Geochemical Perspectives

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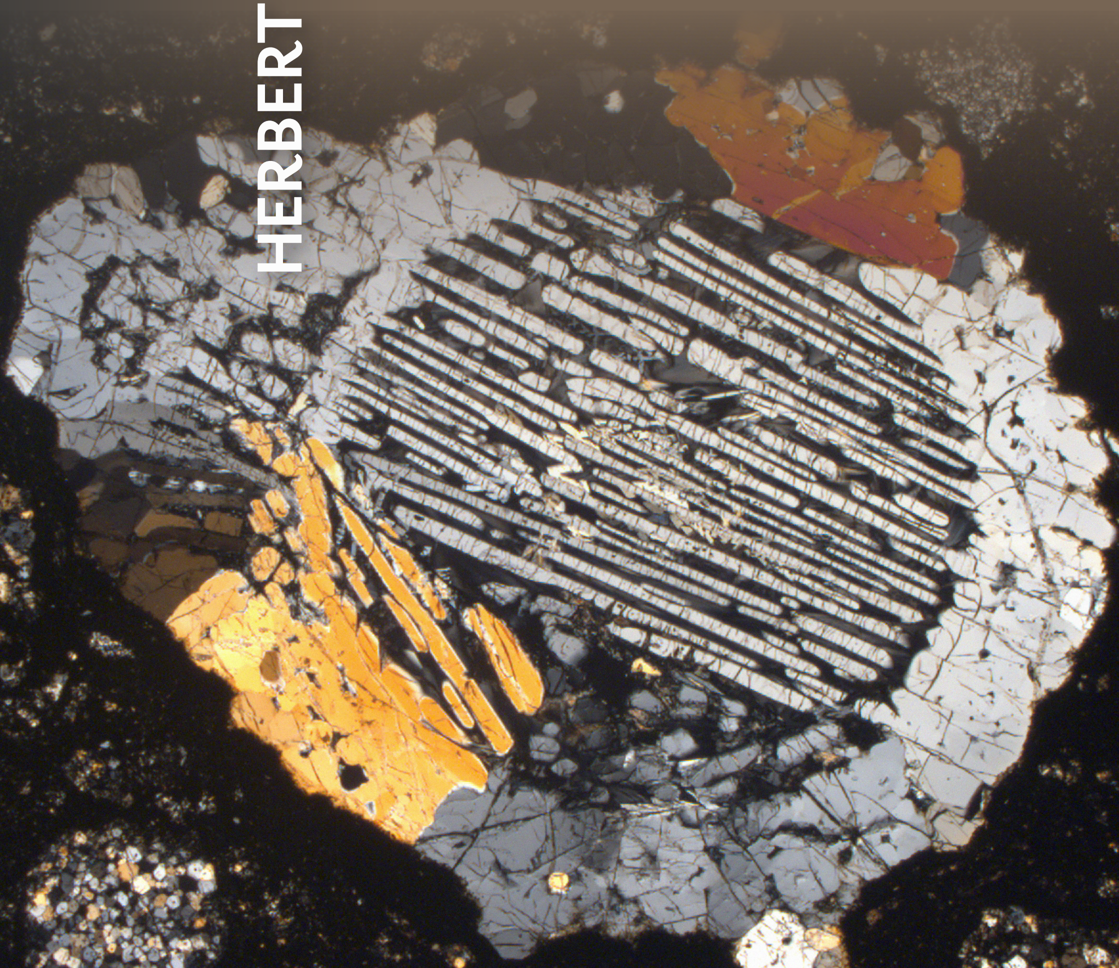
Cosmochemistry along the Rhine

HERBERT PALME



Geochemical Perspectives

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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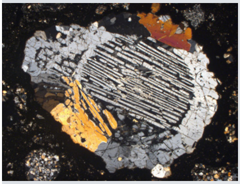

About the cover

Barred olivine chondrule from the Allende meteorite, in transmitted light. The chondrule is surrounded by a broad, coarse grained rim. The diameter of the object is about 2 mm.

Photo credit for the front and back cover:
J. Zipfel, Senckenberg, Frankfurt

CONTENTS

PREFACE

In the second half of the 19th century the cosmochemistry department of the Max-Planck-Institute for Chemistry in Mainz was one of the leading research institutions worldwide, studying the chemistry and evolution of meteorites and planets using multi-element chemical analyses. Many new and innovative ideas and concepts were developed under the leadership of Heinrich Wänke, director of the Department of Cosmochemistry since 1968. From 1971 on, I was actively participating in the research of the cosmochemistry department.

During the festivities of the 100th birthday of the Max-Planck-Institute for Chemistry in 2012, the scientific achievements of the cosmochemistry and also of the geochemistry departments were barely mentioned. I realised that, very soon, all of this will be forgotten. This made me decide to write up the history of Mainz cosmochemistry as I experienced it during the more than 20 years I spent in Mainz. Since I was deeply involved in the research of the cosmochemistry department I also describe here my own contributions to cosmochemistry. When I left Mainz in 1994 to take a position at the University of Cologne, I continued some of the work I had begun in Mainz and started new projects. What was initially planned as a history of the Mainz cosmochemistry evolved to some extent into a description of my own scientific career, which is inseparably connected with the evolution of cosmochemistry in Mainz and Cologne.

A major incentive for my research on meteorites and lunar rocks is the fascination of extraterrestrial materials, which Alexander von Humboldt expressed in his *Kosmos* from 1844.

Wir erhalten durch einen Meteorstein die einzig mögliche Berührung von etwas, das unserem Planeten fremd ist. Gewöhnt, alles Nichttellurische nur durch Messung, durch Rechnung, durch Vernunftschlüsse zu kennen, sind wir erstaunt, zu betasten, zu wiegen, zu zersetzen, was der Außenwelt angehört.

(Meteorite stones provide us with the only possibility of touching something foreign to our planet. Getting to know non-telluric materials by measuring, calculating, reasoning, we are amazed to finger, to weigh, to decompose what belongs to the outside world).

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COSMOCHEMISTRY ALONG THE RHINE

ABSTRACT

At the beginning of this paper I give a short description of the history of the Max-Planck-Institute for Chemistry in Mainz. I then describe my activities in cosmochemistry, from spring 1971 to 1994 at the Cosmochemistry Department of the Max-Planck-Institute for Chemistry under the directorship of Heinrich Wänke, and then from 1994 on at the University of Cologne. In 2008 I retired from the university and joined the meteorite group at the Senckenberg Research Institute in Frankfurt.

I started my job at the Max-Planck-Institute for Chemistry in spring of 1971. After some time I actively participated in the chemical analyses of lunar rocks and meteorites. I helped to improve analytical schemes, devised new analytical methods and participated in the interpretation. After some time I began to pursue my own cosmochemical projects. I studied, among other things, the behaviour of trace elements in the Moon, identified the host phase of refractory metals in Ca, Al-inclusions of Allende and identified the first ultra-refractory inclusion in the Ornans meteorite.

From 1976 to 1977 I spent a year in Chicago with Ed Anders and his group analysing trace elements with radiochemical neutron activation analysis in samples from the Moon and from terrestrial impact craters. After my return from Chicago I continued the crater work for some time. I further initiated routine analyses of terrestrial and meteorite samples, leading, among other things, to an improved estimate of the composition of the mantle of the Earth. I still worked together with Heinrich Wänke on the bulk composition of planets and various problems in cosmochemistry. We made the first analyses of the Acapulco meteorite, determined the chemistry of Rumuruti the only fall of the Rumurutiites, and produced early analyses on CH-chondrites.

In 1994 I took a position as professor of geochemistry and mineralogy at the University of Cologne. From then on I spent quite some time preparing lectures, but I was also completely independent and had the possibility to attract excellent students.

In Cologne I continued to work on meteorites and samples from the upper mantle of the Earth. I was lucky to fill a six year assistant position, first with Sumit Chakraborty and then with Frank Brenker. Astrid Holzheid and Andreas Pack were post-docs with me. All four are presently professors at various universities in Germany.

Among the projects I pursued with PhD students and post-docs were bulk analyses of carbonaceous chondrites, studies of forsteritic olivines in chondritic meteorites, solubilities of Fe, Ni and Co in silicate melts, partition coefficients of Ni and Co between metal and silicate melts at various temperatures, pressures and oxygen fugacities, solubilities of noble metals in silicate melts, studies of chondrules in CR-meteorites, the complementarity of chondrules and matrix in carbonaceous chondrites etc. These projects are related to fundamental questions in cosmochemistry. How did Earth's core form? What is the composition of the mantle of the Earth? Can we identify early formed forsterites as condensates from the solar nebula and why are they so widespread? How did chondrules form in the early solar nebula? How does the chemical compositon of chondritic meteorites fit with solar abundances? Some of these questions still keep me busy at the Senckenberg Forschungsinstitut und Naturmuseum in Frankfurt.

1. INTRODUCTION

In this contribution I want to describe my activities in the Max-Planck-Institute for Chemistry in Mainz and later in the Institute of Mineralogy at the University of Cologne. My field of activity is cosmochemistry. The term cosmochemistry as I use it throughout the paper implies the chemical and isotopic analysis of extraterrestrial matter. I will begin with a short history of the Max-Planck-Institute for Chemistry, followed by a discussion of the beginning, and the development of cosmochemistry in Germany during the second half of the 19th century. At this time the cosmochemistry and later the geochemistry departments of the Max-Planck-Institute for Chemistry in Mainz were widely considered to be the leading research institutions in geo- and cosmochemistry in Germany and among the most important worldwide. Both departments were closed by the Max-Planck-Society some years ago, cosmochemistry in 2005 and geochemistry in 2008 (Schiermeier, 2003).

The appointment of Friedrich Paneth as director at the Max-Planck-Institute for Chemistry in 1953 marked the beginning of cosmochemistry in Germany. Heinrich Wänke, a post-doc of Paneth in Durham (England), became director of the Department of Cosmochemistry in Mainz in 1968 and stayed at this position until his retirement in 1996. I joined the Max-Planck-Institute in Mainz in spring of 1971. In 1994 I took a position as professor of mineralogy and geochemistry at the University of Cologne. In 2008 I retired from this position and joined the Senckenberg Research Institute in Frankfurt as honorary scientific member.

In the following, I will first give a short overview of the history of the Max-Planck-Institute for Chemistry and its Department of Cosmochemistry followed by a short description of my early years in Mainz. I will then discuss the central role of neutron activation analysis in the cosmochemistry department and continue with descriptions of various projects that I worked on in Mainz and later in Cologne. The major emphasis is on the development of cosmochemistry in Mainz, which provided important stimulations for the growing cosmochemistry research in Germany and abroad.

I will also mention the major scientific achievements of Heinrich Wänke until I left Mainz. He shaped the structure and the research directions of the Department of Cosmochemistry and he introduced me to cosmochemistry. When I came to Mainz I had no background, neither in cosmochemistry, nor in geochemistry and mineralogy. During my first years I was very much under Heinrich Wänke's influence and I benefited tremendously from cooperation and extensive discussions with him.

I will not discuss projects in strictly chronological order, I will rather discuss research related to the Moon, Earth and meteorites. After I had left Mainz in 1994 Heinrich Wänke focused his attention on Mars. As I was not really involved in Wänke's Mars projects, I will not discuss them here. Also, I will not describe the activities of Heinrich Wänke before the time of the Apollo missions. Some information regarding the early activities of Heinrich Wänke is given in Palme (2012).

2. A SHORT HISTORY OF THE MAX-PLANCK-INSTITUTE FOR CHEMISTRY

The history of the Max-Planck-Institute for Chemistry (Max-Planck-Institut für Chemie) is described in several articles in a recently published book edited by Horst Kant and Carsten Reinhardt (Kant and Reinhardt, 2012).

In 1911 the Kaiser-Wilhelm-Gesellschaft zur Förderung der Wissenschaften (KWG- Kaiser-Wilhelm-Society for the Promotion of Sciences) was founded in Berlin. It was the progenitor of the Max-Planck-Society, a name given to the society in 1946, after the Second World War. One of the first institutes of the KWG was the Kaiser-Wilhelm-Institute (KWI) for Chemistry with its director Ernst Otto Beckmann, founded in 1912. Initially the KWI for Chemistry had three departments: inorganic and physical chemistry (Ernst Beckmann), organic chemistry (Richard Willstätter) and radioactivity (Otto Hahn). In the following years research activities focused increasingly on radioactivity and nuclear physics. In 1928 Otto Hahn became director of the KWI für Chemie. At this time the institute had two departments: (1) radioactivity with a chemistry section headed by Otto Hahn and a physics section headed by Lise Meitner and (2) organic chemistry with Kurt Hess as director. At long last, Lise Meitner, who had joined the institute in 1912 to work with Otto Hahn, had her own section. After the Nazis had come to power in 1933 the situation for Lise Meitener, who was of Jewish origin, became increasingly difficult, not least because Kurt Hess (the head of organic chemistry) was a fanatical Nazi. In 1938, after the occupation of Austria, Lise Meitner could no longer claim foreign nationality (Austrian). As a German citizen she was subject to the Nuremberg Laws of 1935 and, as she was denied emigration, she had to flee from Germany through the Netherlands to Sweden. Fortunately, Kurt Hess was not successful in informing the authorities of her planned departure (see Kant, 2012 and references). On December 19th 1939 Otto Hahn and Fritz Straßmann detected the fission of uranium by identifying barium in neutron bombarded uranium samples. In 1944 the institute moved from Berlin to Tailfingen (Württemberg), because the institute in Berlin-Dahlem had been partly destroyed by Allied bombardment. In 1946 Otto Hahn became the first president of the Max-Planck-Society after World War II and Josef Mattauch was appointed director of the Max-Planck-Institute for Chemistry. In 1949 the institute moved from Tailfingen to Mainz. At this time the institute had two departments: mass spectrometry (Mattauch) and nuclear chemistry (Fritz Straßmann). The new buildings were partly modified airforce barracks on the campus of the University of Mainz (Fig. 2.1). The official opening of the new institute facilities was in summer of 1956 (Fig. 2.2). Apparently, there were many fights between the chemists (Straßmann) and the physicists (Mattauch). Mattauch was very power-conscious. He was Austrian and described by insiders as having the charm of a Prussian and the organisational skills of a Viennese. In 1953 Mattauch finally gained the upper hand and Fritz Straßmann left the institute and took a position at the University of Mainz, in the Institute for Nuclear

Chemistry. He had been a professor at the university since 1946. On the initiative of Fritz Straßmann a TRIGA Mark II nuclear research reactor was set up at the campus of the university, in the immediate vicinity of the Max-Planck-Institute for Chemistry. The reactor was officially opened by Otto Hahn in 1967, just in time to prepare for neutron activation analysis of lunar samples. Up to 2005 the reactor was widely used for neutron activation analysis in the cosmochemistry department. Hundreds of terrestrial and extraterrestrial samples were irradiated and subsequently counted for characteristic gamma rays to determine the concentrations of major, minor and trace elements.

The search for a successor to Straßmann was difficult. On October 1st 1953 Friedrich Paneth was appointed director of the Department of Radiochemistry, shortly after his retirement as professor at the University of Durham. Paneth studied chemistry at the University of Vienna and then took various positions at universities and scientific institutions in Austria and Germany. In 1929 he was appointed professor of chemistry at the University of Königsberg. When Hitler became Chancellor of Germany on January 30th 1933, Friedrich Paneth was on a lecture tour in England and decided not to return to Germany. In 1939 he became professor at the University of Durham, where he established the Londonderry Laboratory for Radiochemistry. Paneth had a long-lasting interest in meteorites and spent much of his time in Durham trying to measure the age of iron meteorites with the U-He method. The rare gas instrument, that could measure small amounts of He, was transferred from Durham to Mainz. Heinrich Wänke, who had just graduated from the Radiuminstitut in Vienna with Professor Berta Karlik (the first female professor at the University of Vienna) had taken a position as assistant of Friedrich Paneth some eight months before Paneth left Durham. When Paneth decided to take the position in Mainz, Heinrich Wänke (his young assistant) went with him.

Figure 2.1 The main building of the Max-Planck-Institute for Chemistry in Mainz at around 1953 (source: Archiv, Max-Planck-Gesellschaft, Berlin-Dahlem).

Figure 2.2 Fritz Straßmann, Lise Meitner and Otto Hahn on the occasion of the official opening of the new Max-Planck-Institute in Mainz in 1956 (source: Archiv, Max-Planck-Gesellschaft, Berlin-Dahlem).

3. THE BEGINNING OF COSMOCHEMISTRY IN GERMANY

3.1 Early Efforts in Geochronology using Radiogenic Isotopes

When Lise Meitner left the Max-Planck-Institute for Chemistry in 1938, Otto Hahn hired Josef Mattauch (a specialist in mass spectrometry from the University of Vienna) to replace her. Mattauch had earlier analysed a Sr fraction which Hahn and his co-workers had separated from Canadian micas with high Rb and low Sr contents. Hahn wanted to know which of the two Rb isotopes is radioactive. He only knew that the element Rb is a β-emitter. Josef Mattauch could show that the Sr fractions from the Canadian micas were almost pure ^{87}Sr by using the double focusing mass spectrometer, which he and Richard Herzog had constructed (Hahn *et al.*, 1937; see also Reinhardt, 2012). Otto Hahn had realised the potential of the Rb-Sr method for geologic age determinations and he was fully aware of the potential of the U-Pb method (*e.g.*, Hahn and Walling, 1938). A chemist separating elements and a physicist operating a mass spectrometer were ideal prerequisites for further developing methods for dating of geological samples. But this did not occur. After the second world war Mattauch was absent from the institute for several years, because of health problems and Straßmann was acting director. Shortly after Mattauch had returned, Straßmann left the institute. The physicist and the chemist did not get along very well. The physicist, Josef Mattauch and his former student Heinrich Hintenberger dominated the Max-Planck-Institute for Chemistry. The lack of chemists in the institute had two consequences. Age dating was not further pursued, because it required careful chemical separations. The physicists tried to improve the precision of mass determinations rather than work on chemical separation schemes. The physicists also realised that the easiest way to use their mass spectrometers, aside from mass determinations, was the analysis of noble gases. No chemistry was involved, samples were just heated up to release the rare gases. Hintenberger's contributions to the Apollo programme were primarily noble gas analyses of lunar soils. The preference of physicists for noble gas analyses is a worldwide phenomenon. In Switzerland, for example, there was Peter Signer in Zürich focusing on light rare gases and Johannes Geiss in Bern with a preference for heavy rare gases, both are physicists. Heinrich Wänke was an exception. He was interested and knowledgeable in chemistry and he also worked on radiochemical separation schemes.

3.2 Cosmochemistry in Mainz

On October 1st 1953 Friedrich Paneth (1887-1958) became director at the Max-Planck-Institute for Chemistry (Fig. 3.1). There were several directors *at* the institute and Paneth was one of them, but there was only one director *of* the institute, Josef Mattauch. The day of Paneth's appointment may be considered as the beginning of cosmochemistry in Germany (the term *cosmochemistry* was invented by Harold Urey). The Max-Planck-Institute for Nuclear Physics (Max-Planck-Institut für Kernphysik) in Heidelberg also did research in cosmochemistry (rare gases, mineralogy, dating), but was not founded until 1958.

Paneth's interest in meteorites established a new direction of research at the Max-Planck-Institute for Chemistry. The age determination of iron meteorites, Paneth's pet project was, however, not pursued in Mainz. Heinrich Wänke was apparently not convinced of the method. In his interview with Ursula Marvin (Marvin, 2002) Heinrich Wänke mentioned his visit to Chicago to see Harold Urey. In his interview with Ursula Marvin he said: '*Eventually, Urey asked me: "By the way, does your boss, Paneth, still believe in those high uranium figures he has been reporting in iron meteorites?" I said: "Well, I think so." Urey responded: "Then you have to understand, my young friend, that this is hopeless; impossible. Uranium is a strictly lithophile element. It would never go into the metal phase in such concentrations."*'

Figure 3.1 Friedrich Fritz Paneth (with an uplifted finger), to his right Berta Karlik, to his left Otto Hahn, at around 1955.

In 1957 Paneth invited Friedrich Begemann to join his group in Mainz. Begemann had studied physics in Göttingen and had moved with Friedrich Houtermans from Göttingen to Bern, where he finished his PhD. In 1954 he took a post-doc position with Willard F. Libby at the Institute for Nuclear Studies of the University of Chicago. There he worked in Harold Urey's group on the distribution of tritium (^{3}H) in water and in the atmosphere of the Earth. In 1978 Friedrich Begemann became director at the Institute, following Heinrich Hintenberger, who had retired. Begemann was now head of the Department of Isotope Cosmology. One of the first things he did, after he had become director, was to dismantle the world's largest mass spectometer. The pet project of Mattauch and Hintenberger was supposed to improve the determination of atomic masses by a factor of 10. The construction of the mass spectrometer took more than 20 years. A huge amount of money was spent, but the mass spectrometer never produced any real data (see Reinhardt, 2012 for details).

In 1995 Friedrich Begemann retired but was still active in science for many more years.

In 1958 Paneth died unexpectedly on a trip to Vienna after his 70th birthday (Fig. 3.2). The sudden death of Friedrich Paneth caused problems for Heinrich Wänke and Friedrich Begemann, who had joined the cosmochemistry department of the institute in 1958.

Figure 3.2 A dinner party on the occasion of the 70th birthday of Friedrich Paneth. Friedrich Paneth and Heinrich Wänke are sitting at a round table in front of the rows of seats in the lecture hall of the Max-Planck-Institute for Chemistry in Mainz. To the right of Wänke are Hermann Wäffler (1910-2003) and Josef Mattauch (1895-1976).

Wänke described the situation in his interview with Ursula Marvin (Marvin, 2002): *'And this created a problem because, at that time, if your boss passed away, this was very, very bad for a young scientist anywhere in Europe. It was a problem for me and also for Friedrich Begemann who was in Mainz by that time. We two sat together and discussed what we should do. Of course, we could try to get positions at Heidelberg or at Bern, where there were groups working on such things as we were, but it was Fred who came up with the best idea. He said it probably would take years for the Max-Planck Society to find a successor for Paneth, and perhaps we should just try to stay for a while.'*

The director Josef Mattauch let Wänke and Begemann stay at the institute. The vacant director's position was offered to Hans Suess, who finally declined, apparently his wife did not want to stay in the provincial town of Mainz. After several years of successful research, Heinrich Wänke was appointed Scientific Member (Wissenschaftliches Mitglied) of the Max-Planck-Society and in 1968 he became director of the Department of Cosmochemistry at the Max-Planck-Institute for Chemistry. He remained at this position until his retirement in 1996, but he was still active in research until 2008, when he finally left the institute.

3.3 Cosmochemistry in other German Institutions

The extent of cosmochemical research in Germany in 1969 can be judged from the German research groups receiving lunar samples for analysis from NASA. Each research group was represented by a Principal Investigator (PI), who was responsible for proper use of the lunar samples. In Germany there were six PIs: Heinrich Wänke and Heinrich Hintenberger from the Max-Planck-Insitute for Chemistry in Mainz, Josef Zähringer and Paul Ramdohr from the Max-Planck-Institute for Nuclear Physics in Heidelberg, Wofgang von Engelhardt from the University of Tübingen and Wilfried Herr from the University of Cologne.

3.3.1 Max-Planck-Institute for Nuclear Physics in Heidelberg

On the initiative of Wolfgang Gentner the Max-Planck-Institute for Nuclear Physics in Heidelberg was founded in 1958. Wolfgang Gentner was a prominent German experimental nuclear physicist, who was involved in the foundation of CERN. Gentner had, besides nuclear physics, a strong interest in cosmochemistry. He asked Josef Zähringer (his PhD student from the University of Freiburg) to join him and pursue his work on K-Ar age dating of meteorites in Heidelberg. Hugo Fechtig and Hans-Joachim Lippolt were also among the first scientists at the new Max-Planck-Institute hired by Wolfgang Gentner. As director of the Max-Planck-Institute for Nuclear Physics Gentner began to collect meteorites, and build a laboratory for cosmochemistry with a mass spectrometer and a low-level laboratory to count cosmic ray induced radionuclei in meteorites. He offered a position to Paul Ramdohr to join his institute after he had retired from his professorship at the University of Heidelberg. In 1958, Ramdohr was a famous German mineralogist and ore deposit researcher. Only after his retirement from university did Paul Ramdohr start to work on meteorites. In 1973 he published a book with the title *'Opaque Minerals in Stony Meteorites'*, a standard reference for anybody studying opaque minerals in meteorites. In 1963 Ahmed El Goresy (Ramdohr's last and best student) took a position at the cosmochemistry department of the Max-Planck-Institute for Nuclear Physics. After his retirement in Heidelberg in 1989, Ahmed worked in Mainz for 6 years and then moved to Bayreuth. In 2013 he was awarded the Leonard Medal of the Meteoritical Society. Early on I had contact with Ahmed and we published several papers together.

I also remember talking to Paul Ramdohr on occasional visits to Heidelberg. In 1975 I travelled together with Paul Ramdohr to the Meteoritical Society Meeting in Tours. At this time Ramdohr was 85 years old.

A severe setback for the cosmochemistry in Heidelberg was the fatal traffic accident of Josef Zähringer in 1970. Nevertheless cosmochemistry in Heidelberg remained strong with a variety of research groups, among them: Till Kirsten (rare gases, ^{40}Ar-^{39}Ar dating), a cosmic dust group (Hugo Fechtig, Eberhard Grün), crater counting (Gerhard Neukum) and the strong mineralogy-petrology group with Paul Ramdohr and Ahmed El Goresy. Chemical analyses of meteorites and lunar samples were performed by Otto Müller and Ernst Pernicka. Later Heinrich J. Völk did theoretical studies of the early solar nebula, in part together with Gregor Morfill and Werner Tscharnuter. The Heidelberg cosmochemistry group was always seen as competition for Mainz, although their research was different from Mainz; more physical and less chemical. The main research activities of the Heidelberg institute were still in nuclear physics.

3.3.2 Impact research at the University of Tübingen

In 1960 Gene Shoemaker discovered coesite, a high pressure phase of quartz, in the suevite from the Ries crater, Nördlingen. This finding contradicted the hypothesis of a volcanic origin of the Ries crater, prevalent at the time. Wolf von Engelhardt (professor of mineralogy at the University of Tübingen) immediately got interested and began to study samples from the Ries crater in search of mineralogical pressure indicators. His students had to work on all kinds of Ries samples to find more shock indicators. Two of his post-docs, Dieter Stöffler and Fred Hörz, joined him in high pressure research. When the availability of lunar samples was announced Wolf von Engelhardt wrote a proposal to DFG (Deutsche Forschungsgemeinschaft-German Science Foundationton) to study shock effects in lunar samples. The proposal was accepted and Wolf von Engelhardt and Dieter Stöffler began to work on lunar samples, supported by Wolfgang Müller and Jörg Arndt. By this time, Fred Hörz had a position with NASA in Houston.

In 1974 Dieter Stöffler was appointed professor of mineralogy at the University of Münster, where he continued to work on lunar samples. In 1968 he established the Institute of Planetology at the University of Münster, the only such institute in Germany. In addition to Dieter Stöffler, Tilman Spohn (a planetary geophysicist) was appointed professor in the same institute. In 1993 Dieter Stöffler took a position at the Natural History Museum in Berlin. Elmar Jessberger succeeded Dieter Stöfller in Münster and after Jessberger's retirement, Thorsten Kleine took this position in 2009. The second professor position at the Institute of Planetology has, since 2006, been occupied by Harald Hiesinger, a former student of Gerhard Neukum. Hiesinger's research focuses on planetary surfaces.

During Stöffler's time in Münster we had a number of collaborations with him and his group. We provided the chemical data and they did the mineralogy and petrology of lunar rocks and meteorites that we had analysed. We wrote several papers together and I visited Münster quite frequently. I had, and still have, a particularly good relationship with Addi Bischoff (a student of Dieter Stöffler) who still is in Münster. Together, we produced several highly cited papers on CR and CH chondrites as well as on Ca, Al-rich inclusions (see below). In Mainz we never considered the Münster people as competitors. They rather complemented our chemical data with mineralogical characterisations and mineral analyses.

3.3.3 Cosmochemistry in Cologne

Wilfried Herr was a nuclear chemist, who worked together with Fritz Straßmann in the Department of Radiochemistry at the Max-Planck-Institute in Mainz. When Straßmann left the Max-Planck-Institute in 1953, Wilfried Herr joined Mattauch's mass spectrometry department. In 1955 he proposed the Re-Os dating method (Herr and Merz, 1955). In this paper the isotopic composition of Os was determined with neutron activation. In 1958 the Institute of Nuclear Chemistry was established at the University of Cologne and Wilfried Herr was appointed director of the institute. He primarily concentrated his efforts on the analysis of cosmogenic nuclei, such as ^{53}Mn, but he also worked on thermoluminescence and nuclear tracks. At one point Wilfried Herr started in rare gas analysis. He acquired a rare gas mass spectrometer and hired W.A. Kaiser, a rare gas specialist. But the cooperation of Herr and Kaiser did not last very long. After Herr's retirement in 1985 the institute became part of the Department of Biochemistry, but was still active in the analysis of cosmogenic nuclei in meteorites. Ulrich Herpers was leading the group of cosmochemists. Peter Englert, Rolf Michel and Silke Merchel among others, did their PhD work in this institute.

4. MY START IN MAINZ

In spring 1971 I joined the cosmochemistry group at the Max-Planck Institute in Mainz. Rudolf Rieder (an assistant to Heinrich Wänke in Mainz) had decided to go back to Vienna, his hometown. Wänke asked the director of the Institut für Radiumforschung und Kernphysik in Vienna, Prof. Berta Karlik, for a replacement from her institute, which he had graduated from in 1952. As I had just finished my PhD in nuclear physics, Prof. Karlik mentioned to me the possibility of taking a job in Mainz. At the time I was very interested in nuclear physics and intended to do a post-doc outside Austria. I wrote several letters to nuclear physics research institutions and universities in the US and England applying for a post-doc position. I was not successful, most of the answers I received pointed out that money for nuclear physics research was severely cut and personnel reduced. I realised that there was no future in this area and decided to have a closer look at the job in Mainz. After a visit to Mainz I decided to take the job, as this was also a possibility to escape a 9 month military service in Austria. In addition, I was supposed to work on radiogenic isotopes, produced by the interaction of cosmic rays with meteorites and lunar surface rocks and soils and I thought I could use my previous experience in nuclear physics. As my wife had finished her studies of slavonic languages in Vienna at the same time, we moved to Mainz in spring of 1971.

In 1971 the Max-Planck-Institute in Mainz had four departments: (1) mass spectrometry (Hintenberger), (2) nuclear physics (Wäffler), (3) atmospheric chemistry (Junge) and (4) cosmochemistry (Wänke). At the time the Max-Planck-Institute had two main buildings for three departments and a mechanical workshop building, shown in Figure 4.1. Part of the Nuclear Physics was later replaced by the building of the atmospheric chemistry department at the top on Figure 4.1. This was the time after the Apollo 14 mission had been successfully completed. There was an enormous enthusiasm in Wänke's group and in the rest of the institute. They were all very proud that the Max-Planck-Institute had received so much lunar material for investigation. I was ignorant about every aspect of the research that was done on lunar samples and meteorites. I started to work in Begemann's group with Emil Jagoutz, who had come to Mainz a few years earlier and with Else Vilcsek, a chemist from Vienna who had worked in the institute for a couple of years. We did γ- and β-counting of ^{26}Al, ^{22}Na, ^{36}Cl and ^{39}Ar, which required a bit of chemistry. At this time many groups worldwide studied radionuclides in rocks and soils on the lunar surface. Today the interaction of cosmic rays with planetary surfaces is pretty well understood and cosmic ray exposure ages can be calculated from cosmic ray produced nuclei. The activities for research on cosmic ray products in meteorites and lunar rocks declined in Mainz (and everywhere else) and I did not see a great future in this kind of research. I was beginning to get more interested in the chemical analysis of lunar samples and meteorites and the interpretation of the results. I thought a lot about a change in research activities and finally decided to leave cosmic rays. Wänke consented and I shifted my main activities to neutron activation analysis (NAA). In retrospect, I think it was the right decision. The study of the interior of planets and planetesimals seemed to be more interesting than the response of a thin planetary crust to the exposure of cosmic rays.

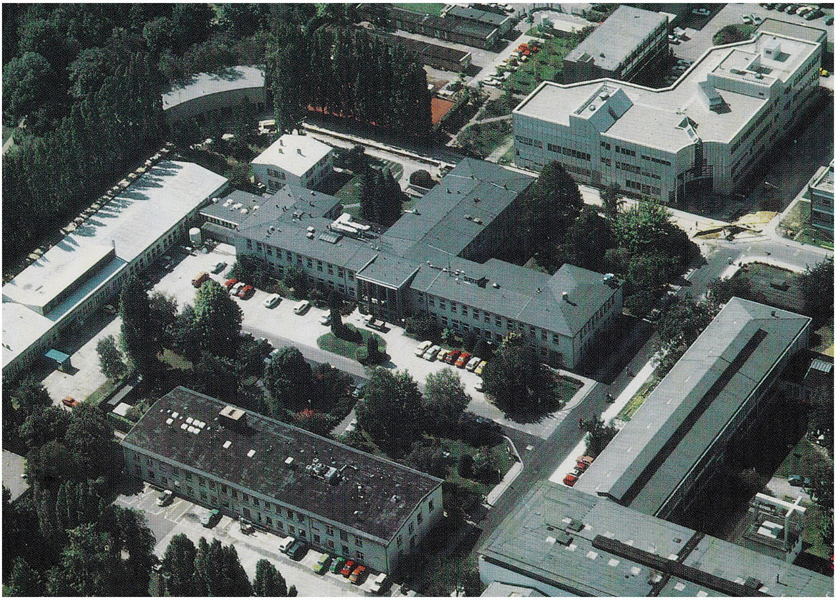

Figure 4.1 The Max-Planck-Institute for Chemistry on the campus of the University of Mainz at around 1987. The main building is in the middle. In the building below was Friedrich Begemann's Department of Isotope Cosmology and later parts of Al Hofmann's Department of Geochemistry. The building on the left side was the mechanical workshop. In the rear the building of the atmospheric chemistry department is visible. It was finished in 1985 and in 2012 the Max-Planck-Institute moved to a new building about 1 km away from the location shown here. The four Max-Planck buildings in the figure are presently deserted (source: Archiv, Max-Planck-Gesellschaft, Berlin-Dahlem).

Nevertheless, the basis for understanding the interaction of cosmic rays with matter was established by experimental and theoretical work during the years after Apollo 11. Nowadays, with high precision isotope analyses, cosmic ray produced nuclei have become important again. A good example is the neutron capture of ^{181}Ta which produces ^{182}W (a decay product of ^{182}Ta) and thus disturbs the Hf-W dating system, which is based on the decay of ^{182}Hf to ^{182}W (Leya *et al.*, 2000). Also, one should not forget that the present analyses of terrestrial samples for ^{26}Al and other radionuclides with accelerator mass spectrometry (AMS) are based on early meteorite and lunar work. Nobody would analyse ^{26}Al in a terrestrial sample, if it were not known that meteorites contain substantial amounts of ^{26}Al. The shielding of cosmic rays by the Earth's magnetic field is very strong, but the residual flux of protons is still high enough to allow dating of surfaces with the very sensitive AMS (Accelerator Mass Spectrometry), a method unknown at the time of the Apollo missions. A similar progress is apparent in ^{14}C dating, where AMS analyses are orders of magnitude more sensitive than the traditional β-counting.

5. THE CENTRAL ROLE OF NEUTRON ACTIVATION ANALYSIS

5.1 Thermal Neutron Activation Analysis

During the 1960s, before Apollo 11, Heinrich Wänke and his group had begun to set up radiochemical procedures for trace element analyses with neutron activation. They tested their methods with analyses of meteorites. With the construction and easy availability of the TRIGA low power research reactors, neutron activation had become the most important tool for chemical analyses of small samples. The TRIGA reactors were constructed in the US in the 1950s. They are inherently safe, because they have a negative temperature coefficient of reactivity, meaning that as the temperature of the core increases, the reactivity rapidly decreases, making a meltdown impossible. The neutron flux is, with a thermal neutron flux of 3.7 x 10^{11} neutrons/second/cm^2, very low and very constant over many years as there is very little ^{235}U used up by fission, implying low heat production. These reactors are ideal for neutron activation analysis (NAA). In NAA samples are exposed to thermal neutrons and neutron-rich nuclei are produced by neutron capture. Some nuclei are radioactive and decay with various half lives whereby they release γ-rays with characteristic energies. The number of γ-rays is proprtional to the number of nuclei of a specific isotope present in the sample. The NaI(Tl)-scintillation crystals used at the time for γ-counting had poor energy resolution, which required extensive radiochemical procedures. With the advent of a new generation of semi-conducting detectors (Li-drifted Ge crystals) for γ counting, a powerful new tool was available for NAA. The new large volume, Li-drifted Ge detectors had high energy resolution and high efficiency. It was now possible to analyse samples without chemical dissolution and isolation of elements. This variant of NAA is called instrumental neutron activation analysis (INNA) in contrast to radiochemical neutron activation analysis (RNAA), where samples are chemically processed after neutron activation. The concentrations of up to 40 elements can be determined with instrumental (non-chemical) analysis of bulk rock samples. In Mainz and other places radiochemical procedures were used for the analyses of some rare elements. The group of Ed Anders at the University of Chicago did exclusively radiochemical analyses for very rare elements such as Ag, Bi, Br, Cd, Cs, Te, U (*e.g.*, Keays *et al.*, 1974). Roman Schmitt's group at Oregon State University started in the 1960s with instrumental neutron activation analysis. They analysed a large number of meteorites and their components (*e.g.*, Osborn *et al.*, 1978) for Mn, Fe, Na, Sc, Cr, Co, Ni, Ir. Later Roman Schmitt and his group also applied radiochemical procedures, in particular for the determination of REE concentrations. And there was the group of John Wasson at UCLA, who made extensive use of neutron activation, initially with radiochemistry, later with both instrumental and radiochemical analyses. There were, of course, many more groups working with neutron activation analysis, but they were less important for cosmochemistry.

The sensitivity of elements for NAA is, besides the number of target nuclei of an element (which are proportional to the concentration of an element), dependent on several nuclear properties that do not scale with abundance. In particular the neutron capture cross section of the target nucleus and the half life and decay scheme of the radioactive, neutron-rich nuclei produced by neutron irradiation are important parameters. Some elements are particularly well suited for NAA, for others the method does not work at all. For example, the rare element Ir is very sensitive to NAA, while the abundant element Si cannot be determined by NAA. The analysis of Mg and Al, both with short-lived radionuclides requires neutron irradiation of a short duration.

5.2 14 MeV Neutron Activation Analysis

Several institutions, including the cosmochemistry department in Mainz had set up 14 MeV neutron generators for the analysis of major elements that could not be determined by neutron activation analysis, primarily oxygen and silicon but also Al and Mg. The accelerator was based on the $^2H + ^3H = ^4He + n$ reaction. Because the reaction is strongly exothermic, a 200 KeV accelerator of deuterons is sufficient to produce 14 MeV neutrons. That the accelerators require radioactive tritium (^3H) for operation was very problematic and ultimately led to the extinction of these instruments for analytical purposes. At the beginning of the Apollo missions the 14 MeV generator in Mainz was regularly used for the analysis of lunar and meteoritic samples, primarily for determining the concentrations of O, Mg, Al and Si. It was a particularly useful method for determining the total amounts of oxygen and silicon (Teschke and Wänke, 1974).

5.3 My Participation

I was actively participating in the analyses of lunar samples, which I found very exciting. Initially, fast and thermal instrumental neutron activation procedures were applied to lunar samples. For rare elements such as W, Ge, REE *etc*. radiochemical procedures had been developed. For Li and halogens special procedures were used. Descriptions of analytical methods are summarised in Wänke *et al.* (1970a, 1977a) and Dreibus *et al.* (1977). After some time the 14 MeV deuteron accelerator used for major element analysis was replaced by X-ray fluorescence analysis and the thermal neutron analysis of short lived radionuclides, such as ^{28}Al for the Al analysis and a few other elements (in particular Mg, V, and Ti) were added. As the TRIGA reactor was only about 200 metres away from the Max-Planck-Institute, we carried the radioactive samples, after a three minutes irradiation with thermal neutrons, in small lead containers from the reactor to our counting systems at the institute. The challenge was to get enough counts from the decay of ^{28}Al with 2.25 minutes half life.

The first important goal was to produce good data. If the data were not accurate enough one was excluded by NASA from receiving samples from later Apollo missions, which happened to several of the principal investigators of Apollo 11 samples. It was therefore important to compare results with other groups applying different techniques. In this way we could continually improve accuracy and precision of our analyses. Particularly important as reference samples were lunar soils such as 10084 (Apollo 11) and 14361 (Apollo 14), which were widely distributed by NASA. The soil samples seemed to be fairly homogeneous in chemical and isotopic composition.

The Department of Cosmochemistry with Heinrich Wänke as director, received samples from all landing sites and later from all Russian LUNA missions. The analyses of lunar rocks and the interpretation of the results was the major activity of the Department of Cosmochemistry in the 1970s. When I joined the cosmochemistry group in late spring 1971, samples from Apollo 11 and 12 had been analysed and Apollo 14 samples were distributed. About a year later I started to work with neutron activation. Each year a paper reporting the new analytical results was published in the *Proceedings of the Lunar Science Conference* (from 1978 on it was the Lunar and Planetary Science Conference). Besides a wealth of high quality analytical data these papers also contained interpretations and discussions of a more general nature. In preparation of the Proceedings papers I had numerous lengthy and fruitful discussions with Heinrich Wänke. These discussions and occasionally disputes formed the basis of my knowledge and understanding of cosmochemistry. Heinrich Wänke's ability to quickly comprehend the essence of a problem and immediately propose more or less detailed solutions was impressive. Some of the success of the cosmochemistry group was that neither Wänke nor I were geoscientists. We approached problems from a physicists' point of view, often neglecting mineralogical and geological constraints, which made things easier, but caused problems for reviewers of our papers. There was in fact a mineralogist in our group, Frank Wlotzka and later a geologist, Emil Jagoutz (who graduated from the University of Mainz while working in the cosmochemistry group). Also Gerhard Brey, who joined the group in 1978, had a geology background. But Frank Wlotzka, Emil Jagoutz and Gerhard Brey had worked on their own projects for most of the time.

5.4 My Early Projects

As time went on I had more of my own projects and cooperated less in Heinrich Wänke's projects, a natural evolution. Nevertheless, in many cases I discussed problems with his research projects with him and *vice versa*. In 1984 I did the habilitation for geosciences at the University of Mainz, which officially enabled me to advise students with their diploma theses and their PhD work. Within the framework of my habilitation I had to give a talk, which was entitled "*Die chemische Zusammensetzung des Erdmantels*" (The chemical composition of Earth's mantle), and, in addition, I had to give an "Antrittsvorlesung" (inaugural lecture) for which I chose the title *"Über die kosmischen Häufigkeiten der Elemente"* (On the cosmic abundances of elements). Apparently these two subjects kept me busy until my retirement and later. Each semester I also had to give a lecture at the university. But the teaching load was very limited. Among others, Katharina Lodders and Jutta Zipfel were my students. Later, both did their PhDs under my supervision. Stephan Weinbruch, now professor at the Technische Hochschule Darmstadt also attended my lectures. He had three PhD advisers; Ahmed El Goresy, Ernst Zinner and I. He travelled frequently between Heidelberg, Mainz and St. Louis.

In 1994 I left the Max-Planck-Institute in Mainz and took a position as professor of mineralogy and geochemistry at the University of Cologne. Here I continued to work on problems I had started earlier in Mainz and I also began some new research programmes. But in addition, I had to give lectures on various subjects in geochemistry, cosmochemistry and mineralogy. Since I had never studied geosciences at a university, I had to spend a fairly large amount of time preparing my lectures adequately.

Although my position at Mainz was permanent, there was no way to advance to a higher level within the system. This is typical of the Max-Planck system. There is a very powerful director and a few steps below are the scientific assistants. Since Heinrich Wänke was very generous about these issues, Emil Jagoutz, Gerhard Brey and I could do more or less whatever we wanted. In the end we had our own groups, even our own small budgets. But, of course there was always a formal dependence on the director.

5.4.1 Zr and other trace elements

After I had begun to participate in neutron activation, I realised that activation analysis with 14 MeV neutrons was a good method for determining Zr, Nb and Y concentrations. The concentrations of these elements were determined in some lunar samples with 14 MeV neutron activation analysis (*e.g.*, Wänke *et al.*, 1975).

During this work I came across the papers of Bill Ehmann and his group. They worried about Zr and Hf contents and the Zr/Hf ratios in terrestrial and extraterrestrial samples. This ratio is important as both elements are chemically very similar and one would expect little variation of this ratio in chondritic meteorites as well as in differentiated rocks. In a paper by Ehmann and Rebagay (1970) the authors had determined Zr and Hf concentrations of chondritic meteorites. For a number of reasons, I concluded that the concentrations reported by these authors were far too high. In their contribution to the famous and very influential *Handbook of Elemental Abundances in Meteorites* by Brian Mason (1971), Ehmann and Rebagay (1971) list 9 and 11 ppm Zr and 0.32 ppm Hf for CI chondrites, about a factor of three higher than presently accepted CI chondrite concentrations. Radiochemistry of Zr is difficult and has to be corrected for radioactive Zr isotopes produced by fission of U. The 14 MeV accelerator seemed to be the right instrument. At high mass numbers (n, 2n) reactions dominate and neutron-poor radioactive isotopes are produced, in contrast to thermal neutron activation where radioactive neutron-rich isotopes dominate. This offered new possibilities. I irradiated two samples of Orgueil for an unusually long period of 48 hours, together with appropriate standards, which is not trivial because the neutron source is basically a point source. In the end I could determine the concentrations of Zr, Y and some other trace elements in the two Orgueil samples. In the two samples I obtained 3.65 ± 0.7 and 4.3 ± 0.5 Zr and 1.55 ± 0.3 ppm Y. The presently best estimates are 3.63 ± 0.2 ppm Zr and 1.46 ± 0.7 ppm Y, well within the range of my earlier analyses (Palme *et al.*, 2014a). This was my first independent work in Mainz. I presented the results at a conference in Vienna and they were published in a book (Palme, 1974).

For some time we continued to do analyses of Zr, Nb and Y in lunar samples (see Wänke *et al.*, 1975) with 14 MeV neutrons. In combination with Hf and Ta, which were determined with thermal neutron anylysis, I found significant variations in Zr/Hf and Nb/Ta ratios between KREEP and Apollo 11 and 17 basalts (Wänke *et al.*,1975). The ratios of the two 'geochemical twins', Zr, Hf and Nb, Ta (Münker *et al.*, 2003) were assumed to stay constant during magmatic fractionations. Münker *et al.* (2003) found very similar variations in lunar samples. In addition, they reported variations of these ratios in Earth and Mars. Their analyses were done with higher precision, using isotope dilution and plasma source mass spectrometry.

The 14 MeV neutron activation procedure was, in the end, unsuitable for routine analyses. It was increasingly difficult to get tritium targets for the accelerator and handling of tritium became extremely difficult in view of more stringent radiation safety laws.

5.4.2 γ-activation anlysis

At the same time there was a 200 MeV electron accelerator for nuclear research at the campus of the University of Mainz. The accelerator was jointly run by the University and the Max-Planck-Institute. The high energy γ-rays (Bremsstrahlung) could be used for γ-activation analysis. Again neutron-poor radioactive nuclei were produced with sometimes useful decay schemes. After some testing I analysed a large Ca, Al-rich inclusion (see below) for Zr, Nb and Y and a number of lunar samples were anlysed for the same elements. The facility was also unsuitable for routine analyses.

5.5 Hildegard Baddenhausen and Bernhard Spettel

When I came to Mainz, Hildegard Baddenhausen and Bernhard Spettel were the two technicians working exclusively for Heinrich Wänke (Figs. 5.1 and 5.2). They were responsible for the chemical analyses. Hildegard Baddenhausen, an experienced chemist, had earlier worked with Otto Hahn. Heinrich Wänke and Hildegard Baddenhausen had set up the chemical separation schemes after neutron irradiation. Bernhard Spettel was employed by Fritz Paneth in 1957. He initially operated the rare gas separation schemes and was later responsible for instrumental neutron activation analysis, but his contribution to radiochemistry was also essential.

Figure 5.1 Hildegard Baddenhausen and Heinrich Wänke.

I worked closely with both Hildegard Baddenhausen and Bernhard Spettel, and with the latter I had a very close relationship. During my stay in Mainz I had almost daily contact with Bernhard. We spent hours discussing improvements in analytics, looked at results of recent analyses, tried to create new plots and discussed general scientific problems in cosmochemistry. Bernhard was not only interested in analytics, he also had a good knowledge of current scientific issues in cosmochemistry. Bernhard was extremely conscientious, competent and very helpful. He would come in very late in the morning and often stay until after midnight. He changed samples for γ-counting on the various detectors and did most of the data reduction. He only released final data after carefully checking the individual countings. He and Hildegard Baddenhausen were often co-authors of papers produced from Wänke's group. The two technicians often participated in Meteoritical Society meetings and other conferences. Heinrich Wänke knew how important they were for his operation.

Figure 5.2 Bernhard Spettel.

In those days accuracy and precision was an important issue. We spent much time improving procedures, preparing standards, analysing standard rocks and comparing our data with literature data obtained with other analytical methods.

I should also mention here Hartwig Kruse, who did computer programming for many years. He was so good at it, that I gave up writing programmes myself, which in the end was not good for me as I lost the ability to write programmes myself.

An invaluable helper with technical questions was Joachim Huth, who was there before I had arrived. Well known to all visitors was Friedl Künstler, who prepared thin sections for the electron microprobe work for the geochemistry and cosmochemistry departments. He was constantly thinking how to improve his facilities and he liked it when people came with unconventional problems. He was so skilled that many visitors wanted to have thin sections prepared by him long after they had left Mainz.

6. THE MOON

6.1 Lunar Samples in Mainz: First Results

The methods for analysing meteorite samples had been developed by Heinrich Wänke (Fig. 6.1) and his coworkers in the 1960s, in part I suspect, in the hope of receiving samples from the Apollo missions by demonstrating analytical competence. The Max-Planck-Institute for Chemistry in Mainz sent 12 proposals to NASA, seven of which were accepted. In addition to chemical analytics, there were also proposals to study rare gases (Hintenberger) and cosmic ray produced nuclei (Begemann). Two months after the return of Apollo 11 Hans Voshage (a scientist working with Heinrich Hintenberger) travelled to Houston and picked up 105.9 grams of lunar samples designated for Mainz. On the following weekend samples were shown to the public at the Max-Planck-Institute. Hundreds of citizens from Mainz took the chance to have a look at the samples from the Moon.

Samples were quickly analysed to present the first results at the Lunar Science Conference in Houston in January 1970. There were many stories told about the exchange of data among scientists travelling to the conference. Nobody knew if their data were correct and there were apparently many last minute changes after discussions with other groups.

On January 30th 1970, the first publications of the results of investigations of lunar samples appeared in *Science*. The Mainz institute had two publications out of 145 contributions. Wänke *et al*. (1970b) reported chemical data on Apollo 11 soils and rocks and some data on cosmic ray produced nuclei by Friedrich Begemann's group. The second publication by Hintenberger *et al*. (1970) focused on rare gas data and some analyses of nitrogen and hydrogen.

Figure 6.1 Heinrich Wänke with a sample from the Moon (1969).

Gene Simmonds, chief scientist at the Manned Spacecraft Center (MSC), later Johnson Space Center (JSC), remarked at the end of the first Lunar Science Conference '*There is a large amount of undigested data and very little interpretation*'. At this time the only thing that seemed to be clear was that the Moon was not a primitive, chondritic planet as Harold Urey had envisioned. This was to some extent even clear before the Apollo missions. Based on α-backscatter data of Surveyor missions (1966 to 1968), which showed high Ti in some rocks, Harold Urey revised his earlier ideas about the Moon as a primitive solar system body.

6.2 Element Correlations and the Bulk Composition of the Moon

Heinrich Wänke was eager to apply the results of neutron activation analyses to problems related to the origin of the Moon and its evolution over geologic time. He began to plot the analytical data as correlations between various elements and he understood soil samples to be mixtures of local materials and a wide-spread trace element-rich component, later termed KREEP (for high concentrations of K, REE, P). It was clear from earlier work of Larimer (1967, 1971) and Larimer and Anders (1967) that the elements condensing at high temperatures (the refractory elements) occur in the same ratios in various types of chondrites, albeit with different absolute abundances. This contrasted with the more volatile elements which had variable abundances and variable abundance ratios in different types of chondritic meteorites. Many of the KREEP elements are refractory elements (*e.g.*, REE, Ba, Sr, Hf, Nb, U, Th), but ratios among them were different from ratios in chondritic meteorites. In Wänke *et al.* (1972) numerous correlations of trace elements were plotted and it was soon clear that the chondrite-normalised refractory element pattern of KREEP was different from patterns in lunar mare basalts: most evident for the high content of the heat producing elements U and Th in KREEP and the low contents in mare basalts. In our paper for the *Proceedings of the Third Lunar Science Conference* (Wänke *et al.*, 1972) we calculated the heat production from the decay of U, Th and also K. We concluded that even a thin layer of KREEP near the lunar surface would have led to complete melting of the outer layers of the Moon, because of the high U and Th contents of KREEP samples, so prominent in Apollo 14 rocks.

In later papers (Wänke *et al.*, 1973, 1974) the focus was on element correlations that included non-refractory lithophile elements such as alkalis, W, and P. These elements fit into the sequence of KREEP elements, except that they are depleted, *i.e.* their ratios with refractory elements are much lower than ratios in CI chondrites, and we calculated depletion factors for these elements. For example, K/La, P/La and W/La ratios were all lower than the corresponding solar ratios, represented by CI chondrites.

The importance of some of these correlations is that they are valid for KREEP-dominated lunar highland samples and at the same time also for mare basalts. The K/La ratio is the same in KREEP and in mare basalts. The reason is the similar incompatibility of K and La, suggesting that the K/La reflects the ratio in the bulk Moon. Wänke attempted to apply this reasoning to other planets. An example is given in Figure 6.2.

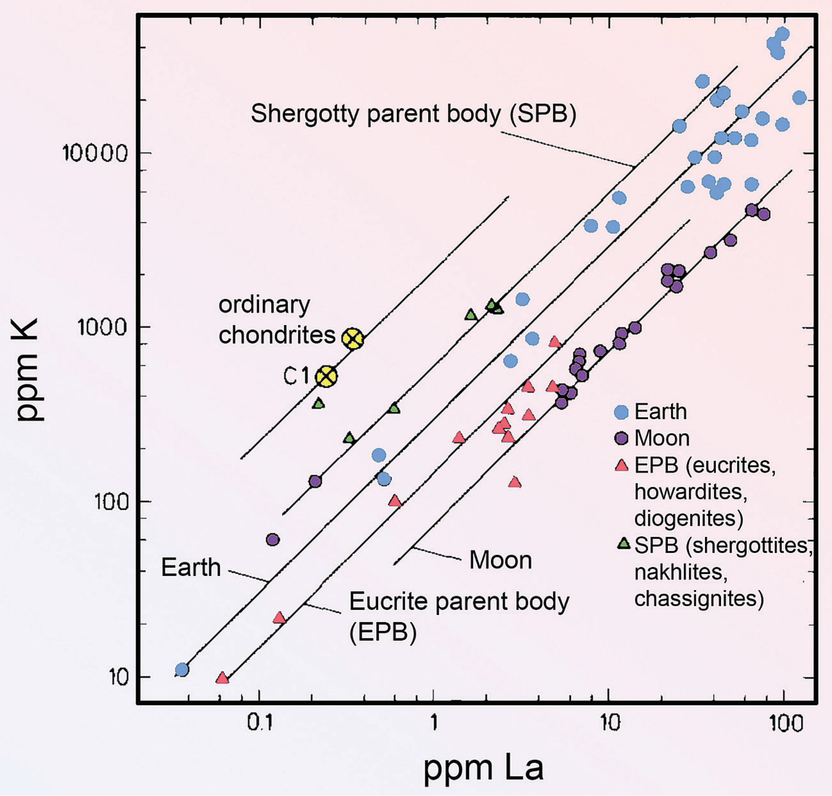

Figure 6.2 Correlation of the incompatible, moderately volatile element K with the similarly incompatible, refractory element La in the Moon and three other planets. The respective K/La ratios are assumed to be representative of the four planets (modified from Dreibus and Wänke, 1987).

From such element correlations Wänke calculated the bulk composition of the Moon and later of other planets. The bulk Moon composition calculated in this way by Wänke *et al.* (1974) was, to my knowledge, the first such estimate. I was involved in these calculations and we concluded that the Moon is strongly enriched in refractory elements, based on a simple two-component model with a chondritic (represented by K) and a high temperature (represented by La) component and using the excellent K *vs.* La correlation which yielded a representative bulk Moon ratio. Later we realised that the low K and Rb contents of the Moon are not indicative of a low chondritic fraction of the Moon, but that the alkalis are low because all volatiles are depleted in the Moon. But in 1974 a large high temperature fraction (designated as HTC or high temperature component) was suggested by the evidence from Ca, Al-rich inclusions, which demonstrated the reality of a pure refractory component. In our 1973 paper the estimated bulk Al content of the Moon was 12 % which dropped to 8.5 % in 1977 (Wänke *et al.*, 1977b). But the principal approach was new. I remember that Heinrich Wänke gave a talk on this subject at the Meteoritical Society Meeting in Davos in 1973. After his talk Ed Anders from the University of Chicago got up and said, *'we thank Prof. Wänke very much for his encouraging approach'*. A year later Ganapathy and Anders (1974) published a much more sophisticated paper estimating the bulk composition of Moon and Earth using many element correlations in defining six basic components based on meteorites. The six components were derived from chondritic meteorites. These authors estimated 5.8 % Al for the bulk Moon. More recent estimates are between 1.95 % and 3.38 % Al (Taylor *et al.*, 2006). One way to estimate the bulk Moon's Al content is by estimating the thickness of the anorthositic crust, with Al approaching the Al content of anorthite. But unfortunately the seismic data are not good enough to constrain the parameter narrowly. Although element abundances in the Moon are often given with an accuracy of a few percent, we are rather ignorant about the bulk Al content of the Moon. We also do not have a good idea about the Mg/Si ratio of the bulk Moon. Overall we know the bulk composition of the Earth much better than that of the Moon (see below).

6.3 KREEP and Trace Elements in the Moon

Most Apollo 14 samples, including soils, contained fractions of a single trace element-rich component, KREEP. Breccias containing this component were found at all landing sites. Since most KREEP-containing rocks had significant amounts of siderophile elements such as Ir and Ni (indicative of a meteoritic component), these rocks were all considered to be breccias formed by impacts on the surface of the Moon. A few, rare siderophile-free KREEP-rich rocks such as 15386 (7.5 grams, with igneous texture) are correspondingly described as magmatic rocks, the so called KREEP basalts (Warren and Wasson, 1979).

The KREEP component was inhomogeneously distributed over the surface of the Moon, but was apparently derived from a single source. The major element composition and the absolute enrichment of the KREEP component were (and are) unknown, later the hypothetical endmember was termed ur-KREEP by Warren and Wasson (1979).

I found the constant trace element ratios in KREEP, independent of the absolute level of trace elements, very striking. I thought that it must represent a Moon-wide event and I set up a model for the trace element evolution of the Moon and the strongly contrasting mare basalts (Palme and Wänke, 1975). In Figure 6.3 the KREEP-rich soil sample 14163 represents the KREEP component. Elements

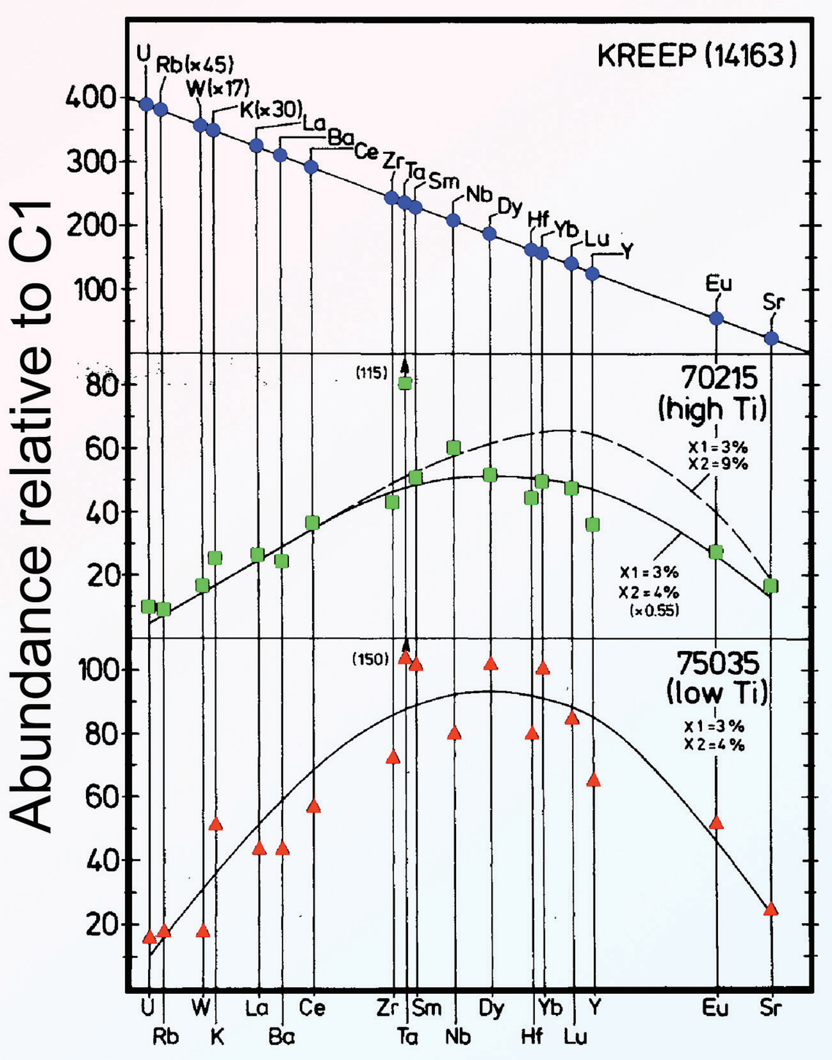

Figure 6.3 Double extraction model for the trace element systematics in the Moon. Elements arranged in the sequence of enrichment in KREEP (here soil sample 14136). Effective partition coefficients calculated from the first extraction are used for calculating trace elements in Apollo 17 basalts. Xi is degree of partial melting (modified from Palme and Wänke, 1975).

in the upper part of the figure are arranged in order of decreasing CI-normalised abundance in KREEP. The sequence thus reflects the degree of incompatibility during crystallisation of the lunar magma ocean. In the lower part of Figure 6.3 the data of two mare basalts from Apollo 17 are plotted. The sequence of elements is the same as for KREEP. Elements with very high enrichment factors in KREEP are low in mare basalts, *e.g.*, U and Ba. More compatible elements such as Yb and Lu are less enriched in KREEP and less depleted in mare basalts.

The first event in my model was a partial melt from bulk Moon representing KREEP. Effective partition coefficients that produce the observed pattern are calculated. These partition coefficients were then used for a second partial melting event from the same source (but depleted in incompatible elements) that produced the mare basalt patterns. In Figure 6.3 I have assumed the first partial melting event produced KREEP with 3 % melting and the second event with 3 or 5 % respectively. It is, however, now assumed that KREEP is the residual melt of a global crystallising magma ocean. In terms of calculations there is little difference between producing a small residual melt by fractional crystallisation or making the same fraction of melt by partial melting. In the case of equilibrium the results are identical. So far only refractory lithophile elements are involved and it is assumed that the bulk Moon has chondritic relative abundances of refractory elements.

The abundances of W in Apollo 14 soil 14163 (KREEP) and in two Apollo 17 mare basalts can be fitted into this scheme by placing W between the elements La and U. Thus, in the lunar environment, W is more incompatible than La but less so than U. From Figure 6.3 it is clear that the Hf/W ratio of KREEP is below the lunar bulk ratio and that of mare basalts is above. Overall W is depleted relative to the refractory lithophile elements by a factor of 17 (newer data suggest a factor of 25). The positions of the depleted moderately volatile elements Rb and K in Figure 6.3 are determined in the same way.

The high Ta content does not fit this scheme. It is the result of ilmenite cumulates which precipitated from Ti-rich KREEP liquids and were added to the source region of mare basalts. In terrestrial rocks Ta is one of the most incompatible elements. In lunar KREEP-rich samples it is less enriched and incompatible, due to ilmenite crystallisation and separation which preferentially removes Ta from KREEP liquids (see next section).

When I wrote this double extraction paper, one reviewer did not understand the underlying idea at all. The other reviewer was John Wasson, who was extremely helpful. Due to his efforts the paper got finally published.

I also presented the model at a Royal Society Meeting in London but I was not particularly successful. Gerry Wasserburg told me that my talk was not understandable. It was one of my first talks and I suspect that I did not produce a very clear presentation. The papers I wrote about this model are rarely cited. I still think that this double extraction model is very useful in trying to understand incompatible elements in the Moon, in particular the depletions of W and the alkali elements. Al Hofmann, who was director of the geochemistry department used a similar approach (Hofmann, 1988) for explaining the trace element patterns of mid-ocean ridge basalts (MORB). I pointed this out to him, but at the time he was not interested in the Moon.

6.4 Analysis of Mineral Grains from Mare Basalt 75035

Figure 6.4 Location and orientation of 75035 at rim of Camelot Crater, Apollo 17. It is a medium-grained subophitic high-Ti basalt texturally similar to the Apollo 11 ophitic basalt (photo credit: NASA).

In a further project with Frank Wlotzka I separated mineral grains from lunar mare basalt 75035 (Fig. 6.4), after having gently crushed the rock (Palme and Wlotzka, 1976a). I picked plagioclase, pyroxene and ilmenite grains with masses from a few micrograms to several hundred micrograms. For this purpose we bought a microbalance, which turned out to be very useful. The mineral grains were irradiated and separately counted on Ge(Li)-detectors. After sufficient cooling they were embedded, polished and analysed with the electron microprobe (EMP) to determine major element concentrations and Mg zoning patterns. There are fairly large differences in trace element concentrations of individual grains as determined by INAA which could be correlated with EMP data. Figure 6.5 shows an example where the average Mg contents of ilmenite grains correlate negatively with the

Ta contents determined with neutron activation analysis. Tantalum is rejected by the major minerals including pyroxene as it is concentrated in the residual melt which becomes, with crystallisation of mafic minerals, increasingly depleted in Mg. In 1975 this was the only way to detemine major and trace elements on the same single mineral grain. Also mineral-melt partition coefficients for a number of trace elements could be derived from these data. Particularly important are the high contents of Ta in ilmenites (Palme and Wlotzka, 1976a). The data show that a mare basalt such as 75035 can be regarded as a melt that crystallised in a closed system. Similar results on mare basalt 70135 were obtained by Haskin and Korotev (1977), although these authors did not analyse single mineral grains.

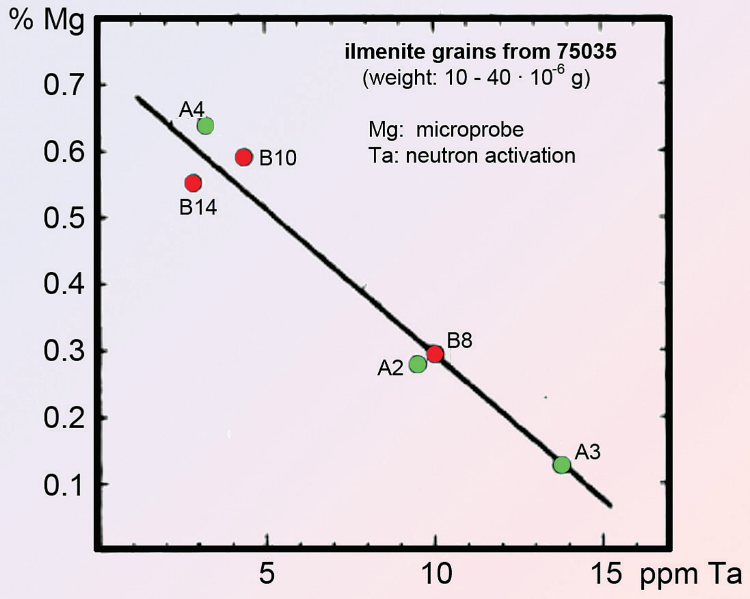

Figure 6.5 Anti-correlation of Mg with Ta in single ilmenite crystals from mare basalt 75035. This figure demonstrates the strong preference of Ta for ilmenite. Ta was determined by INAA on separated mineral grains and Mg by the EMP on the same grains. The later a grain crystallised the higher is the Ta, and the lower the Mg, content (modified from Palme and Wlotzka, 1976a).

6.5 Analysis of Plagioclase Grains from Lunar Highland Rocks

I applied the same procedures that I had used for the analysis of mineral grains from mare basalts to separates from lunar anorthosites. If plagioclase is a crystallisation product of a lunar magma ocean, the plagioclase with the lowest incompatible trace elements should give some indication on the abundance level of incompatible elements in the lunar magma ocean at the onset of plagioclase crystallisation. This was the reasoning behind these analyses. It turned out that the LMO (lunar magma ocean) was about ten fold enriched in Eu and Sr at the time when plagioclase started to crystallise. I also determined the contents of Fe, Cr and Co in plagioclase. With a knowledge of partition coefficients one could calculate the concentration of mafic elements in the LMO at the time when plagioclase started crystallising (Palme *et al.*, 1984). At a Lunar and Planetary Science Conference Bill Phinney (from the Johnson Space Center) pointed out to me that the contents of mafic elements in lunar trace element-poor lunar highland plagioclase separates may reflect late metamorphic exchange with mafic phases rather than igneous crystallisation (Phinney, 1992). This may be different for the less mobile REE. Recently these attempts were resumed (*e.g.*, Sharp *et al.*, 2015).

6.6 The Significance of W in Lunar Samples

6.6.1 W as an incompatible element

The radiochemical separation scheme developed by Wänke and Baddenhausen in the 1960s produced data on W. At this time very little was known about W. After the analyses of Apollo 11, 12 and 14 samples it became clear that W behaved as an incompatible element and Wänke plotted W concentrations in soils, breccias and basalts from the Moon against a variety of incompatible elements. He found that W concentrations correlate quite well with La contents. The La/W ratio arising from these correlations was about a factor of 19 higher than typical chondritic ratios. Wänke *et al.* (1973) ascribed this to the metallic character of W (Fig. 6.6). He suspected that during core formation some fraction of W was removed together with metallic Fe-Ni to the metallic core of Earth, Moon and Vesta. I remember that we spent hours discussing these issues.

6.6.2 Metal-silicate partitioning of W

In order to test this hypothesis Heinrich Wänke planned to undertake metal-silicate partition experiments. Werner Rammensee, a student of chemistry at the University of Mainz, started to do partition experiments for W between metal and silicates. This was one of the first metal-silicate partition experiments, where oxygen fugacity was controlled. I remember well when Wänke offered this project to Werner Rammensee. Werner was a bit uncertain about the project and he asked the chemists and mineralogists he knew, what they thought about the planned partition experiments. Their answers were discouraging. They told him that the project was too complicated and that we did not know enough about these things *etc*. Despite these comments Werner started the project. Experimental charges were doped with radioactive W and after separation of metal, activities of W in silicates and metal were counted separately. The results were parameterised in

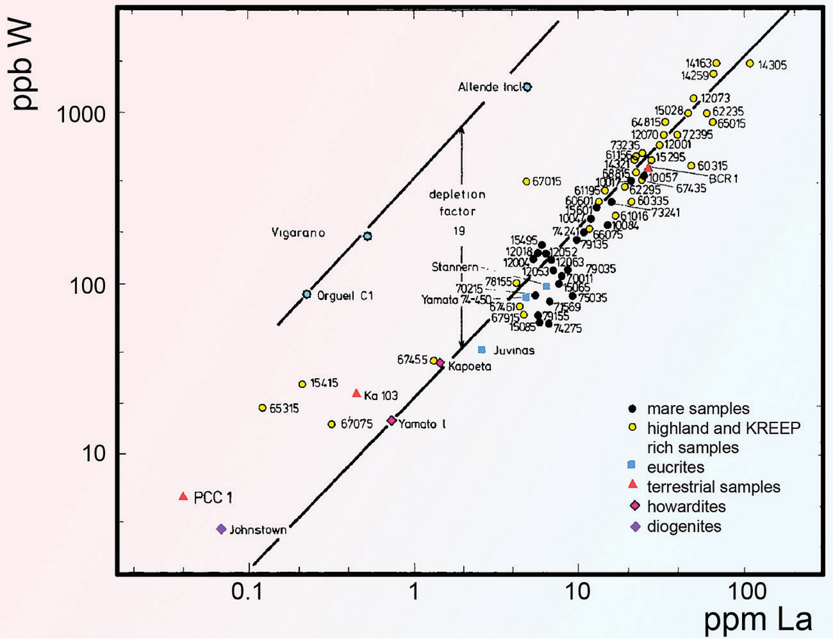

Figure 6.6 A W *vs*. La plot provides evidence for the depletion of W in Earth, Moon and eucrites (modified from Wänke and Dreibus, 1979).

terms of oxygen fugacity and temperature, just as is done today. Rammensee and Wänke (1977) calculated the amount of metal necessary to achieve the observed depletion, using the measured partition coefficients. The depletion of W in the Moon is so large that much more metallic iron is required to produce this depletion than could be present in the lunar core. In addition, it was found that the La/W ratio of terrestrial rocks is identical to the lunar ratio within uncertainties. As a consequence, removal of W into a metal phase must have occurred before accretion of the Moon, preferably in the Earth. A strong hint that the Moon is made of Earth's mantle material. Later Newsom and Drake (1982) argued that these results assume complete melting of silicates, which may not have occurred. As W is very incompatible it will be quantitatively concentrated in a smaller melt fraction and less metal is needed to extract W to the core. If the lunar core metal equilibrated with a large melt fraction the Rammensee and Wänke (1977) argument would be valid. It may be worthwhile to pursue this question further.

The similarity in W/U ratios of Earth and Moon (this is essentially the same as W/La ratios, as both U and La are refractory elements with a constant ratio in meteorites and bulk planets) and the nearly identical $^{182}W/^{184}W$ ratio of Earth and Moon, where ^{182}W is the decay product of ^{182}Hf with a half life of 9 million years (Touboul *et al.*, 2007) support the model of Rammensee and Wänke (1977). In current models of Moon formation, the Moon is the result of a collision of a Mars-sized embryo with the Earth. The similarity in the $^{182}W/^{184}W$ ratio and the Hf/W ratio of Earth and Moon require that the contribution of the projectile to the bulk Moon is very small. It is very unlikely that the W isotopic composition and the fraction of oxidised W in the mantle of the impactor are identical in Earth and Moon. A single source for W isotopes and the Hf/W ratio in Earth and Moon is presently the most reasonable assumption. Either the Moon formed out of the Earth or both the Moon and Earth formed from a homogeneous mixture of Earth and the projectile.

6.6.3 A new method for the analysis of W and other siderophile elements

After my return from Chicago (see next section) Werner Rammensee and I developed a new method for analysing siderophile elements in meteorites, based on his partition experiments. A neutron irradiated sample was equilibrated at reducing conditions with a similar mass of metal. The temperature was so high that the metal melted and formed a spherule. The spherule was then dissolved in acid and the solution was counted. In this way major γ-activities of lithophile elements such as Mn, Na and Sc were removed and the backgound was considerably reduced. The method proved particularly useful for W and in some cases also for Mo (Rammensee and Palme, 1981). We analysed all kinds of samples. We determined a new Mo abundance for CI chondrites and found constant Mo/Ir ratios of about 1.95 for most carbonaceous chondrites (Palme and Rammensee, 1981a). Only Karoonda had, with a Mo/Ir ratio of 0.5, a nearly four times lower Mo content. The Karoonda meteorite is thermally metamorphosed and Mo may have been lost as volatile MoO_3. In this case one would also expect loss of the volatile WO_3 (Palme *et al.*, 1998), but Kleine *et al.* (2004) have shown that W is quite 'normal' in Karoonda, based on the Hf/W ratio. The experiments of Köhler *et al.* (1988) on Allende have, however, shown that heating at high temperatures and oxidising conditions may lead to severe loss of Mo but not of W. Apparently volatile WO_3 is re-trapped in the silicates; a process also observed in opaque assemblages of Allende (Palme *et al.*, 1994).

In another project we analysed eucrites for W using our newly developed analytical scheme (Palme and Rammensee, 1981b). At the time there were very few data available on W in eucrites. From our new data we concluded that U is better correlated with W than La, and we calculated depletion factors for W of 22 ± 8 for the Moon and 31 ± 8 for eucrites. The main message was that, if W behaves as an incompatible element during partial melting, the source region must be free of metal. If metal were present it would buffer the W concentrations and the W contents in the melt would be essentially constant, independent of the degree of partial melting. Thus, eucrites cannot be partial melts from a chondritic source containing metallic Ni-Fe as postulated in Ed Stolper's classic paper (Stolper, 1977). I remember well that Ed Stolper had given a plenary talk about eucrites and shergottites at the Meteoritical Society Meeting in St. Louis in 1982, where he explained his model claiming that eucrites are partial melts from an H chondrite parent body. I pointed out to him that the eucrite source region could not have contained any metal. He told me that he does not care about W. I was a bit disappointed. But I still think that the argument is valid, although I realise only a few people pay attention to it.

7. EARTH

7.1 The Elemental Composition of Earth's Mantle

After having done numerous analyses of lunar samples and after having attempted to estimate the bulk composition of the Moon, we wanted to apply our analytical procedures to terrestrial rocks and estimate the bulk composition of the Earth in a similar way as for the Moon. People had complained that high quality chemical and isotopic data of lunar rocks were not available for terrestrial rocks, in particular the concentrations of rare trace elements that were reasonably well known for many lunar rocks were uncertain for samples from the Earth. For example, we had at the time a pretty good idea about the W content of the Moon. But almost nothing was known about W in terrestrial rocks, particularly in rocks with low concentration of W.

In 1979 it was generally accepted that the composition of the Earth's mantle is not very different from the pyrolite composition, a synthetic mixture of 20 % basalt and 80 % harzburgite as suggested by Ringwood (1962). Some of the peridotitic rocks come close in composition to this synthetic pyrolite composition. Peridotitic rocks occur in a variety of geologic settings as discussed in detail by O'Neill and Palme (1998): (1) as sections in ophiolites, (2) as massive peridotites, variously known as Alpine peridotites, (3) as abyssal peridotites, dredged from the ocean floor, (4) as spinel (rarely garnet) peridotite xenoliths from alkali basalts, mostly from the subcontinental lithosphere, and (5) as garnet peridotite xenoliths from kimberlites and lamproites. We focused our study on peridotitic xenoliths brought to the surface of the Earth by alkali basaltic magmatism. For this purpose Emil Jagoutz had selected six xenoliths from worldwide ocurrences. Only xenoliths visibly free of alteration and with the highest fraction of clinopyroxene (*ca.* 20 % modal) were chosen. The results for all xenoliths analysed were very similar. After averaging they were considered to represent a new, more precise estimate of the composition of the Earth's mantle. Ratios among refractory lithophile elements were approximately chondritic, except for the most incompatible elements. Light rare earth elements (LREE), U, Th, Ba, Ta *etc*. showed more variation and were excluded from the averaging procedures. The peridotitic host rocks must have lost a very small fraction of melt, enriched in highly incompatible elements (Jagoutz *et al.*, 1979). Their abundances were calculated assuming chondritic ratios among all refractory elements. The major elements displayed some fine systematics as shown in the Al/Mg *vs.* Si/Mg plot (Fig. 7.1). I remember well, that after I had made this plot, I went to Heinrich Wänke's office and showed him the figure. He took his pen and wrote on the line connecting the meteorite data, *cosmochemical fractionation* and on the line connecting the peridotite data, *terrestrial fractionation*.

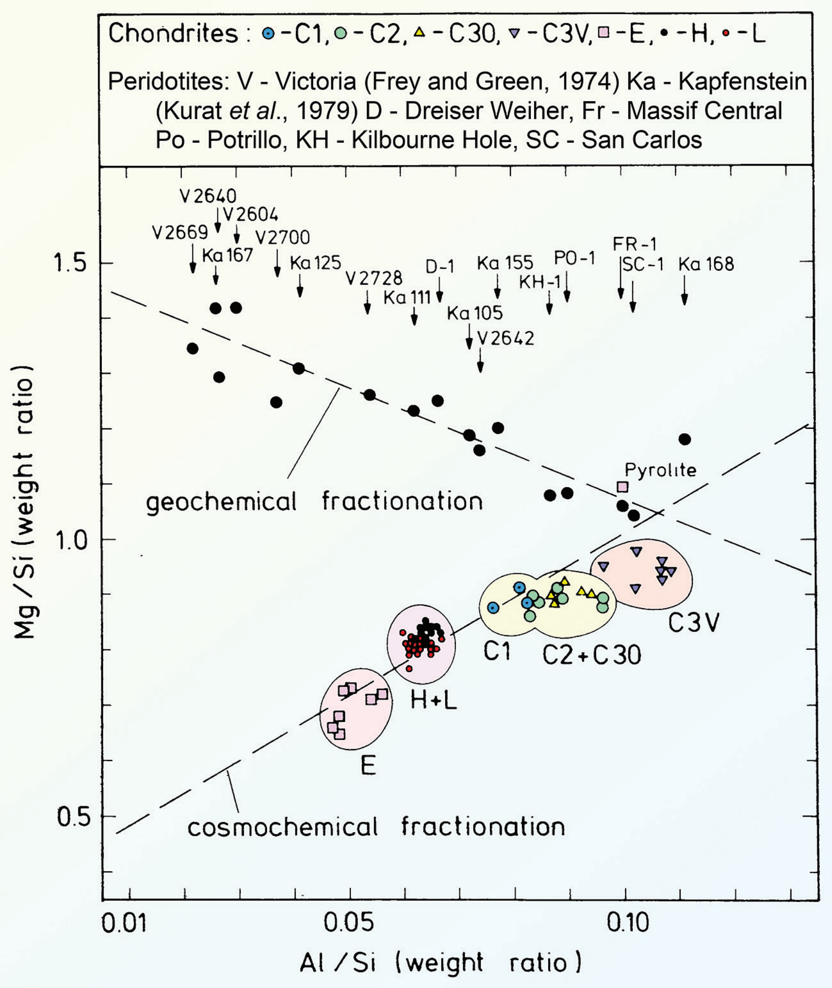

Figure 7.1 Mg/Si *vs.* Al/Si ratios of unfractionated meteorites and terrestrial ultramafic xenoliths. Unfractionated or chondritic meteorites do not have a unique, well defined Mg/Si ratio. The upper mantle composition is assumed, where the geochemical fractionation line reflecting removal of melt intersects the cosmochemical fractionation line (modified from Jagoutz *et al.*, 1979).

The Al/Si *vs.* Mg/Si relationship (Fig. 7.1) may be understood in terms of the chemical composition of residual rocks reflecting continuous loss of the 'basaltic elements' Al and Si and enrichment of compatible elements, such as Mg and Ni by partial melting.

Palme and Nickel (1985) demonstrated that the primitive upper mantle may be defined when ratios among refractory compatible elements become chondritic. This is the point in Figure 7.1, where the cosmochemical and geochemical trends intersect. An example of a chondritic ratio of lithophile, refractory elements in peridotitic rocks with the highest Al is demonstrated in Figure 7.2, where Yb is plotted against Al_2O_3. Most whole rock orogenic, ophiolithic and abyssal peridotites have non-chondritic Yb/Al ratios, but the two refractory elements converge to a chondritic ratio, which is the Yb/Al ratio of the primitive upper mantle (PUM), according to Palme *et al.* (2014a). Some of the estimates for the composition of the upper mantle have used an average of peridotites, with most rocks having lower Al and Yb values than the PUM value in Figure 7.2 (Maaloe and Aoki, 1977; Lyubetskaya and Korenaga, 2007), resulting in lower lithophile refractory element concentrations (*e.g.*, Al, Ti, Yb), and also fractionated lithophile refractory elements, such as the Yb/Al ratio (Fig. 7.2). The PUM values of Palme and O'Neill (2003, 2014) are similar to those of McDonough and Sun (1995).

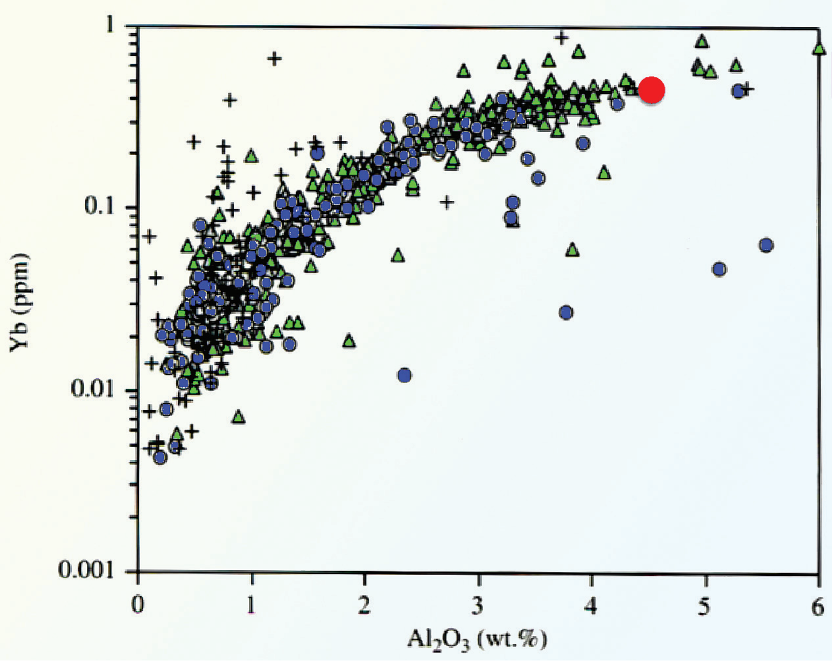

Figure 7.2 Whole rock orogenic, ophiolithic and abyssal peridotites converge to a chondritic Yb/Al ratio, which is indicated by a large red circle on upper right. All other rocks have lower than chondritic Yb/Al ratios. Data from xenoliths in alkali basalts plot exactly on the same curve. The ratio of the primitive upper mantle (PUM) as listed by Palme and O'Neill (2014) is: Al_2O_3 = 4.50 %, Yb = 0.477 ppm, Al/Yb = 49,800. CI chondrites Al/Yb ratio:49 900 (after Bodinier and Godard, 2003).

An exception to chondritic ratios among lithophile refractory elements in PUM seems to be the Ca/Al ratio, which for most peridotites is slightly super-chondritic (see Fig. 9 in Pearson *et al*., 2003). Palme and Nickel (1985) ascribed this to retention of Al in garnet at depths below 60 km, as most of the peridotites studied are from the spinel stability field. However, xenoliths from the Tariat depression (spinel and garnet peridotites) have close to chondritic Ca/Al ratios (Ionov and Hofmann, 2007). It is thus not really clear what these data mean. Even more unexpected are the approximately constant Ca/Al ratios in peridotitic rocks (xenoliths and massive peridoties). Partial melting models of a spinel-peridotitic source predict high Al/Ca ratios for small degree partial melts. As the degree of partial melting increases the ratio decreases and eventually reaches the chondritic value (*e.g.*, Baker and Stolper, 1994). The geochemical fractionation line in Figure 7.1 may thus represent a mixing line, between a high degree partial melt and a residual, clinopyroxene-free residue, rather than a sequence of melts produced by various degrees of partial melting.

The cosmochemical fractionation in Figure 7.1 is still a mystery. The variable Mg/Si and Al/Si ratios of the various types of chondritic meteorites cannot be ascribed to igneous processes. Such trends cannot produce a parallel enrichment of Al and Mg. It is therefore often believed that the cosmochemical fractionation line of Figure 7.1 reflects the removal of an early condensed forsteritic olivine component from the source region of chondritic meteorites. In a recent contribution Dauphas *et al.* (2015) found a correlation of the isotopic composition of Si (δ^{30}Si) with the Mg/Si ratios of chondritic meteorites. The isotopic variations of Si are explained by removal of various fractions of early condensed olivine, leading to the observed sequence of Mg/Si ratios in carbonaceous, ordinary and enstatite chondrites. Using his correlation Dauphas *et al*. (2015) then made predictions regarding the Mg/Si ratios of Mars, the Angrite parent body and other meteorite parent bodies. The Earth's mantle does not plot on this correlation, because of some Si in the core. About 3.6 % Si is required in the core of the Earth to bring the bulk Earth on the δ^{30}Si *vs*. Mg/Si ratio correlation. If correct, this would provide a simple explanation for the correlation of Si isotopes with the bulk chemistry of planets and planetoids.

In the late 1980s, Bill McDonough spent some time in Mainz working in the group of Al Hofmann. I was impressed by the enormous spreadsheet which Bill had constructed with all the literature data available at the time. We had several discussions about the composition of the Earth's mantle and also produced common publications (*e.g.*, Jochum *et al*., 1989).

Later we did more analyses of upper mantle rocks, spinel and garnet peridotites from Vitim and Tara (Siberia). Dimitri Ionov gave us these samples when he spent some time at the Max-Planck-Institute. There are now thousands of samples with compositions falling along the correlations shown in Jagoutz *et al*. (1979) or O'Neill and Palme (1998) and others (Fig. 7.1). This includes samples from xenoliths and massive peridotites. Pearson *et al*. (2003) and Bodinier and Godard (2003) show many such plots with a large number of samples. There are so many publications of the chemistry, mineralogy and isotopic composition of peridotitic rocks that I have lost track of them. But whenever I see a new paper with data on the chemical composition of spinel and/or garnet lherzolites I check the major and trace element compositions. Most of the time they fit with the known element trends.

In summary: the anti-correlation of Al_2O_3 *vs*. MgO in upper mantle rocks (Fig. 7.1) is universal. PUM has the highest Al and the lowest Mg content in this sequence. At this composition the relative abundances of refractory compatible elements (Al, Ca, Sc, Yb *etc*.) are chondritic and the modal abundance of clinopyroxene is close to 20 %. Since the primitive upper mantle (PUM) has lost some fraction of its very incompatible elements (such as the LREE), the criterion of chondritic relative abundances can only be applied to the more compatible refractory elements.

The Mg/Si weight ratios of PUM-like rocks are about 1.045, close to the solar ratio of 0.89, indicating some deficit of Si in the mantle of the Earth. There are no samples from other planets and differentiated planetoids (Moon, Mars, Vesta) with similarly high Mg/Si ratios. For example, the highest Mg/Si ratios in the Moon are about 0.2 or lower, typical of basaltic melts from the interior of these bodies. The lack of high Mg samples from other planets is the reason for the poor knowledge we have on their bulk composition.

The 15 % lower Mg/Si ratio of the primitive upper mantle, compared to CI chondrites has been variously interpreted, either as loss of Si to the core, evaporation of Si from the hot mantle, or as initial Si deficiency of the bulk mantle (see Palme and O'Neill, 2003). Ringwood (1989) has suggested that the Mg/Si ratio of the Earth's mantle is identical to the ratio in the Sun and that the carbonaceous chondrite ratio is fractionated relative to the solar ratio. This seems unlikely to me, considering the overall fit of solar elemental abundances with abundances in type 1 carbonaceous chondrites.

In earlier work I had suggested using the Yb/Sc ratios to define the extent of fractionation in terrestrial and extraterrestrial matter (Palme *et al*., 1978a). Partial melts from a primitive planetary interior have higher than chondritic Yb/Sc ratios whereas residues have lower ratios. During partial melting of an olivine-orthpyroxene-rich interior, Yb is more incompatible than Sc. In the Earth, PUM-like peridotitic rock samples have chondritic Sc/Yb ratios, whereas basalts have higher (and harzburgites lower) ratios. The advantage of using the Yb/Sc ratio is that both elements are not strongly incompatible and that both elements are resistant to metasomatic alteration.

Another feature indicative of the primitive nature of mantle rocks is the $^{187}Os/^{188}Os$ ratio. As Re is incompatible and Os compatible, a small fraction of partial melting will decrease the Re/Os ratio in the residue. There is indeed often a good correlation of the Os isotopic ratio with Al or other elements indicative of the fertility of the rock (the ability to produce basaltic melts). Only PUM rocks have meteoritic $^{187}Os/^{188}Os$ ratios, which are within the range of enstatite chondrites or at the low end of ordinary chondrites but outside the range of carbonaceous chondrites (Meisel *et al*., 1996). This was interpreted to indicate that the composition of the late veneer is similar to ordinary or enstatite chondrites (see Walker, 2009).

8. A YEAR IN CHICAGO

In the mid-1970s it was more or less mandatory for Germans active in research to spend at least a few months in the US. After having returned to Germany, people were awarded with the title iAg (in Amerika gewesen - having stayed in America). It increased the reputation and facilitated the next step in the career. At this time the US were leading scientific progress in many areas, in particular in cosmochemistry, and a research stay in the US was absolutely necessary. Today this is certainly less important. For example, Thorsten Kleine, Carsten Münker and Andreas Pack (professors in Münster, Cologne and Göttingen) have made major contributions to cosmochemistry. None of them ever did research in the US. A stay in an European country or Australia is as good, or even better.

In 1976 I applied for a grant from the National Research Council of the United States (NRC). I planned a stay with John Philpotts and Charlie Schnetzler at Goddard. I knew John from meetings and I was impressed by his, and Charlie Schnetzler's work, on lunar samples. They analysed REE and a few other elements by isotope dilution mass spectrometry and they always had interesting interpretations. In Mainz, we had made comparisons of their data with ours and found very good agreement. I also wanted to learn a new analytical technique with higher precision than INAA. One morning I received a telegram from NRC telling me that my application was accepted. A few weeks later John wrote me a letter and told me that their analytical facilities were to be shut down by NASA. He pointed out that I could nevertheless come and stay for a year, if I wanted to have a good time. But they would not be able do serious science. Some time later, I do not remember exactly when, Ed Anders asked if I would like to spend some time in his lab in Chicago. I was honoured and agreed to participate in his radiochemistry group. As a consequence, I spent a year at the University of Chicago, from autumn 1976 to 1977.

8.1 Hyde Park, South Chicago

In 1977 it was known that South Side Chicago, where the University of Chicago is located, is not the best place to live. But Ed Anders had sent his potential postdocs reports indicating that the crime rate in Hyde Park was lower than in most parts of Chicago. This is because there is, in addition to the normal police, a separate campus police. After having arrived in Chicago, I went through customs and the lady there would not believe that I wanted to go to South Chicago. Apparently the reputation of South Chicago is really bad and she did not know that this was the location of the University of Chicago. When I finally had arrived, I immediately got the advice, not to go West of Cottage Grove, North of 46th or 47th street and South of 64th or so. This is a little strange for Europeans. But in the end I never had any problems with safety in Chicago. Often I spent late evenings at the Regenstein Library (which was open all night) very uncommon for Europeans at this time, and I walked back in the middle of the night to 53th street and lake-side where I lived. My family spent some time with me, and I myself loved to stay in Hyde Park. It was a very vivid community. There was always discussion whether one should stay in Hyde Park or move outward to the suburbs. Ed Anders and Bob Clayton lived in Hyde Park, like Barack Obama, while Larry Grossman moved out.

8.2 Research in Europe and the US

I was quickly learning the difference between the way research was done in a Max-Planck-Institute and in an American research laboratory. In Mainz, money was no problem, when we needed something we contacted Wänke and he would simply buy the piece of equipment we wanted to have. We used to spend hours discussing various aspects of our work. The number of papers at the end of the year was not the most important issue, in contrast with Anders, for whom efficiency had the highest priority. The money came from grants, I suppose mostly NASA grants. Papers had to be written to demonstrate proper use of the money and ensure further grant money. There was not much time for discussions, everything had to be done quickly and efficiently and Ed Anders was very good at this. A Japanese post-doc, Hiroshi Takahashi (an excellent chemist who was working in our group), used to say that Ed Anders writes papers faster than he could read them. Anders' output was indeed gigantic. He may have been on the extreme side. Things were more relaxed with Bob Clayton, who had his lab on the same floor as Ed Anders in the Enrico Fermi Institute. Often I attended Bob Clayton's morning coffee. Tosh Mayeda was there and Bob's students and post-docs. At the beginning Larry Grossman was also a frequent participant. His favourite theme was, in addition to CAIs, the stock market. I learned a lot from the scientific discussions at Bob Clayton's morning coffee. I had frequent discussions with Richard Becker (one of Bob Clayton's post-docs) who was really very knowledgeable. He later took a position with Robert Pepin in Minnesota.

Another aspect, when comparing the European and American systems, is that funding of long term projects is very difficult in the US system. In a Max-Planck-Institute this is not a big problem. This is good and bad. Large promising projects can be funded, and plans can be made for five years or more. On the other hand, if there is no review, projects may get out of control. The world's largest mass spectrometer in Mainz was funded with a huge amount of money over a long period of time without any outcome. Only after Heinrich Hintenberger had retired, did his successor Friedrich Begemann end the operation.

I was on the NASA review panel several times and I was impressed by the efficiency and in most cases the fairness of the review procedure. I felt that for the comparatively small amount of money, some 10 million dollars if I remember right, a lot of science is done. We used to carry home from Houston three large yellow abstract volumes full of mostly interesting projects. It is not clear to me if we are similarly efficient in the German system. Most of the money for science in universities comes from DFG (Deutsche Forschungsgemeinschaft-German Science Foundation). The procedure for getting grants with DFG is similar to the American system. Max-Planck researchers cannot apply for DFG money. They are funded by the Max-Planck-Society, of course this is in reality still tax-payers' money (altogether close to 2 billion euros per year for some 85 institutes). Only directors can apply for this money, and academic staff members are dependent on their director, certainly a disadvantage. There is no peer review system for proposals by the directors.

In Anders' group we did radiochemical analyses of lunar highland rocks under the guidance of Jan Hertogen and Marie-Josée Janssens from Belgium. They were real experts in radiochemistry and I had (and still have) good contact with them. And there was also Roy Lewis with his rare gas instrument. It was the time when s-process signatures in rare gases were detected and the ongoing research for presolar materials, with the search for 'Q' and the discovery of presolar diamonds in Anders' lab. I had also many discussions with B. (Chino) Srinivasan, a rare gas post-doc of Ed Anders. During my stay in Chicago, Chino moved to Rolla (Missouri) to work with Oliver Manuel. He left us his VW beetle for a couple of weeks under the condition that we deliver the car to his new place in Rolla before leaving Chicago. We did this and I remember well sitting in the porch of Oliver Manuel's house in Rolla and discussing the iron-rich Sun, a residual core of a supernova explosion, Oliver Manuel's pet idea, which nobody else seemed to believe.

At the end of my stay in Chicago I was invited to give a talk in La Jolla. I had applied for a job there. I talked about the refractory metal grain we had found in Mainz and the condensation calculations of refractory metals that I had done. I remember this so well because Harold Urey was present at the talk. I noticed that he was sleeping most of the time. But at the end he told me that he liked the talk. Of course, I felt honoured, whether he really remembered anything of my talk was unclear to me.

8.3 Siderophile Elements in the Lunar Highlands

It was also the time of the dispute about the origin of siderophiles in the lunar highlands. Almost all lunar highland rocks that were analysed for siderophile elements showed substantial amounts of Ir, Ni and other metallic elements. The concentrations of these elements in mare basalts were extremely low. It was therefore generally assumed that Ir in highland rocks was delivered with chondritic projectiles of basin-forming asteroids impacting the Moon after its differentiation, *i.e.* after formation of the lunar crust. But here ended the agreement. Ted Ringwood and his group from the Australian National University in Canberra assumed that Ir was delivered by H chondrites. For each analysis of highland rock, an H chondrite component, based on the Ir content, was subtracted. The remaining metallic elements were then ascribed to the inventory of the Moon, implying that they are indigeneous to the Moon and thus were not supplied by impacts of meteorites. They are rather the result of lunar magmatic processes in the interior of the Moon, which, according to Ringwood, had Earth mantle-like composition. At the other extreme, Anders and his group ascribed a larger fraction of highland siderophiles to meteoritic contamination. This required a change in the composition of lunar basin-forming projectiles with time. As an indicator characterising the extra-lunar component they used Au/Ir ratios which were assumed to characterise the impactors (*e.g.*, Morgan *et al.*, 1974; Janssens *et al.*, 1978). The older the impactor the lower the Au/Ir ratios. Wänke and his group (including myself) attempted to show that Au is not a reliable indicator for meteoritic components as it may be volatilised through impacts. Experiments demonstrated the high volatility of Au at elevated temperatures (Dreibus *et al.*, 1981). Some of the scatter of Au in Apollo 16 breccias may have been caused by Au mobilisation. The extent of this effect is unclear.

Wänke's main concern, however, was to show that lunar highland rocks are more or less mechanical mixtures of several components; the anorthositic outer layer of the Moon (delivering Al and Ca), the result of flotation of plagioclase from a cooling lunar magma ocean, a KREEP component distributed over the front side of the Moon by impacts and a Mg-rich component of Earth mantle composition. This was the main carrier of Mg thought to be representative of a late accreting component with Earth's mantle composition, which was impacting the Moon during or after cooling of the magma ocean. A fourth, chondritic component would deliver Ir and other highly siderophiles. The binary mixing diagram of the two main components of lunar highland breccias as suggested by Wänke considered pure anorthositic highland rocks (nearly mono-mineralic rocks of anorthite composition) on one side and the mafic endmember on the other side (see Fig. 8.1). The KREEP component and the late infall of a meteoritic component would not contribute much to the major element composition. If lunar highland breccias were indeed random mechanical mixtures of several components, phase diagrams of highland rocks would be useless.

As the mafic endmember of the mixing diagram of Wänke (Fig. 8.1) did not fit with the composition of the mantle of the Earth, Ringwood *et al.* (1986) suggested that some olivine fractionation had occurred on the Moon leading to a residual melt resembling terrestrial komatiites and thus producing a component with less MgO than Earth's mantle, which would better fit with the mafic endmember of the mixing diagram of highland rocks.

Thus Ringwood and Wänke favoured a terrestrial origin of the Moon, whereas Anders preferred an independently formed Moon, composed of components derived from chondritic meteorites (Ganapathy and Anders, 1974). At the Annual Lunar and Planetary Science Conferences in Houston there was a very high attendance whenever Ed Anders and Ted Ringwood gave their talks, not because people were interested in the origin of siderophiles on the Moon, but because they expected lively discussions.

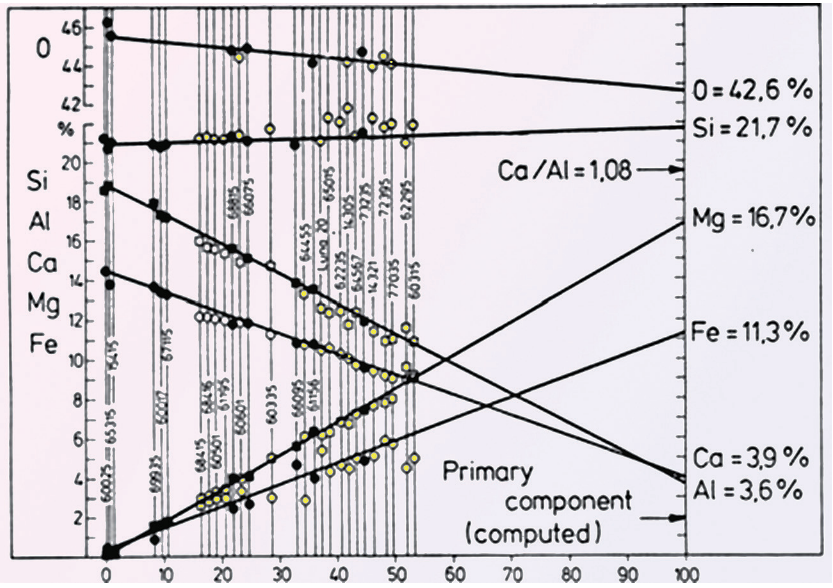

Figure 8.1 Mixing diagram modified from Wänke *et al.* (1975). Lunar highland rocks are essentially mixtures of two major components. Anorthite (left) is one endmember. The extrapolation to the mafic endmember is uncertain. If it is fixed at a chondritic Ca/Al ratio, it is not of Earth's mantle composition, as Fe is too high and Mg too low. Ringwood *et al.* (1986) suggested that this composition is the result of komatiite-like fractionations of a melt of Earth's mantle.

Before I took a one year leave from Mainz I had discussed these questions with Wänke many times. In Chicago I tried to understand better the signatures of projectiles. I wanted to talk about some of the problems with Ed Anders. But he was too busy, he told me that John Morgan and he had studied these problems for several years and that there was no need for additional discussions.

8.4 My Contribution

I contributed to this debate in a paper on the indigenous Ni and Co contents at the Apollo 16 and 17 sites (Palme, 1980). I used Ir-Ni and Ni-Co correlations of highland rocks, which were successful in identifying projectiles of terrestrial impact craters. My conclusion was that there was a difference between the indigeneous (*i.e.* intrinsic lunar) components at the Apollo 17 and the Apollo 16 sites. At Apollo 17 I found 40 ± 15 ppm Ni and 21.6 ± 3.5 ppm Co. These values are essentially defined by the large Apollo 17 boulders. The chondritic Ni/Co ratios of most Apollo 16 rocks suggested no, or only a very small amount of, indigeneous siderophiles. The conclusion that the Moon had different Co concentrations at different landing sites was based on a chondritic Ni/Co ratio of the meteoritic component at both landing sites. The Ni/Co ratio is about 20 in chondritic meteorites, in contrast to the Ni/Ir ratio, which is more variable as Ir is a refractory element. The abundances of refractory elements in meteorites are more variable than Ni and Co. Based on the precise analyses of HSE (highly siderophile elements; Ir, Os, Ru *etc.*) in lunar highland rocks Fischer-Gödde and Becker (2012) claimed that iron meteorites were among the projectiles having impacted the Moon. This hypothesis is required to explain the enhancement of Ru, Pt, Rh and Pd over Ir in some lunar highland rocks. Iron meteorites would also shift the chondritic Ni/Co ratio to lower ratios, as iron meteorites are in most cases enriched in Co relative to Ni. This new hypothesis adds more complications to the interpretation of the meteoritic components in lunar highland rocks. The question of the origin of siderophiles in lunar highland rocks is not yet fully understood.

In a recent attempt to solve these questions Gleißner and Becker (2017) tried to derive Re-Os ages from KREEP-rich highland rocks. Although there are significant variations in Re/Os of different lithologies, there is no common isochron implying that these rocks were never completely molten; they are breccias and different parts may have different ages and also record different meteoritic signatures. More than one meteoritic signature in a single rock is a serious problem, which makes the identification of meteoritic signatures much more difficult, as most analyses of HSE were done on bulk rocks.

8.5 On the Age of KREEP

Besides my activities in Anders' group I wrote a paper on the age of KREEP, a result of the element correlations we did in Mainz (Palme, 1977). In highland rocks KREEP is usually the dominant source of incompatible elements. The late heavy bombardment of the Moon 3.9 to 4.0 Ga ago reset the ages of many highland rocks, in particular those of KREEP-containing rocks. The incompatible elements were not fractionated, but alkali elements were often mobilised, which led to variations in ratios of refractory to volatile element pairs, such as Sm/Rb. By assuming constant Sm/Rb ratios before this late bombardment, one gets much better defined model ages for Apollo 14, 16 and 17 KREEP-enriched rocks, based on existing measurements of ^{87}Sr/^{86}Sr ratios. The model ages were around 4.4 Ga, dating the formation of KREEP-rich magmas. These ages are different from the crystallisation ages of around 3.9 to 4.0 Ga for KREEP-rich rocks. These ages date the distribution of KREEP over the front side of the Moon. Today one would say that the KREEP model age dates the crystallisation of the anorthositic crust of the Moon, which resulted in massive removal of Sr and Eu with crystallising anorthite. High Rb/Sr and large negative Eu anomalies are characteristic features of KREEP.

9. IDENTIFICATION OF PROJECTILES OF TERRESTRIAL IMPACT CRATERS

9.1 Terrestrial Impact Craters

Ed Anders suggested that samples from terrestrial craters should be analysed. The idea was to see if impactors of terrestrial craters can be identified by their high siderophile element contents, similar to that assumed for the Moon. In Chicago samples were analysed with the same procedures as lunar samples. The first attempt failed. Breccias from the Ries crater had no obvious meteoritic contamination. Morgan *et al.* (1979) suggested a differentiated meteorite with no or very low concentrations of metallic elements.

Richard Grieve from the Geological Survey of Canada provided samples of large Canadian Craters, which we analysed in Chicago. In the 1960s Canadians had drilled holes in winter through thick ice layers in lakes presumably of impact origin. This was apparently easier than drilling holes from a boat in summer. The Clearwater lakes are two impact craters on the Candian Shield, East Clearwater is 22 km and West Clearwater is 32 km in diameter, and the rims of both craters are separated by only a few kilometres (Fig. 9.1). West Clearwater lake has a large ring of islands with exposed impact melt, at East Clearwater a 50 metre thick impact melt sheet was encountered at a depth of about 300 metres. Samples of this melt layer have high contents of Ir, Ni and other siderophiles, reflecting some 7 % of a chondritic component (Palme *et al.*, 1978b, 1979). This is the highest fraction of meteoritic material in a large terrestrial crater so far detected. Back in Mainz I attempted to identify the host phase of the meteoritic elements in East Clearwater samples. I could isolate, by activation analysis and following the Ir activity, a tiny grain with roughly a 1,000 fold enrichment of highly siderophile elements. The millerite (NiS) particle may represent an altered piece of the East Clearwater projectile (Grieve *et al.*, 1981). Interestingly, impact melt from West Clearwater does not have a meteoritic component. The reason is unclear. It was long believed that the two Clearwater craters were produced by a double asteroid, in part based on Rb-Sr ages which suggest ages of 285 to 300 Ma for both craters (Reimold *et al.*, 1981). Recently Schmieder *et al.* (2015) reported new ^{40}Ar/^{39}Ar age data for both craters and found a difference of 180 Myr between the formation ages of both craters, with a younger age of West Clearwater (286.2 ± 2.2 Ma). Thus the origin of the Clearwater craters is still a mystery.

After returning to Mainz we did more analyses of terrestrial crater samples. But it turned out that only a few have a measurable meteoritic component (*e.g.*, Göbel *et al.*, 1980; Palme *et al.*, 1980, 1981a).

The meteoritic component is preferably dissolved in the melt component of the impact crater where it is rather homogeneously distributed. Impact melt is, in general, chemically very homogenous, due to extensive and very rapid mixing (*e.g.*, Grieve *et al*., 1977). There are several possibilities for impact melts low in, or free of, meteoritic elements: differentiated projectiles with little or no siderophiles, and very little formation of impact melt in sedimentary targets, because all the energy is needed to heat up and vaporise water (*e.g.*, Ries crater in Germany). High impact velocity produces large amounts of melt and the meteoritic component is diluted or the projectile is completely evaporated. Thus one possibility for the high meteoritic component in East Clearwater is a low impact velocity, which leads to a small fraction of melt and consequently a high meteoritic component (see O'Keefe and Ahrens, 1977). In the late 1970s I found the O'Keefe and Ahrens papers very useful and impact modellers of today tell me that their conclusions are still valid.

Figure 9.1 The two Clearwater Lakes, former impact craters, in the Canadian Shield. On the right Clearwater East with a diameter of 22 km, on the left Clearwater West with a diameter of 32 km and a ring of islands. It has been suggested that both craters formed simulatneously by a double asteroid. This was challenged recently by Schmieder *et al*. (2015) claiming a difference in formation ages of 180 my between the two craters (photo credit: ESA).

In summary: good meteoritic signals in impact melts of large terrestrial craters are rare, *e.g.*, East Clearwater, Brent, Lappajärvi *etc*. In many cases the siderophile element signature is very low or absent, *e.g.*, West Clearwater, Mistastin, Manicouagan, Nördlinger Ries (see Palme, 1982).

More recently Cr isotopes have been used as evidence for the extraterrestrial origin of Cr in impact derived lithologies. Chromium is low in the crust of the Earth, but high in chondritic meteorites. I had earlier emphasised the potential of Cr to identify the meteoritic nature of impactors. The problem is that mafic Cr-rich rocks may contribute to the impact melt in which the meteoritic impactor is dissolved. With the improved accuracy of Cr isotope analyses an extraterrestrial origin of Cr can be established (Koeberl *et al.*, 2007).

9.2 The Cretaceous-Paleogene Impact

At the 44th Meeting of the Meteoritical Society in Bern in 1981, Bob Pepin (from the University of Minnesota) invited me to a meeting in Snowbird (Utah) in October 1981. The meeting was intended to bring together specialists of very different disciplines to discuss the connection between the worldwide ocurrences of Ir-rich layers and the mass extinction at the Cretaceous-Paleogene boundary. I was supposed to talk about the meteoritic signatures of terrestrial impact craters and the extraterrestrial signatures of the K-Pg boundary layers. I found the meeting very interesting, in particular its interdisciplinary character. My main conclusion was that elements, indicative of a meteoritic component, do not occur in chondritic ratios in Ir-rich K-Pg layers, although they seem to be well correlated. For example, the Ni/Co ratio in K-Pg boundary layers at Stevens Klint (Denmark) and Caravaca (Spain) is about 10, compared to the meteoritic ratio of 20. Moreover the element As in Stevens Klint samples is well correlated with Ni but has an over-abundance of As by a factor of more than 300. It appears that meteoritic elements were mixed with terrestrial siderophiles to form a single component, which then formed the boundary layers (see Palme, 1982).

We later analysed Stevens Klint samples, collected by Günther Graup (a mineralogist who has studied Ries sediments), but we were unable to isolate a meteoritic component (Graup *et al.*, 1992). Thus we could not resolve the nature of the extraterrestrial material at the K-Pg boundary. The extraterrestrial nature of some of the elements in the K-Pg boundary layer was established with the non-terrestrial Cr isotopes (Shukolyukov and Lugmair, 1998).

10. METEORITES AND THEIR COMPONENTS

10.1 General Remarks

Meteorites are the prime source for information about the composition of extraterrestrial materials. Meteorites were released during collisions as fragments from asteroidal bodies or planetesimals in the asteroid belt or from the surface of planets, such as Moon and Mars. In most cases meteorites recovered on the surface of the Earth only spent a few million years as individual bodies, so called meteoroids, in space. For most of their lifetime they were buried in the interior of larger planetesimals completely shielded from cosmic rays. Two different types of such planetesimals can be distinguished, those which were once molten and subsequently differentiated into core, mantle and crust and those which were not heated enough to reach melting temperatures, although they may have experienced variable degrees of thermal metamorphism. The latter are called chondritic meteorites because most of them contain sub-mm to mm sized spherules, the chondrules, which were molten in space before accreting into the meteorite parent body. Chondritic meteorites have approximately the same chemical composition for rock forming elements as the average solar system *i.e.* the Sun. They are therefore often referred to as primitive meteorites (Figs. 10.1 and 10.2).

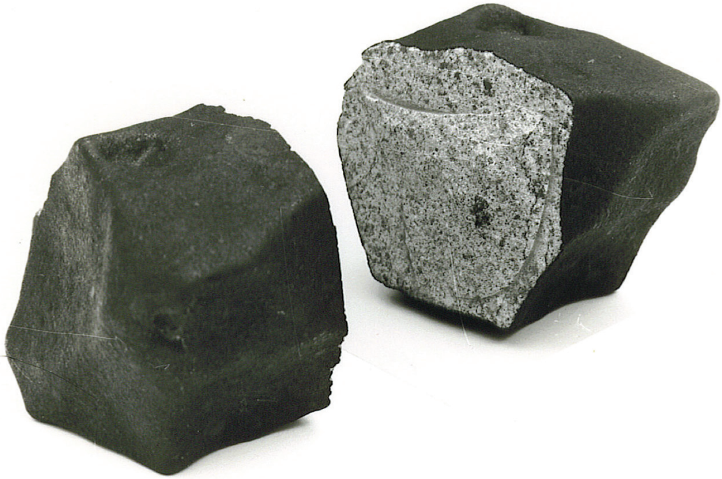

Figure 10.1 Two pieces of the L-chondrite Mocs. The dark and complete fusion crust and the bright, unaltered interior indicate that this is a meteorite fall and not a meteorite find. Diameter of samples *ca.* 5 cm.

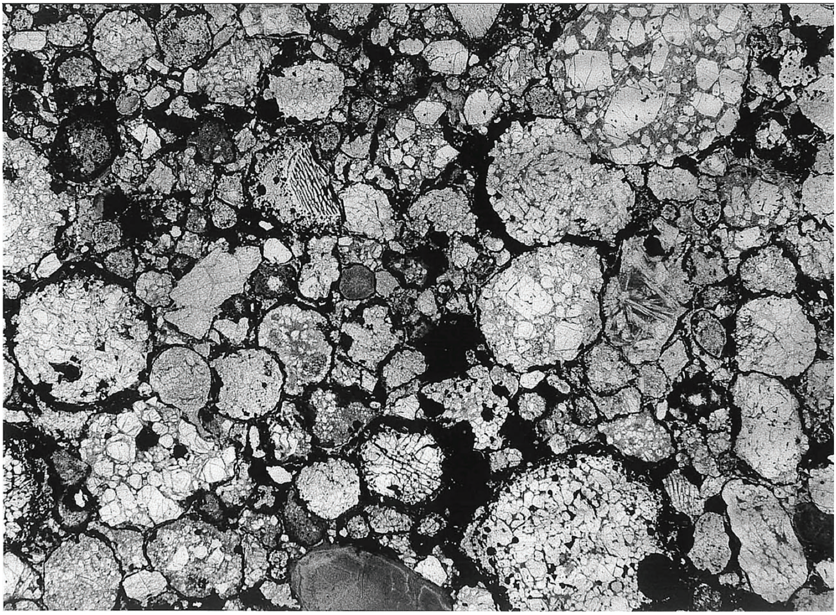

Figure 10.2 The Tieschitz H/L 3.6 chondrite. Thin section in transmitted light. Dark areas are metal and/or sulfide. The chaotic mixture of various types of chondrules, chondrule and lithic fragments with metal and sulphide has a well defined bulk composition on a gram scale. Long side of section is about 3 mm.

Melting of chondritic planetesimals leads to two major events: formation of a metal core by gravitational settling of metallic FeNi-alloys, and formation of an Al-rich silicate crust by partial melting of the Mg-rich silicate mantle. A variety of meteorite classes are derived from such differentiated planetesimals, iron meteorites from the cores (or segregated metal ponds), stony irons from the core-mantle boundary and achondrites (basaltic meteorites) from the crust (Figs. 10.3 and 10.4). The composition of these meteorites is very different from the average solar system composition. It is likely but difficult to prove in detail that differentiated meteorites come from once molten planets with chondritic bulk composition (Palme and Zipfel, 2017).

Throughout his time as director of cosmochemistry at the Max-Planck-Institute, Heinrich Wänke bought meteorites from collectors and meteorite dealers. Between 1977 and 1982 the cosmochemistry department acquired parts of the Glenn Huss collection at the American Meteorite Laboratory in Denver. Heinrich Wänke was not a collector. He did not buy meteorites because they looked nice. He was only interested in the results of chemical analyses. Therefore the collection has interesting and important meteorites, but not necessarily the best exhibit specimens.

Figure 10.3 Iron meteorite, representing the core of a planetesimal. The irregular shapes of the surface, so called regmaglypts, are the result of ablation of material by passage through the atmosphere of the Earth (photo credit: A. Pack).

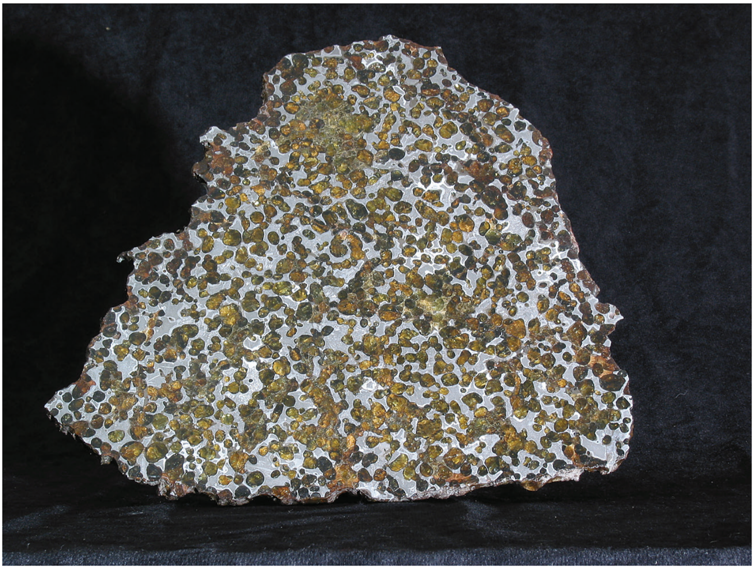

Figure 10.4 A cut and polished surface of a Pallasite, a mixture of olivine and metal, probably representing the core-mantle region of a planetesimal. Width of sample *ca*. 20 cm (photo credit: A. Pack).

One day, I think it was in the 1980s, I got a call from a mineral dealer in Berlin, who wanted to get rid of his Allende materials. I bought about ten kilogram of Allende for the Mainz cosmochemistry and roughly the same amount for Gero Kurat at the Natural History Museum in Vienna. I remember that the price was 1.25 DM per gram (Deutsche Mark, 1 euro is 2 DM). Today Allende is at least ten times more expensive. Later I regretted not having bought all of the Allende meteorite the dealer had offered.

After the end of cosmochemistry in Mainz in 2005, the meteorite collection was transferred to the Senckenberg Museum and Research Institute in Frankfurt. The curator of the collection is Jutta Zipfel. The collection has now about 2,000 individual meteorites.

We did many routine analyses of all types of meteorites with INAA and RNAA. We analysed bulk meteorites as well as components of meteorites, such as chondrules, metals, sulphides and Ca, Al-rich inclusions (CAI) from carbonaceous chondrites.

In some cases we cooperated with Klaus-Peter Jochum from Al Hofmann's group. Klaus-Peter analysed terrestrial and extraterrestrial materials by spark source mass spectrometry (SSMS). We often discussed our results. His data for Y, Nb and Zr were particularly useful to us, because these elements cannot be determined with thermal neutron activation analysis. A good example is our paper on the chondritic abundances of Nb, Ta, and Y (Jochum *et al.*, 1986). Niobium and Y were determined with SSMS, whereas for analyses of low Ta contents we developed a radiochemical procedure. The data we obtained are not very different from newer analyses.

During the period of lunar sample analyses and later we continually analysed meteorites and their components. Here I cannot mention all studies, but I will point out a few special cases.

10.2 Ca, Al-rich Inclusions

When Heinrich Wänke returned to Mainz from the Meteoritical Society Meeting in Chicago in 1972, he told us about Larry Grossman's work on Ca, Al-rich inclusions in the Allende meteorite (Fig. 10.5). He mentioned that some of these inclusions could be fairly easily removed from the meteorite. Frank Wlotzka checked an Allende sample from our collection and a cm-sized CAI fell out of the meteorite. The right size to apply our neutron activation prodecdures. It was a type B CAI with uniform enrichment factors of refractory lithophile and refractory siderophile elements of about 20 (relative to CI abundances), in perfect agreement with Grossman's hypothesis, that CAIs are high temperature condensates, which removed about 5 % of the total condensible matter (Grossman, 1980). Later we analysed more CAIs and found them to be fairly variable in their trace element patterns. The fine grained CAIs had REE patterns that were different from anything we knew from terrestrial samples. It was Bill Boynton who found the right explanation, that condensation of REE and Y occurred from a gas that had earlier lost a super-refractory condensate (Boynton, 1975). On one of my first trips to the United States I visited Bill Boynton in Corvallis. We talked about neutron activation and he showed me the calculations he did to explain the unusual REE patterns, which we also had found, and I showed him the calculations we made to explain the refractory metal nuggets. There is, in my mind, no doubt that condensation processes must have occurred in the early solar sytem.

Figure 10.5 A slice of a 5 cm wide chunk of the Allende meteorite. A large cm-sized fine grained, convoluted inclusion is visible on the lower left side. These spinel-rich inclusions contain REE with so called group II patterns. These patterns reflect condensates from a gas phase which has lost super-refractory elements.

The study of CAIs became a new field and findings of unusual CAIs were frequently reported at Meteoritical Society meetings. We analysed more CAIs from Allende and other carbonaceous chondrites (*e.g.*, Palme and Wlotzka, 1979), some together with Gero Kurat in Vienna. But in the end it was not clear what we were looking for. I sympathise with John Wood who described the situation in a review paper (Wood, 1988):

> *'The literature of refractory inclusions (RI) is mostly descriptive, consisting in large part of long, densely packed petrographic treatises. The properties of RI are so diverse that it is difficult to generalize about them. No conclusion can be drawn about one subset of RI that is not inconsistent with observations made in other inclusions. It is hard to isolate the scientific issues addressed by RI research, and it is hard even to define the class of objects referred to.'*

Nevertheless CAIs have provided us with some fundamental insights. They have the oldest ages of any solar system object. They show that condensation processes must have occurred in the early solar system. If CAIs formed near the Sun, then CAIs must have been transported outward to the region where water-bearing meteorites formed. Also, the stable isotopes may give us some clues for the range of isotopic variabilty in meteorites. The chemical and isotopic composition of CAIs may also provide constraints for astrophysical modelling, although one should not take these models too seriously. On one occasion I talked to Al Cameron, the dominant astrophysicist in the second half of the last century, about some of our data which fitted his models (I forget details). He showed little interest and told me, *'this was last year, this year I have a different model'.*

10.2.1 A super-refractory inclusion

Bill Boynton's explanation for the unusual REE patterns and later for all refractory lithophile elements in fine grained, spinel-rich Allende inclusions, requires a super-refractory component, enriched in the most extreme refractory lithophile elements. This component was removed from the source of the later condensing fine grained inclusions with group II REE patterns. During routine analyses of chunks of the Ornans meteorite I noticed in one sample some enhancement of Ir (Palme *et al.,* 1982). The inclusion was separated from the small Ornans sample. By following the Ir activity, many further separation steps led finally to the isolation of *ca*. 1 µg sample material. The enrichment in Hf, Sc and Zr as well as Os and Re, suggested an ultra-refractory inclusion. These elements have condensation temperatures above the REE which are assumed to condense with hibonite (Lodders, 2003). The mineralogy of the inclusion was determined by Ahmed El Goresy in Heidelberg. Later, more super-refractory inclusions were found (*e.g.*, Davis, 1984). But, as far as I know, none in the Allende meteorite. This is of some significance, since it indicates that the the whole CV parent body may have been devoid of a super-refractory component, relative to the CI pattern of refractory elements. A clear indication is the overall slightly group II fractionated REE pattern of bulk Allende (see Stracke *et al*., 2012 and references therein).

10.2.2 Refractory metal nuggets and opaque assemblages

One aspect of the Ca, Al-rich inclusion research was particularly interesting to me. Coarse grained, type B CAIs are usually high in Ir and other refractory metals. What is the host phase of the refractory metals? I crushed a previously irradiated CAI with high Ir and analysed sub-samples and with the help of a magnet I could finally isolate a tiny 30 µm metal nugget with an estimated mass of about 1 µg and high γ-activities of all refractory metals. After decay of the high activities Frank Wlotzka made a section of the grain and we both travelled to Vienna to analyse the section at the Natural History Museum with Gero Kurat, who was in charge of the electron microprobe (EMP). Although the spatial resolution of the ARL-probe was poor, compared to modern EMPs, we could measure the concentrations of six refractory metals using appropriate metal standards. The INAA data showed roughly chondritic ratios among the refractory metals, but the EMP data indicated local concentrations, Mo was primarily associated with sulphides. The hcp (hexagonal close packed)-metals Os and Ru formed separate phases, and the Ni-Fe core of the particle was high in Pt and Rh (bcc metals). Back in Mainz, and with the help of Jack Larimer (see section on vistors at the institute) we did some condensation calculations, which showed that refractory metals should condense as alloys with some Ni and Fe present, even before the calculated condensation temperatures of pure Fe and Ni (Palme and Wlotzka, 1976b).

Refractory metal alloys were also reported by Wark and Lovering (1976), who suggested a pre-solar origin, as did El Goresy *et al.* (1978). I remember well the Lunar Science Conference in 1976. There was a special session organised by H. Nagasawa on Allende inclusions. I gave a report there about our refractory metal grain and the good fit of the refractory metal abundances with condensation calculations. It was in one of the rooms on the first floor of Gilruth Center. After the talk somebody (I do not remember who it was) stood up and said: '*This cannot be true*.' Then John Lovering from the University of Melbourne stood up and said that they found exactly the same type of alloys. Next day he gave his talk during the normal conference, confirming the existence of refractory metal alloys (Wark and Lovering, 1976). David Wark found the first occurrence of these alloys on May 24th 1973 as he mentions in his thesis (Wark, 1983). As I cannot give a date for our detection of the refractory metal alloys, we agreed that we found them at the same time. Over the years I have had a good relationship with David. He sent me many results of his SEM analyses. Some would fit the condensation sequence, others did not. There are a number of possibilities for this. Calculations are based on ideal solid solution, because we have virtually no knowledge of any activity coefficient of an element in these unusual alloys. Also condensation may start later and/or end abruptly because of shielding by condensing silicates or oxides *etc*. As bulk CAIs usually have bulk volatility-related refractory metal patterns, it seems reasonable to assume a condensation origin for the bulk of the refractory metals.

El Goresy *et al.* (1978) also observed refractory metal nuggets embedded in refractory mineral grains. These assemblages were so unusual that El Goresy *et al*. (1978) named them '*Fremdlinge*' (German for strangers). The authors thought that these alloys have a non-solar system origin. When Hutcheon *et al*. (1987) analysed the isotopes of Mg, Fe, Mo, Ru and W in Fremdlinge, they found no evidence for an extra solar system origin. For this reason, Fremdlinge were later named *opaque assemblages* (Palme *et al*., 1994). With Addi Bischoff from Münster I did more work on opaque assemblages (Fig. 10.6, Bischoff and Palme, 1987). All these data show that refractory metals condense as alloys and later, during nebular cooling, exsolve into hcp alloys with Os and Ru, and bcc metals with Fe, Pt, Rh, W. Later reaction with sulphides may form MoS_2. Often W and sometimes also Mo are oxidised and may form solid solutions of scheelite and powellite (Bischoff and Palme, 1987). The variability in alteration of opaque assemblages and their CAI hosts reflect the various environments the CAIs have experienced before they were assembled in the parent body. These alterations are so diverse that they could not have formed in the homogeneous environment of the Allende parent body. The CAI alterations must have occurred before the final assemblage of the meteorite.

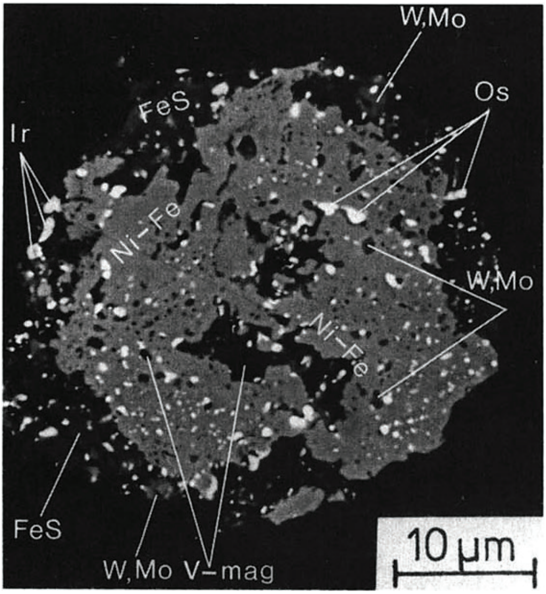

Figure 10.6 Opaque assemblage (OA, earlier Fremdling) from a CAI in the Allende meteorite. The Ni-Fe matrix in the center contains small grains of 0s (white), Ca(W,Mo)O4 (grey), and V-magnetite (dark). Other dark areas of the Fremdling mainly consist of FeS also enclosing 0s-particles. Some Ir-rich metals were found at the edge. The bulk OA pattern of CI-normalized refractory elements follows a pattern expected from condensation calculations. SEM-image in back-scattered electrons (from Bischoff and Palme, 1987 with permission from Elsevier).

10.2.3 Recent activities on the study of refractory metal nuggets (RMN)

Several years after my retirement from the University of Cologne, Uli Ott in Mainz had a student, Thomas Berg, who was looking at acid insoluble residues of chondrites. He was fascinated by the refractory metal nuggets that he frequently found in these residues. I participated in this work and Thomas Berg analysed the metal grains with the SEM and made condensation calculations. It turned out that many of the metal nuggets came compositionally close to predictions by single phase condensation calculations. From simple growth calculations we could calculate a cooling rate of the nuggets of 0.5 K yr^{-1}, much slower than estimated cooling rates of CAIs (Berg *et al.*, 2009). Some of sub-micrometre sized refractory metal nuggets were further studied by Harries *et al.* (2012). With the focused ion beam technique (FIB) samples were prepared and then crystallography, microstructures, and internal compositional variations using transmission electron microscopy (TEM) were studied. All grains were monophase alloys with hexagonal close packed (hcp) crystal structures despite considerable variations in their bulk compositions. There are no compositional heterogeneities. No evidence was found for condensation into separate phases, such as bcc or hcp alloys, as suggested by Sylvester *et al.* (1990). In some of the RMN selected from a type B CAI metallic Nb was identified, attesting to the reduced nature of these grains (Harries *et al.*, 2013).

More work on the RMN was done by a PhD student Daniel Schwander in Mainz, who further pursued the work of Thomas Berg. He studied RMN in acid resistant residues and later in fragments of CAIs earlier analysed with INAA by Bernhard Spettel and I. Schwander *et al.* (2015) claim that RMN compositions not fitting with the results of condensation calculations were established by dissolving and exsolving the RMN in CAI liquids. I have some problems with this hypothesis, but maybe some exchange among RMN in a CAI liquid may have modified the compositions. It is also conceivable that some of the grains were released from oxidised opaque assemblages (Fig. 10.6). From bulk CAI and OA data it seems clear that the refractory metals ultimately must have formed by condensation from a gas of more or less solar composition. Daly *et al.* (2017) have recently studied a large number of RMN in carbonaceous chondrites.The RMN are found in CAIs, chondrules and matrix. Some of them may have had an interstellar origin. But it appears that they experienced a variety of environments, which indicates that they travelled as isolated metal nuggets or as larger opaque inclusions through the early solar system before they were incorporated in the material that formed meteorite parent bodies.

10.2.4 W and Mo anomalies in CAIs

It is often stated that CAIs could either have formed by condensation or by evaporation. Both processes could produce refractory element enriched material. One of the striking features of many CAIs is the uniform abundance pattern of CI-normalised refractory metal patterns, including Mo and W. Both elements require very reducing conditions to condense with the other refractory siderophile elements in a single metal alloy. Indeed W and Mo are often missing in bulk CAIs as well as in refractory metal nuggets. One possibility is that conditions during condensation are more oxidising than the canonical solar nebula. Another possibility is evaporation of silicates and/or water. Early on I had some contact with Bruce Fegley and Alan Kornacki about Allende inclusions and meteorites in general. Fegley and Kornacki (1984) were the first to point out that bulk Allende may have a slightly fractionated REE pattern resembling the famous group II pattern of Mason and Taylor (1982). When Bruce Fegley came over to Mainz we worried about the condensation behaviour of W and Mo. Even at reducing condition W oxides dominate the gas species of W. Only a small fraction of W is present as gaseous metal atoms. As a conseqence the W condensation should be extremely dependent on oxygen fugacity. With our metal condensation programme we calculated the depletions of Mo and W that would occur at more oxidising conditions. Isolated metal grains, opaque inclusions and bulk CAIs often show depletions of W and/or Mo. In some cases refractory metal patterns with W and Mo anomalies could be reproduced by condensation calculations at more oxidising conditions (Fegley and Palme, 1985). It turns out that in incomplete condensates, Mo depletion factors should in all cases be larger than those of W. If evaporation were the major process for the formation of refractory metal alloys and for CAI formation in general, massive depletions of W and Mo would be expected and the losses of W would exceed those of Mo, the opposite to the condensation behaviour. While condensation occurs in the highly reduced solar nebula, dominated by hydrogen, evaporation through local heating will ocurr in a very oxidising environment. Tungsten and Mo would not even enter the alloys of highly refractory metals and would behave as volatile elements. If W and Mo containing refractory metal alloys were heated under oxidising conditions W would be the first element to be lost from the alloy, followed by Mo and at still more oxidising conditions, by Os (Palme *et al.*, 1998). The interesting point is that W as WO_3 will be easily trapped in silicates while volatile MoO_3 may escape (see Palme *et al.*, 1994). Thermal metamorphism at oxidising conditions may have produced loss of Mo from Karoonda, as discussed above, but the volatile WO_3 that was formed under the same conditions was trapped in the silicates.

Bruce Fegley's stay in Mainz had another consequence. Katharina Lodders, who did her diploma and PhD theses with me, became Bruce Fegley's wife.

10.3 Acapulcoites

We did, for example, the first analysis of Acapulco, the worthy father of Acapulcoites. The Acapulco study was in cooperation with Mireille Christophe Michel-Levy and Jean-Claude Lorin from the Université Pierre et Marie Curie in Paris, and Ludolf Schultz and Hartwig Weber from Begemann's group in Mainz. The Paris group looked at the mineralogy and petrology and studied tracks of cosmic rays and Pu, Ludolf Schultz and Hartwig Weber analysed rare gases and we determined the chemistry of the bulk meteorite and of various fractions. We defined Acapulco as a member of a completely new group of chondritic meteorites (Palme *et al.*, 1981b). As of July 7th 2017 there are 148 Acapulcoites, but Acapulco is the only fall.

The bulk composition of Acapulco is not very different from H chondrites, but Acapulco and the other Acapulcoites differ in several important aspects from ordinary chondrites (OC). Acapulcoites contain olivine with an average olivine fayalite content of about 10 mole %. They are much more reduced than ordinary chondrites and the oxygen isotopes are richer in ^{16}O than oxygen isotopes in OC. They plot below the terrestrial fractionation line (Clayton, 1993). The low fayalite content suggests some relationship to silicate inclusions in IAB iron meteorites and forsteritic chondrites, such as Mount Morris and Pontlyfni. Acapulcoites have experienced equilibration temperatures of about 1,000 to 1,100 °C, higher than those in OC. They mark the transition from chondritic meteorites to molten plantesimals. The beginning of melting is evident from inhomogeneous distribution of metal, sulphide, chromite, and phosphate (Palme *et al.*, 1981b; Zipfel *et al.*, 1995a; see review by Keil and McCoy, 2017). The degree of melting in acapulcoites is minor, as the major element composition is still roughly chondritic. Acapulco may be considered as a plagioclase lherzolite equilibrated at more reducing conditions and at higher temperatures than terrestrial plagioclase lherzolites. Jutta Zipfel (a PhD student in Mainz) had worked with Gerhard Wörner on these rocks for her diploma thesis at the University of Mainz. For her PhD work she applied the results to Acapulco. The two-pyroxene thermometer of Köhler and Brey (1990) gave temperatures of 990 °C, while the Ca in olivine thermometer records much lower temperatures, reflecting fairly rapid cooling and the higher Ca diffusivity in olivine compared to pyroxenes. Thus, zoning of Ca in olivine mineral grains contains information about the thermal history of these rocks at temperatures from 500 to 600 °C.

10.4 Ca in Olivine

These observations led to a more systematic study of Ca in olivine. There is an enormous range of Ca in olivine, from several thousand ppm in early condensed forsteritic olivines (Weinbruch *et al.*, 2000; Pack *et al.*, 2004) to 20 ppm in some equilibrated chondritic meteorites. Therefore it seemed promising to study the origin and history of olivine in primitive meteorites.

We were particularly interested in olivines with similar fayalite contents as the Earth's mantle olivines. We therefore performed EMP analyses of Ca zoning in olivine of Acapulco, Pontlyfni, Winona and silicate inclusions of Landes and El Taco in IAB iron meteorites. In 1991, we made a first attempt to quantify the Ca distribution in olivine (Köhler *et al.*, 1991). The quantification was done with the method of Köhler and Brey (1990). The cooling rates were very high for all studied meteorites, from 1,000-50,000 °C/Ma, with large uncertainties. This was a reflection of the high diffusion coefficients, which were taken from an earlier study of Jurewicz and Watson (1988) and extrapolated to the much lower temperatures, where Ca zoning in olivine was established.

After her studies on Acapulco, Jutta Zipfel started a systematic investigation of Ca in olivines of unfractionated meteorites containing olivines with low fayalite contents. Figure 10.7 demonstrates a strongly zoned Ca pattern in an olivine grain of a silicate inclusion of the Caddo County IAB iron meteorite (Zipfel *et al.*, 1992). These analyses were done with an ion probe during her stay at Caltech. Jutta Zipfel could show that the pattern and consequently diffusion coefficients depend on the orientation of olivine.

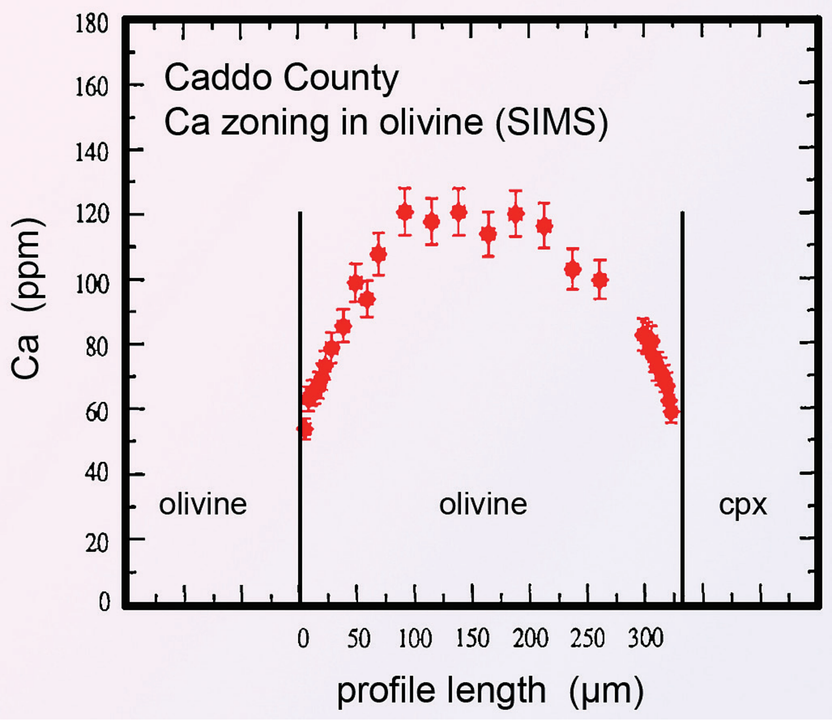

Figure 10.7 Ca profile in an olivine grain from the Caddo County IAB iron meteorite with silicate inclusions. The zonation of Ca reflects a cooling interval between 600 to 500 °C (modified from Zipfel *et al.*, 1992).

The temperature recorded by the highest Ca in the Caddo County olivines is about 200 °C lower than the orthopyroxene-clinopyroxene equilibration temperature. As mentioned above, this difference and the zoned olivines are the combined effect of the cooling and fast diffusion of Ca in olivine. The zoned Ca profiles in olivine (Fig. 10.7) record a similar temperature range as the kamacite-taenite exsolution in iron meteorites. In type IAB iron meteorites with silicate inclusions, such as Caddo County, both thermometers could be used simultaneously. Since the iron meteorite cooling rates changed almost annually with new modelling (Goldstein *et al.*, 2009), Ca in olivine could provide an independent measure of cooling rates. One prerequisite is the precise determination of the diffusion coefficient of Ca in olivine at temperatures as low as possible and at the appropriate oxygen fugacity.

Still in Mainz, I started to get involved with the experimental determination of Ca diffusion coefficients in olivine. The first thing I did was to invite Sumit Chakaraborty from the Bayerisches Geoinstitut in Bayreuth to give a talk about diffusion in Mainz. Sumit was at the time a well established researcher in the field of diffusion. Subsequently I had some contact with people in chemistry at the University of Giessen and a student there, Achim Hain, began to do experiments on Ca diffusion. He was funded by the German Science Foundation (DFG). For a number reasons the results were not satisfactory, and it took nearly ten years more before final results on Ca diffusion were obtained by Sumit Chakraborty's group in Bochum using their new equipment (Coogan *et al.*, 2005). However, it turns out that extrapolation of the diffusion coefficients down to 500-600 °C is still not very precise. The reason is the correlation of the diffusion coefficient with 1/T, which leads to a considerable expansion of the temperature scale and correspondingly large uncertainties. This is the same problem as with metallographic cooling rates. I am still thinking that the method could ultimately be very useful for comparison with metallographic cooling rates in IAB iron meteorites. Even if absolute cooling rates are difficult to obtain, one could compare Ca zoning derived cooling rates and metallographic cooling rates determined in silicate inclusions and metal within the group of IAB iron meteorites (Fig. 10.8). We know that IAB iron meteorites differ significantly in metallographic cooling rates as well as in absolute Ca contents in olivines and their Ca zoning (Köhler *et al.*, 1991).

Earlier Jutta Zipfel had attempted to apply the method to ordinary chondrites (Zipfel *et al.*, 1995b). Indeed she found that the enormous spread in Ca contents of olivines in type 3 to 4 ordinary chondrites is significantly reduced in type 5 to 6, where Ca contents may be very low. The determination of absolute temperatures is difficult because of the high fayalite contents of olivines in ordinary chondrites, as calibrations by Köhler and Brey (1990) were made with peridotitic olivines (Fa *ca*. 10 %). I think there is some potential in the method, but an important first step would be to calibrate the Ca thermometer in olivines with higher FeO contents.

Figure 10.8 The Widmanstätten figure or pattern of this iron meteorite is due to the differential etching of kamacite (α-iron with about 5.5 % nickel) and taenite (γ-iron with between 13 % and 48 % nickel). The kamacite is in the form of plates that have exsolved, parallel to the faces of the octahedron, from taenite. The width of the kamacite lamellae is a measure of cooling rate (photo credit: A. Pack).

10.5 Rumurutiites

We also made the first chemical analysis of Rumuruti, the only observed fall of the group of Rumurutiites (Schulze *et al.*, 1994). This group now comprises 182 meteorites (as of July 7th 2017). Rumuruti fell in Kenya in 1934. A 67 g piece was given to the Museum für Naturkunde in Berlin in 1938 by E. Reuning (a collector of African minerals and meteorites), who had received this piece from District Commisioner H.H. Trafford in Kenya. In 1993 the meteorite was re-detected in the collection of meteorites at the Museum für Naturkunde in Berlin. Rumuruti had several siblings, known before, such as Carlisle Lakes, and several Antarctic meteorites. They were earlier called Carlisle Lakes-type chondrites. These meteorites are the extremely oxidised variety of chondritic meteorites, with chondritic Fe contents but almost no metal and a fayalte content of olivine of about 40 %. The oxygen isotopes are depleted in ^{16}O, more than in any other bulk chondrite. Metals, more siderophile than Fe are in separate phases, with some refractory metal-rich nuggets containing more volatile metals, such as Au. In addition, there are also arsenides and tellurides (see review by Bischoff *et al.*, 2011). The bulk composition of Rumurutiites has some affinity to the composition of ordinary chondrites, but not to carbonaceous chondrites: little or no depletion of refractory elements and of the moderately volatile elements Mn and Na. Newer stable isotopes confirm the classification as non-carbonaceous chondrites (see Warren, 2011).

10.6 CH chondrites

We did early analyses of CH chondrites with Addi Bischoff. Acfer 182 is somewhat similar to ALHA85085 found earlier in Antarctica (Bischoff *et al.*, 1993). We proposed the term CH chondrites, which should indicate affinities with carbonaceous chondrites, although not with regard to the carbon content. But the enrichment of refractories and the depletion of moderately volatile elements such as Zn, Na, Mn and Se are similar to the depletion sequence in carbonaceous chondrites but different to ordinary chondrites. The H in CH should indicate the excess of Fe in the bulk analysis, as in EH. The affinity of the CH chondrites to carbonaceous chondrite has been confirmed by stable isotope analyses (see Warren, 2011 and references).

10.7 Eucrites

From the beginning eucrites were analysed in the same way as lunar samples (*e.g.*, Wänke *et al.*, 1972). We found that, compositionally, eucrites have similarities with lunar basalts. They are very low in volatiles as, for example, reflected in their low K/La ratios and they have similar depletions in W (Wänke *et al.*, 1973). But lunar basalts have lower Mn and higher siderophiles than eucrites, indicating that Earth and Moon are made from the same material, whereas material for the eucrite parent body must have come from a different feeding zone (see also Ruzicka *et al.*, 2001).

Based on oxygen isotopes it is generally thought that howardites, eucrites and diogenites (HED meteorites) come from a single parent body. The fourth largest asteroid Vesta is often identified as the parent planet of HED meteorites. Eucrites are melts from the interior of Vesta, diogenites are residual mafic rocks and howardites are mechanical mixtures of eucrites and diogenites produced by impacts on the surface of Vesta. Analyses of many HED meteorites were possible because of the large Mainz meteorite collection. The collection contained a very nice piece of Ibitira, a special eucrite with many vesicles. A picture of this piece can be found in Wasson (1974; Fig. VI-6). Unfortunately, this piece is lost forever. Aviva Brecher from MIT did magnetic measurements on all kinds of rocks. She emphasised the non-destructive nature of her analyses. One day she asked Wänke for the Ibitira slice and it was sent to her. After some time we got notice that the piece was lost. I remember I talked to her at a lunar science conference and she told me that the student who was supposed to measure the magnetic properties of the piece lost it on his way from his office to the lab. He was later interrogated by psychologists but he could not remember where he put the meteorite, a very strange story.

10.8 Meteorites from Moon and Mars

In 1982 the American Antarctic meteorite search party brought back an unspectacular, but unusual meteorite with the designation ALHA81005 (Fig. 10.9). Brian Mason at the Smithsonian Institution in Washington recognised this as a lunar meteorite. Two years before, the Japanese had brought back an Antarctic meteorite (Yamato 791197), which was identified as a lunar meteorite only after ALHA81005 was classified as a piece of the Moon. At the 14th Lunar and Planetary Science Conference there were a number of talks confirming the lunar origin of ALHA81005, including a contribution from Mainz (Palme *et al.*, 1983). Nobody doubted the lunar origin. Before the detection of ALHA81005, an only slightly shocked lunar meteorite, it was thought that *'lunar ejecta should be very heavily shocked (40–50 GPa) and Martian ejecta should be vaporised (100–200 GPa)'* according to Melosh (1987). The evidence from ALHA81005 caused some rethinking *'so that near-surface material may be accelerated to high speed and still escape compression to correspondingly high pressure'* (Melosh, 1987). This example told me that one should not take predictions from modellers too seriously. We also analysed lunar highland meteorites and we realised that at least some of them should come from the far side of the Moon, containing no KREEP and a low level of siderophiles. From these data we suggested an average chemical composition for the lunar highlands (Palme *et al.*, 1991).

The recognition of lunar meteorites was important for the identification of Martian meteorites. If impacts on the Moon can eject lunar rocks and breccias without major damage, this could also be possible with meteorites from Mars. Heinrich Wänke was among the early proponents favouring a Martian origin of SNC (Shergottites, Nakhlites, Chassignites) meteorites (see review by Wänke, 1991). We therefore analysed most of the Martian meteorites available at the time (*e.g.*, Burghele *et al.*, 1983). Martian meteorites had higher contents of volatile elements and they were more oxidised than terrestrial rocks. Wänke's two-component model that was constructed for the Earth could now be applied to Mars. The early reduced accretionary component was higher in Earth than in Mars which contained more of the later accreting, oxidised component (Dreibus and Wänke, 1989). Recent research has come to similar conclusions (Wood, 2008; Schönbächler *et al.*, 2010; Rubie *et al.*, 2011).

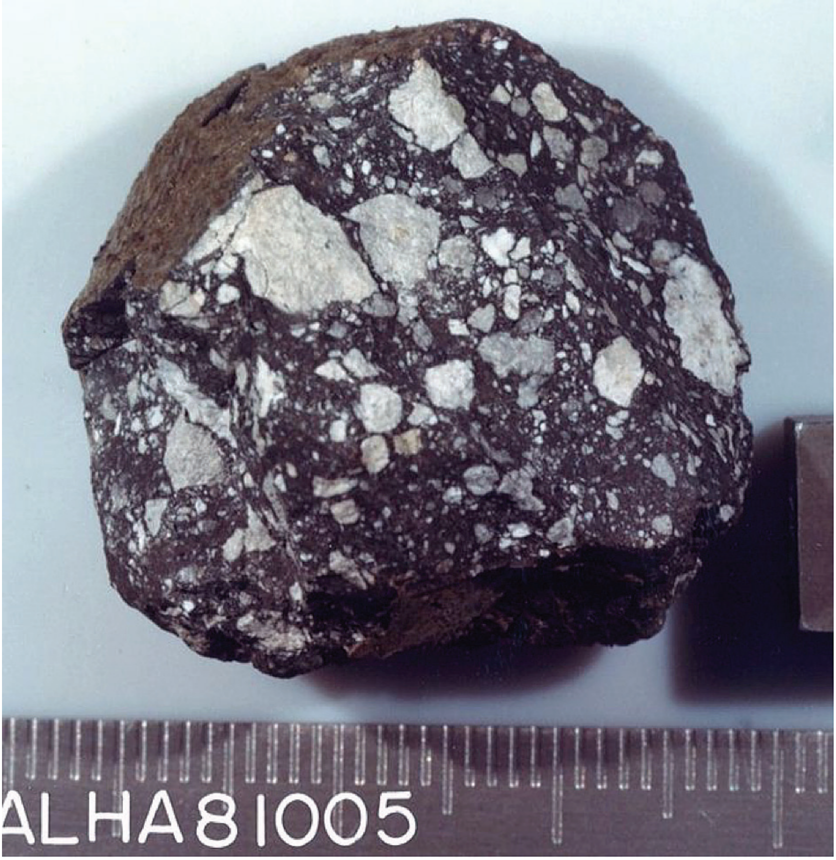

Figure 10.9 The first lunar meteorite, ALHA81005, a regolith breccia with many anorthositic clasts of various sizes. On the upper left side, a piece of the greenish fusion crust is visible (photo credit: NASA).

10.9 Desert Meteorites

One day during the late 1980s, I received a call from Peter Horn from the Institute for Mineralogy in Munich. Peter told me that some German geologists and/or engineers, who worked in Libya exploring oil fields, showed him some dark rocks which they believed were meteorites and he wanted to know if we were interested in purchasing some of these meteorites. I went down to Munich and looked at the meteorites. They were all very weathered, but I thought we should buy a few of them. Some time later two or three of the engineers came to Mainz and showed us their meteorites. Alltogether we finally bought 54 stones, which were all identified as ordinary chondrites by Frank Wlotzka. Because they were heavily weathered, we did not really know what to do with the new chondrites. Finally we decided to ask Tim Jull to determine their terrestrial ages by the ^{14}C method. Eleven of the ages ranged from 3,500 to 7,600 years, with only two samples having ages in excess of 10,000 years. The cut off in ages may be related to the timing of climatic changes in the Hammadah al Hamra desert where the meteorites were found (Jull *et al.*, 1990).

It turned out that the geologists had taken lots of meteorites from Libya, in the hope of making some additional money. They had even begun a systematic search for meteorites. They told me that it was not too difficult to get the meteorites through Libyan customs. Sometimes suitcases full of meteorites were confiscated. Apparently they must have accumulated at the Libyan customs. I suppose, in the end, they were all thrown away.

At this time, I had no idea that desert meteorites would become so important. I thought that the distribution of meteorite types among different classes would be the same in the desert as in our collections, so we could not expect much new information. Besides, these meteorites are all heavily weathered. If at all we should rely on Antarctic meteorites, which are much less altered. A couple of years later, we had a workshop about meteorites in Mainz. I do not recall details, but I remember that I talked about Antarctic and desert meteorites and I pointed out that we now have more meteorites from poorly populated groups and that in addition we are finding completely new types of meteorites. I also mentioned how inexpensive and effective this comparatively cheap research is. After my talk, Jim Arold from La Jolla, who was at the meeting, took me aside and told that I should not emphasise these aspects too much, because such reasoning would be counter-productive for new space missions. I am not so sure about this.

11. MODERATELY VOLATILE ELEMENTS

Around 1986 John Kerridge asked me to contribute to a new meteorite book. I was supposed to summarise the data on moderately volatile elements, together with Mike Lipschutz, and Jack Larimer who joined us later. I defined moderately volatile elements as those with condensation temperatures between Mg silicates and troilite (FeS). Highly volatile elements have condensation temperatures below FeS. Interestingly the abundances of the latter elements are variable in the different petrologic types of ordinary chondrites. In most cases they are increasingly depleted from type 3 to type 6, whereas moderately volatile element abundances do not vary between the petrologic types. For example, S and Zn concentrations in OC are independent of petrologic type, whereas Cs, Tl or Br are highly variable. This is very nicely shown in Keays *et al*. (1971; their Fig. 1).

Our main conclusions from this study were that the depletion of moderately volatile elements is independent of the chemical character of the element and that only meteorites with depletions are known, never enrichments (Palme *et al*., 1988). Both findings argue for incomplete condensation as the cause for the depletions. There are now more arguments against the evaporation of moderately and highly volatile elements. One of my PhD students, Andrea Wulf, did evaporation experiments on chunks of the Allende meteorite at various oxygen fugacities and at temperatures from 1,050 ° to 1,300 °C. Most samples showed loss of Na but no loss of Mn (Wulf *et al*., 1995). Chondritic meteorites have more or less CI chondritic Na/Mn ratios, making losses of Na by evaporation unlikely. Only Mn/Na ratios in small telluric bodies (STBs: Mars, Moon, eucrite parent body) show losses of Na relative to Mn, characteristic of evaporation (O'Neill and Palme, 2008). The Earth has essentially a chondritic Mn/Na ratio, suggesting that its components were never subject to the temperatures required for evaporation of Na. Therefore the depletion of volatiles in the Earth should be an inherited nebular feature. This is supported by the low terrestrial $^{53}Cr/^{52}Cr$ ratio of the Earth, suggesting very early removal of Mn (Palme *et al*., 2012a; Palme and O'Neill, 2014).

12.

TSCHERNOBYL

The most unusual event I encountered with neutron activation occurred a few days after April 26th 1986. Bernhard Spettel and I were doing some γ-counting on Ge(Li) crystals when we noticed unusual lines in the spectrum, which we quickly identified as arising from the decay of ^{131}I with a half life of 12.36 h. We had no explanation and thought of some kind of unknown contamination of the sample. We opened the lead shield of the detector expecting a lower signal to background ratio. But instead the line grew faster. Then the first rumours of a reactor accident in Tschernobyl came on the radio. I went downstairs and sampled some grass in front of the institute and put it back on the detector. Quickly we could see γ-radiation from the decay of ^{134}Cs, ^{137}Cs, ^{141}Ce and some other REE activities that were produced in a reactor 2,000 kilometres away from Mainz. In the following weeks Bernhard Spettel counted numerous samples that people brought to him to check the radioactivity: sand from playgrounds, game meat, mushrooms *etc.* first for radioactive Iodine, later for ^{135}Cs and ^{137}Cs activities.

We constructed a sampling apparatus, which would allow us to take soil samples to a depth of about 30 cm. Samples from all over Germany showed a strong correlation of ^{137}Cs activities with rainfall. Half the ^{137}Cs activity ($T_{1/2}$ = 30.17 years) in soils is, of course, still there, perhaps a little smeared out. We did quite a few analyses and found that the volatile radioactive species were much more abundant than refractory radioactive nuclei, which led us to conclude that the volatiles were transported through the atmosphere with winds. Based on surveys of ^{137}Cs I estimated that most of the inventory of ^{137}Cs of the reactor was distributed over Europe, contrary to some official statements. Refractory (non-volatile) elements were much less abundant, based on our fisson REE data. This also means much less of the dangerous ^{90}Sr with a similar half life as ^{137}Cs. A paper, which I submitted to *Nature*, was not considered, because at this time they had closed their journal for anything from Tschernobyl. The total radiation exposure of the German population from Tschernobyl was about the natural radiation exposure of one year. It was, of course, much worse, closer to the reactor. It took, however, a second accident in Fukushima in March 2011 until nuclear power in Germany was finally brought to an end.

13.

VISITORS TO THE COSMOCHEMISTRY DEPARTMENT

During my stay at the Max-Planck-Institute in Mainz, we had many visitors, some for a few days only, others stayed a year or more. I cannot give a complete list here. I had good contacts with most visitors, some of whom were invited by me. Heinrich Wänke encouraged his coworkers to invite people from other research institutions. Money was no problem at the time.

One of the first visitors was John Wasson. I was in Mainz only for a very short time, when John spent a year in Mainz. I could not really talk about meteorites to him as I did not know enough about meteorites. But I remember that we talked about neutron activation analysis. John and his group had so far done primarily radiochemistry and I think that they started their instrumental neutron activation after John's return from Mainz.

Shortly after my arrival, Stewart Ross Taylor and his family spent several months in Mainz. It was also too early for me to benefit much from his stay. But I remember that I pointed out to him the low ^{87}Sr/^{86}Sr isotopes in lunar samples and we speculated about the consequences.

Ermanno Rambaldi, an Italian mineralogist stayed a couple of years with us. He produced grain size fractions of metals from ordinary chondrites. The size fractions as well as silicates were then analysed with neutron activation analysis. His data showed that W in unequilibrated chondrites is primarily in silicates. During thermal metamorphism the major fraction of W partitions into metal (Rambaldi *et al.*, 1979). A similar finding was reported by Kleine *et al.* (2008). This has always been a mystery to me, because P does the opposite. In unequilibrated chondrites P is in metal and during thermal metamorphism it provides P for apatite and merrilite, it begins as metals and ends up as oxide, whereas W does exactly the opposite. I thought a lot about this problem. My solution is that W is not really in silicates in unequilibrated chondrites. A major fraction is in refractory metal alloys which are enclosed in silicates. During metamorphism W partitions into Fe-Ni metal.

Don Fraser from Oxford also spent some time in Mainz. He worked with the Knudsen cell, which Werner Rammensee had developed. We three, Don, Werner and I, regularly went for lunch and most of the time ended up in political discussions. Werner was very active in the anti-nuclear power movement and explained to us that the end of capitalism was coming soon, which still has not occurred. However the end of nuclear power, at least in Germany, has definitely come.

Louis Ahrens, the great geochemist from the University of Cape Town, also stayed in Mainz for some time. On one occasion he took me aside and told me the essence of his scientific life: *'Follow your interest.'* The Ahrens group in Cape Town was famous for their precise XRF analyses of lunar and terrestrial rocks. They determined in addition to the major and minor elements, also trace elements such as Zr, Nb and Y. James Willis from Louis Ahrens' group spent a year in Mainz, learning neutron activation analysis. We had numerous interesting discussions with him.

At around 1970 Edward Anders at the University of Chicago was the authority in cosmochemistry. He had pioneered the primitive nature of carbonaceous chondrites, contradicting Harold Urey, who thought that meteorites were of secondary origin and chunks of a larger planet. John Larimer (a post-doc of Ed Anders) had calculated the condensation behaviour of major and trace elements and concluded that chondrites formed by condensation from a gas of solar composition. Trace element abundances would provide information about condensation temperatures. After his post-doc John Larimer took a job at the Arizona State University in Tempe. Before he moved to Tempe he spent a year in Mainz, accompanied by his family. I interacted a lot with him. He introduced me to equilibrium thermodynamics and he was of great help in setting up the metal condensation programme. I benefited immensely from his knowledge in meteoritics. He was very important for my further career.

A frequent visitor to the institute was Gero Kurat from the Natural History Museum in Vienna. He was a famous meteorite petrographer, interested in Ca, Al inclusions, chondrules and Earth's mantle rocks. We analysed many samples from the Museum in Vienna and wrote a number of papers together (*e.g.*, Kurat *et al.*, 1980).

Hans Suess was a regular visitor to the institute. We had special birthday parties for him on the occasion of his 70th, 75th and 80th birthday, if I correctly remember. When Hans Suess came to Mainz his foremost activity was to plan further trips to various places in Europe. He asked me once if I would accompany him on a trip to Vienna by car, because as he said, he tends to fall asleep while driving. There are many stories about Hans Suess in Mainz and of course, even more in La Jolla. Hans Suess was responsible for Klaus Keil's departure from communist East Germany. Klaus Keil had studied mineralogy and geochemistry at the University of Jena. Fritz Heide, who had written a book about meteorites, was one his teachers in Jena. Klaus Keil wanted to do meteorite work in the US. Hans Suess, who knew Fritz Heide, visited him in Jena and offered his help to support Klaus Keil, after he had left East Germany. Hans Suess had conspiratorial meetings with Klaus Keil in a car, because they did not want to be taped. On one of these occasions Klaus pointed out that there may be a problem as he wanted to take another person with him, when leaving for West Germany. Hans Suess said something like '*Oh this is no problem there are many young and beautiful women in America*'. When I met Klaus a few years ago I asked him about this story and he confirmed it, mentioning that Hans Suess did not only speak of young and beautiful women in America, but he said young, beautiful and rich women. Of course Klaus took his wife (or girl friend) with him when he escaped from East Germany through Berlin, which was easy at the time as it was a few months before the Berlin Wall was built in 1961. Klaus Keil immediately travelled to Mainz, where he stayed a few months to get his PhD in mineralogy and geochemistry. He then travelled to the US. It was all organised by Hans Suess.

I did not talk much about science with Hans Suess. He was too busy with his travel arrangements. But it was due to the initative of Hans Suess that I started to compile data of CI chondrites and put together a table of cosmic abundances. Hans Suess organised a meeting with Heinz Dieter Zeh, a physicist from Heidelberg and a good friend of his. They published early papers on cosmic abundances of elements, also using Suess' empirical abundance rules (Zeh and Suess, 1973). At this time Zeh was retired and wanted to get rid of any responsibility. Suess and Zeh asked me to continue with compiling meteoritic abundances and compare them with predictions from nucleosynthesis and abundance data from the photosphere of the Sun. I regularly updated the meteoritic abundances, first with Suess and Zeh (Palme *et al.*, 1981c) and then with Hermann Beer, a nuclear physicist from Karlsruhe with special interest in s-processes (Palme and Beer, 1993). Later I contributed to the *Treatise on Geochemistry*, together with Anthony Jones (Palme and Jones, 2003) and an update with Katharina Lodders (Palme *et al.*, 2014a). In 2009 we had a new update and some discussion about solar abundances with Katharina Lodders (Lodders *et al.*, 2009). It is now clear that solar abundances fit extremely well with type 1 carbonaceous chondrites, in particular the Orgueil meteorites. The difference between Orgueil and the solar photosphere is less than one percent for the Mg/Si ratio, about 5 % for Fe/Si, 7 % for Al/Si and about 2 % for S/Si, where Al represents refractory elements and S volatiles. The S content is along with other volatile elements solar, only in CI chondrites, but significantly lower in all other types of chondritic meteorites.

Horton Newsom did his PhD with Mike Drake at the University of Arizon in Tucson. In his thesis he studied the partitioning of W and P between metal and silicates. After he had finished his thesis he decided to stay in Mainz for some time, where he concentrated his efforts on the analysis of Mo. With conventional and newly developed methods he established lunar and eucritic Mo abundances. The problem with neutron activation analysis of Mo was that there is always fission Mo present, which requires the knowledge of the U content for appropriate corrections. There is still a lack of highly accurate data for Mo in the Moon and also in eucrites, considering the precise analyses which are possible with mass spectrometry. I had many fruitful discussions with Hort and we had some common projects.

Earlier I had mentioned Bruce Fegley who spent about a year in Mainz (see section 10.2.4.)

Yukio Ikeda (Ibaraki University) came to Mainz with his family. We worked together on chondrules and eucrites. He seemed to have enjoyed his stay in Mainz.

Later, in the 1980s, Heinrich Wänke encouraged Gerhard Brey, Emil Jagoutz and I to invite scientists from other institutions to spend some time in our institute. I invited Richard Grieve, Bill Boynton, Uwe Reimold, Addi Bischoff and Ian Hutcheon.

All these vistors and many more not explicitly mentioned here were a great source of inspiration. Al Hofmann had, as director of the Department of Geochemistry, many vistors coming through, some were staying for years; Bill White, Nick Arndt, Catherine Chauvel, Bill McDonough, Bruce Watson and many others, and I was always learning new things. When I met Nick Arndt for the first time he told me that the spinifex textures in komatiites which he studied had the same origin as the barred olivine chondrules, by rapid cooling from a Mg-rich melt. At this time I had only a very faint idea about komatiites, but I began to read about them. I remember having had lots of discussions with Bruce Watson, we even analysed some of his samples, but I forget the details. My understanding and knowlege of Pb isotopes I owe to Steve Galer who was and still is employed by the Max-Planck-Institute in Mainz.

14. METAL-SILICATE AND METAL-SULPHIDE PARTITIONING

14.1 Trace Elements in Disko Island Samples

One of my first PhD students from the University of Mainz was Wolfgang Klöck. He studied trace elements in metals from Disko Island, Greenland. This is the largest known occurrence of metallic iron on Earth. Nils Nordenskiöld, who discovered the metallic iron in Ovifak on the south coast of Disko Island in 1870, believed that the metallic masses were meteorites. The trace element signature of siderophile elements in these metals clearly has a crustal origin (Klöck *et al.*, 1986). Separated phases in a Disko Island basalt allowed sulphide-silicate partition coefficients to be derived for a number of trace elements (Klöck and Palme, 1987). Wolfgang Klöck later took a position in Houston to work with David McKay on IDPs (interplanetary dust particles). He detected the so called LIME olivines (low iron manganese enriched) in IDPs. Olivines with high Mn and low Fe are expected to form in a gas of solar composition, but are rarely found. Under solar nebula conditions Fe condenses as metal and not as oxide which could replace MgO in olivine (Klöck *et al.*, 1989).

14.2 Chalcophile Molybdenum?

It is generally believed that Mo partitions preferentially into sulphides. Katharina Lodders (a chemistry student at the University of Mainz) experimentally determined silicate-metal and silicate-sulphide partition coefficients of Mo and W, using a similar procedure as Rammensee and Wänke (1977). The surprising result was that neither W nor Mo are chalcophile, both elements have much higher metal-silicate than metal-sulphide partition coefficients. The stronger depletion of Mo compared to W in the Earth's mantle is a result of its strongly siderophile character (Lodders and Palme, 1991).

Katharina was very much focused on sulphides. She did lots of partition experiments and also looked at metal, sulphide and silicate phases in enstatite chondrites and achondrites. She demonstrated that REE partition into sulphides, if conditions are sufficiently reducing. The depletion of V and Cr in aubrites could be explained by sulphide extraction of these elements (Lodders *et al.*, 1993) and she continued this work in St. Louis (Lodders,1996). Katharina also started to do condensation calculations in Mainz, before she left with her husband Bruce Fegley for St. Louis, where she published her condensation calculations (Lodders, 2003).

14.3 Metal-Silicate Partition Coefficients

After the success of the experimental determination of the W metal-silicate partition coefficients, a student was hired to do more partition experiments using the same method with radioactive tracers (Schmitt *et al.*,1989). This was one of the earlier studies of metal-silicate partitioning, which has now become a large field in experimental petrology. At this time the only other group doing partition experiments was Mike Drake's group at the University of Arizona. The experiments of Werner Schmitt were all done at one atmosphere, but under variable oxygen fugacites and some spread in temperature. In the paper we compared the abundances of the moderately siderophile elements in the present upper mantle with abundances predicted by applying the measured partition coefficients. We got reasonable agreement, given the comparatively large uncertainties. But Co and Ni did not fit at all. The solution to the problem came with the Li and Agee (1996) paper, which showed a strong dependence of the Ni and Co partition coefficients on temperature and pressure.

I also began to determine more metal-silicate partition coefficients with Werner Rammensee. Wänke had postulated that the depletion of Cr and V in the Earth's mantle is the result of core formation at reducing conditions, when Cr and V partition into metal. Indeed we found that at reducing conditions Cr and V become siderophile and that the low Cr and V in the Earth's mantle is the result of more reducing conditions at an earlier stage of core formation (Rammensee *et al.*, 1983). This is the basis for the two-component model of Wänke (*e.g.*, Wänke, 1981), where reducing material accretes first followed by oxidising and more volatile-rich material. That our data were obtained at only one bar was no problem, as it turned out later that the pressure dependence of the Cr and V metal-silicate partition coefficients is not very strong (Mann *et al.*, 2009). The low Cr content of the Earth's mantle has been and still is one of the keystones for heterogeneous accretion models. More recent diamond anvil cell experiments seem to indicate that at very high pressures Cr partitions into metal, even at fairly oxidising conditions (Siebert *et al.*, 2013). If this is true, the heterogeneous accretion models lose an important piece of evidence.

14.4 Noble Metal Solubilities in Silicate Melts

A logical next step was to study the partitioning of noble metals between metal and silicate. This research received a new boost by an initiative within the framework of a priority programme of the German Science Foundation (DFG). With Hugh O'Neill and Don Dingwell in Bayreuth and my group in Mainz (primarily Sasha Borisov and myself), we started a systematic study of the solubilities of noble metals in silicate melts. At this time, both Don Dingwell (Canadian) and Hugh O'Neill (English) were civil servants of the Bavarian Government working in Bayreuth. They told me that they were the first civil servants in Bavaria with foreign passports. Fritz Seifert had employed both within the first years of the Bayerisches Geoinstitut, which was founded in 1986 through the initiative of the then prime minister of Bavaria, Franz-Josef Strauss, who was persuaded by geophysicists that the state of Bavaria could show her excellence with such an institute. The Bayerische Geoinstitut has indeed been a centre of excellence since its foundation. It is now part of the University of Bayreuth, but still has good funding. Don Dingwell and Hugh O'Neill could have stayed there until retirement with all the privileges of a Bavarian civil servant, which are not small.

In our projects we focused on solubilities, because from an analytical point of view the determination of metal-silicate partition coefficients was impossible with the expected low contents of Ir, Pd, Au, *etc.* in the silicate melts. With 'natural concentrations' the contents of noble metals in silicates of a metal-silicate equilibration experiment would be far too low to be analysed with neutron activation analysis. If silicates were equilibrated with pure noble metals, noble metal concentrations in silicates would be much higher and one could extrapolate from solubilities to metal-silicate partition coefficients, if one knew the activity of the respective noble metal in the metal phase (mostly Fe-Ni alloys). In many cases the activity coefficients are not very different from unity, with the notable exception of Pt (*e.g.*, Borisov *et al.*, 1994). In Mainz we performed our experiments with tiny noble metal loops containing silicate droplets while the Bayreuth people used large (expensive) pure noble metal cups, where silicate melt was continuously stirred with noble metal rods of the same composition as the container. On the occasion of a visit to Caltech I talked to Ed Stolper at Caltech about these experiments and he told me that he considers the massive and very expensive Bayreuth set up as a typical German approach (huge and expensive). After I pointed out that neither Don Dingwell nor Hugh O'Neill are Germans, he told me that Don Dingwell has adopted German thinking. Taken together, these experiments provided a wealth of information on noble metals and it became clear for the first time that noble metals are primarily dissolved as oxides in silicate melts. I knew that Pt contamination is a problem for the production of glasses melted in Pt containers. I therefore contacted a large glass producing firm in Mainz, as I thought they might be interested to find out how Pt is dissolved in silicate melts and would perhaps support some further research. The sobering answer was that they had found ways to avoid Pt contamination, and although they had no idea why their procedures work, they had no interest at all in finding the reason, a demonstration of the difference between applied and fundamental research.

We had done our first solubilty tests with silicate melts in Ir and/or Pt crucibles by simply heating the charges in a furnace in one atmosphere. Astrid Holzheid (who was a student in Mainz at that time) did preliminary experiments and it turned out that the Ir content in each experiment was different, in part the result of Ir metal nuggets that may form. The Bayreuth experiments showed that it may take days or even weeks before a larger amount of silicates is fully equilibrated with a pure noble metal foil (O'Neill *et al.*, 1995). Experiments at various oxygen fugacities demonstrated that the opposite process, reduction of dissolved Ir is faster. Also different noble metals behave differently, equilibration with Pd is easier than with Ir. We performed a number of experiments with Pd and demonstrated that at oxidising conditions Pd is stable as PdO_2, gradually converting to PdO at more reducing conditions and in the end possibly leading to metallic Pd (Fig. 14.1; Borisov *et al.*, 1994; Borisov and Palme 1995, 1997). Sasha Borisov (a geochemist from the Vernadski Institute in Moscow) worked with me in Mainz and later in Cologne, more or less annually funded by some grant money from the German Science Foundation (DFG). He is an excellent experimentalist who would take every effort to repair the equipment, if it did not work. He is, like most Russian experimentalists, very good at improvising.

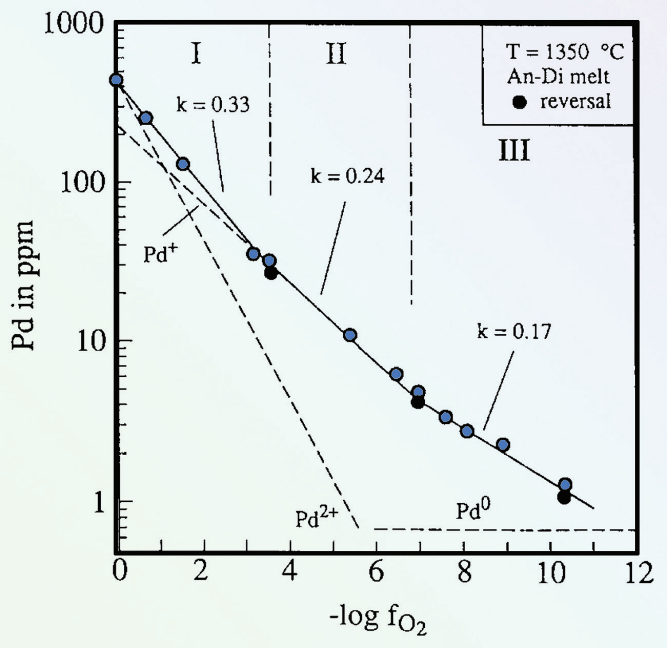

Figure 14.1 Results of Pd solubility experiments at 1,350 °C. Full circles are reversed experiments with initially high Pd in the melt. Slopes corresponding to three Pd valences are indicated (modified from Borisov *et al.*, 1994).

We found large differences between the solubilities of Pd, Ir and Pt, at least at one bar. This is clear support for the late veneer hypothesis, where highly siderophile elements are delivered to Earth by a late chondritic veneer, as HSE occur in roughly chondritic ratios in the mantle of the Earth. Metal-silicate partition coefficients for the highly siderophile elements (*e.g.*, Ir, Pt, Pd) are so high that only a small amount of core forming metal is required to remove them from the silicate mantle of the Earth. The observed abundance pattern of HSE in the mantle of the Earth is thus imposed by the abundance pattern of the late veneer elements. The late veneer hypothesis was intitially proposed by Chou (1978) and Kimura *et al.* (1974) had provided the first experimental data.

A *Science* paper by Rama Murthy (Murthy, 1991) stirred up the community. He maintained that metal-silicate partition coefficients would be significantly lower at high temperatures and could thus explain the presently observed concentration level of HSE in the mantle of the Earth. A late veneer is not needed. Murthy (1991) estimated a decrease in the Ir metal-silicate partition coefficient from 1,660,000 at 1,573 °K to 260 at 3,500 °K. Although newer experiments confirm the trend predicted by Murthy (1991), the measured effect is not as large as expected and differences in the behaviour of HSE still persist (Holzheid *et al.*, 2000; Mann *et al.*, 2012). The idea of a late veneer has survived until the present, although with some modifications:

1. The HSE pattern of the Earth is not strictly chondritic. Enhancement of Pd and Ru were found by several authors. Gerhard Schmidt (a student from Heidelberg) had spent a year with John Wasson, before he came to Cologne (although he stayed most of the time in Mainz, at the reactor building of the Institute of Nuclear Chemistry). He did neutron activation of HSE (highly siderophile elements) by extracting them with NiS, a common method at the time. He primarily focused his work on mantle peridotites. His data on samples from the Zabargad peridotite and on xenoliths clearly defined non-chondritic abundance ratios of the HSE in Earth's mantle, evident from enhanced Ru/Ir and Pd/Ir ratios (Schmidt *et al.*, 2000). Similar results were obtained earlier by Pattou (1996) and Lorand *et al.* (1999). These findings were later confirmed with the more precise LA-ICP-MS by Becker *et al.* (2006). The enhancement of Ru and Pd in the Earth's mantle can be explained by involving sulphides in accretion and differentiation models of the Earth (Rubie *et al.*, 2016). Laurenz *et al.* (2016) have experimentally shown that Ru and Pd are less chalcophile than Pt and Ir and are therefore less efficiently extracted from the mantle into the core, ultimately leading to the observed enhancement of Ru and Pd in the present upper mantle.
2. In accretion models the element Ru is a typical late veneer element, *e.g.*, it is delivered with the late veneer into a basically Ru-free mantle, except in the model of Rubie *et al.* (2016) where some Ru is retained in the mantle, before arrival of the late veneer. The isotopic composition of Ru in the Earth is different from all meteorite groups analysed so far (Fischer-Gödde and Kleine, 2017), excluding known meteorites as source of the late veneer. In earlier suggestions the late veneer was either of carbonaceous or ordinary chondrite origin. A CI chondritic late veneer would have also delivered water. This possibility is excluded on the basis of Os isotopes (Meisel *et al.*,1996). Others have suggested ordinary chondites as source of the late veneer (O'Neill, 1991), in line with the evidence from Os isotopes mentioned above. Recent research has demonstrated that the Earth is richer in s-process nucleosynthetic components than any meteorite group. This is not only valid for the typical late veneer element Ru (Fischer-Gödde and Kleine, 2017) but also for other elements, such as Mo (Burkhardt *et al.*, 2011). The

consequence is that Earth is isotopically different from any known chondrite group. Models where Earth is a mixture of existing types of meteorites have to be discarded (Palme and Zipfel, 2016).

14.5 The Ni-Co Problem

The success with HSE solubilities led to similar experiments with Mo, Ni and Co. Astrid Holzheid (a student from the University of Mainz) did the experiments with gas mixing furnaces. The results demonstrated once again the +2 valence for Ni and Co in silicate melts, but for Mo she could show, for the first time, a change in valence from Mo^{6+} to Mo^{4+} as conditions get more reduced. The steeper slope of the solubility *vs.* fO_2 correlation reflects a higher valence (Holzheid *et al.*, 1994). From these solubility data it is clear that siderophility increases from Fe to the more siderophile Co and finally to Ni. Molybdenum is more siderophile than Ni at reducing conditions, but less siderophile at oxidising conditions (>0.5 $\log_{10}$ units below the iron-wüstite buffer). The Ni experiments were also performed because Colson (1992) had maintained that a large fraction of Ni, even at moderate oxygen fugacities, would be present as metal in silicate melts. The experimental data of Holzheid *et al.* (1994) and Holzheid and Palme (1996) did not give any indication of the presence of neutral Ni. In continuation of this work, later in Cologne, Astrid did more work studying the activity coefficients of Fe, Co and Ni in silicate melts. This information is needed to calculate partition coefficients from solubilities. The results confirm that Fe, Ni and Co are dissolved as +2 ions in silicate melts. The activity coefficients reflecting the difference between thermodynamically calculated and measured solubilities are not very far from unity (Holzheid *et al.*, 1997). The data also show that the solubilities of Ni, Co, and Fe are not dependent on the composition of the melt. The dependence of metal-silicate partition coefficients on melt composition emphasised so much by Righter and Drake (see Righter, 2003, 2011) does not exist for the +2 ions Fe, Co and Ni.

The fairly low Ni and Co metal-silicate partition coefficients at high p, T, that were found by Li and Agee (1996) and by others were surprising to me, because extrapolating these partition coefficients to lower temperatures and pressures yields much lower partition coefficients than observed at one bar. At this point I decided to do more experiments to understand this discrepancy better. Philipp Kegler wanted to do his PhD with me, so I suggested that he perform basic experiments determining Ni-Co partition coefficients. His initial results confirmed our data obtained from solubilities. Further results of experiments, done in Bayreuth, at elevated pressures gave similar results to those in the literature. The obvious conclusion is that there must be a kink in the correlation of Ni and Co metal-silicate partition coefficients *versus* temperature and/or pressure. We could indeed demonstrate a transition at around 3 to 5 GPa as shown in Figure 14.2. The $K_D{}^{\text{Ni-Fe}}$ plotted in Figure 14.2 is the ratio of Ni (metal-silicate) to Fe (metal-silicate) partition coefficients. Values above one indicate that the siderophile character is stronger than that of Fe. Our conclusion from the Kegler *et al.*

(2008) experiments was that the strong pressure and temperature dependences of $K_D^{Ni\text{-}Fe}$ and $K_D^{Co\text{-}Fe}$ at atmospheric pressure change abruptly between 3 and 5 GPa to much weaker dependences at higher pressures. As a consequence the pressure dependences of $K_D^{Ni\text{-}Fe}$ and $K_D^{Co\text{-}Fe}$ cannot be regressed with a single fit over the entire pressure range (Kegler *et al.*, 2008). In a review paper Righter (2011) maintained that the difference in Ni and Co partition coefficients between atmospheric pressure and high pressures is the result of experiments done at different melt composition. Since we believe that this is not true we wrote a comment about the Righter (2011) paper (Palme *et al.*, 2012b). Our conclusion on the Kegler *et al.* (2008) paper was that the results of the experimental data obtained and those from the literature are not sufficiently accurate to exclude single stage equilibration unambiguously. But the results exclude that Fe, Ni and Co contents of the present upper mantle were established by metal-silicate equilibration at upper mantle conditions (*ca.* 25 GPa).

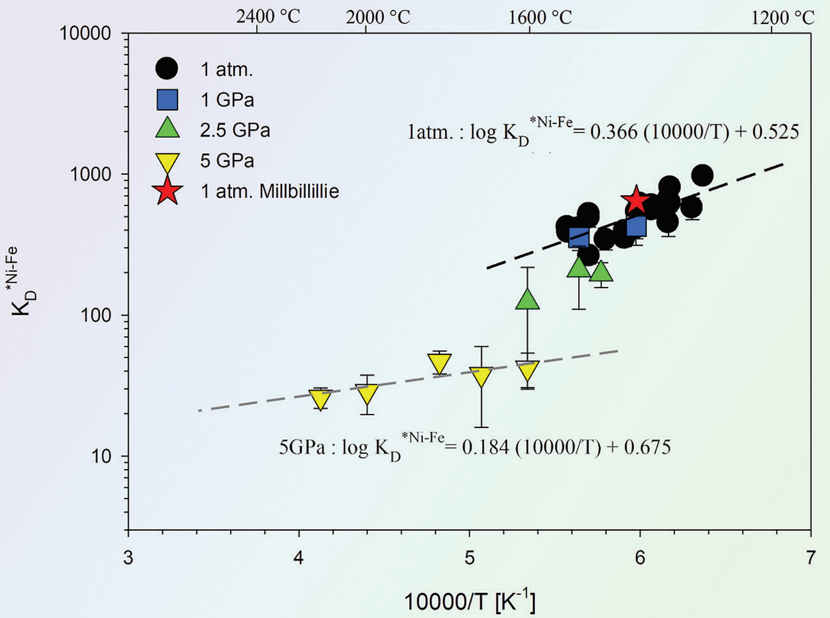

Figure 14.2 Exchange metal-silicate partition coefficients, Ni-Fe and Co-Fe as function of inverse temperature at one atmosphere and at various pressures (after Kegler *et al.*, 2008). Partition data at 5 GPa and higher are lower and the correlation has a lower slope than data at one atmosphere up to 2.5 GPa. Data from Kegler *et al.* (2008). The data point labeled Millbillillie is from partition experiments at atmospheric pressure with eucritic melts as silicate phase (Holzheid and Palme, 2007).

15. COLOGNE

15.1 General Remarks

As mentioned above, in 1994 I moved to Cologne to take a position as professor of mineralogy and geochemistry at the University of Cologne. I have described some of my activities in Cologne in the preceding sections of this paper.

My colleagues at Cologne were H.-A. Seck, Eberhard Seidel and Werner Rammensee and in the neighbouring Institute of Crystallography there were Ladislav Bohatý and Manfred Mühlberg. Initially my teaching obligations were for students at an advanced level. Later after the retirement of Hans Seck I had to teach beginners. Since I never studied mineralogy at a university I had to read textbooks instead. Rolf Hollerbach (museum curator), Rainer Kleinschrodt (research and teaching assistant) and Gudrun Witt-Eickschen were of great help to me in preparing my lectures. With their help I still had time for research. I continued some work from Mainz and started new projects.

I found that scientific activities at the university are different from research at a Max-Planck-Institute. The advantage of a position at a German university is that nobody tells you what to do, as long as you teach the required courses. At a Max-Planck-Institute the director has the full power. He can tell you what you should do and what you shouldn't do. This was not a real problem for me, because Wänke did not tell any of his scientific assistants or coworkers what they should work on. At best he made some suggestions but did not insist. Another big problem for Max-Planck-Institutes in general is to get good students. At the university one can follow the career of beginners and support good students by employing them as teaching assistants *etc*. The disadvantage of a position at a German university, compared to a position at a Max-Planck-Institute, is that funding and travelling is more difficult. I had to write proposals and apply for research grants. In Germany the main source for research grants was and still is the German Research Foundation (DFG). During my stay in Cologne I had written some 40 proposals, most of them were successful, but not all.

While I was in Cologne the institutes for mineralogy, crystallography and geology were combined into a single institute for the geosciences. The official name is now Institute for Geology and Mineralogy. Some efforts on my part were necessary to establish this new name. The palaeontologists wanted their field to be included in the name but I finally convinced them that palaeontology is part of geology. There is now a single curriculum for the geosciences in, I suppose, all German universities covering geosciences. I supported these trends, because I think that separate institutes for mineralogy, crystallography and geology are too small to survive. Larger geoscience departments are more flexible, and research and teaching directions can be easily changed. It was a great satisfaction and a question of prestige for the chair of a mineralogy institute (in German: Lehrstuhlinhaber), that he had a successor and it was even better if his successor was also a professor of mineralogy. Establishing new research directions, which are not represented by the traditional subjects, is difficult in such a system.

When I started my job in Cologne I could fill an assistant position for six years. I asked Sumit Chakraborty from Bayreuth and he agreed to come to Cologne, where he did his habilitation. This is an academic degree above PhD which qualifies for a professorship at a university. Although nowadays habilitation is no more a prerequisite for applying for a professorship, it is still advisable to have the habilitation as it may support a job application. In Cologne, Sumit continued his work on diffusion. He had his office next to mine and we had numerous discussions about all kinds of problems in geo-and cosmochemistry, both before and after midnight. His experience and knowledge were of great help in my first years in Cologne.

In Cologne we had two furnaces with controlled oxygen fugacity, where Sasha Borisov (who came annually to Cologne for about three months), Sumit Chakraborty and Astrid Holzheid (who had come with me from Mainz) did their experiments. There was also the Knudsen cell, which was initially built in Mainz by Werner Rammensee. The Knudsen cell accompanied Werner to Göttingen and later to Cologne. A physics student of Werner Rammensee, Ralf Dohmen, helped to set up the instrument in Cologne. He did his thesis work by studying diffusion in the system Mg-rich olivine and metal. The equilibration of the metal-olivine diffusion couple was monitored by the Knudsen cell. It turned out that besides the expected vapour pressure of Fe there was also a significant partial pressure of metallic magnesium. The increase in the fayalite component of olivine during the reaction was accompanied by release of Mg to the gas phase. This so far unknown loss of Mg to the gas phase may have been important in the early solar system. Perhaps some variations in MgO in chondritic meteorites were due to loss of Mg. Metamorphic temperatures in ordinary chondrites are, however, not high enough to produce such losses, whereas the formation of fayalite-rich rims in olivines of carbonaceous chondrites, if it occurred in the nebula, would have to be accompanied by Mg loss to the gas phase. Sumit Chakaborty and Ralf Dohmen wrote a long paper about these findings in the *American Mineralogist* (Dohmen *et al.*, 1998). In 1999 the paper was chosen as *"the best paper of the year"* for the *American Mineralogist*. It would certainly be worthwhile to further pursue this direction. Sumit also did a number of diffusion studies in Cologne (*e.g.*, Petry *et al.*, 2004), before he took a professorship at the Ruhr-University in Bochum, where he has established a centre for diffusion studies with a worldwide reputation.

After Sumit Chakraborty had left Cologne, Frank Brenker, who did his PhD in Frankfurt with Gerhard Brey took his position. Frank Brenker is known for his research on tiny inclusions in diamonds. He also got contaminated with cosmochemistry. He studied for example, the mineralogy and crystallography of 20 to 50 µm rounded to subrounded aggregates of Ca, Fe-rich minerals in the Allende matrix. He concluded from the structure of Ca, Fe-rich pyroxenes that they must have formed at temperatures above 1,050 °C, which is significantly above temperature of the Allende parent body, suggesting a nebular origin for these aggregates (Brenker *et al.*, 2000). Frank Brenker also participated from the beginning in the stardust mission, in which he is still active. In 2004 he took a position as professor at the University of Frankfurt.

15.2 Further Studies of Earth's Mantle Chemistry

Long before I started my new position in the Department of Mineralogy at the University of Cologne, Hans Seck, Heinz-Günther Stosch, Gudrun Witt-Eickschen and others had studied peridotitic xenoliths from young Eifel volcanos for many years and they had made important contributions to the chemistry and mineralogy of these rocks, in particular their pressure and temperature history. Also they had common projects with Dimitri Ionov, who was a guest at the institute for some time. Dimitri Ionov is presently professor of geochemistry at the University of Montpellier. Very early on he began to study the mineralogy and chemistry of mantle xenoliths from the Tariat Depression in Mongolia and the Vitim volcanic field in the Baikal region. He is author and coauthor of a large number of papers dealing with all aspects of mantle rocks.

Heinz-Günther Stosch analysed radiogenic isotopes in cooperation with Günter Lugmair in La Jolla (*e.g.,* Stosch and Seck, 1980; Stosch *et al.*, 1980).

During my stay in Mainz I had connections with Hugh O'Neill at the Bayerisches Geoinstitut in Bayreuth. After I had moved to Cologne I was successful in applying for a Humboldt professorship for Hugh, who spent a couple of months in our department and we did some work on elemental Earth mantle abundances. After he had left Cologne, Gudrun Witt-Eickschen spent a few months in Canberra with Hugh O'Neill analysing major elements, and a large number of trace elements, in peridotitic xenoliths. About 30 trace elements were measured *in situ* in minerals from peridotites on polished thin sections by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Research School of Earth Sciences, Australian National University. As all samples were well equilibrated, equilibrium temperatures could be determined and new calibrations were established (Witt-Eickschen and O'Neill, 2005). In a follow-up paper we reported data on As, Cd, Ga, In and Sn in various minerals from mantle peridotites (Witt-Eickschen *et al.*, 2009). It turned out that, except for As, these elements primarily reside in clinopyroxene. The results of this study produced better estimates for the primitive upper mantle abundances of these elements than previous data. The comparatively high In abundance for the upper mantle was confirmed. The CI-normalised PUM In abundance is slightly higher than the well established Zn abundance. This is strange, since In is more volatile, judging from its calculated condensation temperature, and more siderophile and chalcophile than Zn. Indium should have been extracted into the core much more efficiently than Zn.

At the Goldschmidt Conference in Heidelberg in 1996, I had several discussions with Hugh O'Neill about the chemical composition of meteorites. The result was a paper in the Ringwood memorial volume (O'Neill and Palme, 1998). Further continuation of this work led to Palme and O'Neill (2003, 2014). These studies reveal that there are similarities in chemistry between Earth and carbonaceous chondrites, particularly with CV chondrites. Both, Earth and CV chondrites are similarly enriched in refractory lithophile elements and their moderately volatile element patterns are similar. Stable, neutron-rich isotopes (*e.g.*, ^{50}Ti, ^{54}Cr, ^{48}Ca) are, however, different in the Earth's mantle and in carbonaceous chondrites (see Warren, 2011). Thus, based on stable isotopes, Earth can only have a small fraction of carbonaceous chondrite (CC) material. Chemically Earth is different from ordinary and enstatite chondrites. Chemistry thus limits the amount of non-carbonaceous (NCC) material. Although bulk Earth may be considered in a broad sense chondritic, only a small fraction of parental material can be derived from existing chondritic meteorites (Palme and Zipfel, 2016). This is important because there are models making the Earth out of a mixture of existing chondritic meteorite groups. The opposite is the case. The Earth consists primarily of material not present in existing chondritic meteorites. This may also be true for Mars and Venus. Thus high precision stable isotope data have fundamentally changed our understanding of planet formation.

15.3 Forsteritic Olivines

After several years in Cologne we had a fairly big cosmochemistry group. One day Susanne Klerner (a PhD student who worked on the chemical complementarity between chondrules and matrix) told me about a promising young scientist from the University of Bonn, who would be interested in cosmochemistry. It turned out it was her boyfriend Andreas Pack, who later became her husband. She had met him while both were studying at the University of Bonn. Andreas Pack started as post-doc in Cologne, after I had received some funding from DFG. He studied forsteritic olivines from chondritic meteorites. We had earlier analysed such olivines by INAA in Mainz and their trace element patterns suggest an origin by condensation in a gas of solar composition (Weinbruch *et al.*, 2000). Andreas Pack found that all chondritic meteorites have a population of forsteritc olivine grains with similar characteristics: high Ca, Al and Ti contents and with fractionated patterns of refractory lithophile trace elements. This includes very reduced (enstatite chondrites) and very oxidised chondrites (Rumurutiites), as well as all types of carbonaceous chondrites. In addition, these olivines are low in Fe, Ni, Co and Mn and fairly high in ^{16}O (Pack *et al.*, 2004, 2005). The refractory forsterites formed at high temperatures, either as nebular condensates or by crystallisation from a very refractory, CAI-like melt. Experiments have shown that the Ca content of normal chondrules is far too low to allow crystallisation of forsteritic olivines with high Ca contents (Pack and Palme, 2003).

The refractory olivines were present at all locations where chondrites formed. Either they came from a single location and were then distributed to chondrite formation locations in the early solar nebula, or they formed at very different locations under similar conditions.

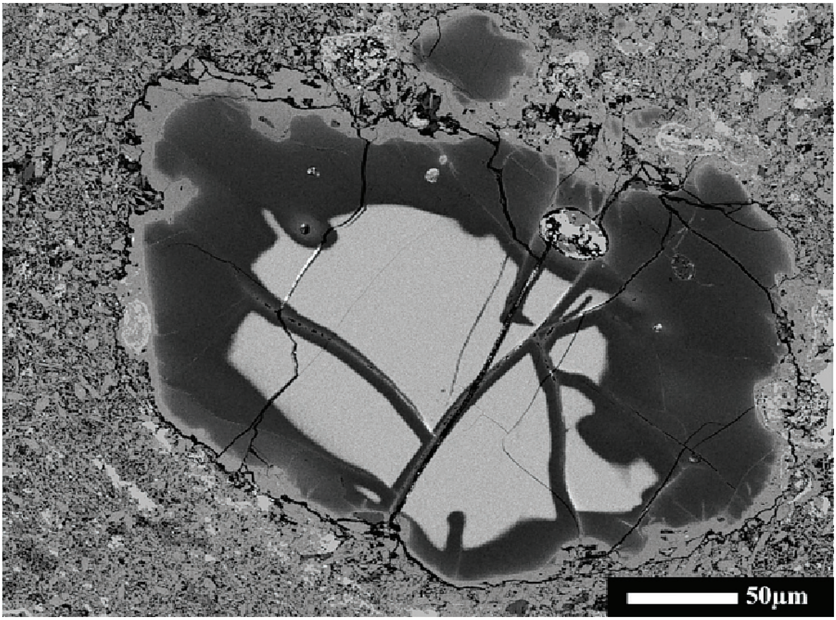

Figure 15.1 Isolated refractory forsterite grain from the Allende meteorite. This is a combined SEM (secondary electron microscopy) and CL (cathodoluminescence) picture. The bright interior indicates a homogeneous, very FeO-poor (0.4 %) forsteritic composition with 0.6 % CaO and 0.3 % Al_2O_3. In the dark band, surrounding the forsteritic core, FeO increases to about 0.6 % and CaO and Al_2O_3 decrease. The bright outer rim of the fragment is much higher in FeO (*ca*. 10 %). The grain is embedded in Allende matrix (from Klerner, 2001).

Daly *et al*. (2017) suggested that refractory metal nuggets (RMN) were exposed to different environments before they were incorporated in CAIs or bulk chondrites. Also, CAIs must have been transported in the early solar nebula. They have been detected in cometary material, far away from the Sun. There is apparently a variety of "free floating" high temperature grains formed in the early solar nebula. Some may have been incorporated in chondrule precursors; others were accreted to meteorite parent bodies together with chondrules and matrix.

After his post-doc in Cologne, Andreas Pack spent some time in Nancy at the Centre de Recherches Pétrographiques et Géochimiques (CRPG). He is now professor at the University of Göttingen and studies, among other things, the behaviour of ^{17}O in the terrestrial environment. An example for the impact of cosmochemistry on geochemistry.

15.4 Pd as a Sensor for Activities of Lithophile Elements

When the first reports of a new technique for the experimental determination of activities of oxides in silicate melts and minerals, using Pd metal, came out I was fascinated by the simplicity of the method and the large amount of information that can be obtained (Chamberlin *et al.*, 1995). The principle of the method is to equilibrate a melt or a mineral with Pd metal at fixed P, T, and fO_2. A small fraction of each oxide will be reduced to metal and dissolve into Pd metal. Metallic Mg, Al, Si, Ti *etc*. dissolve into the Pd in amounts easily measurable with the electron microprobe at oxygen fugacities which can be achieved with conventional gas-mixing techniques.

I thought we should try this method and apply it to determine the activities of oxides in melts formed by partial melting in the upper mantle. A PhD student, Jörg Fechner, started with experiments calibrating Pd metal by equilibrating a Pd wire with melts of known activities. We also studied Rh and Pt metal, which are promising. Jörg Fechner did many experiments in our furnaces with controlled oxygen and could precisely determine the activity of SiO_2 at the forsterite enstatite equilibrium. Ultimately however, it turned out that the method does not give sufficiently reproducible results. The reason is unclear. But I still think that with new improved analytical trace element techniques (laser induced ICP-MS) it should be possible to determine the activities of a large number of oxides in melts or minerals with this technique. It may require intensive calibration, but it is very powerful, because the disturbance of the melt or mineral system with the noble metal sensors is minimal.

15.5 Bulk Chemistry of Meteorites

Chondritic meteorites sample primitive solar system material. Bulk chondrites have not been modified by melting and crystallisation processes. Their major element compositions closely match solar abundances. Small chemical differences among chondritic meteorites reflect fractionation processes in the solar nebula. Based on chemical composition and stable isotopes there are two major groups of chondritic meteorites: carbonaceous chondrites with eight known subgroups and non-carbonaceous chondrites with at least six subgroups (see Krot *et al.*, 2003). For a proper understanding of the chemical differences among chondritic meteorites, knowledge of the chemical compositions of chondritic meteorites is essential. But a number of questions arise, such as for example: how much material is needed for a representative bulk composition? What are the effects of thermal metamorphism and aqueous alteration on the bulk chemical composition?

After I had started my new position in Cologne, we bought a new Philips X-ray fluorescence analyser. The group of Louis Ahrens (von Michaelis *et al.*, 1969) in Capetown as well Gene Jarosewich in Washington (Jarosewich, 1990) have shown that high quality data can be obtained for meteorites, using X-ray fluorescence. Most terrestrial applications of X-ray fluorescence involve the dissolution of several grams of material. This is often not possible with meteorites, where only a much smaller amount of material is available for analysis. We therefore started an extensive calibration programme using only 120 mg of sample material. Dieter Wolf, a PhD student did all the work (Wolf and Palme, 2001). Another advantage of X-ray fluorescence analysis is that it provides data on Si, which is not determined by INAA data published on meteorites (*e.g.*, Kallemeyn and Wasson, 1981).

We finally analysed a large number of carbonaceous chondrites (Wolf and Palme, 2001). The data were similar to earlier bulk chemical data (see Palme *et al.*, 2014b, for references), but in addition we focused on phosphorus and titanium, which gave us new CI chondrite reference values for these elements (Wolf and Palme, 2001). We also analysed a couple of ordinary chondrites. For meteorites with metallic iron it is necessary to oxidise the metallic iron before producing a powder.

With the XRF data in mind I began a new project. On what scale are carbonaceous chondrites chemically homogeneous? In other words, do chondrites have a well defined bulk composition? Is a single analysis of a one gram Allende chunk representative of the whole meteorite? In order to study this problem I took a slice of Allende from the Senckenberg meteorite collection and cut out thirty nine equally sized pieces with an average weight of *ca*. 0.6 g each. The pieces were powdered and aliquots were analysed for major and trace elements. One sample contained a large CAI, another sample was dominated by a dark inclusion (DI). Dark inclusions are common lithologies in many carbobaceous chondrites. They are macroscopically structureless and may reach a size of more than a cm. Their chemical composition is similar to the composition of matrix, although there are some characteristic differences (Bischoff *et al.*, 1988). Excluding the two samples with a CAI and a DI, the concentrations of the major elements Mg, Si and Fe are constant within less than 3 %, which is the analytical uncertainty (see Stracke *et al.*, 2012). More volatile, but geochemically very different elements such as Mn, Cr, Ni, Co, P, Zn and Pb are similarly homogeneously distributed. The refractory elements Al, Ca, Ti *etc*. are more variable, probably the result of different proportions of CAIs. Another important result of this study was the absence of variations in concentrations of so called fluid-mobile elements, such as Ba, Cs, U and W. It had been suggested that water flowing through the Allende parent body would have dissolved and redistributed these elements (Young *et al.*, 1999), leading to a very inhomogeneous distribution. This is not the case as the Hf/W ratios are, for example, constant within analytical uncertainty (Stracke *et al.*, 2012). During weathering W is very mobile, but Hf is not affected. Aqueous alteration certainly occurred in Allende, but it is a very local process. On a mm scale Allende is homogeneous for elements easily mobilised by the action of water. Some of the aqueous alteration may have occurred in the nebula, by reaction of solid mineral assemblages with gaseous oxygen. Some of the analyses of this study were done at the ETH in Zürich, where I stayed for several months after my retirement. Tungsten and some other trace element concentrations were determined by Carsten Münker in Cologne.

Determining bulk meteorite compositions will help to indentify new types of meteorites. The north-west Africa meteorite NWA 5492 is a good example (Fig. 15.2). This is clearly a chondritic meteorite, but there are small compositional differences with other chondrites which indicate a unique type of meteorite. This is supported by the structure and mineralogy of this meteorite. The meteorite has a chondritic texture, enstatite-rich mineralogy and bulk chemistry indicating FeNi-excess and volatile element depletion (Friend *et al.*, 2011; see also Weisberg *et al*. 2012).

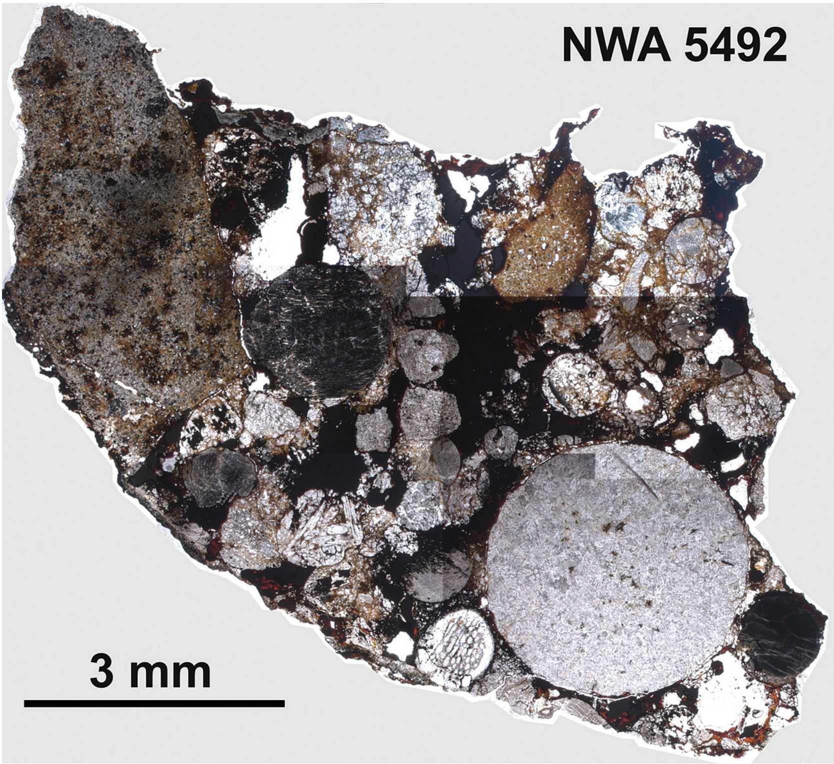

Figure 15.2 Photomosaic of a thin section of NWA 5492 in transmitted light. Metal and sulphides are dark. The meteorite belongs to a completely new group of chondrites. On the left upper side is a lithic clast. There is an enormous range in chondrule sizes (photo credit: J. Zipfel, Senckenberg, Frankfurt).

15.6 Origin of Chondrules

At the beginning of the 1990s in Mainz we started to analyse chondrules from the Allende meteorite. Some of the work was done together with Gero Kurat in Vienna, who was very interested in the problem of chondrule formation. We noticed an enormous spread in the chemical composition of chondrules from a single meteorite. In Palme *et al.* (1992) we discussed the first results and concluded:

> *'The essential point in the present model is that coarse grained chondrule precursor material and fine grained matrix are both products of processes that occurred in the solar nebula. The chemical complementarity of these two components requires a closed system. The inferred nebular processes must have occurred in a small nebular region providing evidence for a highly turbulent nebula with large local variations in temperature and cooling rates. This view is inherent in our notion of unequilibrated chondrites, which are generally thought to represent the most primitive meteorites and thus record a variety of nebular processes.'*

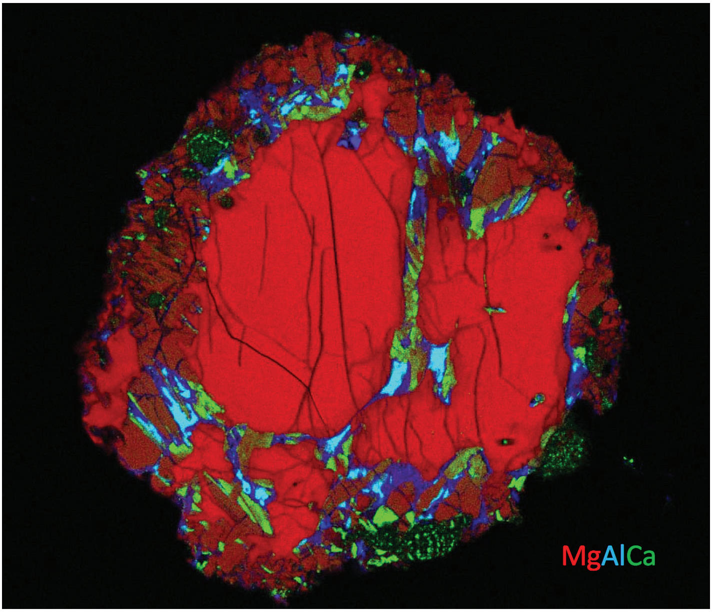

Figure 15.3 A false colour, electron microscope image of a chondrule from the carbonaceous (CV) chondrite Mokoia. The colours reflect compositional differences (red- magnesium, blue- aluminium, green- calcium). The darkening red on the edge of the chondrule indicates reaction of the Mg-rich minerals of the chondrule with an FeO-rich environment. The compositional contrast between the chondrule interior and the FeO-rich matrix reflects the chondrule-matrix complementarity discussed in this contribution (image credit: Dr. J. Claydon, courtesy of the Trustees of the Natural History Museum).

In 1992 I received an invitation for the Annual Symposium of Antarctic Meteorites in Tokyo. I decided to go there and talk about the chondrule and matrix relationship in Allende (Palme, 1992). Figure 15.4 illustrates the physical relationship of chondrules set within a fine grained matrix. The chondrule-matrix complementarity is shown in Figure 15.5 where only an appropriate mixture of chondrules and matrix can achieve the bulk composition of the meteorite. Since the major element composition of Allende is not far from the solar photospheric composition a certain well defined mixture of chondrules and matrix is required (see Fig. 15.5). The Ni content of chondrules is far too low, whereas the matrix has excess Ni. This reflects the generally low contents of metallic elements in chondrules, which is also observed in ordinary chondrites (*e.g.*, Grossman and Wasson, 1985). Similar, but less pronounced differences are found for Cr. The solar Cr abundance clearly lies between the compositions of chondrules and matrix. The Cr/Ni ratio of the solar photosphere fits with bulk.

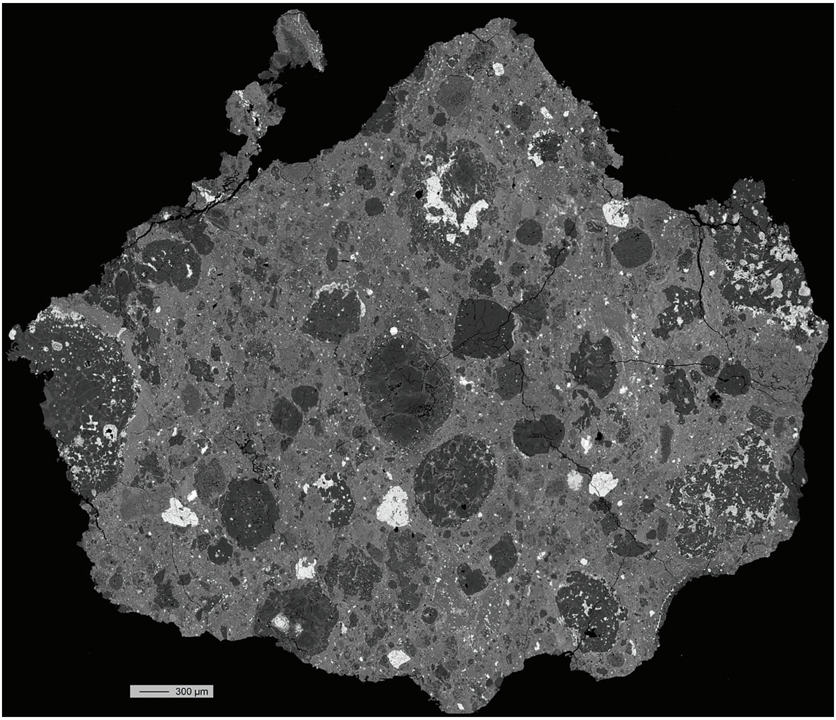

Figure 15.4 Back scattered electron image of Y-86751, a CV chondrite. The meteorite belongs to the same group as the Allende meteorite. The dark, Mg-rich, Fe-poor chondrules can be clearly distinguished from the fine grained greyish matrix (from Hezel and Palme, 2008 with permission from Elsevier).

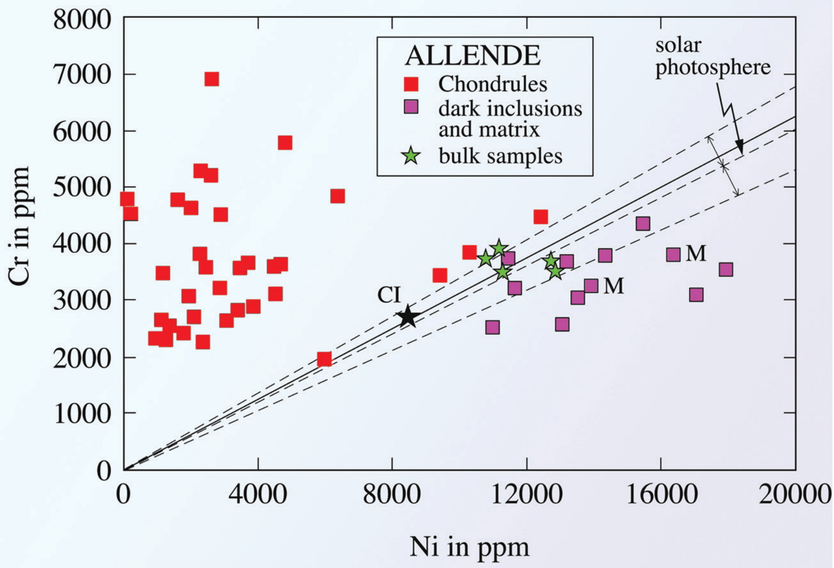

Figure 15.5 A Cr *vs*. Ni diagram for Allende chondrules, matrix (M) and dark inclusions. All data by INAA (Bischoff *et al*., 1988; Palme *et al*., 2014b). The Cr/Ni ratio of the solar photospheric abundances with error bars is included (modified from Palme, 1992).

Another feature from my talk demonstrated the absence of igneous fractionation in chondrules. Large radial pyroxene chondrules in Allende have no excess of Sc, which is expected if this is a mineral effect, as pyroxenes take Sc much more readily than REE. The chondrule did not know that it would become a pyroxene chondrule when it incorporated Sc and REE. The diversity of bulk chondrule compositions is not the result of assembling various mineral grains of a preceding chondrule population.

At the same conference, I listened to a talk by Murakami (Murakami *et al*., 1992; Murakami and Ikeda, 1994). These authors had analysed various components of Y-86751 a CV chondrite very similar in bulk composition and mineralogy to the Allende meteorite. Yet, it turned out that the matrix of Y-86751 is high in Al but low in Ca, whereas chondrules are high in Ca and low in Al, contrary to Allende and some other carbonaceous chondrites. I thought that these findings might be of relevance for the unresolved problem of chondrule formation. In particular it excludes parent body processes as origin of Ca-Al fractionation. But I soon realised that nobody was interested. I gave a talk at the Albuquerque chondrule meeting in 1994. Nobody considered my arguments seriously. It was all parent body redistribution. The arguments are now published in Hezel and Palme (2008).

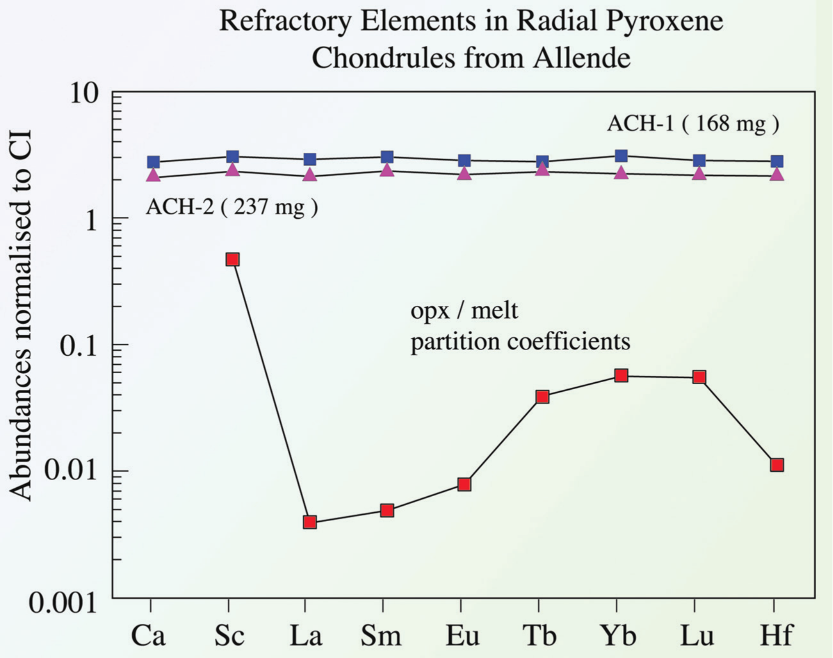

Figure 15.6 Lithophile refractory element patterns of two large radial pyroxene chondrules of Allende. The CI-normalised patterns are flat. They cannot be produced by igneous fractionation, as demonstrated by the cpx-melt partition coefficients. The high Si contents of these chondrules is not the result of preferred aggregation of clinopyroxene grains, which crystallised in an earlier generation of chondrules (modified from Palme,1992).

After I had started my new job in Cologne, a student from the Institute of Mineralogy in Bonn wanted to work with me. Susanne Klerner began her PhD thesis in Cologne in 1998 (Klerner, 2001). She resumed the Allende work with more samples, excellent petrographic skills and a lot of enthusiasm. She not only looked into the chondrule-matrix relationship in Allende, but she also studied Renazzo in great detail. The outcome was a clear complementary relationship of chondrules and matrix in both meteorites. She also noticed high Ti/Al ratios in Renazzo chondrules and low ratios in Renazzo matrix. When she presented this at the Meteoritical Society Meeting in Chicago she was heavily attacked. Again, we could not convince the chondrule community about our findings and their relevance for chondrule formation models. In the meantime we found the complementary Ti-Al relationship in more carbonaceous chondrites, but not in all of them. For example, Allende chondrules do not have enhanced Ti in chondrules. Non-chondritic ratios of refractory elements in matrix samples of some carbonaceous chondrites are commonly reported in the literature, *e.g.*, Wasson and Rubin (2009) and Abreu and Brearley (2010). Brearley (1996) reports strongly fractionated abundances of Al, Ca and Ti in the matrix of the ordinary chondrite Semarkona. It is not clear whether the low Ti in the matrix reflects Ti depletion or Al enrichment. As in some matrix analyses of primitive carbonaceous chondrites Ca and Al are fractionated and, looking at a large number of matrix analyses, it appears that the culprit is Al and not Ti, as the Ca/Ti ratios seem to be closer to chondritic (Brearley, 1996; Abreu and Brearley, 2010). A fractionated Al/Ti ratio in the matrix of a carbonaceous chondrite implies that the Ti/A ratio in chondrules is fractionated in the opposite sense, since bulk carbonaceous and ordinary chondrites have chondritic Ti/Al ratios and since there are approximately equal fractions of chondrules and matrix. A fractionated Ti/Al in an ordinary chondrite matrix has little significance for chondrules as there is only little matrix in these meteorites. But it indicates that the matrix in carbonaceous and in ordinary chondrites is made by similar processes. A more systematic approach to these phenomena seems to be required.

Dominik Hezel (a student from Heidelberg) wanted to get involved in cosmochemistry. He came to Cologne to do his PhD in meteoritics, following Susanne Klerner. He initially studied the origin of SiO_2-rich phases in chondrites, mostly cristobalite. Bob Hutchison's pet theory was that these phases are the residues of extensive igneous processes in chondrites. However, Dominik could clearly demonstrate that this is not the case (Hezel *et al.*, 2006). It is much more likely that these phases formed as late condensates in a SiO(g) saturated, rapidly cooling nebula. By now the absence of evidence for igneous processes in chondritic meteorites seems to be widely accepted by the meteoritic community. After this work Dominik Hezel began to work on the origin of chondrules by analysing chondrules and matrix in a series of carbonaceous chondrites (Hezel and Palme, 2007, 2010). He also studied in more detail the Ca-Al relationships in Allende and in Y-86751, a meteorite very similar in structure and chemistry as Allende, but with high Ca/Al ratios in chondrules and low ratios in the matrix, the opposite of the Ca, Al relationship in Allende, as discussed in the above section. Dominik Hezel significantly enlarged the data base for chondrules in chondritic meteorites. He defined the uncertainties involved in transforming 2D thin section analyses of chondrules into 3D chondrule compositions (Hezel, 2007). With a student at the University of Cologne he recently compiled all chondrule data available in the literature (Hezel *et al.*, 2018). He also found evidence that some changes in chondrule composition may arise from reaction of chondrule melts with the ambient gas. A good example is the conversion of forsteritic olivine, the first phase to crystallise in a molten chondrule, to pyroxene. Friend *et al.* (2016) have compiled textural evidence. Pia Friend (a student of Dominik Hezel) has also enlarged the data base of evidence for complementary. The Mg-rich chondrules, abundantly present in CM chondrites, represent a reservoir very high in Mg and comparatively low in Si. Removing this reservoir from the bulk meteorite composition would leave a strongly non-chondritic meteorite. Mg-rich, type 1 chondrules in CM chondrites are an essential part for a chondritic bulk composition.

Recently we finally published the data on Allende chondrules (Palme *et al.*, 2014b). In Figure 15.7 a spectacular (untypical) chondrule from the Allende meteorite is shown. Our data on Allende chondrules together with the data of Rubin and Wasson (1987) on Allende chondrules and the Jones and Schilk (2009) data on Mokoia clearly demonstrate the chemical complementarity between chondrules and matrix in carbonaceous chondrites. In Figure 15.8 data for the CV meteorite Mokoia are plotted in an Fe *vs.* Mg diagram. The chondrule data are from Jones and Schilk (2009) and the matrix data are from Palme *et al.* (2015). Similar plots can made for all CV chondrites. The CI chondrite Fe/Mg ratio is within a few percent identical to the ratio in the solar photosphere.

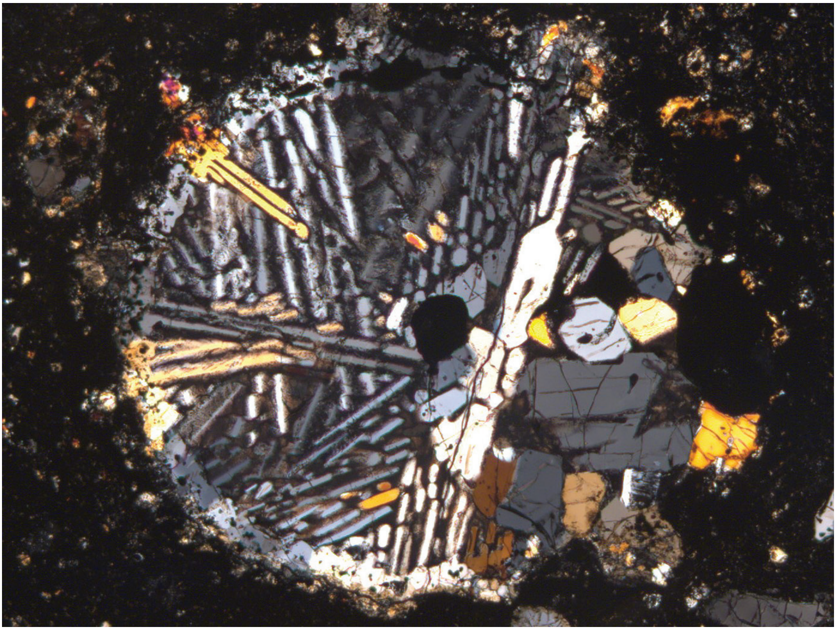

Figure 15.7 A compound chondrule from the Allende meteorite. The left side is a barred olivine chondrule, the right side represents a porphyritic chondrule. The diameter of the chondrule is about 1 mm (photo credit: J. Zipfel, Senckenberg, Frankfurt).

The chemical complementarity of chondrules and matrix constrains chondrule formation models, because it requires a single reservoir for both chondrules and matrix. Recently the concept of complementarity was further strengthened by complementary W/Hf ratios and and W isotopes in chondrules and matrix of Allende (see Becker *et al.*, 2015; Budde *et al.*, 2016).

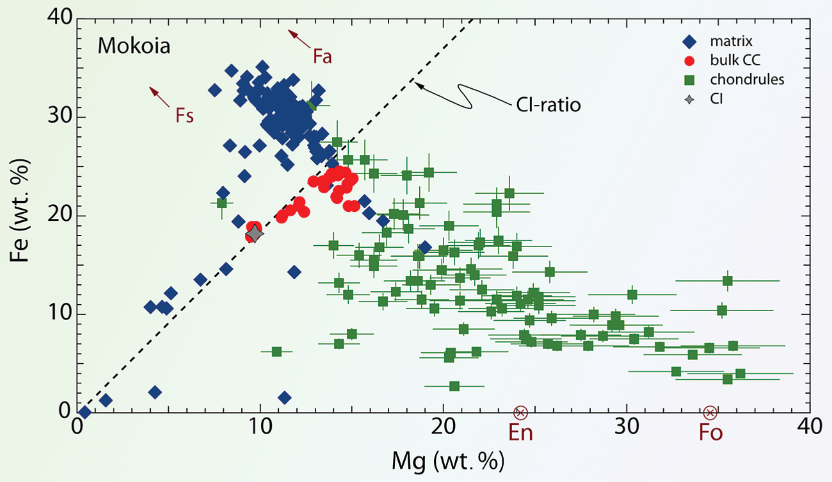

Figure 15.8 Fe *vs.* Mg Mokoia chondrules and matrix (from Palme *et al.*, 2015 with permission from Elsevier). The bulk carbonaceous chondrites (red full circles) have rather constant Fe/Mg ratios which are within a few percent identical to the solar ratios. The matrix has high Fe/Mg ratio and chondrules have variable, but mostly lower than solar, Fe/Mg ratios. Both components are needed to make a good chondrite. For details see Palme *et al.* (2015).

We hope that after 25 years, the concept of complementarity, so evident in carbonaceous chondrites (Wood, 1963), is now beginning to be recognised by the meteoritic community and that it will hopefully serve in the future as basis for astrophysical modelling of chondrule formation.

15.7 W Isotopes in Meteorites and Moon

During my stay in Cologne I had some contact with Klaus Mezger at the University of Münster. I knew Klaus from his stay with Al Hofmann in Mainz, where we had many scientific and non-scientific discussions. When his student Thorsten Kleine began to determine W isotopes in meteorites, we had frequent discussions about the significance of the new data and the geo- and cosmochemical significance of W. This is the reason for my participation in the early W papers of Thorsten Kleine. I was not involved in the analytical work. Later, I suggested extracting metal from lunar samples for W isotope analyses, in particular mare basalts, because I knew from earlier experience that they all contain at least a small fraction of metal and that this metal is an important host phase of W. This is important because lunar metal is free of the lithophile Ta and is thus not affected by the ^{182}W from the decay of ^{182}Ta produced by neutron capture of ^{181}Ta (Leya *et al.*, 2000). This is the reason for my participation in the papers by Touboul (*e.g.*, Touboul *et al.*, 2007).

16.

VISITORS IN COLOGNE

As in Mainz, we had a number of visitors in Cologne. Hugh O'Neill spent several months in Cologne. As discussed above he had received the prestigious Humboldt Prize which enabled him to come to Cologne several times. I had extensive collaboration with Hugh, which is evident from the preceding sections.

Another visitor was Ping Kong from Beijing. She has been interested in meteorites for a long time and had spent some time with Mitsuru Ebihara in Japan, where she did extensive neutron activation analyses of meteorites and their components. In Cologne, she used the neutron activation analysis facility that was installed when I came to Cologne. Gerd Weckwerth, who came to Cologne from Mainz, set up the facility. He was mostly interested in environmental problems, but also did some cosmochemistry work.

Ping Kong found for the first time a significant fraction of REE in sulphides of ordinary chondrites. Her results were confirmed with ion probe analyses of the REE-bearing sulphides in Nancy (Kong *et al.*, 2000). Some of her work in Cologne involved analyses of chondrules and other phases in Renazzo and other CR chondrites. She found complementary siderophile element patterns of CR chondrules and matrix fragments of Renazzo (Kong and Palme, 1999).

17. GOLDSCHMIDT CONFERENCE

While I was in Cologne the European Association of Geochemistry and the Geochemical Society accepted our offer to host the Goldschmidt Conference at the University of Cologne. The conference was held on the university campus (Fig. 17.1).

There were about 2,300 delegates, the largest Goldschmidt Conference at the time. But the Goldschmidt Conferences in Europe are still growing. The 2017 Goldschmidt Conference in Paris had more than 4,500 delegates. This is too big for a university campus. Only large conference centres are possible locations.

The organisation of such a big conference is quite an adventure. Although most of the organisation was done by Paul Beattie's company (Cambridge Publications), there was enough left for us to do. We aimed at registration costs as low as possible, however Paul wanted the opposite. Ultimately, we found a reasonable compromise. All the money was collected by Cambridge Publications and Paul sent us the money we needed for local business. At one point I thought that we would not get enough money to cover all the expenses we had. That cost me a sleepless night. Fortunately, I detected an error in Paul's calculation. In the end we had no financial problems at all, mainly because there were so many late, on-site registrations.

Figure 17.1 Poster announcing the Goldschmidt Conference in Cologne, from August 19th – 24th 2007.

We had a conference dinner at the Gürzenich, Cologne's traditional ballroom and reception hall. About 1,500 participants attended the dinner party. Gerry Wasserburg and Claude Allegre gave short speeches. It was the last time the two Crafoord Prize winners of 1986 met. We had charged only 20 euros to make the party attractive to students. Some time after midnight when the party was over, I had to sign a form indicating the total consumption of beverages. I looked at the forms and calculated that every visitor (including women) would have consumed more than half a litre of beer. I complained to the representatives of the Gürzenich hall, that this is impossible. They offered to show me the empty barrels in the cellar, which I declined. That is the way things work in Cologne.

18.

SUMMARY AND OUTLOOK

In this *Geochemical Perspectives* I discuss the beginning and growth of cosmochemistry in Germany and my contributions to the development of this field. Cosmochemistry, in the sense I use it, implies chemical and isotopic analyses of extraterrestrial materials including relevant terrestrial samples. Theoretical and experimental studies of the early solar system, the formation of planets, remote sensing, asteroid and comet research as well as impact-related research are not included in the present discussion.

With the appointment of Fritz Paneth in 1953 as director at the Max-Planck-Institute in Mainz cosmochemistry was established as a major research area in Germany. For the rest of the century the Mainz group, and later also the Max-Planck-Institute in Heidelberg, were the leading research institutions in this field. The Mainz cosmochemistry group under the leadership of Heinrich Wänke, made fundamental contributions to cosmochemistry with precise chemical analyses of a large number of extraterrestrial and terrestrial rocks, the development of models for the accretion and chemical composition of planets, the experimental determination of metal-silicate partition coefficients and with the analysis of rocks and soils on the surface of Mars. Initially I participated in his activities, later I did my own projects. I continued some of my earlier work in Cologne and added new aspects.

In 2005, about fifty years after Paneth's appointment in Mainz the cosmochemistry department was shut down by the Max-Planck-Society. This was particularly disturbing, because it happened right at the time when two instruments that had been built in Mainz gathered data on the Martian surface. Arguably the Alpha Particle X-Ray Spectrometer (APXS) was the most important and successful instrument on the Mars landers of the NASA Mars Exploration Rover (MER) missions. The instrument was initiated by Heinrich Wänke and designed and built by Rudi Rieder. An earlier version of the APXS had already worked successfully on Mars on NASA's Mars Pathfinder mission in 1997. The numerous chemical data obtained with the APXS were to a large extent responsible for the enormous scientific success of these NASA missions. It is clear that further development of such instruments was and is an important task for the future. Yet, the Max-Planck-Society decided otherwise and further development of the APXS instrument is now done in Canada. Germany missed the chance to take a leading role in Mars research.

Four years later the geochemistry department was also closed, after several attempts failed to find a replacement for Al Hofmann, who retired in 2005. No one who is even vaguely familiar with the situation in Mainz could understand why the two departments with their excellent worldwide reputation and scientific success were closed and why no efforts were made to keep and further develop the APXS instrument in Germany. There was a general notion among German geo- and cosmoscientists that this *'double blow to chemistry'* (Schiermeier, 2003) will have a devastating effect on the geosciences in Germany.

Figure 18.1 The now deserted main building of the Max-Planck-institut für Chemie.

Figure 18.2 The end of the cosmochemistry and geochemistry in Max-Planck-Institute in Mainz. The buildings are still there, but they are empty.

Fortunately, things developed better than expected. The cosmochemical research in Germany is presently in good shape. There are several excellent research groups, mostly concentrating on stable and radiogenic isotopes, but also on trace elements. There is Carsten Münker (my successor in Cologne), Thorsten Kleine in Münster, Stefan Weyer in Hannover, Harry Becker in Berlin, Andreas Pack in Göttingen, Frank Brenker in Frankfurt and Mario Trieloff in Heidelberg. They are all professors at universities and they work to a large extent on cosmochemical problems, using mass spectrometer, ion probe and transmission electron microscopy (TEM) as their analytical tools. Carsten Münker and Stefan Weyer spent some time in Klaus Mezger's lab in Münster, where Thorsten Kleine did his pioneering work on W isotopes under the guidance of Klaus Mezger, who had earlier spent several years in the geochemistry department of the Max-Planck-Institute in Mainz. Andreas Pack and Frank Brenker were postdocs in my group at the University of Cologne. Mario Trieloff graduated at the University of Heidelberg, where he is now professor. There is also the group of Peter Hoppe at the Max-Planck-Institute for Chemistry with ion probe analyses of presolar grains. This is the only research group left over from the old cosmochemistry and geochemistry sections. There are more active cosmochemists in Germany, but the continuation of the field in the future depends to some extent on permanent professor positions who will lay out the path for the next generation of cosmochemists.

The driving forces behind progress in cosmochemistry are (1) attempts to determine increasingly more precise formation ages of extraterrestrial materials and (2) efforts to establish chemical and isotopic differences between terrestrial and extraterrestrial samples. This has led and probably will lead to enormous improvements in the analysis of small extraterrestrial samples. Studies of lunar rocks and meteorites have improved the accuracy of the traditional dating systems, such as for example Rb-Sr and U-He and at the same time completely new methods for age determinations were established (Sm-Nd, Mn-Cr Hf-W *etc*.). In turn, geochemistry has benefitted strongly from these developments. In some sense, cosmochemistry is a forerunner of geochemistry.

The new classification of meteorites based on stable isotopes (section 15.2), the extreme isotopic variation of presolar materials (not discussed here), and the roughly solar composition of the smallest and largest objects in our solar system are essential in understanding the origin and the formation of the solar system and the accumulation and aggregation of source material for the formation of planetesimals and planets in our solar system (Palme and Zipfel, 2016). These data together with the age data are the real constraints for any modelling.

Further sample return missions from solar system objects as well as meteorites from planetary bodies (Moon, Mars, perhaps one day Venus and Mercury) will provide us with new samples that require highly sophisticated instrumentation for analysis. The few grains from asteroid Itokawa brough back to Earth with the Hayabusa mission give us some idea of the problems we are facing with such asteroid missions.

If we want to better understand the formation of our solar system and the evolution of other planetary systems we need strong cosmochemical research groups.

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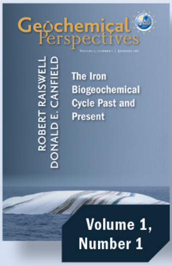
INDEX



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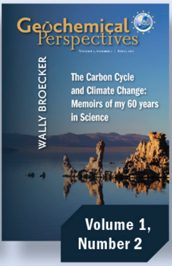

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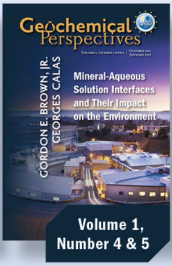

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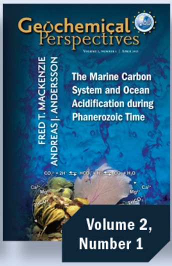

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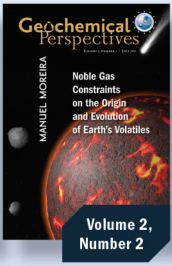

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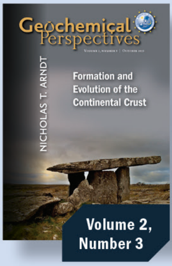

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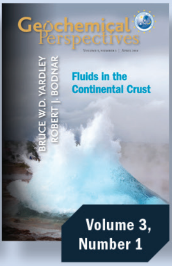

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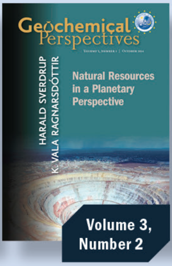

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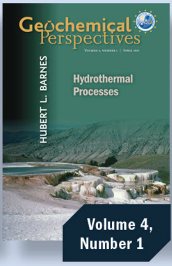

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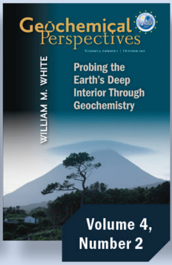

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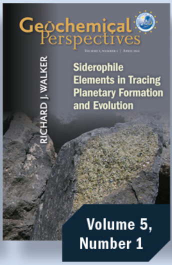

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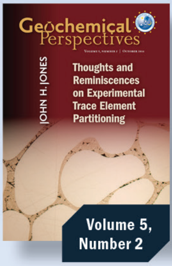

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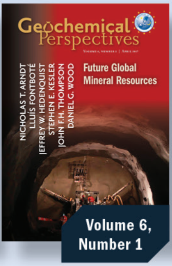

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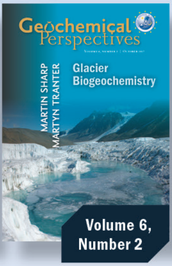

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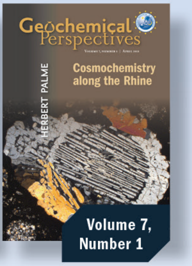

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Image: Zircon megacryst from a southern African kimberlite. Credit: Jon Woodhead

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HERBERT PALME studied physics and mathematics at the University of Vienna. After his PhD at the Institut für Radiumforschung und Kernphysik with Prof. Berta Karlik, he moved to Mainz to take a post-doc position with Heinrich Wänke at the Cosmochemistry Department of the Max-Planck-Institut für Chemie. From 1976 to 1977 he spent a year with Ed Anders at the University of Chicago. In 1984 he did his habilitation for mineralogy at the University of Mainz. From 1994 to 2008 Herbert Palme was professor of mineralogy and geochemistry at the University of Cologne. After his retirement he became honorary collaborator at the Senckenberg Museum and Research Institution in Frankfurt.

Herbert Palme is a Fellow of the Meteoritical Society, as well as of the Geochemical Society and European Association of Geochemistry. In 2003 he was awarded the Leonard Medal of the Meteoritical Society and from 2005 to 2006 he was President of the Meteoritical Society. In 2006 he received the Urey Award of the European Association of Geochemistry and in 2011 the Abraham-Gottlob-Werner Medal of the German Mineralogical Society. He is a member of the Academy of Natural Sciences Leopoldina, a corresponding member of the Austrian Academy of Sciences and since 2014 a member of the Academia Europaeae. Asteroid 7378 carries his name.

Herbert Palme worked on the chemistry and mineralogy of lunar samples, meteorites and rocks from the upper mantle of the Earth. Of particular interest to him were high temperature components of chondrites. Together with Frank Wlotzka, he identified for the first time refractory metal alloys in a chondrite, unequivocally demonstrating condensation processes in the early solar nebula. He also found the first super-refractory inclusion from a carbonaceous chondrite. Together with Susanne Klerner and Dominik Hezel he provided evidence for the chemical complementarity of chondrules and matrix in carbonaceous chondrites. With the help of Alexander Borisov he experimentally determined the solubilities of noble metals in silicate melts and derived metal-silicate partition coefficients. This work was extended to Fe, Ni and Co. Together with Katharina Lodders he worked on the abundances of elements in the solar system and with Hugh O'Neill he published elemental abundances of the upper mantle of the Earth.