

Geochemical Perspectives



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BERNARD MARTY

Origins and Early Evolution of the Atmosphere and the Oceans





Each issue of *Geochemical Perspectives* presents a single article with an in-depth view on the past, present and future of a field of geochemistry, seen through the eyes of highly respected members of our community. The articles combine research and history of the field's development and the scientist's opinions about future directions. We welcome personal glimpses into the author's scientific life, how ideas were generated and pitfalls along the way. *Perspectives* articles are intended to appeal to the entire geochemical community, not only to experts. They are not reviews or monographs; they go beyond the current state of the art, providing opinions about future directions and impact in the field.

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DEDICATION

This volume is dedicated to my colleague and friend Pete Burnard, who tragically passed away in 2015. Pete's technical and scientific skills were fundamental in making the noble gas lab at CRPG what it is today, and we continue to miss his endless good sense of humour and kindness.



PREFACE

When Janne Blichert-Toft came to me with the invitation of writing a volume of *Geochemical Perspectives*, I already had in mind the desire to write something that was neither strictly a terse scientific article, nor a general undergraduate text. In this sense, *GP* was a perfect fit, encouraging, as it does, a narrative of scientific advance in a specialised field, blended with personal experience. In my case, the specialised field is the geochemistry of the so called “atmophile” elements (H, C, N, and the noble gases), according to the nomenclature of Victor Moritz Goldschmidt.

I jumped at the invitation... and immediately realised that I had failed to comprehend the difficulty of the project. After several failed starts, I began to wonder: *How could my life and work be of any interest to people other than myself?* These doubts were exacerbated by the challenge of writing in a language not my own. This somewhat robbed me of the ability to express subtle nuance, or to convey the sense of humour inherent to so many personal stories from daily scientific life. But then I shared a few fragments of preliminary tentative sections with some benevolent colleagues, who were kind enough to return them with guidance and encouragement. Eventually, I threw myself fully into the writing, stumbling haphazardly between personal anecdote, scientific discourse, and incoherent nonsense.

During the course of the writing process, I came to the conclusion that there were three important criteria the finished article had to meet. These were to produce a paper that was not unbearably dull, that I would enjoy reading



myself, and from which I might learn something. It is my sincere hope that the readers of this volume will find that I have, at least partially, succeeded in these goals.

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I am grateful to Janne Blichert-Toft who invited me to write this volume. Without her encouragement and advice, I am not sure it would have come to completion in a reasonable interval of time. Confinement also helped!

Science can be a solitary existence but most of the time it is a group effort. I had the good luck of benefitting from guidance and collaborations with great scientists, among them, Minoru Ozima, Yuji Sano, Igor Tolstikhin, Marc Javoy, Keith O’Nions, Chris Ballentine, Francis Albarède, Rainer Wieler, François Robert, and Albert Jambon. I enjoyed the vibrant atmosphere of research at the CRPG with Jean Carignan, Marc Chaussidon, Christian France-Lanord, Guy Libourel, Etienne Deloule, John Ludden, and Laurie Reisberg, as well as the CRPG staff, especially Isabelle Geoffroy and Bruno Porcu. Members of the noble gas lab, past and present, at CRPG – Allan Bauer, Pierre-Henri Blard, Evelyn Füre, Raphaël Pík, Pete Burnard, Bouchaib Tibari, and Laurent Zimmermann – are thanked for making this whole adventure possible.

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ORIGINS AND EARLY EVOLUTION OF THE ATMOSPHERE AND THE OCEANS

ABSTRACT

My journey in science began with the study of volcanic gases, sparking an interest in the origin, and ultimate fate, of the volatile elements in the interior of our planet. How did these elements, so crucial to life and our surface environment, come to be sequestered within the deepest regions of the Earth, and what can they tell us about the processes occurring there? My approach has been to establish geochemical links between the noble gases, physical tracers *par excellence*, with major volatile elements of environmental importance, such as water, carbon and nitrogen, in mantle-derived rocks and gases. From these analyses we have learned that the Earth is relatively depleted in volatile elements when compared to its potential cosmochemical ancestors (*e.g.*, ~2 ppm nitrogen compared to several hundreds of ppm in primitive meteorites) and that natural fluxes of carbon are two orders of magnitude lower than those emitted by current anthropogenic activity. Further insights into the origin of terrestrial volatiles have come from space missions that documented the composition of the proto-solar nebula and the outer solar system.



The consensus behind the origin of the atmosphere and the oceans is evolving constantly, although recently a general picture has started to emerge. At the dawn of the solar system, the volatile-forming elements (H, C, N, noble gases) that form the majority of our atmosphere and oceans were trapped in solid dusty phases (mostly in ice beyond the snowline and organics everywhere). These phases condensed from the proto-solar nebula gas, and/or were inherited from the interstellar medium. These accreted together within the next few million years to form the first planetesimals, some of which underwent differentiation very early on. The isotopic signatures of volatiles were also fixed very early and may even have preceded the first episodes of condensation and accretion. Throughout the accretion of the Earth, volatile elements were delivered by material from both the inner (dry, volatile-poor) and outer (volatile-rich) solar system. This delivery was concomitant with the metals and silicates that form the bulk of the planet. The contribution of bodies that formed in the far outer solar system, a region now populated by comets, is likely to have been very limited. In that sense, volatile elements were contributed continuously throughout Earth's accretion from inner solar system reservoirs, which also provided the silicates and metal building blocks of the inner planets.

Following accretion, it took a few hundred million years for the Earth's atmosphere and oceans to stabilise. Luckily, we have been able to access a compositional record of the early atmosphere and oceans through the analysis of palaeo-atmospheric fluids trapped in Archean hydrothermal quartz. From these analyses, it appears that the surface reservoirs of the Earth evolved due to interactions between the early Sun and the top of the atmosphere, as well as the development of an early biosphere that progressively altered its chemistry.



1.1 Education

I became interested in volcanoes when I was around six. The trigger was an extraordinary movie on active volcanoes, “*Les Rendez-Vous du Diable*” (released as “*Volcano*” in the UK, where it won a British Academy award in 1962) in which lava lakes, lava flows, and Strombolian explosions could be seen as if you were looking into the torrid mouths of volcanoes (Fig. 1.1). Some of the shots were amazing: the intrepid volcanologist in short pants standing on the rim of Stromboli crater while incandescent lava bombs blasted out way above his head, propagating the wall of the crater just in front of him. In another sequence, the man was running along a black sand beach in the Azores, chased by volutes of silent black and white smoke during a phreatomagmatic eruption. There were scientific animations explaining how volcanoes work. At that time, plate tectonics was not universally accepted, and the movie showed mantle convection beneath the crust, although in a liquid state. The creator of the movie was Haroun Tazieff, a famous volcanologist in France and Belgium at that time. He was a unique blend of adventurer, scientist, writer, movie maker, and an excellent communicator, with a background in engineering geology. He was born in 1914 in Warsaw to a chemist mother and a Tatar prince who was killed in the war shortly after. He emigrated with his mother to Belgium in 1921, where he obtained a degree in geology, while participating in sports that were not for the faint-hearted like boxing, rugby, speleology, and alpinism. During WWII he joined the Resistance and participated in acts of sabotage, as he liked to recall in his numerous autobiographical books. In the forties he served as a field geologist in Katanga (then Belgian Congo, now the Democratic Republic of Congo), where he observed an eruption for the first time at Kituro Volcano near Lake Kivu. Fascinated by active volcanoes, he led several expeditions to study them, with a preference for lava lakes.

As an intrepid scientist, he was active in the same playgrounds as other famous alpinists and oceanographers like Gaston Rébuffat and Jacques-Yves Cousteau. This was in a France that was slowly recovering from the physical and societal damage of WWII, and which was engulfed in colonial wars, first in Vietnam, then in Algeria. A younger generation was looking for evasion and new spaces. At that time the world was not yet covered by Google Earth, and many territories awaited brave explorers. Tazieff, with his magnificent adventurer’s face and his gravelly, Slavic accent, hugely popularised volcanology and geological sciences including geochemistry with his thrilling books (Tazieff, 1951). He argued that the goal when exploring volcanoes is to use scientific tools to understand the processes in action. He put together teams including alpinists



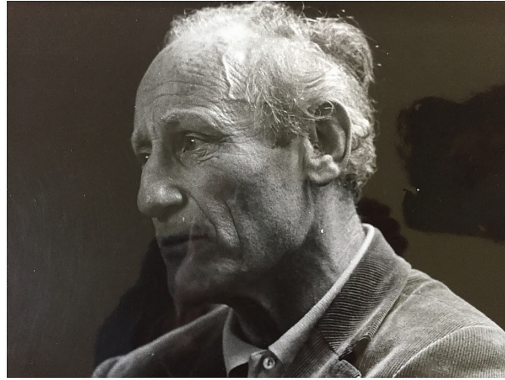


Figure 1.1 Left: *Les Rendez-Vous du Diable*, an award winning movie by Haroun Tazieff (1959). Right: Haroun Tazieff in Toulouse (1971). Photo credit: public domain and B. Marty.

and scientists for expeditions to exotic and dangerous places like Mount Erebus, Nyiragongo, and Erta Ale, all of them hosting active lava lakes, and, of course, to European volcanoes like Stromboli in the Eolian Island and Mount Etna in Sicily.

I once met Tazieff in Toulouse in 1973 where he was giving a conference paper. He was a kind person, attentive to others, and more than happy and willing to share his experience with young scientists. Many young people dreamed of joining Tazieff's teams and living life to the full, and he became an icon for those attracted by adventure, exploration, and outdoor sports. Later, several scientists, including prominent geochemists, questioned the validity of his research, some arguing that he was more of a movie maker than an experienced field scientist. He also adopted controversial positions on volcanic forecasting without having all the elements at his disposal, or on societal subjects where he had little expertise, although he was sometimes right, like on the role of CO₂ in climate change (<https://www.youtube.com/watch?v=tPjHLRYZiHM>). His scientific contributions might not have been commensurate with his media success (which probably did not help him gain respectability from some prominent scientists), but he attracted a generation of young people to the geological sciences, and geochemistry in particular.

Tazieff argued that volcanoes should not only be studied with geological means, as had been the case for centuries, but also through the investigation of the volcanic gas phase, the key driver of eruptions. His teammates developed field gas analysers which operated in harsh conditions and permitted them to follow changes in gas composition in real time even in lava lakes at temperatures



above 1000 °C. Among the scientists following him on these exciting expeditions were François (Fanfan) Le Guern and Werner Giggenbach, a gas geochemist from New Zealand, who established the fundamentals of volcanic gas thermodynamics (Giggenbach and Le Guern, 1976). One of their most famous expeditions took place when teams from the French Centre National de la Recherche Scientifique (CNRS) and the Italian Consiglio Nazionale delle Ricerche (CNR) joined efforts to establish the geological map of Afar, Ethiopia, where three tectonic plates interact with a mantle plume (Barberi *et al.*, 1972). There they monitored variations in gases directly emitted from the Erta Ale lava lake at temperatures above 1000 °C (Allard *et al.*, 1977).

The academic system in France was oriented towards the “hard” sciences rather than natural sciences or literature, and a guidance counsellor, to whom I mentioned my intention to work on volcanoes, recommended studying mathematics and physics rather than geology. As a result, my geology background is thin and informal, mainly gained by reading papers and doing field work with students and fellow geologists. I still like field geology, a kind of detective story in which the murder was committed millions of years ago. Physics gives a different perception of Nature, with the desire to discover principles in action without the fear of equations. Combining the two disciplines, of course, has the great advantage of requiring field work, generally done in exciting places. I studied mathematics and physics at Université Paul Sabatier in Toulouse, and prepared a Master’s degree in physics, with geology as a minor. Higher education in France was strongly compartmentalised and the curriculum did not leave room for other subjects like chemistry, which in fact did not bother me at the time but later on guided me towards physical tracers like noble gases. I was playing in a band during that period but soon realised that my chances of living off music were even slimmer than living off science – and I was still interested in volcanoes. Camping overnight close to the craters of Stromboli and Etna, staring at fireworks and intermittent lava lakes, was breathtaking.

I prepared a “3rd cycle” thesis, which, in the French system at that time, was more like today’s Master’s thesis than a PhD, in an applied physics lab. It was about developing a potassium-argon method, without a ^{38}Ar spike as was usual, in order to measure precisely not only radiogenic ^{40}Ar but also the ratio of the other two argon isotopes, ^{38}Ar and ^{36}Ar . K-Ar dating was trendy, and its application to “young” objects (say, less than a million years) was emerging. The idea proposed by a geology professor at Toulouse University was to date the rise of the Acheulean industry (an archeological industry of stone tool manufacture) in North Africa. The amount of ^{40}Ar in such young samples is tiny and it was essential to discriminate against other causes of ^{40}Ar variations such as isotope fractionation. A paper by Krummenacher (1970) reported co-variations of the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios with $^{38}\text{Ar}/^{36}\text{Ar}$ ratios for geologically young samples and it appeared essential to measure the three isotopes of argon in order to determine the exact contribution of ^{40}Ar from the decay of ^{40}K . With the conventional K-Ar method, this was not possible since ^{38}Ar is added as a spike to determine ^{40}Ar with precision. The lab had experience in vacuum and mass spectrometry, and



this seemed like a good opportunity to use my physics background to address geological questions and coincidentally, stay in Toulouse with my music mates. Most of my three years were devoted to building a high vacuum line in metal, with a custom furnace, a calibration system, and an isotope analyser. The mass spectrometer, an MS10 model from AEI®, consisted of a Nier-type source, a vertical housing surrounded by a permanent magnet, and a Faraday cup, making quite a basic assemblage. The detector was a Vibrating Reed electrometer instead of an electron multiplier as is used widely now. There was no computer—only paper—and the isotope ratios were determined by drawing lines through the peak tops (the peaks were not flat at all) with a pencil and a ruler, so the sharpness of the pencil and its inclination relative to the paper mattered. It was a robust and quite reliable instrument, and a precision of the order of 1% on isotope ratios could be reached after some practice. Because there was no spike to determine the absolute abundances, the calibration system I designed consisted of a high precision, temperature regulated membrane manometer (which cost the lab a fortune) and a calibrated volume to obtain absolute amounts of air aliquots. Then I could determine the age of the sample, which turned out to be as expected, with no isotope fractionation, and the geological problem was solved albeit with a negative result. I also analysed a few modern basalts from Mount Etna and obtained (better) precision on an age of about 20,000 years, which was not bad considering the antiquity of the system. The thesis was complete, with only one technical paper published (Marty and Pagani, 1982) and no volcanic gas analysis. On the positive side, I learned the basics of high vacuum technology and mass spectrometry, how to do an isotopic measurement and, importantly, to what extent to believe in its value.

I was not attracted by geochronology because it seemed difficult to me to do research in volcanology with this tool. In the centralised France of the seventies, isotope geochemistry was blossoming mostly in Paris and its suburbs, especially at the Institut de Physique du Globe de Paris (IPGP) under the leadership of young professors (Claude Allègre, Marc Javoy, and others), and in the south of Paris at the Commissariat à l’Energie Atomique (CEA). Tazieff and his team were based in one of the CEA labs in Orsay and I went there to discuss the possibilities for work. Of course, there were none in a place like that—where hundreds of young scientists dreamt of going—for someone like me, who came from an unknown laboratory in the provinces (*i.e.* not Paris). At the CEA I met passionate people, in particular Patrick Allard, an energetic young CNRS scientist. Patrick mentioned an emerging discipline, the geochemistry of terrestrial noble gases, which appeared to be an excellent tool for studying volcanic gases. He lent me a new book, *“Terrestrial Noble Gases”*, edited by Minoru Ozima, professor at the University of Tokyo, and Calvin Alexander, professor at the University of Minnesota. The book was a collection of papers on the applications of these newly developed tracers to geological and geophysical processes. The range of problems that could be investigated with noble gases was wide, such as the mantle sources of magmas, eruption dynamics, the origin of terrestrial



volatiles, the degassing history of the Earth, and the growth of continents. And the experimental techniques to study noble gases were similar to those used in K-Ar dating.

1.2 The Noble Gases: Early Studies

In an excellent volume of the “*Geochemical Perspectives*” series, Manuel Moreira described in detail the geochemical properties of the noble gases and their applications to many areas within the geosciences (Moreira, 2013). There are also several textbooks on this topic, in particular the classic “*Noble Gas Geochemistry*” book by Ozima and Podosek (2002), the Reviews in Mineralogy and Geochemistry volume “*Noble Gas Geochemistry and Cosmochemistry*” (Porcelli *et al.*, 2002) and, more recently, “*The Noble Gases as Geochemical Tracers*” book edited by Pete Burnard (2013). Instead of focusing only on noble gases, my approach has been to use noble gases, which are trace elements without direct impact on natural systems, to investigate the fate of major “useful” volatiles such as water, CO₂, and N₂.

Noble gases form the right-most column of the periodic table, as their outer electron shells are saturated. They cannot accept more peripheral electrons and they do not need to establish partnerships with other elements in order to saturate their outer electron shells. Consequently, they are chemically inert at Earth’s surface conditions. There are five stable noble gases: helium (atomic mass: 4.00 u), neon (20.18 u), argon (39.95 u), krypton 83.80 u), and xenon (131.29 u). Radon, another noble gas, has two radioactive isotopes which decay in a matter of days or hours. This element, useful in several environmental applications, is not considered here. The isotopes and abundances of noble gases can vary only through physical processes such as phase changes and isotopic fractionation, and as a result of nuclear reactions. The different noble gases cover the whole spectrum of masses and their behaviour in natural systems, such as solubility in minerals, magmas, and water, is mainly governed by their contrasting atomic sizes. Furthermore, they are “rare” on Earth (hence also named “the rare gases”) and their isotopes produced by nuclear reactions, such as spallation, neutron capture, radioactive decay, and fission, can be easily identified. In short, they have the potential to act as geochronometers as well as to be excellent indicators for the origin and history of their host phases.

The golden age for isotope chemistry was in the thirties and forties, partly due to the US Manhattan Project building the first atomic bomb, thereby triggering research on isotope characterisation and separation. During this period, geochronology—the art of dating rocks and minerals—was also developed, mainly exploring the decay schemes which produce lead isotopes from radioactive uranium and thorium isotopes. Potassium-40, discovered by Alfred O. Nier (Nier, 1935), was found to be radioactive, producing ⁴⁰Ca by beta decay, but it was suspected that another decay path could produce ⁴⁰Ar. Carl Friedrich von Weizsäcker, a German physicist, proposed that the high abundance of ⁴⁰Ar



in the atmosphere was due to this decay in rocks with the ^{40}Ar produced being subsequently released into the atmosphere (Von Weizsäcker, 1937). This was a nice idea that proved to be correct, paving the way to models of Earth's degassing and the origin of the atmosphere. Argon makes up almost 1% of air (0.934%) and is mostly ^{40}Ar ; the two other argon isotopes, ^{36}Ar and ^{38}Ar , being at the ppm volume level (the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of atmospheric argon is now established at 298.6 (Lee *et al.*, 2006)). The anomalously high atmospheric concentration of ^{40}Ar stood in sharp contrast to that of other noble gas isotopes, and no nucleosynthetic process (the way stars craft isotopes before dissipating them into interstellar space when they explode) could produce sufficiently abundant argon-40. Later, analysis of meteorites demonstrated that the production of ^{40}Ar is very low in stars compared to ^{36}Ar and ^{38}Ar , with an upper limit of 0.003 for the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio at the birth of the solar system (Begemann *et al.*, 1976). Hence the decay of ^{40}K offered a new dating tool to geologists, but it was difficult to use. Even though potassium is relatively abundant in rocks, ^{40}K is a rare isotope, accounting for only 0.01167% of total potassium and, when it decays (with a half life of 1.25 Gyr), it produces mainly ^{40}Ca . Unfortunately, calcium is abundant in nature, with ^{40}Ca the most abundant isotope. In geochronology, it is essential to have an elevated parent/daughter ratio in order to have sufficient radiogenic isotopes to obtain precise ages. Thus ^{40}K - ^{40}Ca was almost impossible to use - although it can now sometimes be used owing to the high sensitivity and precision achieved by modern instruments. In contrast to Ca, ^{40}Ar was expected to be present in low abundance in rocks, not being chemically retained during high temperature processes, and hence the ^{40}K - ^{40}Ar dating system appeared to open a promising avenue for geochronology. However, the amount of radiogenic ^{40}Ar produced by ^{40}K in rocks also generally is very low (of the order of a few picomoles) as a result of the low abundance of ^{40}K , of its long half life of 1.25 Gyr, and because the yield of ^{40}Ar production is also low (only 10.48% of atoms produced by ^{40}K decay to ^{40}Ar , the rest decaying to ^{40}Ca).

The modern design of mass spectrometers was established by Alfred O. Nier, a physicist at the University of Minnesota, who determined the isotopic composition of most elements with such high precision that his numbers have only recently been improved for some, including the noble gases (Nier, 1950). At that time, mass spectrometers worked in dynamic mode, where atoms of the analysed element produced by an ion source were continuously pumped out. This maintains a low enough vacuum to permit ions to travel in the flight tube in a molecular regime without being neutralised. Such instruments require significant quantities of atoms to be analysed and could not be applied routinely to ^{40}K - ^{40}Ar geochronology. In order to improve sensitivity, John Reynolds, a physicist at the University of Berkeley, designed an instrument working in static mode, *i.e.* with the pumping system of the tube shut down during the purification and analysis of argon. It was made of glass (Fig. 1.2), a material which has a low degassing rate and which did not contribute much to atmospheric contamination during analysis.





Figure 1.2 **Left:** Glass mass spectrometer of the type developed by John Reynolds. This instrument was bought by Claude Allègre and is now on display at the Institut de Physique du Globe de Paris. Photo credit: G. Avice. **Right:** A modern metal noble gas mass spectrometer at the CRPG (MC SFT by Thermo Fisher Co). Photo credit: B. Marty.

With this, the noble gas mass spectrometer was born and one could analyse noble gas isotopes in quantities as low as a few million atoms. The K-Ar dating method rapidly expanded and found applications in several domains of Earth Science. For example, it allowed geologists to determine the age of lava flows with precision, which, together with palaeomagnetic measurements on the same rocks, demonstrated the reality of plate tectonics. Among other successes, the Ar-Ar method, an improvement of the K-Ar method, enabled the dating of lunar rocks brought back by the Apollo missions (Turner, 1970).

The geochemistry of noble gases blossomed with the advent of static mass spectrometry. In the early sixties, it was suspected that noble gases could tell us a lot about the origin and history of meteorites. Solar-like noble gases, resembling the relative abundances of these elements in the Sun, were discovered in primitive meteorites, and intensive research was carried out, mostly in Russia and the USA, to search for primitive substructures (Signer and Suess, 1963; Ozima and Podosek, 2002, and references therein). The age of meteorites and of the Earth had been set at 4.5 Ga by Clair Patterson at the California Institute of Technology using the parallel decay of uranium isotopes to give two lead isotopes (Patterson *et al.*, 1955). Nucleosynthetic models predicted that some of the isotopes synthesised in stars, having half lives shorter than the age of the solar system, could have been alive when the solar system started to condense. Iodine-129 is a radioisotope that decays to ^{129}Xe with a half life of a few Myr ($T_{1/2} = 15.7$ Myr) and should have been produced in massive stars together with the stable isotope of iodine, ^{127}I (Fig. 1.3).

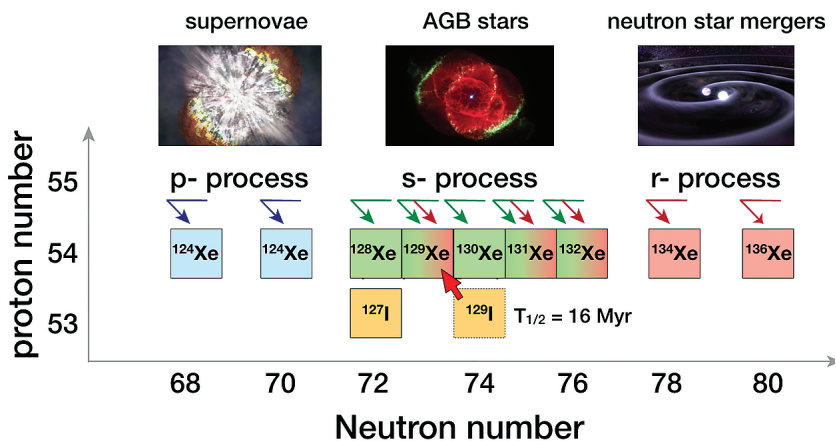


Figure 1.3 The nine isotopes of xenon were produced in several generations of stars by different nucleosynthetic processes before being incorporated into solar system objects. Rapid (r-) neutron nucleosynthesis produced the two isotopes of iodine, stable ^{127}I , and radioactive ^{129}I which subsequently decayed to ^{129}Xe with a half life of 16 Myr.

John Reynolds undertook the analysis of xenon isotope compositions in meteorites with his high sensitivity mass spectrometer and, as predicted, found a monoisotopic excess of ^{129}Xe , the presumed daughter isotope of ^{129}I , in the Richardton meteorite (Reynolds, 1960). This was the first experimental evidence that extinct radioactivities – that is, radioactive isotopes having half lives much shorter than the age of the solar system – were alive when the solar system formed. But an important question remained: had this decay been produced *in situ* – that is, after the meteorite formed – or was it an interstellar inheritance? In the first case, it would mean a short period of time between the last peak of stellar nucleosynthesis and the formation of the first solids in the solar system. The second case would be consistent with continuous production of radionuclides in the galaxy and both possibilities would have strong implications for the formation of stellar systems. Jeffery and Reynolds carried out a clever experiment consisting of irradiating a sample of the Abee meteorite with thermal neutrons in a nuclear reactor (Jeffery and Reynolds, 1961). Irradiation by neutrons with an appropriate kinetic energy, a widely used technique in geochemistry and nuclear physics known as neutron activation, results in nuclear transformations of targeted atoms. Here, neutrons will transform the stable isotope of iodine, ^{127}I , into ^{128}I , a radioactive isotope that decays to stable ^{128}Xe with a half life of 25 min. After waiting some time for the decay of ^{128}I , they analysed the xenon isotopes by incrementally increasing the temperature (Fig. 1.4). This is another common technique based on the fact that isotopes which have similar activation energies (that is, for which a certain amount of energy is needed to release them)



occupy similar retention sites in the crystalline matrix of a rock. They found that ^{128}Xe produced by irradiation of ^{127}I was released together with ^{129}Xe at the same temperature steps, whereas ^{131}Xe , produced by neutron irradiation of tellurium-130, was released at different temperatures. This crystal clear experiment demonstrated that ^{129}Xe had been produced in the sites where iodine was trapped when the meteorite formed, thus establishing that iodine-129 was alive when the minerals of the meteorite trapped iodine. Because ^{129}I is produced together with ^{127}I (the stable iodine isotope) during the so called rapid neutron capture process (r-process) in supernovae, the presence of live ^{129}I implied that an episode of element formation in stars occurred not long before the solar system formed, presumably within a few tens of Myr at most (Jeffery and Reynolds, 1961).

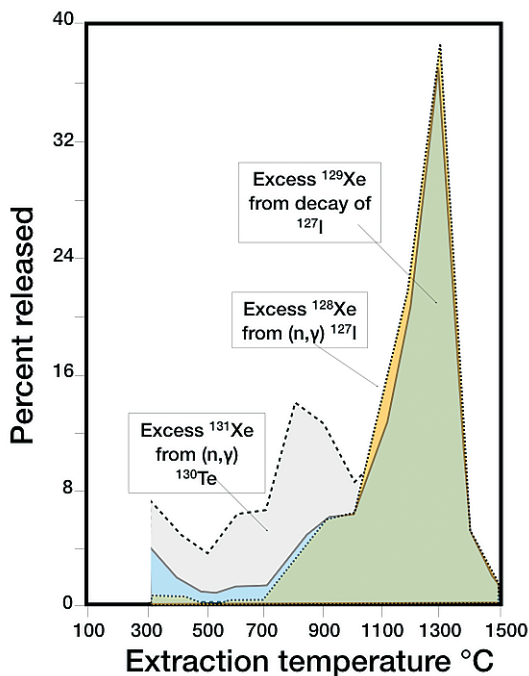


Figure 1.4

Release of xenon isotopes from irradiated meteorite Abee as a function of extraction temperature (each step lasting 1 hour). I-Xe dating requires neutron irradiation of samples (similar to Ar-Ar) and stepwise heating to disentangle the radiogenic ^{129}Xe fraction (see Hohenberg and Pravdivtseva, 2008). Note that ^{129}Xe produced by the decay of ^{129}I is released at the same temperature as ^{128}Xe produced by artificial irradiation of ^{127}I in a nuclear reactor, meaning from the same sites as ^{128}Xe produced by this artificial irradiation. This proves that radiogenic ^{129}Xe was produced where iodine was trapped in the meteorite. In contrast, ^{131}Xe also produced artificially by the irradiation of ^{130}Te is released from different sites. Adapted from Jeffery and Reynolds (1961).



This amazing result (published in a 1.5 page article) had far reaching implications. It demonstrated that neutron-rich stars exploded “just” (on a galactic timescale) before the formation of the solar system, and that meteorites formed shortly after the start of solar system condensation. In order to date objects, one needs to have solids that have trapped parent isotopes, in this case ^{129}I , and which have remained closed until their analysis in order to have retained the daughter isotopes, here ^{129}Xe . In the absence of solid phases formed before solar system condensation, it is difficult to establish directly the time interval between the last nucleosynthetic production of parent isotopes and the formation of meteorites, but the ^{129}I - ^{129}Xe dating system allows us to establish relative formation ages among meteorites (Fig. 1.5). Several other extinct radionuclides were discovered in the following years, including ^{26}Al ($T_{1/2} = 700,000$ yr) (Papanastassiou *et al.*, 1977), permitting the formation interval of solids in the nascent solar system to be narrowed down and the identification of early sources of radioactive heat for early planetesimals to differentiate. The ^{129}I - ^{129}Xe system may also permit us to set constraints on the “age” of the solar system following isolation. Based on ideas current in 1960, John Reynolds assumed steady state evolution of the galaxy over $T = 2 \times 10^{10}$ years prior to isolation, *i.e.* $(^{129}\text{I}/^{127}\text{I})_0 = T_{129}/T = 0.00125$ and hence a solar system “age” of ~ 60 Myr (G. Turner, personal communication). This simple model assumes a uniform average iodine ratio throughout the region of the galaxy from which the solar system formed, which is not realistic given the short half life of ^{129}I . The time interval between the last nucleosynthetic event which produced the two iodine isotopes and the formation of the solar system can also be approximated by assuming from nucleosynthetic models that the production rates of ^{127}I and ^{129}I are comparable (Clayton, 1975). This would give ~ 200 Myr (Fig. 1.5). This time interval would be an upper limit since stable ^{127}I could have been inherited, lowering the $^{129}\text{I}/^{127}\text{I}$ ratio at the onset of isolation of the molecular cloud from the galaxy. All these estimates are much longer than other estimates obtained from short lived radioactivities like ^{26}Al , thus requiring several generations of stars and/or different processes to have seeded the local interstellar medium (Gounelle and Meynet, 2012).

Prompted by the discovery of extinct ^{129}I , several laboratories in Russia, Switzerland, Germany, and the USA started extensive studies of noble gas isotopes in primitive meteorites, unveiling numerous pre-solar components and subcomponents, inherited from the interstellar medium or produced by cosmic ray irradiation and implantation of solar wind ions. These studies in turn permitted the development of increasingly sensitive and precise methods, setting the scene for the study of terrestrial samples for which isotopic variations presumably were smaller.



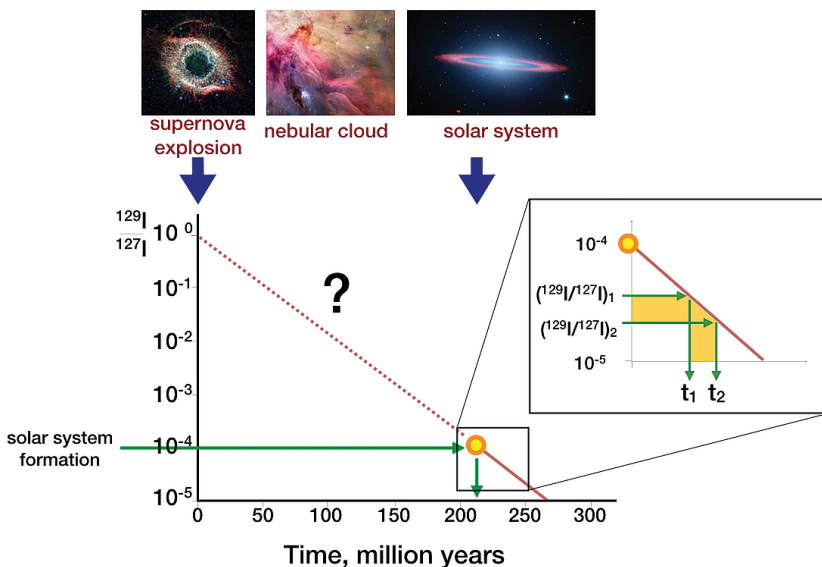


Figure 1.5

Principle of ^{129}I - ^{129}Xe dating. A supernova exploded at some time before the onset of solar system formation, producing two isotopes of iodine, radioactive ^{129}I (half life of 16 Myr) and stable ^{127}I with a ratio of about unity (Clayton, 1975). Debris from the explosion was mixed with other stardust in a giant molecular cloud which evolved for several tens of Myr. ^{129}I decayed, decreasing the ambient $^{129}\text{I}/^{127}\text{I}$. The decay product of ^{129}I , ^{129}Xe , vanished as it was held in ambient xenon. At some stage, a new stellar system formed, namely the solar system at 4.567 Ga. At that time, the $^{129}\text{I}/^{127}\text{I}$ ratio had decreased to about 10^{-4} . Iodine was incorporated into forming solids, now represented by meteorites. Further decay of ^{129}I produced ^{129}Xe within the meteorite minerals which can be identified by excesses of ^{129}Xe . Once iodine was trapped in meteorites, the chronometer became quantitative, allowing the determination of interval formation ages between two meteoritic materials (box on the right hand side). By measuring the $^{129}\text{I}/^{127}\text{I}$ ratios (determined by the excess of ^{129}Xe and stable ^{127}I) in two meteoritic phases, it is possible to determine the time interval between their respective formations with a precision better than 1 Myr for events that took place at 4.567 Ga. A number of other extinct chronometers have been developed since the milestone studies of John Reynolds and his group, permitting outstanding insight into the timing and nature of solar system formation processes.

Xenon is the heaviest stable noble gas and has nine isotopes. The analysis of xenon in meteorites has shown that terrestrial atmospheric xenon has a distinct isotopic composition (Fig. 1.6). It is depleted in its light and enriched in its heavy isotopes, by about 3.5 % *per* atomic mass unit (u), a remarkable feature attributed to mass dependent fractionation of, until recently, unclear origin. The analysis of palaeo-atmospheric samples of Archean age has now provided an



explanation for this pattern (see Section 8). In addition to this unique feature, atmospheric xenon presents a small mono-isotopic excess of about 7% compared to either solar wind Xe or meteoritic Xe, and this excess was attributed to the decay of radioactive ^{129}I trapped during Earth's formation together with stable ^{127}I (Wetherill, 1980). The ratio of ^{129}I to ^{127}I at the start of solar system formation (ASSF) could be determined by analysing xenon in the most ancient meteorites, yielding a $(^{129}\text{I}/^{127}\text{I})_{\text{initial}}$ ratio of 1.0×10^{-4} (Fig. 1.5; Swindle and Podosek, 1988, and references therein).

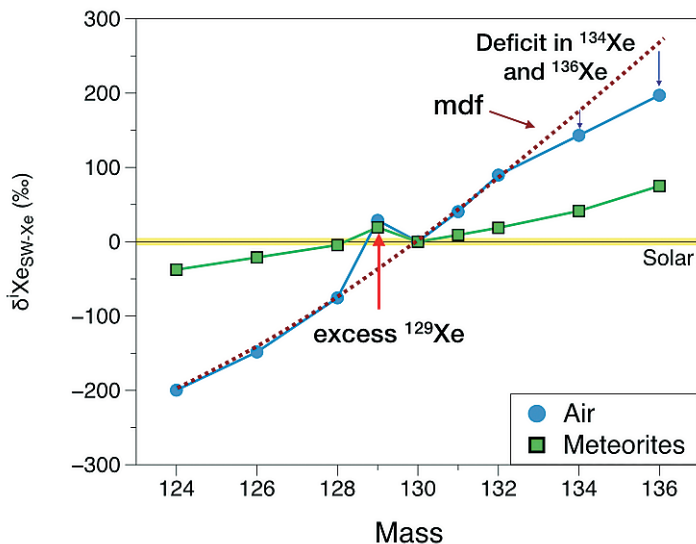


Figure 1.6

Xenon isotope diagram. The nine Xe isotopes are normalised to one of them, here ^{130}Xe , and to a specific reference composition, here solar wind (SW) Xe, which is supposed to represent the composition of the solar nebula from which planetary bodies formed. The isotopic deviations from the reference composition (solar) are given in the classical δ notation: $\delta i\text{Xe} = [(i\text{Xe}/^{130}\text{Xe})_{\text{sample}} / (i\text{Xe}/^{130}\text{Xe})_{\text{SW}} - 1] \times 1000$ (parts per mille, ‰). In this format, a solar-like isotope composition yields a horizontal pattern similar to SW ($\delta i\text{Xe} = 0$ ‰). Atmospheric xenon differs from SW by three important features: (i) It contains a monotopic excess of ^{129}Xe from the decay of ^{129}I ; (ii) It is isotopically fractionated by 35 ‰ per atomic mass unit relative to SW (mdf: mass dependent fractionation), which is extraordinarily high for an element with high mass (mass dependent fractionation decreases with increasing mass number); and (iii) It is depleted in the heavy Xe isotopes ^{134}Xe and ^{136}Xe relative to a line that passes through the other Xe isotopes and which characterises mass dependent isotopic fractionation. Features (ii) and (iii) have implications that are discussed in Sections 7 and 8. Meteoritic Xe is isotopically fractionated relative to SW to a lesser extent than atmospheric Xe and contains excess ^{129}Xe that allows for relative chronology as shown in Figure 1.5.



For the atmosphere, it is possible to do a mass balance to estimate its “age”. The total amount of xenon in the atmosphere is precisely known (Ozima and Podosek, 2002) and the number of ^{129}Xe atoms can be straightforwardly estimated. It is more difficult to obtain the total ^{127}I content of the Earth, for which geochemical estimates vary between 3 ppb (parts per billion, by weight) and 13 ppb (Armytage *et al.*, 2013; Deruelle *et al.*, 1992). Assuming that the excess of ^{129}Xe in the atmosphere is due to the decay of terrestrial ^{129}I , and that produced ^{129}Xe was quantitatively degassed from the solid Earth, one obtains a time interval of 80-120 Myr after the start of solar system formation for the age of the atmosphere (Allègre *et al.*, 1995; Wetherill, 1980). Here the age means the time at which the Earth-atmosphere system started to retain xenon isotopes quantitatively. Strictly speaking, ^{129}Xe could also have been lost from the planetary bodies from which the Earth grew. This age has been questioned since: (i) there is now evidence that atmospheric xenon has been subsequently lost through geological periods of time (Pujol *et al.*, 2011), and (ii) a significant fraction of atmospheric ^{129}Xe excess might have been inherited from comets (Marty *et al.*, 2017). Nevertheless, the idea that the Earth-atmosphere system formed in a few tens of Myr at most after the “start” of solar system formation (defined as the time of condensation of its most refractory phases) still holds and is supported by studies of other extinct radionuclides such as ^{182}Hf ($T_{1/2} = 9$ Myr), ^{244}Pu (82 Myr), and ^{142}Sm (106 Myr).

The study of the xenon isotopic composition of natural gases led to another major discovery. A mono-isotopic excess of ^{129}Xe , relative to the atmospheric composition, was found in CO_2 -rich gas in New Mexico (Butler *et al.*, 1963). No known nuclear process accounts for this excess, which therefore was attributed to the decay of extinct ^{129}I within the solid Earth. This discovery showed that two distinct reservoirs, the atmosphere and the Earth’s interior, had been formed while ^{129}I was still alive, that is, within a few tens of Myr after the start of solar system formation. It also suggested that volatiles had been preserved in the solid Earth since its formation and had never exchanged with atmospheric gases.

Confirmation came from measurements in the late sixties of helium isotopes in volcanic gases and in the oceans. Helium is not retained in the Earth’s atmosphere due to its low mass, and escapes to space continuously, with an atmospheric residence time of ≤ 1 Myr. Consequently, its atmospheric abundance (5.24 ppmv) is low compared to other non-radiogenic noble gases like neon (18.18 ppmv) and its isotopic composition is the result of its two isotopes, ^3He and ^4He , degassing from the Earth. Helium-4 is produced continuously in rocks mainly by the decay of the two radioactive uranium isotopes ^{235}U and ^{238}U and radioactive ^{232}Th , with minor production from other heavy elements. Helium-3 also is produced by nuclear reactions and the radioactive production $^3\text{He}/^4\text{He}$ ratio is of the order of 10^{-8} - 10^{-9} . However, the atmospheric $^3\text{He}/^4\text{He}$ ratio was measured to be 1.39×10^{-6} (Mamyrin *et al.*, 1970), thus requiring a supplementary source of ^3He . Two teams, in Russia and the USA, developed mass spectrometers sensitive enough to measure the rare ^3He isotope with precision. They found excess ^3He (relative to the atmospheric composition) in volcanic gases from Kamtchatka (Mamyrin *et al.*, 1969) and in hydrothermal



fluids from mid-ocean ridges (Clarke *et al.*, 1969), respectively. Gases trapped in meteorites have $^3\text{He}/^4\text{He}$ ratios of the order of 10^{-4} and, after eliminating other potential sources of ^3He , these scientists concluded that the solid Earth contains primordial helium that was trapped when the Earth formed. These discoveries prompted the analysis of volcanic gases and rocks worldwide and it was found that the $^3\text{He}/^4\text{He}$ ratios of fluids and rocks sampled along mid-ocean ridges show a remarkable homogeneity at around 7-9 times the atmospheric value (Kurz and Jenkins, 1981; Graham, 2002, and references therein). Because ^3He and ^4He have different origins, such consistency implies that primordial volatiles (*i.e.* ^3He) have been efficiently mixed with refractory elements producing radiogenic ^4He through mantle convection. Furthermore, volcanic gases sampled at arcs contain mantle-derived ^3He with an upper limit value within the MORB range, attesting to the contribution of the mantle wedge to arc magmas. Gases and rocks collected in some mantle plume areas such as Iceland (Polyak *et al.*, 1976) and Hawaii (Craig and Lupton, 1976) were found to have $^3\text{He}/^4\text{He}$ ratios higher than the MORB range, implying that the sources of mantle plumes have experienced less primordial gas degassing than the convecting mantle feeding mid-ocean ridges.

For other noble gases, atmospheric contamination is always problematic because it tends to mask the original sample signature. Only specific types of samples are suitable for noble gas analysis since the vast majority of rocks and minerals on the Earth's surface have exchanged noble gases with the atmosphere. The structures of certain minerals like olivine and pyroxene are tight enough to prevent extensive contamination by atmospheric noble gases but they also contain extremely small amounts of noble gases. Volcanic glasses coating MORB pillow lavas recovered along ridges are formed by the rapid quenching of lavas in contact with seawater, which minimises extensive degassing of mantle gases and exchange with atmospheric gases dissolved in seawater. Mid-ocean ridge basalt glasses often have apparent ages in excess of those determined for pillow basalts (generally zero age for rocks sampled at the apex of ridges), indicating that MORB glasses contain excess radiogenic ^{40}Ar (Funkhouser *et al.*, 1968). Because MORB derive directly from the mantle, this implies that mantle argon has $^{40}\text{Ar}/^{36}\text{Ar}$ ratios higher than the atmospheric value of 298.6. Minoru Ozima, a palaeomagnetician who developed the K-Ar dating method in his lab in Tokyo, realised that the difference between atmospheric and mantle values offers important information about the dynamics of the Earth and its atmosphere in the distant past (Fig. 1.7).

There was no ^{40}Ar when the Earth formed (stars produce only ^{36}Ar and ^{38}Ar) and the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the mantle increases over time. If mantle degassing had occurred, say, yesterday, mantle and atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratios would be the same, which is not the case. If massive degassing had happened early, most primordial ^{36}Ar and ^{40}Ar already produced at the time of degassing would have been transferred to the atmosphere, and the atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio would reflect that of the ancient mantle. It would evolve due to subsequent



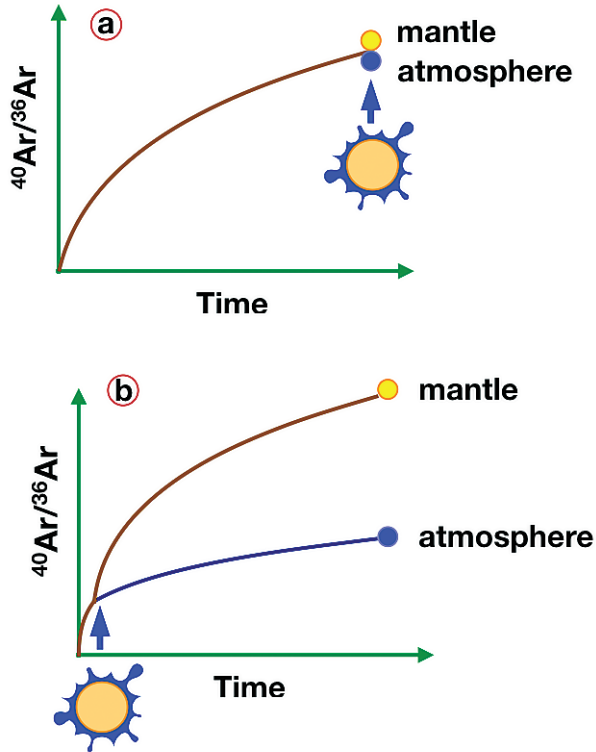


Figure 1.7

How the difference in the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios between the mantle and the atmosphere can give information about the timing of terrestrial degassing. ^{40}Ar has been produced through time by the decay of ^{40}K in the mantle and ^{36}Ar is a stable isotope. **(a)** The first case shows degassing of the atmosphere from the mantle yesterday. In this case, the mantle and the atmosphere would have a similar $^{40}\text{Ar}/^{36}\text{Ar}$ ratio. **(b)** In the second case, degassing took place early. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the mantle, now depleted in ^{36}Ar , will increase sharply. The atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ will still rise due to continuous degassing of the mantle and the crust, but at a slower pace. The timing of degassing will be a function of the contrast in the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios between the mantle and the atmosphere.

degassing of the mantle and the crust. However, the mantle ratio would be much higher because this reservoir would have lost most of its primordial ^{36}Ar , and ^{40}Ar would still be produced by mantle potassium-40. Therefore, there would be a marked difference in the respective argon signatures of the mantle and the atmosphere. The larger the difference, the more ancient and massive degassing would have been. Minoru Ozima built models of terrestrial degassing, based on boxes (the mantle, the atmosphere, and the growing continental



crust) between which potassium and the two isotopes of argon of interest are transferred through time (Ozima, 1975). Both degassing and radioactive isotope production can be written as first order reactions, resulting in the solution of first order differential equations. Measurements of MORB glasses are consistent with terrestrial degassing having taken place within a few tens to a few hundreds of Myr after the start of solar system formation.

In the eighties, Claude Allègre, Thomas Staudacher, and Philippe Sarda at the IGP included argon and xenon in a model of terrestrial degassing (Allègre *et al.*, 1983). This was supported by noble gas data obtained with their state-of-the-art mass spectrometers built around the glass flight tube from Berkeley (Fig. 1.2). They confirmed early atmospheric degassing within a few tens of Myr followed by a decreasing rate throughout Earth's geological time periods. Another area of research was pioneered by Ichiro Kaneoka, who found that argon in mantle plume rocks and minerals, associated with high $^3\text{He}/^4\text{He}$ ratios, had an $^{40}\text{Ar}/^{36}\text{Ar}$ ratio lower than those of MORB and close to the atmospheric value (Kaneoka and Takaoka, 1978). The less degassed lower mantle contained more primordial ^{36}Ar than the upper mantle, explaining its lower $^{40}\text{Ar}/^{36}\text{Ar}$ ratio relative to MORB. This view paralleled three box models (the lower mantle, the upper mantle, and the continental crust) in which incompatible elements were extracted from the upper mantle and stored in the continental crust while the lower mantle, little affected by trace element extraction, kept a composition close to that of primitive meteorites. This type of model was also consistent with strontium and neodymium isotope systematics in mantle plumes which were close to those of the primitive Earth, while those of MORB showed deviations due to the different behaviour of the parent and daughter elements during partial melting. The boundary between the two mantle domain models was the transition zone, where seismic waves change velocity due to contrasting densities. The problems were solved, and scientists could henceforth explore detailed geochemical signatures and relationships among different volcanic provinces. It turned out that things were not as simple as expected: this type of model became inconsistent with the new geophysical evidence that plates are subducted well below the transition zone. The classical model of a two reservoir mantle, with an upper convecting mantle above the transition zone sourcing MORB and a more stagnant mantle region below the 660 km discontinuity, is not the paradigm anymore. Nevertheless, noble gas isotopes strongly suggest the occurrence of some mantle regions less degassed than others and therefore less processed than those feeding mid-ocean ridge basalts.

The variability of mantle degassing through time has physical grounds. During the early stages of Earth's formation and evolution, large regions of the silicate Earth were molten. Due to the low solubility of noble gases in silicate melts (for example, about 2 nanomoles of argon are dissolved in a basaltic melt in equilibrium with an atmospheric pressure of argon), any noble gas atoms trapped in the growing solid Earth were readily degassed quantitatively to the overlying atmosphere, with minute amounts of residual noble gases retained in crystallising silicates. Later, Earth's degassing through magmatism was also efficient.



Most regions of the mantle are made of crystalline solids, and mantle degassing requires magma generation following decompression melting (mid-ocean ridges), excess heat (mantle plumes), or the addition of fluids which depress the melting point (subduction zones). During their ascent, major volatiles dissolved in magmas begin to exsolve; first CO₂, the noble gases and then water, partition into the gas phase and enter the atmosphere. The process of mantle degassing is very efficient for noble gases because these elements are incompatible (Heber *et al.*, 2007), *i.e.* they partition quantitatively from minerals into the forming magmas, and then end up in the atmosphere when the magmas erupt. Even plutonic bodies trapped in the crust are extensively degassed due to water circulation leaching minerals at depth. Incompatible elements such as noble gases are sampled from a mantle volume one order of magnitude larger than the magma volume generated by mantle melting. It is straightforward to calculate that, for a present day magma production rate of about 16 km³/yr (mostly at mid-ocean ridges; Crisp, 1984; Le Voyer, 2019), the mass of the mantle (with a specific gravity of ~3) which is degassed *per* year is about 6 10¹⁷ g. For an age of the Earth of 4.5 Ga, the total mantle mass that has been degassed should be ~2.7 × 10²⁷ g, comparable to the estimated mass of the mantle of 4 × 10²⁷ g. Because the Earth was hotter in the past than today (both short and long lived radioactive isotopes were more abundant early on), magma production rates were higher too, meaning that the whole mantle should have been processed and degassed. Thus, it is remarkable to have primordial isotopes still trapped in the mantle. This is because convection mixing can prevent efficient loss of incompatible volatiles. Gonnermann and Mukhopadhyay (2009) showed that through degassing, the concentration can never be brought down to zero because mixing continuously lowers the mantle concentration, which in turn decreases degassing efficiency even in the absence of a change in magma production rates. As a result of convective mixing, concentrations approach zero with an exponential decay but never get to zero. Conversely, in the absence of convective mixing, the mantle concentrations can be brought down to zero quickly. The presence of primordial helium in the mantle is no longer challenged, but the existence of less degassed mantle regions, as suggested by high ³He/⁴He ratios in mantle plume magmas, has often been questioned and explained by other processes (Anderson, 1998). This view is nevertheless built on solid arguments and is now supported by two other noble gas isotope systems, those of neon and xenon (*e.g.*, Mukhopadhyay and Parai, 2019).

1.3 Parisian Days

With my training, I felt that I would be able to analyse noble gases and carry out research on exciting science, but there was a catch: how and where to do that? I read a few more papers, then wrote to two prominent noble gas scientists, John Reynolds at the University of Berkeley and Minoru Ozima at the University of Tokyo. It took some time to receive an answer in those pre-email times, but I eventually got a nicely written, kind letter some months later from John



Reynolds, apologising that he did not have financial support for a post-doc position. Minoru Ozima answered that I was welcome in his lab but that he also did not have post-doc support. If I could find funds, he would be pleased to have me with him. I then submitted a proposal to the French Ministry of Foreign Relations and at that time it was easier to get a fellowship for Japan than for the USA. Unfortunately, my application arrived a few days too late and I had to spend some time in France waiting for the next funding opportunity. In September 1979, I headed to Paris and inhabited a beautiful, Haussmann-like apartment with a friend in the Quartier Latin at walking distance from the IPGP. There, I divided my time between teaching maths and physics in a private school in a wealthy suburb, taking guitar lessons in a renowned Parisian jazz school, and working in the laboratory of Marc Javoy, a prominent stable isotope geochemist at the IPGP and a colleague of Claude Allègre. As I wanted to work on volcanic gases and mantle degassing, he kindly gave me access to his up-to-date glass lines and mass spectrometers.

Claude Allègre, the leader of geochemistry in France, headed one of the best isotope teams in the world. Passionate about science, he was a somewhat difficult person that you would not go to meet without a certain measure of apprehension. Between other outstanding developments, Claude Allègre went to Berkeley to get two glass tubes from John Reynolds (Fig. 1.2) to build custom noble gas mass spectrometers at the IPGP. The members of the new noble gas laboratory were Thomas Staudacher, a young scientist trained in noble gases in the German laboratory of Till Kirsten, and Philippe Sarda (then a Ph.D. student). The IPGP was in charge of the French volcano observatories, with Tazieff being the director of this department, but things did not turn out well between him and Allègre. La Soufrière, a volcano in Guadeloupe, French Lesser Antilles, began to exhibit explosive activity in 1977 and there was a fierce debate concerning the nature of these explosions. Tazieff argued they were purely phreatic and affected only the summit, whereas Allègre, who was then director of the IPGP and in charge of advising the authorities on this small, but populated island, feared phreatomagmatic activity involving uprising magma that could affect much wider areas. Eventually part of the island was evacuated for months, but no catastrophic event ever occurred. This episode led to a severe clash between Allègre and Tazieff which was widely covered by the media, https://www.youtube.com/watch?v=DYaR06U3QGY&ab_channel=ArchipelDesSciences. As a consequence, Tazieff and his team and Tazieff and his team decided to leave the IPGP and to migrate to a CEA laboratory in Orsay. One interesting consequence was that the volcanic crisis prompted an extensive geochemical survey, and in particular, fumarolic gases near the crater were regularly sampled and analysed in Javoy's lab for major and minor volatile species. These analyses were carried out on a commercial 24-collector mass spectrometer developed by Cameca® for industrial fume monitoring. I learned how to use this instrument and started to play with the abundant data, trying to understand the logic of this natural system. It seemed to me that the data were telling us something but that the necessary framework within which to interpret them was missing.



During another trip to Mount Etna, I realised that what was missing was a reference to compare gaseous species to. It was a successful time for analysis of trace elements in rocks, particularly with more and more accurate measurements of rare earth element (REE) abundances in rocks. Terrestrial REE abundances generally are normalised to chondritic abundances. The latter yield a flat pattern by construction. Deviations from the flat chondritic pattern implied magma fractionation, opening an avenue to investigate the mode and extent of melting in the source regions. When this effect was taken into account and corrected for, the source of mantle-derived magmas appeared fractionated, implying that the mantle sources had experienced previous melting episodes in the distant past. Development of the isotope geochemistry of strontium, neodymium, lead, and hafnium permitted not only confirmation of the message from trace element data, but also an estimation of the kinetics of mantle convection and subduction processes. It seemed interesting to develop a similar framework for major volatiles (water, carbon, nitrogen, sulfur, halogens) but these species could not be normalised to a reference composition and therefore required a different approach. Noble gases had potential to fulfil this role because they are chemically inert, and their abundances would only be affected by phase changes. Noble gases degassed from solid Earth reservoirs accumulate in the atmosphere and only extremely small quantities can be trapped in subducting plates and recycled back into the mantle. Identifying recycled crustal material from pristine material should therefore be easier than for other tracers. This assumption proved to be not entirely correct because, even though noble gas recycling is indeed quantitatively small, the different mantle domains are extremely noble gas-poor and sensitive to subduction of material that was once in contact with the atmosphere. Furthermore, the extreme depletion of mantle noble gases and their tendency to degas from ascending magmas during vesiculation driven by major volatile species make them very sensitive to contamination by abundant atmospheric noble gases in the country rocks or fluids. However, primordial ^3He recently discovered in mantle-derived rocks and gases had an interesting potential for normalisation: (i) its mantle origin is unambiguous and (ii) the atmospheric contamination problem is generally limited since the abundance of atmospheric ^3He is extremely low (7.3×10^{-12} mol ^3He *per* mol air).

Back in Paris, I checked the literature, but gas data sets that included helium isotopes were scarce and more measurements were needed. I was not the only one thinking about developing a normalisation frame for volcanic emanations. In Japan, Sadao Matsuo, Professor at the Tokyo Institute of Technology (then nicknamed TIT, which was later changed to the more politically correct TokyoTech), was a stable isotope geochemist who pioneered a modern approach to the study of volcanic gases. He studied in detail the evolution of fumarolic gases from Showa-Shinzan, a monogenic volcano in Hokkaido that had erupted only once in 1944-1945. He found that initially gases had a high N_2/Ar ratio of 2,200 then gradually evolved towards 98, close to the atmospheric ratio of 83. Together with other volcanic gases having high N_2/Ar ratios, Matsuo concluded that excesses of N_2 relative to the atmospheric composition signalled



the contribution of subducted sediments to the magma-forming region. As crustal fluids percolated into the cooling magma body, volcanic gases gradually equilibrated with atmospheric gases (Matsuo *et al.*, 1978).

The flux of primordial ^3He from the mantle to the surface was quantified by Harmon Craig and John Lupton at Scripps Oceanographic Institution in San Diego, USA. They established a two dimensional map of ^3He excesses in the Pacific Ocean by measuring the helium isotope ratios of seawater sampled at different depths and locations (Craig and Lupton, 1976). They reported ^3He excess in deep water centred above mid-ocean ridges and deflected by oceanic circulation. Knowing the ^3He excess above the helium-3 background of seawater (due to solution of atmospheric He) and the velocity of deep seawater established from carbon-14 measurements, they established the global flux of ^3He from the mantle at ~ 1000 moles *per* year by extrapolating their results to all oceanic basins. This value has been scaled down to 640-850 mol/yr with more data and more refined ocean circulation models (Holzer *et al.*, 2017). For the first time, a flux of mantle-derived volatiles could be quantified and this discovery opened the interesting possibility of estimating the flux of other volatiles, for example, CO_2 , by normalising them to ^3He in mantle-derived fluids and rocks (Marty and Jambon, 1987).

1.4 Tokyo Years

I finally got financial support from France and landed in Tokyo in September 1979, after a long flight through Anchorage, Alaska, as flight paths over Siberia were forbidden during the Cold War. There were not as many gaijins (foreigners) in Tokyo as there are now, and all the noble gas laboratory staff at the Geophysical Institute did their best to make me feel comfortable both in the lab and in the city. I was thrilled to be in a world class laboratory contributing to one of the most exciting areas of the geosciences. Japan was on the rise economically and intellectually, Tokyo was a vibrant city, and gaijins were well-accepted and in fact had more privileges than the average Japanese citizen.

Working in a Japanese lab is different from working in a French lab. Each lab is headed by a professor, with one or two assistant/associate professors, and several students, and rarely any technical staff. The model is similar to that of most British, American, and German labs. French labs are more “socialist” in their set-up, with common analytical facilities for several scientists and technical staff associated with the facilities. In Japan, the head of the lab is highly respected and his advice is rarely discussed, which was a bit strange for me since French students often challenge their advisors and are encouraged to express their own views. Because Ozima had spent a long time outside Japan working in North America, he was quite understanding of my non-Japanese behaviour. Japanese scientists and students were hard working, or at least spent a lot of time working in offices. This was not challenging to me since I had been waiting for this opportunity for a long time and I quickly adapted to the Japanese pace



of work. As a matter of fact, I did not feel disoriented in Japan, communication was not really a problem since many Japanese scientists spoke English, and in everyday life it was always possible to find someone with a little knowledge of English. I slowly learned some kind of survival Japanese, which allowed me to travel on my own and sample volcanic gases along the archipelago.

The first task that Ozima asked me to do was to explain the isotopic fractionation (a change in the isotopic composition of a given element) of noble gases measured in soil gases and fumaroles by another noble gas group led by Keizuke Nagao (Nagao *et al.*, 1981). Because noble gases are chemically inert, only physical processes, such as differential velocity of gaseous atoms, can change their isotopic composition. This can take place in the molecular regime when collisions with the walls of the container exceed inter-atomic collisions, but only at low pressures that are not relevant to natural environments. In these pre-Google times, we could not find documentation with a few mouse clicks but had to go to the library to search for relevant articles and xerox them. Isotopic fractionation was extensively studied in both its analytical and theoretical aspects, but the literature was generally not available since these studies were motivated by the development of nuclear weapons. It took me several weeks to find a study by a Russian group on isotopic separation in the gas phase at ambient pressure, published under the auspices of the United Nations (Gverdsiteli *et al.*, 1958). The process can operate at high pressure and the principle is simple. A current of steam (or any major gas) circulates along a porous tube in which external trace gases are competing between injection to the flow and retention by inter-atomic collisions within the main gas flowing in the tube. Light isotopes are retained better than heavy isotopes, resulting in an isotope fractionation whose extent depends on the reduced mass (see Marty, 1984, for definition) of the trace gas and the major gas. The effect of isotope fractionation differs from pure diffusive fractionation since it is not proportional to the inverse square root of the mass of the trace isotopes, but to the inverse square root of the reduced mass that also involves the mass of the major gas. Hence the extent of fractionation will depend on the nature of the major gas flowing in the tube. I could satisfactorily reproduce the isotope fractionations of neon and argon assuming the major gas was H₂O or CO₂. The natural process was attributed to a volcanic gas phase flowing through the soil in which atmospheric noble gases from soil pores are entrained by the uprising flow (Marty, 1984).

So I passed this first test but wanted to carry out analyses with the lab's noble gas mass spectrometer. There was only one noble gas mass spectrometer in the lab, for two scientists and four students, so getting machine time was challenging. I had a few shiny MORB glasses that had been given to me by Françoise Pineau at the IPGP and I wanted to measure their noble gas compositions. Among these samples was a so called "popping rock", a gas-rich sample from the Mid-Atlantic Ridge, so rich in gas bubbles that rocks on the deck of the dredging ship would jump due to decompression and gas-rich bubble explosion (this is not the well-known "popping rock" analysed later at the IPGP by Manuel Moreira; Moreira *et al.*, 1998). Finally, I got a few days of machine time



and I could extract gases by stepwise heating, a method consisting of incrementally heating the sample under vacuum and recovering extracted gases for analysis. The results were interesting and I quickly drafted a manuscript for *Nature*. I argued that two noble gas components existed in the sample, a result of mixing of a residual batch of magma which had interacted with the atmosphere and a new rising volatile-rich magma, whose gases had not equilibrated with those from the residual magma. It was not a breakthrough discovery, but original enough to be published rapidly (Marty *et al.*, 1983). My Japanese hosts were getting somewhat intrigued and I gained more access to lab facilities, though still restricted by the pressure of other scientists and Ph.D. students. I did more work on MORB glasses, analysed neon, argon and xenon isotopes, and was also seeking an opportunity to sample Japanese volcano gases and apply my $\text{CO}_2/{}^3\text{He}$ normalisation.

The lab's mass spectrometer was partly funded by another lab, the Earthquake Research Laboratory of the University of Tokyo headed by Professor Hiroshi Wakita. There, Yuji Sano, then a Ph.D. student, was successfully developing the helium isotope analysis of volcanic and geothermal fluids. They demonstrated the volcanic gas behaviour around Mt. Ontake volcano (Sano *et al.*, 1984) (which produced lethal phreatic explosions in 2014) and established a two dimensional map of He isotope ratios in Japan clearly showing the relationship between mantle helium isotope distribution and subduction (Sano and Wakita, 1985). I learned how to analyse the isotopic composition of helium with Yuji who generously and patiently dedicated plenty of his machine time to training me. Ozima managed to introduce me to Professor Sadao Matsuo, who opened to me his stable isotope laboratory at TokyoTech and invited me on his volcanic gas sampling missions. We went to Satsuma Iojima, south of Kyushu, a tiny island with only a few dozen people living there (who were very curious and amused to see a real gaijin other than on TV) and a small volcano with fumarolic temperatures above 800 °C. We spent five great days between two boats, lodging in a small ryokan (Japanese inn) and sampling gases on top of the volcano. We also went to Mt. Usu volcano in Hokkaido to sample high temperature gases. Later, I bought a motorbike that allowed me to sample other volcanic areas and gave me the pleasure of seeing another side of Japan, riding on small mountain roads and lodging in traditional inns with warm spring baths in small mountain villages. Many of these volcanoes had already been studied for He isotopes by Yuji so I had to find another research topic. I managed to measure the gas compositions at Matsuo's lab and the He isotopes with Yuji and obtained $\text{CO}_2/{}^3\text{He}$ values for several volcanoes in Japan. The results showed a large range of variation, in part due to interaction of volcanic gases with underlying aquifers, but volcanic gas $\text{CO}_2/{}^3\text{He}$ ratios were systematically higher than those of the MORB glasses I had brought with me from Paris. It was tempting to attribute the excess carbon dioxide (relative to mantle-derived ${}^3\text{He}$) in arc gases to the contribution of subducted carbon trapped as carbonates and organic C in the oceanic crust, but I did not have enough time left in Tokyo to develop this hypothesis further.





Figure 1.8

The Tokyo years. **Top left:** Winter view from my office. **Top right:** The Geophysical Institute, University of Tokyo, in the early eighties. **Bottom left:** Party with members of the Geophysical Institute in honor of Ed Anders and his wife. First row, on the left-hand side, Minoru Ozima. Left-hand side on the third row, bending: Ichiro Kaneoka. When I first came to Japan I had a thick moustache (bottom left), and sometime later I shaved it off (bottom right). The first day I came into the lab with my new look, people were somewhat worried, because in Japan the shaving of your hair can be associated with the taking of an important life decision. In this case however, my decision was purely an aesthetic one! **Bottom right:** International conference in Nikko where I met Igor Tolstikhin (second row, second from the left) and John Lupton (second row, first from the right) for the first time. In the centre of the first row, my colleague and friend Yuji Sano. Photo credit: B. Marty.

1.5 Back to France

I came back to France in 1984 to work in the geothermal energy department of the Bureau de Recherches Géologiques et Minières (BRGM, the French geological survey) which was interested in developing the isotope geochemistry of helium for its fluid applications. Oil was expensive and research for alternative energies was on the move. As member of the team of Christian Fouillac, head of the geochemistry group, we worked on scientific boreholes in the Cezallier province in the Massif Central. During field work, I met Keith O’Nions who was



professor at the University of Cambridge and running one of the few European noble gas labs. Keith was one of the internationally prominent geochemists of the same calibre as Claude Allègre and Al Hofmann in Mainz, Germany, during the golden age of mantle geochemistry. We had exciting chats about noble gases from the mantle and their relationship with major volatile species, and Keith invited me to come to his lab (Fig. 1.9). There I met several students and post-docs who would go on to become prominent geochemists, such as Chris Ballentine, Derek Vance, Dave Hilton, Kevin Burton, and others. A significant part of our time was spent in the bar of Clare College and in the nearby Eagle pub, forging links and friendship that still last today.



Figure 1.9 Helium analysis in Cambridge in Keith O'Nions' lab. **Left:** Keith and Jane, the lab secretary. **Right:** Discussing noble gases in the pub. Photo credit: B. Marty.

In 1985, the price of oil fell, geothermal research slowed as a consequence, and, as I was on a short term contract, I had to find another position. I was recruited by the Air Liquide company in 1986 to work in their research centre. Meanwhile I was encouraged by Francis Albarède to apply for a junior scientist position at the Centre National de la Recherche Scientifique (CNRS). So I was interviewed and, to my surprise, the committee offered to hire me. I spent an evening at a Montmartre café with a friend weighing the pros and the cons and decided to cut my salary in half in order to resume fundamental research at the CNRS. The following day, when I arrived at the Air Liquide campus, I told my boss that I had decided to quit. He understood because he himself came from the academic world, but the other executives did not approve, to say the least. I had to keep working for a few more days and, the next day, my boss arrived in my office holding, with a smile, the *Le Monde* newspaper asking me if I had read the news. I had not and discovered with dismay that the whole CNRS selection process for that year, for all disciplines, had been declared void due to some legal issues! Needless to say, if I had known of the cancellation the day before, I would have kept my mouth shut and might have spent my career working in industry.



There was, however, some hope that the unfortunate CNRS candidates could be hired the following year. After that, we spent some amazing holidays driving in the Sahara Desert, then went back to do some part time jobs, including starring as an extra in a movie shoot (of which I shall not give the title), and in September I was given a short term contract by the CNRS until the following year.

I started setting up a new noble gas lab with Albert Jambon, a newly hired professor at Université Pierre et Marie Curie in the Quartier Latin. Albert, an experienced petrologist and geochemist, had completed some seminal studies on the solubility and diffusivity of noble gases in molten silicates, and was as interested as I in the origin and behaviour of terrestrial volatiles. Claude Allègre's lab at the same Jussieu campus was just a few towers away from ours, but he did not attempt to stop us, either because he was favourably impressed (the wishful way of thinking) or because (more likely) we were not considered a threat. We had good working relations with Thomas Satudacher and Philippe Sarda from the IGP noble gas lab. I had time to develop a new noble gas system including a VG5400[®] mass spectrometer partly funded by an industrial partnership and worked to set up the analysis of nitrogen isotopes together with those of noble gases, continuing to visit the Cambridge lab from time to time to measure He isotopes.

1.6 Research at the CRPG, Nancy, France

In the early nineties a professorship opened up at the Ecole Nationale Supérieure de Géologie (ENSG) in Nancy as Francis Albarède moved from Nancy to the Ecole Normale Supérieure in Lyon. Research had to be carried out at the Centre de Recherches Pétrographiques et Géochimiques (CRPG) in Vandoeuvre-lès-Nancy and both the ENSG and the CRPG had excellent reputations in terms of both the quality of their students and cutting edge research. The French system is based on the so called Ecoles Nationales Supérieures, which are for the most part engineering schools which select students through an entrance examination after two or three years of intensive training in "Classes Préparatoires". After obtaining an engineering diploma most students turn to industry to work in the fields of energy, water management, or mining, but a few are attracted by fundamental research. The CRPG was at a turning point with some of its best scientists having departed, which left free space for newly hired young scientists like Marc Chaussidon, Etienne Deloule, Christian France-Lanord, Guy Libourel, and Laurie Reisberg (Fig. 1.10). A new large sector ion probe had been ordered, justifying the opening of a professorship in geochemistry. I was hired and we moved from Paris to Nancy in 1992. I started to teach fundamental geochemistry, which was not highly regarded at that time by the ENSG management as it was not considered to be "useful" engineering science. One of my graduate students was once told that if he wanted to be jobless, he should go into fundamental research (he is now professor at a leading US university). The state of mind at the ENSG fortunately has changed since then. The management



now values research accomplishments, and a Ph.D. is increasingly accepted as a valuable diploma by the French industry. Teaching fundamental geochemistry was an opportunity for me to get the few students interested in fundamental research hooked.



Figure 1.10 Left: Young CRPG scientists and students in the nineties. The photo was taken during a three-day seminar in the Vosges mountains focusing on xenology led by Igor Tolstikhin during his stay at the CRPG. First row, from left to right: Christian France-Lanord, Estelle Rose-Koga, Igor Tolstikhin, Laurie Reisberg, Jean Carignan. Second row: Anne-Catherine Pierson-Wickmann, myself, Marc Chaussidon, Albert Galy, Lena Tolstikhin, and Franck Humbert. Right: The CRPG building (recent photo). Bottom: Double Scotch live at EGU Vienna (2018). Photo credit: B. Marty, E. Rose-Koga.

Mantle geochemistry was already well developed, and the CRPG team was willing to develop new areas of research such as cosmochemistry, planetary sciences, or erosion/alteration and the geological cycle of carbon. Thus, the CRPG scientists were developing an up-to-date facility for the analysis of extra-terrestrial materials, Archean rocks, and alteration/erosion products focusing on the Himalayas, with an array of newly developed techniques, including the large sector ion probe Cameca 1270. A new low pressure, high temperature



experimental facility was developed to mimic conditions of the birth of the solar system, and new field work campaigns were launched in Nepal, Bangladesh, Ethiopia, and, of course, on active volcanoes.

A CRPG team of scientists and technicians (including Jean Carignan, Nathalie Vigier, Claire Rollion-Bard, Bruno Porcu) and I got together to form an in-house 'lab' rock band, calling ourselves first 'Big Bang', and later 'Double Scotch'. Double Scotch has played at several geochemistry and geoscience conferences, giving us the opportunity to play in front of large rock-fan audiences in Davos, Prague, Florence, Paris, and Vienna, and voiding my frustration of being only an amateur, as opposed to a professional, musician. At EGU in Vienna, I was particularly proud to wear a badge labelled "musician" instead of "geoscientist"! I will never be Brian May, but then I doubt he knows much about xenon isotopes. Just like any research team, the Double Scotch lineup has evolved over the years with the arrivals and departures of musician-geochemists at the lab like Reika Yokochi, Alice Williams, David Bekaert and, as a guest star, Nick Arndt. Besides these big rock star events, we continue to play in local bars and at thesis defense parties.

Thanks to the help of senior scientists in Nancy, I was able to raise funding rapidly for a new noble gas-nitrogen installation equipped with a GV5400[®] mass spectrometer and I greatly benefitted from the support of Laurent Zimmermann, a young engineer hired by the CNRS. The analytical system was partly funded by the oil company Total and by ANDRA, the French agency for nuclear waste. Consequently, I also worked on crustal fluids, which I had already done in Paris, and which was very interesting and scientifically rewarding (Marty *et al.*, 2003a). At the beginning of the 2000s, we had the chance to attract Pete Burnard to the noble gas lab. Pete was a geologist trained in noble gas geochemistry by Grenville Turner at Manchester University. We had already been in touch during the nineties as Pete had wanted to join our group at CRPG, but no positions were available at the time. He and his family therefore moved to Pasadena instead where Pete worked as a research scientist with Ken Farley at Caltech. At the beginning of the 2000s I was about to take on the directorship of the CRPG. John Ludden, who had directed the centre efficiently since 1995, was moving to Paris to become head of Earth Sciences at the CNRS. We requested an engineer position for the noble gas lab and Pete accepted the move from California to Lorraine with his family. His arrival permitted considerable expansion of the noble gas lab at the CRPG. Pete automatized the lines and we were able to order two mass spectrometer prototypes from the company GV Instruments (GVI), one with dual collection for helium isotopes, and the other with five collectors. Unfortunately, GVI went bankrupt and instead we received a kit to build the dual collection analyser ourselves, which Pete managed to do, and the resulting instrument is still being used for cosmogenic He measurements today. The second mass spectrometer was intended for analysis of other noble gases with improved precision at the per mille level, something that was not attainable with conventional, single collector noble gas mass spectrometers. However, its electron multipliers never worked properly and their efficiency faded away with



time. Consequently, we still use the instruments for analysing large noble gas using faraday detectors only. Later on, we received a complementary MC Plus[®] (Thermo-Fisher Co) mass spectrometer and, later again, we bought an MC SFT (Thermo-Fisher Co) and a Noblesse[®] (Nu Instruments) mass spectrometer. All instruments and related lines are functioning, thanks to the dedication of the noble gas lab scientists, technical staff, post-docs, and students, and, not the least, to the impetus of Pete.

Pete was a wonderful person and a great scientist always eager to help and undertake challenging projects. An accomplished and intrepid sportsman, he was also always looking for new adventures around the globe. He sadly passed away in a hang gliding accident in the Jura mountains in 2015, an event that left us heartbroken. His dedication to the training of young scientists is recognised by the Peter G. Burnard Award given annually to a promising early career scientist.



2. THE DUAL ORIGIN OF THE ATMOSPHERE AND THE OCEANS

The terrestrial atmosphere is a thin layer of gas (Fig. 2.1) which protects the surface of our planet from lethal interactions with outer space and permits the ambient temperature to be maintained between that of boiling water and ice. It is a nicely tuned system that has been autoregulating its composition and temperature for billions of years.



Figure 2.1 The atmosphere of the Earth and the Moon, photographed by the Expedition 28 crew aboard the International Space Station. The troposphere, the lowest and densest portion of the Earth's atmosphere, ends abruptly at the tropopause, which appears in the image as the sharp boundary between the orange and blue coloured atmosphere. Photo credit: NASA.

The volatile elements discussed here are those defined as atmophile elements by Viktor Moritz Goldschmidt. They include H, C, N, S, halogens, and noble gases. It is more appropriate to refer to them as the surface inventory of volatiles rather than the gaseous atmosphere *sensu stricto* since several of them are locked into liquid and solid reservoirs at the Earth's surface. In fact, hydrogen is mainly hosted by liquid water and halogens constitute the salinity of the oceans. Carbon is present in trace concentrations as atmospheric CO₂, but its main surface reservoir is locked into crustal rocks in the forms of carbonates and organic carbon. Nitrogen is mainly present as atmospheric N₂, but other N-bearing species are present in significant quantities in the biosphere and



as ammonium in crustal rocks. The main reservoir of noble gases by far is the atmosphere. Sulfur has a specific chemical speciation that makes it behave more like a non-volatile element and is not considered further.

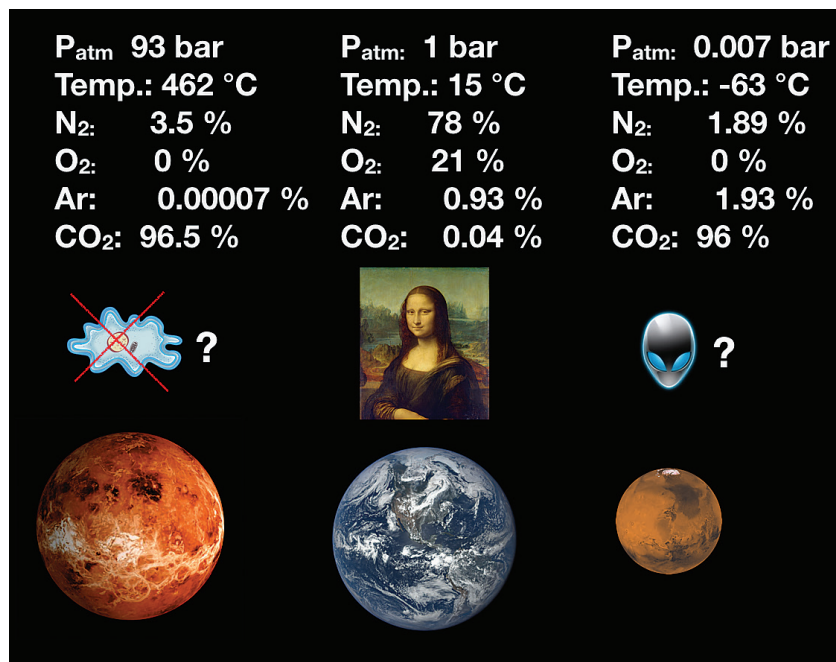


Figure 2.2

The atmospheres of Venus, Earth, and Mars. The atmosphere of Earth contains free oxygen as a result of biological activity, and most carbon is sequestered in surface rocks. If this C was converted to CO₂, the terrestrial atmosphere would have a CO₂/N₂ ratio similar to Venus and Mars, and atmospheric pressure and surface temperature comparable to those of Venus. Venus does not have oceans since water presumably escaped early in its history. The development of life on Venus may be impossible given its extreme environmental conditions, although the occurrence of phosphine in Venusian clouds that could sign biological activity has been reported (Greaves *et al.*, 2020). Life on Mars might have existed, possibly during the first hundreds of Myr when the atmosphere was denser than today. Photo credit: ESA, NASA, public domain.

The atmospheres of Venus, Earth, and Mars differ drastically both in their abundances and compositions (Fig. 2.2). The atmosphere of our planet is dominated by N₂, the next most abundant gas being O₂, which is secondary in origin as it is a by product of life. Argon, the third most abundant gas, is also secondary since it is dominated by ⁴⁰Ar, which is produced in the silicate Earth by the decay of ⁴⁰K ($t_{1/2} = 1.25$ Gyr) and degassed from the mantle and crust over time. As stated above, CO₂ is a trace gas (≥ 400 ppmv) in the atmosphere



with the majority of surface carbon residing in carbonates and organic matter. If the total surface carbon was released as CO_2 , the composition of the terrestrial atmosphere would have a C/N ratio comparable to that of Venus and Mars with an atmospheric pressure of ~100 bar. In fact, the atmospheric pressure would probably be even higher because the high temperature caused by a strong greenhouse effect would allow liquid water to vapourise. The Venusian atmosphere is poor in H_2O , presumably as a result of water loss early in its history. The reason why Venus and Earth evolved differently is not fully understood (Kasting, 1988).

Martian atmospheric pressure is two orders of magnitude lower than that of the Earth. The size of Mars should have allowed the planet to retain its atmosphere so non-thermal escape processes (*i.e.* independent of gravity, such as interactions with solar wind ions) have therefore been advocated to account for this depletion (McElroy *et al.*, 1976). The discrepancies between the atmospheres of the inner planets are partly linked to the respective origins of volatile elements, their different sizes and distances from the Sun, the intensities of their magnetic fields, tectonic activities, as well as the presence/absence of an active biosphere.

2.1 Historical Perspectives

The origin of the atmosphere and oceans has been a fundamental question since at least the Age of Antiquity. Many myths from different cultures seek to explain the origin of the atmosphere and oceans and a few are recalled here. According to Greek mythology, an original ocean surrounded the land. Its God, Okeanos, the elder of the Titans, was the son of Gaia, the Mother Earth, and of Uranos, who personified the sky, the firmament, and the spirit. Hence, the ocean was born from the mating of the sky and the Earth. In Japanese mythology, the god of the oceans was Ryūjin (龍神, dragon god). Interestingly, an ongoing mission, Hayabusa2 by the Japanese Space Agency (JAXA), is currently sampling a volatile-rich asteroid baptised Ryūgū (竜宮), the name of the palace where Ryūjin lived. The *Book of Genesis* (first book of the Hebrew Bible and the Christian Old Testament) describes the simultaneous creation of Heaven and Earth. James Usher (1581-1656), Archbishop of Armagh for the Church of Ireland, dated Earth's creation to the beginning of the night preceding the 23rd day of October, the year before Christ 4004, which, in the Julian calendar, would be around 6 p.m. on October 22, 4004 BC. In Christian mythology, the flood was a fundamental act that fixed the modern world (Richet, 2007).

Scientists and philosophers followed a different agenda. Anasthasius Kircher, a German Jesuit scholar (1602-1680), established various geological concepts and suspected that the Earth was much older than just a few thousand years. Travelling in southern Italy in 1638, he was impressed by active volcanoes and geothermal features. He suggested the existence of a subterranean ocean and hypothesised that the atmosphere and the oceans came from both the interior of the Earth and “celestial winds” (Fig. 2.3), a vision which is not too far from modern concepts.



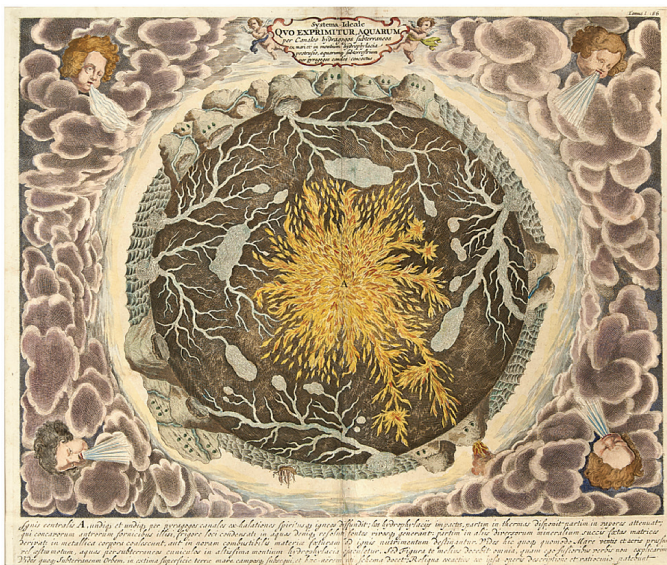


Figure 2.3

Athanasius Kircher (1602-1680). A great scholar, he published about 40 major works in the fields of comparative religion, medicine, theory of music, oriental language, and geology. During a trip to southern Italy, he became fascinated by volcanic and geothermal features. He imagined underground fire and water releasing volatiles to the atmosphere, as illustrated above in his book *Mundus Subterraneus* published in 1660. Credit: public domain.

In 1715, Edmund Halley noted that rivers contributed to the salinity of the oceans and, based on mass balance, suggested that the Earth might be much older than previously thought according to religious dogma. Longer chronologies were in agreement with geological observations such as those of Henri Gauthier in his book *Nouvelles Conjectures sur le Globe de la Terre* (1721) concerning the erosion rates required to form valleys. This approach was revisited on a quantitative basis by John Joly in 1899, who advocated a lower limit of ~100 Ma for the age of our planet based on ocean salinity and the time it may have taken to accumulate salts from river discharges. Other attempts at dating our planet and the Sun, based on the time required for surface cooling of a molten sphere, led to ages of a few 10^4 yr to several Myr. By the beginning of the 20th century, the discovery of radioactivity meant that these concepts were dismissed by providing an internal source of heat, and the U-Pb chronology of planetary objects finally permitted the age of solar system and planetary objects, including the Earth, to be established at 4.5 Ga (Patterson *et al.*, 1955).

By the end of the forties, the debate around the origin of the atmosphere and oceans focused on two possibilities: either the capture of nebular gas (the solar component; Signer and Suess, 1963), similar to the atmospheres of the giant



planets, or degassing of volatile elements trapped in Earth's building materials (the planetary component). The first possibility postulated the existence of an H₂-rich primary atmosphere, as seen around the giant planets. This primary atmosphere would have evolved to an N₂-rich atmosphere as found today due to chemical reactions. The second possibility required the accretion of planetary bodies rich in "secondary volatiles" as seen in meteorites. The first quantitative approach to this problem was carried out by Harrison Brown, a chemist at the University of Chicago, who demonstrated two important features from the analysis of atmospheric noble gases (Brown, 1949). First, the atmospheric noble gas pattern was not solar, being richer in heavy relative to light noble gases compared to the solar abundances (Fig. 2.4). This pattern instead resembled that of meteorites and, therefore, was designated "planetary". Second, atmospheric noble gases, when normalised to the mass of the Earth, are highly depleted relative to either solar or meteoritic compositions. Hence, the Earth appeared to be a volatile-depleted, "dry" planetary body compared to outer solar system planets. In this scenario, the atmosphere of the Earth was "secondary", *i.e.* formed by secondary accretion processes.

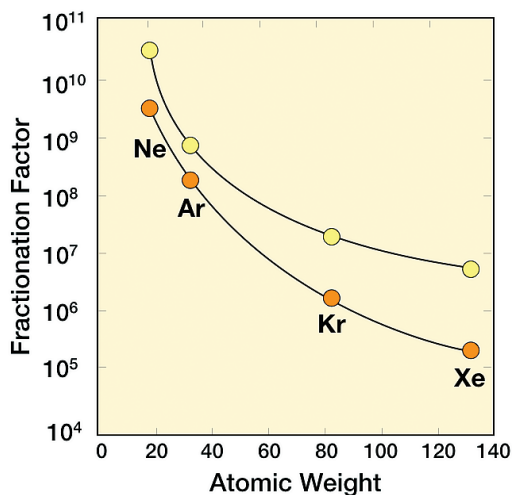


Figure 2.4

Elemental fractionation of noble gases in the terrestrial atmosphere (orange dots) and in the bulk Earth (yellow dots) compared to the cosmic abundance (redrawn from Brown, 1949). Elements are normalised to Si. The cosmic noble gas/Si ratio is divided by the noble gas/Si ratio of the terrestrial atmosphere of the bulk Earth (Si from the bulk Earth in both cases). The terrestrial atmosphere is depleted in noble gases by several orders of magnitude relative to the cosmic abundance. Furthermore, terrestrial noble gases are elementally fractionated compared to solar, *e.g.*, light noble gases are more depleted than heavy noble gases. Brown argued that the terrestrial atmosphere is not primary in origin similar to the giant planets which captured solar nebula gas.



In 1951, William W. Rubey, a geologist at the United States Geological Survey, published a seminal paper entitled “*The Geological History of Seawater*” (Rubey, 1951). He tested the possibility that the atmosphere and oceans could have resulted from the accumulation of volatile elements liberated by the erosion of rocks present at the Earth’s surface. He noted that the relative proportions of “atmospheric” volatiles (those contained in the oceans, atmosphere, and sedimentary rocks) were comparable to those found in igneous rocks, but very different from those of the solar nebula. He further noted that erosion and metamorphism of rocks at the planet’s surface could not supply enough volatile elements over all of Earth’s history, hence implying that other sources of volatiles were required, volcanism being an obvious candidate. Rubey had limited means at that time to test this model quantitatively but the study of noble gases in the present day mantle permitted a semi-quantitative approach. From ^{40}K - ^{40}Ar and ^{129}I - ^{129}Xe isotope systematics (Staudacher and Allègre, 1982; Allègre *et al.*, 1983; Sarda *et al.*, 1985) (Section 1), it became clear that terrestrial degassing could not be a continuous process and that some sort of “catastrophic” degassing event must have occurred during the first tens of Myr after the start of solar system formation. In the eighties this model of early terrestrial degassing of a secondary atmosphere prevailed, supported by discoveries made in Tokyo, Paris, and Berkeley. There were, however, a few observations that did not fit into this scenario. First, the isotopic composition of neon measured in mantle-derived rocks, such as MORB and OIB glasses analysed in Paris (Sarda *et al.*, 1988) and Canberra (Honda *et al.*, 1991), suggested the existence of more than one reservoir for terrestrial volatiles. Second, the systematics of xenon isotopes produced by extinct and extant radioactivities did not fit well with this single component, two reservoir model.

2.2 The Neon Alphabet: A key to Understanding the Origin of Terrestrial Volatiles

2.2.1 The three Ne isotope diagram

Neon is another noble gas with exceptional properties that allow the origin of terrestrial volatiles to be traced. It is not in itself a radiogenic system, although some of its isotopes are produced by nuclear reactions, and major information is derived from its stable isotopes. The relative abundances of its three isotopes, ^{20}Ne , ^{21}Ne , and ^{22}Ne , show large variations in nature. Reynolds and Turner (1964) were the first to develop the widely used Ne triple isotope diagram where $^{20}\text{Ne}/^{22}\text{Ne}$ ratios are plotted against the $^{21}\text{Ne}/^{22}\text{Ne}$ ratios. This format is convenient because data points for two-component mixtures lie along straight lines by construction (Fig. 2.5). What is important here is the nature of the end members. Because atmospheric contamination always affects the composition of mantle-derived noble gases, atmospheric Ne defines one of the end members ($^{20}\text{Ne}/^{22}\text{Ne} = 9.80$; Fig. 2.5). In 1976, Harmon Craig and John Lupton



reported excesses of ^{20}Ne , with $^{20}\text{Ne}/^{22}\text{Ne}$ ratios around 10.3, in volcanic gases from Kilauea, Hawaii, that could not be attributed to nuclear reactions in the mantle (Craig and Lupton, 1976). ^{21}Ne is produced in the mantle through time by known natural nuclear reactions. However, since no natural reaction produces significant amounts of ^{20}Ne , or destroys ^{22}Ne , in the mantle, the slight excess of ^{20}Ne was attributed to the occurrence of a new Ne component within the Earth. Alternatively, it could also have resulted from isotope fractionation, a naturally occurring kinetic process able to slightly modify the isotopic composition of natural gases (Nagao *et al.*, 1981; see Section 1). In the early eighties, Ozima and his group reported $^{20}\text{Ne}/^{22}\text{Ne}$ ratios higher than the atmospheric value, and submitted a letter to *Nature*, which was not accepted. Philippe Sarda, a graduate student of Claude Allègre, found excesses of ^{20}Ne and ^{21}Ne relative to ^{22}Ne in a suite of MORB samples, clearly showing the occurrence of a new Ne component (Sarda *et al.*, 1988). $^{21}\text{Ne}/^{22}\text{Ne}$ ratios higher than the atmospheric value were correctly attributed to nucleogenic ^{21}Ne produced in the mantle over time by the reactions $^{24}\text{Mg}[\text{n},\alpha]^{21}\text{Ne}$ and $^{18}\text{O}[\alpha,\text{n}]^{21}\text{Ne}$ (Wetherill, 1954), while excesses of ^{20}Ne were attributed to a solar Ne component contribution to the mantle source of MORB (Sarda *et al.*, 1988).

In 1964, Craig Merrihue measured high $^3\text{He}/^4\text{He} \geq 10^{-4}$ in red clays from the Pacific Ocean. Such high ratios cannot be of terrestrial origin, and rather characterise meteoritic/cometary material irradiated by solar winds. He concluded that oceanic sediments are accumulating fine extraterrestrial particles (Merrihue, 1964), a result confirmed by Ozima *et al.* (1984). These particles were identified and labelled Interplanetary Dust Particles (IDP) (Brownlee, 1985). Because they are tiny (typically a few microns), IDPs do not completely melt upon entry in the atmosphere. Instead, they degas, continuously “snowing” on Earth’s surface, and constitute the largest flux of extraterrestrial material to Earth, on the order of 10^4 tons/yr (Brownlee, 1985). Subduction of oceanic crust loaded with IDPs could introduce solar-like neon into the mantle and account for the high $^{20}\text{Ne}/^{22}\text{Ne}$ component (Sarda *et al.*, 1988). However, this suggestion faced two difficulties: (i) neon can readily diffuse out of submicron particles during subduction metamorphism, preventing Ne from entering the mantle; and (ii) mass balance considerations suggested that the amount of potentially subducted Ne was quantitatively too small to account for solar-like mantle Ne (Hiyagon, 1994). While in Japan, I analysed Ne isotopes together with those of other noble gases in the few MORB glasses I had brought with me from Paris and also observed high $^{20}\text{Ne}/^{22}\text{Ne}$ ratios. Together with information from Xe isotope data (see below), I argued that two cosmochemical sources supplied volatiles to Earth, which breached the canonical model of early mantle degassing being the origin of the oceans and atmosphere (Marty, 1989). In 1991, Masahiko Honda, a former student of Minoru Ozima and then a post-doc with Ian McDougall, professor at the Australian National University in Canberra, published Ne isotope data for the Hawaiian mantle plume, which also showed excesses of ^{20}Ne and ^{21}Ne . They suggested that solar neon is still trapped in the deep mantle sourcing the Hawaiian plume (Honda *et al.*, 1991). Furthermore, the Hawaiian data defined a



mixing correlation which differed from that of MORB in having a steeper slope, confirmed by further analyses of other mantle plume material (Fig. 2.5). The slope of a given isotope correlation relates to the $^{20}\text{Ne}/^{21}\text{Ne}$ ratio of the mantle source, where ^{20}Ne is primordial and ^{21}Ne has been produced by time dependent reactions. Therefore, the value of the slope depends on the amount of primordial gas in a given mantle reservoir and gives an indication on the degassing state of this reservoir, as does the $^3\text{He}/^4\text{He}$ ratio. Reservoirs that have suffered little degassing will have a mantle end member closer to the solar value than that of a degassed reservoir, resulting in a steeper slope of the former compared to the latter (Fig. 2.5). Neon isotopes therefore fully confirm the observation from helium isotopes that some regions of the mantle are less degassed (contain more primordial isotopes) than those feeding mid-ocean ridges.

2.2.2 Which solar neon component?

The occurrence of solar-like neon in the mantle, and the different Ne isotope correlations of mid-ocean ridge basalts derived from the convecting mantle and ocean island basalts sampling deep mantle sources, were successfully confirmed by subsequent studies (Fig. 2.5) (Moreira *et al.*, 1998; Yokochi and Marty, 2004; Mukhopadhyay, 2012; Péron *et al.*, 2019; Williams and Mukhopadhyay, 2019). However, an important question with far reaching implications remains: what is the exact composition of mantle Ne (Fig. 2.5) and what is its origin?

Solar material cannot be collected directly on the solar surface but the Sun emits solar wind (SW) ions that can be sampled from a distance. Solar wind ions originate in the Sun's upper atmosphere and are accelerated by the solar magnetic field to velocities of typically ~400-800 km/s, depending on the solar activity regime (Wiens *et al.*, 2004). The first successful attempt to collect SW ions was carried out by the Apollo 11 astronauts. A nicely thought out experiment designed by Johannes Geiss's group at the University of Bern (Switzerland) consisted of unfolding a pure aluminum foil screen as soon as possible after lunar landing, exposing it to the Sun for a few hours to a few days depending on the mission, and returning it to Earth for laboratory analysis (Geiss *et al.*, 2004, and references therein, see Fig. 5.1). One of the first things Neil Armstrong did after exiting the Lunar Excursion Module was to plant a pole stretching the Al-coated foil, which was then irradiated for 77 min. The results of the SW exposure experiments and those of the subsequent analysis of lunar soils were amazing: from measurements of solar wind D/H and $^3\text{He}/^4\text{He}$ ratios, Geiss and Reeves (1972) demonstrated that the solar nebula D/H ratio was much lower than the ocean value, prohibiting a genetic link between the solar nebula and terrestrial volatiles (see Wieler, 2016). During this limited Apollo 11 exposure experiment, enough implanted SW neon was collected to measure a $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of 13.5 ± 0.6 (Geiss *et al.*, 1970), clearly different from the atmospheric composition (9.80). More precise values were obtained from longer exposure times during subsequent Apollo missions and from the NASA Genesis spacecraft which collected SW ions for 27 months on a pure target material ($^{20}\text{Ne}/^{22}\text{Ne} = 13.78 \pm 0.03$; Heber *et al.*, 2009).



More than 99 % of solar system material is concentrated in the Sun, which makes our star the best sample of the solar nebula from which the planets formed. However, the process of acceleration of SW ions fractionates the abundances and isotopes of solar photospheric elements, rendering the composition of the solar wind markedly different from that of the Sun. Fortunately, the Genesis experiment was carefully designed to sequentially collect SW ions with different velocities corresponding to different regimes of solar activity (Wiens *et al.*, 2004). The extent of SW isotope fractionation depends on the energy of solar events, and Ne isotope data for different events have allowed the $^{20}\text{Ne}/^{22}\text{Ne}$ ratio of solar Ne to be estimated by extrapolation to a value of 13.36 ± 0.10 (Heber *et al.*, 2012). This value is considered to be representative of the ambient nebular gas during Earth formation (Fig. 2.5).

Another solar Ne component was identified in lunar soils and gas-rich meteorites and named Ne-B ($^{20}\text{Ne}/^{22}\text{Ne} = 12.5 \pm 0.2$; Black and Pepin, 1969). It is also of solar wind origin, but its isotopic composition is fractionated relative to that of SW. The velocities of SW ions are equal and heavier ions have higher kinetic energies (of the order of ~ 1 KeV/u) than lighter ions, which leads to their implantation at greater depth (typically ~ 10 -30 nm). Erosion of the outer layer of the grains by impacting material or corpuscular irradiation light ions (preferentially distributed close to the surface) and, in a steady state, lunar and asteroidal soil particles are therefore enriched in ^{22}Ne relative to ^{20}Ne . Mid-ocean ridge basalt glass analysis shows that their $^{20}\text{Ne}/^{22}\text{Ne}$ ratios present an upper limit consistent with the Ne-B value (Moreira *et al.*, 1998; Péron *et al.*, 2019). Hence several authors have proposed that solar neon was incorporated into the forming Earth as dust loaded with solar gases (Trieloff and Kunz, 2005; Ballentine *et al.*, 2005; Moreira, 2013; Moreira and Charnoz, 2016; Fig. 2.5, bottom right). In their view, particles embedded in the cloud of gas and dust forming the solar nebula were irradiated by solar wind ions emitted by the active young Sun in nebular gas-free regions. Subsequent dust compaction and incorporation into growing planetesimals that then accreted to form the Earth provided solar neon to the mantle, consistent with numerical modelling of the disk evolution (Moreira and Charnoz, 2016).

However, some of the $^{20}\text{Ne}/^{22}\text{Ne}$ data for mantle-derived samples showed values higher than Ne-B, suggesting the occurrence of another solar Ne component in the mantle (Fig. 2.5). Precise measurement of Ne isotopes in neon-poor samples is always a difficult exercise but with accumulation of data it became clear that values higher than 12.5 were not due to an experimental artefact. Neon isotopes could also fractionate in natural systems, but other noble gas isotopic compositions measured together with Ne did not show evidence for this (Yokochi and Marty, 2004; Mukhopadhyay, 2012; Williams and Mukhopadhyay, 2019). It is also possible than the Ne-B value is not unique and that the range of $^{20}\text{Ne}/^{22}\text{Ne}$ ratios for irradiated dust could go up to 12.75 (Moreira and Charnoz, 2016), not very far from the inferred proto-solar nebula value of 13.4 ± 0.2 (Fig. 2.5). Nevertheless, multiple high $^{20}\text{Ne}/^{22}\text{Ne}$ data have been acquired to date and, remarkably, they are all related to mantle plumes with high $^3\text{He}/^4\text{He}$ ratios



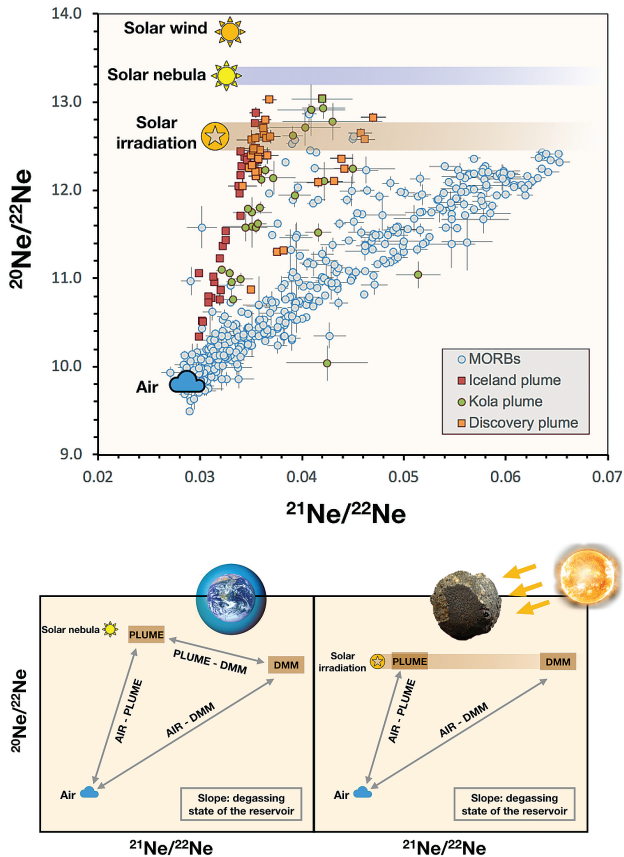


Figure 2.5

Top: Neon isotope data of mid-ocean ridge basalts (MORB) and mantle plume samples. MORB data from compilation by M. Moreira (personal communication), Icelandic subglacial glasses from Mukhopadhyay (2012), Kola mantle plume carbonatites from Yokochi and Marty (2004), and submarine glasses from the Discovery plume area from Williams and Mukhopadhyay (2019). The solar wind value was measured on the Moon and more recently in solar wind ions collected by the Genesis mission (Heber *et al.*, 2009). The solar nebula value is inferred from the composition of the Sun, corrected for isotope fractionation during solar wind generation (Heber *et al.*, 2012). The solar irradiation value represents the end member value found in lunar soils and solar gas-rich meteorites. It is fractionated relative to solar wind by soil processing on the Moon and on asteroids. In this isotope format, two component mixing yields straight lines. In both cases the arrays defined by sample data result from mixing between the composition of atmospheric neon contaminating the samples and a mantle end member composition. The slopes of correlations relate to the degassing state of the respective mantle reservoirs. The single array defined by MORB worldwide indicates efficient mantle



homogenisation of the convecting mantle (DMM: Depleted MORB Mantle). **Bottom:** Two interpretations of the Ne isotope data. **Bottom left:** The solar end member is defined by the inferred composition of the solar nebula. A primary atmosphere of nebular composition surrounded the proto-Earth and nebular gases were dissolved in silicates during magma ocean stages (Yokochi and Marty, 2004; Williams and Mukhopadhyay, 2019). **Bottom right:** Mantle end member values are consistent with solar-like neon from the contribution of dust irradiated in the early solar system (Moreira and Charnoz, 2016, and references therein). The different DMM end member value could result from either a heterogeneous Ne contribution (Ballentine *et al.*, 2005) or mixing between different mantle components (Williams and Mukhopadhyay, 2019).

sourced in the less degassed deep mantle, and not in the convecting mantle associated with MORB (Fig. 2.5). The highest $^{20}\text{Ne}/^{22}\text{Ne}$ ratios ever measured are similar (within errors) to the inferred proto-solar nebula value. Yokochi and Marty (2004), Mukhopadhyay (2012), and Williams and Mukhopadhyay (2019) proposed that solar Ne was incorporated into the growing Earth by dissolution of a nebular-like, primary atmosphere into the proto-Earth or planetary embryos. This possibility, already advocated by Sasaki (1990) based on modelling, is supported by the inference drawn from other stellar systems that the lifetime of the nebular gas present in the early solar system was probably of the order of a few Myr (Podosek and Cassen, 1994). During this time interval differentiated Mars-sized planetary embryos were already present (Dauphas and Pourmand, 2011) and the retention of a H_2 -rich nebular atmosphere could have occurred for embryos with diameters over a few thousand km (Sasaki, 1990). Growing embryos were partially molten as a result of highly energetic events such as collisions or enhanced greenhouse effects, allowing dissolution of nebular-like gases into molten silicates at high atmospheric pressure (Sasaki, 1990; Yokochi and Marty, 2004). Dissolution of solar neon as now observed in the mantle plume source would have required moderate atmospheric pressure from ~ 10 bar (Marty and Yokochi, 2006) to ~ 100 bar (Porcelli *et al.*, 2001). Hence the proto-Earth might have resembled a small Jupiter, since Jupiter-like exoplanets are observed very close to the central stars (Brucalassi *et al.*, 2016). The presence of solar xenon in the Martian mantle, as sampled by the Chassigny meteorite (Ott, 1988), is in line with the formation of the Red Planet in a short time interval when the solar nebula was still present. This primary-like atmosphere would have been cleared by enhanced activity of the young Sun as it entered the T-Tauri stage.

The two models presented above for the origin of terrestrial Ne are not mutually exclusive, and one could consider a hybrid origin for noble gases. Solar nebula-like neon was trapped in what is now the deep mantle when the proto-Earth was embryo-sized. Solar wind-like gases, which now dominate the mantle source of MORB, were supplied later when the solar nebula dissipated, with SW irradiated material predominantly contributing to the growing Earth (Ballentine *et al.*, 2005). This possibility would however require specific processes for the contribution of extraterrestrial material to the proto-Earth, because during its late stages of accretion, large bodies rather than dust might have added volatile elements to the proto-Earth (Morbidelli *et al.*, 2000). Resolving



this important planetary science problem will require higher-precision data for mantle-derived neon, which will be provided by a new generation of noble gas mass spectrometers.

The case of major volatiles (H, C, N) is different from that of light noble gases and will be discussed in the following Sections. Although solar Ne is now well documented in the mantle, other volatile species mainly originate from asteroidal sources. The Sun is rich in He and Ne compared to planetary solids (meteorites, inner planets) and so a binary mixing between a solar and a planetary component will result in the solar contribution mostly impacting the light noble gas budget, whereas planetary sources still dominate other volatiles.

Regardless of the ultimate origin of solar neon in the mantle, these studies have confirmed that atmospheric neon ($^{20}\text{Ne}/^{22}\text{Ne} = 9.80$) has an isotopic composition drastically different from that of mantle neon ($^{20}\text{Ne}/^{22}\text{Ne} \geq 12.5$). In terms of stable isotope notation, this corresponds to a ^{20}Ne enrichment of ≥ 275 ‰ in the mantle relative to the atmosphere, which, given its magnitude, cannot be easily explained by stable isotope fractionation in magmatic systems. In the framework of atmosphere formation by mantle degassing, this dichotomy would require extreme isotope fractionation of atmospheric Ne. Hydrodynamic escape of the early atmosphere, a process in which massive loss of hydrogen drags heavier elements and causes their escape to space, could have severely depleted light noble gases and fractionated their isotopes in favour of the heavy ones (e.g., Hunten *et al.*, 1987). This possibility is however not consistent with the elemental/isotopic abundances of neon and argon (Marty, 2012), nor with the fact that Xe is isotopically fractionated relative to planetary precursors whereas Kr is not (see next section).

2.3 The Paradoxes of Xenon

Zeno of Elea (490-430 BC) was a Greek philosopher best known for having developed several paradoxes, such as the arrow and the target. He imagined that during a sufficiently small interval of time, an arrow would appear immobile. Adding a series of such small intervals will result in an immobile arrow which will not be able to reach the target. As such, he was the precursor of the concept of infinity in mathematics. He might have also thought about other paradoxes pertaining to xenon if he had known about the mysteries of its isotopes. Xenology (Staudacher and Allègre, 1982), the art of playing with Xe isotopes, is often perceived as too complicated and too model dependent to be usable in practice. At international conferences, I have noticed quite often that, just before a talk on xenon starts, the attendance in the room becomes sparse. It has, however, its circle of aficionados worldwide, and recent advances in this discipline have led to insightful constraints not only on the origin(s) of planetary volatiles but also on atmospheric and mantle evolution during the first billion years of Earth history. I do not think that the prejudice about xenology is justified because its apparent complexity can be simplified if we consider that it is as a multi-radiogenic system



combined with stable isotope systems in which isotope abundances can vary according to mass dependent laws. These two aspects can be disentangled by a step by step approach.

Stable isotope fractionation offers unique information about escape processes of planetary atmospheres and the evolution of the terrestrial atmosphere (Sections 1 and 8). It can be identified and corrected for with the light Xe isotopes (^{124}Xe , ^{126}Xe , ^{128}Xe , ^{130}Xe) which are not produced by radioactive decay. Besides this, xenon has three built up chronometers. Some Xe isotopes are produced by three independent decay reactions whose half lives cover key periods of time: Earth's formation by the decay of ^{129}I to ^{129}Xe with a half life of 16 Myr (see Section 1); the Hadean eon by the fission of ^{244}Pu to produce heavy Xe isotopes with a half life of 82 Myr; and the whole of Earth history by the fission of ^{238}U ($T_{1/2} = 4.47$ Gyr), which is still extant at present (Fig. 2.6).

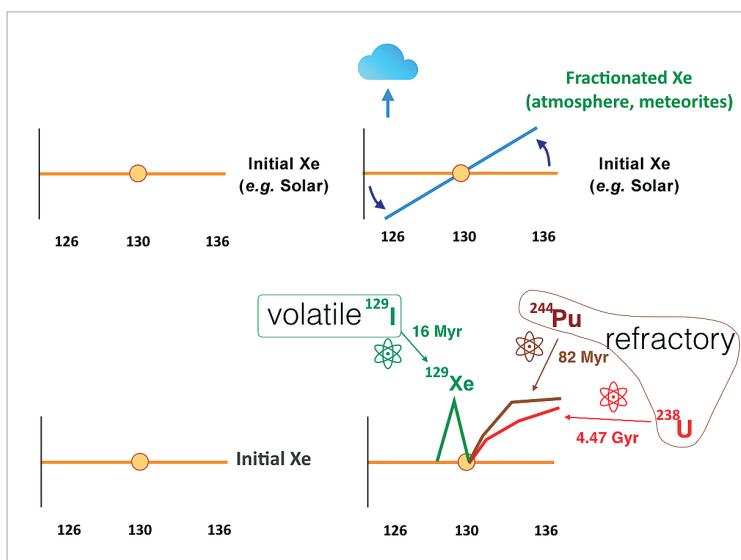


Figure 2.6

Principles of xenology. Xenon has nine isotopes (see Fig. 1.3; only three are represented here including ^{130}Xe used for normalisation) that can be isotopically fractionated like any stable isotope system. It requires physical, not chemical, processes since Xe is chemically inert. For example, planetary atmosphere escape can fractionate the isotopes of noble gases, including Xe, in favour of light isotopes under specific conditions. In addition to stable isotope fractionation, three radioactivities produce Xe isotopes. ^{129}I with a half life of 16 Myr was present when the solar system formed and produced ^{129}Xe . This radioactive production is easy to detect and identify as it forms a monoisotopic excess at mass 129. ^{244}Pu with a half life of 82 Myr was also present at that time and produced ^{131}Xe , ^{132}Xe , ^{134}Xe , and ^{136}Xe by spontaneous fission. The same isotopes were produced by the spontaneous fission of ^{238}U with a half life of 4.47 Gyr. These two latter radioactivities are more

difficult to quantify since they both produce the same isotopes and because mass dependent fractionation also can produce excesses of these isotopes. This effect can be corrected for with the light Xe isotopes not produced by radioactivity (^{124}Xe , ^{126}Xe , ^{128}Xe , and ^{130}Xe). The contributions of ^{244}Pu and ^{238}U to the heavy Xe isotopes can be disentangled with precise measurements since their fission spectra differ. These three radioactivities are advantageous in that they cover three distinct periods of terrestrial evolution: (i) the nebular accretion period (decay of ^{129}I); (ii) the Archean eon (fission of ^{244}Pu); and (iii) the whole of Earth history (fission of ^{238}U). Another interesting property is that parent iodine-129 is volatile, whereas parents ^{244}Pu and ^{238}U are refractory. This difference in behaviour can provide information about the nature of accreting bodies.

2.3.1 The first paradox of xenon: The “missing Xe” problem

The xenon isotopic composition of air is highly fractionated by 3.5 % *per* atomic mass unit (u) compared to any cosmochemical component (Section 1, Fig. 1.6). Such a huge fractionation could have happened during atmospheric escape, which favours light isotopes (*e.g.*, ^{126}Xe) relative to heavy isotopes (*e.g.*, ^{136}Xe), and hence would have left the atmosphere depleted in light Xe isotopes as observed. The paradox is that krypton, which is elementally lighter than Xe, is much less isotopically fractionated, even though it should have been more affected by mass dependent escape processes than xenon. Furthermore, as an element, Xe is depleted relative to the other noble gases (*e.g.*, Kr, Fig. 2.7), contrary to what would be expected if atmospheric escape were responsible for Xe depletion and isotopic fractionation. Escape processes of planetary atmospheres are generally attributed to the so called thermal, or Jeans, escape in which light gases are less gravitationally bound to planets than heavy gases. Atmospheric gaseous species also can be entrained by escaping hydrogen atoms during so called hydrodynamic escape, again preferentially affecting light species (Hunten *et al.*, 1987). Neither of these two processes would have been able to fractionate only xenon without also affecting the other noble gases.

In order to solve this paradox, several models have been developed in which mainly xenon escaped from the proto-Earth, becoming elementally depleted and isotopically fractionated (Pepin, 2000; Tolstikhin and O’Nions, 1994; Shcheka and Keppler, 2012; Dauphas, 2003). The other noble gases would have been locked into the proto-Earth and subsequently released, either due to differential solubilities in molten silicates (Pepin, 2000; Tolstikhin and O’Nions, 1994) or to selective melt/mineral partitioning (Shcheka and Keppler, 2012). In another model, noble gases were contributed by cometary bodies which, being poor in Xe, did not impact the reserve of residual Xe (Dauphas, 2003). These models are somewhat *ad hoc* because they require fine tuning of a specific sequence of events. Furthermore, they could not account for Martian Xe which presents similarities with terrestrial atmospheric Xe in terms of both elemental depletion and isotopic fractionation. In yet other models, xenon “missing” from the atmosphere is still sequestered in the solid Earth due to its affinity with silicates



(Leroy *et al.*, 2018) or metal (Zhu *et al.*, 2014) at high pressures. These possibilities need, however, to account for atmospheric Xe isotopic fractionation and the similarities of terrestrial and Martian xenon, since these two planets have drastically different characteristics in terms of mass, core volume, and chemical composition.

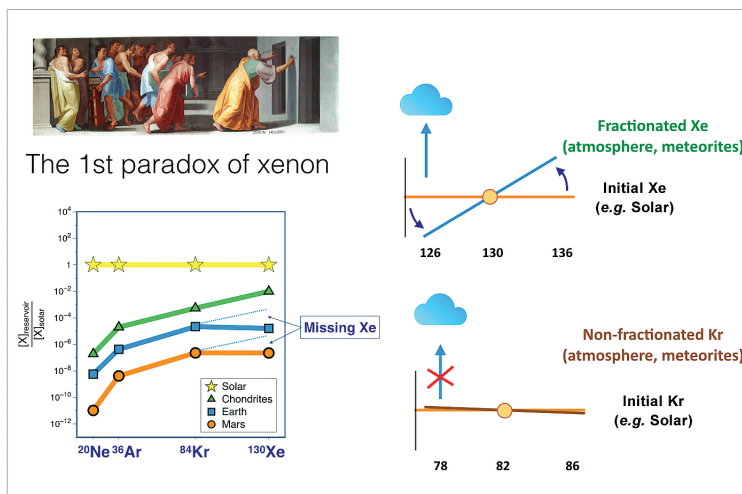


Figure 2.7

As an element, atmospheric xenon is depleted relative to other noble gases (e.g., krypton) when compared to primitive material in the solar system such as chondrites (left). The chondritic pattern resulted from better incorporation/retention of the light noble gases in solids compared to the heavy noble gases. Isotopically, xenon is depleted in light compared to heavy isotopes, a feature that could have resulted from atmospheric escape. However, xenon, which is heavier than krypton, is depleted relative to Kr and is isotopically fractionated while Kr is not. This difference constitutes the first xenon paradox. Interestingly, Martian atmospheric xenon is also depleted and isotopically fractionated (not shown) similar to terrestrial atmospheric Xe. This resemblance suggests a common process for Xe depletion and isotopic fractionation for both planets despite their different gravities. Illustration: Zeno showing the doors of Truth and Falsity (*Veritas et Falsitas*). Fresco in the library of El Escorial, Madrid. Credit: public domain.

Recently, our group may have found a clue to solve the missing xenon problem. Magali Pujol and Guillaume Avice, former Ph.D. students at CRPG, analysed palaeo-atmospheric noble gases trapped in fluid inclusions in a series of Archean and Proterozoic hydrothermal quartz samples (see Section 8). Archean atmospheric Xe was found to be isotopically intermediate between the presumed cosmochemical ancestor of terrestrial Xe and modern atmospheric Xe (Pujol *et al.*, 2011), whereas the other palaeo-atmospheric noble gases were not isotopically fractionated. The degree of isotopic fractionation of atmospheric Xe

relative its ancestor increased with time, reaching the modern value at around 2 Ga and remaining the same until present (Avice *et al.*, 2018a). This strongly suggests that isotopic fractionation of xenon was not exclusively an early Earth process, but lasted for about 2 Gyr. We hypothesised that the preferential escape of xenon resulted from its preferential ionisation compared to other atmospheric gases by far-ultraviolet light from the young Sun (Hébrard and Marty, 2014; Zahnle *et al.*, 2019). This process, which requires an external cause (*i.e.* solar irradiation of atmospheres), has the advantage of being applicable to other planets like Mars (Section 8). In addition, we have also recently interpreted data from the analysis of the coma of 67P/Churyumov-Gerasimenko to argue that comets could have made a modest, but significant, contribution to terrestrial noble gases (Marty *et al.*, 2017; Section 7).

2.3.2 The second paradox of xenon

As discussed in Section 1, ^{129}Xe was produced by the extinct radioactivity of ^{129}I ($T_{1/2} = 16$ Myr), implying that any difference in the $^{129}\text{Xe}/i\text{Xe}$ ratio (where $i\text{Xe}$ is a stable isotope of xenon used for normalisation, generally ^{130}Xe) between terrestrial reservoirs happened early in Earth's history, within the first few tens of Myr. There is another interesting xenon puzzle. The heavy isotopes of xenon, $^{131-136}\text{Xe}$, are also produced by two nuclear reactions, namely the fission of ^{238}U ($T_{1/2} = 4.47$ Gyr) and the fission of extinct ^{244}Pu ($T_{1/2} = 82$ Myr). The two fission spectra are slightly different and can be disentangled with sufficient analytical precision. Hence the Xe system comprises three nuclear schemes, two extinct radioactive decays (^{129}I : 16 Myr, and ^{244}Pu : 82 Myr) and one long lived radioactive decay (^{238}U : 4.47 Gyr). This plurality of potential chronometers has made xenon a tracer of choice for dating events that occurred in the early Solar system. During my early Tokyo years, I obtained some Xe isotope data having ^{129}Xe excesses and used the following reasoning to show that the atmosphere could not derive exclusively from the mantle (Fig. 2.8). In a given reservoir with fixed $^{244}\text{Pu}/^{129}\text{I}$, the ratio between a heavy Xe isotope, say $^{136}\text{Xe}_{\text{Pu}}$, produced by the fission of ^{244}Pu , and $^{129}\text{Xe}_{\text{I}}$, produced by the decay of ^{129}I , would decrease rapidly during the first tens of Myr given that $^{129}\text{Xe}_{\text{I}}$ would be produced at a faster rate than $^{136}\text{Xe}_{\text{Pu}}$. The $^{136}\text{Xe}_{\text{Pu}}/^{129}\text{Xe}_{\text{I}}$ ratio can be estimated for the atmosphere, after correction for the long term contribution of ^{238}U to ^{136}Xe , obtained from the amount of radiogenic ^{40}Ar in the atmosphere and the $^{40}\text{Ar}/^{136}\text{Xe}_{\text{U}}$ production ratio. Similarly, the corrected $^{136}\text{Xe}_{\text{Pu}}/^{129}\text{Xe}_{\text{I}}$ ratio can be estimated for the mantle from MORB data, and it transpires that the atmospheric $^{136}\text{Xe}_{\text{Pu}}/^{129}\text{Xe}_{\text{I}}$ ratio is higher than the actual mantle ratio (Fig. 2.8). This would therefore imply that the mantle degassed after the atmosphere was formed, which contradicts the classical model of atmospheric degassing from the mantle. This simple mass balance led me to conclude, in agreement with neon isotope systematics, that several sources of terrestrial volatiles are required, having not only different Ne isotope compositions, but also different refractory (plutonium)/volatile (iodine) ratios (Marty, 1989). Interestingly, another solution to this paradox would be



that some ^{129}Xe -rich material was added to the surface after the mantle became closed to extraterrestrial contributions and the new cometary data from the Rosetta mission seem to support this possibility (Section 7).

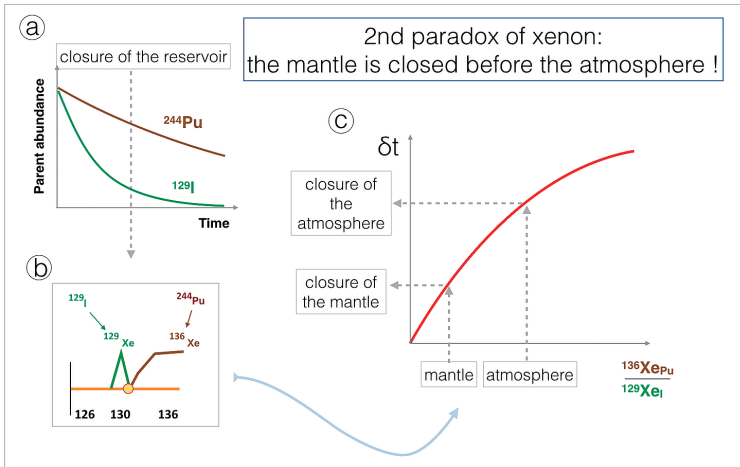


Figure 2.8

The paradox of atmospheric degassing from the mantle. In the classical model, atmospheric volatiles were degassed from the mantle during early episodes of Earth's evolution. This possibility is tested here with the extinct radioactive decay of ^{129}I and ^{244}Pu producing ^{129}Xe and $^{131}\text{-}^{136}\text{Xe}_{\text{Pu}}$ isotopes, respectively (here $^{136}\text{Xe}_{\text{Pu}}$ represents the latter). The parent abundances decrease with different half lives. (a) When a given reservoir stops losing its volatiles, including xenon (reservoir closure), residual ^{129}I and ^{244}Pu produce Xe isotopes in proportions depending on the time of closure. (b) The ratio between these radioactivity products, here $\frac{^{136}\text{Xe}_{\text{Pu}}}{^{129}\text{Xe}_{\text{I}}}$, depends on the time of closure. This ratio can be estimated from Xe isotopic measurements of the mantle and the atmosphere with relevant geochemical parameters, and the respective times can be computed accordingly. (c) The paradox is that the mantle became closed before the atmosphere, in contradiction to the classical model with atmospheric volatiles derived from mantle degassing. Therefore, either atmospheric volatiles and mantle volatiles were derived from sources with different Pu/I ratios, or atmospheric volatiles have a different origin from mantle volatiles, or both. The classical model does not hold and terrestrial volatiles require different cosmochemical sources, in qualitative agreement with neon isotope systematics (Fig. 2.5).

2.3.3 The third paradox of xenon indicates heterogeneous accretion of the Earth

The reservoir closure approach can be extended to the different domains of the mantle. Mid-ocean ridge basalts and continental CO_2 -rich gases are sourced by the homogenous convecting mantle which has a near constant $^3\text{He}/^4\text{He}$ ratio. In contrast, some of the mantle plumes presenting high $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^{21}\text{Ne}$



values originate from presumably deeper regions in the mantle that have experienced less degassing and therefore must have been decoupled from mantle convection. To apply the closure approach to the mantle, it is necessary to identify the respective contributions of extinct radioactivities to Xe isotopes, which is challenging for noble gas-poor, mantle-derived samples (Kunz *et al.*, 1998; Moreira *et al.*, 1998; Yokochi and Marty, 2005). Sujoy Mukhopadhyay and his group at the University of California in Davis pioneered a new area of research by drastically improving the precision of noble gas isotopic measurements in mantle-derived rocks (Parai and Mukhopadhyay, 2015; Mukhopadhyay, 2012). As a result, they could clearly quantify the Xe isotope contributions from ^{244}Pu and ^{238}U . These data were supplemented by CO_2 -rich continental gas data for which high precision can also be statistically obtained by duplicating noble gas analyses (Holland and Ballentine, 2006; Bekaert *et al.*, 2019). It was concluded that the convecting mantle and the plume mantle have different $^{136}\text{Xe}_{\text{Pu}}/^{129}\text{Xe}_{\text{U}}$ ratios (<0.1 and >0.8, respectively) which, when converted to reservoir closure chronology, would imply that the convecting mantle became closed for volatile degassing before the deep mantle (Fig. 2.9).

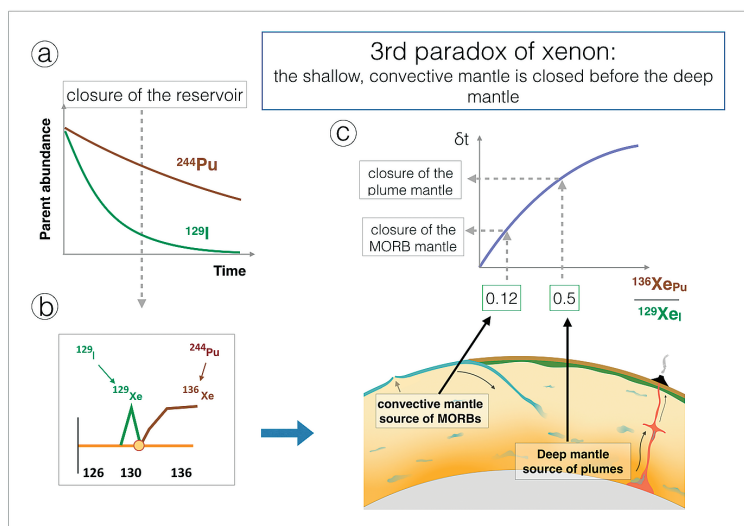


Figure 2.9

The paradox of mantle xenon. (a) and (b), same format as in Figure 2.8. Precise analysis of Xe isotopes in MORB (Parai and Mukhopadhyay, 2015) and mantle plume materials (Mukhopadhyay, 2012) permitted the $^{136}\text{Xe}_{\text{Pu}}/^{129}\text{Xe}_{\text{U}}$ ratio of the respective mantle sources to be estimated (c). This ratio depends on the time of reservoir closure (Fig. 2.8 and text). For a chemically homogeneous mantle (common Pu/I ratio), the convecting mantle, which sourced MORB, should have closed before the less degassed deep mantle sourced mantle plumes, which evidently is absurd. A way to turn this problem around is to



infer chemical inhomogeneities in the mantle that date back to Earth's accretion when ^{129}I and ^{244}Pu were still alive. The deep mantle would represent dry material that accreted first, depleted in volatile iodine relative to refractory plutonium, while the convecting mantle would be related to volatile-rich material that accreted later.

This third xenon paradox indicates that a model in which the mantle is chemically homogenous and has a unique Pu/I ratio was no longer tenable. Because the Pu/I difference is observed for extinct radioactivity products, such heterogeneity must date back to the period of Earth's formation. The Pu/I ratio could have been differentially fractionated during episodes of core formation (Jackson *et al.*, 2018), although this model would require somewhat *ad hoc* episodes of giant impacts and magma oceans (Mukhopadhyay and Parai, 2019). Alternatively, the accretion of the Earth might have been heterogenous, with the proportion of volatile relative to refractory elements increasing with time. Dry, iodine-depleted material dominated the first episodes of Earth's accretion and its signature is now found in deep mantle material with a high Pu/I ratio. Later, other material, richer in volatile elements, contributed to terrestrial formation, leaving its signature in the convecting mantle (Mukhopadhyay, 2012; Caracausi *et al.*, 2016; Mukhopadhyay and Parai, 2019).

The tales of xenon are not over yet. This peculiar element also provides outstanding insights into the origin of terrestrial volatiles (Section 7), the evolution of the atmosphere during the first 2 Gyr of Earth history, and the recycling of volatile elements into the mantle (Section 8). As a final note of this section, I would like to emphasise the ability of the isotopes of xenon to decipher the degassing state and thus the convection rate of the mantle, as do helium and neon isotopes.

The reasoning is illustrated in Figure 2.10. High precision analysis of volcanic rocks and gases worldwide have shown that a dichotomy in Xe isotopes exists between deep sourced plumes and the convecting mantle sampled by MORB and CO_2 -rich gases (see 2.3.2 above). This dichotomy extends to the relative proportions of heavy Xe isotopes produced by the fissions of ^{244}Pu ($T_{1/2} = 82$ Myr) and ^{238}U ($T_{1/2} = 4.47$ Gyr). For a given mantle reservoir, Xe isotopes produced by the fission of ^{244}Pu will dominate, or not, over those produced by the fission of ^{238}U (Fig. 2.10), depending on the timing and extent of degassing. Hence fissiogenic Xe isotopes constitute another powerful tracer of mantle degassing and have shown that the mantle source of plumes is indeed much less degassed than the convecting mantle which feeds mid-ocean ridges, in complete agreement with He and Ne isotope systematics. Because both Pu and U are refractory and presumably incompatible, the view of a less degassed, deep mantle source for plumes is even more robust than in the case of other noble gases for which different origins and/or geochemical behaviour of parent/daughter isotopes were advocated as alternative possibilities (Anderson, 1998).



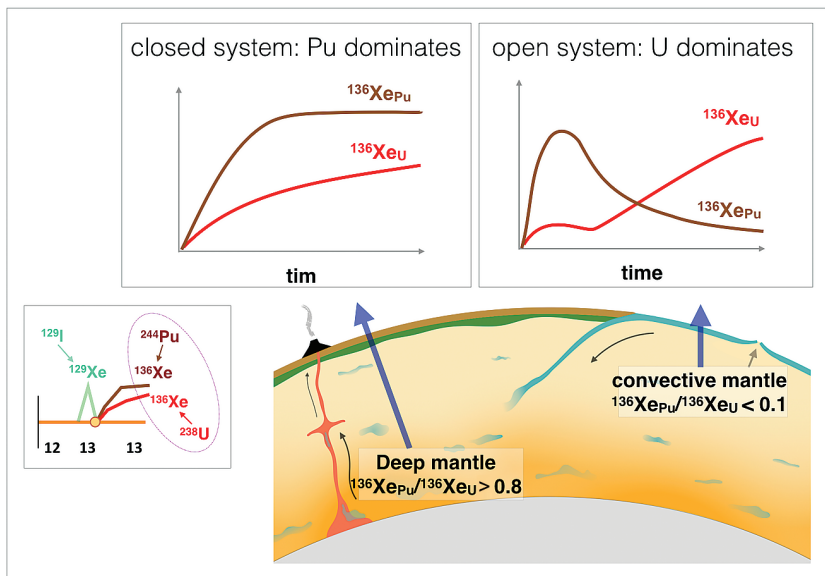


Figure 2.10 Probing mantle degassing with xenon isotopes) ratio is >0.8 , corresponding to the first case (limited degassing) whereas in MORB and CO_2 -rich gases, $^{136}\text{Xe}_{\text{Pu}}/(^{136}\text{Xe}_{\text{U}} + ^{136}\text{Xe}_{\text{Pu}})$ is <0.4 , showing extensive degassing of this reservoir.

Xenology and other related puzzles are currently discussed during international seminars and events by the friendly noble gas community (Fig. 2.11).





Figure 2.11

Some of the noble gas folks. **Top:** Banquet in honour of Minoru Ozima who was awarded the Goldschmidt medal in 2010, Knoxville, USA. First row, from left to right: Noriko Kita, Masahiko Honda, Nobu Shimizu, Minoru Ozima, Frank Podosek, Marc Caffee, Bernard Marty. Second row: Takayuki Ushikubo, Chris Ballentine, Takuya Tatsumoto, Mitsuru Ebihara, Keiko Sato, Sujoy Mukhopadhyay, Junji Yamamoto, Takanori Yamada. Third row: Yuri Amelin, Magali Pujol, Nicolas Dauphas, Doug Hamilton, Mark Kendrick, Kevin Zahnle, Hiroshika Sumino, unidentified. **Centre left to right:** Bob Pepin and David Black (the neon guys), LPSC 2010, Houston, USA; Mark Kurz enjoying pastis at home; Daniele Pinti and Christine Boucher. **Bottom left to right:** Rolf Kipfler, Grenville Turner, and Chris Ballentine. Albrecht Hofmann (left) and Igor Tolstikhin (behind them Julie Hofmann) during a seminar held at the Max Plank Institute for Chemistry, Mainz (Germany) for the 75th birthday of Igor. Photo credit: B. Marty.



3.1 The Earth as an Old British Hotel Room

When I was young, the hotel rooms in the United Kingdom had the reputation of having a strange plumbing system, with noisy and leaking taps and irrational water flows along endless pipelines. This was of course a cliché entertained by the Froggies, but I like to visualise the cycle of terrestrial volatiles a bit like this. The Earth is a carefully tuned system which continuously exchanges its life-supporting elements between its interior –the mantle– and its surface –the atmosphere, the oceans and the crust– through main flow paths (ridge, arc and intraplate magmatism *vs.* subduction) but also through a number of leaks which are more difficult to spot (*e.g.*, diffuse degassing, faults, plate foundering).

The geological record reveals that optimal conditions for the development of biochemistry, *i.e.* clement temperatures allowing liquid water to persist, have existed for at least 4 Gyr. Aside from their biogeochemical relevance, water and carbon-bearing species affect mantle rheology and lower the melting temperature of mineral assemblages constituting the mantle. Without volatiles in the mantle, the Earth would have followed a different evolution, and plate tectonics might have been overridden by discrete catastrophic events which would have then released its internal heat (Sleep, 2007).

The content of mantle volatiles and their elemental and isotopic ratios bear key information on the nature of terrestrial building blocks and on the processes and timing of accretion. For refractory and moderately volatile elements, a good analogue of the Earth's composition is given by that of primitive meteorites, but for H, C, N, and noble gases, such an analogy does not hold because their compositions were drastically modified by accretionary processes and/or by processing of parent planetesimals. Furthermore, cosmochemical sources other than chondrites, such as the proto-solar nebula gas or comets, might have also contributed volatiles to the growing proto-Earth. Thus, knowledge of the nature and composition of volatiles trapped in the mantle has the potential to shed light on solar system formation as well as on planetary accretion processes.

Three decades ago, the nature and content of mantle volatiles were not well known (and are still a topic of debate), but primordial noble gases had been identified and isotopes produced by extinct and extant radioactivities had been found in mantle-derived gases and rocks (Section 2). It was also known that the deep mantle contains hydrogen which is isotopically different from surface water with δH values down to -125‰ in Hawaiian xenoliths, where the standard is ocean water (Deloule *et al.*, 1991) and possibly down to -220‰ in samples from Baffin Island, another mantle plume province (Hallis *et al.*, 2015). But mantle carbon has a similar isotopic signature ($\delta^{13}\text{C}$ around -5‰ , where the standard is



carbonate C; Javoy *et al.*, 1986) to that of surface carbon (a mixture of carbonates and organic C). Nitrogen trapped in diamonds was found to be depleted by a few per mille relative to atmospheric N, a signature that may indicate a cosmochemical origin (Javoy *et al.*, 1984). There are still significant unknowns, but dramatic progress has been achieved since then, notably thanks to the development of high precision analysis as well as *in situ* ion and laser probe measurements.

I have been trying to contribute to the field with a novel analytical setup allowing the simultaneous analysis of carbon, nitrogen, and noble gases at high sensitivity. In this Section I will develop my approach to the use of noble gases as key tracers of the origin and composition of major volatiles (carbon, water, and nitrogen) in the mantle. First, I will address the carbon flux from the mantle to the atmosphere, a major player in the geological cycle of carbon, for which the calibration to mantle-derived ^3He allowed us to obtain estimates that are still up to date. I will then describe a method of quantifying the geological nitrogen cycle by normalising this element to argon isotopes. At the end of the Section, I will present my estimates for the composition of mantle volatiles and compare the resulting numbers with those obtained by other methods.

3.2 Natural Fluxes of Mantle Carbon

During its geological history, the Earth has been degassing its volatile elements— H_2O , CO_2 , N_2 , $\text{SO}_2/\text{H}_2\text{S}$, halogens, noble gases—through volcanism, plutonism, and tectonic processes (Section 2). This geological degassing constitutes the volatile flux out of the silicate Earth (Fig. 3.1). Conversely, volatiles are recycled back into the mantle, mainly through subduction of the hydrated and carbonated oceanic crust (Plank and Manning, 2019). The efficiency of Earth's degassing and ingassing is related to the thermal evolution of the mantle: In the distant past, a hotter Earth would have released its volatiles more efficiently than today due to higher melting and mantle convection rates. At present, the largest volume of magmas produced by partial melting of the mantle is generated at mid-ocean ridges ($\sim 16\text{--}20 \text{ km}^3/\text{yr}$) during mantle adiabatic decompression. Intraplate magmatism, including mantle plume volcanoes such as those in La Réunion, Iceland, and Hawaii, generates lavas with an estimated volume of the order of $1 \text{ km}^3/\text{yr}$. However, in the past, gigantic eruptions occurred, producing large igneous provinces with poorly known magma generation rates. Finally, magmas generated at subduction zones may account for an additional $\sim 3\text{--}4 \text{ km}^3/\text{yr}$ on average (Crisp, 1984). Hence, estimating the volatile flux at mid-ocean ridges gives a first order estimate of the mantle flux. Mid-ocean ridge magmatism mostly occurs beneath the oceans, releasing magmatic volatiles into seawater. This setting opens up the possibility of tracing magma degassing by analysing mantle-derived isotopes in the oceans.

In Japan, I measured the amount of CO_2 and helium and the $^3\text{He}/^4\text{He}$ ratio for a few MORB samples with the goal of calibrating the carbon flux from the mantle to that of helium-3. I tried to publish the $\text{C}/^3\text{He}$ ratio of MORB in a paper



submitted to *Geochimica et Cosmochimica Acta* when I was in Japan, supplementing a study on noble gas partitioning in MORB. One reviewer, not convinced by the potential of this approach, recommended dropping the carbon-helium aspect and keeping only the noble gas partitioning story (Marty and Ozima, 1986). The article I wrote later with Albert Jambon on $C/{}^3\text{He}$ systematics became one of my most cited papers (Marty and Jambon, 1987).

In the MAGIE (Magmatologie et Géochimie Inorganique et Experimentale) laboratory established by Albert Jambon at Université Pierre et Marie Curie in Paris, we started to brainstorm the relationship between carbon and helium in my samples and other samples analysed by Albert. From the small data set (something like 10 samples) we had at the time, we proposed a mean $\text{CO}_2/{}^3\text{He}$ molar ratio of MORB of $\sim 2 \pm 0.5 \times 10^9$ (Marty and Jambon, 1987) (Fig. 3.1). From the mantle ${}^3\text{He}$ flux of ~ 1000 mol/yr estimated at that time, the carbon flux from mid-ocean ridges was calculated to be $\sim 2 \times 10^{12}$ mol/yr, which was one order of magnitude lower than previous estimates (Javoy *et al.*, 1982).

Later, we expanded the MORB database. We analysed 45 glasses from different locations and of different types –depleted or N-type, transitional or T-type, enriched or E-type (Marty and Zimmermann, 1999). We also corrected the C/He ratio for fractional degassing using the ${}^4\text{He}/{}^{40}\text{Ar}$ radiogenic production/accumulation ratio to finally estimate the magmatic ratios before degassing. These ratios are representative of the mantle sources as both helium and carbon are incompatible during partial melting of mantle minerals. We found that the mantle source $C/{}^3\text{He}$ ratios are heterogeneous (Marty and Tolstikhin, 1998; Marty and Zimmermann, 1999). “Normal” or N-MORB ($C/{}^3\text{He}$ around 1×10^9) are mid-ocean ridge basalts depleted in incompatible elements as a result of previous episodes of mantle source melting. “Enriched” MORB (E-MORB) have $C/{}^3\text{He}$ ratios that are a factor of 3-5 higher than the N-MORB average. This “excess” carbon relative to primordial ${}^3\text{He}$ is regarded as reflecting a contribution from subducted carbon, in line with trace element and radiogenic isotope systematics of E-MORB which independently suggest the contribution of recycled crust. We calculated a mean MORB mantle source $C/{}^3\text{He}$ ratio by averaging the different MORB type values weighted by the proportions of N-MORB, T-(transitional) MORB, and E-MORB (LeRoex, 1987), obtaining a value of $2.2 \pm 0.9 \times 10^9$. Meanwhile, the mantle ${}^3\text{He}$ flux into the oceans was revised from 1000 mol/yr to 640-850 mol/yr (Holzer *et al.*, 2017) and the CO_2 flux from mid-ocean ridges became $1.6 \pm 1.0 \times 10^{12}$ mol/yr. Calculation of mid-ocean ridge CO_2 flux values yielded comparable numbers even when following different approaches: $(1.3 \pm 0.8) \times 10^{12}$ mol/yr from a compilation of CO_2 measurements in MORB (Le Voyer *et al.*, 2019), and $(1.6 \pm 0.2) \times 10^{12}$ mol/yr (Tucker *et al.*, 2018) from extended calibration of CO_2 to mantle ${}^3\text{He}$ flux into the oceans. Hence the annual CO_2 flux from the convecting mantle which produces the highest magma volume is probably well characterised to within a factor of two or better (Fig. 3.1).



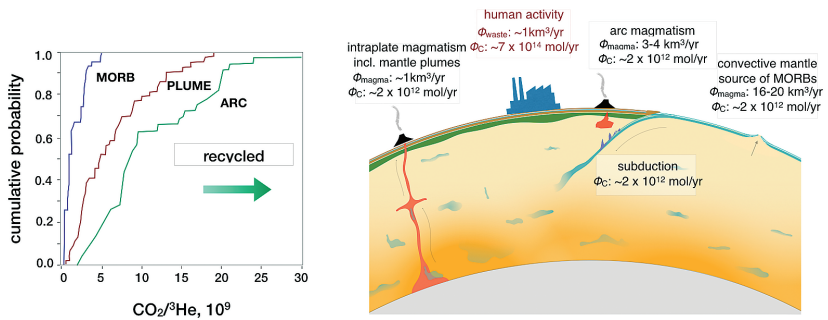


Figure 3.1

Top: $\text{CO}_2\text{-}^3\text{He}$ systematics. In this cumulative probability plot (@ Matlab), values showing low dispersion present a steep distribution. $\text{CO}_2/{}^3\text{He}$ ratios have limited dispersion with values generally lower than 5×10^9 . Arc volcanic gases show a larger dispersion and are rich in carbon compared to MORB, an observation that we interpreted as a fingerprint of subduction (Marty *et al.*, 1989). Plume-related gases have intermediate values, suggesting contribution of subducted material to their deep mantle source. **Bottom:** Respective volcanic fluxes of magmas and CO_2 (Marty and Tolstikhin, 1998) for the three main types of volcanism. “Unseen” diffuse degassing through continents is not taken into account here. The panel compares the total volcanic flux to the natural flux of carbon required by the BLAG carbon cycle model (Berner *et al.*, 1983) and to the flux of CO_2 generated by human activity. “Waste” represents the volume of waste generated by human activity.

Quantifying the volatile flux for the two other types of volcanism (arc and intraplate) is complicated by the fact that, contrary to the case of mid-ocean ridges, volcanoes release gases into the atmosphere where they are readily diluted to background levels. Estimates can be obtained by compiling single measurements on individual volcanoes using relevant tracers, but the natural variability from one system to another makes this approach difficult. Subaerial volcano measurements are generally undertaken on active volcanoes presenting large C and S fluxes, with the assumption that a limited number of volcanoes with strong open degassing dominate fluxes from dormant volcanoes and geothermal areas quantitatively (Allard, 1992; Brantley and Koepenick, 1995). There is a confidence in his assumption resting on some ground given the statistical distribution of measured volcanic fluxes. For instance, Mt. Etna degasses $\sim 2\text{-}4 \times 10^{11}$ moles of CO_2 per year at present (Allard *et al.*, 1991), which is a large fraction of the total flux of carbon dioxide emitted annually by subaerial volcanoes ($\sim 1\text{-}2 \times 10^{12}$ mol CO_2/yr ; Aiuppa *et al.*, 2019). Quiescent degassing from strong degassers also tends to dominate over eruptive degassing, although estimates are based on a low number of cases. Nevertheless, simple mass balance suggests that “unseen” magmatic degassing, not directly measured in volcanic plumes, is significant. Crisp (1984) estimated that erupted lavas at arcs ($\sim 1 \text{ km}^3/\text{yr}$) account for about 1/3 of magma generation at arcs at most ($\sim 3\text{-}4 \text{ km}^3/\text{yr}$), given that most magmas are trapped as plutons in the crust overlying the wedge. Granitic plutons will



also degas magmatic volatiles through fractures and dissolution in groundwater over large areas without being detected. Hence, the quantification of “unseen” degassing in tectonically active areas remains one of the principal unknowns in the geological carbon cycle.

The absorption of solar light by sulfur dioxide (SO₂) in volcanic plumes allows an estimate of its flux to be achieved as the atmospheric background of S species is low, contrary to the case of CO₂ for which human activity produces a high background. This method to estimate flux requires measurements of both the mass loading of SO₂ and the velocity of the plume, using spectroscopic means (e.g., Aiuppa *et al.*, 2019). By compiling individual measurements for key volcanoes, some global numbers can be determined and, together with C/S ratios in volcanic fumaroles, the CO₂ flux from subaerial volcanoes can be derived (Allard, 1992; Aiuppa *et al.*, 2019). With Marie-Françoise le Cloarec, a geochemist at the CEA measuring uranium decay chain products in volcanic gases, we attempted to estimate the CO₂ flux independently by calibrating this species to polonium-210. The rationale is that about half of ²¹⁰Po atoms in the atmosphere are volcanic in origin, the rest being mobilised by fires and anthropic activity. ²¹⁰Po is released mostly in high temperature volcanic gases, which considerably restrains the number of sampled volcanoes. From our limited database, we came to the conclusion that the CO₂ flux from the small number of analysed subaerial volcanoes is of the order of $2 \pm 1 \times 10^{12}$ mol/yr, with the problematic assumption that such volcanoes are the largest CO₂ emitters among all volcanoes including those that are dormant (Marty and Leclourec, 1992).

Extensive efforts to quantify fluxes of carbon in and out of the solid Earth have been made through the Deep Carbon Observatory, a decennial programme supported by the Sloan Foundation (<https://deepcarbon.net>) which aims to understand better the geological cycle of carbon. Up to date estimates of geological carbon fluxes can be found in recent review papers (Plank and Manning, 2019; Kelemen and Manning, 2015). From the sulfur flux calibration of a much larger number of active volcanoes, the flux of carbon from subaerial volcanoes, mostly arcs, was found to be about $2 \pm 1 \times 10^{12}$ mol C/yr (Aiuppa *et al.*, 2019; Plank and Manning, 2019; Kelemen and Manning, 2015), comparable to the CO₂ flux at ridges. However, the magma production rate at arcs is one order of magnitude smaller than at ridges, implying that most carbon released at arcs is not from the mantle but from recycled oceanic crust.

The calibration of volcanic CO₂ to mantle ³He also proved to be promising. When I was in Japan, I sampled gases from several active volcanoes and found that they had systematically higher C/³He ratios than gases trapped in MORB fluid inclusions (Marty *et al.*, 1989). After ruling out elemental fractionation during gas transfer in the crust, we suggested that this excess CO₂ relative to mantle helium-3 was due to the addition of carbon trapped in the subducting crust. Yuji Sano (who visited me in France on several occasions) went a step further by adding carbon isotope measurements to C/³He ratios (Sano and Marty, 1995). Carbon trapped in subducting oceanic crust is locked in organic matter



and carbonates, which have different isotopic compositions, allowing identification of the original phases (Fig. 3.2). This approach led us to conclude that gases released by arc volcanoes contain less than 30% carbon from the mantle wedge and that most of the CO₂ released by arc volcanoes is from the subducting slab. It is therefore of surface origin, consistent with the mass balance presented above.

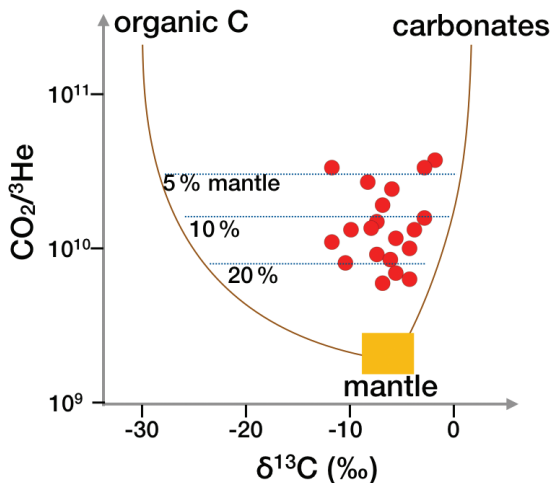


Figure 3.2

CO₂³He and δ¹³C systematics of arc volcanic gases. Carbon in organic matter and in carbonates have isotopic compositions around -30 ‰ and 0 ‰ in the δ¹³C notation, respectively where δ¹³C is the deviation of the ¹³C/¹²C ratio of the sample relative to a carbonate standard, in parts per mille. Red dots represent volcanic and geothermal gas data in arc settings. Brown curves represent mixing between the mantle and crustal end member compositions, respectively. The relative proportions of gases from the mantle wedge assumed to have a MORB-like composition are represented by horizontal blue dotted lines. The data suggest that only ≤30% carbon is from the mantle wedge, the rest being supplied by the subducting slab (Sano and Marty, 1995; redrawn from Figure Box 1 in Plank and Manning, 2019).

Igor Tolstikhin from the Russian Academy of Sciences (whom I mentioned in Section 1) visited the CRPG for several months in the nineties. Igor, one of the leading experts in noble gas geochemistry, co-discovered mantle ³He (Section 1) and invented the ³H-³He dating method for young groundwaters, among other discoveries. Unfortunately, his achievements were not well rewarded in the then bipolarised world. Thanks to his energy and fighting spirit, he managed to exchange science and ideas with western countries. We attempted to estimate the global flux of carbon from the solid Earth by summing the C flux at ridges (~2 × 10¹² mol/yr), arc volcanoes (~2 × 10¹² mol/yr), and volcanoes in mantle plume provinces (~3 × 10¹² mol/yr, taking into account large igneous provinces). The resulting global carbon flux (6 × 10¹² mol/yr, range: 4-10 × 10¹² mol/yr) fits



well with the geological flux of C required to balance the global carbon flux ($6\text{--}11 \times 10^{12}$ mol/yr; Berner *et al.*, 1983). The geological flux of carbon is 2-3 orders of magnitude smaller than the anthropogenic carbon flux ($\sim 7 \times 10^{14}$ mol/yr) (Friedlingstein *et al.*, 2010), which confirms that we are heading towards serious climate problems due to man made carbon fluxes.

Knowledge of the volcanic CO₂ flux has dramatically improved during the last decade under the leadership of the Deep Carbon Observatory thanks to novel techniques and equipment, including miniaturised field gas sensors, drones, and satellite observations. Flux measurements are carried out on several tens of active volcanoes continuously and are monitored in real time from space. Flux measurements are available for 91 active volcanoes and yield 0.9×10^{12} mol/yr (Aiuppa *et al.*, 2019), and the global subaerial volcanic flux has been estimated at $1.8 \pm 0.2 \times 10^{12}$ mol/yr (Plank and Manning, 2019; Kelemen and Manning, 2015), not far from our original estimate based on CO₂/³He measurements. However, it became evident that other natural sources of CO₂ critically require identification and quantification. Soils, faults, volcanic lakes, and aquifers could account for up to as much as 2×10^{12} mol/yr (Fischer and Aiuppa, 2020), thus doubling previous estimates. Improving these estimates will require a tremendous amount of work, such as thousands of soil and water flux measurements, as well as large scale extrapolations.

3.3 Tracing Modern Carbon Fluxes with Atmospheric Helium Isotopes

During the last decade, in order to improve our knowledge of the aeronomical problem of helium (Kockarts, 1973), we have developed the measurement of the ³He/⁴He ratio of air with a precision at the per mille level (Mabry *et al.*, 2013). The primary idea was to investigate potential variations of atmospheric He isotope composition due to the release of crustal carbon by mining and oil industries. Natural gases, oil, and coal are rich in crustal helium dominated by radiogenic ⁴He and depleted in mantle ³He. Helium is chemically inert, not gravitationally bound to Earth, and its atmospheric abundance is low, 7.3×10^{-12} vol/vol (He content: 5.24×10^{-6} vol/vol air, atmospheric ³He/⁴He = 1.39×10^{-6} ; Ozima and Podosek, 2002). Previous studies have suggested that the atmospheric He isotopic composition could have varied through time and space, which opens the interesting possibility of investigating the contributions of different sources of atmospheric He isotopes (Sano *et al.*, 1989). The sources of anthropogenic CO₂ –combustion of fossil fuels, land change, and cement manufacturing– are well identified and quantified thanks to mining, agriculture, and industry statistics. But atmospheric CO₂ sinks –biosphere greening or oceanic capture– are more uncertain as they operate over longer periods of time. Helium does not have this problem since the sources of its isotopes –the crust for ⁴He, and the mantle for ³He– are known, and their sinks, such as escape to space, although not precisely known ($10^4\text{--}10^6$ yr; Torgersen, 1989), operate over timescales exceeding those of human activity. Hence the amount of atmospheric ⁴He might have increased



from the onset of industrial activity (starting in the middle of the 19th century). Assuming constant release of mantle-derived ³He over this period of time, the ³He/⁴He ratio of the atmosphere would have declined at the same rate, and variations of a few per mille were anticipated over the last decades (Sano *et al.*, 1989; Brennwald *et al.*, 2013), as were geographical heterogeneities between the southern and northern hemispheres because the major sources of industrially released ⁴He are located in Europe, the USA, India, and the People's Republic of China. The atmosphere is rapidly (≥ 1 year) mixed but steady state sources could locally induce He isotope heterogeneities. Besides this potential new tracer of global change, there is another practical outcome for noble gas geochemists. Atmospheric helium is used as an international standard and local or temporal isotopic variations could have implications for long term studies using helium as a monitor of unrest activity (*e.g.*, earthquakes, volcanoes).

In 2011, we received the grant NOGAT (for Noble Gases in the Atmosphere through Time) from the European Research Council to study the origin and evolution of the atmosphere at different timescales. One of the aims of the NOGAT programme was to investigate noble gas isotope variations during the Anthropocene (*e.g.*, Sano *et al.*, 2010) and to that end we developed a new analytical facility to measure the atmospheric ³He/⁴He ratio at the per mille level, a precision that was rarely attained previously. Thanks to the efforts and expertise of Pete Burnard, Jennifer Mabry (then post-doc), Tefang Lan (then post-doc), and Christine Boucher (then graduate student), the facility which included an automated line and a new two collector noble gas mass spectrometer, became operational in 2012, one single determination taking several days of continuous data collection (Mabry *et al.*, 2013).

We collected, or had collected by others, air samples in stainless steel bottles worldwide, from Svalbard at 79 °N to Dome C station at 80 °S. However, we could not detect any geographical variation of the atmospheric ³He/⁴He ratio within the precision of our measurements. The only exceptions were Antarctica with an excess of ³He (or deficit of ⁴He) of 2.0 ± 1.4 ‰ (95 % confidence level) and (possibly) Tokyo (1.7 ± 1.5 ‰) (Boucher *et al.*, 2018a). Jennifer and Christine also investigated temporal variations by analysing helium sampled in Tasmania and stored in large stainless steel bottles by the Commonwealth Scientific and Industrial Research Organisation (the research institution of Australia) since 1976 (Mabry *et al.*, 2015), in pétanque balls, and in the carburettor floater from a 1910 Renault car (in perfect shape) belonging to the family of my colleague Christian France-Lanord (Fig. 3.3). All ³He/⁴He data were indistinguishable from air sampled in 2016 at the Brabois Park in Nancy (France) (Mabry *et al.*, 2015, Boucher *et al.*, 2018b). These negative results were somewhat unexpected and not very rewarding, but they had their value in that they showed that atmospheric helium can be used safely as an international standard since its isotopic composition does not vary with space or time. This is important in studies focusing on temporal He isotope variations for monitoring natural hazards like volcanoes and earthquakes. They also showed that the mining statistics (helium content of natural gases) on which previous claims of temporal variations were based were



biased towards gases containing exploitable, high content He. Subtle variations appeared to exist in Antarctica, presumably due to injection of ^3He -rich solar wind at the poles (Boucher *et al.*, 2018a), providing a potential tool to investigate interactions between the Sun and the terrestrial atmosphere.

Using high precision ^3He measurements, we tried to quantify the flux of volcanic gases on a regional scale. Excesses of magmatic gases in the atmosphere, *e.g.*, CO_2 and S species, can hardly be detected, given the large atmospheric background of CO_2 and the trapping of S-bearing species in the subsurface. The detection of ^3He excess in air over tectonically active areas, coupled with meteorological measurements, could, in principle, permit the identification and quantification of regional magmatic degassing. We went to sample air in Afar (Ethiopia), a tectonic triple junction where a mantle plume is interacting with three rifting segments. This area is the locus of present day volcanism, as seen in the active Erta Ale volcano which hosts a permanent lava lake. We did not detect any He isotope variation in air sampled along the Afar roads, but a 15 ‰ ^3He excess was observed over the Erta Ale lava lake and higher excesses were measured in soil gases around the crater, allowing us to map degassing over larger areas than that of the crater (Boucher *et al.*, 2018c). Air mixing quickly reduced ^3He excesses from volcanic degassing on a regional scale and our approach was not entirely successful, as so often happens in geochemistry.

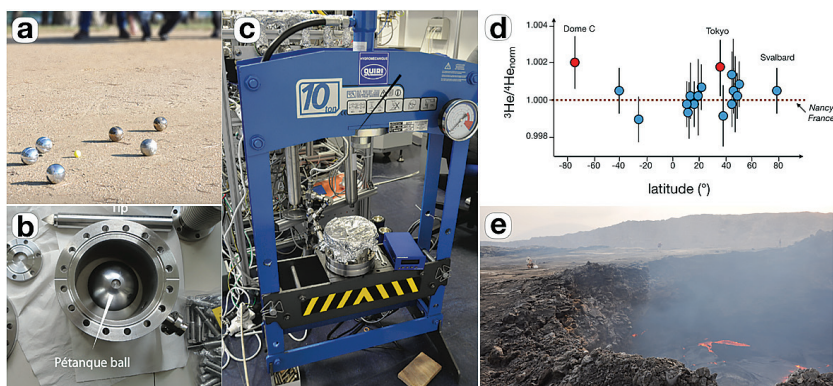


Figure 3.3

Measuring the isotopic composition of atmospheric helium at high precision. (a) The pétanque ball game in France is very popular. It consists of throwing a metal ball as close as possible to a small wooden ball called the cochonnet. Each pétanque ball is made of two hemispheres of stainless steel that are welded together, leaving inside a volume of air of about 80 cm^3 that was trapped at the time of manufacturing. The Obut company provided us with balls manufactured back to the sixties. (b) and (c) Trapped air was extracted under vacuum using a tip fitted to a press. Other ancient air samples were provided by CSIRO (Australia) which has archived air in stainless steel bottles since 1978 (courtesy of R.L. Langenfelds, CSIRO). Air trapped in the carburettor floater of a 1910 Renault car was also analysed and we could not detect any He isotope variation in air since the beginning of the 20th century (Mabry *et al.*, 2015; Boucher *et al.*, 2018b). (d) Air samples taken at different places



worldwide from 79 °N to 80 °S have an isotopic composition similar to that of Nancy (France) within 2σ , with the exception of Dome C air (Antarctica) and possibly that of Tokyo air. (e) Air aliquots were sampled in Afar (Ethiopia), including the Erta Ale volcano which hosts a permanent lava lake, with the aim of using ^3He excesses in air as a proxy for volcanic CO_2 degassing in a tectonically active province. The He isotope composition was also similar to that of Nancy air, except for air sampled around the crater and above the lava lake which showed a ^3He excess of 1-2%. Photo credit: Y. Marrocchi and B. Marty.

3.4 Terrestrial Nitrogen

Nitrogen is a particularly interesting element because N_2 makes up 78 % of the modern atmosphere and N is also key in the development of the biosphere. Nitrogen can be biologically reduced to NH compounds, which can then enter the silicate cycle by substitution for potassium in sediments. It can be oxidised (denitrification) by bacteria with a significant and trackable isotopic fractionation and return to the atmosphere, or it can stay locked in sedimentary rocks and be returned to the mantle at subduction zones. Therefore, its behaviour in the Earth-atmosphere system is strongly dependent on bacterial metabolism. The N_2 triple bond makes this molecule particularly resistant to degradation even at high temperature, which makes dinitrogen inert in most inorganic reactions. Thus, N_2 is often referred to as the “6th noble gas”. In oxidising conditions characteristic of terrestrial magmas, N_2 behaves like argon. It is incompatible, just as Ar during partial melting (Miyazaki *et al.*, 2004), and also has a solubility similar to that of Ar in basaltic melts (Libourel *et al.*, 2003; Miyazaki *et al.*, 2004). Hence, Ar can be used as a proxy for understanding the geochemical behaviour of N. Under reducing conditions, N bonds with hydrogen, carbon, silicon, or titanium and its solubility in silicate melts increases dramatically (Grewal *et al.*, 2020; Libourel *et al.*, 2003; Miyazaki *et al.*, 2004) (Fig. 3.4). These conditions might have occurred in the proto-Earth and considerable amounts of N (and H and C) might have been sequestered in silicates during magma ocean episodes. If or when the proto-Earth evolved toward more oxidising conditions, H, C, and N could have been released as H_2O , CO, CO_2 , and N_2 into the atmosphere and oceans, and possibly lost during atmospheric escape events (Grewal *et al.*, 2020).

The major flux of nitrogen from the mantle to the surface takes place at mid-ocean ridges and from hot spot volcanism, and is reasonably well known, whereas its return flux requires bacterial reduction and depends on whether or not sedimentary N survives the subduction barrier. The efficiency of nitrogen degassing from the subducted plates depends on the thermal regime of subduction and is likely to have been low in the distant past when the Earth was hotter than today. Last but not least, the ratio of its two stable isotopes, $^{15}\text{N}/^{14}\text{N}$, presents extreme variations among solar system objects and reservoirs, only second in magnitude after the D/H ratio, which makes nitrogen the cosmochemical tracer of choice.



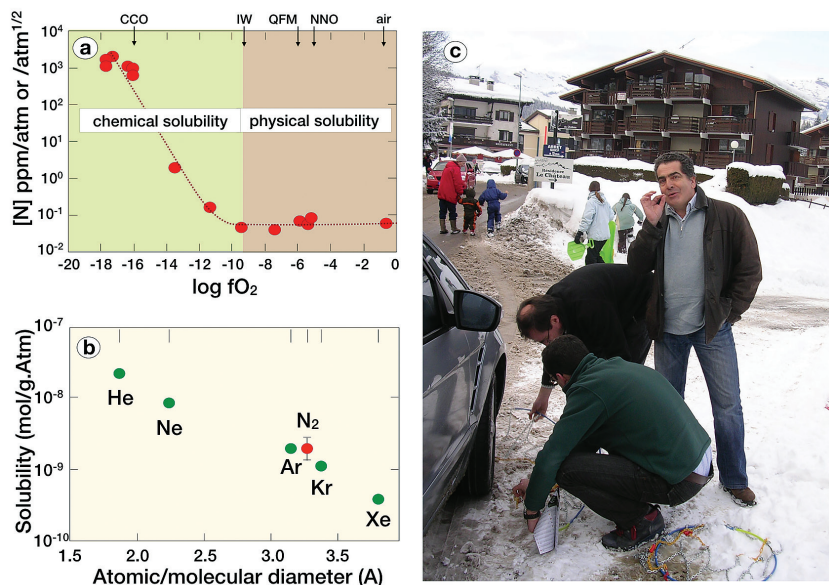


Figure 3.4 (a) Nitrogen solubility in silicate melt as a function of oxygen fugacity (f_{O_2}), which is an index of the redox state of magmas (after Libourel *et al.*, 2003). This work was part of the thesis of Franck Humbert. Iron-wüstite (IW) corresponds to the coexistence of metallic Fe with FeO. The present day f_{O_2} of the mantle is higher than IW and around the QFM buffer, corresponding to oxidising conditions (brown area). Nitrogen is mostly present as N_2 and has a low and constant solubility. Before core differentiation, the proto-Earth might have had a f_{O_2} slightly below IW. The green area below IW corresponds to reducing conditions, which can be found in some planetary bodies like enstatite chondrite parent bodies or Mercury. Under reducing conditions N solubility increases drastically as nitrogen can bind with carbon, silicon, or titanium (Libourel *et al.*, 2003; Grewal *et al.*, 2020). (b) Comparison of the solubility coefficients of noble gases (data from Carroll and Draper, 1994) and N_2 under oxidising conditions. Dinitrogen behaves similar to argon in that of radiogenic ^{40}Ar produced by the decay of ^{40}K . (c) Guy Libourel enjoying the fresh air in the French Alps while Marc Chaussidon and I were attaching the snow chains, *en route* to the Les Houches Winter School of Physics (February 2009).

In the sixties and seventies, the stable isotope geochemistry of nitrogen was comparatively less developed than that of carbon, hydrogen, and oxygen because N is not abundant in rocks and minerals, often only present at the ppm level or less. At that time, dynamic mass spectrometry required large amounts of material to yield precise measurements, of the order of 1 micromole for N. Consequently, N isotope studies mostly focused on extraterrestrial materials, notably lunar samples brought back by the Apollo missions, or on



N-rich biological material. Bob Pepin and his colleagues at the University of Minnesota went a step further by developing static mass spectrometry analysis of nitrogen, which led to an impressive increase in sensitivity of several orders of magnitude compared to stable isotope dynamic analysis (Frick and Pepin, 1981). The rationale was to analyse N together with noble gases using noble gas techniques after the dedicated purification procedure. Little work had been done on terrestrial samples, and, while in Paris, I started to develop a similar system to analyse noble gases and nitrogen which had been extracted from rocks and minerals together, either by vacuum crushing or stepwise heating, as was usual for noble gases (Marty *et al.*, 1995). We continued working on MORB and OIB glasses and analysed the abundances and isotopic compositions of volatile elements, including nitrogen, together. The detection limit for N was extremely low (about 1×10^{-12} mol N_2) compared to dynamic mass spectrometry and Ar isotopes were used as index of atmospheric contamination so that the N mantle signal could be identified. We crushed MORB glasses under vacuum to recover gases trapped in vesicles and discovered that the $N_2/^{36}Ar$ ratio correlates strongly with the $^{40}Ar/^{36}Ar$ ratio over two orders of magnitude (Fig. 3.5) (Marty, 1995). The correlation of Figure 3.5b is consistent with mixing between an atmospheric end member ($^{40}Ar/^{36}Ar = 298.6$, $N_2/^{40}Ar = 40$ (air saturated water) - 83.6 (air), $N_2/^{36}Ar = 1.4\text{-}2.5 \times 10^4$) and a MORB mantle end member with $^{40}Ar/^{36}Ar$ up to 40,000 and $N_2/^{36}Ar$ up to 3×10^6 .

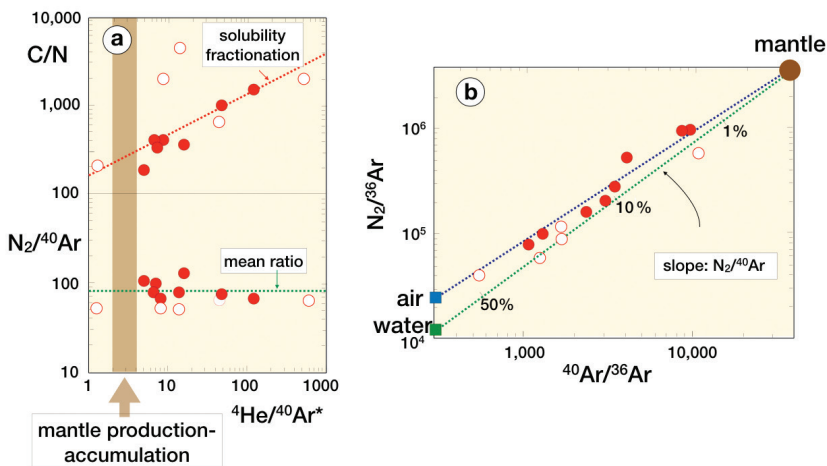


Figure 3.5

Variations of carbon, nitrogen, and argon isotope abundances in a set of mid-ocean ridge basalts (MORB; red dots: N-MORB; red circles: T- and E-MORB). These elements were analysed together by static mass spectrometry following vacuum crushing of MORB glasses (modified from Marty, 1995). (a) C/N and $N_2/^{40}Ar$ ratios as a function of the $^{4}He/^{40}Ar^*$ ratio (* means corrected for atmospheric ^{40}Ar). During magma degassing, the relative abundances of C, N, and Ar vary as a function of their solubilities in basaltic melt. Consequently, residual gases trapped in MORB glasses are often fractionated



compared to their initial abundances in mantle-derived magmas. In order to reconstruct the mantle source composition, we used the $^4\text{He}/^{40}\text{Ar}^*$ ratio as an index of elemental fractionation. Its mantle source value is inferred from the parent $(\text{U} + \text{Th})/^{40}\text{K}$ ratio in the mantle to be 2-3. ^4He is ~10 times less soluble than Ar. In contrast, N_2 has a solubility comparable to that of Ar and the N_2/Ar ratio is not expected to vary as a function of $^4\text{He}/^{40}\text{Ar}^*$, which is effectively the case (green dotted line, lower panel in a). This is different for C because the solubility of CO_2 is intermediate to those of He and Ar or N_2 . Accordingly, the C/N ratios vary as a function of degassing (upper panel in a); the red dotted line represents fractionation following Rayleigh distillation). The correlation suggests that the C/N ratio of the source is about 200-300. Note that some E-MORB data suggest higher C/N ratios. (b) The correlation between $\text{N}_2/^{36}\text{Ar}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ is consistent with mixing between an atmospheric contaminant (air or seawater) and a mantle end member. The slope of the correlation gives the $\text{N}_2/^{40}\text{Ar}$ ratio of the mantle source, which is comparable to that of the atmosphere. In contrast, the atmospheric and mantle $\text{N}_2/^{36}\text{Ar}$ ratios differ by two orders of magnitude. The comparable $\text{N}_2/^{40}\text{Ar}$ ratios of the atmosphere and the mantle permit the concentration of nitrogen to be estimated at around 1 ppmw (see Fig. 3.4). Numbers along the correlation represent the percentage of atmospheric contamination for N_2 .

These analyses showed that the atmospheric $\text{N}_2/^{36}\text{Ar}$ is lower than the mantle ratio by two orders of magnitude, the latter being within the range of chondritic values (~ 10^6 , for carbonaceous chondrites). This difference will be discussed later with C data. In contrast, the $\text{N}_2/^{40}\text{Ar}$ ratio of MORBs, given by the correlation slope in Figure 3.5b, is near constant and comparable to that of the atmosphere. Calculating the bulk N content of the silicate Earth from the radiogenic ^{40}Ar budget is straightforward, because the parent isotope (^{40}K) abundance in the silicate Earth (mantle and crust) is reasonably well known. The reasoning is simple: (i) about half of the ^{40}Ar produced during Earth's history is now in the atmosphere, while the rest is still contained in the mantle; (ii) the N_2/Ar ratio of the mantle is comparable to that of the atmosphere; (iii) therefore, about the same amount of nitrogen as present in the atmosphere is still in the mantle, which corresponds *grosso modo* to 1 ppmw (Fig. 3.6).

Further analyses confirmed that N_2 and radiogenic ^{40}Ar abundances correlate well in MORB and OIB glasses from different localities worldwide (Marty and Zimmermann, 1999; Marty and Dauphas, 2003). Consequently, the N content of the mantle can be estimated from that of ^{40}Ar produced by ^{40}K decay. This is because the potassium content of the bulk silicate Earth (BSE) is reasonably well known (280 ± 60 ppm K; Arevalo *et al.*, 2009) and the duration of decay is also known as it corresponds to the age of the Earth. About half *i.e.* 42 (+32 or -18%) of radiogenic ^{40}Ar is now in the atmosphere as a result of terrestrial degassing (Allège *et al.*, 1996). The surface reservoirs (atmosphere, sediments, and crust) account for about 1 ppmw N (Hirschmann, 2018). Using the $\text{N}_2/^{40}\text{Ar}$ ratios of the atmosphere and the mantle, the mantle N concentration was estimated to be ~1 ppmw (Marty, 2012) and, more recently, refined to 1.1 ± 0.5 ppmw (Hirschmann, 2018). Hence nitrogen is a trace element on Earth. Available constraints on the global inventory of N in the Earth's mantle and surface constitute a solid basis for estimating the volatile content of the BSE



(Marty, 2012; Halliday, 2013; Johnson and Goldblatt, 2015; Hirschmann, 2018). The Earth is nitrogen-poor compared to primitive meteorites which contain several tens to hundreds of ppm nitrogen (Kung and Clayton, 1978), and also compared to comets (Marty *et al.*, 2016). This depletion could have resulted from partitioning into the core (Marty, 2012; Roskosz *et al.*, 2006, 2013), losses to space (Tucker and Mukhopadhyay, 2014; Bergin *et al.*, 2015), and/or thermal or impact metamorphism of the planetary bodies that accreted to form the Earth (Marty *et al.*, 2020).

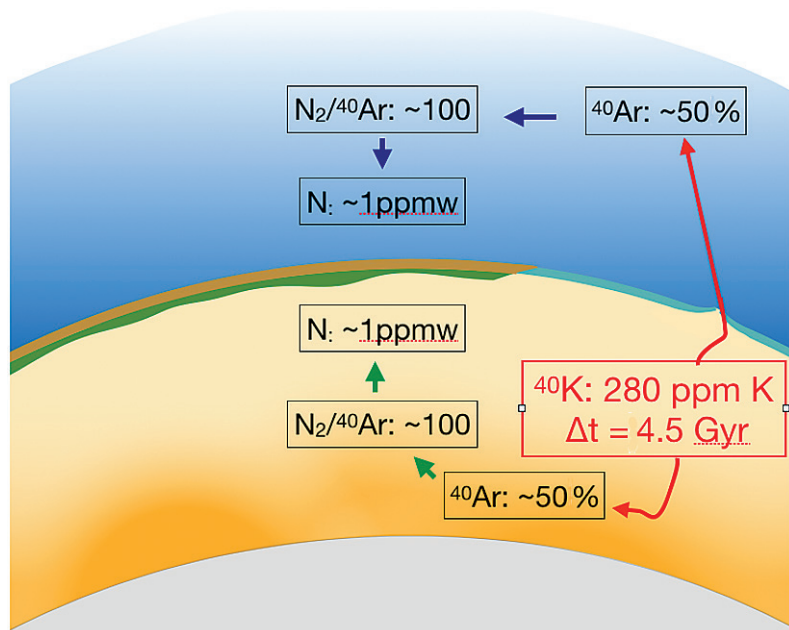


Figure 3.6

Principle of mantle nitrogen content determination. The amount of K is known and one can compute the amount of ^{40}Ar produced in silicates over 4.5 Gyr. The amount of ^{40}Ar in the atmosphere is well measured and corresponds to about half of its production. The $N_2/^{40}\text{Ar}$ ratios of the atmosphere and the mantle are comparable. Therefore, the total amount of nitrogen (atmosphere plus mantle) can be calculated. As the amount of atmospheric N_2 is also well measured, that of mantle N can be deduced by mass balance and corresponds to a mean concentration of 1 ppmw for a mantle mass of 4×10^{27} g (Marty, 2015). This budget has been refined by including further $N_2/^{40}\text{Ar}$ data for MORB and OIB glasses (Marty and Dauphas, 2003) and taking into account crustal nitrogen (Johnson and Goldblatt, 2015; Hirschmann, 2018).

During some of these experiments, the isotopic composition of mantle nitrogen trapped in MORB glasses was also measured, which yielded an average value of $\delta^{15}\text{N} = -3.3 \pm 1.0\text{ ‰}$ relative to atmospheric N (where $\delta^{15}\text{N} = [(^{15}\text{N}/^{14}\text{N})$



sample/ $^{15}\text{N}/^{14}\text{N}_{\text{atm}} - 1] \times 1000$). This signature is consistent with the average $\delta^{15}\text{N}$ value of diamonds (-5 ‰) and is considered to be representative of the mantle sampled by diamonds and MORB. Most primitive meteorites have $\delta^{15}\text{N}$ values ranging from about -30 ‰ (enstatite chondrites) to $\geq +20$ ‰ (carbonaceous chondrites), and the terrestrial values are therefore consistent with an asteroidal (Marty 2012) rather than solar (-400 ‰, see Section 6) or cometary ($\sim +800$ ‰, Section 7) origin. Interestingly, some rare diamonds show $\delta^{15}\text{N}$ values down to -30 ‰ (Cartigny and Palot, 2012) and might have preserved the primordial nitrogen composition. This ^{15}N -depleted signature is within the range of enstatite chondrite values (Javoy *et al.*, 1986), suggesting that this type of material might have largely contributed to the growing Earth, as also suggested by other geochemical tracers (Dauphas, 2017).

Nicolas Dauphas, then a Master’s student at the CRPG, analysed N-Ar concentrations and isotopes in a suite of ocean island basalts which presumably sample the deep mantle (Dauphas and Marty, 1999; Marty and Dauphas, 2003). The N-Ar isotopes define two different mantle correlations representing mixing between the atmosphere and two different end members, respectively (Fig. 3.7). One end member with $\delta^{15}\text{N}$ around -5 ‰ represents the convecting mantle also sampled by diamonds, but the other correlation defined by OIB data points to an end member characterised by positive $\delta^{15}\text{N}$ values, in the same range as sedimentary and crustal values. We proposed that the OIB signature

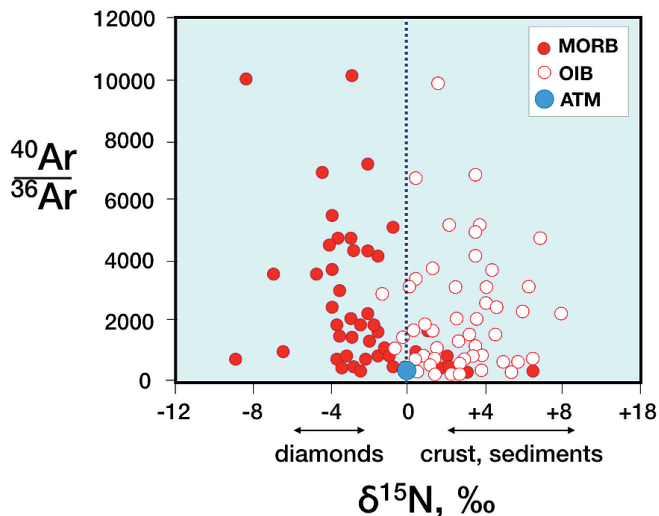


Figure 3.7

N and Ar isotope variations in mid-ocean ridge basalt (MORB) glasses and ocean island basalt (OIB) and mantle plume samples (adapted from Marty and Dauphas, 2003). OIB samples are from Iceland, Kola, the Society islands, Hawaii, and the East Pacific Rise at 15-19 °S.



was imprinted by recycling of sedimentary N deep in the mantle (Dauphas and Marty 1999). If the initial $\delta^{15}\text{N}$ value of the Earth was -30‰ , then the MORB mantle signature already represented a homogenised mixture of primordial and recycled N, whereas the mantle source of OIB might have been contributed to more efficiently by surface N (Marty and Dauphas 2003). An alternative interpretation has recently been proposed by Labidi *et al.* (2020) who confirmed that mantle plumes have positive $\delta^{15}\text{N}$ values using N isotopologues, but argued that they represent a primordial, rather than recycled, signature. The N isotope systematics, together with those of noble gases like Ne, illustrate the diversity of cosmochemical sources which contributed to the construction of our planet.

3.5 The Mantle C/N Ratio and the Carbon Content of the Silicate Earth

Given the importance of the carbon cycle on Earth, knowledge of the concentration of carbon in the major terrestrial reservoirs is essential, and several efforts, notably supported by the Deep Carbon Observatory programme, have been devoted to this task during the last decade. This is a difficult exercise because CO_2 has a low solubility in basaltic magmas and tends to degas at several km depth before magmas reach the surface. Hence, the concentrations observed in mantle-derived samples are in no way representative of the source composition, as only residual CO_2 is left in lavas. In order to estimate the C content of the convecting mantle, two approaches have been attempted, both focusing on mid-ocean ridges. One method, based on global mass balance, considered the carbon flux from mid-ocean ridges ($1.3\text{--}1.6 \times 10^{12}$ mol/yr, Section 3.2), the magma production rate at ridges ($16 \text{ km}^3/\text{yr}$, Le Voyer *et al.* 2019), and the average partial melting rate of the MORB mantle ($12 \pm 3\%$, LeRoex, 1987). Marty (2012) and Tucker *et al.* (2018) calculated a MORB mantle source concentration of 20–30 ppm C.

The other method was to estimate the ratio between CO_2 and a non-volatile element such as Nd or Ba for which the abundance in the convecting mantle is known. This approach yielded a similar estimate of 20 ± 7 ppm C (Rosenthal *et al.*, 2015). Carbon was also scaled to water, which has a higher solubility than CO_2 and tends to degas less (Hirschmann and Dasgupta, 2009; Dasgupta and Hirschmann, 2010), giving comparable results. One potential caveat with this approach is that it requires estimation of the CO_2 content of basalts prior to degassing, which can be problematic in the case of C-rich mantle sources. There is evidence (see below) that the mantle C concentration is heterogeneous as a result of C recycling, primordial heterogeneities, and variable states of degassing. Besides the convecting mantle sampled by MORB, other mantle reservoirs, such as those sampled by mantle plumes, could contain an order of magnitude more volatiles, as suggested by variations in noble gas isotope ratios. Unfortunately, the size of such mantle reservoirs is not known. In order to circumvent this problem, Rosenthal *et al.* (2015) and Hirschmann (2018) estimated the CO_2/Ba



ratio for samples from different tectonic settings. They proposed that a CO₂/Ba ratio of 100 ± 20 (ppmw) is representative of the mantle sources of the analysed lavas, and taking a Ba concentration of the convecting mantle to be 4.0 ± 0.4 ppm (Palme and O'Neill, 2013), the concentration of C in the mantle was thereby estimated at 110 ± 40 ppm (Hirschmann, 2018). With a similar estimate and a mantle concentration of 1.1 ± 0.5 ppm N (see Section 3.4), Bergin *et al.* (2015) estimated that the C/N ratio of the mantle is about 80.

We have adopted another approach based on the determination of the mantle N content (Section 3.4). The idea was to determine the C/N ratio in mantle-derived samples and also volumetrically analyse CO₂ on the same series of ocean basalts as analysed for N and noble gases (Marty, 1995; Marty and Zimmermann, 1999). Because gases trapped in ocean basalt glasses always constitute a residual fraction of the initial volatile content, it is necessary to correct observed abundances for degassing fractionation, which depends on the respective solubilities in basaltic melt. The solubilities of N₂ and Ar are comparable ($K_{N_2} \sim K_{Ar} \sim 2-3 \times 10^{-12}$ mol/g.hPa; where K_i is Henry's solubility coefficient; Carroll and Draper, 1994; Libourel *et al.*, 2003; Fig. 3.4) and not expected to fractionate upon degassing, which is effectively observed in MORB glasses. However, CO₂ and He are ~3 and ~10 times more soluble than N₂ or Ar, respectively ($K_{CO_2} = 9 \times 10^{-12}$ mol/g.hPa; Dixon *et al.*, 1995; $K_{He} = 2.5 \times 10^{-11}$ mol/g.hPa; Carroll and Draper, 1994). Accordingly, He and CO₂ will be depleted (relative to N₂-Ar) in the first fractions of gas escaping from a magma and enriched in residual gas trapped in erupted lavas. One way to correct for degassing fractionation is to use the radiogenic ⁴He/⁴⁰Ar* ratio. Its production/accumulation ratio in the mantle is estimated from the parent (U + Th)/K abundance ratio to be ~2 (range: 1.8-3.0; *e.g.*, Marty, 2012; Mukhopadhyay and Parai, 2019). Mid-ocean ridge basalts systematically have higher values in the range of 3-96 (Marty and Zimmermann, 1999), demonstrating the effect of elemental fractionation following Raleigh-type distillation. The initial (before degassing) (C/N)_i ratio of the mantle source can be calculated from the measured (C/N)_{meas} ratio according to:

$$(C/N)_i = (C/N)_m \times \left[\frac{\left(\frac{{}^4\text{He}}{{}^{40}\text{Ar}} \right)_m}{\left(\frac{{}^4\text{He}}{{}^{40}\text{Ar}} \right)_i} \right] \left[\frac{(K_{N_2}^{-1} - K_{CO_2}^{-1})}{(K_{He}^{-1} - K_{Ar}^{-1})} \right]$$

where K_j is the basaltic melt/gas partition coefficient for species j and suffixes "i" and "m" stand for initial and measured, respectively. After correction, the mean MORB C/N ratio was calculated to be ~500 (Marty and Zimmermann, 1999) with a large disparity of C/N values, E-MORB (1000-2000) being richer in C (relative to N) than N-MORB (100-300). This study indicated that the C/N ratio of the MORB mantle is much higher than that of the surface inventory ((C/N)_{surface} = 21 ± 6; Hirschmann, 2018). The MORB C/N ratios are generally higher than the estimate of Bergin *et al.* (2015) of ~90 (here molar) for the bulk



mantle (Fig. 3.8). Although some of the N-MORB data are consistent with the latter estimate, most MORB C/N ratios, as well as those for CO₂-rich gases of mantle derivation (see below), indicate that the C content of the mantle is high and heterogeneous. Further evidence for mantle C heterogeneities arises from co-variations of N, C, ³He, and trace elements (Fig. 3.9). The C/N ratio increases with the K₂O/TiO₂ ratio (Fig. 3.9a), which is an indicator of MORB mantle enrichment. E-MORB are rich in incompatible elements (like K) relative to compatible elements (like Ti) as a result of addition of crustal material. The higher C/N ratios of E-MORB compared to N-MORB are therefore consistent with addition of crustal C to the convecting mantle sourcing MORB. Furthermore, the C/³He and C/N ratios grossly correlate (Fig. 3.9b), which can be regarded as the contribution of a carbon-rich end member depleted in both mantle nitrogen and primordial helium to a depleted N-MORB component. The recycled crustal component is devoid of primordial ³He and N relative to C during subduction metamorphism (Busigny and Bebout, 2013).

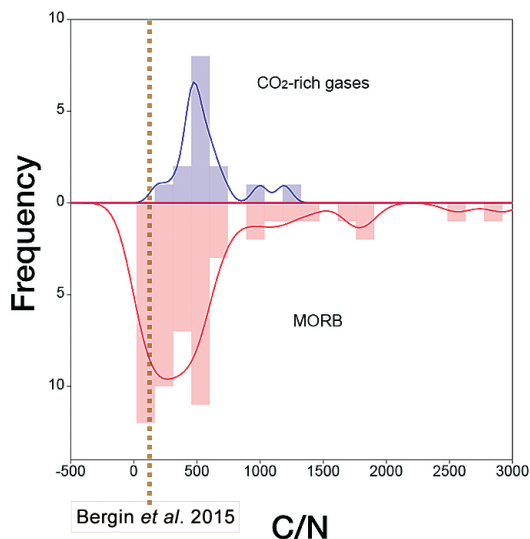


Figure 3.8

Kernel density distribution of C/N ratios in MORB and CO₂-rich gases. For comparison, the mantle C/N estimate of Bergin *et al.* (2015) is indicated by the vertical dotted line. All ratios are molar (adapted from Marty *et al.*, 2020).

The validity of correction for fractional degassing of MORB was questioned by Bergin *et al.* (2015) and we have recently considered another type of mantle-derived gas. We selected natural CO₂-rich gases which contain primordial ³He, have ⁴⁰Ar/³⁶Ar ratios above the atmospheric value, Ne isotope ratios which lie along mantle correlations (Section 2), and present excess ¹²⁹Xe produced

by the extinct radioactivity of ^{129}I (Section 1). These gases have $^4\text{He}/^{40}\text{Ar}^*$ ratios close to the mantle production/accumulation value and therefore have suffered little degassing fractionation (Marty *et al.*, 2020). They present both $\text{CO}_2/{}^3\text{He}$ ratios and C/N ratios that are within the range of MORB values (Fig. 3.8). If the mantle has a C/N ratio around 90, as proposed by Bergin *et al.* (2015), how could basalts and mantle-derived gases have up to one order of magnitude higher C/N ratios? This question is unsolved at present.

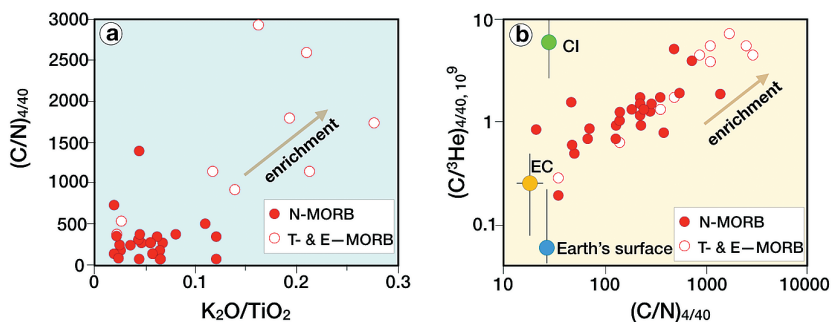


Figure 3.9

(a) Variation of the MORB C/N ratio (corrected for fractional degassing using the $^4\text{He}/^{40}\text{Ar}^*$ ratio) as a function of the $\text{K}_2\text{O}/\text{TiO}_2$ ratio. The latter is an index of MORB enrichment. (b) Variation of the MORB $\text{C}/{}^3\text{He}$ ratio as a function of the C/N ratio. Since ${}^3\text{He}$ is primordial, *i.e.* not recycled, covariations are due to addition of a C-rich component to an N-MORB component. These variations are likely to result from recycling of a crustal C-rich component which has lost N during subduction metamorphism. Both figures adapted from Marty and Zimmermann (1999).

Taking CO_2 -rich gas and MORB data together, we recently estimated the mean mantle C/N ratio to be within 350–470 (Marty *et al.*, 2020). Using again a mantle N concentration of 1.1 ± 0.5 ppm, the corresponding mean C concentration of the mantle would be around ~300–400 ppm, significantly higher than the value of 110 ± 40 ppm proposed by Hirschmann (2018) based on the CO_2/Ba approach. Estimates for the C concentration of OIB sources extend to values as high as 300–1800 ppm (Dixon *et al.*, 2002; Miller *et al.*, 2019). Clearly, the carbon content of different mantle domains, including the source of mantle plumes, is uncertain. Progress will require better understanding of the structure of the mantle, the nature of Earth’s building block materials, as well as of phase relationships of the mineral assemblages constituting the mantle.



4.

INTERMEZZO: VOLCANOES AND FIELD WORK

One of the great advantages of being a geoscientist is being able to do field work, or at least justifying adventures in exotic countries by the need to get well-characterised samples. Fieldwork is also a social exercise where you meet and get to know people of diverse cultures and collaborate in sometimes harsh conditions.

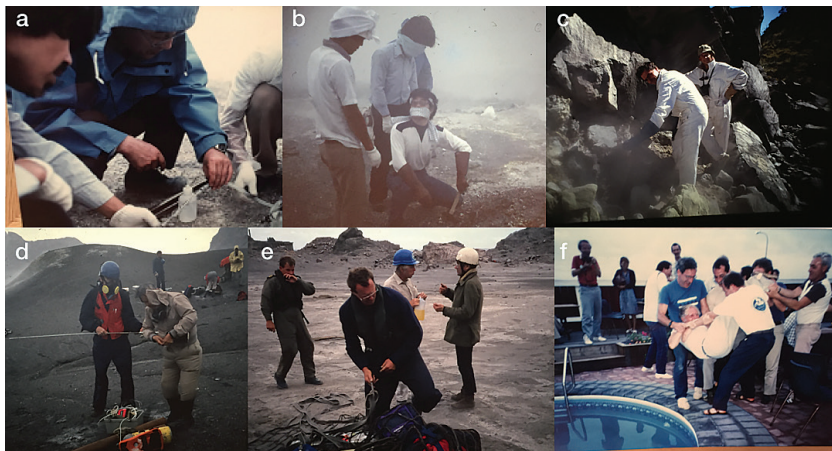


Figure 4.1

(a, b) Mt. Usu in 1983. (a) Sadao Masto (centre). (b) Sitting: Hiroshi Shinohara, now at the Geological Survey of Japan. (c) Sampling gases at Merbabu volcano, Java, Indonesia, with Patrick Allard, right. (d, e, f) White Island volcano, New Zealand, during a volcanic gas workshop. (d) Moto Sato (centre) trying to measure hydrogen fugacity in harsh weather conditions. (e) Werner Giggenschach, with a blue helmet. (f) Werner being thrown in the hotel swimming pool by some of the nasty participants. Photo credit: B. Marty.

During my career I joined several field campaigns on active volcanoes in Japan, Italy, and New Zealand to collect high temperature gases. In 1988, Werner Giggenschach, a New Zealander geochemist whom I mentioned earlier, organised a volcanic gas workshop on White Island, an active volcano off the north-eastern coast of New Zealand. Werner, a true chemist by training (and not a geochemist like most of us), was a master of gas sampling methods as well as chemical thermodynamics. He developed methods to perform *in situ* chemical analysis of eruptive gases in harsh conditions and could monitor thermodynamic temperatures of magmas in real time. A companion of Tazieff, he was once bombarded by chunks of molten lava while hanging on a rope over the lava lake of Mt. Erebus in Antarctica. He unfortunately passed away from a stroke while collecting gases in Papua New Guinea. The White Island trip was a nice opportunity to meet



with colleagues and friends of the volcanic gas community like Patrick Allard, Yuji Sano, Marie-Françoise Le Cloarec, Franco Italiano, and many others. We suffered from exceptionally bad weather that prohibited landing on the island by boat. So instead Werner organised transfers by helicopter from the coast to an Australian navy ship, where another helicopter then transferred participants from the moving ship to the White Island shore four people at a time. The helicopter pilot did an incredible job. The wind was so strong that four crew members had to hold hooks to retain the helicopter on the ship's deck and, at a given order, removed the hooks all at once while the helicopter was rising at full speed and moving away from the ship horizontally over several tens of metres. Landing also required extreme expertise, and the exhausted pilot, who did ten rotations a day, needed a nap in between landings. White Island is not a hospitable place, especially in rough weather, for collecting high temperature gases in the mist, and it reminds us that volcanoes are very dangerous places to visit and to work. There, one feels Earth's extraordinary energy. Volcanoes are eminently unstable high enthalpy systems that can break down at any time. One gas workshop ended dramatically in Central America, when a sudden explosion killed or injured several gas geochemists who were working on the lava dome at the time. The recent tragic event at White Island when a group of tourists was engulfed in an eruption while visiting the crater was deeply unfortunate; these phreatomagmatic eruptions are by their nature very difficult to forecast, and these people had been given the green light by the tour company to visit one of the most exciting, but dangerous, places on Earth.

4.1 Vanuatu

One of the most fascinating volcanic areas in the world is the archipelago of Vanuatu. It is an arc formed by the collision/subduction of two oceanic plates in the South Pacific and it hosts some of the most persistently active volcanoes. Vanuatu was called New Hebrides when it was a British-French condominium, a political exception where two colonial empires were fighting to increase their influence in the countries furthest from Europe. There are still remnants of this period in the Capital Port Vila. On one side of the road is a French brasserie where one can enjoy a *pastis* and a "steak-frites" on the terrace, and on the other side is a typical British pub with ale, darts, and chips. I went there in 1990 with a colleague from the French institute for overseas studies (ORSTOM, now IRD), Michel Lardy, to carry out a gas reconnaissance survey along the archipelago. The island of Tanna, a quick hop by plane from the capital island Vate, hosts a very active volcanic cone, Yasur, which stands about 380 m above sea-level and has continuous strombolian explosions within its 400 m diameter crater. The crater can be reached by car, making Yasur an enjoyable touristic spot. There were no accessible fumaroles so we started measuring trace gas concentrations in ambient air with so called Draeger tubes, which are glass tubes filled with colorimetric material that give concentrations directly. With a simple camera on a tripod and a chronometer, we could obtain semi-quantitative measurements



of the flux rate and dimensions of the volcanic gas plume. We estimated the total flux of SO₂, a key measurement in volcanic flux studies which allows the calibration of other gaseous species such as CO₂. The number we got with this crude method, 1200 ± 600 tons SO₂/day, was confirmed years later by teams working with absorption spectrometers. Compared to other active arc volcanoes, this flux is at the upper end of the scale relative to the persistent activity of Yasur volcano. There were some hot streams gushing along the coast and, in order to sample these, we asked for permission from the chief of a nearby village, located 3 km from the crater. From the village you could see the explosions rising over the roofs, without disturbing the inhabitants. Permission was given in a friendly way and the old chief asked to see me as he had a message to convey. I met with him in his house and he encouraged me to make a movie of our encounter. His community was raised with the religious belief that a superman, called John Frum, protects them from natural hazards (within a visible distance) and deprivation. One day he will come back to bring them all to the land of plenty. The legend apparently started during WWII, when the Vanuatu islands were a base for the US army fighting the Japanese army in the Pacific. When the war ended, the US army left major infrastructure on site and sunk a lot of machinery to the bottom of the sea, including trucks and facilities, before flying back to their country. The village where I went was organised like an army camp, with long huts mimicking soldiers' barracks. The US flag (or a piece of fabric resembling it) was raised every morning and the important men of the village wore clothes that also resembled US army uniforms. One night, a couple of men suggested we go to the forest for a special event, the kava ceremony, as a mark of friendship. Kava is prepared from the root of a pepper-like plant (*piper methysticum*) and is consumed for its relaxing properties. The men started to knead kava roots and a venerable elder chewed pieces of them until it became a kind of viscous pulp which he then spat out into a piece of fabric. The other participants squeezed the fabric over an empty coconut bowl and we drank it several times during the night, while the volcano roared in the distance. I do not know if it had a relaxing effect but I had strange dreams all night, in one of which a Tibetan monk was pursuing me with a long knife.

After Tanna, we flew to the island of Ambrym in a small bush airplane and landed in a meadow near the coast. There was no car on the island and we hired several enthusiastic young men to carry the equipment and bivouac gear. They had comfortable sport shoes and often played football, but they preferred to walk barefoot in the jungle to avoid wearing out the soles. After a few hours walk in the dense jungle, we reached the 12 km wide caldera of Ambrym, a flat surface where several volcanic cones were emitting volutes of gas. The helpers, except one, were not enthusiastic about following us towards the cones. We discovered a new crater of approximately 100 × 70 m, full of smoke and gas, that, following our helper's suggestion, we called Niri M'buelesu Taten, which means the son of the wild pig, in relation to the adjacent M'buelesu cone. I descended into the crater to measure temperatures and collect gases, but my gas mask rapidly became saturated and my colleague had to pull me out with the rope



I fortunately had attached around my chest. The last temperature I was able to measure before the thermocouple broke was 625 °C. Nearby were two cones, the M'ebuelesu and the Niri M'ebuelesu Tamo (elder son). We carefully approached the crater rim of Tamo and discovered silent explosions projecting cauliflower-like volutes of black and grey ash as well as blocks, some of them obviously fresh, sprinkling the flanks of the cone. We did not stay long. The other cone was emitting a noisy engine-like blast and we climbed to the rim of the crater where we discovered an amazingly loud jet of hot yellow gases gushing out almost horizontally at the bottom of the crater. The impression of power was absolutely overwhelming. These two cones were probably the result of lava migration from the nearby Marum cone. The other cone, the Bembow, often hosts a lava lake. We did not check but a strong blue plume rising from the crater signalled the presence of hot material. We did not write up any papers for peer reviewed journals although a report exists in the archives of ORSTOM, but this was one of the most impressive field trips of my career.



Figure 4.2 Vanuatu in 1990. **(a)** The team. Second row, right: Michel Lardy from ORSTOM. **(b)** Explosion at M'ebuelesu Tamo volcano, Ambrym. **(c)** Sampling high-temperature gases; the thermocouple broke down at 625 °C. **(d)** Staring at an explosion at M'ebuelesu volcano. Photo credit: B. Marty.

This was not the end of my Vanuatu experience. Six years later, I was on board the French oceanographic vessel l'Atalante sailing from Noumea, New Caledonia, to Port Vila, Vanuatu. The project was headed by Jean-Philippe



Eissen, a scientist at ORSTOM who unfortunately passed away a few years ago, and the goal was to make a detailed bathymetric map of a 20 km wide submarine caldera and dredge rock samples. This caldera might have been the result of a gigantic eruption in the 13th century that possibly triggered global cooling of the atmosphere. The vessel managed to reach Port Vila just before Bastille Day, and we were all invited to the 14th of July reception at the French Embassy, where everybody greeted the crew of the vessel –which was considered to be the jewel of the French scientific fleet– with champagne. The following day we embarked on the cruise and within 24 hours the vessel was on site and circling around the caldera edge beside emerged land. We were working round the clock with three hour shifts and the following morning a colleague and I were enjoying coffee in the sunshine on the upper deck. We spotted flashes of light from inhabitants with mirrors on the nearby coast and we naively thought they were doing that as a sign of welcome. Suddenly we heard a continuous thump and could feel a strong vibration everywhere on the ship. Bending over the edge of the deck we could see arrays of nearby coral reefs shining in the morning sun. The boat was perched on a coral reef and the captain applied full power to clear the barrier. The thumping ceased and we were excited to think that a ship could be sailed like a four wheel drive, by accelerating over an obstacle when stuck. However, this was absolutely not the case; the damage to the ship was extremely severe. Going down to the science room, we found all of our colleagues deeply worried, and we too became worried when the ship started to bend laterally. I was in contact with my graduate student, Franck Humbert, by internet. I told him I could not comment on his manuscript today because the ship was sinking. It was an attempt at humour, but the word spread quickly at the CRPG. The ship hull was torn open over several tens of centimetres and the ballasts were filling up with ocean water. Fortunately, people in the machine room were able to evacuate quickly, and the hull was breached at a level where there was double wall so that water could not enter. Once the ballasts were full, the vessel was stabilised. The signals from the local people had probably been a warning that we were entering a coral reef zone. A previous bathymetric map had been produced by a small vessel but it did radial back and forth trips over the caldera and could not see circumspherical corals. Our vessel was equipped with a multibeam sonar which was vertical and could not see ahead of the ship. When the seafloor suddenly rose quickly, it was too late. We headed back to Port Vila at moderate power, fortunately with beautiful weather. Once we arrived the captain decided to run the boat aground on the beach in front of the city instead of anchoring at the small harbour which had deeper water, in case the hull broke down. The local media had a field day when they reported that the jewel of the French scientific fleet, complete with the latest technological equipment, had returned discretely a few days after its much trumpeted departure. A diver inspected the hull, did some makeshift repairs, and finally the ship returned to Noumea where we debarked. A cruise that was supposed to last a month ended after just a couple of days. We had to wait a week for a return flight to France. Meanwhile, we explored the restaurants and beaches of New Caledonia, feeling sort of sad for Jean-Philippe who had been organising this expedition for years. The end of the story



was that the entire schedule of the ship had to be set back for months, and many cruises were cancelled. Notably, the nearest dry dock where the hull could be fixed was far away in the Fiji Islands. This was my first, and last, scientific cruise: sampling volcanoes appeared to me less dangerous than sailing on the oceans.

4.2 The Ethiopian Magmatic Province

Ethiopia stands on an exceptional tectonic setting where three rift segments, the Red Sea, the Gulf of Aden, and the Ethiopian Rift (which terminates the East African Rift system) meet to form a triple junction. Along the northern border of the continental rift, the Ethiopian Highlands were formed by km-thick continental flood basalts and ignimbrites/rhyolites covering an uplifted Pan-African crust. Within the locus of the triple junction, the crust is stretched and delaminated, forming the Afar Triangle. Active volcanism takes place along the Ethiopian Rift and in Afar. The interplay between tectonics and magmatism has been studied for decades and, in particular, was central in the joint exploration programme by the French and Italian research agencies (the CNRS and CNR, respectively) in the early seventies (Barberi *et al.*, 1972). This programme established a detailed geological map of Afar and explored active volcanoes including Erta-Ale and its permanent lava lake. In 1974-1975, the fall of Emperor Hailé Selassié and the seizing of power by Mengistu Haile Mariam drove the country into a bloody dictatorship, with millions of people imprisoned, tortured, and/or executed. The country was isolated from the scientific world until the fall of Mengistu in 1991. Then timid exchanges with former western allies resumed, and, for cultural and historical reasons, France and Italy were among the first countries to re-initiate collaboration with Ethiopian geoscientists. The country had been torn apart by years of war and found itself in a desperate economic situation, but liberation infused a new wave of enthusiasm, hope, and curiosity, especially among the young. French scientists were among the first to be allowed to work there, and in 1994, we were asked if we were interested in doing field work. I was of course interested, the noble gas lab at the CRPG was operational and there was a long standing debate about the origin of East African magmatism and the relationship between rifting, continental flood basalts (CFB), and continent breakup. In the seventies Harmon Craig and colleagues analysed geothermal waters and gases along the Ethiopian Rift for stable isotopes and helium isotopes. The study was never published in a peer reviewed journal (as was the case for many of Craig's projects) but data were reported in a United Nations report. The $^3\text{He}/^4\text{He}$ ratios varied between some crustal end member values and values above the MORB range (7-9 Ra) up to 13 Ra, suggesting a mantle plume source feeding modern volcanism. Since the rift magmatism is at most 2 Ma, what was the potential relationship between 30 Ma old Ethiopian CFB, crustal uplift, rifting, the Afar triple junction, and continental breakup? Raphael Pik was then a Ph.D. student, supervised by Philippe Vidal and Christian Coulon, studying the origin of basaltic volcanism in Ethiopia. A field trip was organised with the support of the French Ministry of Foreign Relations and I flew to Addis Ababa to meet



Raphael and two other students and post-docs at the Café de la Gare. This was a bar/restaurant/hotel near Addis train station where the train line from Djibouti built by the French in 1902 ended. I also met Gezahegn Yirgu, a professor at the University of Addis who would become a long term close colleague and friend, and Dereje Ayalew, then an undergraduate student at the University of Addis Ababa. The Café de la Gare, with its provincial atmosphere and little garden, was a turning point for traffic of all genres, gossip, rumours, more or less (un)verified information, and was the ideal place to plan a trip into the wild.



Figure 4.3 Sampling mantle plume gases in Ethiopia. **(a)** Raphael Pik explaining the geology of Afar (November 2017). **(b)** Dereje Ayalew and Antonio Caracausi sampling mineral spring gases at Ambo, Ethiopian Highlands (April 2018). **(c)** Transporting equipment in central Afar (January 2011). **(d)** the lava lake inside the Erta Ale central crater. **(e)** Northern crater of Erta Ale, with fumarolic temperatures up to 1080 °C. Photo credit: B. Marty.

It just so happened that I was the most senior participant (Gezahegn could not come) but had absolutely no experience with field work in African countries. Raphael had already participated in weeks-long field trips in the Highlands and was the most experienced but also the youngest participant. In Ethiopia, as in many African countries, seniority matters so our crew was a little awkward for our Ethiopian partners. Two drivers were recruited, one having already worked for French geologists before. The other, a former seminarian, had absolutely no experience with field work or, more concerning, with driving; he was also myopic and a little bit psychotic. We embarked into two aged four wheel drive cars and headed to Afar, along one of the most dangerous roads in the world.



The War of Liberation was largely won thanks to the support of the Eritrean people. After the war, Eritrea, which had been annexed by Ethiopia during the dictatorship, declared its independence. As a result, Ethiopia lost direct access to the Red Sea through which all goods, including oil, transited to Addis Ababa. The only access left was through the Republic of Djibouti, linked to Addis by the French-built railway that was falling apart (there is now a brand new railway built by the People's Republic of China) and a partially paved road used by most of the commercial truck traffic. Most trucks were wrecked, some with tires where one could see the metal grid beneath the rubber. The only speed limit was that determined by the degradation of the road; and horribly twisted truck frames punctuated the sides of the road every ten metres or so. We managed to spend ten days in Afar, collecting basalts and geothermal gases during daytime and spending nights in trucker hotels which were also brothels, bars, discos, and restaurants with never ending loud music. It was not possible to camp outside for security reasons. The country was coming out of years of turmoil and civil war, and the price of a Kalashnikov was about that of a sheep. In fact, the drivers selected our hotels for drinking and prostitutes, rather than for rest as we had requested. We also had to hire a local "guide", who was a friend of some person in the authority and spent his time asking for more money and bottled water. Finally, the rain came, in a desert where such events are very rare, and we were forced to stop driving off road. To add to the charm of the local travelling conditions, there were plenty of fleas and mosquitos, but fortunately we did not get malaria. So this first trip was not the best we had in Ethiopia but we collected sufficient samples in Afar and in the Ethiopian Rift to get a good snapshot of the regional helium isotope distribution.

We went back to Afar several times since, until very recently, and conditions have drastically improved. The road to Djibouti is now fully paved, the state of most trucks is reasonable, and going off road is not a problem anymore, provided that you travel with local policemen or militia and with good drivers in decent cars. We worked for the last decade with a French gentleman and his wife who provided us with excellent logistics. We were able to enjoy the beauty of this arid country, the culture and habits of its inhabitants, and work in relaxing conditions. One limitation is the size of Afar but helicopter support was out of our academic budget. We have recently been collecting soil and geothermal gases along one of the rift axes, in the Erta Ale area and in regional air, to try to detect ^3He excesses with our high-He isotope system designed to investigate atmospheric helium isotope variations (see Section 3). Surprisingly, we could not find evidence of mantle degassing even in the geothermal gases, suggesting discontinuous localised pulses of magmas, and Raphael, Pete Burnard, post-doc Alice Williams, and Ph.D. student Sarah Medynski worked for a long time to unravel processes of magma generation and rift propagation along some of the Afar rift segments, using geochemistry and dating young lava flows with cosmogenic isotopes (Medynski *et al.*, 2013).



One of the Ethiopian government's priorities was and still is education: there are about 25 universities in Ethiopia, with an elite system that aims at selecting the best students for the best universities such as the University of Addis Ababa. Vincent Courtillot at the IPGP was very supportive of further Ethiopia-France collaboration and managed to raise funds for Ethiopian students. After a Master's degree in Addis, Dereje Ayalew went to the CRPG to prepare a Ph.D. supervised by Pierre Barbey, a petrologist at the CRPG, and myself. Modern studies on the petrology and geochemistry of Ethiopian CFB were well explored by Raphael Pik, who demonstrated a mantle plume origin for some of the (high Ti) basalts, whereas others (low Ti) showed a contribution from the lithosphere and the Pan-African crust (Pik *et al.*, 1999). It seemed interesting to us to investigate the origin and timing of Ethiopian ignimbrites and rhyolites which are abundant in the Highlands and along the recent rifts. Little work had been done before and it was quite old, so the study required new sampling all along the Ethiopian Highlands and Rift. This was an excellent opportunity to discover a fascinating country on a large scale. When one thinks of Ethiopia it is often about famine and despair as was the case, for example, in the eighties, largely as a result of the politics of the dictator. The rural areas are not prosperous, but people are generally self sustaining thanks to local farming, at least in the Highlands which are well watered. Afar is another story. The people are nomads who move depending on vegetation and water, and the Ethiopian government is attempting to settle them with water tanks. During the first trips, the country was barely recovering from the War of Liberation and one could find wrecked Soviet tanks, trucks, and cannons all along the Highland roads. The field conditions were very basic, no possibility of camping and you were advised to remember to go to the natural toilet during the day because those at the hotels were, let us say, adventurous at best. No matter how remote, it was always possible to find a cool beer at night, injira (a traditional sort of crepe made with teff, a local cereal) or pasta, the other choice, covered with hot tomato sauce. Mornings woke you up with scrambled eggs and a piece of bread, delicious home made coffee and a Fanta®. Progressively, conditions improved and decent hotels can now be found everywhere. The landscapes are sumptuous, biblical, with amazing gorges sculpted into piles of flood basalts, and cold rivers in the depths. The people are welcoming, with myriads of children whirling around with big smiles and laughter. Ethiopia has never been colonised, except for a relatively short period of time by Italy in the thirties, prices everywhere are generally the same for foreigners and locals, and bargaining is very rare. Most tourism takes place in a few areas like Lalibela with its churches carved in stone, which are linked by buses and regional planes. Maybe one day these places will resemble Kyoto or Amsterdam, crowded with tourist groups, which by the way would be fortunate for such a country, lacking energy and commercial resources.

With all the helium data we collected and the detailed geochronology completed/carried out at the IPGP, we built a model for the generation and evolution of the Ethiopian mantle plume (Marty *et al.*, 1996). The mantle plume



reached the surface 32 Myr ago and provoked crustal uplift of 1-2 km in central Ethiopia and flooding of about 1 million km³, 1-2 km thick lava flows, in less than a million years, over a surface area of ~1000 km diameter in central Ethiopia and Yemen before continental breakup (Hofmann *et al.*, 1997). The ³He-rich mantle plume component (up to 20 Ra) was already present and rifting developed later along the Ethiopian Rift and in Afar, leading to a complex array of rift segments and oceanisation of the crust. This breakup in the already extending crust might have been facilitated by regional heating of the lithosphere by the plume. Rifting then focussed volcanism along the rift segments where it is still active. Mantle plume helium is still present today in the Ethiopian Rift, the Gulf of Tadjoura, and along the Red Sea (Marty *et al.*, 1993), with slightly lower ³He/⁴He, perhaps marking progressive dilution of deep seated material by the surrounding convecting mantle and the lithosphere. Geophysical imaging suggests that the Ethiopian-Afar mantle plume is rooted at the core-mantle boundary below West Africa/Atlantic Ocean and is deflected towards the Horn of Africa over several thousands of kilometres. We confirmed the relationship between CFB and mantle plumes, suggested independently for the case of the Deccan traps (Basu *et al.*, 1993). The study of Oligocene ignimbrites and rhyolites located on top of the Ethiopian Highlands has shown that they originated from mantle-derived magmas that differentiated in the upper crust and are closely associated with the development of the Ethiopian mantle plume (Ayalew *et al.*, 2002). Their thickness can reach 500 m and, because they require differentiation of basaltic melt about 5 times their volume, part of the crustal uplift could be due to the injection of giant sills in the Pan-African crust from the Oligocene to the present. In the Rift and Afar, lavas are generally younger than 2 Ma and are composed almost exclusively of differentiated products in the form of central stratovolcanoes and of thick deposits along the Rift axis, with basalts making up less than 10%. This feature seems to characterise the first steps of rifting and continental breakup prior to large basalt eruptions.

The occurrence and location of mantle plumes in Africa is a classic example of interactions between continental breakup and mantle plumes. The African plate has been near-static since at least the Tertiary, and the plate could be anchored by several mantle plumes, the surface expressions of which are intracontinental volcanic provinces such as Kenya, Hoggar, Tibesti, Darfur, and Cameroon. However, for most of them, their ³He/⁴He ratios are lower than, or equal to, MORB, characterising the convecting, presumably upper mantle (Pik *et al.*, 2006). Only Ethiopian lavas and gases show He isotope ratios higher than those of MORB. Likewise, there are other large igneous provinces in Africa, such as in Kenya and Cameroon, with formation of domes and voluminous lava outflows, but only in Ethiopia are these features associated with both high ³He/⁴He ratios and deep roots, suggesting the occurrence of different types of mantle uplift (Courtillot *et al.*, 1999). Thus, the Afar mantle plume may be of a similar nature as the Icelandic, Yellowstone, Réunion-Indian, or Hawaiian mantle plumes. However, Halldórsson *et al.* (2014) proposed the existence of



a single deep-rooted mantle plume beneath Ethiopia and Kenya, from He-Ne isotope relationships in rocks from the Rungwe volcanic province, south of the Kenyan dome.

4.3 Oldoinyo Lengai in the Maasai Country: The Coolest Volcano on Earth

The amount of noble gases in terrestrial rocks is very low, of the order of 10^{-14} - 10^{-18} mole *per* gram, and a way to improve precision was to analyse “large” samples like natural gases that could be duplicated many times while keeping their isotope homogeneity. Remarkable work had been carried out on CO₂-rich well gases in the US and Australia, with a demonstrable mantle origin which allowed us to unravel detailed isotopic structures of primordial noble gases, in particular xenon (Caffee *et al.*, 1999) and krypton (Holland *et al.*, 2009). The nature of the mantle source of these gases was, however, uncertain, and we thought it would be interesting to extract mantle gases directly from an active volcano. Most volcanic gases including fumaroles and bubbling geothermal waters are heavily contaminated by atmospheric noble gases as indicated by low ⁴⁰Ar/³⁶Ar ratios close to the atmospheric value. A possible exception could be carbonatitic volcanism, because carbonatites are lavas composed almost entirely of calcium or magnesium carbonates. We expected that carbonatites might be rich in noble gases if the carbonates had originated from a CO₂-rich volatile phase. Carbonatites are found all over the world and in all geological eras, and most of them occur in continental areas. The origin of carbonatites is debated to be either the resurgence of mantle carbonate-rich fluids or immiscibility of carbonate-rich phases from silicates, or a combination of the two. There is currently only one active volcano on Earth erupting (magnesium) carbonatitic lavas, Mt. Oldoinyo Lengai (Mountain of Gods) in the northern Tanzanian Rift, south of Lake Natron. We drafted a small proposal to CNRS, designed special glassware to sample large amounts of noble gases in volcanic fumaroles, and asked Toby Fisher, a volcanic gas geochemist at the University of New Mexico, if he would like to join us. We flew to Tanzania in July 2005 and ended up in a Masai village close to the volcano. The volcano is often visited by adventure tours and the business of guides and porters is well developed. Talking with the head of the Masai porters, we were informed that tariffs would be double what we had been told. Negotiation was difficult with someone carrying a spear and we had to cut one day of our planned three day expedition to stay within our budget. Climbing to the volcano was strenuous because Masai trails go directly upward without any turns even when the slope is >40 °. In the early morning we reached the crater filled with white carbonatites, with several small pits (Fig. 4.4).





Figure 4.4 (a) Oldoinyo Lengai, Tanzania, an active carbonatitic volcano located on the eastern branch of the East African Rift Valley. (b) Crater filled with carbonatite lavas in July 2005. Several hornitos (cones) were spilling out fresh lava. Originally black, carbonatites rapidly turned white (in a matter of days) as they became hydrated. (c) Pete Burnard and Masai porters. (d) Cascade of liquid carbonatite continuously flowing from a 10 m high hornito. Photo credit: B. Marty.

Carbonatites are black when they erupt and turn white within a day as they readily become hydrated in contact with moisture from the air (Fig. 4.4c). The carbonatite crater was a peaceful, silent, white landscape with a little stream of water-like fluids making its way through snow. We discovered a nice cascade of molten black carbonatites from one of the cones flowing downstream in lava flows with low viscosities, similar to water or oil, at a temperature of 550 °C (Fig. 4.4d). We had a cook with us, with four live chickens in a cage, who suggested camping under a small lava rampart, shielded from the wind. We were not enthusiastic about the site because a stream of molten carbonatite was flowing, albeit quietly so, only 50 m away from the spot. We would rather go to the other side of the crater but the Masai insisted on staying at the first site because they were poorly protected against the cold clothing-wise. So we stayed and set up our tents for the first night, which was particularly harsh for one colleague since he was suffering from “turista” (diarrhea) and frequently had to go outside in the night, knowing that there was an active volcano very close by with a flowing lava stream, as well as a leopard thought to be wandering



around the crater. The following morning, we went to sample and we found a nice fumarolic area where we started sampling gases in our big glass, Giggenbach-type, bottles. The site was a little bit exposed as it was right beneath a pit where molten lava was flowing on the opposite flank, so we moved to another spot where a hole in the ground was strongly degassing. Toby, who is an experienced volcanologist, had had the good idea of bringing a swimming pool pole to which we could attach a funnel connected to Tygon[®] tubing (Fig. 4.5a). We could then quietly sample 175 °C gases in our Giggenbach bottles while sitting at the surface and this resulted in some of the least air contaminated gas ever sampled on a volcano. The following night we were awakened by yelling and screaming which we thought were our porters arriving as this was our last day on the crater. But when we woke up, we discovered that the Masai camp had been flooded by molten carbonatite from which they barely escaped (Fig. 4.5c). They saved most of their material, but the two remaining chickens were lost. Nevertheless, they managed to prepare breakfast with the pans heating directly on the still viscous lava (Fig. 4.4d). In 2007, a major eruption destroyed the flat crater we visited and now there is a large, deep crater with carbonatite erupting at the bottom and no pristine fumaroles can be accessed.



Figure 4.5

(a) Sampling gas at Oldoinyo Lengai. The best gas samples with temperatures up to 175°C were collected from a hole with a funnel attached to a swimming pool pole. (b) Our initial base camp. (c) The same base camp after lava flooding. (d) The cook prepared our breakfast directly on the cooling lava. Photo credit: B. Marty.



The data proved to be very interesting. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio was up to 947, attesting to the limited air contamination, while the $^3\text{He}/^4\text{He}$ ratio was about 6.9 Ra, slightly below the MORB range but within the range of mantle values typically found for volcanoes in continental settings. The C/N/He ratios were little fractionated from a MORB-like mantle composition and the carbon and nitrogen isotopic ratios were mantle-like. Contrary to the case of trace elements, which are highly enriched and fractionated in carbonatites by partial melting, volatile elements including noble gases were not fractionated, suggesting that the formation of carbonatites took place at low pressure when a gas phase was already present. We proposed that the carbonatitic liquids formed from a MORB-like source with a very low partial melting rate. This enriched the liquid in carbon-bearing phases which experienced immiscibility at low pressure (Fischer *et al.*, 2009). Unfortunately, our five collector mass spectrometer never worked properly and we could not achieve our primary goal of analysing xenon isotopes. We had to wait for a new analyser and a new set of magmatic gases which were collected not very far from Nancy a decade later.

4.4 The European Magmatic Province

Antonio Caracausi, a gas geochemist at the Instituto Nazionale di Vulcanologia e Geofisica (INGV) at Palermo, Sicily, came to visit Pete Burnard and myself at the CRPG on a sabbatical position. Having worked for a long time on gas compositions and stable and helium isotopes, he wanted to expand his knowledge to heavy noble gases. It is rare to find natural gases that are not air contaminated for noble gases so Antonio did a literature search on the composition of gaseous emanations in western Europe, finding an extensive survey in the Tertiary-Quaternary volcanic province of Eifel carried out by a German group (Bräuer *et al.*, 2013). From this, Antonio targeted sites with elevated $^{40}\text{Ar}/^{36}\text{Ar}$ up to 3,000. Current debate about the origin of this volcanism centres around rifting of the European plate in response to the Alpine collision or a mantle plume channelled by regional tectonics. At Victoriaquelle, vigorous bubbling of CO_2 -rich gas is taking place in a charming forest, and the site has been known for its curative effects since Roman times as attested to by ruins of a thermal facility. Antonio went there to collect plenty of gas, which, after purification, permitted duplicate high precision analysis of xenon isotopes. Previously, Holland and Ballentine found that krypton isotopes in mantle-derived CO_2 -rich gases point to a chondritic, rather than a solar, origin for mantle volatiles (Holland *et al.*, 2009). Likewise, Antonio found that the stable isotopes of xenon pointed to a chondritic, rather than a solar, origin, as also indicated by neon and helium isotopes (Caracausi *et al.*, 2016). Hence, a dual origin for volatiles trapped in the mantle was confirmed, with light noble gases, which are enriched in a solar component, deriving from the solar nebula (or from solar wind-implanted material) and heavy noble gases, krypton, xenon and, presumably argon, originating from inner solar system material. From mass balance, we suggested that major volatiles such as C and N were derived from asteroidal-like material. We also claimed that the



xenon isotopes produced by the decay of ^{129}I and by fissions of ^{244}Pu and ^{238}U (Section 2) pointed to similarities with Icelandic Xe (Mukhopadhyay, 2012), and that the Eifel magmatic province might have affinities with a mantle plume. This proved to be incorrect when, with David Bekaert and Michael Broadley, graduate student and post-doc at the CRPG, respectively, we sampled the Victoriaquelle gas again and analysed Xe in a less air contaminated gas sample. These samples were collected during the summer season when the amount of atmospheric gases dissolved in rainwater is low, and we used Giggenbach bottles, which had not been the case of Antonio's sampling. The Giggenbach bottle, originally designed by Werner Giggenbach, is a smart and simple device consisting of a glass bottle half filled with a 5 N NaOH solution, with the dead volume above the solution pumped away. The alkaline solution traps water vapour, CO_2 , and sulfur species which are by far the major constituents of volcanic and geothermal gases. After purging the connecting tubes, the gas is pumped into the bottle by the evacuated space in which minor residual species, mostly N_2 , noble gases, and sometimes CO , CH_4 , and H_2 , accumulate. The bottle is able to pump two to three orders of magnitude more gas than its physical volume, and major species abundances and isotope ratios can be determined by titration and after solution degassing, respectively. The evacuated space volume contains noble gases which are enriched by several orders of magnitude, increasing greatly the signal/contamination ratio. Using this method, we collected gases with $^{40}\text{Ar}/^{36}\text{Ar}$ ratios up to 8,000, which has improved our understanding of Earth's formation. While the high precision Xe isotope analysis confirmed the chondritic origin, it did not corroborate the mantle plume affinity as the noble gases of the Eifel sample were closer in composition to those from the convecting mantle sampled at mid-ocean ridges (Bekaert *et al.*, 2019).

4.5 Gases from the Deep Mantle: Yellowstone National Park (USA)

In 2018 we started a systematic noble gas study of geothermal fields in Yellowstone National Park (YNP) under the leadership of Michael Broadley (CRPG) and Pete Barry (Woods Hole Oceanographic Institution, USA) (Fig. 4.6d-g). Yellowstone is the surface expression of a mantle plume which pierces a Precambrian basement where He isotope ratios of geothermal manifestations show dilution of mantle plume-like $^3\text{He}/^4\text{He}$ (with values higher than those of MORB) by crustal radiogenic He. The idea was to obtain high precision isotope data for noble gases (especially Kr and Xe) sampled in large amounts using the Giggenbach bottle technique to check if they differed from compositions typical of the convecting mantle sampled at mid-ocean ridges. So far, the data show neon isotope variations with a similar slope (in a 3-Ne isotope diagram, Section 3) to those from Hawaiian volcanism. The data further indicate the occurrence of carbonaceous chondrite-like Kr and Xe in the mantle source of plumes as also seen in samples from the convecting mantle, hence demonstrating an inner solar system origin for volatile elements trapped during the early stages of Earth's accretion (Broadley *et al.*, 2020). Field work resumed in September 2019 in order



to extend the geographic diversity of the sites sampled. A novel study on nitrogen isotopologues on gases from YNP and other locations led by Jabrane Labidi and Ed Young at UCLA opened a novel avenue to decipher the origin of N in the deep mantle (Labidi *et al.*, 2020). We were supposed to return to YNP in September 2020, but the ongoing COVID-19 pandemic has frozen all planned field work.



Figure 4.6

(a) Sampling volcanic gases at the crater of Mt. Etna with INGV scientists (2014). (b) Sampling gases at Mt. Etna Voragine crater with Evelyn Fűri (centre) and Tefang Lan (right). In the background, Marteen de Moor. (c, d) Sampling mineral spring gases at Victoriaquelle spring (Eifel, Germany) with Michael Broadley (left) and David Bekaert (2018). (e, f, g) Sampling geothermal gases at Yellowstone National Park. (f) On the left-hand side, Pete Barry. (g) Sampling train at Yellowstone. From left to right, metal funnel, two copper tubes for long-term helium storage, and a Giggenbach bottle for stable and noble gas isotopes. Photo credit: (a, b, c, d) B. Marty, (e, f, g) D. Bekaert.



In the nineties, geochemists turned more and more to cosmochemistry, the geochemical study of extraterrestrial (ET) material. It seemed to many that mantle geochemistry was going round in circles and was no longer the branch of geochemistry where paradigm changing discoveries could be made. This was quite arrogant and inexact, as new concepts and novel tools including terrestrial extinct radioactivities and chemical geodynamics turned out to still have good days ahead. New instruments were being delivered to the CRPG, starting with the Cameca IMS 1970 large sector ion probe, the first model ordered by Etienne Deloule and Marc Chaussidon. Guy Libourel developed experimental setups targeting low pressure, high temperature runs in vertical furnaces to investigate chemical reactions in the nascent proto-solar nebula. Laurie Reisberg, specialist in Re-Os isotope geochemistry, also watched ET samples closely. As I installed a new noble gas facility, I naturally became interested in volatile elements in the solar system. However, a lot of noble gas studies had been carried out since the discovery of non-terrestrial noble gases in meteorites in the early sixties (see Section 1). Noble gases were central to the discovery of extinct radioactivities in the solar system, and to the identification of pre-solar material that had survived the birth of the solar system. Since several laboratories worldwide already specialised in noble gas cosmochemistry there were fewer opportunities for breakthrough. However, with my new static mass spectrometry technique I thought about analysing nitrogen isotopes together with noble gases.

Nitrogen isotopes were until then mainly analysed by conventional stable isotope (dynamic) mass spectrometry, which required about 1 ppm N in samples, but our static mass spectrometry method decreased the detection limit by about six orders of magnitude and therefore paved the way for microsample analysis such as individual lunar or meteoritic grains. Based on the analytical performance developed at the CRPG with ion probe and static mass spectrometry, we have been able to analyse ET material from every sample return mission, that is, lunar samples collected by the Apollo and Luna missions, solar wind collected by the Genesis mission, cometary grains collected by the Stardust mission, and asteroidal samples collected by the Hayabusa mission. We are now awaiting the arrival of new asteroidal material to be returned by the Hayabusa 2 and Osiris Rex missions to carbonaceous chondrite-type asteroids. This makes the CRPG somewhat unique among geochemistry labs.

The exploration of the Moon and lunar sample returns by the Apollo and Luna missions led to fantastic discoveries that changed the paradigm on the origin of terrestrial planets and their early history, not only for the Earth-Moon system, but also for the composition of the Sun and its evolution through geological time. One of the remarkable features of the Moon is the absence of erosion, weathering, and tectonics over the past several billion years, meaning



that ancient lunar surfaces can be tracked back to 4.3 Ga. On Earth, in contrast, the oldest available rocks are 3.8-4.0 Ga old, and many Precambrian terranes have been buried, subducted, or metamorphosed. The lunar surface, unlike the Earth, has preserved a record of the impact history of the inner solar system, which has allowed establishing a crater density-surface age relationship, used in turn to place age constraints on surfaces of planetary bodies such as Mars, Venus, and some satellites of the Giant planets.

One important question was the occurrence and origin of lunar volatiles. Looking back to the Apollo 11 mission, lunar volatiles were characterised and different components were disentangled using a variety of techniques available in the Apollo era, fifty years ago. One particular focus was the lunar regolith, a "soil" on average 10 m thick covering most of the lunar surface. Lunar soils are made of different sized fragments resulting from the fracturing of rocks by meteoritic impacts, which lead to a periodic mixing process known as "gardening". Lunar soils also preserve a record of the bombardment by ET material from planetary surfaces not protected by atmospheres. Once at the surface, lunar soil particles are exposed to the continuous flux of solar wind ions and to cosmic rays made of high energy protons which produce new isotopes. The surface exposure duration of lunar soil grains, calculated from the accumulation of cosmic ray-produced isotopes, varies between a few Ma and several Ga. Long durations are expected since no tectonic processes are renewing lunar surfaces, which are only being reworked by impacts. Solar wind ions are implanted within the first tens of nanometres of the surface of the grains whereas cosmic rays can penetrate up to several tens of centimetres and synthesise new isotopes.

It was soon discovered that lunar soils contain abundant noble gases and that their noble gas concentrations increase with decreasing grain sizes and therefore increasing surface/volume ratios (Eberhardt *et al.*, 1970, 1972; Fig. 5.1). This property shows that lunar noble gases are not trapped within grains but instead appear to have been deposited on their surfaces, as if they had been delivered by an external flux. The most obvious candidate for irradiation was solar wind, which consists of ions from the Sun accelerated by the solar magnetic field to velocities of several hundreds of km/s. The direct analysis of solar wind ions implanted in aluminum foils deployed by Apollo astronauts confirmed a solar wind origin for lunar soil noble gases. The case of other volatile elements, in particular nitrogen, was not so clear, nor was the occurrence of indigenous volatiles.

A long-standing, unresolved problem concerning the isotope variability of nitrogen in lunar soils was pointed out by Rainer Wieler, a noble gas cosmochemist at ETH Zürich well experienced in analysing lunar samples. The Zürich laboratory was established by Peter Signer who came back from Al Nier's (the pioneer of modern mass spectrometers) lab with two analysers. This facility was among the first to analyse lunar rocks returned by the Apollo astronauts. Analyses from the seventies using dynamic mass spectrometry showed that nitrogen trapped in lunar soils presents remarkable isotope variability, with $\delta^{15}\text{N}$



ranging from -240 ‰ up to +250 ‰. In particular, cosmic rays produce ^{15}N and the highest $\delta^{15}\text{N}$ values found in bulk lunar soil grains were correctly attributed to the contribution of ^{15}N produced by cosmic rays at the lunar surface. Using other cosmic ray-produced isotopes, such as ^{21}Ne or ^{38}Ar , ^{15}N could be corrected for cosmogenic contributions. Nevertheless, even after correction, lunar nitrogen still showed an impressive variability, which was attributed to the contribution of different nitrogen components (Geiss and Bochsler, 1982). Given the solar wind origin of lunar noble gases, a similar solar origin was attributed to lunar N. This possibility was supported by observations that N and solar noble gases from different lunar soils correlate well (Fig. 5.2) (Kerridge, 1993).

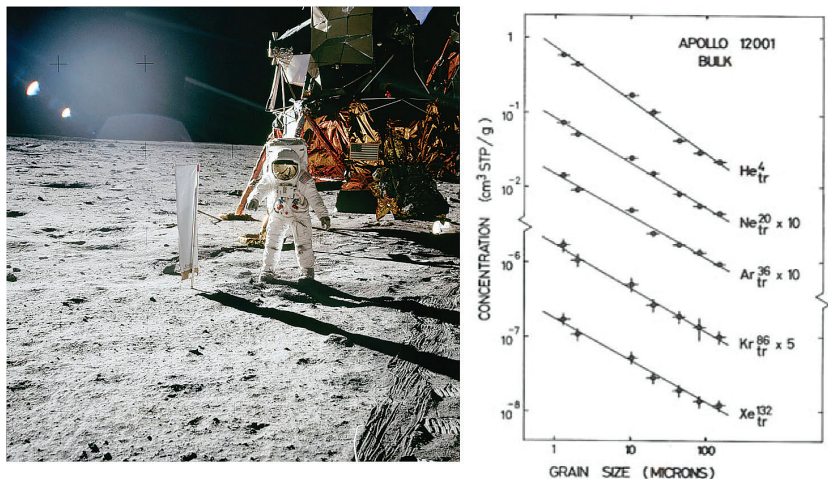


Figure 5.1

Left: The solar wind experiment during the Apollo 11 mission with astronaut Buzz Aldrin standing next to it. This experiment designed by the group of Johann Geiss at the University of Bern (Switzerland) consisted in exposing a foil of aluminum to solar radiation during the duration of the mission in order to collect solar wind ions (see Section 2). Photo credit: NASA. **Right:** Concentration of noble gases in lunar soils as a function of grain size. The inverse correlation showed that noble gases are surface-correlated and not volume-correlated, demonstrating their solar wind implantation origin (Eberhardt *et al.*, 1972).

There was still a problem with this interpretation. First, it would imply that the N isotope composition of solar nitrogen was variable. Second, the slope of the correlation yielded a nitrogen/noble gas ratio ($^{14}\text{N}/^{36}\text{Ar}$ in Fig. 5.2) higher than the value observed in modern solar wind. This discrepancy was interpreted as resulting from more efficient retention of solar wind nitrogen relative to noble gases. Furthermore, there appeared to be an inverse relationship between $\delta^{15}\text{N}$ and the “antiquity” of the samples, that is, the epoch at which a sample was exposed at the surface of the Moon, estimated from either cosmogenic ages (Fig. 5.3) or a proxy like the inherited $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the sample (Kerridge,

1975; 1993). This inverse relationship was interpreted as a secular change of the solar wind N isotope ratio, whereby ^{15}N production increased over time by either nuclear reaction (spallation) on oxygen in the solar corona or dredges of ^{15}N produced deep within the Sun. These interpretations were not, however, without problems (Geiss and Bochsler, 1982). The physical conditions for coronal spallation are unlikely for the Sun, and it is not clear whether the CNO cycle (a catalytic reaction producing ^4He from H involving ^{15}N) takes place in the Sun. Even if it does, ions synthesised in the radiative zone may not be able to cross the convecting zone and reach the Solar surface.

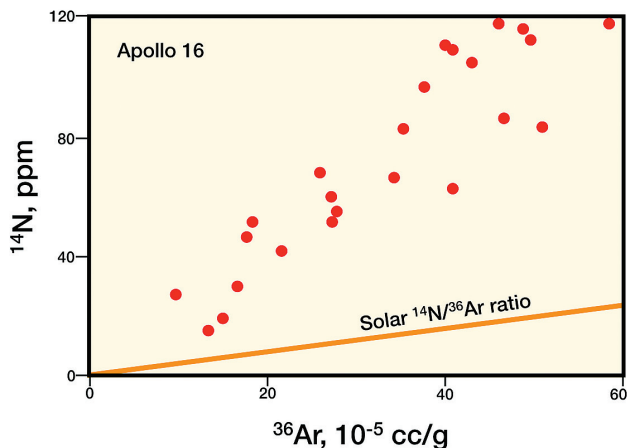


Figure 5.2 Nitrogen versus ^{36}Ar contents for a suite of lunar soils recovered by the Apollo 16 mission (Kerridge, 1993). Both elements/isotopes correlate and, because Ar is of solar wind origin, N was regarded as having the same origin. However, N is overabundant relative to Ar when compared to the solar wind composition (orange line), which was interpreted as due to better retention of N compared to inert ^{36}Ar in soil grains.

Back in the lab, our low blank, high sensitivity system for the simultaneous analysis of N and noble gases opened new avenues of cosmochemistry research. Franck Humbert, who completed his Ph.D. at the CRPG on nitrogen partitioning between gas and silicate melt (Section 3), developed laser extraction of nitrogen together with noble gases from silicates coupled with static mass spectrometry, allowing us to carry out step heating on mg-sized samples. Rainer Wieler came to Nancy to analyse N and Ar in single grains of Apollo 17 lunar soil 71501 and measured the amounts of nitrogen and solar wind ^{36}Ar in fractions extracted from 0.5-1 mm-sized grains in several temperature steps. He had previously performed single grain analysis of noble gases on similar samples and found that they correlate very well with each other. In the present set of data, nitrogen tended to also correlate with noble gases, but careful data analysis showed that, in fact, only a small fraction of N is solar, the rest is of unknown origin (Wieler *et al.*, 1999; Fig. 5.4).



Figure 5.3

Nitrogen isotope variation in Apollo 16 lunar soils as a function of the cosmic ray exposure age determined from the amount of cosmogenic ^{21}Ne . Samples exposed for long durations tend to show more negative (^{15}N -depleted) $\delta^{15}\text{N}$, which was interpreted as evidence for secular variation of solar wind N isotope composition (Kerridge, 1975).

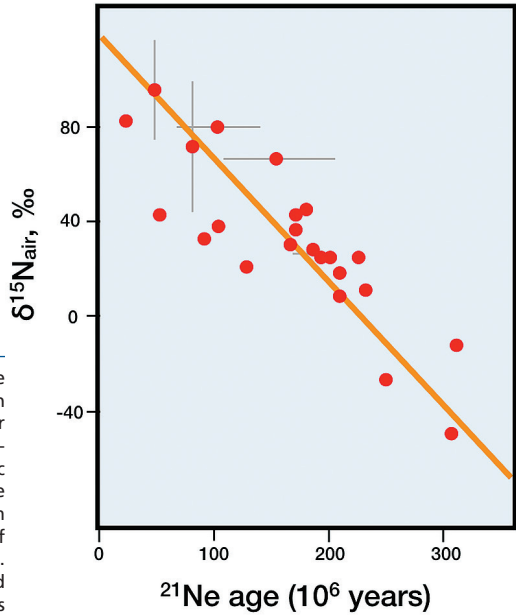
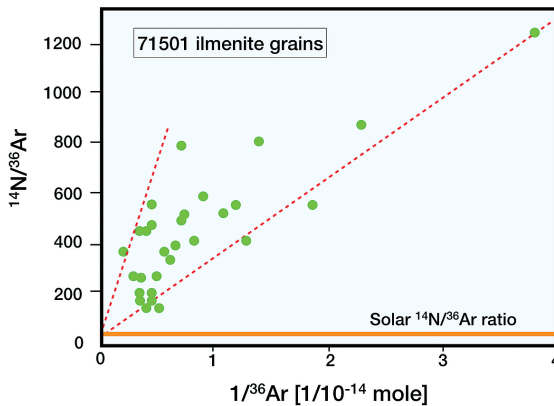


Figure 5.4

$^{14}\text{N}/^{36}\text{Ar}$ versus the inverse of the ^{36}Ar concentration in individual grains from soil 71501, Apollo 17. If nitrogen was solar, the $^{14}\text{N}/^{36}\text{Ar}$ ratio should remain constant whatever the concentration of solar ^{36}Ar . This is not the case, as the ratio increases with increasing $1/^{36}\text{Ar}$ (decreasing ^{36}Ar), demonstrating the contribution of non-solar N in roughly constant proportion (adapted from Wieler *et al.*, 1999).



A further step was achieved when Ko Hashizume, then assistant professor at Osaka University (Japan) came to our lab for a sabbatical. Ko implemented a new analytical procedure in order to measure the N isotope composition together with N and Ar contents (Hashizume *et al.*, 2002). This development allowed him to correct individual grain data for ^{15}N contribution using measured cosmogenic ^{38}Ar . After correction, he could obtain the N isotopic composition of the trapped components. Ko analysed grains from three Apollo 17 soils, one (71501) that had been exposed at the lunar surface over the last 100 Myr and another two (79035 and 79135) presumably irradiated long ago at 1-2 Ga. He found the same variability of N and Ar isotopic compositions in the three soils, covering the whole range of values found in bulk analysis of lunar rocks (Fig. 5.5). Impacts had destroyed large areas of lunar lithologies and had dispersed fragments all over the lunar surface. Clearly, a spoonful of lunar regolith contained microscopic fragments originating from large regions of the lunar surface which had experienced histories comparable to those of bulk soils from different lunar regions.

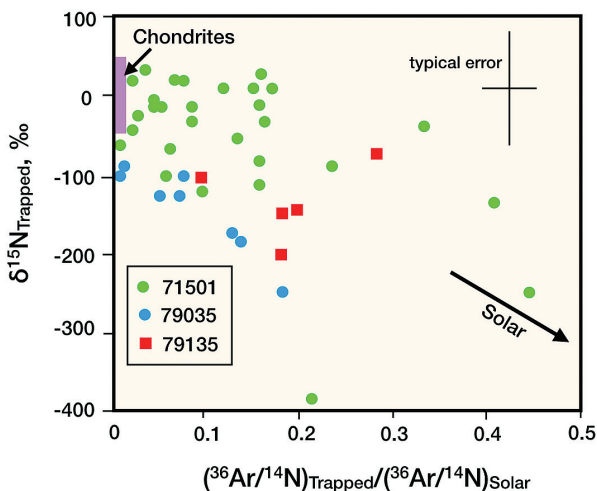


Figure 5.5 Nitrogen isotope variation in three Apollo 17 200 mm soil grains as a function of a solar N content index. Given this normalisation, a value of 1 for x would mean 100% solar N and a value of 0 would imply chondritic (asteroidal) N. All grains contain non-solar N and the spread of the data is consistent with a contribution of asteroidal N to the soil grains, presumably carried by micro-meteorites (adapted from Hashizume *et al.*, 2002).

In the format of Figure 5.5, an x axis value equal to one would mean pure solar, and a value close to zero would imply non-solar, presumably indigenous or meteoritic, since these two components are both plausible for the lunar surface, which has been battered by planetary material. Ko found that grains with the largest proportion of solar N (towards the right hand side of the diagram) had negative $\delta^{15}\text{N}$ values no matter the regolith considered. Overall, this tendency



was consistent with mixing between a solar component depleted in ^{15}N ($\delta^{15}\text{N} < 0$) and a non-solar component with $\delta^{15}\text{N}$ values around -0 ± 50 ‰, which is in the range of primitive meteorites. Hence a secular change in the isotopic composition of solar wind nitrogen was no longer necessary as lunar N variations could simply be explained by mixing between solar wind N and another nitrogen component, either indigenous or contributed by asteroidal material impacts. From the mixing ratio of the two nitrogen components, and adopting the modern influence of solar wind, Hashizume *et al.* (2002) estimated the flux of planetary material to the Moon to be within a range of 7,000-75,000 tons/yr, in qualitative agreement with the contemporary flux of micrometeorites on Earth (MMs, 40000 ± 20000 tons/yr; Love and Brownlee, 1993).

The surface of the Moon constitutes a perfect record of irradiation and bombardment of planetary surfaces in the terrestrial region by solar wind particles, cosmic dust, micrometeorites, meteorites, asteroids and, possibly, comets, and the antiquity/age of some of its soils permits investigations into past fluxes deep in time. We attempted to estimate the flux of non-solar matter onto the lunar surface using available bulk soil data (Fig. 5.6). We assumed binary mixing between SW N and meteoritic N, dominated by micrometeorites. We further assumed a $\delta^{15}\text{N}$ value of -375 ‰ for SW N (as measured in Jupiter's atmosphere, no direct measurement being available at that time) and of $+100$ ‰ for micrometeoritic N, as well as a mean value of CM and CR chondrites, which are the dominant types of Antarctic micrometeorites (Kurat *et al.*, 1994). For each batch of soil data, the N isotope ratio was corrected for a cosmogenic ^{15}N contribution using associated noble gases (*e.g.*, cosmogenic ^{21}Ne) and the respective amounts of SW and meteoritic nitrogen were calculated from the N contents and isotope ratios. Solar N contents correlate well with cosmogenic ^{21}Ne ages, as expected for a constant SW flux (Fig. 5.6b). The concentration of SW N in a given layer near the regolith surface depends on the average volume of the regolith that has been exposed to solar radiation. Noble gas isotopes produced by cosmic rays (here $^{21}\text{Ne}_c$) accumulate mainly in the first tens of cm below the surface, hence cosmic ray exposure ages are relevant only to soil grains located in this depth interval. In Figure 5.6b, the dotted lines correspond to the accumulation of solar nitrogen with a modern flux value in the 0.3-1 m depth range. The fact that all data are consistent with the modern solar wind flux strongly suggests that the SW flux has not varied from its present day value over the last Gyr. The same exercise for non-solar N leads to a surprising outcome (Fig. 5.6a). The two dotted lines represent the accumulation of micrometeoritic nitrogen (with an average N content of 1000 ppm) for a modern flux of $40,000 \pm 20,000$ tons/yr, corrected for gravitational differences between the Earth and the Moon. For samples with exposure ages higher than ~ 500 Ma, the data correlate well and are consistent with a contribution of micrometeorites with the modern flux value. However, data with exposure ages lower than 500 Ma support non-solar nitrogen fluxes a factor of 2-5 higher than today. Clearly the flux of ET material to the Moon and, by extension, in the inner solar system, has not been constant over the last ~ 500 Myr but significantly higher by up to a factor of ~ 5 . This is consistent with the findings of Culler *et al.* (2000) who reported an increase in the impact frequency on the Moon in the last 500 Myr based on ^{39}Ar - ^{40}Ar ages of lunar



glassy spherules from meteoritic impacts. Changes in the fluxes of ET material in the inner solar system could be linked to the breakup of an L-parent body at 466 Ma that resulted in a drastic increase of ET material and which might have triggered major environmental changes on Earth (Schmitz *et al.*, 2019). In fact the breakup of the L-parent body around 500 Myr was a major conclusion of the very first Ar-Ar age determinations (Turner *et al.*, 1966)! The potential of the lunar surface to trace inner solar system events is only in its infancy, and the exploration of other lunar terranes than those visited by the Apollo and Luna missions will certainly bring its share of great discoveries.

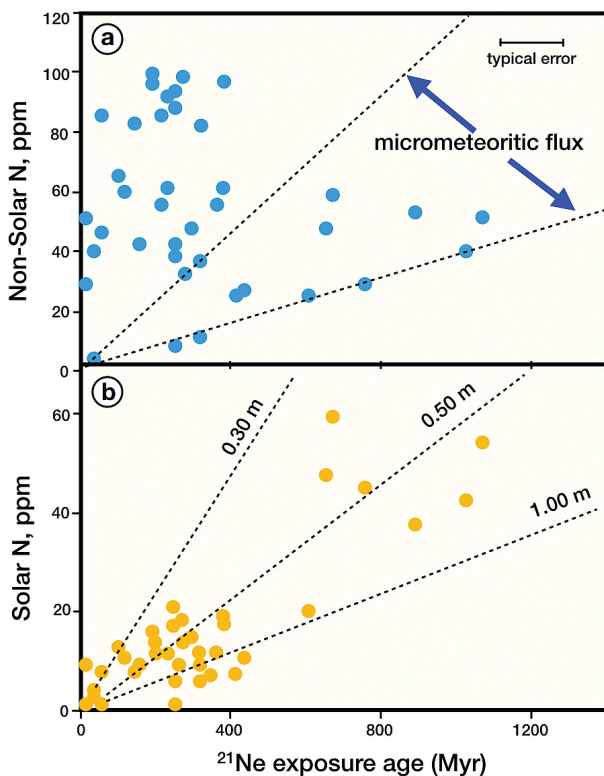


Figure 5.6

Solar N and non-solar (presumably chondritic) N versus cosmogenic ^{21}Ne exposure age for lunar soils. The latter is a function of the duration of soil irradiation by cosmic rays at the lunar surface. **(a)** Non-solar, presumably micrometeoritic flux was not constant over time and appears to have been enhanced by a factor of up to 5 during the last ~500 Myr. This possibility is consistent with the breakup of an asteroid family during this time period (Marty *et al.*, 2003b). **(b)** Solar N from solar wind correlates with exposure age, suggesting that solar wind flux was constant over time. The dotted lines represent depths of soil over which regolith grains were irradiated and correspond to typical depths for irradiation by energetic galactic cosmic rays.



6.1 Sampling Solar Ions with a Spacecraft

Every year my CRPG colleagues and I attend the Lunar and Planetary Science Conference (LPSC) in Houston, Texas, which used to be held on the NASA campus south of the city (not so anymore). This was a thrilling place, immortalised in reports on the Gemini and Apollo missions and in Hollywood movies. You would enter the campus through a gate where you were checked by guards, and then you would drive past a Saturn V rocket lying on the side of the entrance road. The conference, quite tiny compared to the LPSC today, was held in the sports facilities of the campus, meals could be taken in the astronaut canteen, and it was possible to stroll around, open a door, and enter the control room of the Apollo missions. The science was excellent and competitive. Most of our American colleagues were supported by NASA grants and therefore were obliged to present their results and discussions were often lively. After the 9/11 terrorist attack in 2001, the campus was closed to non-accredited people and the conference was moved to a nearby complex, somewhat losing its vintage charm of recalling space exploration in the sixties.

Rainer Wieler was well aware of our N-noble gas analytical facility performance as he himself had used it (Section 5). He encouraged us to participate in the Genesis sample return mission and during an LPSC he introduced me to Don Burnett, professor at the California Institute of Technology. Besides being a respected petrologist and geochemist, Don was also the Principal Investigator of the Genesis mission in the NASA discovery programme. The idea was simple: the Sun contains ~99.9% of the mass of the solar system and is at present the best representation we have of the composition of the proto-solar nebula from which the planets formed. Hence the Sun has retained memories of the genesis of our world. The Sun's chemical composition is known from spectral analysis of the light it emits, but the isotopic composition of its elements cannot be resolved spectroscopically, in particular not for its most abundant components (H, C, N, O, noble gases). The Sun's composition of refractory elements can be obtained by analysing primitive meteorites, such as carbonaceous chondrites, as the refractory elements were quantitatively trapped in these during condensation and accretion processes, but the volatile elements were not. Hence it was timely to have pristine samples of the Sun in the lab, which obviously could not be taken at the solar surface, but particles emitted by the Sun, *i.e.* the solar wind, could be sampled at a distance. This was already the idea of the lunar aluminum foil experiment during the Apollo missions (Sections 2 and 5), which permitted the isotopic composition of solar wind light noble gases to be determined to some extent. Heavy noble gases could be analysed in lunar soils irradiated by solar wind particles (Section 5), but elements other than noble gases were present in too small abundances to be distinguished from the lunar background.



The solar wind is a stream of ionised atoms generated in the solar corona at temperatures of several million kelvin, which are accelerated by the solar magnetic field at energies varying between 1 KeV per atomic mass unit up to several KeV during solar energetic events. During these processes, significant elemental and isotopic fractionations occur but models are not clear on whether they would depend on the element's first ionisation potential (FIP), or on the first ionisation time (FIT) (Burnett and Genesis Sci, 2011). Understanding these processes would allow a better knowledge of the Sun's composition, which also has implications for its internal structure (Burnett and Genesis Sci, 2011). The prioritised objectives of the mission were to resolve two important problems in cosmochemistry: the triple isotope (^{16}O , ^{17}O , ^{18}O) composition of oxygen, and the $^{15}\text{N}/^{14}\text{N}$ ratio of proto-solar nitrogen. Don Burnett asked me if we were interested in analysing nitrogen isotopes in Genesis targets with our low-blank N noble gas facility. Another team, led by Bob Pepin and Richard Becker at the University of Minnesota, planned to extract nitrogen from gold targets by mercury amalgamation.

The Genesis mission lifted off on August 8, 2001, and after navigation settled around Lagrangian point L2. There the respective gravitational attractions of the Sun and the Earth cancel out and navigation is less energy consuming. The spacecraft stayed at a near-constant distance from the Sun for 27 months, and solar wind was passively implanted onto several panels covered with targets composed of layers of pure material such as gold, chemical vapour deposition (CVD) diamond, or aluminum on sapphire. Solar wind particles were implanted at typical depths of one nanometer *per* atomic mass unit, which is enough to retain them firmly in the target material. It was a very well-designed mission which comprised kinetic energy sensors for solar wind particles, permitting different targets to be exposed or shielded as well as the sampling of different solar wind regimes. Because solar ions are accelerated and isotopically fractionated under variable regimes corresponding to different bursts of energy, isotopic fractionation is expected to depend on the velocity of solar wind ions, thus providing insight into these processes.

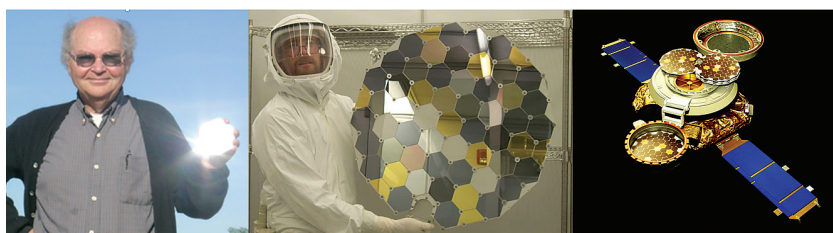


Figure 6.1

The Genesis mission. **Left:** Don Burnett, PI, holding one of the targets. **Centre:** An array holding targets made of ultrapure material (gold, sapphire on gold, diamond-like carbon, aluminum, silicon, silicon carbide). **Right:** The Genesis spacecraft collecting solar wind ions with its panels deployed. Photo credit: NASA.



On April 1st, 2004, the spacecraft completed sampling and closed the re-entry capsule which then entered the Earth's atmosphere and landed in the Utah Test and Training Range in Dugway, Utah. Two helicopters, flown by experienced stunt pilots (who otherwise worked in Hollywood movies), were waiting to retrieve the sample canister. The idea was to prevent the canister from being contaminated by terrestrial dust during landing by slowing it down with a parachute and then catching it on a pole, attached to the helicopters... At the CRPG, we were following the descent of the capsule live in the lecture theatre, accompanied by journalists, including three TV crews. We watched the capsule containing the samples whirling towards the ground...without a parachute...and crashing! The NASA commentator continued to talk calmly about the end of the fall. Immediately the TV crews came to me asking if the mission was compromised. It was obviously not a good thing; all the targets were broken into thousands of shards. I was torn between despair and anger, but I tried to look confident and answered that nobody had been hurt and that the analysis of SW ion isotopes should still be possible as the samples had not been lost to space (Fig. 6.2). The expectation was that SW ions were implanted in the target material at a greater depth (several tens of nm) than the adsorbed atmospheric atoms and species (0.1-1 nm). During the days that followed we received mixed messages from the Genesis team, with a nice photo of Don sorting out the debris with a somewhat forced smile. Don also insisted that the scientific targets of the mission were not compromised. Although most of target material was broken and fragments were mixed up, Don anticipated this possibility: a key design feature was that target disks had different thicknesses so that, if necessary, broken fragments could be sorted using a micrometer.

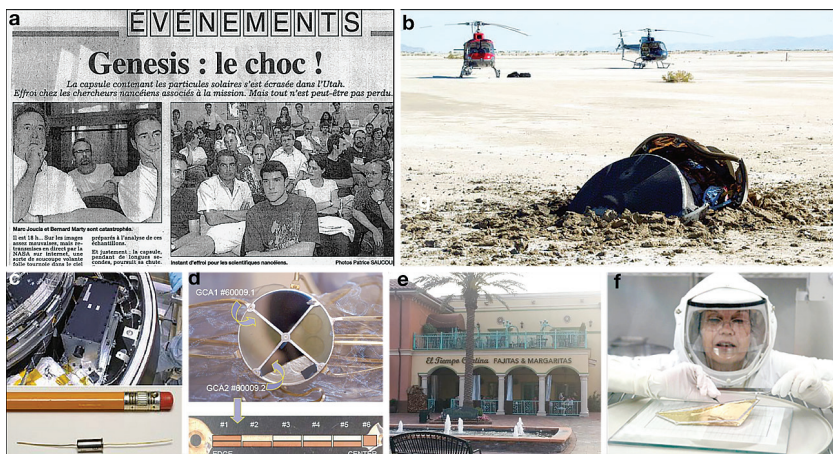


Figure 6.2

Crash of the sample return capsule. (a) News in Le Républicain Lorrain, a regional newspaper, on CRPG members watching the crash of the capsule live. (b) The capsule after its hard landing in the Utah desert; behind it, the



two helicopters that were supposed to hook the parachute. (c) The parachute did not open because an accelerometer, which should have triggered its deployment, was not mounted in the correct direction. (d) The concentrator target after hard landing. We analysed N and noble gas isotopes by laser ablation and static mass spectrometry in a branch of the gold plated cross and N isotopes with the 1280 HR2 Cameca ion probe at the CRPG. (e) The Mexican restaurant near Houston International Airport where Judy Allton gave me a piece of the concentrator target. (f) Judy Allton recovering target material debris at the Johnson Space Center curation facility.

An investigation was launched to understand the cause of this catastrophic failure and it concluded a few years later that an accelerometer had been incorrectly mounted on the electronic board of the spacecraft. During the high temperature entry into the atmosphere, communications between the entry capsule and the control room were shut down, and the signal commanding the deployment of the parachute therefore had to be automatic. At the shock of entry, an accelerometer should have started a timer which would have triggered explosive bolts liberating the parachute. However, the accelerometer was mounted upside down and could not be activated (Fig. 6.2c). Ten years after the landing, we had a Genesis memorial meeting at the Jet Propulsion Laboratory, and it seemed that NASA did not fully appreciate the mission which, in the eyes of their administrators and engineers, technically had failed, despite the outstanding scientific outcomes that had resulted from it. In fact, all scientific objectives were met despite the crash. And nobody was hurt.

6.2 Solar Oxygen and the Origin of the Solar System

The University of Chicago is where the geochemistry of stable isotopes was developed before WWII under the guidance of Harold Urey. There, Robert Clayton achieved outstanding advances in the field and, among other important discoveries, observed, with Toshiko Mayeda, that the isotopic composition of oxygen in meteorites does not follow a mass dependent isotope fractionation (MDF) (Clayton *et al.*, 1976). On Earth, most oxygen isotope variations are proportional to the relative mass difference between two isotopes, a behaviour common to stable isotope systems on Earth. In an $^{17}\text{O}/^{16}\text{O}$ versus $^{18}\text{O}/^{16}\text{O}$ diagram (Fig. 6.3), terrestrial data define a fractionation trend with a slope close to 1/2, because $^{18}\text{O}/^{16}\text{O}$, which has a relative mass difference $\Delta M/M$ of 2/16, varies twice as much as $^{17}\text{O}/^{16}\text{O}$ for which the relative mass difference is 1/16. Primitive and differentiated meteorites from a given family originating from a given parent body follow this trend. However, in addition to this effect, different families form parallel trends, implying that there is also a mass independent isotope fractionation (MIF) effect. Clayton *et al.* (1976) analysed calcium-aluminum- rich inclusions (CAI), which are refractory inclusions in primitive meteorites. Mineral phases forming CAIs were presumably the first to condense in the cooling solar nebula gas, in agreement with U-Pb and ^{26}Al - ^{26}Mg ages showing that CAIs are the most ancient objects of the solar system. Oxygen in CAI does not define a 1/2 trend



but instead falls on a line with a slope close to 1 (Fig. 6.3). This implies that these objects were subject to isotope variations of the same extent for both $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ and therefore these variations were independent of the respective isotopic masses. Furthermore, planetary material accreted regionally with variable mass and independently fractionated oxygen. This discovery permitted genetic relationships amongst meteorite family members to be established, and the isotopic composition of oxygen in extraterrestrial materials became one of the most powerful tracers in cosmochemistry. In the O isotope diagram (Fig. 6.3), variations could be accounted for by two different processes, mass dependent and mass independent, with the origin of the latter being unclear (still is today to some extent). They could result from the contribution of an exotic ^{16}O -rich nucleosynthetic component, possibly from the explosion of a nearby supernova, to a “normal” (Earth-like) component. The alternative view was that the proto-solar nebula was poor in ^{16}O , and that a process was able to conjointly enrich ^{17}O and ^{18}O relative to ^{16}O , either by addition of nucleosynthetic products, or by MIF. The best way to decide between these far-reaching possibilities was to determine where the Sun would plot in the oxygen isotope diagram.

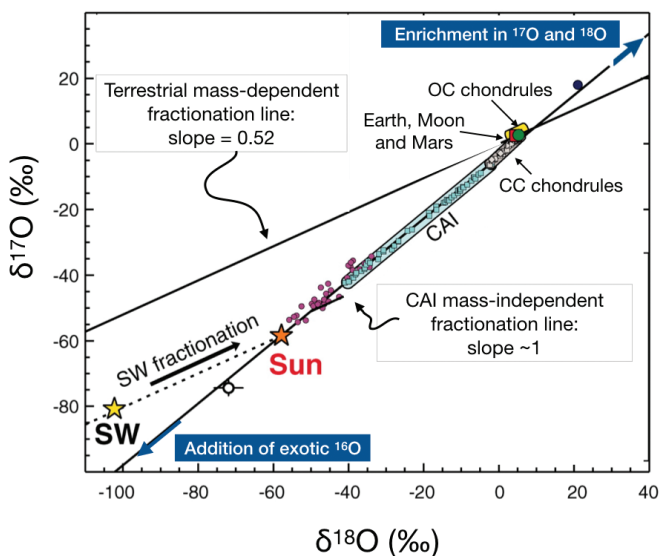


Figure 6.3

Three oxygen isotope diagram. The coordinates are the $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios, in parts per mille relative to terrestrial O (ocean water). Two types of isotope variations are depicted: mass dependent fractionation, the usual type of isotopic fractionation, which has a slope of about 0.5; and mass independent fractionation, first defined by refractory inclusions (CAI) in primitive meteorites, which has a slope of about 1. Before the Genesis mission, two possibilities were advocated: (i) The solar nebula had a composition similar to that of Earth, to which was added an exotic component rich in ^{16}O ; or



(ii) CAI defined an end member solar nebula, to which was added oxygen rich in ^{17}O and ^{18}O . Solar wind oxygen analysed by Genesis (yellow star) permitted extrapolation of the solar nebula value (orange star labelled Sun) after correction for mass dependent fractionation during solar wind generation (dotted line). This composition demonstrated that the second hypothesis was correct (adapted from McKeegan *et al.*, 2011).

In order to analyse oxygen isotopes, Kevin McKeegan and his team at UCLA designed a specific secondary ion mass spectrometry (SIMS) instrument with very high mass resolution in order to distinguish the rare ^{17}O isotope from contributing isomasses. For this key analysis, they used target material that was enriched in solar wind ions. This enrichment was obtained during the Genesis mission thanks to a solar wind concentrator consisting of a reflector and a small target. This device permitted an increase in solar wind fluence (the number of ions received *per* surface unit) by a factor of up to 20. However, the concentrator significantly fractionated isotopes depending on the radial distance from the centre of the target. Veronika Heber, post-doctorate fellow, and Rainer Wieler at ETH Zürich had been working on this problem of isotope fractionation, which was also affecting the oxygen isotopes, with a careful experiment. They lasered different spots on the targets and analysed neon isotopes, thus establishing the relationship between position and isotope fractionation. McKeegan and his colleagues succeeded in measuring the three O isotopes in a silicon carbide quadrant of the concentrator. They corrected the data for mass discrimination using the Ne isotope relationship and obtained the SW value represented in Figure 6.3 by a yellow star. To obtain the solar value (and therefore that of the proto-solar nebula), the measured SW oxygen isotope composition had to be corrected for isotope fractionation during solar wind acceleration, according to the so called inefficient Coulomb drag model (which corrects for retardation of ionised species according to their charge state and kinetic energy). McKeegan obtained the red star composition which falls perfectly as an end member of the mass independent fractionation line (McKeegan *et al.*, 2011). This composition is fully consistent with data obtained for CAI, the earliest solids to form in the solar system from condensation of the nebular gas. Thus, all solar system objects and reservoirs except CAI (and some other rare meteoritic mineral phases) were enriched to a comparable extent in ^{17}O and ^{18}O relative to ^{16}O , implying that solar system oxygen was not contributed by late stage injection of nucleosynthetic ^{16}O , but that processes able to enrich solids in the rare, heavy isotopes of oxygen operated. These enrichments likely took place during self-shielding of nebular CO and further photochemistry with hydrogen to form icy grains. Self-shielding is a process that enriches rare isotopes with respect to the abundant ones when a gaseous isotopic mixture is ionised by photons. Given a homogeneous distribution of wavelengths, photons that ionise abundant isotopes become more exhausted than those ionising rare isotopes when light proceeds within the gas cloud. Icy grains hosting isotope enrichments were transported towards the centre of the disk where its isotopes exchanged with those of silicates due to increase in ambient temperature.



6.3 Solar Nitrogen and the Origin of Terrestrial Volatiles

The nitrogen isotope problem was of a different nature. Because nitrogen has only two stable isotopes it is not possible to detect MIF, but its two isotopes show the largest variations (after hydrogen) among solar system objects and reservoirs. The $^{15}\text{N}/^{14}\text{N}$ ratio varies by up to 5,000 ‰, while other volatile elements like carbon show much more modest variations of only a few tens of per mille. The nitrogen isotope variability was posited with the return of the Apollo samples in the seventies, when N isotope analysis of lunar soils revealed variations of several hundreds of per mille, which at that time were attributed to secular change in solar wind composition (Section 5). The analysis of Jupiter's atmosphere by spectroscopy (Fouchet *et al.*, 2000) and mass spectrometry onboard the NASA Galileo probe (Owen *et al.*, 1999) revealed that Jovian nitrogen is depleted in ^{15}N by about 400 per mille. The analysis of N in the solar wind-irradiated grains of lunar soils suggested that the Sun is poor in nitrogen-15, with an upper limit for $\delta^{15}\text{N}$ of -250 ‰ (Hashizume *et al.*, 2000). Furthermore, an osbornite (TiN) inclusion in a CAI showed a ^{15}N depletion of -360 ‰ (Meibom *et al.*, 2007). In contrast, enrichments in ^{15}N are common in the solar system, with $\delta^{15}\text{N}$ in some meteorites of the CR-CB clan up to +1,500 per mille (Grady and Pillinger, 1990) and comets being systematically rich in ^{15}N by about 1,000 per mille (Arpigny *et al.*, 2003). So, a timely measurement of the nitrogen isotope composition of the proto-solar nebula was necessary in order to resolve this puzzle (Fig. 6.4).

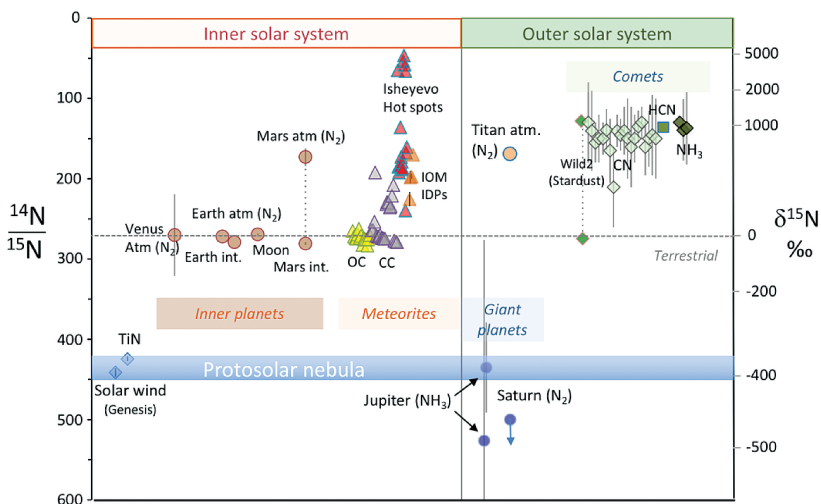


Figure 6.4 Nitrogen isotope variation among solar system objects and reservoirs. The left hand axis gives the values as $^{14}\text{N}/^{15}\text{N}$, a notation used by astronomers, and the right hand axis is the $\delta^{15}\text{N}$ notation used by geochemists and cosmochemists. Jupiter's atmosphere, a TiN inclusion in a CAI, and solar wind analysed by



Genesis define the composition of the proto-solar nebula (horizontal blue bar). Other objects and reservoirs are 15N-rich. Adapted from Fűri and Marty, 2015, and refs. therein.

The task of recovering SW nitrogen from the target material was problematic for different reasons. The amount of solar wind ions implanted during the 27 months of exposure was very low when it came to some key isotopes (4,000 atoms for the rare ^{124}Xe and ^{126}Xe isotopes, for example), requiring ultrasensitive methods. In addition, the material itself contained ions from the terrestrial environment, which required the development of techniques to identify them and correct for the contamination. This problem was particularly crucial for nitrogen, which is abundant in the terrestrial environment. Furthermore, the target material after the crash needed to be extensively cleaned up to remove dust and adsorbed species without affecting implanted SW ions. Selected laboratories worldwide developed different cleaning techniques using laser photon and ion bombardments.

At the CRPG we worked to improve the performance of our nitrogen noble gas facility in two ways. We first attempted to decrease the analytical blanks. The amount of nitrogen to be extracted from about one square cm was about 1×10^{-12} moles, and the analytical blank of our system, mainly from the purification section, was 3×10^{-12} moles, so we needed to decrease the blank level by at least one order of magnitude. It took the CRPG noble gas facility lab manager, Laurent Zimmermann, four years to improve all the steps of the analysis and finally reach this goal (Zimmermann *et al.*, 2009). Second, we needed to extract nitrogen from the smallest possible depth below the target surface, in order to maximise the SW N amount relative to the sample blank, and we also needed to remove the target material's outer skin, which was loaded with contamination, as much as possible. Pete Burnard and Laurent developed a laser rastering technique using a 193nm beam. With non-flight target material, Laurent patiently calibrated depth profiles of laser pits by atomic force microscopy. After many tests and much practice, it became possible to remove an outer skin of the target material 5 nm thick over cm-sized areas. Then the following 50 nm of depth would be rastered in order to release implanted SW. The best target material for analysis was gold which is chemically inert and would release N ions as N_2 , whereas other target materials would have chemically trapped nitrogen. After five years of intensive tests, our analytical system was finally ready and we started to analyse broken fragments of gold target material. Unfortunately, it emerged that the isotope ratios of the extracted nitrogen were atmospheric. Furthermore, the amount of extracted nitrogen and its isotopic composition from flight and non-flight material were about the same. Clearly, the gold target material had already been contaminated before the flight during manufacturing, and we learnt that gold vapour deposition was not done under ultra high vacuum conditions. As a result, the contamination level was well above the expected amount of SW nitrogen. It may seem strange to send material into space that was contaminated to the point where the expected signal would be overwhelmed,



but in fact, when the mission was designed, analytical methods sensitive enough to analyse N at such low levels did not yet exist. The target material was thought to be pure because background N was below the detection limits of the conventional analytical techniques available at the time. At this point, we had spent several years and significant funding from the Centre National d'Études Spatiales (CNES, the French space agency) to arrive at the conclusion that the flight material could not be analysed.

Fortunately, the mission's careful design allowed a plan B and we turned to the concentrator target material analysed by McKeegan. There, the signal/blank ratio should have been favourable, and, after discussion with Don and the team, we decided that it was worth a try. Most of the target material was not gold, but the four quadrants of the concentrator that were maintained by a metal cross with gold deposited onto its surface (Fig. 6.2c) and we attempted to laser sections of this cross. We measured N together with neon isotopes and could correct N isotopes for isotope fractionation by comparison with data from the Zürich group. Again, we found nitrogen isotope ratios quite close to the atmospheric value, attesting to terrestrial contamination of the golden cross material as well. The golden cross was not designed to be analysed and no special precautions had been taken when covering it with a thin film of gold. Nevertheless, nitrogen showed slight deviations from the air composition and, as we analysed neon and nitrogen together, a $^{15}\text{N}/^{14}\text{N}$ vs. $^{20}\text{Ne}/^{14}\text{N}$ mixing diagram of the same kind as those for lunar samples permitted extrapolation of the non-atmospheric, solar wind nitrogen isotopic composition to -388 ± 182 ‰ (95 % confidence level; Marty *et al.*, 2010). The large error was not analytical but the result of the extrapolation to obtain the solar N end member composition since only ≤ 4 % N was of solar origin. The Minnesota group also working on N isotopes in Genesis samples reached the opposite conclusion to us. They claimed that SW nitrogen was not ^{15}N -poor, but ^{15}N -rich by about 300 ‰ relative to terrestrial values, from their analysis of nitrogen, which was released from golden material by amalgamation with mercury vapour. As noted by some of our colleagues at the 2008 LPSC where both groups presented their data, the numbers were approximately the same, several hundreds of per mille, only the signs were different. Two groups using different techniques obtained completely different results, which was quite embarrassing and required further verification. It just so happened that our results were corroborated by a different type of analysis (see next paragraph), suggesting that the results from the Minnesota group had been affected by some unexpected chemical contamination during amalgamation.

Another technique, secondary ionisation mass spectrometry (SIMS), appeared promising in the light of the recent data obtained by Kevin McKeegan and his group at UCLA for oxygen. Marc Chaussidon and I decided to try analysing N isotopes in Genesis target material, specifically a concentrator's target material made of silicon carbide. A high mass resolution SIMS, recently delivered to the CRPG (Cameca ims HR2), was able to analyse N isotopes such as $^{12}\text{C}^{14}\text{N}^-$ and $^{12}\text{C}^{15}\text{N}^-$ ions. In this analyser, a primary beam of ions, generally O^+ or Cs^+ , sputters the surface of the sample and extracts secondary ions. These



are then analysed with a high resolution mass spectrometer, which filters ions according to their energy and mass. We requested the loan of the silicon carbide quadrant of the concentrator, probably the most valuable sample of the Genesis mission as it was also used to analyse oxygen and noble gases. Judy Allton, who was in charge of the curation of the Genesis targets, asked me to come to Houston in person to pick up the sample to minimise risks of damage or loss. I flew to Houston where Judy and a colleague were waiting for me at the airport. We went to a nearby Mexican restaurant where they gave me the sample and I signed several forms, taking some of them with me for customs, just in case (Fig. 6.2). They then gave me a ride back to the airport where I took a late afternoon flight back to France. Flying home in economy class, I was thinking that the sample I had in my hand baggage was much more expensive, in terms of mission costs, than the plane itself.

Thanks to the quality of the ion probe and Marc's expertise, the measurement was straightforward. The sample was first rastered to a depth of a few nanometres with the primary ion beam to remove terrestrial contamination, and then both N isotopes were analysed continuously as the primary beam dug below the surface. The N isotope depth profile was just what was expected, forming a bell shaped distribution culminating at a few tens of microns depth. Terrestrial contamination was negligible as the material was much purer than the golden cross holding it, and the depth profile analysis allowed us to focus on the zones enriched in SW ions, maximising the signal/blank ratio. The results fully confirmed those from previous mass spectrometry sessions, namely that solar wind nitrogen is ^{15}N -poor, but now with a precision improved by one order of magnitude ($\delta^{15}\text{N}_{\text{SW}} = -407 \pm 7 \text{‰}$; 95 % confidence interval). After correction for isotope fractionation (using Ne isotopes analysed at ETH Zürich and the so called Coulomb drag model) and solar processing (solar diffusive element settling plus radiative levitation), we proposed that the proto-solar nebula, now represented by the Sun, had a composition of $\delta^{15}\text{N}_{\text{SW}} = -383 \pm 8 \text{‰}$, 95 % confidence interval, relative to air (Marty *et al.*, 2011).

This result had straightforward planetary implications. The Sun, which contains more than 99 % of present day solar system matter, had captured the largest share of dust and gas present in the proto-solar nebula. In contrast, all solar system objects except the atmospheres of giant planets are rich in ^{15}N by more than 60 % (Fig. 6.4). With the new SW N data, nitrogen isotope variations among solar system objects defined an evolution trend with ^{15}N excess relative to the solar composition increasing with the distance from the Sun.

The cause of these remarkable isotopic variations is debated and several models have been put forward. Isotopic fractionation during ion-molecule exchange could have taken place in the outer parts of the disk or in the molecular cloud before disk collapse where temperatures of about 10 K would have been required to yield such large isotopic excursions (Rodgers and Charnley, 2008). One problem with this is the low probability of reactions at these temperatures. It would also require extended periods of time that are not necessarily



consistent with the time lags of stellar system formation. Alternatively, contributions from diverse nucleosynthetic material could also account for N isotope diversity among solar system objects since ^{14}N and ^{15}N are produced in different stellar environments (e.g., Füri and Marty, 2015, and references therein). Nucleosynthetic heterogeneities are well documented in primitive meteorites for refractory elements such as Cr, Nd, Ti, and Mo, and are also identified in the so called pre-solar grains which represent relics of forming material that survived high temperature processing of stellar dust. However, the isotopic variations for these elements in primitive meteorites are extremely small, of the order of a few parts per mille or less, which is three orders of magnitude less than those of nitrogen isotopes.

Two other possibilities proposed in the literature require illumination of the gas by UV photons, capable of triggering photodissociation of N_2 (presumably the main phase of nitrogen in the nebula) and photochemistry to form organic molecules. Hard UV photons (≤ 100 nm in order to ionise or dissociate N_2) were abundant in a newly born stellar system derived from the early Sun or from nearby stars. In order to be effective, the gas would have needed to be transparent enough to permit penetration of photons and these conditions might have been met at the surface or at the outskirts of the disk, illuminated by nearby stars (see Appendix). Isotopically fractionated N would then be isolated from the gas in solid form (organics or ice grains), hampering isotope re-equilibration. Self-shielding is a process known in stellar systems in which rare isotopes are enriched by a statistical effect (see previous subsection). Photodissociation is a quantum effect that takes place at finite wavelengths. For a given distribution of wavelengths from a UV source, molecules hosting the major isotopes, here, ^{14}N , will be consumed more rapidly than molecules hosting minor isotopes like ^{15}N (the solar $^{14}\text{N}/^{15}\text{N}$ ratio is 440) (Thiemens and Heindenreich III, 1983; Clayton, 2002). Consequently, the photodissociation of the latter –creating ^{15}N -rich new molecules– will take place at greater depth in the gas than the former. To avoid homogenous distribution of N-bearing molecules with different isotopes, some kind of sorting process favouring the preservation of ^{15}N -bearing molecules should occur, due to either specific transport conditions, or to the destruction of ^{14}N -bearing molecules which would have been generated closer to the disk surface. An alternative possibility has been advanced by Sumit Chakraborty and Mark Thiemens at UCSD, while experimentally studying photon induced chemistry in a gas phase made of H_2 and N_2 , illuminated by photons below 110 nm from a synchrotron light source. They found enrichments up to 12,000 % in produced NH_3 , observed independently of the experiment temperature, that they attributed to preferential exchange of ^{15}N -bearing molecules in their excited states (Chakraborty *et al.*, 2014). At the CRPG, we followed another path by dissociating N_2 with electrons and forming solid organics from a $\text{CO} + \text{N}_2$ gas. Maia Kuga, then a graduate student, succeeded in forming solid organics which resembled meteoritic organic matter and which trapped noble gases presenting similar mass dependent fractionation to that observed in primitive meteorites (Kuga *et al.*, 2014; 2015). However, trapped nitrogen was depleted, and not



enriched, in ^{15}N , with a modest isotopic effect of 15–25 ‰. Ionisation by electrons occurs over a continuous, and not quantum, spectrum of energy. Hence it seems that photons are a key ingredient to achieving extreme ^{15}N enrichments in solids as they form. These solids, ice or organics, could then be incorporated in accreting grains during formation of small bodies and planets. The fact that ^{15}N enrichments (relative to Solar) occur in the inner solar system where ice would not have been stable suggests that ^{15}N -rich grains were preferentially hosted in organics before being distributed among high temperature metal and silicate phases during planetary differentiation. In the outer solar system, ice could have been the main host of these isotopic excursions, as suggested by the relative homogeneity of cometary N signatures (Fig. 6.3). A recent experiment led by Evelyn Füri at the CRPG demonstrated that the ^{15}N enrichment in the inner solar system occurred very early, within a few hundred thousand years after the start of solar system formation, as defined by the condensation of CAI. A large CAI showing “canonical” ^{26}Al (an extinct radioactivity chronometer able to date the first ~4 Myr of solar system history), *i.e.* the time zero signature, in fact already contained ^{15}N -rich nitrogen, suggesting that such enrichments occurred during the condensation sequence that led to the first solids, or could have even preceded condensation of solids, being synthesised by photons (Füri *et al.*, 2015).

The isotopic composition of hydrogen, that is, the deuterium/protium (D/H) ratio, also shows extreme variations among solar system reservoirs, with a tendency to increase dramatically from the nebular value of 25×10^{-6} to 150×10^{-6} for the inner solar system up to 500×10^{-6} in comets. As for nitrogen, Jupiter (and presumably the other giant planets as well) has a solar-like composition, showing that the Jovian atmosphere is primarily of nebular gas origin with limited, if any, contribution from comet-like material. The processes at the origin of hydrogen isotope variations are likely to be different from those that led to ^{15}N enrichments, but nevertheless N and H isotope covariations with heliocentric distance allow us to constrain the origin of terrestrial water and associated volatile elements (Marty, 2012; Alexander *et al.*, 2012). When combining the two isotope systems (Fig. 6.5), the Earth, the Moon, and the interior of Mars have D/H and $^{15}\text{N}/^{14}\text{N}$ compositions comparable to those of primitive meteorites, and different from both the proto-solar nebula and cometary values. This comparison led to the idea of a mainly asteroidal (local), rather than cometary or nebular, origin for the terrestrial atmosphere and oceans. However, this does not exclude minor contributions from either the proto-solar nebula (*e.g.*, neon; Section 2) or comets (Section 7). Altogether, it appears that some major elements of the proto-solar nebula, H, C, N, and O, that existed as gaseous molecules (H_2 , CO, N_2) were rapidly enriched in their rare and heavy isotopes just before, or during, the collapse of the nebula and the formation and early evolution of the protoplanetary disk. Understanding the processes at work will provide insight into the formation of a stellar system and the conditions necessary for the rise of habitable planets.



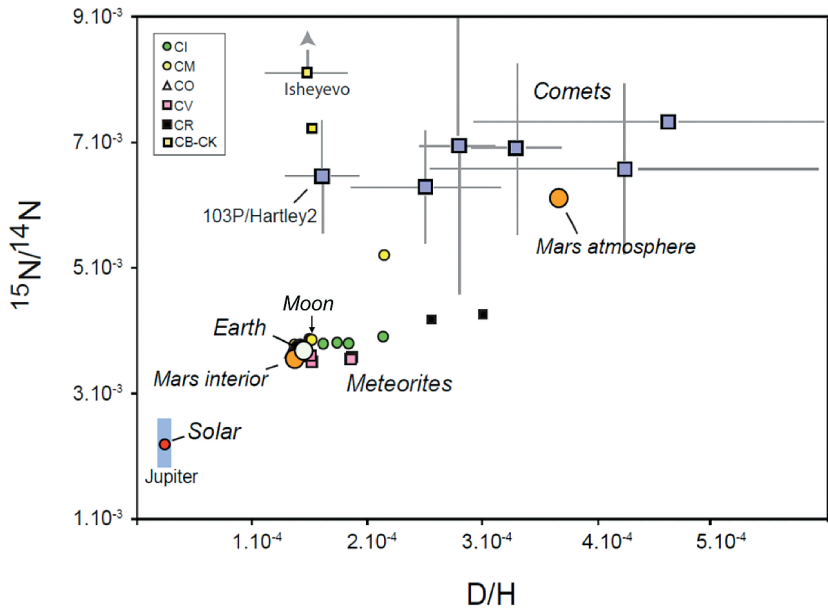


Figure 6.5

Nitrogen and hydrogen isotope covariations among solar system objects and reservoirs (adapted from Marty, 2012). The data seem to define three reservoirs: the proto-solar nebula (Solar and Jupiter), inner planets and chondrites, and comets. This distribution was taken as evidence for a chondritic origin of volatile elements on Earth. Note that Moon and Earth have comparable $\delta^{15}\text{N}$ values (Mathew and Marti, 2001a; Füri *et al.*, 2015) and D/H values (Tartèse *et al.*, 2013; Füri *et al.*, 2014), highlighting comparable isotopic sources for these two planetary bodies.



7. COMETS AS WITNESSES OF THE OUTER SOLAR SYSTEM

Comets are small (km-sized) icy bodies that consist of a large proportion of H₂O ice accounting for between 10 and 50 % of their mass. They contain organic matter, ice, and silicates/metal in comparable proportions (Greenberg, 1998). Comets have elliptic trajectories that crosscut the midplane of planetary orbits, which mean they can impact planets. In 1994, comet Shoemaker-Levy 9 crashed into Jupiter at a velocity of 60 km/s after orbiting the planet for ~30 years. This event, which left visible scars on Jupiter's surface, illustrates well the comet delivery of volatile elements to a planet. The contribution of comets to the atmosphere and oceans was long an open question, some models suggesting that about half of the material delivered after the main phases of terrestrial accretion was derived from comets, the rest being asteroids (Gomes *et al.*, 2005). The nature of cometary material, interstellar and solar system alike, has been another longstanding question.

Many comets seen in the inert solar system are periodic, *i.e.* they return regularly to the inner solar system, with periods ranging from a few years to hundreds of years. The original location of comets can be tracked from their trajectories, which led to the identification of two main cometary reservoirs, the Kuiper Belt and the Oort Cloud. The Kuiper Belt, with a total mass estimated to be a few percent of Earth's mass, extends to about 30 AU (where 1 AU or astronomical unit is the Sun-Earth distance) beyond the orbit of Neptune on the ecliptic plane. Comets with large eccentricities originate from a spherical reservoir with a very large radius of up to 10⁵ AU, the Oort Cloud. Some comets may be extrasolar: the Sun was born in a swarm of close stars and some of the solar system's icy bodies might have been ejected to other stellar systems or, conversely, icy material from other protoplanetary disks might have been injected into the outer solar system (Levison *et al.*, 2010). Oort Cloud and Kuiper Belt comets are thought to have been scattered from their original position in the trans-Neptunian disk to their present day position by gravitational disturbances induced by dynamic instabilities of the giant planets (Brasser and Morbidelli, 2013). From time to time, some of these objects are gravitationally destabilised and deviate towards the inner solar system. On their way they can be captured by the gravity field of giant planets and may modify their trajectories to smaller eccentric orbits. The so called Jupiter family comets have short periodicities of a few years to tens of years. One of the most famous comets, Halley, was represented on the Bayeux tapestry (1082 AD) and led Edmund Halley to infer the periodicity of comets (76 yr for Halley).

We know very little about comets and their origin because samples are scarce, degraded, and generally in very small abundance, and because *in situ* measurements performed by analysers on past spacecrafts lacked precision. However, two recent missions, Stardust, which sampled grains from comet 81P/Wild 2, and Rosetta, which analysed *in situ* volatiles released by comet



67P/Churyumov-Gerasimenko (hereafter 67P/C-G), have drastically changed our view. At the CRPG, we were lucky to be involved in both of these missions, being in charge of the analysis of noble gases in the cometary samples collected by the Stardust mission and of the interpretation of the noble gas data obtained by the Rosetta mission.

7.1 The First Cometary Samples Returned to Earth: The Stardust Mission

Sampling a comet is challenging. Their velocities of several tens of km/s require energy efficient and delicate spacecraft operations to reach low differential velocities between the spacecraft and the comet. Don Brownlee, professor at the University of Washington and a specialist in micrometeorites and interplanetary particles, was the Principal Investigator (PI) of the NASA Stardust mission (Brownlee *et al.*, 2006). The aim of this mission was to recover grains from comet 81P/Wild 2, a Jupiter family comet with a diameter of about 5 km and a periodicity of 6.4 yr. Wild 2 was captured by the Jovian gravitational field in 1974, which ensured its “freshness” as it had not experienced too much thermal processing near the Sun. The Stardust spacecraft was launched in 1999 and, after sophisticated navigation that involved three gravity assisted manoeuvres around the Sun (spacecrafts can use the gravity field of the Sun or planets to gain velocity), encountered Wild 2 on January 2, 2004. The spacecraft crossed the coma at a distance of 230 km from the nucleus and passively collected grains with a differential velocity of 6.1 km/s. The collector, a tennis racket-shaped aluminum grid, was deployed before collection. Its hollows were filled with aerogel, a silica foam of extremely low density to best preserve the grains. The sample return capsule landed successfully on January 15, 2006, in a US army facility in Utah (Fig. 7.1).

As we were already involved in Genesis and our analytical performances were known, we became involved in the mission at another LPSC. Several participating scientists met in a room to discuss which analyses should be rapidly carried out first. We were assigned the analysis of noble gases and nitrogen in some of the grains. The samples had been identified just after the capsule landed, and there were not many grains in the aerogel. Most of them were micron-sized, so scientists rushed to acquire the biggest ones. The samples embedded in the aerogel had left tracks of several tens of microns in length which finished with black residual grains, while the upper parts of the tracks were bubble-shaped, the result of the explosion of the volatile-rich icy grains upon impact (Fig. 7.1f). If noble gases and N had been preserved, they might have impregnated the walls of the bubbles, which were sometimes peppered with black dust. Hence, we requested fragments of the walls instead of the competitive terminal grains.

The analysis was straightforward compared to the nitrogen analyses of the Genesis targets. In the newly commissioned clean room at the CRPG, we carefully and somewhat apprehensively loaded the small transparent aerogel chips into a laser chamber which was connected to our N-noble gas line. Gases were



extracted upon heating the aerogel chips with a CO₂ infrared laser. Nitrogen, argon, krypton, and xenon signals were those of the line blank, but we could detect and measure the abundances and isotopic ratios of helium and neon. Bob Pepin's group, which was also in charge of noble gas analysis, identified He and Ne as well, so we decided to team up and publish our data together (Marty *et al.*, 2008). The proto-solar nebula ³He/⁴He ratio is estimated at 1.4×10^{-4} from the composition of the Jovian atmosphere and from meteoritic data. The ³He/⁴He ratio of the protosun evolved rapidly due to burning deuterium which yielded helium-3. As a result, the solar He isotope ratio increased from the proto-solar nebula value to about 4.4×10^{-6} , as analysed in modern solar wind (Heber *et al.*, 2009). Once the star reached the main sequence, the He ratio did not vary further. We found ³He/⁴He cometary ratios intermediate to these two end member values, suggesting that matter trapped in comet Wild 2 had recorded a snapshot of the early evolution of the protosun 4.567 Gyr ago. The neon isotopic composition was different from that of the Sun and close to values identified in meteoritic Phase Q, a poorly identified host of primordial noble gases in chondrites which is closely linked to organic matter. Both He and Ne abundances were very high, even higher than in solar wind-irradiated material like lunar soils. Cometary ice is unlikely to be the host of helium and neon as light noble gases could not be cryo-trapped at comet formation temperatures, hence these elements likely were hosted in refractory silicates or metal. We proposed a scenario in which metal/silicate grains were irradiated at high fluence, presumably close to the early active Sun, during its deuterium burning phase.

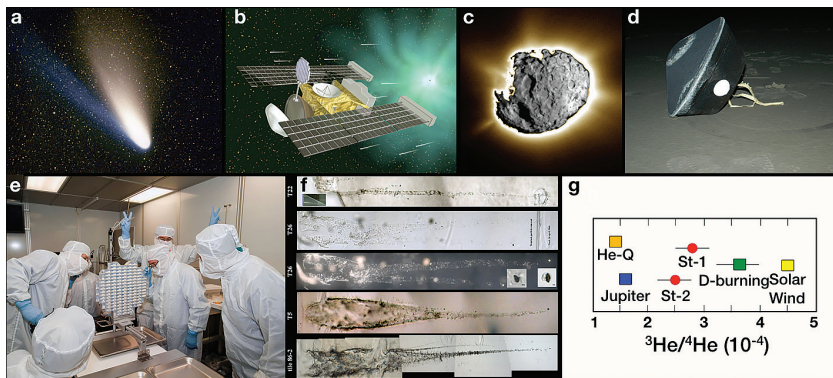


Figure 7.1

The Stardust mission. **(a)** Comet Hale Bopp seen from Earth. The two tails are made of ionised particles (blue), orientated away from the Sun, and the coma is made of gas and dust released by the nucleus. **(b)** Artist's view of the Stardust spacecraft with its vertical collector deployed to catch cometary grains. **(c)** Nucleus of comet 81P/Wild 2 viewed from the Stardust spacecraft (false colours). **(d)** Sample return capsule after landing in the Utah desert. **(e)** Examination of the collector at the Johnson Space Center. Don Brownlee, PI of the mission, flashes victory signs to celebrate the discovery of cometary grains trapped in the aerogel. **(f)** Tracks of cometary grains that entered the aerogel



from left to right. Large cavities at the entrance were formed by explosions of gas-rich phases and black debris along the tracks are solid dust particles. (g) $^3\text{He}/^4\text{He}$ isotope ratios of two cometary samples (ST-1 and ST-2) compared to other cosmochemical end member values. He-Q: helium trapped in Phase Q, a ubiquitous reservoir of chondritic noble gases; Jupiter: atmosphere of Jupiter which is thought to have trapped gas from the solar nebula. (These two values may represent the composition of solar nebula gas). D-burning: composition of the protosun before reaching the main sequence; Solar Wind: modern SW thought to represent the solar composition after deuterium burning. The observation that Stardust helium has an intermediate isotopic composition suggests that cometary matter might have sampled the evolving protoSun. Photo credit: (a) Public domain (b-f) JPL and NASA (g) Adapted from Marty *et al.* (2008).

Results obtained by several labs worldwide changed our vision of solar system formation. Several of the components found in Stardust grains were high temperature mineral assemblages commonly found in primitive meteorites such as CAI, chondrules, pre-solar grains, crystalline and amorphous silicates, metal sulfides, and oxides, as well as organics. These findings imply that rocky components that accreted to form 80P/Wild 2 originated from the inner regions of the solar system (Brownlee *et al.*, 2006). These components were mixed with low temperature phases like H_2O , CO_2 , and CO ices, providing direct evidence of large scale transport of solid phases across the solar nebula. Prebiotic organics like glycine were found, as well as was evidence for liquid water. Unfortunately, the size of the grains and their degradation during the capture process did not permit direct analysis of cometary ice and its compounds, but another remarkable mission was about to do this *in situ*.

7.2 The Rosetta Mission: Origin of Cometary Matter

This ESA-led mission with NASA participation was designed to study a comet *in situ*. The mission built on the success of the ESA Giotto mission which, together with two Russian probes and two Japanese probes, approached and analysed comet Halley in 1985. The 1.4 billion Euro Rosetta mission comprised a spacecraft with 11 instruments to analyse the physical and chemical characteristics of the comet, and a lander called Philae, which was equipped with a chemical analyser and a few sensors. The spacecraft was launched on March 2, 2004, from Kourou, French Guyana, with an Ariane 5 rocket, and travelled for 10 years thanks to outstanding, sophisticated navigation comprising two Earth and one Mars gravity assists. The probe visited asteroids Steins and Lutetia before switching off electricity and entering space hibernation in order to save energy. After three years and with some apprehension, the spacecraft was successfully switched back on, and it reached its final destination, comet 67P/Churyumov-Gerasimenko around 500 million km from the Earth, in August 2014 (Fig. 7.2). At this distance, signals took about 8 minutes at the speed of light to transit between the spacecraft and the Earth, so all manoeuvres had to be perfectly anticipated. The Philae lander was sent off in November 2014 but unfortunately failed to grip the cometary



surface and bounced several times before falling into a cavity where its solar panels could not work efficiently. The lander power went down in a matter of days, hampering extensive *in situ* measurements. It was nevertheless a huge success since it was the first time that a man made instrument had landed on such a small body, furthermore a comet. The spacecraft accompanied the comet during its approach to the Sun and recorded all morphological and chemical changes with increasing temperature. The mission, which was programmed to end in November 2015, was extended for several months as all instruments were working normally. The bandwidth for space communications is limited, and the manpower to follow a mission is costly, so it was decided that the mission would end in November 2016. The spacecraft approached the comet and finally landed at low velocity to switch off the power supply. The story may not be over since there are projects to visit 67P/C-G, which is well documented, again and to return samples from its surface to Earth.

The morphology and physical properties of 67P/C-G were astounding and unexpected (Fig. 7.2). The 4 km nucleus consisted of two lobes linked by a depression. The overall density of the comet was very low, about 0.4, implying a porosity of 80 % despite its compact appearance. Its low albedo (which is the fraction of light reflected by a body) of 6.5 % attested to its organic rich composition; blue ice was rarely seen but numerous jets of gases were evidence of sublimation of H₂O ice at a rate of several hundred kg/s. Cometary degassing provided the opportunity to analyse directly the composition of ice, as well as that of expelled grains together.

Among the instruments, the ROSINA (Rosetta Orbiter Spectrometer for Ion and Neutral Analysis) mass spectrometry system was particularly interesting for us. The ROSINA instrument was developed by an international consortium led by Kathrin Altwegg at the University of Bern. The instrument consisted of two mass spectrometers, a time-of-flight mass spectrometer (TOFMS) and a double focusing mass spectrometer (DFMS). We really lacked noble gas data for comets so I contacted Kathrin to ask if it would be possible to join the group even though the mission had already been flying for ten years. One of the main objectives of the DFMS was to analyse noble gases, and my goal was to have access to the data. Kathrin agreed and we met at one of the many ROSINA meetings in, of course, the Swiss Alps. The TOFMS did not function as planned due to electrical issues but the DFMS worked perfectly and provided invaluable data on the composition of cometary volatiles. The DFMS was a Mattauch-Herzog type mass spectrometer which combined separation in electric and magnetic fields to achieve high mass resolution, that is, the ability to separate different ionised compounds with almost identical masses. Compounds from the coma were directly introduced into the Nier-type electron impact source of the mass spectrometer without a pumping system since it was operating in the vacuum of space. Cometary gases were analysed in bulk, without species separation. At a given mass, several contributing compounds could be separated and identified



owing to the high mass resolution of the instrument. Both abundant and trace compounds were analysed conjointly, which required a large range of masses and of sensitivities for the collectors.

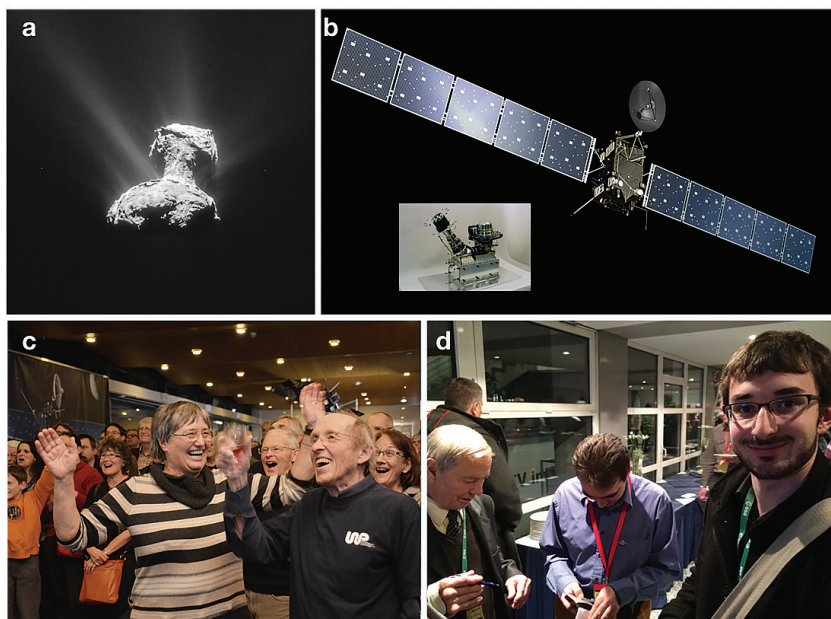


Figure 7.2 Exploration of comet 67P/Churyumov-Gerasimenko by the ESA-NASA Rosetta probe. **(a)** 67P/G-C upon arrival. **(b)** Artist's view of the Rosetta spacecraft, with insert showing the double focusing mass spectrometer (DFMS) of the ROSINA instrument that analysed volatiles released by the comet. **(c) Left:** Kathrin Altwegg. **Right:** Hans Balsiger and the ROSINA instrument team celebrating successful measurements. **(d) Left:** Klim Ivanovitch Tchourioumov (1937-2016) who discovered comet 67P/Churyumov-Gerasimenko with Svetlana Gerasimenko, photographed during an ESA event celebrating the Philae (almost) successful landing. **Right:** Guillaume Avice, then Ph.D. student at CRPG, enjoying the discussion. Photo credit: ESA and B. Marty.

The DFMS made many breakthrough discoveries. Cometary water was found to be rich in deuterium by a factor of 3 relative to oceans (Altwegg *et al.*, 2015), which, together with other cometary data obtained by remote sensing, confirmed that comets are D-rich. Hence, the contribution of 67P/C-G-like H₂O to terrestrial water had to be small. The coma was found to be rich in argon and heavy noble gases, confirming their trapping at low temperatures in cometary ice (Balsiger *et al.*, 2015). From mass balance involving noble gases, the contribution of cometary H, C, N, and halogen-bearing compounds to the atmosphere and oceans also had to be small, of the order of less than one percent (Marty

et al., 2016). Dinitrogen was identified which, together with CO, allowed us to constrain the comet formation and evolution temperatures to be less than 50 K (Rubin *et al.*, 2015). Molecular oxygen was surprisingly abundant, suggesting that water ice was dissociated by irradiation in icy grains before comet formation, and therefore was a pre-solar evolution (Bieler *et al.*, 2015). ROSINA identified glycine, an amino acid commonly found in proteins, phosphorus, a key component of DNA and cell membranes (Altwegg *et al.*, 2016), and aliphatic compounds (Raponi *et al.*, 2020) lending support to the possibility that cometary matter dispersed bio-elements onto early Earth.

I convinced Kathrin of the interest in having xenon isotope data to investigate the famous xenon paradox(es) (Section 2). However, xenon is the least abundant noble gas and, at the operating distance of the spacecraft, generally a few tens to hundreds of km, the Xe signal was too weak to analyse its isotopic composition. Kathrin has a strong personality, able to move mountains even outside Switzerland, and she requested that the spacecraft was manoeuvred closer to the comet surface. The flight engineers and other scientific investigators were not comfortable with this because the instruments risked degradation if hit by ejected particles and the guidance system, which uses fixed stars, could be blurred by ejected cometary grains shining in the solar light. Finally, Kathrin won her case and the spacecraft stayed at a distance of 7-10 km for three weeks to analyse mostly noble gases. In fact, the guidance system failed for a couple of hours, but control of the spacecraft was recovered safely. Not only xenon but all noble gases could be analysed for their abundances and their isotopes, and a magic discovery emerged.

7.3 Contribution of Comets to the Oceans and the Atmosphere

Among noble gases, xenon is probably the most interesting in terms of scientific information, but also the most difficult to decipher (Sections 1 and 2). Xenon has nine isotopes, produced by a variety of stellar processes: p-process in supernovae for the two light ^{124}Xe and ^{126}Xe isotopes; s-process (slow neutron capture) in asymptotic giant branch (AGB) stars for ^{128}Xe , ^{129}Xe , ^{130}Xe , ^{131}Xe , and ^{132}Xe isotopes, and r-process (rapid neutron capture) for ^{129}Xe , ^{131}Xe , ^{132}Xe and exclusively for the heaviest ^{134}Xe and ^{136}Xe isotopes in neutron stars and supernovae (Fig. 1.3). These multiple nucleosynthetic sources for heavy elements which have numerous isotopes are not uncommon, and the thorough mixing of stardust yielded the starting composition of solar system xenon as seen in the solar wind. Xenon trapped in chondritic (primitive) meteorites resembles solar wind although it is slightly enriched in heavy isotopes by about 1% *per* atomic mass unit, as a possible result of isotope fractionation upon ionisation and trapping in solids (Fig. 1.6; Hohenberg *et al.*, 2002; Marrocchi *et al.*, 2005). This Xe component, labelled Q-Xe, is common to all chondritic types but its host phase is not precisely known. It appears associated with, or trapped in, organics. Our current model is that Q-Xe was trapped from the nebula during ionisation of the nebular



gas that led to the formation of organic matter, to the isotopic fractionation of solar Xe, and to its efficient trapping. Organics were then processed and incorporated in meteorites (Marrocchi *et al.*, 2011; Kuga *et al.*, 2015). Chondritic Xe presents a monoisotopic excess of ^{129}Xe due to the decay of extinct ^{129}I .

The terrestrial atmosphere is isotopically fractionated, by 3.5 % *per* atomic mass unit in favour of the heavy isotopes (Fig. 7.3). Furthermore, atmospheric xenon is depleted, relative to other noble gases, by about a factor of 10-20, when compared to the so called planetary abundance, that is, the abundance pattern of noble gases in chondrites (*cf.* the missing Xe problem, Section 2). A simple solution to this paradox was found in the composition of palaeo-atmospheric gases trapped in Archean rocks (Pujol *et al.*, 2011). The analysis of ancient Xe trapped in hydrothermal quartz of different ages showed a smooth evolution of Xe isotope fractionation with time (Avice *et al.*, 2018a; Section 8), as a result of specific

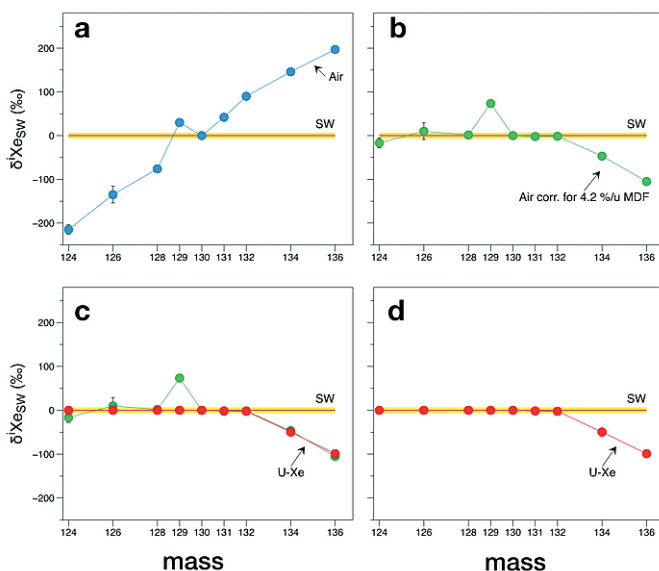


Figure 7.3

(a) Isotopic composition of atmospheric xenon (blue dots), normalised to ^{132}Xe and to solar wind (SW). Isotopic ratios are given in parts per mille deviation relative to SW. In this format, SW yields a horizontal straight line (orange). Mono-isotopic excess at mass 129 is due to the decay of extinct ^{129}I . (b) Atmospheric Xe corrected for mass dependent fractionation (MDF) (green dots) of 4.2 % *per* atomic mass unit (u). (c) Same as (b) with highlighted ^{129}Xe excess. (d) U-Xe (red dots), the putative progenitor of atmospheric Xe, whose isotopic composition is similar to SW (or chondritic) for $^{124}\text{-}^{132}\text{Xe}$ isotopes but is depleted in ^{134}Xe and ^{136}Xe (Pepin, 1991). Such a depletion was found in cometary Xe measured on 67P/C-G, establishing the link between comets and the atmosphere.



atmospheric Xe escape to space. Hence, the modern composition of atmospheric xenon was a secondary and not a primary feature of terrestrial xenon. After correction for isotope fractionation (Fig. 7.3), the primordial composition of terrestrial xenon resembles that of the solar wind (or meteorites, at this scale both are comparable), for all isotopes, except for the two heaviest ones, ^{134}Xe and ^{136}Xe which are significantly depleted. Such depletion cannot be explained by any known nuclear process: the fission of heavy elements like ^{235}U , ^{238}U , or ^{244}Pu produce heavy Xe isotopes like ^{134}Xe and ^{136}Xe which are stable and cannot decay. This primitive Xe component, nicknamed U-Xe (U stands for Ur which means something like original or primordial; Pepin, 1991), has not been found anywhere else than on Earth and its origin had been enigmatic for a long time, until the analysis of Xe isotopes by the ROSINA instrument on Rosetta.

For three weeks, the DFMS system on board Rosetta accumulated about 500 Xe and Kr isotope data. The data reduction team led by Martin Rubin at the University of Bern proceeded to correct for mass discrimination and isobar contributions. The light, rare ^{124}Xe and ^{126}Xe isotopes could not be analysed due to their low abundance, but the other isotope measurements showed a drastically different composition to any other solar system component (Fig. 7.4). Two main features emerged: (i) ^{134}Xe and ^{136}Xe are severely depleted, by 40 % and 60 %, respectively, relative to solar or chondritic compositions; and (ii) cometary Xe is enriched in ^{129}Xe (Marty *et al.*, 2017).

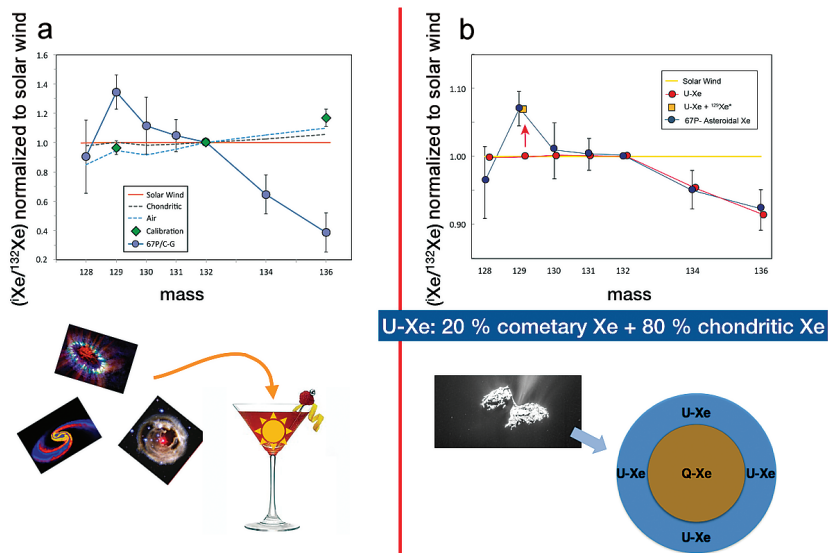


Figure 7.4

(a) Isotopic composition of cometary xenon (dark blue dots) normalised to ^{132}Xe and to solar wind (SW). In this format, SW yields a horizontal straight line (orange). For comparison, atmospheric Xe (dotted blue line), chondritic



Xe (dotted black line), and atmospheric Xe measured on board the spacecraft with embarked aliquots of air (green diamonds). Cometary Xe is highly depleted in heavy ^{134}Xe and ^{136}Xe isotopes, as a result of a stardust cocktail different to that of the bulk solar system (bottom). **(b)** U-Xe characterising atmospheric xenon can be reproduced by mixing 20% cometary Xe with 80% chondritic (Q) Xe trapped in Earth. Note that excess ^{129}Xe in air can also be reproduced by such mixing. This is the first evidence of cometary contribution to Earth. Adapted from Marty *et al.* (2017).

The peculiar Xe isotopic composition of cometary ice raised a number of questions about the origin of cometary matter. The heavy isotope depleted pattern could be due to large isotopic fractionation (although the lightest measured Xe isotope, ^{128}Xe , does not follow this trend). 67P/C-G experienced several heating events during previous travel towards the Sun, and phase changes in ice, *e.g.*, from amorphous to crystalline, may induce isotope separation. This possibility is presently being tested at the CRPG by graduate student Matthieu Almayrac, although it may not account for the magnitude of the observed trend. Isotopic fractionation is not supported by the isotopic composition of krypton, measured at the same time, which is close to that of the solar composition (though with some significant deviations; Rubin *et al.*, 2018). We concluded that the important depletion of the heavy Xe isotopes resulted from a nucleosynthetic mix different from that of the bulk solar system. ^{134}Xe and ^{136}Xe are the only xenon isotopes produced exclusively by the r-process, and their strong depletion was attributed to a deficit of isotopes produced in neutron stars and supernovae, implying that cometary Xe has never been homogenised with the nebular gas, and is *de facto* presolar. Nanodiamonds, SiC among others, host presolar noble gases whose correlations permitted identification of the isotope compositions of several nucleosynthetic components (Huss *et al.*, 2003; Gilmour and Turner, 2007). Using these end member compositions, we could satisfactorily reproduce cometary Xe (Fig. 7.4) on the condition that r-process Xe isotopes were highly depleted. This presolar Xe component hosted in 67P/C-G might have been trapped and preserved in the icy grains that accreted to form the comet, suggesting that cometary ice, at least that trapped in 67P/C-G, is presolar as well, and possibly interstellar. Thus, high temperature silicates and metals, as observed in the refractory phases captured by the Stardust mission, were mechanically mixed with ice derived from the outer solar system or from other stellar systems, requiring large scale transport in the nascent solar system from its hot internal zones towards its most remote outskirts. Furthermore, cometary Xe also contained a large excess of ^{129}Xe , presumably from the decay of extinct ^{129}I , but there was not enough ^{129}I at the birth of the solar system to produce such a large excess. We proposed that the icy grains forming 67P/G-C trapped Xe together with ^{129}I , which had been freshly produced by a nearby supernova tens of Myr before the onset of solar system formation, in agreement with a presolar origin of cometary grains (Marty *et al.*, 2017).



Because ^{134}Xe and ^{136}Xe are depleted in U-Xe, we tested the possibility that this depletion was the signature of cometary contributions. The experiment worked beyond expectations, the U-Xe composition could be well reproduced by mixing solar, or meteoritic, Xe with cometary Xe, the latter accounting for $22 \pm 5\%$ of atmospheric Xe (Fig. 7.4b). Even the excess of ^{129}Xe in air, previously attributed to the decay of ^{129}I in the proto-Earth, could also be inherited from comets. For the first time, a quantitative link between the atmosphere and comets could be established, showing that comets contributed volatile elements to Earth. Then, from the composition of coma volatiles, we calculated the contributions of comets to ocean water and found that this might have been limited to the order of 1% or less, in agreement with D/H or Ar constraints (Fig. 7.5; Marty *et al.*, 2016; Rubin *et al.*, 2019). Hence, the cometary contribution of noble gases to Earth was significant, but that of major volatiles like water, carbon, or nitrogen was not. This is because comets are rich in noble gases compared to inner solar system reservoirs, including the Earth. For example, the Ar, Kr, and Xe contents of the 67P/C-G coma are three orders of magnitude higher than in chondrites. Nebular noble gases were frozen quantitatively in cometary ice whereas they were not retained in the high temperature solids that form meteorites and planetary bodies because they could not establish chemical bonding with metal or silicate atoms. Adding a little bit of cometary material to Earth significantly impacted the noble gas budget while having a very limited effect on major volatiles.

Based on the composition of comets, including 67P/C-G on the one hand and the contribution of cometary Xe on the other, we placed constraints on the total mass of comets which had impacted the Earth. The amount of atmospheric xenon used in this mass balance calculation needed to be corrected for the $\sim 10\times$ to $20\times$ loss of Xe through geological time. The resulting cometary mass ranged from 2×10^{20} to 6×10^{21} g. Xenon trapped in the terrestrial mantle is chondritic, and not U-Xe-like (Caracausi *et al.*, 2016), implying that comets contributed volatiles to Earth when the mantle was already closed to exchanges with the surface, presumably after the Moon-forming event. The so called late veneer, *i.e.* extraterrestrial material added after the moon-forming impact to account for the unfractionated budget of highly siderophile elements in the mantle, accounted for about 0.5% of the terrestrial mass, that is, 3×10^{25} g. Hence the largest share of late contributions to Earth were of asteroidal, rather than cometary, origin, which is also consistent with the stable isotope composition of the atmosphere and oceans.

The case of organic matter may be different. Comets are made of roughly one third organic molecules (Greenberg, 1998), including prebiotic ones like glycine, which was detected in the coma of 67P/C-G (Altwegg *et al.*, 2016). Based on a similar mass balance, comets might have contributed 1.7×10^{18} to 3.4×10^{19} g of organics, which is comparable to the present day biomass (2×10^{18} g) (Fig. 7.5). Hence contribution of comets to early terrestrial environments might have been significant for prebiotic material. Whether or not such organics could have survived impact is not obvious. Cometary material could have partly survived



impacts in oceans at velocities lower than 10 km/s (Chyba *et al.*, 1990). Cometary dust, due to either a rain of tiny cometary-like present day IDP, or their fragmentation high in the atmosphere, might have been able to survive as a result of aerobraking. The survival of cometary organics and their role in prebiotic chemistry are clearly fascinating but open questions.

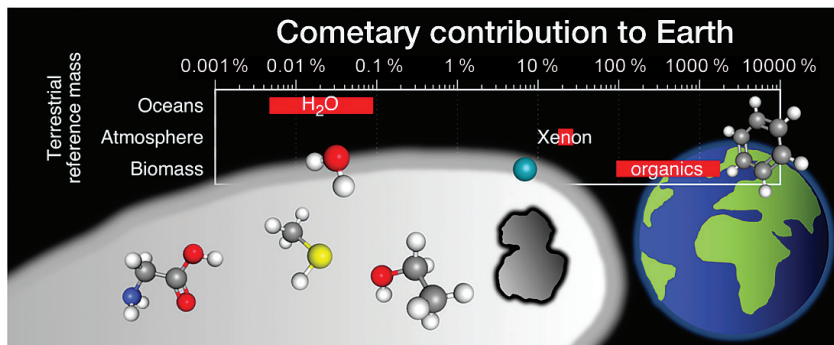


Figure 7.5 Cometary contribution to Earth's surface reservoirs based on Xe isotope mass balance (Marty *et al.*, 2017; Rubin *et al.*, 2019). Adapted from Rubin *et al.* (2019).

Finally, is 67P/C-G representative of all comets? And did all comets sample a common reservoir, or do they represent samples of highly heterogeneous material with diverse origins, including presolar? The observation that all comets have comparable ¹⁵N-rich isotope compositions (Rousselot *et al.*, 2014) would support a common origin or at least trapping of material that was processed together. The ultimate answer will lie in the analysis of either other comets, or a cometary sample return mission.

8.1 Early Environments

Life exists on Earth but its existence has not been definitively proven on other planets/worlds. Biological activity might have existed on Mars and, in this respect, the ancient environments of the Red Planet may shed light on the environmental conditions of the ancient Earth. How life developed on our planet is far from fully understood. Whether the origin of life was exogenous (Section 7) or developed in peculiar and transient niches on Earth is still vigorously debated. However, planetary sciences and the geological record provide significant insight into relevant environmental conditions and timing. Although life can develop and persist in extreme environments (temperatures up to 120 °C, pH ranging from 1 to 11, high pressure, high salinity), its development required certain key conditions: (i) liquid water (to optimise chemical reaction rates); (ii) a relevant temperature range (to avoid H₂O freezing or evaporating); (iii) available carbon, nitrogen, and salts in adequate chemical speciation (as essential ingredients); and (iv) shielding from harmful irradiation from outer space that could destroy organic molecules. This section details recent advances using my preferred geochemical toolbox to place constraints on some of these conditions.

The age of the atmosphere and oceans, defined as the epoch when these reservoirs became cool and stable enough to avoid extensive loss to space, is probably related to the last catastrophic event affecting the proto-Earth: the Moon-forming impact. Traditionally, the atmosphere was “dated” thanks to the 7% atmospheric excess of ¹²⁹Xe from extinct ¹²⁹I (Figs. 1.6, 7.3) which, from estimates of the iodine content of Earth, yielded an age of about 4.46 Ga, that is, ~100 Myr after the start of solar system formation (Wetherill, 1980; Allègre *et al.*, 1995). This age was revisited to 4.51 Ga (~40 Myr after the start of solar system formation) by taking into account atmospheric xenon loss after this major event and the consequent correction of the initial amount of ¹²⁹Xe (Avice and Marty, 2014). While such an “old” age was consistent with other geochemical approaches defining the age of the Moon-forming impact (Kleine *et al.*, 2005), the composition of cometary xenon suggested that part of the atmospheric ¹²⁹Xe excess could be inherited (Marty *et al.*, 2017), thus rendering problematic the use of this chronometer to date the atmosphere. The age of the lunar cataclysm is still controversial (Touboul *et al.*, 2007; Jacobson *et al.*, 2014) but it may be safe to assume that the atmosphere and oceans stabilised within the first 150 Myr, that is, around 4.4 Ga.

The first 600 Myr of Earth history, known as the Hadean eon, were not easy. The Moon-forming event partly melted the proto-Earth (but not completely since solar neon survived in the mantle; Section 2) and might have blown away the atmosphere and oceans, although the latter could have survived (Genda and



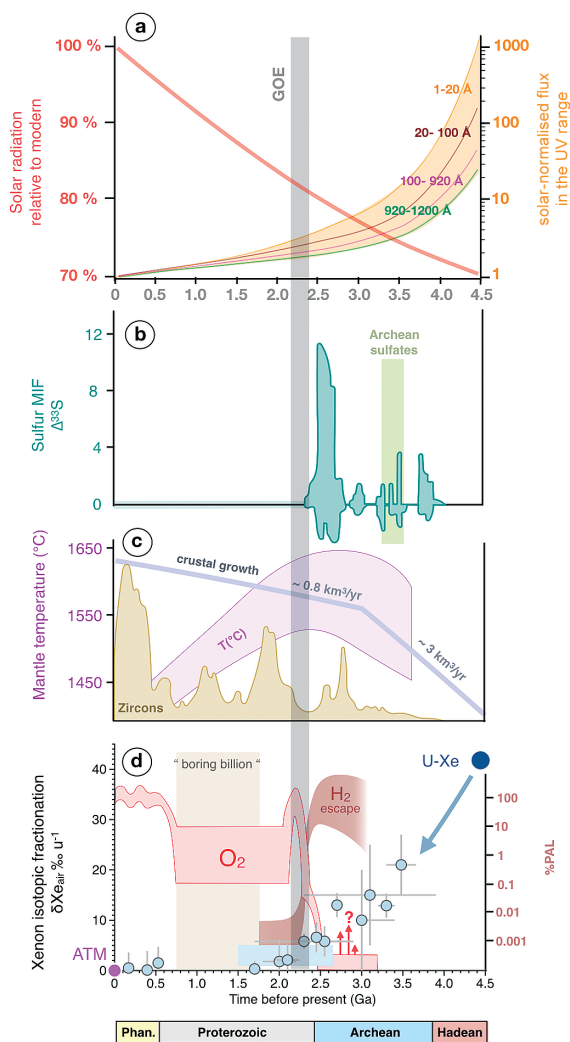


Figure 8.1

(a) Energy delivered by the Sun through time relative to modern- (left; Sagan and Chyba, 1997) and solar normalised flux versus age for different stages of solar-type stars in the far UV range (modern solar flux = 1) (Ribas *et al.*, 2005). (b) MIF-S recorded in sedimentary rocks expressed as $\Delta^{33}\text{S}$ as a function of age (Johnston, 2011). (c) Temporal evolution of the number of zircons (a proxy of continental formation pulses), of the crustal growth rate (Hawkesworth *et al.*, 2019), and of mantle temperature (Herzberg *et al.*, 2010). (d) Evolution of hydrogen escape, atmospheric O_2 concentration (Zahnle *et al.*, 2013), and isotope fractionation of atmospheric xenon (Avice *et al.*, 2017; 2018a). GOE: Great Oxidation Event. Adapted from Bekaert (2020).



Abe, 2005). After this last giant impact, a CO₂ steam atmosphere progressively cooled, permitting water condensation, within a few Myr. The remaining CO₂, equivalent to several tens of bars, was removed from the atmosphere, maybe by carbonate precipitation and burial in the mantle by early subduction-like processes (Sleep *et al.*, 2014), resulting in clement surface temperatures. Major episodes of mantle-crust differentiation took place over 100-200 Myr, as recorded by extinct radioactivity systems of Hadean and Archean rocks (Blichert-Toft and Albarède, 2008; Boyet *et al.*, 2003; Caro *et al.*, 2017). The surface of our planet was battered by asteroid and comet impacts (Section 7), collectively referred to as late accretion. The largest impacts might have frustrated early life forms, but might also have triggered the necessary abiotic reactions for the first living organisms to develop (Bada *et al.*, 1994). There are almost no rocks preserved from this period of time, but the analysis of detrital minerals (zircons) that survived several tectonic cycles suggest that liquid water, continental crust, and possibly modern-like subduction were already present at 4.4 Ga (Blichert-Toft and Albarède, 2008; Harrison *et al.*, 2005; Mojzsis *et al.*, 2001; Wilde *et al.*, 2001).

The ancient Sun was about 20-30 % less energetic than today during the first one billion years (Fig. 8.1). Its energy comes from the fusion in its core of four hydrogen nuclei yielding one ⁴He nucleus. As a result, the concentration of ⁴He in the distant past was lower than at present, just as the Sun's density in its inner regions and, consequently, its temperature and nuclear fusion rate were lower than today. For an atmospheric composition similar to today's, the average temperature of the Earth's surface would have been below 0 °C until about the mid-Proterozoic (Kasting, 2010). If a glaciation period had started, the terrestrial albedo (the fraction of incoming solar energy reflected to space) would have become close to unity and the surface of the Earth could not have been warmed again. However, liquid water was already acting as a weathering agent at 4.4 Ga (Wilde *et al.*, 2001) and the geological record indicates that glaciations were rare and episodic during the Archean and Proterozoic eons. This is the so called "faint young Sun paradox" (Sagan and Chyba, 1997). To counter this effect, the surface of the Earth might have been prevented from freezing by greenhouse gas(es). Carbon dioxide would be an obvious candidate but the atmospheric partial pressure required to maintain a clement temperature is not consistent with the geological record of palaeosols (Rye *et al.*, 1995; but also see Rosing *et al.*, 2010, for an alternative view). Several other greenhouse gas candidates have been advocated, such as NH₃ (Sagan and Chyba, 1997), methane (Pavlov *et al.*, 2000), or ethane (Haqq-Misra *et al.*, 2008). The generally anoxic character of the terrestrial environment before 2.4 Ga might have prolonged the atmospheric residence time of these species. A combination of several greenhouse gases might have also helped (Kasting, 2010). These possibilities require specific (abiotic and/or biotic) sources of gases over long periods of time, but their origins are unclear. Alternatively, higher concentrations of N₂ could have warmed the surface by broadening the absorption lines of CO₂ and H₂O (Goldblatt *et al.*, 2009). Another idea is that the nebulosity during the Hadean and Archean eons was lower than today, decreasing the albedo of our planet (Rosing *et al.*, 2010). The latest



insights on CO₂ concentration in the palaeo-atmosphere, together with recent 3D global climate models, may open a promising avenue to solve this paradox. Indeed warming from cloud feedbacks is more efficient in the 3D models than in the 1D models even for low atmospheric CO₂ partial pressures (Charnay *et al.*, 2020). Clearly, constraints on the composition of palaeo-atmospheric gases are critically needed.

Besides the total flux of solar energy, the quality and intensity of solar radiation itself might have also affected the composition of the ancient atmosphere, by triggering escape processes. Studies of Sun-like stars show that young stars of this type, although delivering less total energy than aged stars (see above), emit up to 1-2 order(s) of magnitude more photons in the UV and X-ray wavelength ranges below 100 nm (Fig. 8.1; Ribas *et al.*, 2005). Such photons are able to ionise and/or dissociate atmospheric atoms and molecules. Ionised particles reaching the exobase (the altitude above which atmospheric particles may escape to space) can be entrained along open lines of the terrestrial magnetic field, if already present, or along those of the solar magnetic field.

The energy delivered by Sun-like stars depends on their rotation. A fast rotating, Sun-like star, could cause the loss of an Earth-like atmosphere in ~100 Myr. For a slow rotating star, only ~40 % atmospheric loss could have taken place over 4.5 Gyr (Tu *et al.*, 2015). Unfortunately, the rotation regime of the young Sun is unknown and the potential of the young Sun to trigger atmospheric escape cannot be predicted. A geomagnetic field (which developed through time due to cooling of the core) weaker than today's could have also favoured atmospheric escape by providing less protection against solar wind ionisation of atmospheric species. Other factors such as the concentration of atmospheric CO₂ (Lichtenegger *et al.*, 2010) or the presence of aerosols might have cooled the upper atmosphere, preventing its escape. Young solar-like stars develop sudden and gigantic energy outbursts, called solar flares, which might have been up to three orders of magnitude more intense than those experienced today. Modern solar flares can already be harmful and present a major threat to astronauts in space and to electronics and telecommunications on Earth. For example, a strong solar flare in 1972 led to the explosions of dozens of US sea mines in the waters of Hong La, Vietnam. Cataclysmic solar flare events could have had profound impacts on ancient environments, being able to reach the terrestrial surface through the atmosphere and ionising atmospheric particles along their paths. None of these processes in the distant past are documented.

The terrestrial environment during the first half of Earth's history was very different from the modern one. The continuous presence of oceans from the Hadean to the Proterozoic is now firmly established, but their physical and chemical characteristics, such as volume and temperature, are poorly known. Atmospheric oxygen levels were as low as only 10⁻⁴ times the present day atmospheric level (PAL) (Holland, 1984; Rye *et al.*, 1995) due to oxygen consumption by iron oxidation and lack of biological activity strong enough to counterbalance it. The transition between the Archean and Proterozoic eons (around 2.4 Ga)



was marked by a rapid shift from anoxic to oxic surface conditions, referred to as the Great Oxidation Event (GOE; Fig. 8.1). Anoxic conditions, first proposed on the basis of sulfur speciation in Archean rocks (Holland, 1984), were later clearly demonstrated by the occurrence of mass independent fractionation of sulfur isotopes (MIF-S) recorded in Archean rocks (Farquhar *et al.*, 2000a). Volcanic SO₂ and SO injected into the Archean atmosphere was disproportionated between elemental sulfur and sulfate by solar UV light, each of them carrying an “anomalous” sulfur isotope (MIF-S) signal (expressed as $\Delta^{33}\text{S}$, which in a multiple isotope ratio plot gives the distance of the measurement to the “normal”, mass dependent fractionation line). This chemistry required very low levels of atmospheric oxygen to allow UV photons to break down SO₂ (such photons are now shielded by ozone, O₃). It would have also required oxidising species, such as H₂O and CO₂, to produce nitrates together with reducing species such as methane, ethane, and ammonia to polymerise elemental sulfur. The extent to which these conditions were met during the Archean eon is a subject of discussion (Farquhar and Wing, 2003). MIF-S stopped abruptly at 2.45 Ga when other indices of low oxygenation also disappeared (*e.g.*, banded iron formations, uranium deposits, specific transition metal compositions in shales, *etc.*) (Fig. 8.1). Interestingly, Martian sulfur trapped in SNC meteorites also presents MIF-S, supporting the absence of O₂ and abundant solar UV light as necessary conditions for their appearance (Farquhar *et al.*, 2000b). The cause(s) of the GOE are discussed in the framework of three types of processes, or a combination of several of them: (i) hydrogen escape to space following H₂O vapour dissociation by solar UV light leading to oxidation of the oceans (Zahnle *et al.*, 2013); (ii) development of an oxygen producing biomass such as cyanobacteria (Schirmermeister *et al.*, 2013); and (iii) tectonic driven change (Hawkesworth *et al.*, 2019) in the oxidation state of volcanic sulfur (Gaillard *et al.*, 2011; Ciborowski and Kerr, 2016) (Fig. 8.1). Based on Xe isotopes we proposed an alternative possibility (Marty *et al.*, 2019) that will be described in this section.

8.2 Ancient Atmospheric Gases Trapped in Tiny Bubbles

The oldest terranes that are not too metamorphosed to have kept a direct record of past environments are meso-Archean in age, *i.e.* ~3.5 Ga. They are found in several localities in northwest Australia in the region of the Pilbara, and in South Africa around the town of Barberton. They consist of the so called greenstone belts, a layered assemblage of volcanics, cherts, and detrital sediments of volcanic origin. They are crosscut by hydrothermal veins of barite and quartz, which were of great interest to us as they might have preserved palaeo-atmospheric gases and palaeo-ocean water. We teamed up with Pascal Philippot, then professor at the IPGP. Pascal is an experienced field geologist with an excellent knowledge of fluid inclusions, whom I knew from my Parisian years as we had nearby offices. Magali Pujol from the ENSG in Nancy, where I teach, signed on for a Ph.D. and we did some field work with a team from the IPGP and the CRPG around a locality ironically named North Pole, NW Australia, because this is where some



of the highest temperatures on the continent are recorded (Fig. 8.2). This area is the focus of extensive studies by several groups from Australia, Japan, the USA, and France. The 3.5 Ga rocks there are exceptionally well preserved, with pillow basalts, stromatolites, and volcanic cinder cones and bombs that look as fresh as if they had been ejected the year before.

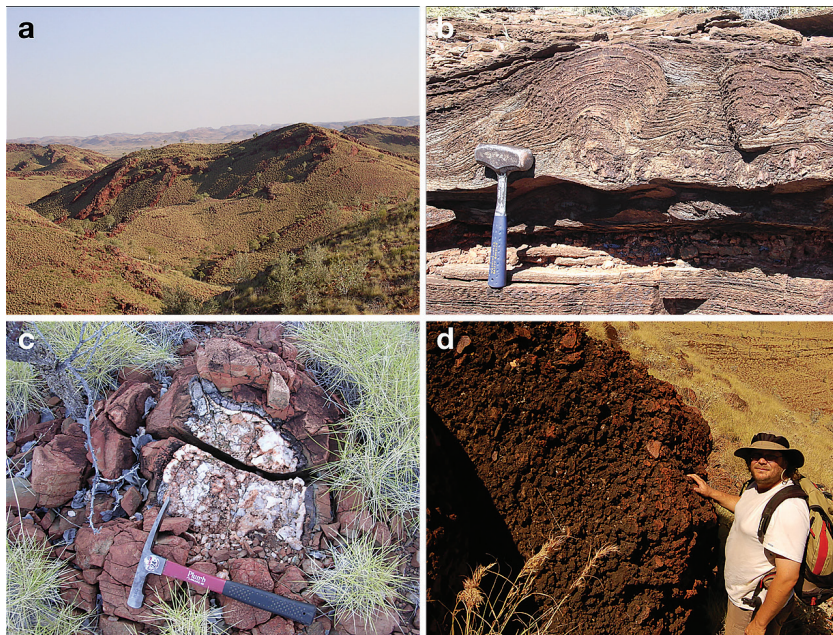


Figure 8.2

(a) 3.5 Ga Archean terranes around North Pole, Pilbara (NW Australia), during a field trip in 2006. The dyke-like structures are hydrothermal veins of barite and quartz crosscutting cherts and detrital sediments of volcanic origin. (b) Stromatoloids in the Strelley Pool formation. (c) 3.54 Ga pillow basalt filled with hydrothermal quartz. (d) Jean Carignan (CRPG, deceased) looking at “fresh” 3.2 Ga volcanic deposits. Photo credit: B. Marty.

We began by analysing noble gases in a 3.5 Ga barite from a drill core, inspired by an early study showing that xenon trapped in North Pole barite has a very different isotopic signature from the modern one (Srinivasan, 1976). We aimed at constraining the half life of ^{130}Ba , which is expected to decay to ^{130}Xe by double electron capture. These double decays are of interest for physicists because they carry information on the ultimate nature of matter, such as the mass of the neutrino. Meshik *et al.* (2001) found a small excess of ^{130}Xe in 170 Ma barite that they attributed to ^{130}Ba decay for which they proposed a half life of 2.2×10^{21} yr. The data that Magali obtained (Pujol *et al.*, 2009) showed a fractionated isotope pattern like that of barite analysed by Srinivasan (1976). Fissiogenic



Xe isotopes produced by the decay of ^{238}U allowed us to verify an Archean age for the sample and a mass fractionation of 2.1 ‰/atomic mass unit (u). The sample had an excess of ^{130}Ba , which led us to propose a half life of 6×10^{20} yr, four times shorter than the one estimated by Meshik *et al.* (2001). The severe isotope fractionation was tentatively attributed to mass dependent isotopic fractionation, combined with a Rayleigh distillation effect which could have occurred during interaction. These conclusions were, however, challenged by Meshik and Pravdivtseva (2017) who argued that the excess of ^{130}Xe we measured was due to a combination of cosmogenic production and isotope fractionation. We also realised that our initial interpretation of the large mass dependent isotope fractionation trend was not consistent with the fact that krypton, also analysed in the study, was not fractionated, and further, that additional analyses of Archean samples of different nature showed a comparable Xe isotope fractionation. The two main conclusions of the study of Pujol *et al.* (2009) proved to be wrong, but it put us on track towards a very fruitful area of research!

We turned our attention to fluid inclusions (FI) trapped in hydrothermal quartz. Pascal Philippot and his team characterised fluid inclusions in chert and quartz as remnants of Archean seawater mixed with several hydrothermal fluids (Fig. 8.3d). The idea is that gases dissolved in fluid inclusions reflect the composition of the palaeo-atmosphere at the time of entrapment. At equilibrium, the concentrations of atmospheric species dissolved in surface waters are determined by their partial pressures in air and their respective solubility coefficients. Solubility coefficients are known from laboratory experiments and for chemically inert species like noble gases or N_2 , it is possible to reconstruct their palaeo-atmospheric compositions from analysis of ancient waters. Noble gases and nitrogen in the atmosphere are overwhelmingly abundant compared to those in the mantle, and their mantle component in groundwaters can be neglected in most cases. Fluids trapped in hydrothermal quartz consist of a mixture of surface water (fresh or seawater) and a crustal end member. The latter contains radiogenic and fissiogenic isotopes produced in the crust and can be identified and corrected for by careful, stepwise analysis. The surface water component reflecting the composition of the palaeo-atmosphere can be estimated.

This method requires the fluid inclusions to be contemporaneous with the host rocks and minerals and therefore the age of trapped fluids to be assessed. We collaborated with Ray Burgess at the University of Manchester to get insight into deposition ages. One of the specialties of the Manchester group is neutron activation to obtain Ar-Ar ages as well as halogen chemistry. Magali and Ray found that Ar-Ar dating of targeted samples yielded fluid ages consistent with those of the host formations. Xenon extracted from fluid inclusions by stepwise crushing under high vacuum also was found to be enriched in light compared to heavy isotopes, just like Xe in North Pole barite. Magali rushed to my office with the new data and we immediately thought of a completely different interpretation. This trend was not a signature of local isotope fractionation but instead reflected a peculiar signature of ancient atmospheric xenon. The Xe isotope spectrum was isotopically intermediate between that of solar Xe and that of modern



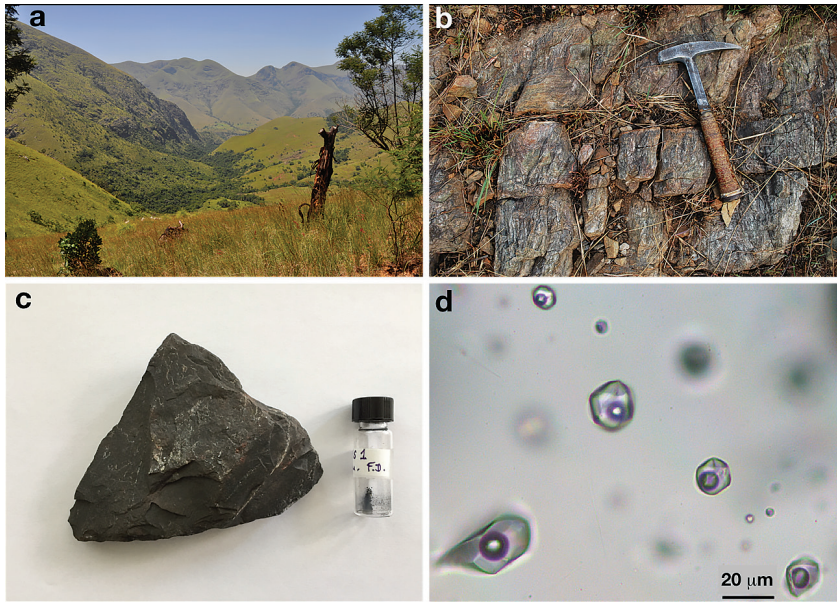


Figure 8.3

(a) Field trips in the Barberton greenstone belt, South Africa, in 2010 and 2013. Meso-Archean terranes consisting of volcanics and cherts. (b, c, d) Three types of samples that are able to retain paleo-atmospheric noble gases. (c) Barite (Pujol *et al.*, 2009). (d) Kerogen extracted from black shales (Bekaert *et al.*, 2018a). (d) Fluid inclusions in hydrothermal quartz (Pujol *et al.*, 2011, 2013; Avicé *et al.*, 2017, 2018a). Photo credit: B. Marty, D.V. Bekaert, M. Pujol.

atmospheric Xe. Archean xenon trapped in these samples recorded a snapshot of an evolutionary trend affecting only Xe (Pujol *et al.*, 2011). Krypton analysed together with xenon had an isotopic composition similar to that of modern air. The most obvious way to fractionate Xe isotopes was to preferentially lose Xe into space by atmospheric escape, which would also explain why xenon in the atmosphere is depleted relative to krypton (the first Xe paradox, Section 2). This possibility raised more questions than it addressed, but it could be tested.

Guillaume Avicé, another Ph.D. student, went to Barberton in South Africa with Axel Hofmann, Nick Arndt, and myself to obtain new quartz samples from a different location. Guillaume found similar Xe isotope trends, demonstrating that the phenomenon was not local but affected the entire atmosphere at that time (Avicé *et al.*, 2017). Guillaume then analysed a suite of hydrothermal quartz from various locations worldwide, with ages ranging from 3.5 Ga to present, which allowed him to reconstruct the secular evolution of atmospheric Xe isotope fractionation (Fig. 8.1d) (Avicé *et al.*, 2018a). The isotopic fractionation of xenon evolved from an initial composition similar to solar or chondritic Xe to a modern-like composition over a period of 2 Gyr, and this evolution stopped

at around 2 Ga. Hence xenon was the second atmospheric element, after sulfur, to exhibit a time dependent isotope evolution through geological time. Remarkably, xenon was the only noble gas to show such an isotopic evolution, with palaeo-atmospheric neon and non-radiogenic argon and krypton having isotopic compositions similar to those of modern air.

The escape of xenon from the atmosphere could not be due to a thermal effect (escape due to mass) since lighter noble gases were not affected. But the Xe ionisation potential is lower than those of other noble gases, as well as those of CO, CO₂, and N₂, rendering Xe prone to ionisation by abundant UV photons from the young Sun and subsequent loss to space. The large atmospheric Xe isotope fractionation of 3.5‰ could have resulted from a cumulative process during Rayleigh distillation escape of atmospheric Xe to space. The instantaneous fractionation factor required to deplete atmospheric Xe by one order of magnitude (to account for “missing xenon”) is about 1‰. Eric Hébrard, an atmosphere modeller (then a post-doc at the CRPG) built a 1D model for the Archean atmosphere in which xenon was preferentially trapped in a growing organic haze, the occurrence of which was proposed on other grounds (Pavlov *et al.*, 2000). Upon ionisation, atmospheric methane and hydrogen would produce an organic haze, such as the one seen in the atmosphere of Titan. Yves Marrochi and Maia Kuga, both Ph.D. students at the CRPG, observed a ≥1‰ isotopic fractionation of xenon trapped in solid organics from a C-rich gas phase during ionisation experiments (Marrochi *et al.*, 2011; Kuga *et al.*, 2017). Eric Hébrard showed that the maximum ionisation rate of Xe occurred at an altitude of about 60–100 km, also the altitude range at which haze production was maximum (Hébrard and Marty, 2014). Xenon trapped in the haze would be enriched in its heavy isotopes as required, while Xe enriched in its light isotopes would escape. Still, this model required Xe ions to escape to space. Kevin Zahnle, a scientist at Ames Laboratory in California, developed a physical model in which atmospheric Xe was ionised, interacted with ionised hydrogen through their Coulomb electric field, and was lifted to the exobase by escaping hydrogen ions (Zahnle *et al.*, 2019). Hydrogen ions were provided by the photodissociation of water vapour. In this model, Xe isotope fractionation would occur by mass segregation during the rising process. One difficulty of the model is, however, to keep xenon ionised during its atmospheric transit because, if neutralised by electrons floating around, it would immediately fall back. Consequently, Zahnle *et al.* (2019) proposed that Xe escape was limited to short episodes of high solar activity, or to transient weakening of the geomagnetic field. A significant fraction of ocean water could have been lost during such events.

The above models assume a steady state, continuous process, but the role of intensive solar activity such as gigantic solar flares, which are known to occur on young solar-like stars, might have triggered short term, enhanced escape, thereby making the process discontinuous. This possibility is potentially testable with the Xe isotope evolution curve, which does indeed suggest that some stepwise evolution occurred. The termination of the escape process around 2 Ga is also poorly defined and it is not clear if it was linked to the emergence of free oxygen in the



atmosphere, as is the case for the end of mass independent isotope fractionation of sulfur. The emergence of free oxygen might have terminated hydrogen escape and, therefore, xenon ions. We continue to study Xe isotope fractionation through time in detail with the hope that Xe isotopes could monitor both the evolution of atmospheric chemistry as well as the activity of the young Sun.

The Xe evolution curve through time could also be used as a new geochronological tool. David Bekaert and Michael Broadley, graduate student and post-doc at the CRPG, respectively, evaluated the possibility of “Xe atmochronology” to test the syngenicity of organic matter. They analysed Xe in ancient organic matter separated from a 3.0 Ga quartzite and found that its degree of isotopic fractionation, when reported on the Xe isotope evolution curve of Avice *et al.* (2018a), yielded a kerogen “Xe age” similar to that of the host quartzite (Bekaert *et al.*, 2018a; Fig. 8.4a). Hence the study showed that (i) kerogen is able to trap atmospheric noble gases over extended periods of time and (ii) “Xe atmochronology” of kerogen can provide a novel method for evaluating the syngenicity of organics in Precambrian rocks. New Ar, Kr, and Xe isotopic data for four kerogens isolated from 3.4 to 1.8 Ga old cherts confirmed that Xe isotopes from the Archean atmosphere can be retained within kerogens, but newly determined “Xe ages” were found to be sometimes younger than expected based on the host rock ages. This indicates that, initially, trapped Xe components were at least partially lost and/or mixed together with Xe carried by younger generations of organic material, therefore complicating the Xe based dating method (Bekaert *et al.*, 2020). Another interesting development of palaeo-atmospheric xenology was the possibility of evaluating the strength of mantle degassing through time (Fig. 8.4b,c). From the deficit of palaeo-atmospheric ^{129}Xe and its secular variations, we proposed that the GOE was provoked by a sudden and massive release of mantle-derived volcanic gases (Marty *et al.*, 2019).

The development of the continental crust through time was constrained by argon isotopes. Fluid inclusions have various shapes, sizes, and chemistry, and cannot be analysed individually because they do not contain enough gas for one analysis. Instead gases were extracted from bulk hydrothermal quartz fractions by crushing them sequentially and/or heating them progressively in order to resolve the seawater and crustal components. After each crushing or heating step, released gases representing a fraction of the total gas were analysed. Data defined linear correlations that permitted an estimation of the two end member compositions. Because samples were neutron irradiated, the amount of chlorine could also be measured from that of radioactive ^{37}Ar produced by the $^{37}\text{Cl}(n,p)^{37}\text{Ar}$ reaction and the $\text{Cl}/^{36}\text{Ar}$ ratio (where ^{36}Ar is a stable isotope of argon that has been conservative in the atmosphere) could be used as an index of mixing between a Cl-rich hydrothermal component and the seawater component with a fixed, low $\text{Cl}/^{36}\text{Ar}$ ratio. Finally, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the seawater and therefore of the palaeo-atmosphere in equilibrium with seawater at that time, was determined. Its value, 143 ± 24 (1 σ), was significantly different from the modern ratio of 298.6. A lower $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in the past atmosphere was not surprising because ^{40}Ar has been produced through time by the decay of



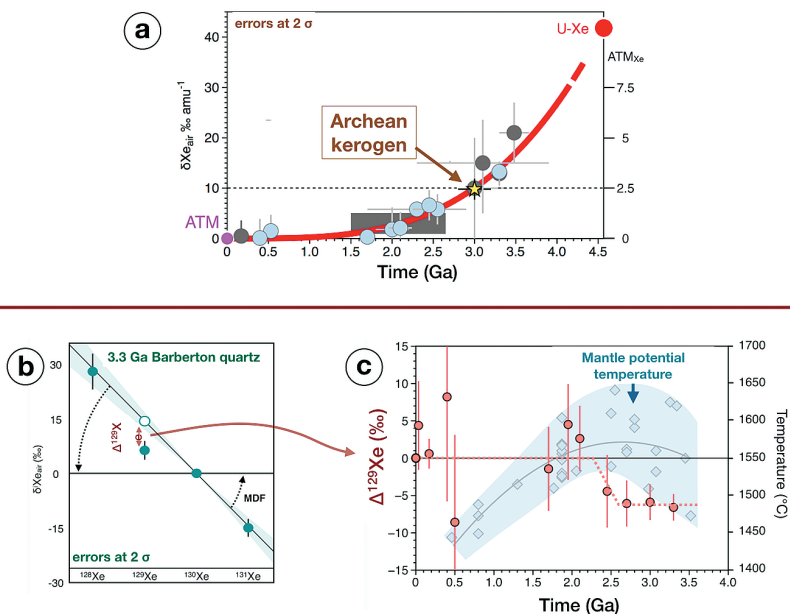


Figure 8.4 (a) Evolution of Xe isotope fractionation with time as a new geochronology tool. Grey and black dots represent data obtained for fluid inclusions trapped in hydrothermal quartz with different ages (Avice *et al.*, 2018a). Archean kerogen contains isotopically fractionated Xe which can be positioned on the curve to estimate the kerogen age. Here age means the time period when atmospheric Xe was trapped in organic matter. The age obtained is consistent with the age of the host rock (Bekaert *et al.*, 2018a). (b) and (c) Determining past volcanic fluxes from the mantle using the ^{129}Xe deficit in palaeo-atmospheric xenon ($\Delta^{129}\text{Xe}$ representing the distance between the measured composition and that expected for fractionated modern-like Xe). (b) The rationale is that, in the distant past, the atmosphere contained less mantle-derived ^{129}Xe than today. (c) Variations of the ^{129}Xe deficit in the palaeo-atmosphere through time permit the secular rate of volcanism to be constrained. A step increase of ^{129}Xe around 2.0-2.5 Ga was interpreted as an increase of magmatic activity, which possibly triggered the GOE (Marty *et al.*, 2019). This event could have been due to sudden release of overheated lavas to cool down the mantle, as suggested by mantle potential temperature variations (Herzberg *et al.*, 2010).

radioactive potassium in the crust and the mantle. However, knowing the exact value at a given time allowed us to place constraints on the growth of the continental crust. Because the continental crust is rich in potassium, its development impacts the release of ^{40}Ar from the solid Earth to the atmosphere. Constructing a box model comprising the mantle, the crust, and the atmosphere, Magali, Ray Burgess, Grenville Turner (the inventor of the Ar-Ar method, amongst other things), and myself proposed that between 3.5 Ga and 2.7 Ga, the continental



crust volume increased from ~30 % to ~80 % relative to the modern volume (Pujol *et al.*, 2013). Such crustal kinetics, derived from the composition of the atmosphere, are in agreement with models of crustal production and evolution based on mantle-derived tracers (Hawkesworth *et al.*, 2019).

8.3 Ancient Oceans

Prokaryotic microbial life was already present during the Archean (Knauth, 2005) and these primitive forms of life developed in the Archean oceans whose properties (salinity, temperature, chemistry) are poorly understood and subject to debate (*e.g.*, Albarède *et al.*, 2020). Holland (1984) estimated that the salinity of the ancient oceans could have been 1.2 times the modern inventory, based on evaporite volume estimates, but these formations barely resist metamorphism and plate tectonics. Knauth (2005) proposed that the salinity could have been twice modern levels. From statistical analysis of fluid inclusions trapped in hydrothermal quartz in Archean terrains worldwide, Weiershauser and Spooner (2005) suggested that the Archean oceans could have been more saline than modern oceans by up to one order of magnitude. A major unknown is the exchange rate of halogens between the surface and the mantle, since subduction of halogens could have depleted the surface budget of these elements but also enhanced the Cl content of arc magmas (Kendrick *et al.*, 2012). The extended Ar-Ar method allows one to determine chlorine, potassium, and natural Ar isotopes in the same extraction (Johnson *et al.*, 2000). Thus, we applied the end member mixing approach to the cases of Cl and K by normalising their fluid contents to that of stable ^{36}Ar (Marty *et al.*, 2018). Mixing trends for different Archean quartzes define several correlations that converge towards a unique seawater end member having both low Cl/ ^{36}Ar and K/ ^{36}Ar ratios compared to the Cl- and K-rich hydrothermal components. The correlation is particularly well defined for a 3.4 Ga Barberton sample (Fig. 8.5) and the Archean seawater component can be compared to the modern ocean water composition. The solubility of noble gases, *e.g.*, here argon, is temperature and salinity dependent, which does not allow us to define a single composition in temperature-salinity space (insert in Fig. 8.5), but data are consistent with a salinity level as defined by the Cl content comparable to the modern level within 20-30 %. The potassium content of the Archean oceans (Cl/K ~50 from the slope of the correlation, compared to the modern ratio of 29) could have been 40 % lower than the modern one, possibly in conjunction with a low continental crust volume at that time. Hence, this study suggests that the early forms of life were not particularly salt tolerant or restricted to dilute estuary/estuarine waters. Also, the limited diversity of eukaryotes in the Proterozoic record may be accounted for by nutrient limitation and/or widespread sulfidic conditions in the ancient oceans rather than by drastically different temperature and salinity conditions. Finally, a near constant salinity through time may set an upper limit of about 30 % for the fraction of ocean water that could have escaped to space, which is consistent with the amount of surface water which would be dissociated in order for hydrogen to escape and entrain atmospheric xenon (Zahnle *et al.*, 2019).



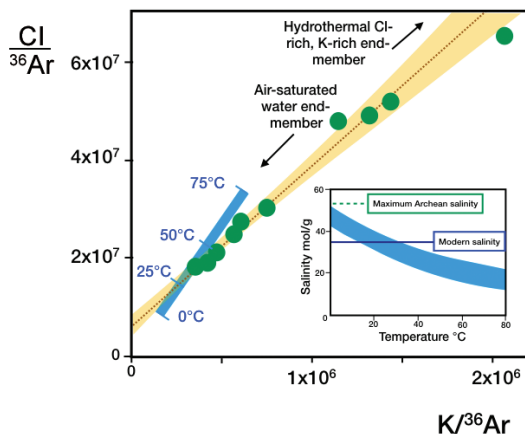


Figure 8.5 Tentative determination of Archean ocean salinity (Marty *et al.*, 2018, see text).

8.4 The Archean Atmosphere

What was the composition of the atmosphere billions of years ago and how did it evolve through geological time? This thin layer of gases permitted clement environmental temperatures at the Earth's surface; it protected the terrestrial environment from lethal irradiation from the Sun; and it supplied nutrients and redox conditions to molecules evolving towards self replication. A key palaeo-atmospheric element is nitrogen which, under the redox conditions inferred from the ancient Earth, was mainly present as N_2 . The partial pressure and isotopic composition of palaeo-atmospheric N_2 holds information on several important processes: (i) atmospheric escape processes potentially recorded in nitrogen isotopes; (ii) the onset of biological activity able to reduce nitrogen and incorporate N into organics; and (iii) the exchange rate of N between the mantle and the surface.

Contrary to Mars, dinitrogen is not presently escaping from the terrestrial atmosphere. The terrestrial exobase extends to altitudes of a few hundreds of km, and atoms heavier than hydrogen and helium are gravitationally bound and cannot reach such altitudes. The magnetosphere expands up to several tens of thousands of km, shielding atmospheric species from interactions with extra-terrestrial charged particles like those of the solar wind (which trigger nitrogen escape on Mars). Conditions were different in the distant past. The Earth's atmosphere might have been less efficiently shielded as the terrestrial magnetic field was weaker than today. Without a magnetic field, the ancient atmosphere might have lost all its N_2 in a few million years, unless a large enough quantity of CO_2 , at least two orders of magnitude in excess of the present concentration,



allowed cooling and shrinking of the thermosphere (Lichtenegger *et al.*, 2010). The top of the atmosphere might have been heated by solar far UV and X-ray photons and the exobase could have extended to several thousand kms, favouring thermal escape. The flux of solar wind particles might have been stronger than today, and exceptional solar flare events were probably more intense and more frequent than today. Energetic radiation could have penetrated deep into the atmosphere and would have altered its chemistry and induced ionisation and escape of atmospheric species. Such intense radiation would have been harmful for biomolecules that were not shielded in the oceans.

We attempted to determine the partial pressure of Archean atmospheric N_2 and its isotopic composition. Dinitrogen and argon abundances and isotopic ratios –extracted from hydrothermal quartz by stepwise crushing and heating– were analysed together. Our data defined correlations between $N_2/^{36}Ar$ and $^{40}Ar/^{36}Ar$, indicating mixing between a hydrothermal end member rich in crustal N and radiogenic ^{40}Ar , and a low $^{40}Ar/^{36}Ar$, low $N_2/^{36}Ar$ end member (Fig. 8.6; Marty *et al.*, 2013). The latter had an $^{40}Ar/^{36}Ar$ ratio comparable to that of the Archean atmosphere, representing atmospheric noble gases and nitrogen dissolved in Archean seawater. There is independent evidence that ^{36}Ar has been conserved in the atmosphere since the events that formed the Earth (Marty *et al.*, 2013), so an Archean seawater $N_2/^{36}Ar$ ratio similar to that of the modern oceans implies that the partial pressure of Archean atmospheric nitrogen, P_{N_2} , 3.5 Ga ago, was comparable to the modern one. Further work on different samples with ages spanning the period from 3.5 Ga to 2.7 Ga confirmed these results and established that the P_{N_2} could have been lower than today by a factor of ~2 (Avicé *et al.*, 2018a). Additionally, the N isotopes showed little variation and were within the range of modern values for water and sediments (Marty *et al.*, 2013). At 3.5 Ga, nitrogen was already conserved in the atmosphere, suggesting that a magnetic field strong enough to protect the top of the atmosphere was in place by that time. This conclusion was consistent with studies indicating a strong palaeomagnetic field in the Hadean and Archean eons (Tarduno *et al.*, 2020).

In fact, the most intriguing result was that atmospheric P_{N_2} might have been similar to, or even lower, than modern N_2 partial pressure, contrary to expectations. In the distant past, N_2 , once degassed from the mantle, should have accumulated in the atmosphere because subduction of volatile elements might have only been effective over the last billion years or so (Parai and Mukhopadhyay, 2018). A hot subduction regime such as that expected during the Archean might have triggered nitrogen degassing back to the surface (Busigny and Bebout, 2013) and not mantle recycling. A high P_{N_2} in the past was independently proposed to resolve the faint Sun paradox (Goldblatt *et al.*, 2009). Dinitrogen is not a greenhouse gas but enhanced P_{N_2} could have facilitated the greenhouse power of other atmospheric species like CO_2 or H_2O by scattering IR photons and a P_{N_2} 2-3 times higher in the Archean epoch could have helped to keep the Earth's surface warm despite a low P_{CO_2} . Goldblatt *et al.* (2009) also called for a palaeo-atmospheric P_{N_2} three times higher than today in order to keep the atmosphere warm by H_2 - N_2 collision induced absorption.



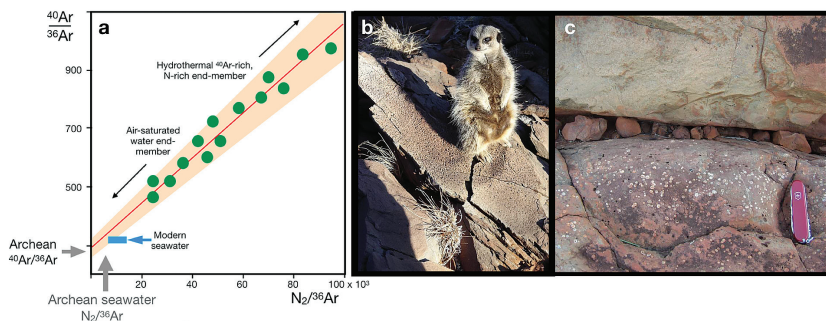


Figure 8.6

(a) Estimating the partial pressure of N_2 in the Archean atmosphere. Data from stepwise heating and crushing of hydrothermal quartz define a linear correlation between a crustal end member rich in N and radiogenic ^{40}Ar , and an Archean seawater component. The latter has $N_2/^{36}\text{Ar}$ comparable to, or lower than, modern seawater. Because ^{36}Ar has been conservative in the atmosphere, the partial pressure of N_2 had to be comparable to, or lower than, that of modern N_2 . Adapted from Marty *et al.* (2013) and Avice *et al.* (2018a). (b) Determination of the total air pressure from fossil airdrop imprints in Archean sediments (Som *et al.*, 2012). (c) Determination of the total air pressure from size distribution of bubbles in Archean basalt (Som *et al.*, 2016). Photo credit: Sanjoy Som.

Our study did not support these possibilities, and other studies also called for low P_{N_2} . Som *et al.* (2012) constrained the total palaeo-atmospheric pressure from morphological analysis of fossil raindrops imprinted in the 2.7 Ga volcanic tuffs of the Ventersdorp Supergroup, South Africa. The rationale behind this approach is that the maximum size a falling raindrop can reach before fragmentation is a direct function of the ambient atmospheric pressure. Assuming that the rocks studied were emplaced at sea level, the distribution of fossil raindrops, together with analogue experiments aimed at reproducing this distribution in the laboratory, allowed the authors to conclude that the total palaeo-atmospheric pressure could not have been more than twice the modern atmospheric pressure, and was more probably comparable to, or lower than, the latter. Recently, Som *et al.* (2016) attempted to estimate the absolute Archean barometric pressure using the size distribution of gas bubbles in lava flows that solidified at sea-level 2.7 Ga ago in the Pilbara craton, Australia. Som *et al.* (2016) proposed that the atmospheric pressure was low, about 0.23 bar. Because this was the total atmospheric pressure, that of N_2 could have been even lower. Stuïken *et al.* (2016) proposed an attractive model to account for a low P_{N_2} in the Archean. Nitrogen, metabolised by ancient organisms, was sequestered in organic matter deposited in the crust at a time when environmental conditions were reducing. Biologically fixed nitrogen could not return to the atmosphere by denitrification and oxidative weathering as today. Later, the increase in oxygen might have allowed sequestered N to return to the atmosphere as N_2 .



These palaeo-barometers are by nature imprecise, and there may be room for a significant amount of CO₂ in the Archean atmosphere in order to resolve the faint Sun paradox. Combining estimates of the total atmospheric pressure (Som *et al.*, 2012; 2016) with those of the P_{N₂} (Marty *et al.*, 2013; Avice *et al.*, 2018a) suggests that there might have been a significant amount of other atmospheric species, up to 0.7 bar, when uncertainties are taken into account, which leaves space to have a high enough concentration of a greenhouse gas like CO₂ to counterbalance low energy delivery by a fainter Sun at that time.

Recent advances in the characterisation of ancient environments suggest a uniformitarian vision of the ancient Earth: with oceans of comparable chemistry and volume; an N₂-dominated atmosphere; clement temperatures (but with transient episodes of glaciation); and limited atmospheric escape to space. However, this broad image does not reflect stepwise dramatic changes like those resulting from intense irradiation by the Sun or nearby stars, astronomical events such as Milankovitch-like cycles, asteroidal or cometary impacts, expansion of the biosphere, and/or catastrophic volcanic events. We are just starting to explore past environments that prevailed during half of Earth's history. A good analogue for the ancient Earth is Mars, which, after a humid period that lasted a few hundreds of Myr, has remained almost frozen for the last 4 Gyr.

8.5 Mars and Early Earth: Common and Divergent Evolutions

The modern Martian atmosphere is much less dense ($P_{\text{atm}} = 600 \text{ Pa}$) than that of the Earth ($P_{\text{atm}} = 101,325 \text{ Pa}$). The major atmospheric species (CO₂, N₂) do not escape by thermal (mass dependent) processes, at least at present, but the isotopic compositions of hydrogen (D/H) and nitrogen are strongly fractionated, by thousands to several hundred per mille, respectively (Leshin *et al.*, 1996; Mahaffy *et al.*, 2013; Avice *et al.*, 2018b). The two stable isotopes of argon are also isotopically fractionated, but krypton is not, and xenon is as fractionated as terrestrial xenon (Atreya *et al.*, 2013; Conrad *et al.*, 2016; Chennaoui Aoudjehane *et al.*, 2012). Thus, Martian volatiles present an intriguing puzzle which is not fully understood. The diversity and extent of isotope fractionation call for several types of escape processes, which would have acted on the atmosphere of the red planet over extended periods of time. The two planets also differ in their distances to the Sun (1 UA *versus* 1.52 AU), their masses ($M_{\text{Mars}} = 0.107 \times M_{\text{Earth}}$), and their magnetic fields (fossil on Mars, still active on Earth). The comparison between Earth and Mars is particularly intriguing since both atmospheres present important atmospheric Xe isotope fractionation (3.5 ‰ for Earth, 3.3 ‰ for Mars) for trapped atmospheric Xe in Martian meteorites (Swindle *et al.*, 1986), or 2.4 ‰ for modern atmospheric Xe directly analysed by Mars Sample Laboratory (Conrad *et al.*, 2016). In contrast, nitrogen is highly fractionated on Mars relative to chondrites (60 ‰ enrichment of ¹⁵N; Nier and McElroy, 1977; Wong *et al.*, 2013) but not on Earth. Fortunately, there are time constraints on the epochs of the respective isotope fractionation processes.



For Earth, we have argued that both missing Xe and Xe isotopic fractionation were due to prolonged escape of Xe alone, and an external cause like interactions between the top of the atmosphere and the atmosphere and solar UV photons could have also acted on Mars. Having a comparable isotopic fractionation for atmospheric Xe on Mars and Earth is striking. The escape process proposed by Zahnle *et al.* (2019) depends on intrinsic planetary parameters such as gravity, ionisation rate of Xe in the atmosphere, solar irradiation activity, and strength and shape of the respective magnetic fields. The model of Hébrard and Marty (2014), in which Xe ions are trapped in forming organic haze, is also appealing as it would point to haze formation on Mars as well.

However, the timing of events presumably is different. Recently, Cassata (2017) argued that >4 Ga ALH84001 and NWA7084 (“Black Beauty”) Martian meteorites contain ancient Martian atmospheric gases with little, if any, Xe isotopic fractionation relative to modern Martian atmospheric Xe. One conclusion of this study is that isotopic fractionation and escape of Martian atmospheric Xe occurred very early in the planet’s history and ceased around 4.4–4.0 Ga. This observation is in line with studies arguing for an early stage of strong atmospheric escape on Mars starting when a steam atmosphere was outgassed from the magma ocean and lasting about 500 Myr. It is thus tempting to link the Xe isotope fractionation with xenon escape, which is related to a major change in the Martian environment and the disappearance of permanent liquid water on Mars by the end of the Noachian. In the case of terrestrial Xe, hydrogen from dissociation of atmospheric H₂O could have played a role in Xe escape and isotopic fractionation (Zahnle *et al.*, 2019), but at different periods for Earth and Mars. It remains to be understood why the extent of Xe isotopic fractionation is comparable for both planetary atmospheres.

The present day isotopic composition of Martian atmospheric N₂ measured by Mars Science Laboratory rover, is $\delta^{15}\text{N} = +572 \pm 90 \text{ ‰}$ (Wong *et al.*, 2013). The initial Martian value could have been $\delta^{15}\text{N} = -30 \text{ ‰}$ as measured in the Chassigny meteorite (Mathew and Marti, 2001b). Thus, either a component rich in ¹⁵N such as cometary material contributed to the Martian atmosphere (see Marty *et al.* 2016) or N isotopes were fractionated during non-thermal escape to space. The modern nitrogen isotopic composition is consistent with values measured in ≥ 1.3 Ga Martian meteorites (Becker and Pepin, 1986; Avice *et al.*, 2018b). However, the 4.1 Ga ALH84001 Martian meteorite contains different N components including a presumed Martian atmospheric end member identified using Xe isotopes, which is less rich in ¹⁵N (Mathew and Marti, 2001b). This suggests that the evolution of the N isotope composition by atmospheric escape processes is younger than ~4 Ga. Figure 8.7 compares the different evolution of N and Xe isotope fractionation through time as constrained by present meteoritic data. Clearly, the history of the Martian atmosphere is not well resolved, and more data for various geological ages are needed. Conversely, more information on the evolution of terrestrial volatiles during the Hadean and Archean eons will certainly help in understanding why the environments of the two planets diverged during the first part of their respective histories. The exercise



of comparative planetology for the solar system cannot be completed without considering the atmosphere of Venus, the Earth's sister planet, for which almost no data exist. Hopefully future Venesian missions involving automated probes or atmospheric sample return will bridge this gap.

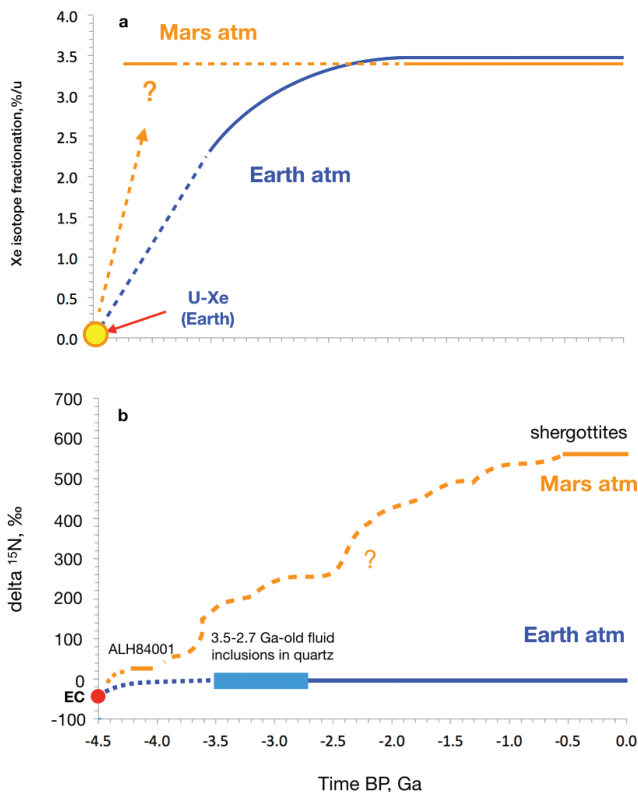


Figure 8.7

Comparative evolution of xenon and nitrogen isotopes in the Martian atmosphere as constrained by available data. (a) Xenon isotope fractionation through time. The terrestrial ancestor of Xe is thought to be U-Xe, an intermediate composition resulting from mixing cometary and solar, or chondritic Xe (Marty *et al.*, 2017). For Mars, a solar Xe composition has been advocated (Conrad *et al.*, 2016) and this component is identified in mantle-derived Xe (Ott, 1988; Mathew and Marty, 2001b). Xenon in >4 Ga Martian meteorites appears already isotopically fractionated (Cassata, 2017). On Earth, this was a continuous process still in progress during the Archean (Avice *et al.*, 2018a). (b) In the case of nitrogen, the situation is reversed. The “old” Martian meteoritic component did not show ¹⁵N enrichment whereas “recent” (<1.3 Ga) Martian meteorites show Xe isotope fractionation similar to that of the modern atmosphere. “EC” means esstaitite chondrite, a potential progenitor of planetary nitrogen. Martian samples (meteorites, future returned samples) with intermediate ages will permit the long term evolution of the Martian atmosphere to be investigated more precisely.



As a final note, I would like to share a few thoughts about the principles of research. I do not believe that there is just one single path for science. Everyone has their own approach, and mine has not been linear, but composed of opportunities, luck, and failures in equal measure. If you want to discover something completely new, you have to be in a state of uncertainty. It is, however, crucial to have general guidelines in an important area of research, to pick problems worth solving, and to find the right people to work with. Another key ingredient is technology, as major advances in geochemistry and cosmochemistry are often driven by the capability to analyse natural materials with the highest possible precision and/or spatial resolution, which generally requires expensive equipment. This is, however, not always the case, and it is also possible to make discoveries with simple setups, addressing problems with an innovative approach. Of course, if you have a genuinely novel idea that requires facilities outside of your lab, then you should not let that get in the way of doing exciting science. Set out to establish new scientific collaborations that can give you access to the facilities you need. All that is required is that you have an exciting question and an idea of how to answer it.

One of the reviewers was curious to know about the future of our discipline. Improving analytical precision towards the per mille level and beyond on noble gas isotope ratios will be a critical development opening new avenues of research. A limiting factor has always been the quantity of the “rare” gases available for analysis. For now, the ionisation efficiency of gas source mass spectrometers is of the order of a few percent. Hence great progress will arise from laser ionisation, already under development in a few labs, and/or spectroscopic measurements of noble gas isotopes. The development of multi-collector dynamic mass spectrometry, currently done for large samples like noble gases in ice, can be applied to other types of large samples like volcanic and geothermal gases. For major volatiles, the development of isotopologue geochemistry as done for example for nitrogen is opening a large array of new tracers that can be combined with noble gases.

Within the next decade, samples will be returned from unexplored regions of the Moon, from asteroids and comets, and from Mars. Volatiles may be analysed with precision in the atmospheres of Venus, Titan, giant planets and their satellites. The analysis of ancient atmospheric gases and of the ancient mantle at different periods of Earth’s history is only beginning to be understood. Models of planetary evolution will increasingly integrate multi-gas data together with new high pressure experimental data. This is certainly an exciting period of research on the origin and evolution of planetary atmospheres, and on the conditions that permitted the development of life on our planet.



We would often have a light lunch (quiche or paté lorrain) at a bakery close to the CRPG. One day, I somewhat presumptuously asked François Robert, who was visiting us at the time, which of his discoveries he was most proud of. François replied: “The one I will make tomorrow”.



Figure 9.1

(a) The noble gas lab at the CRPG (partial view). (b, c, d, e, f) Some of the noble gas folks. (c) From left to right: Bouchaib Tibari, (CNRS engineer), Pete Burnard (CNRS senior scientist), Guillaume Avice (then graduate student), and Laurent Zimmermann (CNRS lab manager) watching the delivery of a mass spectrometer. (c) Jennifer Mabry, then post-doc, succeeded with Pete Burnard in designing a helium isotope facility able to reach the permil precision level. (d) Laurette Piani (then post-doc) and Maia Kuga (then graduate student). (e) Evelyn Fűri, junior scientist (CNRS), not very happy with problems on the nitrogen noble gas line, with Laurent Zimmermann. (f) Pierre-Henri Blard (CNRS junior scientist) developed a system to analyse cosmogenic noble gases in terrestrial samples. Not represented: Raphaël Pik (Fig. 4.3a) who runs a U-He facility in the lab. Some of the post-docs and students can be seen in Figs. 2.11 and 4.6.

APPENDIX: A RECIPE FOR THE ATMOSPHERE AND THE OCEANS



Figure A1 A recipe for the atmosphere and the oceans. Photo credit: Michel Guay.

Ingredients

Nebular gas (mostly H_2 , CO , N_2 , noble gases)

Diverse spices (your choice of nanodiamonds, presolar grains, etc.)

Silicate and metal powder, butter (or any other organics)

Ice cream, ice cubes

Eggs (planetary mantles and cores)

High temperature oven(s)

Intense spot light

Catapult

Preparation

14 Gyr to prepare the gas

100 Myr to isolate basic ingredients from galactic evolution

<1 Myr to form the first solids

~5 Myr to make the first planets (e.g., Mars)

40-100 Myr to make the Earth

~700 Myr for late seasoning with tasty ingredients

2 Gyr for finishing and stabilising the atmosphere and oceans



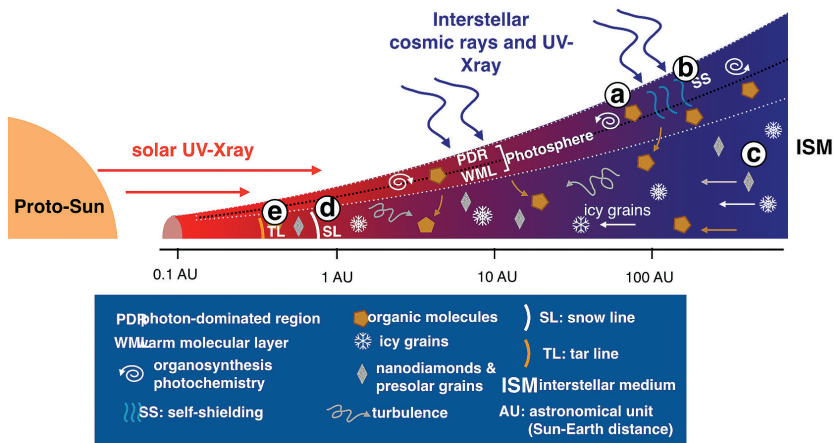


Figure A2 **Preparing the ingredients.** A protoplanetary disk composed of 99% nebular gas (mainly H_2 , CO , N_2 , and noble gases) and 1% dust forms around a central star, here the protosun. Dust consists of presolar grains, silicates, organics, and icy grains (adapted from Kuga *et al.*, 2015, and Bekaert, 2020).

- Organic dust is synthesised by ionisation/irradiation of H_2 , CO , and N_2 gas by photons and protons from nearby stars and/or the central star in the photon-dominated region (PDR) of the disk. Laboratory experiments indicate that such photochemistry can take place at high temperatures (up to 1000 K), typically within the PDR and warm molecular layers (WML), at the surface of the disk. Experiments reproduce to some extent the structure and properties of insoluble organic matter found in chondrites (Kuga *et al.*, 2015) as well as elemental and isotopic fractionation of noble gases observed in primitive meteorites (Kuga *et al.*, 2017; Marrocchi *et al.*, 2011) as well as certain biomolecules (Oró, 1963). Other models propose the synthesis of organics on grains in the interstellar medium (*e.g.*, Sagan and Khare, 1979; van Dishoeck *et al.*, 2013).
- Excesses of ^{15}N observed in solar system objects and reservoirs (Section 6) may result from interaction between gas and stellar photons at the surface of the disk or in the interstellar medium (ISM) during either self shielding (Clayton, 2002) or N_2 photolysis by UV light (Chakraborty *et al.*, 2014). ^{15}N enrichments could also have taken place during ion-molecule exchange at low temperature in dense molecular clouds (Rodgers and Charnley, 2008).
- Presolar material (grains from previous generations of stars) fall from the parent molecular cloud and are mixed with organic dust. Water ice may form in the disk by processes involving thermodynamic equilibrium with nebular N and O and ionisation (Albertsson *et al.*, 2014)



and/or could be inherited from the interstellar medium, hosting strong enrichments in deuterium (van Dishoeck *et al.*, 2013). Solid grains including organics (Laurent *et al.*, 2015; Remusat *et al.*, 2006) are mixed by viscous spreading of the disk and turbulence (Bekaert *et al.*, 2018b; Ciesla and Sandford, 2012).

- (d) In the inner regions of the solar system delineated by the “snow line”, enthalpy was too high to permit ice formation. Consequently, solids formed within ~1 AU (astronomical unit: distance between the Sun and Earth) were devoid of water. They are now represented by the so called non-carbonaceous chondrites (NC), in particular enstatite chondrites, whose isotopic characteristics suggest a genetic link with Earth-building material (Javoy *et al.*, 2010; Dauphas, 2017). Material accreted beyond the snow line was rich in volatile elements, including water. They are now represented by carbonaceous chondrites (CC).
- (e) Organics could have been preserved at distances closer to the protosun than the snow line, given their more refractory character than water ice. The limit of organic preservation is labelled the “tar line” (Lodders, 2004). As a result, material between the snow line and the tar line, such as NC, could host refractory organics while being depleted in hydrated phases.

Take home message. The origin of highly volatile compounds (made of H, C, N, and noble gases) could be interstellar and/or synthesised within the protosolar nebula through ion-molecule exchange and/or interactions between solar/interstellar photons and the gas.

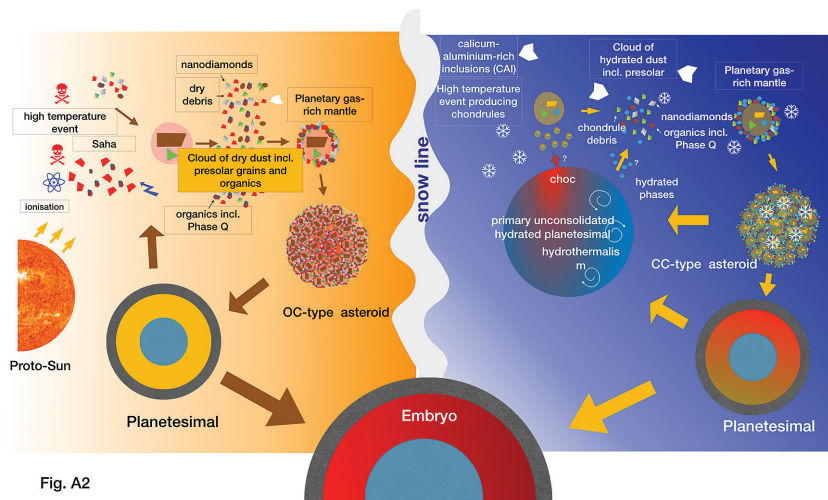


Fig. A2

Figure A3 Assembling the ingredients.



- **Left:** In the inner-most regions of the disk, water ice could not exist. Chondrules are ≤ 1 mm diameter spherical assemblages of refractory silicates formed during high enthalpy events of debated origin. They are generally devoid of volatile elements although some of them can incorporate noble gases (*e.g.*, the subsolar component of enstatite chondrites) by undocumented processes, which are likely to require ionisation. They are mixed together, in a fine grained dust, with presolar material, debris of previous planetary collisions, as well as refractory organics (as they were located within the region delimited by the tar line; Fig. A1). The accretion of chondrules and dust –devoid of water– yielded asteroids of the NC (non-carbonaceous) type and 100-1000 km planetesimals. These early bodies were disrupted by impact shocks that produced more dust, of secondary origin. Some planetesimals survived and accreted to form 1000-5000 km embryos. All these processes were geologically rapid, within a time period of a few Myr after the start of solar system (Johansen and Lambrechts, 2017; Morbidelli *et al.*, 2012).
- **Right:** Beyond the snow line, icy dust was present. Chondrules and other high temperature assemblages were formed in the inner solar system by condensation and high energy events, either locally by impacts (possibly for chondrules) or flash heating close to the Sun (CAI), before being transported outward. These objects travelled through dusty regions with nanodiamonds and presolar grains like those found in NC material, but also icy material and planetary debris from previous collisions. These materials probably repeatedly went through a coagulation, accretion, and fragmentation cycle that lasted several Myr. Some precursor bodies escaped destruction to form CC (carbonaceous chondrite)-like asteroids or larger planetesimals. Two space missions, JAXA Hayabusa2 and NASA Osiris Rex, are currently sampling CC-like asteroids and will return samples to Earth in 2020 and 2023, respectively.

Both types of planetesimals (NC- and CC-like) ultimately accreted to form planetary embryos ($>1,000$ km in diameter). CC-like material is richer in noble gases, C, and N than NC-like material, and contain water under the form of hydrated material. However, NC meteorites also contain hydrogen that could have formed water upon oxidation (Piani *et al.*, 2020).

Take home message. Chondrites are sedimentary objects formed from the debris of previous collisions between early planetary bodies, as well as accretion of a common mix of presolar material, organics and, beyond the snow line, of icy dust.

Isotope systematics allow us to distinguish two types of primitive meteorites. NC (non-carbonaceous) chondrites (*e.g.*, ordinary and enstatite chondrites) have isotopic compositions close to those of the Earth and the Moon. They might have been the main source of Earth-building matter. They formed in energetic regions where liquid or frozen water could not



exist, and are therefore considered to have always been dry. However, hydrogen was recently discovered in enstatite chondrites, suggesting that NC could also be a significant source of terrestrial water (Piani *et al.*, 2020). Carbonaceous chondrites (CC-type) are nucleosynthetically different from the Earth and Moon and are rich in volatile elements. They are thought to be a major source of terrestrial atmosphere's volatiles (Marty, 2012; Alexander *et al.*, 2012; Halliday, 2013; Albarède *et al.* 2013).

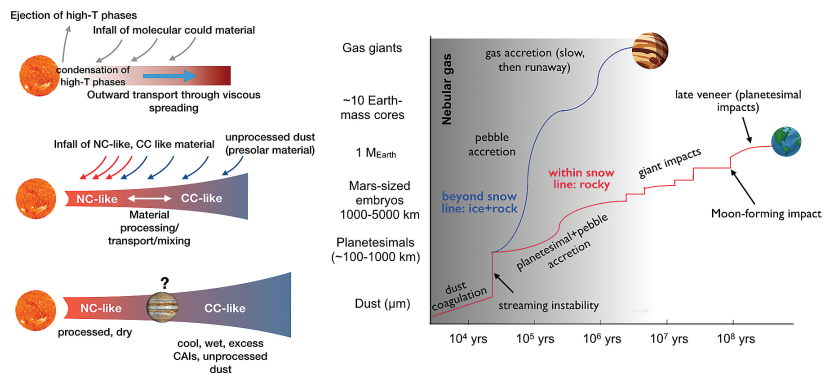


Figure A4 Distributing the ingredients and making the planets.

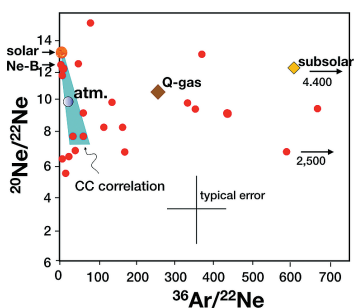
- Left:** Molecular cloud material falling onto the evolving disk. Formation of the first solar system solids started by condensation during cooling of the high temperature nebular gas. Calcium-aluminum-rich inclusions (CAIs) were the first mineral phases to form close to the central star, before being transported outward through viscous spreading of the disk (Pignatale *et al.*, 2018) and/or by ejection caused by X-winds (Shu, 1997). The composition of infalling material from the molecular cloud might have been variable, basically evolving from a CC-like composition to a more NC-like composition (Nanne *et al.* 2019). CC-like materials contain more unprocessed dust than NC-like material due to a lesser extent of thermal processing. Dust transport within the disk was driven by viscous spreading (outward), turbulence (all directions), and radial drift due to gas drag (inward). NC-like material was predominant within the innermost, dryer regions of the disk. CC-like material rich in CAI and unprocessed dust accreted beyond the snowline. The timescale of this epoch is of the order of 0-2 Myr after the start of solar system condensation, as defined by the formation of CAI. Jupiter, which formed within a few Myr, could have played a major role in segmenting the inner solar system and blocking lateral transport of material (Nanne *et al.*, 2019).



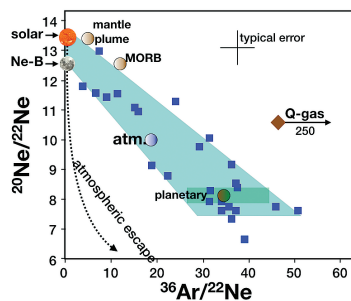
- Right:** Accretion rate as a function of timescale (after Meech and Raymond, 2020). Micron-sized dust aggregated *via* tensile strength and electrostatic gluing until reaching \sim cm sizes. Further growth was hampered by the decrease in sticking efficiency for larger grain sizes and specific conditions, such as pebble accretion, and/or streaming instability, were required to overcome the “cm barrier” (Johansen and Lambrechts, 2017; Johansen and Youdin, 2007). Two types of accretion then took place. In wet, low temperature, icy regions beyond the snow-line, accretion was fast (of the order of one Myr) due to high sticking efficiencies promoted by water ice and low temperature organics. Large planetary objects were able to capture and retain ambient nebular gas. In the innermost region of the solar system, hot and dry conditions slowed planetary accretion. Mars-sized embryos formed within a few Myr (Dauphas and Pourmand, 2011). Larger planets like Earth and Venus formed by collisional accretion of planetary embryos. This accretion phase required several tens of Myr because (i) the density of accreting bodies decreased drastically with time (most available building material had been consumed) and (ii) gravitational focusing (the ability of a planet to deviate impacting bodies) also decreased with increasing embryo size.

Take home message. The nascent solar system was a highly dynamic system, with lateral transport back and forth along the disk plane, and turbulence mixing the material fallen from the molecular cloud to the central plane of the disk.

Giant planets formed more rapidly than inner planets. Early formed Jupiter might have acted as a barrier for the transport of CC-like material towards the inner solar system. Hence terrestrial volatiles might have been contributed early on by CC-like material, and not as a late veneer.



Enstatite Chondrites



Carbonaceous Chondrites (CI and CM)

Figure A5

Investigating the origin of terrestrial volatiles with noble gases trapped in primitive meteorites.



The distribution of hydrogen and nitrogen isotope ratios in primitive meteorites (chondrites) point to a chondritic origin for terrestrial volatiles (Fig. 6.5). Furthermore, the neon isotope composition of mantle volatiles points to the presence of a solar Ne component at depth (Fig. 2.5, Section 2). The composition of terrestrial noble gases permits further identification of cosmochemical ancestors. These two panels present variations of the $^{20}\text{Ne}/^{22}\text{Ne}$ ratios as a function of the elemental $^{36}\text{Ar}/^{22}\text{Ne}$ ratio in different classes of chondrites. In this format, two component mixing results in a straight line, joining the component end members. The above diagrams are based on a compilation of noble gas data in enstatite (NC-type) and carbonaceous (CC-type) chondrites (relevant literature listed at <https://zenodo.org/record/3984898#.XzZU7i3M2iA>). Data were corrected for contribution of cosmic-ray produced Ne and Ar isotopes using the $^{21}\text{Ne}/^{22}\text{Ne}$ ratios.

- **Left:** Compilation of enstatite chondrite (EC) data. Based on isotope systematics, these meteorites represent the best cosmochemical analogue to Earth's accretionary material (Javoy *et al.*, 2010; Dauphas, 2017). Noble gases in EC often present enrichments in ^{36}Ar compared to other chondritic classes, a pattern labelled "subsolar" (Crabb and Anders, 1981). These enrichments result in a large spread of data in the figure, which means they are collectively unable to account for the atmospheric composition. Some of the EC are also rich in solar neon (Ne-B; Section 2) and/or contain Ne-A (Mazor *et al.*, 1970), a presolar Ne component found in nanodiamonds and SiC grains. "Q-gas" refers to the gas trapped in the Phase Q component associated with insoluble organic matter and ubiquitously found in chondrites. Error bars are generally large due to correction for cosmic ray effects and relevant error propagation.
- **Right:** Same diagram for carbonaceous chondrites, represented by CI and CM chondrites. Here, data can be well explained by mixing between a solar-like component and the so called "planetary component" with low $^{20}\text{Ne}/^{22}\text{Ne}$ (Mazor *et al.*, 1970; Black and Pepin, 1969). The composition of the latter is dominated by presolar ^{22}Ne trapped in nanodiamonds. Remarkably, atmospheric and mantle noble gases are intermediate between Solar and Planetary end members, which strongly suggests a CC-like origin for terrestrial volatiles (Marty, 2012). The isotopic compositions of krypton and xenon in the mantle are also most consistent with a CC-like origin (Holland *et al.*, 2009; Broadley *et al.*, 2020). Another important outcome of this diagram is that atmospheric escape to space (outlined by the dotted curve) cannot account for the composition of atmospheric noble gases, as otherwise often advocated (Ozima and Zahnle, 1993; Pepin, 1991).

Take home message. Light noble gases (Ne and Ar) point to a carbonaceous chondrite-like origin for terrestrial atmosphere's volatiles, as does Kr for the mantle. A CC-like origin is consistent with hydrogen and nitrogen



isotope distribution among solar system objects and reservoirs. However, H which would have ultimately oxidised to form water, might have been already present in NC-like material (Piani *et al.*, 2020) as could have been C and N hosted by refractory organics. Hence terrestrial volatiles might have been sourced by different types of primitive material, originating from both within and outside the snowline. Mass balance involving H and N isotopes suggest a NC/CC mix of about 75-95%/15-5%.

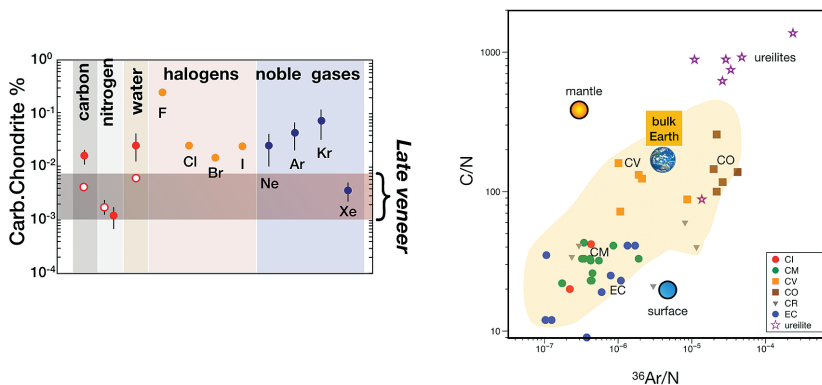


Figure A6 Volatile element trapping and effects of planetary differentiation.

- Left:** Contribution of carbonaceous chondrite-like (CC-type) material to bulk Earth (excluding the core). Estimates are from Marty (2012; closed symbols), and references therein, and Hirschmann (2018; red open symbols). Terrestrial abundances are normalised to those of CM-CI, which directly gives the contribution of CC-like material (in %, y axis). These estimates are consistent with a $2 \pm 1\%$ contribution of CC-like material, except for nitrogen and xenon which appear depleted by one order of magnitude. The Xe depletion is accounted for by protracted atmospheric escape during the Hadean and Archean eons (Section 8). The late veneer (0.1-0.8% of Earth's mass, brown horizontal area) refers to material added after the Moon-forming impact. The terrestrial abundances of volatile elements require more CC-like material than that potentially added by the late veneer. A CC-like contribution might have occurred during major Earth-forming events (*e.g.*, the Moon-forming impact) rather than during late bombardments. An early contribution of CC material is consistent with the presence of CC-like krypton in the deep mantle (Broadley *et al.*, 2020). The depletion of terrestrial nitrogen could have resulted from preferential trapping of N in the core (Marty, 2012; Roskosz *et al.*, 2013) or from other planetary differentiation processes as suggested below.

- Right:** Effects of planetary differentiation on volatile abundance ratios. C/N and $^{36}\text{Ar}/\text{N}$ ratios were calculated from literature data listed at <https://zenodo.org/record/3984898#.XzZU7i3M2iA>. Meteorite families include EC (NC-type) and CM, CI, CV and CO (CC-type) chondrites. CV and CO chondrites are the most evolved and volatile depleted meteorites among the CC family. All meteorite classes define a trend (outlined in yellow) towards elevated C/N and $^{36}\text{Ar}/\text{N}$ ratios upon planetary evolution and differentiation (CV and CO chondrites). Estimates for the surface of the Earth and the terrestrial mantle are calculated with volatile abundance estimates from Marty (2012), Hirschmann (2018) and references therein. Bulk Earth (excluding the core) ratios are obtained by adding the surface and mantle inventories. The position of the Bulk Earth within the field of CV and CO chondrites suggests that the apparent depletion of nitrogen relative to other volatile elements (here C and ^{36}Ar) resulted from thermal processing (*e.g.*, metamorphism) on the planetesimals that contributed to the formation of Earth (Marty *et al.*, 2020).

Take home message. Left: The abundances of volatile elements in the bulk Earth (mantle, atmosphere, hydrosphere and sediments, excluding the core) are consistent with the contribution of a few percent carbonaceous chondrite-type material to a volatile depleted proto-Earth. This contribution was not late and took place during the main stages of Earth's formation. Right: Planetesimals that formed the Earth experienced evolution and differentiation that resulted in volatile element fractionation, in particular nitrogen depletion. Core formation and metal-silicate exchange might have also played an important role.

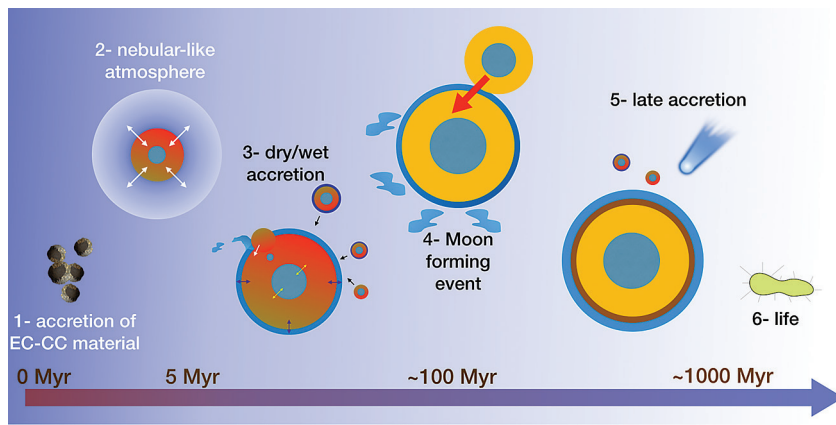


Figure A7 Final recipe.



Time sequence of the main ocean- and atmosphere-forming events, from the condensation of solids (CAI) in the solar system (time not to scale).

- (a) Accretion of chondritic material. From isotope systems (*e.g.*, N, O, Mo, Ti, *etc.*), NC-like material of the EC type was dominant. However, the isotopic composition of noble gas isotopes in the mantle suggests delivery of volatiles by CC-like material early during Earth's building process (Broadley *et al.*, 2020).
- (b) Once the proto-Earth reached a size of several thousands of km, a nebular (H₂-rich) atmosphere would have been retained, whose traces are now found in the neon isotopic composition of the deep mantle (Section 2). This primary atmosphere would have been blown away, together with nebular gas, by impacts and/or intense radiative activity of the young Sun.
- (c) After dissipation of nebular gas, the proto-Earth continued to grow through accretion of planetesimals with chondritic compositions. Based on volatile abundances and isotopic compositions, CC-like material could have contributed a few weight % to the growing Earth (Fig. A5; Albarède *et al.*, 2013; Marty, 2012). Other isotopic systems also point to a moderate contribution of CC-like material to an NC-like proto-Earth (Budde *et al.*, 2019; Dauphas, 2017). A secondary atmosphere developed through impact degassing and equilibration between molten silicates and gas, which might have been partly and periodically removed by razing impacts (Mukhopadhyay and Parai, 2019). Volatiles (H, C, N) were partitioned between the core, mantle and surface according to their speciation and thermodynamic (temperature, pressure) conditions (Dalou *et al.*, 2017; Grewal *et al.*, 2019). There is as of yet no consensus about the abundances of these elements in the core.
- (d) The late stages of Earth's accretion were dominated by impacts of Mars-sized planetary embryos, the last impact being the Moon-forming event around 10² Myr after the start of solar system formation. Any existing atmosphere would have been partially or totally blown away, depending on the existence of oceans (Genda and Abe, 2005). This catastrophic event marked the end of core-mantle differentiation.
- (e) Residual accretion referred to as the late veneer consisted of a mix of NC and CC materials (Dauphas *et al.*, 2004) amounting to less than 1 % of Earth's mass. Cometary material contributed ~20 % argon, krypton, and xenon to the atmosphere and mantle gases were unaffected by these late contributions (Section 7). Cometary contribution was negligible for the oceans and surface C and N.
- (f) Life started to blossom during the first Gyr of Earth's existence, thanks to the establishment of clement conditions (see Section 8).



REFERENCES

- AIUPPA, A., FISCHER, T.P., PLANK, T., BANI, P. (2019) CO₂ flux emissions from the Earth's most actively degassing volcanoes, 2005–2015. *Scientific Reports* 9, 5442, doi: 10.1038/s41598-019-41901-y.
- ALBARÈDE, F., BALLHAUS, C., BLICHERT-TOFT, J., LEE, C.-T., MARTY, B., MOYNIER, F., YIN, Q.-Z. (2013) Asteroidal impacts and the origin of terrestrial and lunar volatiles. *Icarus* 222, 44–52.
- ALBARÈDE, F., THIBON, F., BLICHERT-TOFT, J., TSIKOS, H. (2020) Chemical Archeoceanography. *Chemical Geology* 548, Article 119625.
- ALBERTSSON, T., SEMENOV, D., HENNING, T. (2014) Chemodynamical deuterium fractionation in the early solar nebula: the origin of water on Earth and in asteroids and comets. *Astrophysical Journal* 784, 39.
- ALEXANDER, C.M.O., BOWDEN, R., FOGEL, M.L., HOWARD, K.T., HERD, C.D.K., NITTLER, L.R. (2012) The provenances of asteroids, and their contributions to the volatile inventories of the terrestrial planets. *Science* 337, 721–723, doi: 10.1126/science.1223474.
- ALLARD, P. (1992) Global emissions of helium-3 by subaerial volcanism. *Geophysical Research Letters* 19, 1478–1481.
- ALLARD, P., LE GUERN, F., SABROUX, J.C. (1977) Thermodynamic and isotopic studies in eruptive gases. *Geothermics* 5, 37–40, doi: 10.1016/0375-6505(77)90006-2.
- ALLARD, P., CARBONELLE, J., DAJLEVIC, D., LE BRONEC J., MOREL P., ROBE, M.C., MAURENAS, J.M., FAIVRE-PIERRET, R., MARTIN, D., SABROUX, J.C., ZETTWOOG, P. (1991) Eruptive and diffuse emissions of CO₂ from Mount Etna. *Nature* 351, 387–391.
- ALLÈGRE, C.J., STAUDACHER, T., SARDA, P., KURZ, M. (1983) Constraints on evolution of Earth's mantle from rare gas systematics. *Nature* 303, 762–766.
- ALLÈGRE, C.J., MANHÈS, G., GÖPEL, C. (1995) The age of the Earth. *Geochimica et Cosmochimica Acta* 59, 1445–1457.
- ALLÈGRE, C.J., HOFMANN, A.W., O'NIONS, R.K. (1996) The argon constraints on mantle structure. *Geophysical Research Letters* 23, 3555–3557.



- ALTWEGG, K., BALSIGER, H., BERTHELIER, J.J., BIELER, A., BOCHSLER, P., BRIOIS, C., CALMONTE, U., COMBI, M., KEYSER, J. DE, EBERHARDT, P., FUSELIER, S., GASC, S., GOMBOSI, T.I., HANSEN, K.C., KOPP, E., KORTH, A., LEROY, L., MALL, U., MARTY, B., MOUSIS, O., NEEFS, E., OWEN, T., RUBIN, M., WAITE, H., WURZ, P. (2015) 67P/Churyumov-Gerasimenko, a Jupiter family comet with a high D/H ratio. *Science* 347, 3–6.
- ALTWEGG, K., BALSIGER, H., BAR-NUN, A., BERTHELIER, J.-J., BIELER, A., BOCHSLER, P., BRIOIS, C., CALMONTE, U., COMBI, M.R., COTTIN, H., DE KEYSER, J., DHOOGHE, F., FIETHE, B., FUSELIER, S.A., GASC, S., GOMBOSI, T.I., HANSEN, K.C., HAESSIG, M., JÄCKEL, A., KOPP, E., KORTH, A., LE ROY, L., MALL, U., MARTY, B., MOUSIS, O., OWEN, T., RÈME, H., RUBIN, M., SÉMON, T., TZOU, C.-Y., HUNTER WAITE, J., WURZ, P. (2016) Prebiotic chemicals-amino acid and phosphorus-in the coma of comet 67P/Churyumov-Gerasimenko. *Science Advances* 2, e1600285, doi: 10.1126/sciadv.1600285.
- ANDERSON, D.L. (1998) The Helium Paradoxes. *Proceedings of the National Academy of Science of the United States of America* 95, 4822–4827.
- AREVALO, R., McDONOUGH, W.F., LUONG, M. (2009) The K/U ratio of the silicate Earth: Insights into mantle composition, structure and thermal evolution. *Earth and Planetary Science Letters* 278, 361–369, doi: 10.1016/j.epsl.2008.12.023.
- ARMYTAGE, R.M.G., JEPHCOAT, A.P., BOUHIFD, M. A., PORCELLI, D. (2013) Metal–silicate partitioning of iodine at high pressures and temperatures: Implications for the Earth’s core and ^{129}Xe budgets. *Earth and Planetary Science Letters* 373, 140–149, doi: 10.1016/j.epsl.2013.04.031.
- ARPIGNY, C., JEHIN, E., MANFROID, J., HUTSEMÉKER, D., SCHULZ, R., STÜWE, J.A., ZUCCONI, J.M., ILYIN, I. (2003) Anomalous Nitrogen Isotope Ratio in Comets. *Science* 301, 1522–1524.
- ATREYA, S.K., TRAINER, M.G., FRANZ, H.B., WONG, M.H., MANNING, H.L.K., MALESPI, C.A., MAHAFFY, P.R., CONRAD, P.G., BRUNNER, A.E., LESHIN, L.A., JONES, J.H., WEBSTER, C.R., OWEN, T.C., PEPIN, R.O., NAVARRO-GONZÁLEZ, R. (2013) Primordial argon isotope fractionation in the atmosphere of Mars measured by the SAM instrument on Curiosity and implications for atmospheric loss. *Geophysical Research Letters* 40, 5605–5609, doi: 10.1002/2013GL057763.
- AVICE, G., MARTY, B. (2014) The iodine–plutonium–xenon age of the Moon–Earth system revisited. *Philosophical Transactions of The Royal Society A: Mathematical Physical and Engineering Sciences* 372, 20130260, doi: 10.1098/rsta.2013.0260.
- AVICE, G., MARTY, B., BURGESS, R. (2017) The origin and degassing history of the Earth’s atmosphere revealed by Archean xenon. *Nature Communications* 8, 15455, doi: 10.1038/ncomms15455.
- AVICE, G., MARTY, B., BURGESS, R., HOFMANN, A., PHILIPPOT, P., ZAHNLE, K., ZAKHAROV, D. (2018a) Evolution of atmospheric xenon and other noble gases inferred from Archean to Paleoproterozoic rocks. *Geochimica et Cosmochimica Acta* 232, 82–100, doi: 10.1016/j.gca.2018.04.018.
- AVICE, G., BEKAERT, D. V., AOUDEHANE, H.C., MARTY, B. (2018b) Noble gases and nitrogen in Tissint reveal the composition of the Mars atmosphere. *Geochemical Perspectives Letters* 6, 11–16, doi: 10.7185/geochemlet.1802.
- AYALEW, D., BARBEY, P., MARTY, B., REISBERG, L., YIRGU, G., PIK, R. (2002) Source, genesis, and timing of giant ignimbrite deposits associated with Ethiopian continental flood basalts. *Geochimica et Cosmochimica Acta* 66, 1429–1448, doi: 10.1016/S0016-7037(01)00834-1.
- BADA, J.L., BIGHAM, C., MILLER, S.L. (1994) Impact melting of frozen oceans on the early Earth: Implications for the origin of life. *Proceedings of the National Academy of Sciences of the United States of America* 91, 1248–1250, doi: 10.1073/pnas.91.4.1248.
- BALLENTINE, C.J., MARTY, B., LOLLAR, B.S., CASSIDY, M. (2005) Neon isotopes constrain convection and volatile origin in the Earth’s mantle. *Nature* 433, 33–38.



- BALSIGER, H., ALTWEGG, K., BAR-NUN, A., BERTHELIER, J.-J., BIELER, A., BOCHSLER, P., BRIOIS, C., CALMONTE, U., COMBI, M., DE KEYSER, J., EBERHARDT, P., FIETHE, B., FUSELIER, S.A., GASC, S., GOMBOSI, T.I., HANSEN, K.C., HÄSSIG, M., JÄCKEL, A., KOPP, E., KORTH, A., LE ROY, L., MALL, U., MARTY, B., MOUSIS, O., OWEN, T., RÈME, H., RUBIN, M., SÉMON, T., TZOU, C.-Y., WAITE, J.H., WURZ, P. (2015) Detection of argon in the coma of comet 67P/Churyumov-Gerasimenko. *Science Advances* 1, e1500377, doi: 10.1126/sciadv.1500377.
- BARBERI, F., TAZIEFF, H., VARET, J. (1972) Volcanism in the Afar depression: Its tectonic and magmatic significance. *Tectonophysics* 15, 19–29, doi: 10.1016/0040-1951(72)90046-7.
- BASU, A.R., RENNE, P.R., DASGUPTA, D.K., TEICHMANN, F., POREDA, R.J. (1993) Early and late igneous pulses and a high-³He plume origin for the Deccan flood basalts. *Science* 261, 902–906.
- BECKER, R.H., PEPIN, R.O. (1986) Nitrogen and light noble gases in Shergotty. *Geochemica et Cosmochimica Acta* 50, 993–1000.
- BEGEMANN, F., WEBER, H., HINTENBERGER, H. (1976) On the primordial abundance of Argon-40. *Astrophysical Journal* 203, L155–L157.
- BEKAERT, D.V. (2020) Isotopic constraints on the origin and nature of primitive material in the Solar system and on Earth. Ph.D. Dissertation, Université de Lorraine
- BEKAERT, D.V., BROADLEY, M.W., DELARUE, F., AVICE, G., ROBERT, F., MARTY, B. (2018a) Archean kerogen as a new tracer of atmospheric evolution: Implications for dating the widespread nature of early life. *Science Advances* 4, eaar2091, doi: 10.1126/sciadv.aar2091.
- BEKAERT, D.V., DERENNE, S., TISSANDIER, L., MARROCCHI, Y., ANQUETIL, C., MARTY, B., CHARNOZ, S. (2018b) High-temperature Ionization-induced Synthesis of Biologically Relevant Molecules in the Protosolar Nebula. *Astrophysical Journal* 859, 142, doi: 10.3847/1538-4357/aa7a.
- BEKAERT, D.V., BROADLEY, M.W., CARACAUSI, A., MARTY, B. (2019) Novel insights into the degassing history of Earth's mantle from high precision noble gas analysis of magmatic gas. *Earth and Planetary Science Letters* 525, 115766, doi: 10.1016/j.epsl.2019.115766.
- BEKAERT D.V., BROADLEY, M.W., DELARUE, F., DRUZHININA, Z., PARIS, G., ROBERT, F., SUGITANI, K., MARTY, B. (2020) Xenon isotopes in Archean and Proterozoic insoluble organic matter: A robust indicator of syngeneity? *Precambrian Research* 336, 105505, doi: 10.1016/j.precamres.2019.105505.
- BERGIN, E.A., BLAKE, G.A., CIESLA, F., HIRSCHMANN, M.M., LI, J. (2015) Tracing the ingredients for a habitable earth from interstellar space through planet formation. *Proceedings of the National Academy of Sciences of the United States of America*. 112, 8965–8970, doi: 10.1073/pnas.1500954112.
- BERNER, R.A., LASAGA, A.C., GARRELS, R.M. (1983) The carbonate-silicate geochemical cycle and its effect on atmospheric carbon-dioxide over the past 100 million years. *American Journal of Science* 283, 641–683.
- BIELER, A., ALTWEGG, K., BALSIGER, H., BAR-NUN, A., BERTHELIER, J.-J., BOCHSLER, P., BRIOIS, C., CALMONTE, U., COMBI, M., DE KEYSER, J., VAN DISHOECK, E.F., FIETHE, B., FUSELIER, S.A., GASC, S., GOMBOSI, T.I., HANSEN, K.C., HÄSSIG, M., JÄCKEL, A., KOPP, E., KORTH, A., LE ROY, L., MALL, U., MAGGILOLO, R., MARTY, B., MOUSIS, O., OWEN, T., RÈME, H., RUBIN, M., SÉMON, T., TZOU, C.-Y., WAITE, J.H., WALSH, C., WURZ, P. (2015) Abundant molecular oxygen in the coma of comet 67P/Churyumov-Gerasimenko. *Nature* 526, 678–681, doi: 10.1038/nature15707.
- BLACK, D.C., PEPIN, R.O. (1969) Trapped neon in meteorites, II. *Earth and Planetary Science Letters* 6, 395–405.
- BLICHERT-TOFT, J., ALBARÈDE, F. (2008) Hafnium isotopes in Jack Hills zircons and the formation of the Hadean crust. *Earth and Planetary Science Letters* 265, 686–702, doi: 10.1016/j.epsl.2007.10.054.



- BOUCHER, C., LAN, T., MABRY, J., BEKAERT, D.V., BURNARD, P.G., MARTY, B. (2018a) Spatial analysis of the atmospheric helium isotopic composition: Geochemical and environmental implications. *Geochimica et Cosmochimica Acta* 237, 120-130, doi: 10.1016/j.gca.2018.06.010.
- BOUCHER, C., MARTY, B., ZIMMERMANN, L., LANGENFELDS, R. (2018b) Atmospheric helium isotopic ratio from 1910 to 2016 recorded in stainless steel containers. *Geochemical Perspectives Letters* 6, 23–27.
- BOUCHER, C., LAN, T., MARTY, B., BURNARD, P.G., FISCHER, T.P., AYALEW, D., MABRY, J., MAARTEN DE MOOR, J., ZELENSKI, M.E., ZIMMERMANN, L. (2018c) Atmospheric helium isotope composition as a tracer of volcanic emissions: A case study of Erta Ale volcano, Ethiopia. *Chemical Geology* 480, 3–11, doi: 10.1016/j.chemgeo.2017.05.011.
- BOYET, M., Blichert-Toft, J., ROSING, M., STOREY, M., TELOUK, P., ALBAREDE, F. (2003) Nd-142 evidence for early Earth differentiation. *Earth and Planetary Science Letters* 214, 427–442.
- BRANTLEY, S.L., KOEPENICK, K.W. (1995) Measured carbon dioxide emissions from Oldoinyo Lengai and the skewed distribution of passive volcanic fluxes. *Geology* 23, 933-936, doi: 10.1130/0091-7613.
- BRASSER, R., MORBIDELLI, A. (2013) Oort cloud and Scattered Disc formation during a late dynamical instability in the Solar System. *Icarus* 225, 40–49, doi: 10.1016/j.icarus.2013.03.012.
- BRÄUER, K., KÄMPF, H., NIEDERMANN, S., STRAUCH, G. (2013) Indications for the existence of different magmatic reservoirs beneath the Eifel area (Germany): A multi-isotope (C, N, He, Ne, Ar) approach. *Chemical Geology* 356, 193–208, doi: 10.1016/j.chemgeo.2013.08.013.
- BRENNWALD, M.S., VOGEL, N., FIGURA, S., VOLLMER, M.K., LANGENFELDS, R., PAUL STEELE, L., MADEN, C., KIPFER, R. (2013) Concentrations and isotope ratios of helium and other noble gases in the Earth's atmosphere during 1978–2011. *Earth and Planetary Science Letters* 366, 27–37, doi: 10.1016/j.epsl.2013.01.039.
- BROADLEY, M.W., BARRY, P.H., BEKAERT, D.V., BYRNE, D.J., CARACAUSI, A., BALLENTINE, C.J., MARTY, B. (2020) Identification of chondritic krypton and xenon in Yellowstone gases and the timing of terrestrial volatile accretion. *Proceedings of the National Academy of Sciences of the United States of America* 117, 13997–14004, doi: 10.1073/pnas.2003907117.
- BROWN, H. (1949) *The atmospheres of the Earth and Planets*. University of Chicago Press, Chicago.
- BROWNLIE, D.E. (1985) Cosmic dust : collection and research. *Annual Review of Earth and Planetary Sciences* 13, 147–173.
- BROWNLIE, D., TSOU, P., ALÉON, J., ALEXANDER, C.M.O., ARAKI, T., BAJT, S., BARATTA, G.A., BASTIEN, R., BLAND, P., BLEUET, P., BORG, J., BRADLEY, J.P., BREARLEY, A., BRENKER, F., BRENNAN, S., BRIDGES, J.C., BROWNING, N.D., BRUCATO, J.R., BULLOCK, E., BURCHELL, M.J., BUSEMANN, H., BUTTERWORTH, A., CHAUSSIDON, M., CHEUVRON, A., CHI, M., CINTALA, M.J., CLARK, B.C., CLEMETT, S.J., CODY, G., COLANGELI, L., COOPER, G., CORDIER, P., DAGHLIAN, C., DAI, Z., D'HENDECOURT, L., DJOUADI, Z., DOMINGUEZ, G., DUXBURY, T., DWORKIN, J.P., EBEL, D.S., ECONOMOU, T.E., FAKRA, S., FAIREY, S.A.J., FALLON, S., FERRINI, G., FERROIR, T., FLECKENSTEIN, H., FLOSS, C., FLYNN, G., FRANCHI, I.A., FRIES, M., GAINSFORTH, Z., GALLIEN, J.-P., GENGE, M., GILLES, M.K., GILLET, P., GILMOUR, J., GLAVIN, D.P., GOUNELLE, M., GRADY, M.M., GRAHAM, G.A., GRANT, P.G., GREEN, S.F., GROSSEMY, F., GROSSMAN, L., GROSSMAN, J.N., GUAN, Y., HAGIYA, K., HARVEY, R., HECK, P., HERZOG, G.F., HOPPE, P., HÖRZ, F., HUTH, J., HUTCHEON, I.D., IGNATYEV, K., ISHII, H., ITO, M., JACOB, D., JACOBSEN, C., JACOBSEN, S., JONES, S., JOSWIAK, D., JUREWICZ, A., KEARSLEY, A.T., KELLER, L.P., KHODJA, H., KILCOYNE, A.L.D., KISSEL, J., KROT, A., LANGENHORST, F., LANZIROTTI, A., LE, L., LESHIN, L.A., LEITNER, J., LEMELLE, L., LEROUX, H., LIU, M.-C., LUENING, K., LYON, I., MACPHERSON, G., MARCUS, M.A., MARHAS, K., MARTY, B., MATRAJT, G., MCKEEGAN, K., MEIBOM, A., MENNELLA, V., MESSENGER, K., MESSENGER, S., MIKOUCHI, T., MOSTEFAOUI, S., NAKAMURA, T., NAKANO, T., NEWVILLE, M., NITTLER, L.R., OHNISHI, I., OHSUMI,



- K., OKUDAIRA, K., PAPANASTASSIOU, D.A., PALMA, R., PALUMBO, M.E., PEPIN, R.O., PERKINS, D., PERRONNET, M., PIANETTA, P., RAO, W., RIETMEIJER, F.J.M., ROBERT, F., ROST, D., ROTUNDI, A., RYAN, R., SANDFORD, S.A., SCHWANDT, C.S., SEE, T.H., SCHLUTTER, D., SHEFFIELD-PARKER, J., SIMIONOVICI, A., SIMON, S., SITNITSKY, I., SNEAD, C.J., SPENCER, M.K., STADERMANN, F.J., STEELE, A., STEPHAN, T., STROUD, R., SUSINI, J., SUTTON, S.R., SUZUKI, Y., TAHERI, M., TAYLOR, S., TESLICH, N., TOMEOKA, K., TOMIOKA, N., TOPPANI, A., TRIGO-RODRÍGUEZ, J.M., TROADEC, D., TSUCHIYAMA, A., TUZZOLINO, A.J., TYLISZCZAK, T., UESUGI, K., VELBEL, M., VELLENGA, J., VICENZI, E., VINCZE, L., WARREN, J., WEBER, I., WEISBERG, M., WESTPHAL, A.J., WIRICK, S., WOODEN, D., WOPENKA, B., WOZNIAKIEWICZ, P., WRIGHT, I., YABUTA, H., YANO, H., YOUNG, E.D., ZARE, R.N., ZEGA, T., ZIEGLER, K., ZIMMERMANN, L., ZINNER, E., ZOLENSKY, M. (2006) Comet 81P/Wild 2 under a microscope. *Science* 314, 1711–1716, doi: 10.1126/science.1135840.
- BRUCALASSI, A., PASQUINI, L., SAGLIA, R., RUIZ, M.T., BONIFACIO, P., LEÃO, I., CANTO MARTINS, B.L., DE MEDEIROS, J.R., BEDIN, L.R., BIAZZO, K., MELO, C., LOVIS, C., RANDICH, S. (2016) Search for giant planets in M67. *Astronomy and Astrophysics* 592, L1, doi: 10.1051/0004-6361/201527561.
- BUDDE, G., BURKHARDT, C., KLEINE, T. (2019) Molybdenum isotopic evidence for the late accretion of outer Solar System material to Earth. *Nature Astronomy* 3, 736–741, doi: 10.1038/s41550-019-0779-y.
- BURNARD, P. (Ed.) (2013) *The Noble Gases as Geochemical Tracers, Advances in Isotope Geochemistry*. Springer, Berlin, Heidelberg, doi: 10.1007/978-3-642-28836-4.
- BURNETT, D.S., GENESIS SCI, T. (2011) Solar composition from the Genesis Discovery Mission. *Proceedings of the National Academy of Sciences of the United States of America* 108, 19147–19151, doi: 10.1073/pnas.1014877108.
- BUSIGNY, V., BEBOUT, G.E. (2013) Nitrogen in the Silicate Earth: Speciation and Isotopic Behaviour during Mineral–Fluid Interactions. *Elements* 9, 353–358, doi: 10.2113/gselements.9.5.353.
- BUTLER, W.A., JEFFERY, P.M., REYNOLDS, J.H., WASSERBURG, G.W. (1963) Isotopic variations in terrestrial xenon. *Journal of Geophysical Research* 68, 3283–3291.
- CAFFEE, M.W., HUDSON, G.U., VELSKO, C., HUSS, G.R., ALEXANDER, E.C., CHIVAS, A.R. (1999) Primordial noble gases from Earth's mantle: Identification of a primitive volatile component. *Science* 285, 2115–2118.
- CARACAUSI, A., AVICE, G., BURNARD, P.G., FÜRI, E., MARTY, B. (2016) Chondritic xenon in the Earth's mantle. *Nature* 533, 82–85, doi: 10.1038/nature17434.
- CARO, G., MORINO, P., MOJZSIS, S.J., CATES, N.L., BLEEKER, W. (2017) Sluggish Hadean geodynamics: Evidence from coupled 146,147Sm--142,143Nd systematics in Eoarchean supracrustal rocks of the Inukjuak domain (Québec). *Earth and Planetary Science Letters* 457, 23–37, doi: 10.1016/j.epsl.2016.09.051.
- CARROLL, M.R., DRAPER, D.S. (1994) Noble gases as trace elements in magmatic processes. *Chemical Geology* 117, 37–56.
- CARTIGNY, P., PALOT, M. (2012) Diamond Formation: A Stable Isotope Perspective. *Annual Review of Earth and Planetary Sciences* 42, 699–732, doi: 10.1146/annurev-earth-042711-105259.
- CASSATA, W.S. (2017) Meteorite constraints on Martian atmospheric loss and paleoclimate. *Earth and Planetary Science Letters* 479, 322–329, doi: 10.1016/j.epsl.2017.09.034.
- CHAKRABORTY, S., MUSKATEL, B.H., JACKSON, T.L., AHMED, M., LEVINE, R.D., THIEMENS, M.H. (2014) Massive isotopic effect in vacuum UV photodissociation of N₂ and implications for meteorite data. *Proceedings of the National Academy of Sciences of the United States of America* 111, 14704–14709, doi: 10.1073/pnas.1410440111.
- CHARNAY, B., WOLF, E.T., MARTY, B., FORGET, F. (2020) Is the Faint Young Sun Problem for Earth Solved? *Space Science Reviews* 216, 90, doi: 10.1007/s11214-020-00711-9.



- CHENNAOUI AOUJJEHANE, H., AVICE, G., BARRAT, J.-A., BOUDOUMA, O., CHEN, G., DUKE, M.J.M., FRANCHI, I.A., GATTACCECA, J., GRADY, M.M., GREENWOOD, R.C., HERD, C.D.K., HEWINS, R., JAMBON, A., MARTY, B., ROCHETTE, P., SMITH, C.L., SAUTTER, V., VERCHOVSKY, A., WEBER, P., ZANDA, B. (2012) Tissint martian meteorite: A fresh look at the interior, surface, and atmosphere of Mars. *Science* 338, 1224514, doi: 10.1126/science.1224514.
- CHYBA, C., THOMAS, P., BROOKSHAW, L., SAGAN, C. (1990) Cometary delivery of organic molecules to the early Earth. *Science* 249, 366–373, doi: 10.1126/science.11538074.
- CIBOROWSKI, T.J.R., KERR, A.C. (2016) Did mantle plume magmatism help trigger the Great Oxidation Event? *Lithos* 247, 128–133, doi: 10.1016/j.lithos.2015.12.017.
- CIESLA, F.J., SANDFORD, S. A. (2012) Organic synthesis via irradiation and warming of ice grains in the solar nebula. *Science* 336, 452–4, doi: 10.1126/science.1217291.
- CLARKE, W.B., BEG, M.A., CRAIG, H. (1969) Excess ^3He in the sea: evidence for terrestrial primordial helium. *Earth and Planetary Science Letters* 6, 213–220.
- CLAYTON, D.D. (1975) Extinct radioactivities: Trapped residuals of presolar grains. *Astrophysical Journal* 199, 765–769.
- CLAYTON, R. N. (2002). Solar System - Self-shielding in the solar nebula. *Nature* 415, 860–861.
- CLAYTON, R.N., ONUMA, N., MAYEDA, T.K. (1976) A classification of meteorites based on oxygen isotopes. *Earth and Planetary Science Letters* 30, 10–18.
- CONRAD, P.G., MALESPIN, C.A., FRANZ, H.B., PEPIN, R.O., TRAINER, M.G., SCHWENZER, S.P., ATREYA, S.K., FREISSINET, C., JONES, J.H., MANNING, H., OWEN, T., PAVLOV, A.A., WIENS, R.C., WONG, M.H., MAHAFFY, P.R. (2016) In situ measurement of atmospheric krypton and xenon on Mars with Mars Science Laboratory. *Earth and Planetary Science Letters* 454, 1–9, doi: 10.1016/j.epsl.2016.08.028.
- COURTILLOT, V., JAUPART, C., MANIGHETTI, I., TAPPONNIER, P., BESSE, J. (1999) On causal links between flood basalts and continental breakup. *Earth and Planetary Science Letters* 166, 177–195.
- CRABB, J., ANDERS, E. (1981) Noble gases in E-chondrites. *Geochimica et Cosmochimica Acta* 45, 2443–2464.
- CRAIG, H., LUPTON, J.E. (1976) Primordial neon, helium, and hydrogen in oceanic basalts. *Earth and Planetary Science Letters* 31, 369–385, doi: 10.1016/0012-821X(76)90118-7.
- CRISP, J.A. (1984) The rate of magma emplacement and volcanic output. *Journal of Volcanology and Geothermal Research* 20, 177–211.
- CULLER, T.S., BECKER, T.A., MULLER, R.A., RENNE, P.R. (2000) Lunar impact history from Ar-40/Ar-39 dating of glass spherules. *Science*. 287, 1785–1788.
- DALOU, C., HIRSCHMANN, M.M., VON DER HANDT, A., MOSENFELDER, J., ARMSTRONG, L.S. (2017) Nitrogen and carbon fractionation during core–mantle differentiation at shallow depth. *Earth and Planetary Science Letters* 458, 141–151, doi: 10.1016/j.epsl.2016.10.026.
- DASGUPTA, R., HIRSCHMANN, M.M. (2010) The deep carbon cycle and melting in Earth's interior. *Earth and Planetary Science Letters* 298, 1–13, doi: 10.1016/j.epsl.2010.06.039.
- DAUPHAS, N. (2003) The dual origin of the terrestrial atmosphere. *Icarus* 165, 326–339, doi: 10.1016/s0019-1035(03)00198-2.
- DAUPHAS, N. (2017) The isotopic nature of the Earth's accreting material through time. *Nature* 541, 521–524, doi: 10.1038/nature20830.
- DAUPHAS, N., MARTY, B. (1999) Heavy nitrogen in carbonatites of the Kola Peninsula: A possible signature of the deep mantle. *Science* 286, 2488–2490.
- DAUPHAS, N., POURMAND, A. (2011) Hf-W-Th evidence for rapid growth of Mars and its status as a planetary embryo. *Nature* 473, 489–U227, doi: 10.1038/nature10077.
- DAUPHAS, N., DAVIS, A.M., MARTY, B., REISBERG, L. (2004) The cosmic molybdenum-ruthenium isotope correlation. *Earth and Planetary Science Letters* 226, 465–475.



- DELOULE, E., ALBARÈDE, F., SHEPPARD, S.M.F. (1991) Hydrogen isotope heterogeneities in the mantle from ion probe analysis of amphiboles from ultramafic rocks. *Earth and Planetary Science Letters* 105, 543–553.
- DERUELLE, B., DREIBUS, G., JAMBON, A. (1992) Iodine Abundances in Oceanic Basalts - Implications for Earth Dynamics. *Earth and Planetary Science Letters* 108, 217–227.
- DIXON, J.E., STOLPER, E.M., HOLLOWAY, J.R. (1995) An experimental study of water and carbon dioxide solubilities in Mid-Ocean Ridge basaltic liquids. Part I: Calibration and solubility models. *Journal of Petrology* 36, 1607–1631.
- DIXON, J.E., LEIST, L., LANGMUIR, C., SCHILLING, J.G. (2002) Recycled dehydrated lithosphere observed in plume-influenced mid-ocean-ridge basalt. *Nature* 420, 385–389, doi: 10.1038/nature01215.
- EBERHARDT, P., GEISS, J., GRAF, H., GROGLER, N., KRAHENBUHL, U., SCHWALLER, H., SCHWARZMULLER, J., STETTLER, A. (1970) Trapped solar wind noble gases, exposure age and K/Ar-age in Apollo 11 lunar fine material. In: *Proceedings of the Apollo 11 Lunar Science Conference*, 1037–1070.
- EBERHARDT, P., GEISS, GRAF, H., GRÖGLER, N., MENDIA, M.D., MÖRGELI, M. (1972) Trapped solar gases in lunar fines and a breccia. *Abstracts of the Lunar and Planetary Science Conference* 3, p.203.
- FARQUHAR, J., BAO, H.M., THIEMENS, M. (2000a) Atmospheric influence of Earth's earliest sulfur cycle. *Science* 289, 756–758.
- FARQUHAR, J., SAVARINO, J., JACKSON, T.L., THIEMENS, M.H. (2000b) Evidence of atmospheric sulphur in the martian regolith from sulphur isotopes in meteorites. *Nature* 404, 50–52.
- FARQUHAR, J., WING, B.A. (2003) Multiple sulfur isotopes and the evolution of the atmosphere. *Earth and Planetary Science Letters* 213, 1–13, doi: 10.1016/S0012-821X(03)00296-6.
- FISCHER, T.P., AIUPPA, A. (2020) AGU Centennial Grand Challenge: Volcanoes and Deep Carbon Global CO₂ Emissions From Subaerial Volcanism—Recent Progress and Future Challenges. *Geochemistry, Geophysics, Geosystems* 21, e2019GC008690, doi: 10.1029/2019GC008690.
- FISCHER, T.P., BURNARD, P., MARTY, B., HILTON, D.R., FÜRI, E., PALHOL, F., SHARP, Z.D., MANGASINI, F. (2009) Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites. *Nature* 459, 77–80, doi: 10.1038/nature07977.
- FOUCHET, T., LELLOUCH, E., BÉZARD, B., ENCRENAZ, TH., DROSSART, P., FEUCHTGRUBER, H., DE GRAAUW, TH. (2000) ISO-SWS Observations of Jupiter: measurement of the ammonia tropospheric profile and of the ¹⁵N/¹⁴N isotopic ratio. *Icarus* 143, 223–243.
- FRICK, U., PEPIN, R.O. (1981) Microanalysis of nitrogen isotope abundances: association of nitrogen with noble gas carriers in Allende. *Earth and Planetary Science Letters* 56, 64–81, doi: 10.1016/0012-821X(81)90117-5.
- FRIEDLINGSTEIN, P., HOUGHTON, R.A., MARLAND, G., HACKLER, J., BODEN, T.A., CONWAY, T.J., CANADELL, J.G., RAUPACH, M.R., CIAIS, P., LE QUÉRÉ, C. (2010) Update on CO₂ emissions. *Nature Geoscience* 3, 811–812, doi: 10.1038/ngeo1022.
- FUNKHOUSER, J.G., FISHER, D.E., BONATTI, E. (1968) Excess argon in deep-sea rocks. *Earth and Planetary Science Letters* 5, 95–100.
- FÜRI, E., MARTY, B. (2015) Nitrogen isotope variations in the Solar System. *Nature Geoscience* 8, 515–522, doi: 10.1038/ngeo2451.
- FÜRI, E., DELOULE, E., GURENKO, A., MARTY, B. (2014) New evidence for chondritic lunar water from combined D/H and noble gas analyses of single Apollo 17 volcanic glasses. *Icarus* 229, 109–120.
- FÜRI, E., CHAUSSIDON, M., MARTY, B. (2015) Evidence for an early nitrogen isotopic evolution in the solar nebula from volatile analyses of a CAI from the CV3 chondrite NWA 8616. *Geochimica et Cosmochimica Acta* 153, 183–201.



- GAILLARD, F., SCAILLET, B., ARNDT, N.T. (2011) Atmospheric oxygenation caused by a change in volcanic degassing pressure. *Nature* 478, 229–232, doi: 10.1038/nature10460.
- GEISS, J., REEVES, H. (1972) Cosmic and solar system abundances of deuterium and helium-3. *Astronomy and Astrophysics* 18, 126–132.
- GEISS, J., BOCHSLER, P. (1982) Nitrogen isotopes in the solar system. *Geochimica et Cosmochimica Acta* 46, 529–548.
- GEISS J., EBERHARDT P., BUELHER F., MEISTER J., SIGNER P. (1970) Apollo 11 and 12 solar wind composition experiments. Fluxes of He and Ne isotopes. *Journal of Geophysical Research* 75, 5972–5979, doi: 10.1029/ja075i031p05972.
- GEISS J., BÜHLER F., CERUTTI H., EBERHARDT P., FILLEUX C., MEISTER J., SIGNER, P. (2004) The Apollo SWC experiment: Results, conclusions, consequences. *Space Science Reviews* 110, 307–335.
- GENDA, H., ABE, Y. (2005) Enhanced atmospheric loss on protoplanets at the giant impact phase in the presence of oceans. *Nature* 433, 842–844.
- GIGGENBACH, W.F., LE GUERN, F. (1976) The chemistry of magmatic gases from Erta’Ale, Ethiopia. *Geochimica et Cosmochimica Acta* 40, 25–30, doi: 10.1016/0016-7037(76)90190-3.
- GILMOUR, J.D., TURNER, G. (2007) Constraints on nucleosynthesis from xenon isotopes in presolar material. *Astrophysical Journal* 657, 600–608, doi: 10.1086/510881.
- GOLDBLATT, C., CLAIRE, M.W., LENTON, T.M., MATTHEWS, A.J., WATSON, A.J., ZAHNLE, K.J. (2009) Nitrogen-enhanced greenhouse warming on early Earth. *Nature Geosciences* 2, 891–896, doi: 10.1038/ngeo692.
- GOMES, R., LEVISON, H.F., TSGANIS, K., MORBIDELLI, A. (2005) Origin of the cataclysmic Late Heavy Bombardment period of the terrestrial planets. *Nature* 435, 466–469.
- GONNERMANN, H.M., MUKHOPADHYAY, S. (2009) Preserving noble gases in a convective mantle. *Nature* 459, 560–563.
- GOUNELLE, M., MEYNET, G. (2012) Solar system genealogy revealed by extinct short-lived radionuclides in meteorites. *Astronomy and Astrophysics* 545, doi: 10.1051/0004-6361/201219031.
- GRADY, M.M., PILLINGER, C.T. (1990) ALH 85085 : Nitrogen isotope analysis of a highly unusual primitive meteorite. *Earth and Planetary Science Letters* 97, 29–40.
- GRAHAM, D.G. (2002) Noble gas isotope geochemistry of mid-ocean ridge and ocean island basalts : characterization of mantle source reservoirs. In: D. Porcelli, Ballentine, C.J., Wieler, R. (Eds.) *Noble Gases in Geochemistry and Cosmochemistry: Reviews in Mineralogy and Geochemistry*, 47–318.
- GREAVES, J.S., RICHARDS, A.M.S., BAINS, W., RIMMER, P.B., SAGAWA, H., CLEMENTS, D.L., SEAGER, S., PETKOWSKI, J.J., SOUSA-SILVA, C., RANJAN, S., DRABEK-MAUNDER, E., FRASER, H.J., CARTWRIGHT, A., MUELLER-WODARG, I., ZHAN, Z., FRIBERG, P., COULSON, I., LEE, E., HOGE, J. (2020) Phosphine gas in the cloud decks of Venus. *Nature Astronomy*, doi:10.1038/s41550-020-1174-4
- GREENBERG, J.M. (1998) Making a comet nucleus. *Astronomy and Astrophysics* 330, 375–380.
- GREWAL, D.S., DASGUPTA, R., SUN, C., TSUNO, K., COSTIN, G. (2019) Delivery of carbon, nitrogen, and sulfur to the silicate Earth by a giant impact. *Science Advances* 5, 1–12.
- GREWAL, D.S., DASGUPTA, R., FARNELL, A. (2020) The speciation of carbon, nitrogen, and water in magma oceans and its effect on volatile partitioning between major reservoirs of the Solar System rocky bodies. *Geochimica et Cosmochimica Acta* 280, 281–301, doi: 10.1016/j.gca.2020.04.023.
- GVERDTSITELI, L.G., KUCHEROV, R.Y., TSKHAKAYA, V.K. (1958) Isotope separation by diffusion in a current of steam. In: *Peaceful Uses of Atomic Energy*, United Nations, 608–618.



- HALLDÓRSSON, S.A., HILTON, D.R., SCARSI, P., ABEBE, T., HOPP, J. (2014) A common mantle plume source beneath the entire East African Rift System revealed by coupled helium-neon systematics. *Geophysical Research Letters* 41, 2304–2311, doi: 10.1002/2014GL059424.
- HALLIDAY, A.N. (2013) The origins of volatiles in the terrestrial planets. *Geochimica et Cosmochimica Acta* 105, 146–171, doi: 10.1016/j.gca.2012.11.015.
- HALLIS, L.J., HUSS, G.R., NAGASHIMA, K., TAYLOR, G.J., HALLDÓRSSON, S.A., HILTON, D.R., MOTT, M.J., MEECH, K.J. (2015) Evidence for primordial water in Earth's deep mantle. *Science* 350, 795–797.
- HAQQ-MISRA, J.D., DOMAGAL-GOLDMAN, S.D., KASTING, P.J., KASTING, J.F. (2008) A Revised, Hazy Methane Greenhouse for the Archean Earth. *Astrobiology* 8, 1127–1137, doi: 10.1089/ast.2007.0197.
- HARRISON, T.M., Blichert-Toft, J., MULLER, W., ALBAREDE, F., HOLDEN, P., MOJZSIS, S.J. (2005) Heterogeneous Hadean hafnium: Evidence of continental crust at 4.4 to 4.5 Ga. *Science* 310, 1947–1950.
- HASHIZUME, K., CHAUSSIDON, M., MARTY, B., ROBERT, F. (2000) Solar wind record on the moon: deciphering presolar from planetary nitrogen. *Science* 290, 1142–1145, doi: 10.1126/science.290.5494.1142.
- HASHIZUME, K., MARTY, B., WIELER, R. (2002) Analyses of nitrogen and argon in single lunar grains : towards a quantification of the asteroidal contribution to planetary surfaces. *Earth and Planetary Science Letters* 202, 201-216.
- HAWKESWORTH, C., CAWOOD, P.A., DHUIME, B. (2019) Rates of generation and growth of the continental crust. *Geoscience Frontiers* 10, 165–173, doi: 10.1016/j.gsf.2018.02.004.
- HEBER, V.S., BROOKER, R.A., KELLEY, S.P., WOOD, B.J. (2007) Crystal–melt partitioning of noble gases (helium, neon, argon, krypton, and xenon) for olivine and clinopyroxene. *Geochimica et Cosmochimica Acta* 71, 1041–1061.
- HEBER, V.S., WIELER, R., BAUR, H., OLINGER, C., FRIEDMANN, T.A., BURNETT, D.S. (2009) Noble gas composition of the solar wind as collected by the Genesis mission. *Geochimica et Cosmochimica Acta* 73, 7414–7432.
- HEBER, V.S., BAUR, H., BOCHSLER, P., MCKEEGAN, K.D., NEUGEBAUER, M., REISENFELD, D.B., WIELER, R., WIENS, R.C. (2012) Isotopic Mass Fractionation of Solar Wind: Evidence From Fast and Slow Solar Wind Collected By the Genesis Mission. *The Astrophysical Journal* 759, 121.
- HÉBRARD, E., MARTY, B. (2014) Coupled noble gas – hydrocarbon evolution of the early Earth atmosphere upon solar UV irradiation. *Earth and Planetary Science Letters* 385, 40–48, doi: 10.1016/j.epsl.2013.10.022.
- HERZBERG, C., CONDIE, K. & KORENAGA, J. (2010) Thermal history of the Earth and its petrological expression. *Earth and Planetary Science Letters* 292, 79–88.
- HIRSCHMANN, M.M. (2018) Comparative deep Earth volatile cycles: The case for C recycling from exosphere/mantle fractionation of major (H₂O, C, N) volatiles and from H₂O/Ce, CO₂/Ba, and CO₂/Nb exosphere ratios. *Earth and Planetary Science Letters* 502, 262–273, doi: 10.1016/j.epsl.2018.08.023.
- HIRSCHMANN, M.M., DASGUPTA, R. (2009) The H/C ratios of Earth's near-surface and deep reservoirs, and consequences for deep Earth volatile cycles. *Chemical Geology* 262, 4–16, doi: 10.1016/j.chemgeo.2009.02.008.
- HIYAGON, H. (1994) Retention of solar helium and neon in IDPs in deep sea sediment. *Science* 263, 1257–1259.
- HOFMANN, C., COURTILLOT, V., FERAUD, G., ROCHETTE, P., YIRGU, G., KETEFU, E., PIK, R. (1997) Timing of the Ethiopian flood basalt event and implications for plume birth and global change. *Nature* 389, 838–841.
- HOHENBERG, C.M., PRAVDIVTSEVA, O.V. (2008) I-Xe dating: From adolescence to maturity. *Chemie der Erde - Geochemistry* 68, 339–351.



- HOHENBERG, C.M., THONNARD, N., MESHK, A. (2002) Active capture and anomalous adsorption: New mechanisms for the incorporation of heavy noble gases. *Meteoritics and Planetary Science* 37, 257–267.
- HOLLAND, G., BALLENTINE, C.J. (2006) Seawater subduction controls the heavy noble gas composition of the mantle. *Nature* 441, 186–191.
- HOLLAND, G., CASSIDY, M., BALLENTINE, C.J. (2009) Meteorite Kr in Earth's Mantle Suggests a Late Accretionary Source for the Atmosphere. *Science* 326, 1522–1525, doi: 10.1126/science.1179518.
- HOLLAND, H.D. (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton.
- HOLZER, M., DeVRIES, T., BIANCHI, D., NEWTON, R., SCHLOSSER, P., WINCKLER, G. (2017) Objective estimates of mantle ^3He in the ocean and implications for constraining the deep ocean circulation. *Earth and Planetary Science Letters* 458, 305–31, doi: 10.1016/j.epsl.2016.10.054.
- HONDA, M., MCDUGALL, I., PATTERSON, D.B., DOULGERIS, A., CLAGUE, D.A. (1991) Possible solar noble-gas component in Hawaiian basalts. *Nature* 349, 149–151.
- HUNTEN, D.M., PEPIN, R.O., WALKER, J.C.B. (1987) Mass fractionation in hydrodynamic escape. *Icarus* 69, 532–549.
- HUSS, G.R., MESHK, A.P., SMITH, J.B., HOHENBERG, C.M. (2003) Presolar diamond, silicon carbide, and graphite in carbonaceous chondrites: Implications for thermal processing in the solar nebula. *Geochimica et Cosmochimica Acta* 67, 4823–4848, doi: 10.1016/j.gca.2003.07.019.
- JACKSON, C.R.M., BENNETT, N.R., DU, Z., COTTRELL, E., FEI, Y. (2018) Early episodes of high-pressure core formation preserved in plume mantle. *Nature* 553, 491–495.
- JACOBSON, S., MORBIDELLI, A., RAYMOND, S.N., O'BRIEN, D.P., WALSH, K.J., RUBIE, D.C. (2014) Highly siderophile elements in Earth's mantle as a clock for the Moon-forming impact. *Nature* 508, 84–87, doi: 10.1038/nature13172.
- JAVOY, M., PINEAU, F., ALLEGRE, C.J. (1982) Carbon geodynamic cycle. *Nature* 300, 171–173, doi: 10.1038/300171a0.
- JAVOY, M., PINEAU, F., DEMAÏFFE, D. (1984) Nitrogen and carbon isotopic composition in the diamonds of Mbuji Mayi (Zaire). *Earth and Planetary Science Letters* 107, 598–611.
- JAVOY, M., PINEAU, F., DELORME, H. (1986) Carbon and nitrogen isotopes in the mantle. *Chemical Geology* 57, 41–62.
- JAVOY, M., KAMINSKI, E., GUYOT, F., ANDRAULT, D., SANLOUP, C., MOREIRA, M., LABROSSE, S., JAMBON, A., AGRINIER, P., DAVAILLE, A., JAUPART, C. (2010) The chemical composition of the Earth: Enstatite chondrite models. *Earth and Planetary Science Letters* 293, 259–268.
- JEFFERY, P.M., REYNOLDS, J.H. (1961) Origin of excess Xe^{129} in stone meteorites. *Journal of Geophysical Research* 66, 3582–3583.
- JOHANSEN, A., YODIN, A. (2007) Protoplanetary disk turbulence driven by the streaming instability: Nonlinear saturation and particle concentration. *Astrophysical Journal* 662, 627–641, doi: 10.1086/516730.
- JOHANSEN, A., LAMBRECHTS, M. (2017) Forming Planets via Pebble Accretion. *Annual Review of Earth and Planetary Sciences* 45, 359–387, doi: 10.1146/annurev-earth-063016-020226.
- JOHNSON, B., GOLDBLATT, C. (2015) The nitrogen budget of Earth. *Earth-Science Reviews* 148, 150–173, doi: 10.1016/j.earscirev.2015.05.006.
- JOHNSON, L.H., BURGESS, R., TURNER, G., MILLEDGE, H.J., HARRIS, J.W. (2000) Noble gas and halogen geochemistry of mantle fluids: comparison of African and Canadian diamonds. *Geochimica et Cosmochimica Acta* 64, 717–732.
- JOHNSTON, D.T. (2011) Multiple sulfur isotopes and the evolution of the Earth's sulfur cycle. *Earth-Science Reviews* 106, 161–183, doi.org/10.1016/j.earscirev.2011.02.003.



- KANEOKA, I., TAKAOKA, N. (1978) Excess ^{129}Xe and high $^3\text{He}/^4\text{He}$ ratios in olivine phenocrysts of Kapuho lava and xenolithic dunites from Hawaii. *Earth and Planetary Science Letters* 39, 382–386.
- KASTING, J.F. (1988) Runaway and moist greenhouse atmospheres and the evolution of Earth and Venus. *Icarus* 74, 472–494, doi: 10.1016/0019-1035(88)90116-9.
- KASTING, J.F. (2010) Faint young Sun redux. *Nature* 464, 687–689, doi: 10.1038/464687a.
- KELEMEN, P.B., MANNING, C.E. (2015) Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proceedings of the National Academy of Sciences of the United States of America* 201507889, doi: 10.1073/pnas.1507889112.
- KENDRICK, M.A., KAMENETSKY, V.S., PHILLIPS, D., HONDA, M. (2012) Halogen systematics (Cl, Br, I) in Mid-Ocean Ridge Basalts: A Macquarie Island case study. *Geochimica et Cosmochimica Acta* 81, 82–93, doi: 10.1016/j.gca.2011.12.004.
- KERRIDGE, J.F. (1975) Solar nitrogen: Evidence for a secular change in the ratio of nitrogen-15 to nitrogen-14. *Science* 188, 162–164.
- KERRIDGE, J.F. (1993) Long-term compositional variation in solar corpuscular radiation: Evidence from nitrogen isotopes in the lunar regolith. *Reviews of Geophysics* 31, 423–437.
- KLEINE, T., PALME, H., MEZGER, M., HALLIDAY, A.N. (2005) Hf-W chronometry of lunar metals and the age and early differentiation of the Moon. *Science* 310, 1671–1674.
- KNAUTH, L.P. (2005) Temperature and salinity history of the Precambrian ocean: Implications for the course of microbial evolution. *Palaeogeography, Palaeoclimatology, Palaeoecology* 219, 53–69, doi: 10.1016/j.palaeo.2004.10.014.
- KOCKARTS, G. (1973) Helium in the terrestrial atmosphere. *Space Science Reviews* 14, 723–757, doi: 10.1007/BF00224775.
- KRUMMENACHER, D. (1970) Isotopic composition of argon in modern surface volcanic rocks. *Earth and Planetary Science Letters* 8, 109–117, doi: 10.1016/0012-821X(70)90159-7.
- KUGA, M., CARRASCO, N., MARTY, B., MARROCCHI, Y., BERNARD, S., RIGAUDIER, T., FLEURY, B., TISSANDIER, L. (2014) Nitrogen isotopic fractionation during abiotic synthesis of organic solid particles. *Earth and Planetary Science Letters* 393, 2–13, doi: 10.1016/j.epsl.2014.02.037.
- KUGA, M., MARTY, B., MARROCCHI, Y., TISSANDIER, L. (2015) Synthesis of refractory organic matter in the ionized gas phase of the solar nebula. *Proceedings of the National Academy of Sciences of the United States of America* 112, 7129–7134, doi: 10.1073/pnas.1502796112.
- KUGA, M., CERNOGORA, G., MARROCCHI, Y., TISSANDIER, L., MARTY, B. (2017) Processes of noble gas elemental and isotopic fractionations in plasma-produced organic solids: Cosmochemical implications. *Geochimica et Cosmochimica Acta* 217, 219–230, doi: 10.1016/j.gca.2017.08.031.
- KUNG, C.C., CLAYTON, R.N. (1978) Nitrogen abundances and isotopic compositions in stony meteorites. *Earth and Planetary Science Letters* 38, 421–435.
- KUNZ, J., STAUDACHER, T., ALLÈGRE, C.J. (1998) Plutonium-fission xenon found in the Earth's mantle. *Science* 280, 877–880.
- KURAT, G., KOEBERL, C., PRESPEL, T., BRANSTÄTTER, F., MAURETTE, M. (1994) Petrology and geochemistry of Antarctic micrometeorites. *Geochimica et Cosmochimica Acta* 58, 3879–3904.
- KURZ, M.D. AND JENKINS, W.J. (1981) The distribution of helium in oceanic basalt glasses. *Earth and Planetary Science Letters* 53, 41–54.
- LABIDI, J., BARRY, P.H., BEKAERT, D. V., BROADLEY, M.W., MARTY, B., GIUNTA, T., WARR, O., SHERWOOD LOLLAR, B., FISCHER, T.P., AVICE, G., CARACAUSI, A., BALLENTINE, C.J., HALLDÓRSSON, S.A., STEFÁNSSON, A., KURZ, M.D., KOHL, I.E., YOUNG, E.D. (2020) Hydrothermal $^{15}\text{N}/^{14}\text{N}$ abundances constrain the origins of mantle nitrogen. *Nature* 580, 367–371, doi: 10.1038/s41586-020-2173-4.



- LAURENT, B., ROSKOSZ, M., REMUSAT, L., ROBERT, F., LEROUX, H., VEZIN, H., DEPECKER, C., NUNS, N., LEFEBVRE, J.-M. (2015) The deuterium/hydrogen distribution in chondritic organic matter attests to early ionizing irradiation. *Nature Communications* 6, 8567, doi: 10.1038/ncomms9567.
- LE VOYER, M., HAURI, E.H., COTTRELL, E., KELLEY, K.A., SALTERS, V.J.M., LANGMUIR, C.H., HILTON, D.R., BARRY, P.H., FÜRI, E. (2019) Carbon Fluxes and Primary Magma CO₂ Contents Along the Global Mid-Ocean Ridge System. *Geochemistry, Geophysics, Geosystems* 20, 1387–1424, doi: 10.1029/2018GC007630.
- LEE, J.Y., MARTI, K., SEVERINGHAUS, J.P., KAWAMURA, K., YOO, H.S., LEE, J.B., KIM, J.S. (2006) A redetermination of the isotopic abundances of atmospheric Ar. *Geochimica et Cosmochimica Acta* 70, 4507–4512, doi: 10.1016/j.gca.2006.06.1563.
- LE ROEX, A.P. (1987) Source regions of Mid-Ocean Ridge Basalts: Evidence for enrichment processes. In: Menzies, M.A., Hawkesworth, C.J. (Eds.) *Mantle Metasomatism*. Academic Press Geology Series, 389–422.
- LEROY, C., SANLOUP, C., BUREAU, H., SCHMIDT, B.C., KONŔPKOVÁ, Z., RAEPSAET, C. (2018) Bonding of xenon to oxygen in magmas at depth. *Earth and Planetary Science Letters* 484, 103–110, doi: 10.1016/j.epsl.2017.12.019.
- LESHIN, L.A., EPSTEIN, S., STOLPER, E.M. (1996) Hydrogen isotope geochemistry of SNC meteorites. *Geochimica et Cosmochimica Acta* 60, 2635–2650.
- LEVISON, H.F., DUNCAN, M.J., BRASSER, R., KAUFMANN, D.E. (2010) Capture of the Sun's Oort cloud from stars in its birth cluster. *Science* 329, 187–190, doi: 10.1126/science.1187535.
- LIBOUREL, G., MARTY, B., HUMBERT, F. (2003) Nitrogen solubility in basaltic melt. Part I. Effect of oxygen fugacity. *Geochimica et Cosmochimica Acta* 67, 4123–4135.
- LICHTENEGGER, H.I.M., LAMMER, H., GRIESSMEIER, J.M., KULIKOV, Y.N., VON PARIS, P., HAUSLEITNER, W., KRAUSS, S., RAUER, H. (2010) Aeronomical evidence for higher CO₂ levels during Earth's Hadean epoch. *Icarus* 210, 1–7, doi: 10.1016/j.icarus.2010.06.042.
- LODDERS, K. (2004) Jupiter formed with more tar than ice. *Astrophysical Journal* 611, 587–597.
- LOVE, S., BROWNLEE, D.E. (1993) A direct measurement of the terrestrial mass accretion rate of cosmic dust. *Science* 262, 550–553.
- MABRY, J., LAN, T., BURNARD, P., MARTY, B. (2013) High-precision helium isotope measurements in air. *Journal of Analytical Atomic Spectrometry* 12, 1903–1910, doi: 10.1039/c3ja50155h.
- MABRY, J.C., LAN, T., BOUCHER, C., BURNARD, P.G., BRENNWALD, M.S., LANGENFELDS, R., MARTY, B. (2015) No evidence for change of the atmospheric helium isotope composition since 1978 from re-analysis of the Cape Grim Air Archive. *Earth and Planetary Science Letters* 428, 134–138, doi: 10.1016/j.epsl.2015.07.035.
- MAHAFFY, P.R., WEBSTER, C.R., ATREYA, S.K., FRANZ, H., WONG, M., CONRAD, P.G., HARPOLD, D., JONES, J.J., LESHIN, L.A., MANNING, H., OWEN, T., PEPIN, R.O., SQUYRES, S., TRAINER, M. (2013) Abundance and isotopic composition of gases in the martian atmosphere from the Curiosity Rover. *Science* 341, 263–266, doi: 10.1126/science.1237966.
- MAMYRIN, B.A., TOLSTIKHIN, I.N., ANUFRIEV, G.S., KAMENSKY, I.L. (1969) Anomalous isotopic composition of helium in volcanic gases. *Doklady Akademií Nauk SSSR (Proceedings of the USSR Academy of Sciences)* 184, 1197–1199 (in Russian).
- MAMYRIN, B.A., ANUFRIYEV, G.S., KAMENSKY, I.L., TOLSTIKHIN, I.N. (1970) Determination of the isotopic composition of atmospheric helium. *Geochemistry International* 7, 498–505.
- MARROCCHI, Y., DERENNE, S., MARTY, B., ROBERT, F. (2005) Interlayer trapping of noble gases in insoluble organic matter of primitive meteorites. *Earth and Planetary Science Letters* 236, 569–578.
- MARROCCHI, Y., MARTY, B., REINHARDT, P., ROBERT, F. (2011) Adsorption of xenon ions onto defects in organic surfaces: Implications for the origin and the nature of organics in primitive meteorites. *Geochimica et Cosmochimica Acta* 75, 6255–6266, doi: 10.1016/j.gca.2011.07.048.



- MARTY, B. (1984) On the Noble-Gas Isotopic Fractionation in Naturally-Occurring Gases. *Geochemical Journal* 18, 157–162.
- MARTY, B. (1989) Neon and xenon isotopes in MORB: implications for the earth-atmosphere evolution. *Earth and Planetary Science Letters* 94, 45–56, doi: 10.1016/0012-821X(89)90082-4.
- MARTY, B. (1995) Nitrogen content of the mantle inferred from N₂-Ar correlation in oceanic basalts. *Nature* 377, 326–329.
- MARTY, B. (2012) The origins and concentrations of water, carbon, nitrogen and noble gases on Earth. *Earth and Planetary Science Letters* 313–314, 56–66, doi: 10.1016/j.epsl.2011.10.040.
- MARTY, B., PAGANI, A. (1982) Quantitative-Analysis of Argon Extracted from Recent Rocks by Mass-Spectrometry without Tracer. *Analysis* 10, 225–228.
- MARTY, B., OZIMA, M. (1986) Noble-Gas Distribution in Oceanic Basalt Glasses. *Geochimica et Cosmochimica Acta* 50, 1093–1097.
- MARTY, B., JAMBON, A. (1987) C/³He in volatile fluxes from the solid Earth: implications for carbon geodynamics. *Earth and Planetary Science Letters* 83, 16–26, doi: 10.1016/0012-821X(87)90047-1.
- MARTY, B., LE CLOAREC, M.-F. (1992) He-3 and CO₂ Fluxes from Subaerial Volcanos Estimated from Po-210 Emissions. *Journal of Volcanology and Geothermal Research* 53, 67–72.
- MARTY, B., TOLSTIKHIN, I.N. (1998) CO₂ fluxes from mid-ocean ridges, arcs and plumes. *Chemical Geology* 145, 233–248.
- MARTY, B., ZIMMERMANN, L. (1999) Volatiles (He, C, N, Ar) in mid-ocean ridge basalts: Assessment of shallow-level fractionation and characterization of source composition. *Geochimica et Cosmochimica Acta* 63, 3619–3633.
- MARTY, B., DAUPHAS, N. (2003) The nitrogen record of crust–mantle interaction and mantle convection from Archean to Present. *Earth and Planetary Science Letters* 206, 397–410.
- MARTY, B., YOKOCHI, R. (2006) Water in the Early Earth. *Journal of Volcanology and Geothermal Research* 62, 421–450, doi: 10.2138/rmg.2006.62.18.
- MARTY, B., ZASHU, S., OZIMA, M. (1983) Two noble gas components in a Mid-Atlantic Ridge basalt. *Nature* 302, 238–240, doi: 10.1038/302238a0.
- MARTY, B., JAMBON, A., SANO, Y. (1989) Helium isotopes and CO₂ in volcanic gases of Japan. *Chemical Geology* 76, 25–40.
- MARTY, B., APPORA, I., BARRAT, J.-A.A., DENIEL, C., VELLUTINI, P., VIDAL, P. (1993) He, Ar, Sr, Nd and Pb isotopes in volcanic rocks from Afar: Evidence for a primitive mantle component and constraints on magmatic sources. *Geochemical Journal* 27, 219–228, doi: 10.2343/geochemj.27.219.
- MARTY, B., LENOBLE, M., VASSARD, N. (1995) Nitrogen, helium and argon in basalt: a static mass spectrometry study. *Chemical Geology* 120, 183–195, doi: 10.1016/0009-2541(94)00120-W.
- MARTY, B., PIK, R., GEZAHEGN, Y. (1996) Helium isotopic variations in Ethiopian plume lavas: Nature of magmatic sources and limit on lower mantle contribution. *Earth and Planetary Science Letters* 144, 223–237.
- MARTY, B., DEWONCK, S., FRANCE-LANORD, C. (2003a) Geochemical evidence for efficient aquifer isolation over geological timeframes. *Nature* 425, 55–58.
- MARTY, B., HASHIZUME, K., CHAUSSIDON, M., WIELER, R. (2003b) Nitrogen isotopes on the moon: Archives of the solar and planetary contributions to the inner solar system. *Space Science Reviews* 106, 175–196.
- MARTY, B., PALMA, R.L., PEPIN, R.O., ZIMMERMANN, L., SCHLUTTER, D.J., BURNARD, P.G., WESTPHAL, A.J., SNEAD, C.J., BAJT, S., BECKER, R.H., SIMONES, J.E. (2008) Helium and neon abundances and compositions in cometary matter. *Science* 319, 75–78.



- MARTY, B., ZIMMERMANN, L., BURNARD, P.G., WIELER, R., HEBER, V.S., BURNETT, D.L., WIENS, R.C., BOCHSLER, P. (2010) Nitrogen isotopes in the recent solar wind from the analysis of Genesis targets: Evidence for large scale isotope heterogeneity in the early solar system. *Geochimica et Cosmochimica Acta* 74, 340-355, doi: 10.1016/j.gca.2009.09.007.
- MARTY, B., CHAUSSIDON, M., WIENS, R.C., JUREWICZ, A.J.G., BURNETT, D.S. (2011) A ^{15}N -poor isotopic composition for the solar system as shown by Genesis solar wind samples. *Science* 332, 1533-1536, doi: 10.1126/science.1204656.
- MARTY, B., ZIMMERMANN, L., PUJOL, M., BURGESS, R., PHILIPPOT, P. (2013) Nitrogen isotopic composition and density of the Archean atmosphere. *Science* 342, 101-104, doi: 10.1126/science.1240971.
- MARTY, B., AVICE, G., SANO, Y., ALTWEGG, K., BALSIGER, H., HÄSSIG, M., MORBIDELLI, A., MOUSIS, O., RUBIN, M. (2016) Origins of volatile elements (H, C, N, noble gases) on Earth and Mars in light of recent results from the ROSETTA cometary mission. *Earth and Planetary Science Letters* 441, 91-102.
- MARTY, B., ALTWEGG, K., BALSIGER, H., BAR-NUN, A., BEKAERT, D.V., BERTHELIER, J.-J., BIELER, A., BRIOIS, C., CALMONTE, U., COMBI, M., DE KEYSER, J., FIETHE, B., FUSELIER, S.A., GASC, S., GOMBOSI, T.I., HANSEN, K.C., HÄSSIG, M., JÄCKEL, A., KOPP, E., KORTH, A., LE ROY, L., MALL, U., MOUSIS, O., RÈME, H., OWEN, T., RUBIN, M., SÉMON, T., TZOU, C.-Y., WAITE, J.H., WURZ, P. (2017) Xenon isotopes in 67P/Churyumov-Gerasimenko show that comets contributed to Earth's atmosphere. *Science* 356, 1069-1072, doi: 10.1126/science.aal3496.
- MARTY, B., AVICE, G., BEKAERT, D.V., BROADLEY, M.W. (2018) Salinity of the Archaean oceans from analysis of fluid inclusions in quartz. *Comptes Rendus Geoscience* 350, 154-163.
- MARTY, B., BEKAERT, D.V., BROADLEY, M.W., JAUPART, C. (2019) Geochemical evidence for high volatile fluxes from the mantle at the end of the Archaean. *Nature* 575, 485-488, doi: 10.1038/s41586-019-1745-7.
- MARTY, B., ALMAYRAC, M., BARRY, P.H., BEKAERT, D.V., BROADLEY, M. W., BYRNE, D.J., BALLENTINE, C.J., CARACAUSI, A. (2020) An evaluation of the C/N ratio of the mantle from natural CO_2 -rich gas analysis: geochemical and cosmochemical implications. *Earth and Planetary Science Letters* 551, 116574.
- MATHEW, K.J., MARTI, K. (2001a) Lunar nitrogen: Indigenous signature and cosmic-ray production rate. *Earth and Planetary Science Letters* 184, 659-669.
- MATHEW, K.J., MARTI, K. (2001b) Early evolution of Martian volatiles: Nitrogen and noble gas components in ALH84001 and Chassigny. *Journal of Geophysical Research* 106, 1401-1422, doi: 10.1029/2000JE001255.
- MATSUO, S., SUZUKI, M., MIZUTANI, Y. (1978) Nitrogen to argon ratio in volcanic gases. In: Alexander, E.C.J., Ozima, M. (Eds.) *Terrestrial Rare Gases*. Japan Science Society Press, Tokyo, 17-25.
- MAZOR, E., HEYMAN, D., ANDERS, E. (1970) Noble gases in carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 34, 781-824.
- MC ELROY, M.B., YUNG, Y.U., NIER, A.O. (1976) Isotopic Composition of Nitrogen: Implications for the Past History of Mars' Atmosphere. *Science* 194, 70-72, doi: 10.1126/science.194.4260.70.
- MCKEEGAN, K.D., KALLIO, A.P.A., HEBER, V.S., JARZEBINSKI, G., MAO, P.H., COATH, C.D., KUNIHITO, T., WIENS, R.C., NORDHOLT, J.E., MOSES, R.W., REISENFELD, D.B., JUREWICZ, A.J.G., BURNETT, D.S. (2011) The oxygen isotopic composition of the Sun inferred from captured solar wind. *Science* 332, 1528-1532.



- MEDYNSKI, S., PIK, R., BURNARD, P., WILLIAMS, A., VYE-BROWN, C., FERGUSON, D., BLARD, P.H., FRANCE, L., YIRGU, G., SEID, J.I., AYALEW, D., CALVERT, A. (2013) Controls on magmatic cycles and development of rift topography of the Manda Hararo segment (Afar, Ethiopia): Insights from cosmogenic ^3He investigation of landscape evolution. *Earth and Planetary Science Letters* 367, 133–145, doi: 10.1016/j.epsl.2013.02.006.
- MEECH, K., RAYMOND, S.N. (2020) Origin of Earth's water: sources and constraints. In: Meadows, V., Arney, G., Schmidt, B., Des Marais, D.G. (Eds.) *Planetary Astrobiology*. University of Arizona Press, 325–353, doi: 10.2458/azu_uapress.9780816540068-ch013.
- MEIBOM, A., KROT, A.N., ROBERT, F., MOSTEFAOUI, S., RUSSELL, S.S., PETAEV, M.I., GOUNELLE, M. (2007) Nitrogen and Carbon Isotopic Composition of the Sun Inferred from a High-Temperature Solar Nebular Condensate. *Astrophysical Journal* 656, L33–L36, doi: 10.1086/512052.
- MERRIHUE, C. (1964) Rare gas evidence for cosmic dust in modern pacific red clay. *Annals of the New York Academy of Sciences* 119, 351–367, doi: 10.1111/j.1749-6632.1965.tb47445.x.
- MESHK, A., PRAVDIVTSEVA, O. (2017) Weak Decay of Tellurium and Barium Isotopes in Geological Samples: Current Status. *Proceedings of the 14th International Symposium on Nuclei in the Cosmos 020702*, 2016–2018, doi: 10.7566/JSPSC.14.020702.
- MESHK, A.P., HOHENBERG, C.M., PRAVDIVTSEVA, O. V, KAPUSTA, Y.S. (2001) Weak decay of Ba-130 and Ba-132: Geochemical measurements. *Physical Review C* 64, 6, doi: 03520510.1103/PhysRevC.64.035205.
- MILLER, W.G.R., MACLENNAN, J., SHORTLE, O., GAETANI, G.A., LE ROUX, V., KLEIN, F. (2019) Estimating the carbon content of the deep mantle with Icelandic melt inclusions. *Earth and Planetary Science Letters* 523, 115699, doi: 10.1016/j.epsl.2019.07.002.
- MİYAZAKI, A., HIYAGON, H., SUGIURA, N., HIROSE, K., TAKAHASHI, E. (2004) Solubilities of nitrogen and noble gases in silicate melts under various oxygen fugacities: Implications for the origin and degassing history of nitrogen and noble gases in the Earth. *Geochimica et Cosmochimica Acta* 68, 387–401, doi: 10.1016/s0016-7037(03)00484-8.
- MOJZSIS, S.J., HARRISSON, T.M., PIDGEON, R.T. (2001) Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4,300 Myr ago. *Nature* 409, 178–181.
- MORBIDELLI, A., CHAMBERS, J., LUNINE, J.I., PETIT, J.M., ROBERT, F., VALSECCHI, G.B., CYR, K.E. (2000) Source regions and timescales for the delivery of water to the Earth. *Meteoritics and Planetary Science* 35, 1309–1320.
- MORBIDELLI, A., LUNINE, J.I., O'BRIEN, D.P., RAYMOND, S.N., WALSH, K.J. (2012) Building Terrestrial Planets. *Annual Review of Earth and Planetary Sciences* 40, 251–275, doi: 10.1146/annurev-earth-042711-105319.
- MOREIRA, M. (2013) Noble gas constraints on the origin and evolution of Earth's volatiles. *Geochemical Perspectives*. 2, 229–403, doi: 10.7185/geochempersp.2.2.
- MOREIRA, M., CHARNOZ, S. (2016) The origin of the neon isotopes in chondrites and on Earth. *Earth and Planetary Science Letters* 433, 249–256, doi: 10.1016/j.epsl.2015.11.002.
- MOREIRA, M., KUNZ, J., ALLÈGRE, C.J. (1998) Rare gas systematics in Popping Rock : Isotopic and elemental compositions in the upper mantle. *Science* 279, 1178–1181.
- MUKHOPADHYAY, S. (2012) Early differentiation and volatile accretion recorded in deep-mantle neon and xenon. *Nature* 486, 101–104, doi: 10.1038/nature11141.
- MUKHOPADHYAY, S., PARAI, R. (2019) Noble Gases: A Record of Earth's Evolution and Mantle Dynamics. *Annual Review of Earth and Planetary Sciences* 47, 389–419, doi: 10.1146/annurev-earth-053018-060238.
- NAGAO, K., TAKAOKA, N., MATSUBAYASHI, O. (1981) Rare gas isotopic compositions in natural gases of Japan. *Earth and Planetary Science Letters* 53, 175–188, doi: 10.1016/0012-821X(81)90152-7.



- NANNE, J.A.M., NIMMO, F., CUZZI, J.N., KLEINE, T. (2019) Origin of the non-carbonaceous–carbonaceous meteorite dichotomy. *Earth and Planetary Science Letters* 511, 44–54, doi: 10.1016/j.epsl.2019.01.027.
- NIER, A.O. (1935) Evidence for the existence of an isotope of potassium of mass 40. *Physical Review* 48, 283–284.
- NIER, A.O. (1950) A Redetermination of the Relative Abundances of the Isotopes of Carbon, Nitrogen, Oxygen, Argon, and Potassium. *Physical Review* 77, 789–793, doi: 10.1103/PhysRev.77.789.
- NIER, A.O., MCELROY, M.B. (1977). Composition and structure of Mars' upper atmosphere: Results from the neutral mass spectrometers on Viking 1 and 2. *Journal of Geophysical Research* 82, 434–4349.
- ORÓ, J. (1963) Synthesis of organic compounds by electric discharges. *Nature* 197, 862–867.
- OTT, U. (1988) Noble gases in SNC meteorites : Shergotty, Nakhla, Chassigny. *Geochimica et Cosmochimica Acta* 52, 1737–1748.
- OWEN, T., MAHAFFY, P., NIEMANN, H.B., ATREYA, S., DONAHUE, T., BAR-NUN, A., DE PATER, I. (1999) A low-temperature origin for the planetesimals that formed Jupiter. *Nature* 402, 269–270.
- OZIMA, M. (1975) Ar isotopes and Earth-atmosphere evolution models. *Geochimica et Cosmochimica Acta* 39, 1127–1140.
- OZIMA, M., ZAHNLE, K. (1993) Mantle degassing and atmospheric evolution: Noble gas view. *Geochemical Journal* 27, 4–5.
- OZIMA, M., PODOSEK, F.A. (2002) Noble gas geochemistry. Cambridge University Press, Cambridge, 286 pp.
- OZIMA, M., TAKAYANAGI, M., ZASHU, S., AMARI, S. (1984) High He-3/He-4 ratio in oceanic sediments. *Nature* 311, 448–450.
- PALME, H., O'NEILL, H. (2013) Cosmochemical Estimates of Mantle Composition, 2nd ed, Treatise on Geochemistry: Second Edition. Elsevier Ltd, doi: 10.1016/B978-0-08-095975-7.00201-1.
- PAPANASTASSIOU, D.A., LEE, T., WASSERBURG, G.J. (1977) 2. Evidence for ²⁶Al in the Solar System. *International Astronomical Union Colloquium* 39, 343–349, doi: 10.1017/S0252921100070275.
- PARAI, R., MUKHOPADHYAY, S. (2015) The evolution of MORB and plume mantle volatile budgets: Constraints from fission Xe isotopes in Southwest Indian Ridge basalts. *Geochemistry, Geophysics, Geosystems* 16, 1–17, doi: 10.1002/2014GC005566.
- PARAI, R., MUKHOPADHYAY, S. (2018) Xenon isotopic constraints on the history of volatile recycling into the mantle. *Nature* 560, 223–227, doi: 10.1038/s41586-018-0388-4.
- PATTERSON, C., TILTON, G., INGRAM, M. (1955) Age of the Earth. *Science* 121, 69–75.
- PAVLOV, A.A., KASTING, J.F., BROWN, L.L., RAGES, K.A., FREEDMAN, R. (2000) Greenhouse warming by CH₄ in the atmosphere of early Earth. *Journal of Geophysical Research: Planets* 105, 11981–11990, doi: 10.1029/1999JE001134.
- PEPIN, R.O. (1991) On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles. *Icarus* 92, 2–79.
- PEPIN, R.O. (2000) On the isotopic composition of primordial xenon in terrestrial planet atmospheres. *Space Science Reviews* 92, 371–395.
- PÉRON, S., MOREIRA, M.A., KURZ, M.D., CURTICE, J., BLUSZTAJN, J.S., PUTLITZ, B., WANLESS, V.D., JONES, M.R., SOULE, S.A., MITTELSTAEDT, E. (2019) Noble gas systematics in new popping rocks from the Mid-Atlantic Ridge (14°N): Evidence for small-scale upper mantle heterogeneities. *Earth and Planetary Science Letters* 519, 70–82, doi: 10.1016/j.epsl.2019.04.037.
- PIANI, L., MARROCCHI, Y., RIGAUDIER, T., VACHER, L.G., THOMASSIN, D., MARTY, B. (2020) Earth's water may have been inherited from material similar to enstatite chondrite meteorites. *Science* 369, 1110–1113, doi: 10.1126/science.aba1948.



- PIGNATALE, F.C., CHARNOZ, S., CHAUSSIDON, M., JACQUET, E. (2018) Making the Planetary Material Diversity during the Early Assembling of the Solar System. *Astrophysical Journal* 867, L23, doi: 10.3847/2041-8213/aab22.
- PIK, R., DENIEL, C., COULON, C., YIRGU, G., MARTY, B. (1999) Isotopic and trace element signatures of Ethiopian flood basalts: Evidence for plume-lithosphere interactions. *Geochimica et Cosmochimica Acta* 63, 2263–2279.
- PIK, R., MARTY, B., HILTON, D.R. (2006) How many mantle plumes in Africa? The geochemical point of view. *Chemical Geology* 226, 100–114.
- PLANK, T., MANNING, C.E. (2019) Subducting carbon. *Nature* 574, 343–352, doi: 10.1038/s41586-019-1643-z.
- PODOSEK, F.A., CASSEN, P. (1994) Theoretical, observational, and isotopic estimates of the lifetime of the solar nebula. *Meteoritics* 29, 6–25, doi: 10.1111/j.1945-5100.1994.tb00649.x.
- POLYAK, B., KONOVOV, I.V., TOLSTIKHIN, I.N., MAMYRIN, B.A., KHABARIN, L.V. (1976) The helium isotopes in thermal fluids. In: Johnson, A.I. (Ed.) *Thermal and chemical problems of thermal waters*. International Association of Hydrological Sciences Publications 119, 17–33.
- PORCELLI, D., WOOLUM, D., CASSEN, P. (2001) Deep Earth rare gases: initial inventories, capture from the solar nebula, and losses during Moon formation. *Earth and Planetary Science Letters* 193, 237–251.
- PORCELLI, D., BALLENTINE, C.J., WIELER, R. (2002) (Eds.) Noble Gas Geochemistry and Cosmochemistry. *Reviews in Mineralogy and Geochemistry* 47.
- PUJOL, M., MARTY, B., BURNARD, P., PHILIPPOT, P. (2009) Xenon in Archean barite: Weak decay of ¹³⁰Ba, mass-dependent isotopic fractionation and implication for barite formation. *Geochimica et Cosmochimica Acta* 73, 6834–6846, doi: 10.1016/j.gca.2009.08.002.
- PUJOL, M., MARTY, B., BURGESS, R. (2011) Chondritic-like xenon trapped in Archean rocks: A possible signature of the ancient atmosphere. *Earth and Planetary Science Letters* 308, 298–306. doi: 10.1016/j.epsl.2011.05.053.
- PUJOL, M., MARTY, B., BURGESS, R., TURNER, G., PHILIPPOT, P. (2013) Argon isotopic composition of Archean atmosphere probes early Earth geodynamics. *Nature* 498, 87–90, doi: 10.1038/nature12152.
- RAPONI, A., CIARNIELLO, M., CAPACCIONI, F., MENNELLA, V., FILACCHIONE, G., VINOGRADOFF, V., POCH, O., BECK, P., QUIRICO, E., DE SANCTIS, M.C., MOROZ, L. V., KAPPEL, D., ERARD, S., BOCKELÉE-MORVAN, D., LONGOBARDO, A., TOSI, F., PALOMBA, E., COMBE, J.-P., ROUSSEAU, B., ARNOLD, G., CARLSON, R.W., POMMEROL, A., PILORGET, C., FORNASIER, S., BELLUCCI, G., BARUCCI, A., MANCARELLA, F., FORMISANO, M., RINALDI, G., ISTIQOMAH, I., LEYRAT, C. (2020) Infrared detection of aliphatic organics on a cometary nucleus. *Nature Astronomy* 4, 500–505, doi: 10.1038/s41550-019-0992-8.
- REMUSAT, L., PALHOL, F., ROBERT, F., DERENNE, S., FRANCE-LANORD, C. (2006) Enrichment of deuterium in insoluble organic matter from primitive meteorites: A solar system origin ? *Earth and Planetary Science Letters* 243, 15–25.
- REYNOLDS, J.H. (1960) Determination of the Age of the Elements. *Physical Review Letters* 4, 8–10, doi: 10.1103/PhysRevLett.4.8.
- REYNOLDS J. H., TURNER G. (1964) Rare gases in the chondrite Renazzo. *Journal of Geophysical Research* 69, 3263–3281.
- RIBAS, I., GUINAN, E.F., GUDEL, M., AUDARD, M. (2005) Evolution of the Solar Activity over Time and Effects on Planetary Atmospheres. I. High Energy Irradiances (1–1700 Å). *Astrophysical Journal* 622, 680–694, doi: 10.1086/427977.
- RICHET, P. (2007) *A Natural History of Time*. The University of Chicago Press, XIV + 471 pp
- RODGERS, S.D., CHARNLEY, S.B. (2008) Nitrogen superfractionation in dense cloud cores. *Monthly Notices of the Royal Astronomical Society* 385, L48–L52, doi: 10.1111/j.1745-3933.2008.00431.x.



- ROSENTHAL, A., HAURI, E.H., HIRSCHMANN, M.M. (2015) Experimental determination of C, F, and H partitioning between mantle minerals and carbonated basalt, CO₂/Ba and CO₂/Nb systematics of partial melting, and the CO₂ contents of basaltic source regions. *Earth and Planetary Science Letters* 412, 77–87, doi: 10.1016/j.epsl.2014.11.044.
- ROISING, M.T., BIRD, D.K., SLEEP, N.H., BJERRUM, C.J. (2010) No climate paradox under the faint early Sun. *Nature* 464, 744–747, doi: 10.1038/nature08955.
- ROSKOSZ, M., MYSEN, B.O., CODY, G.D. (2006) Dual speciation of nitrogen in silicate melts at high pressure and temperature: An experimental study. *Geochimica et Cosmochimica Acta* 70, 2902–2918.
- ROSKOSZ, M., BOUHIFD, M.A., JEPHCOAT, A.P., MARTY, B., MYSEN, B.O. (2013) Nitrogen solubility in molten metal and silicate at high pressure and temperature. *Geochimica et Cosmochimica Acta* 121, 15–28, doi: 10.1016/j.gca.2013.07.007.
- ROUSSELOT, P., PIRALI, O., JEHIN, E., VERVOLOET, M., HUTSEMÉKERS, D., MANFROID, J., CORDIER, D., MARTIN-DRUMEL, M.-A., GRUET, S., ARPIGNY, C., DECOCK, A., MOUSIS, O. (2014) Toward a Unique Nitrogen Isotopic Ratio in Cometary Ices. *Astrophysical Journal* 780, L17, doi: 10.1088/2041-8205/780/2/L17.
- RUBEY, W.W. (1951) Geologic history of sea water. *Geological Society of America Bulletin* 62, 1111–1148.
- RUBIN, M., ALTWEGG, K., BALSIGER, H., BAR-NUN, A., BERTHELIER, J.-J., BIELER, A., BOCHSLER, P., BRIOIS, C., CALMONTE, U., COMBI, M., DE KEYSER, J., DHOOGHE, F., EBERHARDT, P., FIETHE, B., FUSELIER, S.A., GASC, S., GOMBOSI, T.I., HANSEN, K.C., HASSIG, M., JACKEL, A., KOPP, E., KORTH, A., LE ROY, L., MALL, U., MARTY, B., MOUSIS, O., OWEN, T., REME, H., SEMON, T., TZOU, C.-Y., WAITE, J.H., WURZ, P. (2015) Molecular nitrogen in comet 67P/Churyumov-Gerasimenko indicates a low formation temperature. *Science* 1–4, doi: 10.1126/science.aaa6100.
- RUBIN, M., ALTWEGG, K., BALSIGER, H., BAR-NUN, A., BERTHELIER, J., BRIOIS, C., CALMONTE, U., COMBI, M., DE KEYSER, J., FIETHE, B., FUSELIER, S.A., GASC, S., GOMBOSI, T.I., HANSEN, K.C., KOPP, E., KORTH, A., LAUFER, D., LE ROY, L., MALL, U., MARTY, B., MOUSIS, O. (2018) Krypton isotopes and noble gas abundances in the coma of comet 67P / Churyumov-Gerasimenko. *Science Advances* 4, eaar6297.
- RUBIN, M., BEKAERT, D.V., BROADLEY, M.W., DROZDOVSKAYA, M.N., WAMPFLER, S.F. (2019) Volatile Species in Comet 67P/Churyumov-Gerasimenko: Investigating the Link from the ISM to the Terrestrial Planets. *American Chemical Society Earth and Space Chemistry* 3, 1792–1811, doi: 10.1021/acsearthspacechem.9b00096.
- RYE, R., KUO, P.H., HOLLAND, H.D. (1995) Atmospheric carbon dioxide concentrations before 2.2 billion years ago. *Nature* 378, 603–605, doi: 10.1038/378603a0.
- SAGAN, C., KHARE, B.N. (1979) Tholins: organic chemistry of interstellar grains and gas. *Nature* 277, 102–107, doi: 10.1038/277102a0.
- SAGAN, C., CHYBA, C. (1997) The early faint sun paradox: Organic shielding of ultraviolet-labile greenhouse gases. *Science* 276, 1217–1221.
- SANO, Y., WAKITA, H. (1985) Geographical distribution of ³He/⁴He ratios in Japan: Implications for arc tectonics and incipient magmatism. *Journal of Geophysical Research* 90, 8729–8741.
- SANO, Y., MARTY, B. (1995) Origin of Carbon in Fumarolic Gas from Island Arcs. *Chemical Geology* 119, 265–274.
- SANO, Y., NAKAMURA, Y., WAKITA, H., URABE, A., TOMINAGA, T. (1984) Helium-3 emission related to volcanic activity. *Science*. 224, 150-151.
- SANO, Y., WAKITA, H., MAKIDE, Y., TOMINAGA, T. (1989) A ten-year decrease in the atmospheric helium isotope ratio possibly caused by human activity. *Geophysical Research Letters* 16, 1371–1374.



- SANO, Y., FURUKAWA, Y., TAKAHATA, N. (2010) Atmospheric helium isotope ratio: Possible temporal and spatial variations. *Geochimica et Cosmochimica Acta* 74, 4893–4901, doi: 10.1016/j.gca.2010.06.003.
- SARDA, P., STAUDACHER, T., ALLÈGRE, C.J. (1985) $^{40}\text{Ar}/^{36}\text{Ar}$ in MORB glasses : Constraints on atmosphere and mantle evolution. *Earth and Planetary Science Letters* 72, 357–375.
- SARDA, P., STAUDACHER, T., ALLÈGRE, C.J. (1988) Neon isotopes in submarine basalts. *Earth and Planetary Science Letters* 91, 73–88.
- SASAKI, S. (1990) The primary solar-type atmosphere surrounding the accreting Earth : H₂O-induced high surface temperature. In: Newson, H.E., Jones, J.H. (Eds.) *Origin of the Earth*. Oxford University, New York, 195–209.
- SCHIRRMESTER, B.E., DE VOS, J.M., ANTONELLI, A., BAGHERI, H.C. (2013) Evolution of multicellularity coincided with increased diversification of cyanobacteria and the Great Oxidation Event. *Proceedings of the National Academy of Sciences of the United States of America* 110, 1791–1796, doi: 10.1073/pnas.1209927110.
- SCHMITZ, B., FARLEY, K.A., GODERIS, S., HECK, P.R., BERGSTRÖM, S.M., BOSCHI, S., CLAEYS, P., DEBAILLE, V., DRONOV, A., GINNEKEN, M. VAN, HARPER, D.A.T., IQBAL, F., FRIBERG, J., LIAO, S. (2019) An extraterrestrial trigger for the mid-Ordovician ice age : Dust from the breakup of the L-chondrite parent body. *Science Advances* 5, eaax4184.
- SHCHEKA, S.S., KEPPLER, H. (2012) The origin of the terrestrial noble-gas signature. *Nature* 490, 531–534, doi: 10.1038/nature11506.
- SHU, F.H. (1997) X-rays and Fluctuating X-Winds from Protostars. *Science* 277, 1475–1479, doi: 10.1126/science.277.5331.1475.
- SIGNER, P., SUESS, H.E. (1963) Rare gases in the sun, in the atmosphere, and in meteorites. In: Geiss, J., Goldberg, E.D. (Eds.), *Earth Science and Meteorites*. North-Holland Publishing, Amsterdam, 241–272.
- SLEEP, N.H. (2007) Plate tectonics through time. In: Stevenson, D. (Ed.) *Treatise on Geophysics, Volume 9: evolution of the Earth*. Elsevier B.V. 145–170, doi: 10.1016/B978-044452748-6.00143-7.
- SLEEP, N.H., ZAHNLE, K.J., LUPU, R.E. (2014) Terrestrial aftermath of the Moon-forming impact. *Philosophical Transactions of the Royal Society A* 372: 20130172.
- SOM, S.M., CATLING, D.C., HARNMEIJER, J.P., POLIVKA, P.M., BUICK, R. (2012) Air density 2.7 billion years ago limited to less than twice modern levels by fossil raindrop imprints. *Nature* 484, 359–362, doi: 10.1038/nature10890.
- SOM, S.M., BUICK, R., HAGADORN, J.W., BLAKE, T.S., PERREAULT, J.M., HARNMEIJER, J.P., CATLING, D.C. (2016) Earth's air pressure 2.7 billion years ago constrained to less than half of modern levels. *Nature Geosciences* 9, 448–451, doi: 10.1038/ngeo2713.
- SRINIVASAN, B. (1976) Barites: anomalous xenon from spallation and neutron-induced reactions. *Earth and Planetary Science Letters* 31, 129–141, doi: 10.1016/0012-821X(76)90104-7.
- STAUDACHER, T., ALLÈGRE, C.J. (1982) Terrestrial xenology. *Earth and Planetary Science Letters* 60, 389–405.
- STUËKEN, E.E., KIPP, M.A., SCHWIETERMAN, E.W., JOHNSON, B., BUICK, R. (2016) Modeling pN₂ Through Geological Time: Implications for Planetary Climates and Atmospheric Biosignatures. *Astrobiology* 16, 949–963
- SWINDLE, T.D., PODOSEK, F.A. (1988) Iodine-Xenon Dating. In: Kerridge, J.F., Matthews, M.S. (Eds.) *Meteorites and the Early Solar System*. University of Arizona Press, Tuscon, Arizona, 1127–1146.
- SWINDLE, T.D., CAFFEE, M.W., HOHENBERG, C.M. (1986) Xenon and other noble gases in shergottites. *Geochimica et Cosmochimica Acta* 50, 1001–1015.



- TARDUNO, J.A., COTTRELL, R.D., BONO, R.K., ODA, H., DAVIS, W.J., FAYEK, M., ERVE, O. VAN 'T, NIMMO, F., HUANG, W., THERN, E.R., FEARN, S., MITRA, G., SMIRNOV, A. V., BLACKMAN, E.G. (2020) Paleomagnetism indicates that primary magnetite in zircon records a strong Hadean geodynamo. *Proceedings of the National Academy of Sciences of the United States of America* 117, 2309–2318, doi: 10.1073/pnas.1916553117.
- TARTESE, R., ANAND, M., BARNES, J.J., STARKEY, N.A., FRANCHI, I.A., SANO, Y. (2013) The abundance, distribution, and isotopic composition of Hydrogen in the Moon as revealed by basaltic lunar samples: Implications for the volatile inventory of the Moon. *Geochimica et Cosmochimica Acta* 122, 58–74.
- TAZIEFF, H. (1951) Cratères en Feu. Arthaud, Paris, 249 pp.
- THIEMENS, M.H., HEINDENREICH III, J.E. (1983) The Mass-Independent Fractionation of Oxygen : A Novel Isotope Effect and Its Possible Cosmochemical Implications. *Science* 219, 1073–1075.
- TOLSTIKHIN, I.N., O'NIONS, R.K. (1994) The Earth's missing xenon: A combination of early degassing and of rare gas loss from the atmosphere. *Chemical Geology* 115, 1–6, doi: 10.1016/0009-2541(94)90142-2.
- TORGENSEN, T. (1989) Terrestrial helium degassing fluxes and the atmospheric helium budget: Implications with respect to the degassing processes of continental crust. *Chemical Geology* 79, 1–14.
- TOUBOUL, M., KLEINE, T., BOURDON, B., PALME, H., WIELER, R. (2007) Late formation and prolonged differentiation of the Moon inferred from W isotopes in lunar metals. *Nature* 450, 1206–1209, doi: 10.1038/nature06428.
- TRIELOFF, M., KUNZ, J. (2005) Isotope systematics of noble gases in the Earth's mantle: possible sources of primordial isotopes and implications for mantle structure. *Physics of the Earth and Planetary Interiors* 148, 13–38.
- TU, L., JOHNSTONE, C.P., GÜDEL, M., LAMMER, H. (2015) The extreme ultraviolet and X-ray Sun in Time: High-energy evolutionary tracks of a solar-like star. *Astronomy and Astrophysics* 577, L3, doi: 10.1051/0004-6361/201526146.
- TUCKER, J.M., MUKHOPADHYAY, S. (2014). Evidence for multiple magma ocean outgassing and atmospheric loss episodes from mantle noble gases. *Earth and Planetary Science Letters* 393, 254–265, 10.1016/j.epsl.2014.02.050
- TUCKER, J.M., MUKHOPADHYAY, S., GONNERMANN, H.M. (2018) Reconstructing mantle carbon and noble gas contents from degassed mid-ocean ridge basalts. *Earth and Planetary Science Letters* 496, 108–119, doi: 10.1016/j.epsl.2018.05.024.
- TURNER, G. (1970) ⁴⁰Ar–³⁹Ar dating of lunar rock samples. *Science* 167, 466–468.
- TURNER G., MILLER J. A., GRASTY R. L. (1966) The thermal history of the Bruderheim meteorite. *Earth and Planetary Science Letters* 1, 155–165.
- VAN DISHOECK, E.F., HERBST, E., NEUFELD, D.A. (2013) Interstellar Water Chemistry: From Laboratory to Observations. *Chemical Reviews* 113, 9043–9085, doi: 10.1021/cr4003177.
- VON WEIZÄCKER, C.F. (1937) Über die Möglichkeit eines dualen-Zerfalls von Kalium. *Physikalische Zeitschrift* 38, 623–624 (in German).
- WEIERSHAUSER, L., SPOONER, E.T.C. (2005) Seafloor hydrothermal fluids , Ben Nevis area , Abitibi Greenstone Belt : Implications for Archean (~ 2.7 Ga) seawater properties. *Precambrian Research* 138, 89–123, doi: 10.1016/j.precamres.2005.04.001.
- WETHERILL, G.W. (1954) Variations in the Isotopic Abundances of Neon and Argon Extracted from Radioactive Minerals. *Physical Review* 96, 679–683, doi: 10.1103/PhysRev.96.679.
- WETHERILL, G.W. (1980) Formation of the terrestrial planets. *Annual Review of Astronomy and Astrophysics* 18, 77–113.
- WIELER, R. (2016) Do lunar and meteoritic archives record temporal variations in the composition of solar wind noble gases and nitrogen? A reassessment in the light of Genesis data. *Geochemistry* 74, 463–480.



- WIELER, R., HUMBERT, F., MARTY, B. (1999) Evidence for a predominantly non-solar origin of nitrogen in the lunar regolith revealed by single grain analyses. *Earth and Planetary Science Letters* 167, 47–60, doi: 10.1016/S0012-821X(99)00012-6.
- WIENS, R.C., BOCHSLER, P., BURNETT, D.S., WIMMER-SCHWEINGRUBER, R.F. (2004) Solar and solar wind isotopic compositions. *Earth and Planetary Science Letters* 222, 697–712.
- WILDE, S.A., VALLEY, J.W., PECK, W.H., GRAHAM, C.M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* 409, 175–178.
- WILLIAMS, C.D., MUKHOPADHYAY, S. (2019) Capture of nebular gases during Earth's accretion is preserved in deep-mantle neon. *Nature* 565, 78–81, doi: 10.1038/s41586-018-0771-1.
- WONG, M.H., ATREYA, S.K., MAHAFFY, P.N., FRANZ, H.B., MALESPIN, C., TRAINER, M.G., STERN, J.C., CONRAD, P.G., MANNING, H.L.K., PEPIN, R.O., BECKER, R.H., MCKAY, C.P., OWEN, T.C., NAVARRO-GONZÁLEZ, R., JONES, J.H., JAKOSKY, B.M., STEELE, A. (2013) Isotopes of nitrogen on Mars: Atmospheric measurements by Curiosity's mass spectrometer. *Geophysical Research Letters* 40, 6033–6037, doi: 10.1002/2013GL057840.
- YOKOCHI, R., MARTY, B. (2004) A determination of the neon isotopic composition of the deep mantle. *Earth and Planetary Science Letters* 225, 77–88.
- YOKOCHI, R., MARTY, B. (2005) Geochemical constraints on mantle dynamics in the Hadean. *Earth and Planetary Science Letters* 238, 17–30.
- ZAHNLE, K.J., CATLING, D.C., CLAIRE, M.W. (2013) The rise of oxygen and the hydrogen hourglass. *Chemical Geology* 362, 26–34, doi: 10.1016/j.chemgeo.2013.08.004.
- ZAHNLE, K.J., GACESA, M., CATLING, D.C. (2019) Strange messenger : A new history of hydrogen on Earth , as told by Xenon. *Geochimica et Cosmochimica Acta* 244, 56–85, doi: 10.1016/j.gca.2018.09.017.
- ZHU, L., LIU, H., PICKARD, C.J., ZOU, G., MA, Y. (2014) Reactions of xenon with iron and nickel are predicted in the Earth's inner core. *Nature Chemistry* 6, 644–648, doi: 10.1038/nchem.1925.
- ZIMMERMANN, L., BURNARD, P., MARTY, B., GABORIAUD, F. (2009) Laser ablation (193 nm), purification and determination of very low concentrations of solar wind nitrogen implanted in targets from the Genesis spacecraft. *Geostandards and Geoanalytical Research* 33, 183–194, doi: 10.1111/j.1751-908X.2009.00021.x.



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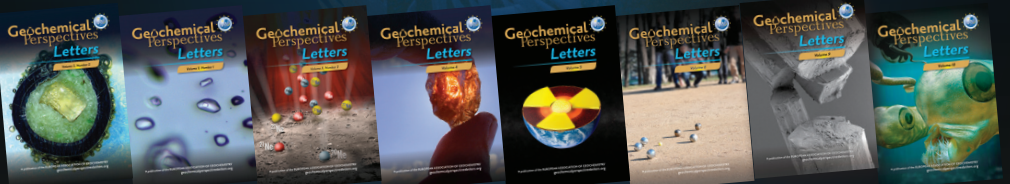
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