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# Core Formation During Early Accretion of the Earth

## Horton E. Newsom and Kenneth W. W. Sims

Recent studies are leading to a better understanding of the formation of the earth's metal core. This new information includes: better knowledge of the physics of metal segregation, improved geochemical data on the abundance of siderophile and chalcophile elements in the silicate part of the earth, and experimental data on the partitioning behavior of siderophile and chalcophile elements. Extensive melting of the earth as a result of giant impacts, accretion, or the presence of a dense blanketing atmosphere is thought to have led to the formation of the core. Collision between a planet-sized body and the earth may have also produced the moon. Near the end of accretion, core formation evidently ceased as upper mantle conditions became oxidizing. The accumulation of the oceans is a consequence of the change to oxidizing conditions.

THE ORIGIN OF THE SOLAR SYSTEM, AS MEASURED BY meteorites, occurred at 4.6 billion years ago (Ga) by collapse of a cloud of dust and gas (1). Evidence from meteorites suggests that this dust accumulated to form planetesimals, which agglomerated to form the planets. Key questions are the size of the material which accreted to form the planets and the location in the solar system where this material originally formed (2). The possibility that accreting material included planet-sized objects has led to the idea that the collision between a planet-sized body and the earth produced the moon and completely melted the earth (3, 4).

The earth's core represents approximately one-third of the mass of the earth. Its formation is thus closely connected with the initial thermal and physical state of the earth and thus also perhaps to the origin of the moon. Knowledge of the origin of the core is thus important for understanding the distribution of elements in the earth, the mysterious absence of any continental crust older than 4.2 Ga, and the history of the solar system [see papers in (5)].

The segregation of metal from the silicate part of the earth as required to form the Fe-rich core is assumed to have depleted the bulk silicate earth (primitive mantle) in the siderophile and chalcophile elements relative to the lithophile elements (6). The original abundances of the siderophile and chalcophile elements in the earth are assumed to be related to those measured in chondritic meteorites. Because the relative abundances of most elements in the CI chondrites are similar to those in the solar photosphere, the assumption is commonly made that the CI chondrites are identical in composition to the solar nebula out of which the planets formed. Other types of chondrites and the earth are not identical to CI chondrites, and thus there are some uncertainties in the initial abundance of siderophile and chalcophile elements in the earth. However, the uncertainties are small compared to the large depletions of siderophile and chalcophile elements, which therefore provide key constraints on the processes of accretion and core formation.

In this article, we discuss this and other evidence as it relates to three general models of core formation. The first is simple homogeneous accretion in which equilibrium is maintained between the mantle and core. The second is inefficient core formation, where metal is left behind in the mantle during core formation. The third is heterogeneous accretion, involving multiple stages of accretion and core formation.

## The Structure and Composition of the Earth

The earth's metal core consists of a solid inner core and a molten outer core. It has long been recognized that the density of the core is $10 \pm 2\%$ by weight less than that of pure Fe (7); this value indicates that the core is not made up of only Fe and Ni, but must instead be an alloy with light elements. Although Fe and Ni in the core are probably alloyed with all other elements to some degree (8, 9), the important issue is to identify the most abundant alloying constituent, as the nature of this light alloying element is important for determining whether core formation was dominated by high-pressure or low-pressure processes. The two elements that are currently considered to be the most likely alloying constituents are S and O; Si and H have also been proposed as possible or less significant constituents (9). Sulfur has been proposed on the basis of the occurrence of Fe-S phases in meteorites and its depletion in the upper mantle. The presence of significant amounts of S in the core would indicate that the core metal became alloyed at low pressures and thus that core formation may have been occurring during earth's accretion. The possibility of Si as an alloying phase is suggested by the presence of reduced Si in Fe metal in some meteorites and the depletion of Si relative to Mg and other refractory lithophile elements in the mantle (10, 11). In contrast the possibility that O or H are the dominant alloying constituents of the core is based on high-pressure laboratory data as neither of the relevant oxide or hydroxide phases are observed at low pressures or in meteoritic assemblages (9, 12). Of these two, O is the most likely because of its high abundance inside of the earth (nearly 60% of the mantle on an atomic basis). Because of the high pressures required, alloying with O and H is only expected to occur deep inside of the earth well after the core has begun to form. Therefore these elements, particularly O, are prime alloying constituents if the core has been evolving over much of the earth's history.

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At the core-mantle boundary, adjacent to the liquid outer core, is the thin D" (D double prime) layer (200 to 300 km thick), which may reflect a chemical reaction zone between the silicate mantle and core. The reaction, which produces the metallic alloys FeSi and (Fe,Mg)O Wüstite, occurs only at high pressures (>30 to 40 GPa for the reaction between (Mg,Fe)SiO$_3$ perovskite, and Fe metal (9).

Because the core originally segregated from the mantle, information about the mantle is essential to understanding this process. Information about the mantle is obtained from seismic data, analysis of mantle rocks and mantle-derived magmas brought to the surface in volcanic eruptions, and laboratory experiments at high pressures. At about 400 to 650 km depth is a transition zone between the upper mantle and the lower mantle, which consists of high-pressure mineral phases, such as (Mg,Fe)SiO$_3$ perovskite. A key question is whether the lower mantle is chemically distinct from the upper mantle (13) or whether convection or plumes originating near the core-mantle boundary (14) allow chemical and mass transport between the upper and lower mantle.

Whereas seismic evidence can only reflect the present structure of the earth, the continental crust contains a record of the chemistry of the mantle for more than 4 billion years. Almost every continent contains Archean rocks, but fragments of continental crust from the first billion years of the earth's history are virtually nonexistent. The few rocks that date back close to the time of formation of the earth include, the West Greenland suite (<3.8 Ga) and the recently discovered Acasta Gneiss (3.96 Ga). In addition, detrital zircons with ages of 4.0 to 4.3 Ga have been found in Western Australia (15).

In this article, we assume that data for samples from the mantle and the continental crust allow us to calculate the depletions, relative to chondrite meteorites, of siderophile elements in the bulk silicate earth, also called the primitive mantle. The present mantle is the main reservoir for many siderophile elements, such as Ni and Co, but the continental crust is a major reservoir for some incompatible siderophile elements, for example, W, As, and Sb. We assume that these depletions reflect fractionations associated with the process of core formation, which occurred during and immediately following the accretion of the earth, before the formation of the continental crust. Therefore, in regard to siderophile elements, we use the term primitive mantle to refer to the bulk silicate earth.

The abundances and isotopic composition of rare gases in the earth's atmosphere also contain clues to the formation of the earth, such as the possible existence of an early dense atmosphere. The presence of such an atmosphere would have important implications for melting of the earth and for oxidation and reduction reactions involving Fe (16). The low abundance of noble gases in the present atmosphere, when compared to solar type gas indicates that the earth lost its initial atmosphere (17). Dissipation of this primitive atmosphere could have resulted from a strong ultraviolet flux during an early T-Tauri phase of the sun (involving a massive stellar wind), or large impacts (16).

## Accretionary Processes and the Origin of Metallic Iron in the Earth

Several mechanisms could have controlled the amount of Fe metal relative to oxidized Fe in the earth and thus the size and composition of the core (18). (i) The earth may have simply inherited the metal content of accreting material, which was established by metal-silicate redox equilibria in the solar nebula. This hypothesis corresponds to the homogeneous accretion theory under the assumption that the composition of the accreting material did not change with time. (ii) Chemical reactions in the accreting earth may have changed the ratio

of oxidized to reduced iron. This hypothesis includes the inefficient core formation theory, where metal is retained in the mantle during core formation but is subsequently oxidized. (iii) The earth may have accreted from planetesimals with variable metal contents, and the more oxidized planetesimals may have accreted late. This scenario corresponds to the heterogeneous accretion theory (11).

*Homogeneous accretion.* The similarities among the abundances of refractory elements in meteorites, other planetary materials and the relative abundances of these elements measured in the sun (19) suggest that the composition of the earth may be related to that of the chondritic meteorites. This assumption leads to a simple end-member model for the formation of the earth by accretion of chemically homogeneous chondrite-like material, and subsequent separation of the metal and silicate parts without any oxidation or reduction of Fe. The composition of the silicate part of the earth is broadly chondritic, for example, refractory trace elements, such as the rare earth elements (REEs) have the same relative abundances as the chondritic meteorites and the sun (19). The composition of the earth, however, does not match the exact composition of any known meteorite group, as discussed by Taylor (20). The lack of a match with known meteorites is not a significant problem for this model, because the known meteorites are probably a poor sample of the early solar system, and they probably did not form at the earth's heliocentric distance. A severe difficulty with a strictly homogeneous accretion model, however, is the strong evidence for the late establishment of oxidized conditions in the mantle. This evidence includes the high abundances of many siderophile elements in the primitive mantle and the presence of the oceans, neither of which reflect equilibrium with the core or Fe metal (21). This late oxidation event requires that a change occurred in either the accretion conditions or in the composition of the accreting material.

*Oxidation and reduction of Fe.* Oxidation of Fe metal can occur at relatively low temperatures (<800°C) in chemical reactions involving water and C (22), such as:

$$C + 2MgSiO_3 + 2Fe_{metal} + 2H_2O \rightleftharpoons Fe_2SiO_4 + Mg_2SiO_4 + CH_4 \tag{1}$$
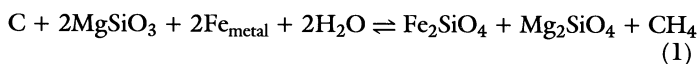
This kind of reaction may have been important during early and late stages of accretion (16). Oxidation of a small amount of metal left behind in the mantle is also a feature of the inefficient core formation model.

The reduction of oxidized Fe to form Fe metal can also occur by gas-solid reactions involving C at high temperatures and low pressures near the surface, for example

$$2FeO + C \rightleftharpoons 2Fe_{metal} + CO_2 \tag{2}$$
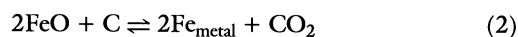
This reaction ceases to operate even at very shallow depths (<0.1 GPa pressure) because the solid side of the reaction is favored with increasing pressure. Arculus et al. (18) pointed out that in the presence of C at pressures greater than 1.5 GPa, CO$_2$ can react with silicates to form partially carbonated assemblages; the reaction may lead to solid-solid reactions that can also produce Fe metal, for example,

$$3Fe_2SiO_4 + C + 2Fe_{metal} \rightleftharpoons FeCO_3 + 3FeSiO_3 \tag{3}$$
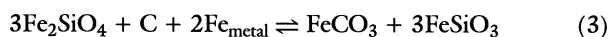
In addition, the formation of an early high-temperature dense steam atmosphere, either by rapid accretion and degassing of impacting planetesimals (16, 23) or by accretion of a primitive atmosphere directly from the solar nebula (24, 25) could have led to melting of the surface of the earth and production of Fe metal by reduction reactions. The formation of a $10^2$- to $10^3$-bar protoatmosphere by rapid accretion requires that accretion took place over a period of about $10^7$ to $10^8$ years, on the basis of a Safronov accretion model (25). The melting point of the silicate mantle at the

surface (1500 K) buffers the temperature of this atmosphere. Abe and Matsui (23) assumed that the uppermost layer of the earth (approximately 20 km thick) was about 10% partially molten. Reduction reactions occurring under such high-temperature conditions (22) could have produced Fe metal by:

$$CO + MgFeSiO_4 \rightleftharpoons Fe_{metal} + CO_2 + MgSiO_3 \qquad (4)$$
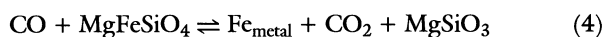
Ahrens (16) developed an accretionary model based on this concept (Fig. 1). A volatile-rich protoearth amounting to 12 to 22% of the earth is first accreted, until the velocity of incoming planetesimals results in significant degassing. Once a massive steam atmosphere develops, conditions become largely reducing near the surface until the waning stages of accretion. The dense atmosphere collapses or is lost during lulls in accretion and as a result of impact erosion or catastrophic collisions with lunar-sized or larger objects (16). The final stage of accretion under oxidizing conditions (amounting to 0.7% of the mantle by weight) establishes the abundances of the highly siderophile elements in the primitive mantle, as in the heterogeneous accretion model described below.

Another way that a dense atmosphere, containing up to one earth mass, could have been created on the earth is by direct accretion from the solar nebula. The abundances and composition of noble gases in the present atmosphere indicate that such a primitive atmosphere must have been lost, which could have occurred by impacts or an enhanced T-Tauri type of solar wind. Sasaki (25) showed that in such a dense atmosphere, the large abundance of $H_2$ would reduce oxidized Fe on the surface to Fe metal and produce excess $H_2O$ in the atmosphere. The excess $H_2O$ causes the opacity of the lower atmosphere to increase, which results in increased temperatures. Such an atmosphere could contain as much as one earth mass, and surface temperatures could be from 2000 K to as high as 4700 K if excess $H_2O$ is present. The corresponding surface pressures range from $10^7$ Pa to $10^9$ Pa (100 to 10,000 bars). An additional complication involving the higher temperatures is that partial evaporation of the surface silicates would occur, but this has not been thoroughly explored (25).
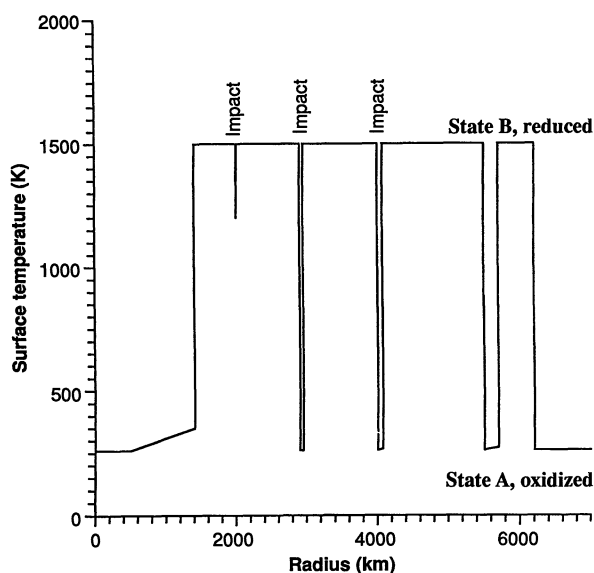


**Fig. 1.** Diagrammatic sketch of the temperature state at the surface of the accreting earth (16). During the initial accretion of the earth, volatiles are retained and oxidizing conditions prevail until complete vaporization of impacting planetesimals occurs (State A). The resulting loss of water to the atmosphere causes thermal blanketing, melting of the surface, and a switch to reducing conditions (State B). Finally, the decline in accretion rate leads to collapse of the protoatmosphere and a late stage of accretion under oxidizing conditions.

The presence of one or several early dense atmospheres depends strongly on the accretion rate of the earth. The resulting oxidation or reduction of metal depends on the proportions of C-H-O in the atmosphere. If massive atmospheres did not form, a balance would have developed between oxidation of accreting Fe metal by water and the reduction of oxidized iron by C.

The grain size of accreting metal is a critical, but unknown parameter for understanding the role of oxidation-reduction reactions and the equilibration of metal with the mantle in terms of siderophile elements. If large planetesimal cores accreted to the earth without being substantially disrupted, chemical equilibration of the metal with the primitive mantle could have been inhibited (26). Gaffey (27) reviewed evidence from meteorite and asteroidal studies suggesting that the degree of melting of asteroids decreased significantly with heliocentric distance. Asteroids that are interpreted to have melted are concentrated in the inner parts of the asteroid belt. This evidence suggests that planetesimals that were accreting to the earth had probably differentiated to form metal cores and lost some volatile elements. Possible heat sources for melting include electrical induction during a T-Tauri phase of solar evolution and the decay of short-lived radionuclides such as $^{26}Al$. Prevention of impact destruction and vaporization of the metal cores during accretion, however, probably requires a low velocity at impact and a dense terrestrial atmosphere. For example, recent Magellan data indicate that Venus, with a surface pressure of 95 bars, lacks craters smaller than 3 km; this observation is consistent with atmospheric breakup of planetesimals smaller than a few hundred meters (28). The resulting meter-to tens-of-meter-sized metal fragments presumably impact the surface at a relatively low terminal velocity. This process would have been more effective during the accretion of the earth, because the accreting planetesimals would have come from nearly the same heliocentric distance as the earth and thus would have entered the atmosphere with a lower average velocity than for Venus. Impact velocities also were much lower during the beginning of accretion because of the lower gravity of the protoearth (16). Sinking of such fragments of metal into the earth's core at a rate rapid enough to prevent equilibrium with the primitive mantle would also require a magma ocean to be present (discussed below).

*Heterogeneous accretion.* A variation in the composition of material accreting to the earth as a function of time is widely called upon to account for the apparent disequilibrium between the Fe metal core and the oxidized crust and upper mantle. A wide range of compositions of accretionary components is suggested by asteroid spectral characteristics and the compositions of primitive meteorites (2). These variations suggest that local processes in the solar nebula, such as differential transport and agglomeration of presolar and solar grains and production of diverse types of chondrules in brief high-temperature events had a strong influence on the variety of sizes and compositions of the cores of the terrestrial planets. Wetherill (29), however, emphasized that radial mixing attributed to the high eccentricities of planetesimals following dissipation of the solar nebula, could have led to compositional variations in accreting material transported from different regions of the solar system. Wetherill (29) suggested that local feeding zones would have been eliminated after the solar nebula dissipated (<3 × $10^6$ years), such that the remainder of material that accreted over $10^7$ to $10^8$ years would have spanned the terrestrial planet region.

## Metal Segregation in the Mantle

An early idea of core formation that has received much attention (30) was that metallic liquid percolated into layers that formed large sinking diapirs as a result of Raleigh-Taylor instabilities. However,

segregation of metallic liquid is inhibited because the high surface tension of metallic liquids relative to silicate solids causes melt droplets to collect at grain boundaries. This process prevents connectivity of melt at low amounts of melting, which would be needed for porous flow to occur (31). Segregation of solid or liquid metal would be facilitated if the mantle was partially molten, but recent work indicates that high degrees of partial melting (much greater than 50%) are needed because of the finite shear strength of partially molten systems (32, 33). In the case of a Bingham plastic melt, the minimum radius required for a diapir to sink ($r^*$) is given by

$$r^* = \frac{3K\sigma_0}{4\Delta\rho g} \qquad (5)$$

where $K$ is a dimensionless constant equal to about 5.0, and $\sigma_0$ is the yield strength. Ryerson et al. (34) have recently determined an empirical relationship for $\sigma_0$ (in dynes per square centimeter)

$$\sigma_0 = 65,000(1 - F)^{2.85} \qquad (6)$$

where $F$ equals the fraction of melt. Using these relations, we calculate that the minimum radii for a metal particle to sink at the earth's surface is 36 cm for $F$ equals 10% melting and 7 cm for $F$ equals 50% melting. The critical size is larger for lower values of gravity within the earth and while the earth was accreting. Metal segregation without a large degree of melting may be possible, however, by sinking of large metal-rich areas (30), although the heterogeneity in the distribution of metal in the protoearth is unknown.

At pressures greater than 6 to 15 GPa, metal segregation from a largely solid mantle by percolative flow may be possible if the increased solubility of oxygen in Fe metal lowers the surface tension of the liquid metal phase and thus allows it to wet the grain boundaries of oxides and silicates. The resulting connectivity of the liquid metal allows it to segregate. Experimental textural data supporting this hypothesis has been presented by Urakawa et al. (35). Segregation of metal from the low-pressure part of the earth still requires that there was a large-scale melting event or convection of shallow material to great depths, however. Convective turn over of the mantle could be a result of the formation of a top-heavy system due to metal segregation from the lower mantle (32).

Stevenson (32) discussed the mechanisms of core formation from a largely or totally molten magma ocean. Immediately after formation of the magma ocean, turbulent shear strain caused by rapid convection produces an emulsion of metallic droplets with radii of the order of 1 cm. These droplets form and settle rapidly into the core. In the case of a shallow magma ocean, the metal could form accumulations that rapidly sink as large diapirs, or percolated as an oxygen-rich metal at depth (Fig. 2). In the early stages of settling the increasing density with depth due to sinking of metal will stifle convection. At a later stage, convection can resume when the metal content of the magma ocean is much less. At this stage convective velocities can be greater than the settling velocities of the metal droplets. Metal segregation can continue, however, because of the existence of a convective boundary layer at the bottom of the magma ocean, where the convective velocity goes to zero, but the Stokes settling velocity is retained.

The chemical implications of these core formation mechanisms can be divided into two possibilities. If oxygen-rich metal percolated downward within the deep mantle, or if core formation occurred by segregation of small droplets at the base of a global magma ocean, then the mantle should reflect metal-silicate equilibrium at very high pressures and temperatures near the core-mantle boundary. Alternatively, metal may have segregated in the upper part of the mantle, perhaps in a shallow magma ocean, and sunk as large diapirs

through the lower part of the mantle. The low ratio of surface area to volume and the rapid settling rate of a metal diapir would have prevented significant reaction with the mantle, such that the mantle could reflect low-pressure equilibrium with metal.

The retention of metal in the mantle is an important element in the inefficient core formation theory. A possible mechanism is stranding of metal at the base of a shallow magma ocean, which could have occurred if the lower mantle was intrinsically more dense than the upper mantle (32). Another possibility is that the lowering of surface tension in oxygen-rich metallic alloys at high pressures is within a narrow critical range such that most of the metal could have percolated downward but a small amount could have been retained (32).

## Siderophile Elements

Different processes of accretion and core formation should result in characteristic depletions of siderophile elements in the primitive mantle compared to their initial abundances. The siderophile-element depletions in the bulk silicate earth are obtained by combining data from several sources, as discussed below. Plotting the siderophile element depletions versus their metal-silicate partition coefficients produces a stepped depletion pattern (Fig. 3). The depletion pattern in the earth is quite different from the depletion patterns for the moon and the parent body of the eucrite meteorites, which are characterized by a correlation between depletion and siderophile nature. The depletion pattern can be divided into three parts. The highly siderophile elements, including the platinum group elements, are depleted by a factor of about 350 in the primitive mantle (normalized to CI chondrites and refractory elements), and are present in chondritic relative abundances. Somewhat less depleted (by factors of 10 to 15) are the moderately siderophile elements, including Co, Ni, W, As, and Sb, which are present in chondritic relative abundances at that depletion level. The third group of elements are the slightly or barely siderophile elements, such as Mn, V, Cr, and Ga.

Siderophile element depletions in the primitive mantle are calculated from the ratio of their abundances in the bulk silicate earth to their abundances in CI chondrites (19). The earth, however, is not identical in composition to CI chondrites. For example, the FeO/(FeO+MgO) ratio for the earth is different from any chondrite groups, although the Fe/Si ratio is identical to that of CI chondrites. Another problem is that other types of chondrites have fractionated abundances of siderophile and chalcophile elements, compared to lithophile elements, indicating fractionation among nebular components. For example, Ni and Co are generally correlated with the

**Fig. 2.** A representation of several core-forming mechanisms that could have played a role early in the earth's history (32). Metal segregation from a rapidly convecting magma ocean may have involved settling of metal grains in a viscous boundary layer. Metal that accumulates into large enough masses may sink as metal diapirs. Alloying of oxygen with metal in the lower mantle may allow percolation of liquid metal into the core.
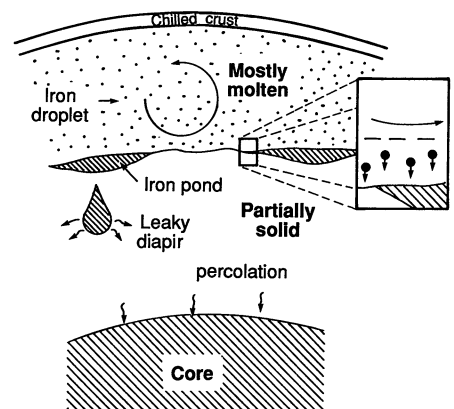
amount of Fe metal, whereas the refractory siderophile elements, such as Ir and Os, were apparently sited in a refractory component. The refractory lithophile elements, such as the REEs were sited in a third component (36). The possibility that the abundances of these three components are also fractionated in the bulk earth relative to CI chondrites adds an uncertainty to the observed depletions, especially for the moderately siderophile elements. For the highly siderophile elements, the observed depletions are so great that this should not be a major problem with our modeling.

Compatible elements, including many siderophile elements, such as Ni, Co, Ir, Ru, and Os, are retained in mantle minerals, such as olivine, and their abundances are not greatly affected by removal of small amounts of melt. Mantle nodules, therefore, provide good information on the abundances of the compatible siderophile elements in the upper mantle (37). For example, the concentrations of Ni in mantle nodules from around the world generally agree within 10% (38). Incompatible elements, including siderophile elements such as As, Sb, W, and Mo, however, concentrate in the melt phase during partial melting. The abundances of these elements in mantle nodules are therefore less likely to reflect actual mantle abundances. Mantle-derived melts, however, can be used to determine the depletions of the incompatible elements in the source regions if the concentrations of the siderophile elements are normalized to equally incompatible refractory lithophile elements, such as the REE, U, Th, and Ba. The assumption is that the ratio of two equally incompatible elements remains constant and identical with the ratio in the source region during igneous processes, because the two incompatible elements will be equally fractionated (39). The measured ratios can then be divided by the ratios of the same elements in CI chondrites to obtain the depletion factor.

Sims et al. recently determined the abundances of several moderately siderophile incompatible elements (As, Sb, W, and Mo) in the present mantle and continental crustal reservoirs and estimated their abundance in the bulk silicate earth (40). They found that As, Sb,
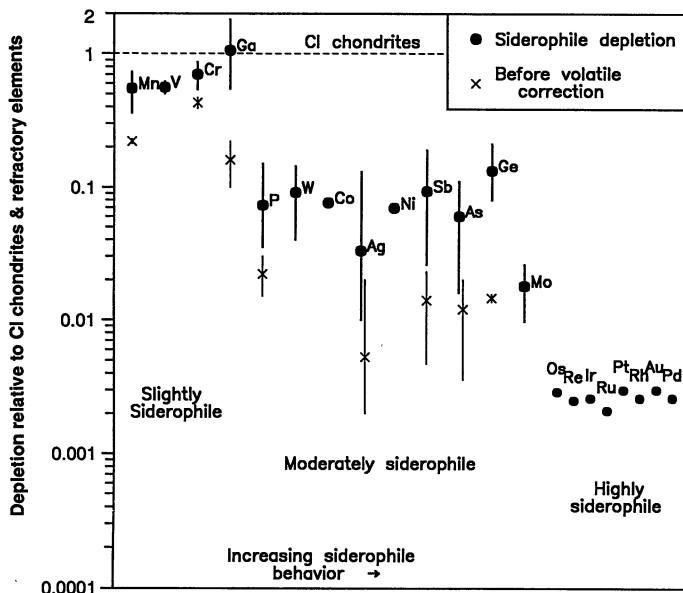


Fig. 3. Depletion of siderophile elements in the earth's primitive mantle (silicate part of the earth), normalized to mean CI chondrites and refractory elements (see text). The slightly siderophile and moderately siderophile elements are arranged roughly in order of increasing siderophile behavior. The uncertainties in the depletions for the highly siderophile elements are not shown (43). The actual depletions of the volatile siderophile elements Mn, Cr, Ga, P, Ag, Sb, As, and Ge in the primitive mantle relative to CI chondrites are indicated by crosses. Because the depletions of these elements are due to both volatility and siderophility, their corrected siderophile depletions are indicated by filled circles.

and Mo are moderately incompatible and correlate with the light REEs La, Ce, and Pr, whereas W is highly incompatible and correlates with U, Th, and Ba. Using these normalized abundances and the relative masses of the crust and mantle reservoirs, they calculated the abundances of these elements in the bulk silicate earth and their depletion relative to the CI chondrites. One important result is that the revised bulk silicate earth abundance for W is considerably higher than earlier estimates (41, 42), and is now consistent with the depletions of most of the other moderately siderophile elements (Fig. 3).

For the refractory siderophile elements (such as W, Co, Ni, and the platinum group elements) the calculated depletions relative to CI chondrites provide direct information about the earth's core formation and accretionary history. In contrast, the depletions of the volatile siderophile elements are a result of both their siderophile behavior and the general depletion of volatile elements in the earth. The depletions for these siderophile elements are obtained by subtracting out the depletion of volatile lithophile elements of similar volatility (43).

Another important question is whether the chemistry of the mantle, especially the abundances of the siderophile elements, has changed over geologic time. The physical models of core formation, described above, indicate that core formation should have been very rapid, at a time scale comparable to the duration of accretion (32). Patterson (44) and other workers (45) showed that the age of the earth (4.55 Ga), as represented by the U/Pb fractionation attributed to core formation in the earth, is close to that of the meteorites (4.56 Ga). This age for the earth is consistent with the assumption that the core formed within 20 ± 10 million years of the accretion of primary solar nebula materials. Continued formation of the core through geologic time has been used as a possible explanation of the lead isotope record in mantle derived oceanic samples (46), which indicates that a late fractionation of U from Pb occurred in some source regions. However, several studies, including data for many of the oldest known rocks (40) indicate that there were no variations in the abundances of siderophile elements caused by metal segregation in the mantle during earth history (47). If the U/Pb fractionation was a result of variable amounts of metal segregation, correlations would be observed between lead isotopes and siderophile element abundances. The absence of these correlations also argues against core formation through time (41).

Siderophile elements provide constraints on several different accretion and core formation models including: (i) equilibrium between the primitive mantle and S-rich metal or O-rich metal (48, 49); (ii) inefficient core formation, involving the retention of Fe-metal and sulfides during core formation (50); (iii) heterogeneous accretion, with multiple stages of accretion and core formation (51); and (iv) giant impacts, which provide components for heterogeneous accretion models.

Equilibrium models. The equilibrium core formation model is a logical extension of the homogeneous accretion theory. Establishment of the siderophile element pattern in the earth by simple equilibrium between the earth's core and primitive mantle is attractive in its simplicity, but this model is not quantitatively successful for the metal-silicate partition coefficients that have been measured at low pressures (43, 50). Physical models that lead to low-pressure equilibrium between metal and silicate include accretion with continuous segregation of metal in a shallow magma ocean. Once the metal has accumulated into large masses at the floor of the ocean, diapiric settling through the mantle can be initiated; settling will be too rapid for significant reequilibration at high pressures to occur. The calculated depletion pattern fits the observed pattern best for equilibrium between a S-rich metallic liquid and a primitive mantle that contains 50% melt (43). In contrast to other theories, the

abundance of Ga is well modeled by this theory, and the calculated abundances of Mn, Cr, P, Co, Ag, Mo, and Re are within a factor of 2 of the observed abundances. Poorly modeled elements having well-known abundances and partition coefficients include V, W, Ni, Ge, and Au. The elements Sb and As do not fit well, but their partition coefficients are poorly known. Another difficulty is that the calculated depletions fail to produce the stepped depletion pattern observed for the siderophile elements. Models in which equilibrium is assumed under more reducing conditions provide a better match for Mn, V, P, and W, but weaken the fits for other elements. Similarly, varying the degree of partial melting helps the fit for some elements, but weakens the fit for others.

In the equilibrium model, a large content of S, greater than or equal to 25% by weight, in the metallic liquid is required to obtain the partition coefficients necessary to explain the siderophile-element pattern in the primitive mantle. This is a significant difficulty because the physical parameters for the present core are best matched with a S content of 11 ± 2% by weight (52). Brett (49) suggested, as a possible solution, that reactions between the lower mantle and sinking metal could have modified the S content of the core, but this would require an extreme enrichment of S in the lower mantle. Another severe problem with S as the light element in the core is that the resulting bulk earth abundance of S would be much greater, relative to chondrites, than the abundance of elements such as K, which have similar volatilities. Brown et al. (53) have shown that a S content of 10% in the core would produce a bulk earth abundance of S that is a factor of 2 greater than that expected by comparison with K.
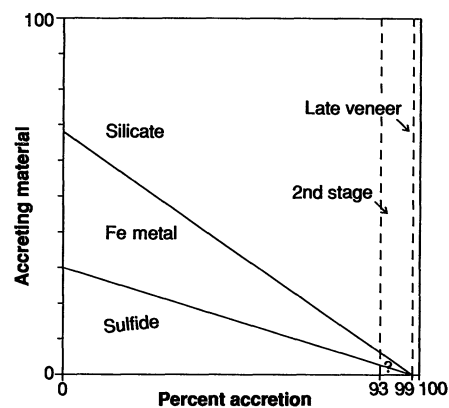
The model calculations discussed above also apply to the possibility that metal-silicate equilibrium was established during core formation events in the planetesimals that accreted to form the earth (26). However, the poor match with the observed siderophile abundances remains a problem, at least for the simple case of homogeneous accretion.

The possibility that the earth's siderophile element depletion pattern was caused by partitioning into metal alloys (containing O or Si) at extremely high pressures (24) cannot be tested yet, because of the lack of metal-silicate partition coefficients at the required pressures. The few data from studies of metal-silicate partitioning at elevated pressures (54, 55) does not indicate any significant effect due to pressure alone, but the available data for pressures where oxygen is soluble in Fe are still too limited. The effects of high temperatures for siderophile element partitioning deep within the earth may be of greater importance than the pressure effects (56).

Inefficient core formation. The inefficient core formation theory (50) quantitatively accounts for the siderophile element abundances by retention of small amounts of solid metal and S-rich metallic liquid in the earth's primitive mantle during core formation. In this model, the first step is equilibrium among solid silicate, liquid silicate, solid metal, and S-rich metallic liquid. The presence of S-rich metallic liquid requires a temperature of about 1250° to 1275°C. Jones and Drake (50) and Newsom (43) showed that the best fit to the abundance data is obtained when the liquid silicate represents 10% of the total silicates. The metallic phases will largely segregate to form a core with 10% S. However, just the right amount of solid metal (0.04% by weight) and S-rich metallic liquid (2.5% by weight) must be left behind in the primitive mantle to contribute a major part of the moderately and highly siderophile elements now observed in the bulk silicate earth. This model is intrinsically inconsistent with the presence of a magma ocean because of the low degree of partial melting (10%) required to account for the siderophile abundances and the physical retention of metal in the mantle.

The calculated depletions agree well for many elements, with the exceptions of V, Ge, and Au. The calculated depletions of V and Ge

are factors of 2 and 4, respectively, from the observed abundances, but their partition coefficients and depletions are well known (43, 57). The calculated abundance of Au is probably at least a factor of 10 too high, in spite of the significant scatter in the abundance of Au in mantle-derived magmas and mantle nodules (37). The partition coefficients for Au, however, are not very well known. In order to oxidize the 0.04% by weight Fe metal left behind in the mantle, water amounting to approximately 0.012% by weight of the mantle must be consumed, which is equivalent to only one-third of the present volume of the oceans.

In the inefficient core formation model, the amount of S in the mantle is constrained by the amount of metallic liquid left behind. The resulting mantle abundance of approximately 6000 ppm of S (43) is too high, although the actual S abundance in the mantle is uncertain. Estimates range from 10 ppm of S, based on mantle nodules (51), up to approximately 1000 ppm of S, based on Archean komatiites (58). As with the equilibrium model, this model also suffers from the problem of requiring too large of a S content in the bulk earth compared to that of other volatile elements.

Heterogeneous accretion. The stepped pattern of siderophile element depletions in the earth can be accounted for by a theory involving multiple stages of accretion and core formation (11, 51). In this theory an additive process controls the abundances of the siderophile elements and results in chondritic relative abundances among moderately siderophile elements and highly siderophile elements. As represented schematically in Fig. 4, the earth begins by accreting from a reduced component containing Fe metal and sulfides. During this stage of growth, core formation depletes the siderophile elements in the primitive mantle to levels significantly below the present observed abundances. This first stage of accretion, amounting to 90 to 95% of the earth, establishes the abundances of the barely siderophile elements such a V, Cr, and Mn in the mantle. A second stage of accretion begins when the accreting material becomes sufficiently oxidized that segregation of Fe metal essentially ceases and the moderately siderophile elements build up in the mantle to their observed level. During this second stage, continued segregation of a small amount of Fe-metal or S-rich metallic liquid depletes Mo and the highly siderophile elements below their present abundances. The final stage of accretion, sometimes called the late veneer, occurs after metal segregation ceases. The addition of the late veneer material, amounting to less than 1% of the mantle, establishes the observed abundance of the highly siderophile elements (37). The progressive oxidation of the mantle in this model reflects either a change in the composition in accreting



Fig. 4. Schematic representation of the heterogeneous accretion theory. The composition of accreting material is represented as a function of the percent accretion of the earth. For clarity, the width of the second stage and the late veneer, beginning at roughly 93 and 99% accretion, respectively, are expanded. The fraction of core material accreting is shown as steadily decreasing, although a straight line function is not required. During the second stage of accretion, small amounts of either metal or sulfide, or both, continue to segregate to the core. The final stage of accretion, the late veneer, is assumed to consist of entirely oxidized silicate material.

material, or changes in the accretion regime of the earth, such as the collapse of a dense steam atmosphere.

Heterogeneous accretion is the most successful model in matching the observed siderophile element abundances (Fig. 5), although this is partly because of the large number of adjustable parameters. The refractory siderophile elements, such as V, Co, Ni, and W, provide the best constraints on this model. Support for this theory comes from the new crustal data for W, which indicate that the depletion of W is indistinguishable from that of Co and Ni (40).

Only a few elements are not consistent with the calculated abundances for the heterogeneous accretion theory. The calculated Ge abundance is below the measured primitive mantle value, but the discrepancy is not as bad as for the inefficient core formation theory. The discrepancy is hard to understand, however, considering the well-known partition coefficients for Ge. A similar discrepancy is observed for the calculated depletion of Ga. The problem with Sb and As may be due to the poorly known partition coefficients.

A significant difficulty with the heterogeneous accretion theory is the need for segregation of small amounts of liquid metal at low degrees of partial melting during the second stage of depletion. The relatively low degree of partial melting is needed to deplete Mo in the silicates while not significantly depleting Ni or Ge. Alternately, O'Neill (59) suggested that Mo suffered an additional depletion by volatilization under oxidizing conditions during accretion of the earth. Manganese, which is probably depleted because of its volatility, has the opposite behavior to Mo and is less volatile under oxidizing conditions; thus, the observed depletion of Mn in the primitive mantle could be construed as evidence against the depletion of Mo because of volatility. However, in the heterogeneous accretion theory the abundance of Mn in the primitive mantle would be controlled by the first stage of accretion, involving reducing conditions, whereas the abundance of Mo would be controlled by oxidizing conditions that affected material added during the second stage.
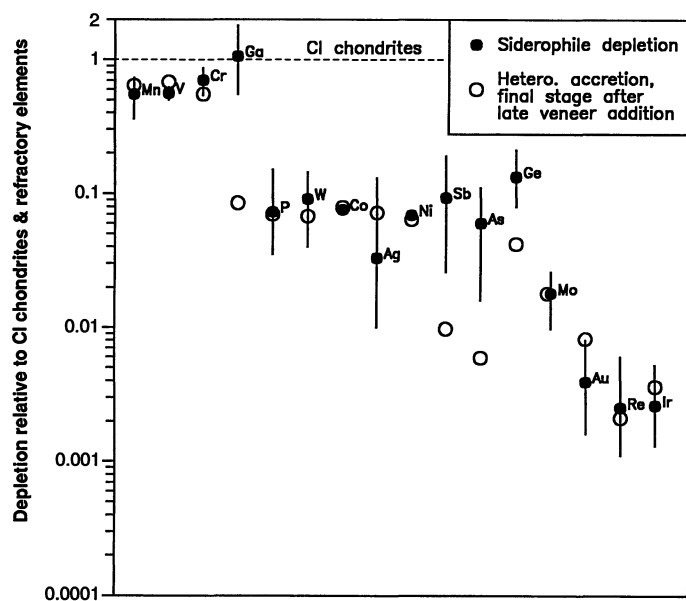


**Fig. 5.** Final results of a model calculation for the heterogeneous accretion theory (43). In the calculation, we assumed that: (i) An initial stage of core formation occurred until approximately 93% of the earth had accreted. Core formation during this first stage occurs under reducing conditions in order to deplete V. (ii) Addition of more oxidized material during the next 7% of accretion is needed to bring the moderately siderophile elements up to their observed primitive mantle abundances. (iii) Segregation of 0.08% Fe metal by weight during the second phase of accretion is needed to deplete the highly siderophile elements below their present abundances. (iv) Addition of the late veneer (0.2%) brings up the abundances of highly siderophile elements to their observed level.

The amounts of the second-stage oxidized component and of the late veneer control the S abundance in the mantle for the heterogeneous accretion model. Newsom (43) calculated that these components represent as little as the last 7% of accretion, which would reduce the amount of S brought in during this stage to about 1400 ppm, depending on the volatile depletion of the accreting material. This is much closer to the estimates of <1000 ppm of S in the mantle, but is still somewhat high.

*Giant impact models.* Giant impacts, which may or may not be associated with the origin of the moon, probably had an important role in the origin and evolution of the earth, including ejection of a primitive atmosphere, a source of energy for melting the earth, and providing accretionary components that contributed to the siderophile-element abundances in the primitive mantle. In numerical calculations of the impact of a Mars-sized differentiated planet with the earth, Benz and Cameron (60) showed that most of the mantle of the impactor would have accreted to the earth, and that the core of the impactor would have likely penetrated to the earth's existing core. Newsom and Taylor (61) suggested that the addition of 3 to 4% of such an impactor's core to the earth's mantle could account for the observed abundances of the highly siderophile elements in the primitive mantle, as in the last stage of the heterogeneous accretion theory. The amount of Fe metal deposited in the earth's mantle amounts to approximately 0.2% by weight of the mantle. Oxidation of this metal by reaction with water requires approximately 0.06% water by weight, or about two times the present mass of the oceans. This amount of water could be supplied to the earth if the last 1% of the mantle was accreted in the form of CI chondrites. Comets could also be an important source of water. In contrast to the inefficient core formation model a negligible amount of S-rich metal is assumed to be left in the mantle in this model.

O'Neill (59) also suggested that a giant impact could provide material to the earth in the context of the heterogeneous accretion model. Following accretion of most of the earth under reducing conditions, he proposed that the material from an undifferentiated impactor provides the moderately siderophile elements in the second stage addition step and establishes the present oxidation state of the mantle. His model then proceeds with the second-stage depletion of highly siderophile elements and the accretion of the late veneer.

Both of these models retain several of the problems associated with the heterogeneous accretion model. One problem is that metal must be segregated during the second-stage depletion step to account for the depletion of Mo relative to Ni. If, however, the extra depletion is a result of the volatility of Mo, the volatile depletion need only be characteristic of the material added during the second-stage addition step, if the model of Newsom and Taylor (61) is correct. In O'Neill's model the extra Mo depletion must be characteristic of the oxidized impactor.

## Summary and Future Directions

Three major questions stand out as critical for understanding accretion and core formation in the earth. First is whether a terrestrial magma ocean was present, second is the nature of the light element in the earth's core; and third is the composition of the lower mantle. The chemical characteristics of the earth's mantle provide conflicting evidence for the presence of a magma ocean. Resolution of this problem bears not only on the origin of the earth, but on the origin of the moon. The nature of the light element in the earth's core is critical for understanding the mechanism of core formation and whether metal-silicate equilibrium in the earth was dominated by low-pressure or high-pressure equilibrium. A better understanding of the accretionary components that made up the earth may bear

on the possible role at the end of accretion of a late veneer or veneers of oxidized material. The major and trace element composition of the lower mantle will be the same as the upper mantle if whole mantle convection is important (14), although some workers suggest that the lower mantle has a different composition (13).

Future advances in understanding accretion and core formation in the earth will require improved understanding of the physics and chemistry of silicate and metal assemblages at both high and low pressures, as well as more complete information on the abundances of siderophile elements in the earth. The available data are not yet sufficient to rule out any of the models we have discussed. The unsuccessful aspects of the core formation models should be the focus of future work (62).

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