



Frontiers

Early Earth differentiation

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Abstract

The birth and infancy of Earth was a time of profound differentiation involving massive internal reorganization into core, mantle and proto-crust, all within a few hundred million years of solar system formation (t_0). Physical and isotopic evidence indicate that the formation of iron-rich cores generally occurred very early in planetesimals, the building blocks of proto-Earth, within about 3 million years of t_0 . The final stages of terrestrial planetary accretion involved violent and tremendously energetic giant impacts among core-segregated Mercury- to Mars-sized objects and planetary embryos. As a consequence of impact heating, the early Earth was at times partially or wholly molten, increasing the likelihood for high-pressure and high-temperature equilibration among core- and mantle-forming materials. The Earth's silicate mantle harmoniously possesses abundance levels of the siderophile elements Ni and Co that can be reconciled by equilibration between iron alloy and silicate at conditions comparable to those expected for a deep magma ocean. Solidification of a deep magma ocean possibly involved crystal–melt segregation at high pressures, but subsequent convective stirring of the mantle could have largely erased nascent layering. However, primitive upper mantle rocks apparently have some nonchondritic major and trace element refractory lithophile element ratios that can be plausibly linked to early mantle differentiation of ultra-high-pressure mantle phases. The geochemical effects of crystal fractionation in a deep magma ocean are partly constrained by high-pressure experimentation. Comparison between compositional models for the primitive convecting mantle and bulk silicate Earth generally allows, and possibly favors, 10–15% total fractionation of a deep mantle assemblage comprised predominantly of Mg-perovskite and with minor but geochemically important amounts of Ca-perovskite and ferropericlaase. Long-term isolation of such a crystal pile is generally consistent with isotopic constraints for time-integrated Sm/Nd and Lu/Hf ratios in the modern upper mantle and might account for the characteristics of some mantle isotope reservoirs. Although much remains to be learned about the earliest formative period in the Earth's development, a convergence of theoretical, physical, isotopic and geochemical arguments is beginning to yield a self-consistent portrait of the infant Earth.

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1. In the beginning

An unfortunate consequence of the Earth's unruly beginnings is that we have essentially no direct rock record of its birth and early childhood. Yet it was during that earliest stage when much of the Earth's personality was shaped. The first 860 Ma of the Earth's lifetime are generally referred to as the 'Hadean', a stage during which the Earth underwent major episodes of differentiation of a magnitude that will unlikely ever be repeated. The metallic core separated from the silicate mantle, and the silicate mantle may have developed much of its internal character.

A detailed sketch of the Earth's birth can now be drawn on the basis of stochastic and hydrodynamic modeling of solar nebula processes. The picture that emerges depicts a violent infancy. The formation of a solar nebula starts with gravitational contraction of a localized dense region in an interstellar molecular cloud, and a supersonic shock event, probably from a nearby supernova or perhaps an AGB star, triggered cloud collapse [1,2]. Within the inner, or 'terrestrial', region of the nebular disc, sticky primordial dust particles coagulate to form a large population of meter- to kilometer-sized objects [3]. Gravity and gas-drag began to affect the larger objects, driving a period of runaway growth lasting on the order of 10^6 years, the product of which includes a vast array of planetesimals and planetary embryos [4,5]. A final phase of coalescence, completed on a time scale of 10^8 years, occurs mainly by infrequent albeit massive impacts among larger objects, resulting in a few terrestrial planets that sweep up the flotsam and jetsam. Importantly, such modeling predicts that the lion's share of a terrestrial planet's mass and energy is acquired during this late-impact stage [6–8]. Vindication of the standard planetary accretion model comes from hydrodynamic simulations which indicate that giant impacts can account for the origin and low density (iron-poor) of the Moon, the spin angular momentum of the Earth–Moon system, as well as the Earth's rotation [8–12].

Giant impacts involve a vast amount of potential and kinetic energy. Physical models show that the energy buried in the proto-Earth from a giant collision with a Mars-sized impactor, such as in a 'moon-forming' event, would have been sufficient to raise

interior temperatures by thousands of degrees, causing high degrees of melting and a global magma ocean [13,14]. During its accretion period, the proto-Earth likely endured several massive impacts and may have experienced transient magma oceans. The birth of Earth was violent and hot. How did such an angry young planet grow and differentiate into the seemingly well-adjusted, mature planet we know today?

2. Core formation

The formation of a metallic core is the most dramatic differentiation event in a terrestrial object involving segregation of dense, iron-rich metal alloy from magnesium-rich silicate. Understanding the core formation process provides insight into accretion and the earliest formative period of a planet, and in recent years, answers have begun to emerge to key questions regarding the timing, physical conditions and mechanisms of core formation.

2.1. When do planetary cores form?

Parent/daughter fractionation of short- and long-lived radionuclides during core formation generates isotopic signals that constrain the timing of accretion and core formation in terrestrial objects (see Table 1

Table 1
Radiogenic isotope systems

Parent–Daughter	Half-life (years)	$D_{\text{parent}}^{\text{met/sil}}/D_{\text{daughter}}^{\text{met/sil}}$	$D_{\text{parent}}^{\text{CP/RM}}/D_{\text{daughter}}^{\text{CP/RM}}$
<i>Short-lived</i>			
$^{26}\text{Al}-^{27}\text{Mg}$	0.7×10^6	~ 1	~ 1
$^{146}\text{Sm}-^{142}\text{Nd}$	103×10^6	~ 1	< 1
$^{182}\text{Hf}-^{182}\text{W}$	9×10^6	$\ll 1$	> 1
<i>Long-lived</i>			
$^{87}\text{Rb}-^{87}\text{Sr}$	49×10^9	~ 1	> 1
$^{147}\text{Sm}-^{143}\text{Nd}$	106×10^9	~ 1	< 1
$^{176}\text{Lu}-^{176}\text{Hf}$	36×10^9	~ 1	< 1
$^{238}\text{U}-^{206}\text{Pb}$	4.5×10^9	$\ll 1$	> 1
$^{235}\text{U}-^{207}\text{Pb}$	0.8×10^9	$\ll 1$	> 1

^a $D_{\text{parent}}^{\text{met/sil}}/D_{\text{daughter}}^{\text{met/sil}}$ = the ratio of partition coefficients, $D^{\text{metal/silicate}}$, during metal–silicate equilibration for parent and daughter elements in radiogenic isotope systems.

^b $D_{\text{parent}}^{\text{CP/RM}}/D_{\text{daughter}}^{\text{CP/RM}}$ = the ratio of partition coefficients, $D^{\text{CP/RM}}$, during fractionation of a deep mantle crystal pile, CP, from residual mantle, RM, for parent and daughter elements.

for review of some relevant isotope systems) [15–17]. The short-lived Hf–W isotope system places severe restrictions on the timing of core formation in planetesimals [18,19]. Iron-rich cores apparently formed in some objects within about 3 million years of t_0 , a time frame that provides important constraints on plausible core formation mechanisms in growing terrestrial bodies.

In contrast, analyses of Earth samples reveal a much later, or more protracted, core formation. The W isotopic composition of mantle silicates suggests core formation at ~ 30 million years after t_0 , but this model ‘age’ requires a wholesale core–mantle reequilibration event at that time [18,19]. But it is unlikely that such a global event ever happened, because Pb and Xe isotopes indicate more than a factor of two longer core formation time scales [20]. Defining a core formation rate for the Earth depends on the degree to which silicate and iron equilibrate between impactors and the proto-Earth, especially during a giant moon-forming impact that might have disturbed the cosmochemically volatile U–Pb system relative to the refractory Hf–W system [20]. Defining an absolute ‘age’ of core formation may have little real meaning for a continuous accretion process, but in a broad sense, the radioisotope data prescribe that the bulk of the Earth’s core formed on a 10^7 - to 10^8 -year time scale, generally consistent with accretion time scales predicted by stochastic modeling.

2.2. How do planetary cores form?

Common wisdom has held that molten iron alloy does not ‘wet’ silicate grain boundaries, rendering the silicate effectively impermeable. For this reason, core formation in planetary bodies has been thought to require extensive silicate melting, enabling dense molten metal droplets to sink through silicate melt [21–23]. To achieve high degrees of silicate melting in a planetesimal requires prodigious heat, and the most important early source of energy may have been the decay of short-lived radioactive ^{26}Al ($t_{1/2} \sim 0.7$ Ma), which is known to have been active in the solar disc [24]. Models of the thermal evolution of a growing planetesimal indicate that for an object large enough to retain heat efficiently ($r \sim 30$ or 40 km), the thermal evolution is dependent on both the timing of accretion

and the initial $^{26}\text{Al}/^{27}\text{Al}$ abundance ratio [25–27]. These models show that bodies with $^{26}\text{Al}/^{27}\text{Al}$ greater than about 1×10^{-5} and which accreted within a few ^{26}Al half-lives of t_0 would have heated internally to temperatures sufficient to melt iron alloy and even silicate, as illustrated in Fig. 1. High initial $^{26}\text{Al}/^{27}\text{Al}$ ratios, as for example the canonical initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of 5×10^{-5} that is based on measurements of calcium–aluminum inclusions (CAI) in meteorites [28], would clearly have produced sufficient heat to melt planetesimals. However, recent measurements on carbonaceous chondrites reveal much lower initial ratios in some cases, of the order 5×10^{-6} [29], indicating that radiogenic heating may not have been sufficient to cause partial melting and implying a larger role for impact heating among planetesimals [29].

Recent experimental results indicate that excess molten iron alloy over a percolation threshold of only about 5 vol.% can create permeability in a solid silicate matrix [27]. The metal content in planetary objects may generally exceed 10 vol.%, so objects heated sufficiently to melt iron alloy could have experienced an incipient albeit inefficient stage of core formation upon melting of iron alloy. Modeling indicates that melting and segregation of iron alloy could have occurred within a few million years of the origin of the solar system, consistent with the short time frame allotted by tungsten isotopes (Fig. 1). Efficient removal of molten iron alloy to a planetary core may have required heating to well above the silicate solidus, such as would have occurred for high initial $^{26}\text{Al}/^{27}\text{Al}$ ratios and rapid accretion or as a consequence of shock-heating among small, porous planetesimals [29]. Alternatively, efficient removal of iron alloy may have been aided by heat advection in the silicate, as recent experiments show that plastic deformation of the silicate matrix promotes connectivity in an otherwise impermeable silicate, possibly even at low melt fractions [32].

2.3. How did the Earth’s core form?

The prevailing evidence indicates early core formation in planetesimals. The Earth acquired most of its mass from giant impacts with Mercury- to Mars-sized objects during late-stage accretion, and these objects, as well as the embryonic Earth, are likely to

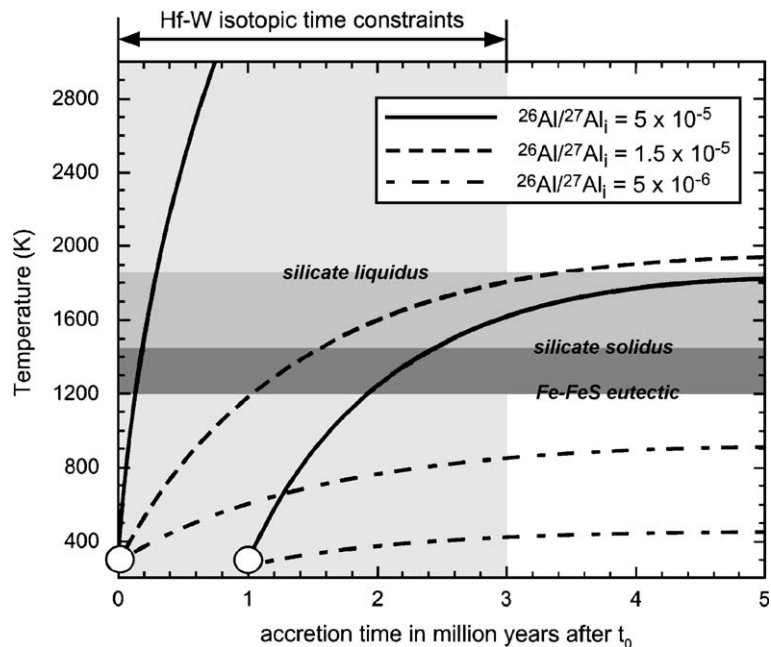


Fig. 1. Thermal models for post-accretion heating of a planetary body of CI chondritic composition and with a minimum radius of 30 km by decay of short-lived ^{26}Al . The silicate/metal proportion is 85:15 (vol.%) and the initial temperature is assumed to be 255 K. Heating trajectories are shown for a canonical initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of 5×10^{-5} (solid lines) [28], as well as for lower ratios of 1.5×10^{-5} (dashed lines) and 5×10^{-6} (long-short dashed lines). Estimated 1 atm melting intervals in the Fe–FeS system (dark shaded region) and Allende silicate (medium shaded region) are shown [30,31]. Heating paths emanating from 0 and 1 Myr show the effects of accretion time. The W isotopic composition of iron meteorites indicates core formation within about 3 m.y. of solar system formation in planetesimals (light shaded region). Both the initial $^{26}\text{Al}/^{27}\text{Al}$ ratio and the timing of accretion have large effects on the rate of heating [26,28], but bodies that accreted within 1 Myr of t_0 may generally have reached the melting points of iron alloy and silicate within 3 Myr.

have had preformed cores [33]. What happens to the metallic core of an impactor during the violent collision with the proto-Earth?

Hydrodynamic simulations of giant impacts indicate a dependence on the angular momentum of the collision but generally show that while some of the impactor core may merge directly with the Earth's proto-core, much of the impactor core would be ejected into low orbit and would fall rapidly back to the Earth [9]. Models are too low in resolution to trace the fate of core materials in detail, but if the iron falls back to the Earth in large fragments, then dense metallic blobs should sink rapidly to the base of the magma ocean produced by the impact. If the entire silicate mantle were molten, the metal blobs would sink directly to the proto-core with little equilibration, but if the base of the magma ocean were solid silicate, then metal might pool until gravitational instability permits movement to the core in large diapirs [22].

Alternatively, metal from the impactor and perhaps even the Earth's proto-core may have become highly fragmented and emulsified in the magma ocean, in which case small metallic droplets could equilibrate rapidly with silicate melt. The fate of the cores of the impactor and proto-Earth during a giant impact and the process of emulsification are poorly understood dynamical problems needing attention.

Direct evidence of core formation is preserved in the siderophile ('iron-loving') element geochemistry of mantle rocks. Siderophile elements partition nearly wholesale into metal during core formation, but trace amounts remain in the silicate. Element partitioning is sensitive to the physical conditions of metal–silicate equilibrium (e.g., P , T , X), and if core formation were a singular, equilibrium event, then the conditions of equilibrium can be deduced from the pattern of siderophile element depletion in mantle rocks.

Compositional models that are based on the assumption that refractory elements are present in chondritic relative proportions in bulk Earth have yielded a generally consistent picture regarding the degree to which siderophile elements are depleted in the mantle, as shown on Fig. 2 [34–36]. The so-called highly siderophile elements (HSE) such as Au and the Pt-group elements exist as a group in near-chondritic relative proportions in the Earth's mantle, meaning that whatever process established their abundances did not fractionate them one from another. Chondritic relative HSE cannot be reconciled with measured low-pressure and -temperature metal/silicate partitioning behavior, which show that within the group, these elements have highly variable siderophile character, with partition coefficients varying by as much as 10^8 [35]. Furthermore, the HSE are present at levels that exceed expectations for metal segregation at shallow mantle conditions by many orders of magnitude. It has been suggested that metal–silicate equilibration at higher pressures and temperatures might potentially explain HSE abundances, but the limited experimental data do not support that contention [37]. The standard model is that core formation effectively stripped all the HSE from the mantle, and subsequently, HSE abundances were raised to observed values by the

final 1% of Earth accretion comprised of meteoric materials with chondritic proportions of HSE [38]. Alternatively, back-mixing of a small amount outer-core materials might also have established HSE abundances in the mantle [39]. In either case, HSE abundances cannot be used as a signal of core–mantle equilibration.

In contrast to the HSE, the abundances of moderately and slightly siderophile elements (MSE and SSE, Fig. 2) would not have been significantly altered by the late addition of meteoric material and so are potentially much more informative about the conditions of core formation. Of these elements, Ni and Co have provided the most powerful constraints on core formation because their abundances in the mantle are most accurately and precisely known, and their partitioning behavior has been relatively well studied experimentally over a wide range of conditions. A fascinating feature of mantle rocks is that within uncertainty, Ni and Co are present in essentially chondritic relative proportions, both having apparently been depleted similarly during core formation (Fig. 2). A relatively complete experimental database that describes Ni and Co partitioning between molten silicate and molten iron alloy at pressures up to ~ 40 GPa and over a range of high

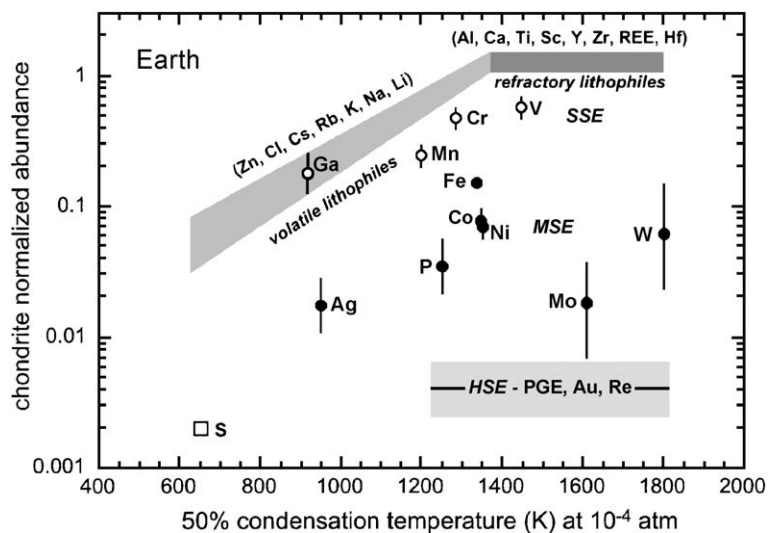


Fig. 2. Elemental abundances in the Earth's upper mantle normalized to chondritic abundance levels [34,35] and plotted relative to 50% condensation temperatures in a vacuum (10^{-4} atm), which is used as a proxy for a nebular condensation sequence. The generalized trends of refractory lithophile and volatile elements are shown as shaded regions. Slightly siderophile elements (SSE) are plotted as open circles and moderately siderophile elements (MSE) as solid circles. The highly siderophile elements (HSE) have nearly constant abundance as a group, and abundance uncertainties are shown for simplicity by a shaded region.

temperatures (e.g., ~2000 to 3000 K) and oxygen content now exists. Experiments show that at constant oxygen content, an increase in pressure and/or temperature causes both Ni and Co to become less siderophile, but at different rates, so that they can have similar partitioning behavior under certain conditions as required by mantle rocks. [40–42].

Fig. 3 shows an example of how experimental partitioning data can be used to deduce a set of conditions at which metal and silicate might last have equilibrated in the Earth. The diagram, which is constructed on the basis of our own parameterizations to high-pressure and -temperature experimental data (see figure caption), shows the locus of pressures and temperatures that satisfies the condition that the ratio of the Ni and Co exchange partition coefficients (K_D) is ~1.1 during metal–silicate equilibrium. In this model, the relative and absolute abundances of Ni and Co in the Earth’s upper mantle are satisfied simultaneously at ~40 GPa and ~2800 K. Modeling like this is used as primary evidence for metal–silicate equilibration in a deep magma ocean [40,41,52],

plausibly linked to large-scale melting during one or more giant impacts during late-stage accretion.

Partitioning models have been developed for other MSE and SSE (e.g., Ga, P, W, and Mo), and a signature of high-pressure and -temperature metal–silicate equilibration is interpreted for these elements as well, although their mantle abundances and partitioning behavior are far less well constrained than for Ni and Co [35,41,52]. It is well to remember that limitations inherent to the partition coefficient parameterization scheme, due for example to correlated effects among variables or nonlinear effects, make extrapolation outside the range of the data precarious at best and misleading at worst. Further constraints on plausible metal–silicate equilibrium conditions require collection of internally consistent sets of partitioning data over a wide pressure, temperature and compositional range for each element in order to more accurately deduce the effects of each variable (e.g., P , T , X) in isolation. A solidly anchored thermodynamic understanding of how intensive properties effect partitioning is needed in order to reliably

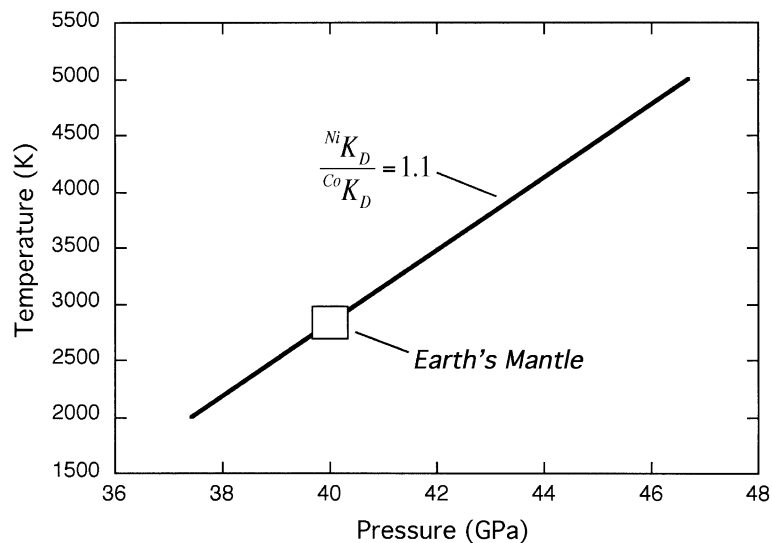


Fig. 3. The locus of solutions in pressure–temperature space for a ratio of $^{Ni}K_D$ to $^{Co}K_D$ of 1.1:1, where K_D is the molten Fe alloy/molten silicate exchange partition coefficient, $K_D = \frac{(^{met}X_M)^{sil}X_{MO}}{(^{met}X_{Fe})^{sil}X_{FeO}}$, where M=Ni or Co and assuming that Fe, Ni and Co are in a divalent oxidation state. The large square shows the ‘unique’ pressure–temperature condition that satisfies the absolute Ni and Co K_D s required to reproduce the observed abundances of these elements in the Earth’s mantle. The diagram is constructed based on parameterizations to high-pressure and -temperature experimental partitioning data [40,42–51]. Data are regressed to the equation, $\ln K_D = \alpha/T + \beta P/T + \gamma \ln(1 - X_S) + \delta \ln(1 - X_C) + k$, where T is temperature in Kelvin, P is pressure in GPa, X_S and X_C are the mol fractions of sulfur and carbon in the iron alloy and k is a constant. Values for fitted coefficients with standard uncertainties are as follows: Ni: $\alpha=9887$ (853), $\beta=-181$ (16), $\gamma=0.17$ (0.19), $\delta=1.03$ (0.5) and $k=-0.12$ (0.42), $n=68$, $R^2=0.90$; Co: $\alpha=6847$ (1113), $\beta=-70$ (15), $\gamma=0.78$ (0.17), $\delta=0.58$ (0.38) and $k=-0.53$ (0.48), $n=44$, $R^2=0.75$.

extrapolate to conditions outside those encompassed by the experimental database.

Presuming that a signal of high-pressure and -temperature equilibration is robust, interpreting exactly what the signal means is a matter of conjecture. In the simplest model, metal segregates from a magma ocean, ponds at the ocean floor, equilibrates essentially isobarically and eventually sinks to the core in diapirs or perhaps by percolation through high-pressure silicate phases [33,41]. This model is probably unrealistic because numerical calculations show that large blobs of metal require several orders of magnitude more time to equilibrate than plausible magma ocean crystallization time scales [53]. Another possibility is that emulsified metal precipitates out of the magma ocean in much the same manner as rain out of clouds [22]. Small metal droplets would equilibrate rapidly with silicate melt as they descend, and deduced metal–silicate equilibrium conditions would reflect the average of a polybaric, polythermal process [42,53].

Geochemically based core formation modeling has typically presumed a singular metal–silicate equilibration event (single-stage). However, accretion theory leads us to expect numerous large impacts among core-segregated objects, each of which could have left an indelible imprint on the siderophile element content of the mantle (multistage). For example, it is conceivable that a large impactor could have been a fragment of a previously differentiated object with overall nonchondritic siderophile element ratios (e.g., Mercury). Another major unknown factor is the degree of metal–silicate reequilibration between impactor and target materials. Whether or not current siderophile element abundances in the mantle reflect a single, final giant impact in which effectively all the silicate and metal were re-homogenized and equilibrated or reflect a multistage history of metal–silicate partial equilibration is a difficult question to assess. Reconstructing the details of a multi-event history of metal segregation is a daunting and perhaps intractable prospect.

3. Mantle differentiation in the Hadean

Large-scale melting of Earth is unavoidable in the standard model of planetary accretion. Deposition of

impact energy when a planetary embryo swallows up planetesimals during late-stage accretion would result in magma ocean formation. Repeated impacts could sustain a magma ocean especially in the presence of a blanketing atmosphere [54]. A giant collision of a ‘Mars-sized’ impactor with proto-Earth is the prevailing theory for the origin of the Moon [9,11,12], and such an impact could deliver sufficient energy to melt the entire planet [13].

Hydrodynamic impact models indicate that shock-induced impact melting would create a melt pond within the impact crater, which upon isostatic readjustment would spread like a blanket over the surface, forming a deep magma ocean [14]. The extent and depth of the magma ocean depend on many factors including the impactor/target mass ratio, impact velocity and initial temperatures of the objects [14]. How would a magma ocean cool and crystallize? Would crystal fractionation occur and be preserved? Does the modern mantle provide physical or geochemical evidence that informs us about magma ocean differentiation processes?

3.1. How would a magma ocean crystallize?

Cooling of a peridotite magma ocean would eventually lead to crystallization from the bottom up because liquidus crystallization curves have dT/dP slopes that are steep relative to an adiabat in a convecting magma ocean, as shown schematically in Fig. 4. Experimental melting studies show that crystallization in the deep mantle (>700 km) would be dominated by Mg-perovskite, with minor amounts of Ca-perovskite and ferropericlase, whereas crystallization at shallower levels would be dominated by olivine and its high-pressure polymorphs, majorite garnet, and lesser amounts of pyroxenes [55–57].

Numerical simulations show that the magma ocean solidification process is sensitive to many factors, including surface temperature, cooling rate, crystal nucleation and growth rates and melt and crystal-mush viscosities [54,58,59]. Surface temperature and cooling rate are highly dependant on whether a rock vapor or steam atmosphere is present during cooling [54]. In the absence of an atmosphere, heat radiation to space is very efficient and the deeper portion of a magma ocean cools rapidly (10^3 years). The upper portion of the magma ocean (e.g., transition zone and

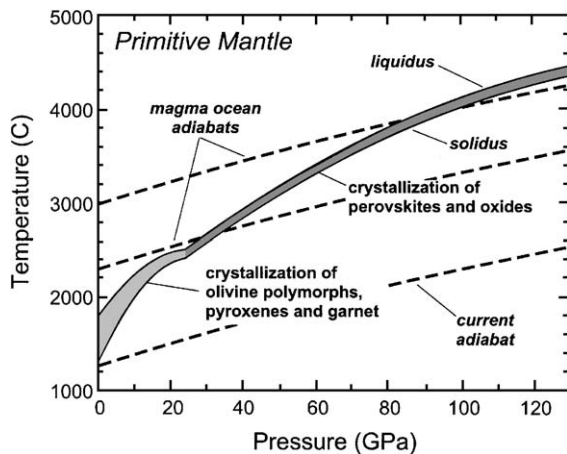


Fig. 4. Generalized pressure–temperature phase diagram for a fertile peridotite mantle [55–57]. Schematic magma ocean adiabats illustrate that crystallization would proceed from the bottom up. At pressures greater than about 25 GPa, crystallization would involve Mg-perovskite, Ca-perovskite and (Mg,Fe)-oxide, and at lower pressures, it would involve olivine polymorphs, garnet and pyroxenes.

shallow upper mantle) could remain hot and molten much longer due to the depression of the solidus at pressures less than about 25 GPa (Fig. 4), especially if a ‘chill-crust’ forms at the surface—heat radiation to space from the surface would be efficient enough to cool and crystallize a surface layer of the magma ocean (D. Stevenson personal communication). If an atmosphere persists, it provides very effective thermal insulation and cooling time scales are much longer (10^6 – 10^7 years) even for deeper portions of the magma ocean.

Hydrodynamic models indicate that vigorous convection during early stages of crystallization might effectively prevent accumulation of crystals if the melt–solid viscosity contrast is sufficiently low [58,59]. The viscosity contrast depends critically on the physical properties of melt at high pressures and the nucleation and growth rates of the crystals, properties that are poorly known for deep mantle phases. The potential for crystal fractionation in a deep magma ocean remains a matter of speculation [54].

An initially stratified mantle after magma ocean solidification would have important chemical and dynamic consequences for mantle evolution. Nearly 4.5 billion years of solid-state convection subsequent

to solidification may have largely erased nascent stratification. However, if lower mantle phases are intrinsically dense and stiff, they could form layers, or ‘deep crystal piles’, that are resistant to convective mixing.

3.2. Is the modern mantle stratified?

The extent, scale and morphology of mantle chemical heterogeneity has long been a hotly debated topic in mantle geophysics, geodynamics and geochemistry, with implications for the nature of mantle convection [60–65]. Geochemical and isotope heterogeneities in mantle derived magmas dictate distinctive geochemical reservoirs, evoking models for chemical layering [60]. Global seismic discontinuities at ~410 and 660 km image mineralogic boundaries separating the ‘upper’ mantle from the ‘transition zone’ and ‘lower’ mantle. These boundaries can be well ascribed to phase transitions based on known phase relations and elastic properties of high-pressure and -temperature mineral assemblages in fertile mantle peridotite [64,66,67]. Seismic tomography indicates that subducting slabs penetrate deep into the lower mantle [68], at least in some regions, and return flow of material from the deep mantle is implicated. The mixing efficiency of mantle convection is linked to the driving forces of subducting slabs and the vorticity or toroidal motion induced by rotation and strike-slip motion of the surface plates [69,70]. Whole-mantle convection, even when moderated by the 660-km phase transition and a high-viscosity lower mantle, is expected to generally erase large-scale heterogeneities over the age of the Earth. Moreover, mixing was probably considerably more vigorous when the Earth was young and hot. These considerations make it likely that the modern mantle is not chemically stratified in a gross sense.

Yet stable chemical domains in the deeper reaches of the lower mantle remain a distinct possibility. Seismic observations and theoretical models have indicated the possible presence of dense, compositionally distinct regions in the lowermost mantle [71,72]. The depth of the upper boundary of this ‘layer’ is thought to be laterally and temporally highly variable [72]. Indeed, numerical simulations suggest that seismic observations might best be explained if dense material is restricted to discontin-

uous piles rather than a continuous, undulating boundary [73].

Massive crystallization differentiation in the Hadean mantle, possibly involving flotation of olivine in the upper mantle, concentration of majorite at transition zone depths or fractionation of lower mantle phases, should have been largely or even completely homogenized by the Earth's convective engine. However, it remains conceivable that some fraction of a crystal pile deposited at the base of the mantle could have become rheologically isolated from the main convecting regime or perhaps slowly eroded as the convecting mantle interacts with the stiffer crystalline mass. The pressure and temperature dependence of density and viscosity is not well known for perovskite and oxide phases at deep mantle conditions. In lieu of direct validation or repudiation of the plausibility for long-term isolation of a deep mantle layer on mineral–physical grounds, it is of interest to investigate what kind of geochemical signal would be expected in the convecting mantle should such a layer actually exist.

3.3. *What is the composition of the primitive convecting mantle?*

Crystal fractionation induces chemical changes in an evolving magma, and isolation of a crystal pile in the deep mantle would impart a chemical imprint on the remaining residual mantle. The search for a geochemical signal involves a compositional comparison among the original magma ocean (i.e., bulk silicate Earth), the isolated crystal pile and the modern convecting portion of the mantle. To properly constrain a magma ocean crystallization model, reliable compositional estimates for each of these reservoirs are required.

Meteorite compositions, either as direct analogues or through deductions from compositional trends, form the basis of most bulk Earth and bulk silicate Earth compositional models [34,74–77]. The relative constancy of cosmochemically refractory element ratios (e.g., Ca/Al, Al/Ti, Sc/REE) in primitive chondritic meteorites of all flavors helps justify the assumption that refractory elements were delivered to the Earth en masse in primitive solar nebula proportions [34,36]. Correlations among refractory lithophile elements in chondritic meteorites and selected sets of

primitive upper mantle rocks have been interpreted to indicate that the bulk silicate Earth has chondritic relative abundances of these elements (such as Ca, Al, Ti, Sc, Zr and REE) [34,74–77].

The crux of the early mantle differentiation issue is whether or not the modern convecting mantle (plus crust) has the same composition as the bulk silicate Earth. Model primitive upper mantle compositions, which may be representative of the convecting mantle, have been constructed based directly on primitive peridotite compositions [78–80], mixtures of depleted peridotite and basalt ('pyrolite') [81] and melt extraction trends in residual peridotites [82]. Fig. 5 shows a set of chondrite-normalized major and trace refractory lithophile element ratios that are most accurately known based on literature assessments of primitive upper mantle composition. Common among these models are superchondritic Mg/Si and Ca/Al ratios by about 20% and 15%, respectively, whereas the Al/Mg ratio is generally subchondritic. Ratios involving Mg and Si may be unreliable as geochemical indicators, however, because they are not constant among various chondrite groups, varying by as much as 20% relative and indicating that a cosmochemical process fractionated these elements prior to Earth accretion [76]. In contrast, the Ca/Al ratio is essentially constant within uncertainty among nearly all chondrite groups, consistent with the highly refractory nature of these elements. Ca/Al is presumably very near the chondritic value in the bulk silicate Earth, in which case the apparently superchondritic ratio in the primitive upper mantle could be a consequence of mantle differentiation [80,82].

Among trace elements Sc, Yb and Sm abundances show a relatively small scatter in primitive mantle rocks, and elemental ratios among these and major elements are typically within about 10–20% of chondritic ratios. Overall, the pattern exhibited in Fig. 5 is one of a primitive convecting mantle with some elemental ratios that are close to chondritic, but with others that may have been fractionated to various degrees away from initially chondritic values.

3.4. *How would crystal fractionation in the deep mantle affect mantle chemistry?*

Crystal–melt separation can be a very efficient mechanism for fractionating major and trace element

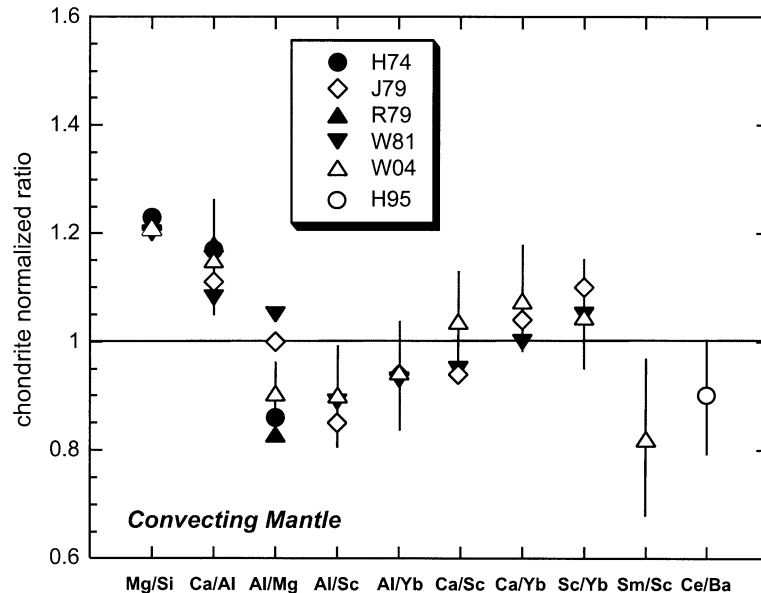


Fig. 5. Elemental ratios in primitive upper mantle rocks normalized to CI chondritic values [34]. Data sources are H74 [78], J79 [79], R79 [83], W81 [84], W04 [80] and H95 [85]. Error bars are best estimates of the mean at the 95% confidence level from the data compilation of [80], with the exception of the Ce/Ba ratio which is based on data from [85].

ratios. Some elements concentrate in the melt phase and are incompatible in minerals (e.g., K, Na, Ba, LREE), whereas others are compatible minerals (e.g., Mg, Ni, Cr). Elemental fractionations are commonly used to retrace the crystallization history of differentiated lavas that erupted at the Earth's surface and in the same way can be used to detect signals of magma ocean fractionation. Mantle convection may have efficiently destroyed initial layering throughout much of the mantle, in which case crystal fractionation in the deep mantle would be the most likely mechanism for imposing long-term geochemical effects. Peridotite crystallization studies show that a deep mantle crystal assemblage would be comprised of Mg-perovskite, Ca-perovskite and ferropericlasite [55,56,86]. Although crystallization experiments have only been made at pressures corresponding to the uppermost lower mantle (~25 to 35 GPa), Mg-perovskite is expected to be the first and proportionally dominant phase to crystallize throughout most of the lower mantle, followed down temperature by ferropericlasite and Ca-perovskite as the magma ocean cools and solidifies.

Mg-perovskite has a subchondritic Mg/Si ratio, so it is not surprising that removal of this phase in the

lower mantle has been envisioned as a way to elevate the Mg/Si ratio in the upper mantle [87]. With this impetus, early partitioning studies concentrated on how Mg-perovskite fractionates major and trace element ratios. Measuring reliable partition coefficients at extreme pressures and temperatures proved challenging, but a general consensus emerged that only very minor amounts of Mg-perovskite fractionation in the lower mantle could be accommodated given near-chondritic refractory element ratios in primitive upper mantle [88,89]. The severe geochemical restrictions imposed by these studies have generally been accepted as evidence against magma ocean crystal fractionation [63,88,89] and have even been used to argue that a magma ocean likely never existed [90].

There are factors, however, that preclude an outright dismissal of at least some fractionation of deep mantle phases. The first of these is that the convecting mantle can be interpreted to have some nonchondritic refractory elemental ratios, most notably the Ca/Al ratio, and these fractionations beg for an explanation (Fig. 5). Second, partition coefficients for all phases were not well known in early magma ocean fractionation models. A recent spate of

experiments has vastly improved our knowledge of partitioning among deep mantle phases with some remarkable new findings [80,91–93]. For example, it has recently been revealed that Ca-perovskite can accommodate copious amounts of trace elements, so that even a small amount in a fractionating assemblage can exert considerable leverage on certain elemental ratios [92,93]. Furthermore, in a surprising number of cases, Ca-perovskite fractionates elemental ratios in a sense opposite to that of Mg-perovskite [80].

The exact proportions in which deep mantle phases might have been removed from a crystallizing magma ocean is not known with any certainty, but simple major element mass balance dictates an assemblage dominated by Mg-perovskite with small amounts of Ca-perovskite and ferropericlaase [80]. By way of example, Fig. 6 shows how the elemental ratios from Fig. 5 change in two scenarios for deep mantle crystallization, which are based on our own modeling [80]. One involves pure Mg-perovskite fractionation, and the other fractionation

dominated by Mg-perovskite but with minor amounts of Ca-perovskite and ferropericlaase. In these examples, the amount of crystal fractionation is chosen to generate a Ca/Al ratio in the residual magma ~15% greater than the chondritic value in order to match the mean estimate of this ratio in the primitive convecting mantle. In one model, 10% of the magma ocean crystallizes as pure Mg-perovskite, whereas in the other model, 15% of the magma ocean crystallizes as an assemblage comprised of 93% Mg-perovskite, 3% Ca-perovskite and 4% ferropericlaase.

The Mg/Si ratio is nominally unchanged in these models, reinforcing the conclusion that the high mantle Mg/Si ratio is either inherited from accretionary materials or that Si was sequestered into the core [75,76,83]. Another feature is that, Mg/Si notwithstanding, the models do not produce elemental fractionations that are grossly discordant with observed element ratios in convecting upper mantle, and it is intriguing that the multiphase deep mantle crystal assemblage produces elemental fractionations

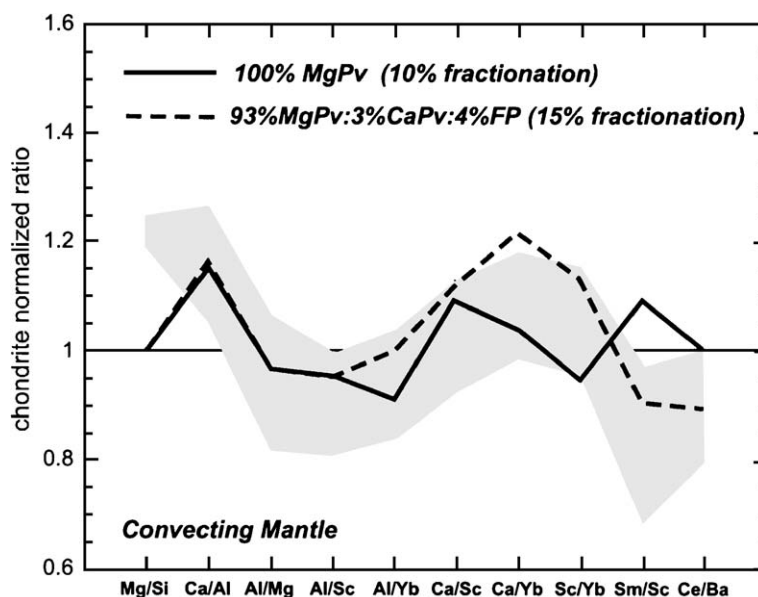


Fig. 6. Two models showing how crystal fractionation of deep mantle phases changes lithophile element ratios away from initially chondritic values in the mantle. The solid line is for the fractionation of 10% of pure Mg-perovskite. The dashed line is for the fractionation of 15% of an assemblage consisting of a mixture of 93% Mg-perovskite, 3% Ca-perovskite and 4% ferropericlaase. Partition coefficients for Mg-perovskite and ferropericlaase are from [80]. Partition coefficients for Ca-perovskite are based on the modeling of [80] for a coexisting melt with 4 wt.% CaO, based on a parameterization of data from [92,93]. Primitive mantle elemental ratios are as in Fig. 5.

that resemble closely those observed in convecting mantle.

Geochemical models such as these are not uniquely required by phase equilibrium constraints, and there are plenty of possible fractionation scenarios involving realistic combinations of deep mantle phases that do not produce chemical fractionations that match well with convecting mantle [80]. Model outcomes are especially sensitive to the amount of Ca-perovskite in the assemblage, as well to the chosen partitioning models for both perovskite phases [80,91–93]. Much needs to be learned about the pressure, temperature and compositional effects on element partitioning at deeper mantle conditions, as all experiments to date are at conditions valid only for the very top of the lower mantle.

Given these caveats, however, it can at least be stated that geochemical modeling indicates that a reservoir of ultra-high-pressure phases constituting something like 10% to 15% of the mantle is plausible.

Such a reservoir, if evenly distributed, would extend about 500 km above the core mantle boundary but might more likely exist as mountainous, discontinuous crystal piles [73]. If such a reservoir has existed for nearly 4.5 Ga, then an obvious place to look for a signal is in radiogenic isotope systems with parent/daughter ratios that are affected by crystal–melt fractionation.

3.5. How would crystal fractionation in the deep mantle effect mantle isotopes?

The isotopic composition of radiogenic daughter nuclides in modern mantle derived magmas that erupted as volcanic rocks at mid-oceanic ridges and ocean islands yield information about time-integrated changes in the parent/daughter ratios in their mantle source rocks. Both long- and short-lived radionuclides provide probes into early mantle differentiation processes (see Table 1). For example, Fig. 7 shows

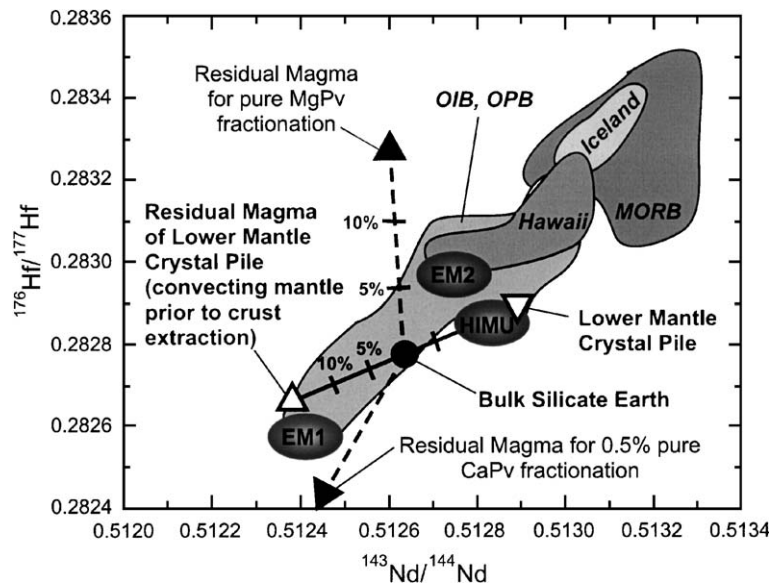


Fig. 7. The $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic compositions of modern, mantle-derived volcanic rocks. The fields for mid-ocean ridge basalt (MORB), ocean island basalt (OIB), ocean plateau basalts (OPB), Hawaii and Iceland, as well as the compositions of bulk silicate Earth and mantle isotopic components (enriched mantle I, EM1; enriched mantle II, EM2; high U/Pb, HIMU) are taken from [94,95]. Models are shown for the time-integrated effects on the residual magma (i.e., residual mantle) of the removal and isolation from the bulk silicate Earth of deep mantle phases in a Hadean magma ocean. The dashed trends show the time-integrated isotopic compositions in the residual magma for removal of up to 15% of pure Mg-perovskite or 0.5% removal of pure Ca-perovskite. The solid hatched line shows isotopic compositions in the lower mantle crystal pile and residual magma (convecting mantle before crust extraction) for removal of up to 15% of an assemblage composed of 93% Mg-perovskite, 3% Ca-perovskite and 4% ferropiclasite, as described in the caption in Fig. 6. In the fractionation models, isotopic growth occurs in a chondritic reservoir for the first 30 Ma. At 4.536 Ga ago, Sm/Nd and Lu/Hf are fractionated due to crystal removal in the deep mantle.

$^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{176}\text{Hf}/^{177}\text{Hf}$ for modern oceanic volcanic rocks. Isotopic compositions form a relatively tight array that passes through an estimated model chondritic bulk silicate Earth reservoir [94]. Correlated positive and negative deviations from bulk silicate Earth are interpreted to reflect mantle components that are relatively radiogenic (e.g., the ‘depleted’ MORB source) and unradiogenic (e.g., the ‘enriched’ OIB sources).

Fig. 7 shows models demonstrating the effect that removal and isolation of deep mantle phases in the early Hadean could have on the isotopic composition of the residual magma, which would now be the modern convecting mantle [80]. Mg-perovskite crystallization produces a marked increase in Lu/Hf, whereas Sm/Nd remains essentially constant. More than about 5% removal of pure Mg-perovskite in the early Hadean would yield a modern convecting mantle with a bulk isotopic composition outside the observed mantle array, a fact used previously as a compelling argument against a buried reservoir of pure Mg-perovskite [95]. Ca-perovskite has considerable leverage on element ratios during crystal fractionation because Lu and REE are extremely compatible in this phase and it has a very high Lu/Hf ratio. Removal of even as little as ~0.2% Ca-perovskite in isolation would move convecting mantle outside its observed field, but importantly, in the opposite sense to Mg-perovskite fractionation (Fig. 7).

Removal of deep mantle phases in the proportions 93% Mg-perovskite, 3% Ca-perovskite and 4% ferropericlase, as in the model shown in Fig. 6, produces a reduction in both Lu/Hf and Sm/Nd in the residual magma from initially chondritic values. Separation of ~15% of this crystalline assemblage in the early Hadean would produce subsequent isotopic compositions in the residual magma (e.g., convecting mantle) that remain internal to the mantle array (Fig. 7) [80]. Furthermore, the Nd and Hf isotopic compositions of the residual mantle are remarkably akin to the modern Enriched Mantle I (EMI) reservoir. The complementary crystal pile at the base of the lower mantle would grow an isotopic composition akin to the modern HiMu reservoir (high U/Pb), at least on this isotope diagram. Interestingly, available partition coefficients, although not well known, make it conceivable that a deep crystal pile could have low

Rb/Sr and elevated U/Pb relative to chondrite [80,91–93], the residual magma acquiring complementary ratios. In such case, the correspondence in Fig. 7 between the isotopic characteristics of the deep crystal pile and residual magma with HiMu and EMI, respectively, might translate to Sr and Pb isotopes as well.

After separation of the crystal pile, the convecting portion of the mantle would have become differentiated further by permanent separation of continental crust material, perhaps initially by late-stage melt expulsion, a considerable portion of which might have been extracted within a few hundred million years of t_0 based on fossil ^{142}Nd observed in Archean rocks [96,97]. This, together with continued continental crust formation, would differentiate the convecting mantle into an incompatible element depleted reservoir (‘MORB mantle’) and enriched continental crust [98].

3.6. Speculations on deep mantle differentiation

As the juvenile Earth grew during the first few tens of millions of years, at some time it would have reached a size large enough for perovskite phases to become stable at the base of the silicate mantle. Accretion models lead one to expect that it is probabilistically favorable that the size threshold for perovskite stability would have been breached during a giant impact between the proto-Earth and a large impactor. Besides the large mass gain in the proto-Earth, the energy deposited in the impact could have been sufficient to substantially melt the silicate mantle (as we have seen, evidence that such a magma ocean stage might have occurred comes from the abundances of Ni and Co in the mantle). Subsequent cooling and solidification of the silicate magma ocean might have involved the fractional removal of deep mantle perovskite and oxide phases. Further impact accretion of the Earth to its final size may have involved more than one magma ocean stage, each possibly involving deep mantle crystal fractionation. Vigorous convection in the silicate mantle of a hot, young Earth may have reworked and homogenized much of the mantle, but some amount of dense, deep mantle crystalline phases might have remained rheologically stable at the base of the deepening mantle. Indeed, proto-

crystalline piles of deep mantle phases may have been eroding at various rates since primordial crystallization. Compositional models involving moderate amounts (e.g., 10% to 15%) of an isolated ultra-high-pressure crystal fraction can produce elemental and isotopic characteristics of the residual magma that are generally consistent with those observed in primitive upper mantle rocks.

4. Perspectives

In spite of the missing rock record documenting differentiation in the infant Earth, important information has been gathered from diverse fields including observational and theoretical astrophysics, cosmochemistry and high-pressure experimental geophysics and geochemistry. What is most intriguing given the present knowledge of early Earth differentiation is the apparent convergence of several different approaches regarding the timing of events. Accretion models predict that giant impacts should occur during the late stages of accretion on a time scale of 10^7 – 10^8 years after t_0 [6]. Radiogenic isotopes yield an ‘age’ of core formation on similar time scales, of the order of 50 million years after t_0 , that could be related to the origin of the Moon and magma ocean formation [18–20]. Siderophile element abundances in mantle rocks apparently preserve a signature of high-pressure–temperature equilibration [52]. Complete crystallization of the magma ocean could occur on a 10^7 year time scale [54]. Long- and short-lived Hf and Nd isotopes indicate very early differentiation in the mantle also on a time scale of 10^7 – 10^8 years after t_0 [96]. Advances in our understanding will likely continue to come from a multifaceted approach.

Advances in numerical modeling and laboratory experiments at high pressures and temperatures will facilitate increased understanding of the physicochemical processes of accretion, terrestrial core formation and magma ocean formation and differentiation. Higher resolution hydrodynamic modeling is needed to address the fate of metal cores during giant impacts and particularly whether metal emulsification is a likely prospect. Determination of the physical properties of metals, minerals and melts at deep mantle conditions is needed to better constrain numerical

modeling of the processes of magma ocean formation, cooling, convection and crystallization in the magma ocean, as well as metal segregation from silicate. A more comprehensive and accurate database on experimentally determined partitioning coefficients for a range of elements between minerals and melts in silicate-dominated systems and between Fe-dominated metal and silicate is also needed.

High-pressure experiments within the stability field of lower mantle materials are challenging. The trade-off between sample volume and pressure applies to multi-anvil experiments using sintered diamond anvils, as well as to diamond anvil cell experiments. Experiments covering the entire lower mantle pressure regime are required in order to realistically constrain early Earth differentiation processes. This is especially important in terms of crystallization in a deep magma ocean. Currently, it is possible to obtain relatively stable and long-duration melting experiments with relatively low thermal gradients across the sample capsule up to about 25 GPa using conventional multi-anvil configurations. A future challenge is to develop corresponding thermal stability at the higher pressures generated by diamond anvils.

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