Geochemical Constraints on the Early Thermal History of the Earth

Michael J. Drake

Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721

Z. Naturforsch. **44a**, 883–890 (1989); received May 16, 1989

Dedicated to Heinrich Wänke on the occasion of his 60th birthday

Theories of the formation of the Earth strongly suggest that the Earth should have been substantially molten during and immediately after accretion. Estimates of the composition of the upper mantle indicate that many elements are present in chondritic ratios. Experimental measurements of element partition coefficients show that segregation of perovskite, majorite garnet, or olivine would fractionate the ratios of these elements away from chondritic values. The implication of these geochemical observations is that the Earth did not undergo extensive fractionation during and immediately following accretion. One possibility is that the Earth did not become substantially molten. Alternatively, if the Earth was indeed substantially molten, then it is possible that minerals were entrained in magma and were unable to segregate. In the former case, the accretional process must have delivered gravitational potential energy more slowly than current theory predicts, and an origin of the Moon in a giant impact would be unlikely. In the latter case, the high Mg/Si ratio in the upper mantle of the Earth relative to most classes of chondrites would be intrinsic to the silicate portion of the Earth. Unless significant amounts of Si exist in the core, the high Mg/Si ratio is a bulk planetary property, implying that the accretional process did not mix material between 1 AU and 2–4 AU.

Introduction

The question of the early thermal state of the Earth is intimately associated with the accretion and primordial differentiation of the Earth. There is a general consensus that the Earth and the other terrestrial planets accumulated from smaller objects, called "planetesimals" (e.g., Greenberg et al. [1], Wetherill [2]). The details of this accumulation process remain uncertain, however (Drake et al. [3]).

A major question is whether the inner solar system was a relatively violent place towards the end of accretion with a large number of Moon-size or larger bodies in orbits characterized by significant eccentricities so that giant collisions were common, or whether it was a quite place characterized by large bodies with almost circular orbits and a dearth of intermediate lunar-sized bodies.

The "violent accretion" hypothesis predicts that the terrestrial planets should resemble each other broadly in composition, because "feeding zones" would overlap towards the end of accretion due to the large eccentricities of the growing planets and their gravitational effects on planetesimals remaining to be accreted. This hypothesis is consistent with (i) the rotational angular momenta and obliquities of the planets, as planets would be expected to have no obliquity and to rotate at best very slowly if they accreted from small planetesimals (Safranov [4]), (ii) the formation of the Earth's moon as a result of a giant impact on the Earth during the final stages of accretion (Benz et al. [5–7]), and (iii) heterogeneous accretion of the Earth and, perhaps, the unexpectedly high abundances of siderophile elements in the upper mantle, because planetary "feeding zones" are likely to overlap very early in the accretion process (Wetherill [2]).

In contrast, the "quiet accretion" hypothesis would lead to the prediction that any compositional and isotopic heterogeneities existing in the inner solar system prior to accretion would be preserved because "feeding zones" would not overlap until the very last stages of planet growth. This hypothesis is consistent with (i) the variation in the uncompressed densities of the terrestrial planets with semi-major axis, (ii) the considerable compositional structure as a function of semi-major axis exhibited by the Main Belt asteroids (Gradie and Tedesco [8]), (iii) noble gas abundance patterns which are characteristic of individual planets (Donahue and Pollack [9]), (iv) the observation based

---

Reprint requests to Prof. Dr. M. J. Drake, Lunar and Planetary Laboratory, University of Arizona, Tucson/AZ 85721, USA.

0932-0784 / 89 / 1000-0883 $ 01.30/0. – Please order a reprint rather than making your own copy.

on analyses of the Earth, Moon, and meteorites that the inner solar system was not well mixed in terms of the isotopes of oxygen (see Drake et al. [3], for a review), and (v) differences in the abundances and abundance ratios of moderately and highly siderophile elements inferred for the mantles of the Earth and Mars (Treiman et al. [10]).

At present, theoretical and observational studies seem unable to distinguish between these two radically different environments of planet growth. The mechanisms by which dust agglomerates to make pebbles, pebbles agglomerate to make boulders, boulders agglomerate to become kilometer scale planetesimals, and so on, are obscure. It is not possible to follow the accretion of kilometer scale planetesimals to final planet assembly using the "particle in a box" physics of Greenberg et al. [1] because the assumptions necessary for calculation break down at diameters in excess of about 500 km. Consequently, by no means can we be certain that the starting conditions assumed by Wetherill [2] ever existed as a natural consequence of the accretion of smaller bodies. Our inferences from theory concerning the thermal state of the Earth during and immediately following accretion depend critically upon how well we understand the details of the accretion process.

Evidence for a Molten Earth

Although the details of accretion theory are poorly understood, there is a general consensus that the Earth should have begun to melt by the time it achieved about the mass of Mars, i.e., about 10% of its present mass (e.g., Stevenson [11]). Strictly, however, such a conclusion depends on a detailed knowledge of the mass distribution of accreting planetesimals and the timescale of accretion, neither of which is well-understood. In the limit of accretion of very small particles, gravitational potential energy is deposited at the very surface of the planet and is readily radiated to space. Larger accreting objects deposit their energy much deeper, and that energy is more efficiently retained in the growing planet. An extreme example of such an accretion process is the giant impact scenario for the origin of the Moon, in which the mantle of the Earth and even portions of the core would be melted and, perhaps, partially vaporized (Benz et al. [5–7], Kipp and Melosh [12, 13]). In spite of the overall uncertainty in the details of the accretion process, it is difficult to see how the Earth could have avoided being substantially melted.

The differentiation of the Moon into a feldspathic crust and a mafic mantle has been interpreted to imply that the Moon was substantially or completely molten, with crust and mantle crystallizing from the lunar magma ocean. See Warren [14] for a review of the hypothesis. It is difficult to understand how the Moon could have been substantially molten without the Earth having suffered simlar consequences, regardless of whether the Moon formed in a giant impact or by some other mechanism (Hostetler and Drake [15]).

There are also experimentally-determined phase equilibrium studies which point to the possibility of significant melting of the early Earth. Takahashi [16] and Ito and Takahashi [17] have shown that for a composition appropriate for the upper mantle of the Earth, the liquidus and solidus converge at about 170 kbar and 2000 °C. At this point, majorite garnet replaces olivine as the liquidus phase. For isobaric melting, an equilibrium partial melt of a multiphase assemblage would be expected to coexist with one or more solid phases, the number depending on the mode of the solid assemblage and the degree of melting. Partial melting of a growing planet would not, of course, be expected to be isobaric. Nevertheless, this convergence is consistent with, although it does not require, the upper mantle being a partial melt of a more primitive material, presumably the primordial mantle (see also Walker [18]).

In summary, both theoretical considerations of planetary accretion and experimental determinations of phase equilibria lead to the expectation that the Earth was substantially molten during and immediately following accretion.

Evidence against a Molten Earth

Surprisingly, a number of geochemical considerations conflict with the conclusions drawn above that the Earth must have been substantially molten during and immediately following accretion. These considerations derive from estimates of elemental abundance ratios for the Earth's upper mantle and from experimental measurements of partition coefficients.

Studies of mantle nodules and basalts lead to the conclusion that a number of elements are present in chondritic ratios and, in some cases, chondritic absolute abundances in the upper mantle of the Earth (e.g.,

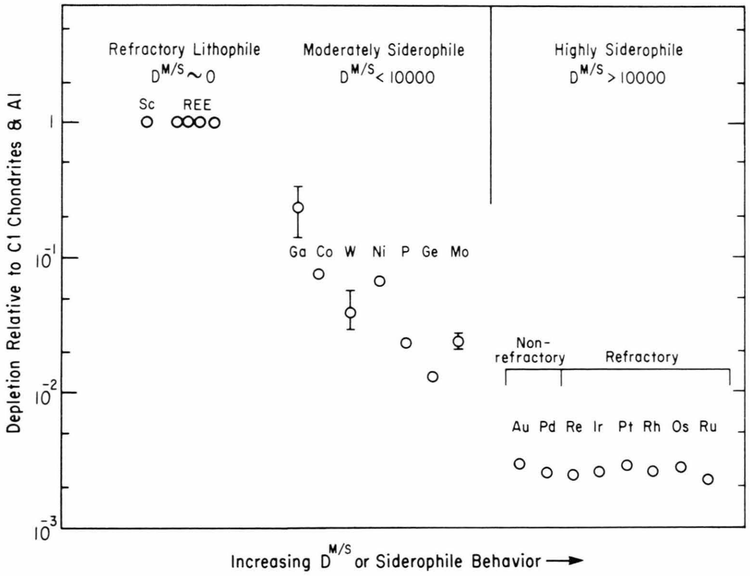

Fig. 1. Abundances of refractory lithophile, moderately siderophile, and highly siderophile elements in the upper mantle of the Earth. Note that the ratios of refractory lithophile elements such as Sc/Sm, moderately siderophile elements such as Ni/Co and P/Mo, and highly siderophile elements such as Ir/Au are all approximately C1 chondritic, although absolute abundances vary widely. After Newsom and Taylor [39].

Jagoutz et al. [19], Chou et al. [20]). For example, refractory lithophile elements such as Sc and Sm are present in chondritic ratios at chondritic abundance levels. Ratios of some moderately siderophile elements such as Ni/Co and P/Mo are also chondritic, but at absolute abundances of between one tenth and one hundreth of chondritic values. Ratios of highly siderophile elements such as Ir/Au are also chondritic, but at absolute abundances of about 0.007 of chondritic. These elements are shown in Figure 1.

The origin of these elemental abundances is not fully understood. Wänke [21] attributes them to heterogeneous accretion of the Earth. Brett [22] speculates that they arise from equilibrium between a Fe–S–O metallic liquid and mantle silicates. Jones and Drake [23] consider the possibility of inefficient core formation. Each of these hypotheses faces problems, some of which are discussed by Jones and Drake [23]. Regardless of the origin of these abundance patterns if the upper mantle is partial melt of more primitive matter, the partial melting and subsequent crystallization process cannot have fractionated these ratios from CI-chondritic values.

The probability that these elemental ratios will remain chondritic may tested against measured partition coefficients of plausible liquidus phases. Ito and Takahashi [17] have shown that Mg-perovskite is the liquidus phase for an upper mantle composition at pressures in excess of about 220 kbars. Between about 170 kbars, majorite garnet is the liquidus phase. Below about 170 kbars, olivine is the liquidus phase. Partition coefficients of elements between these phases and liquids of composition appropriate to the upper mantle may be used to limit the amount of fractionation during a melting or crystallization event.

Kato et al. [24–26] have reported partition coefficients of a substantial suite of major, minor, and trace elements (the minor and trace elements being doped to levels measurable on the microprobe) between Mg-perovskite and silicate liquid. These authors find that most of the partition coefficients deviate from unity. For example, $D(\mathrm{Sc})$ is larger than unity while $D(\mathrm{Sm})$ is much smaller than unity. Kato et al. conclude that ratios of many refractory element pairs would deviate markedly from chondritic values with relatively small amounts (10%–30%) of fractionation of Mg-perovskite. These experiments are extremely difficult technically and are of very limited duration. They are conducted in a considerable temperature gradient. Henry's law has not been demonstrated, and formal reversals demonstrating that equilibrium has been bracketed have not been carried out. Thus, the reported partition coefficients may be in error. A thoughtful analysis of the possible sources of error in such experiments is given by Walker and Agee [27]. Nevertheless, the arguments of Kato et al. are robust. Unless partition coefficients are very small (<0.1) or are essentially unity for elements present in chondritic ratios in the upper mantle, small amounts of fractionation of Mg-perovskite will result in nonchondritic element ratios.

Kato et al. [24, 25] and Ohtani et al. [28] have also reported majorite garnet/melt partition coefficients for a number of elements. The phase equilibrium diagram of Ito and Takahashi [17] shows that the shape of the liquidus slope between the olivine and Mg-perovskite stability fields is such that an adiabat will not intersect the majorite garnet field and, hence, majorite garnet will not be a liquidus phase until relatively late in the crystallization of a terrestrial magma ocean, and will only be the liquidus phase in the intermediate pressure range of about 170 kbars to 220 kbars. As with the above discussion of Mg-perovskite fractionation, the ratios of many refractory element pairs will deviate markedly from chondritic values with relatively small amounts (10% – 30%) of fractionation of majorite garnet.

At pressures lower than about 170 kbars, olivine is the stable liquidus phase. It will be shown below that olivine/melt partition coefficients also may be used to investigate the question of whether the early Earth was ever substantially molten.

Mg/Si Ratios, Olivine Flotation, and the Formation of the Upper Mantle

It has been known for some time that the Mg/Si ratio inferred by most authors for the upper mantle of the Earth is higher than in the chondritic meteorites (e.g., Jagoutz et al. [19]). Figure 2 illustrates this observation. The class of primitive meteorites most similar to the upper mantle is the C3V carbonaceous chondrites. These meteorites are not good candidates for proto-Earth matter as their Ir/Au ratio is almost twice as high as the CI ratio and estimates for the Earth's upper mantle (Kallemeyn and Wasson [29]).

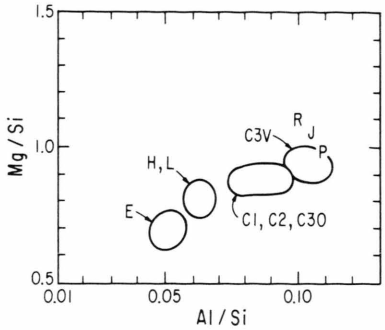

Fig. 2. Mg/Si vs. Al/Si weight ratios in various classes of undifferentiated meteorites and three estimates of the composition of the upper mantle of the Earth. R = pyrolite of Ringwood [40], J = preferred composition of Jagoutz et al. [19], P = preferred composition of Palme and Nickel [31].

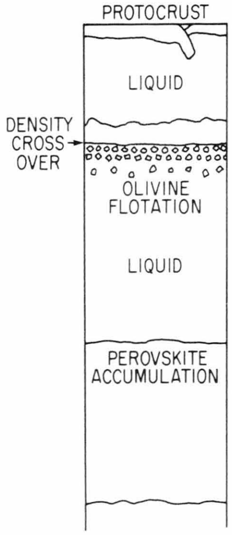

Fig. 3. Schematic cross-section of the Earth's mantle after accretion is largely over and heat loss from the Earth by radiation to space exceeds heat input from core formation and gravitational potential energy of accreting objects. A protocrust founders and dissolves, perhaps leaving refractory olivine to settle to the neutrally bouyant zone at about 80 kbar, to which olivine floating upwards from below the neutrally bouyant zone is added. At great depth, perovskite is on the liquidus and sinks. After Agee and Walker [30].

Recently Agee and Walker [30] have offered an innovative proposal to produce such a high ratio from initially chondritic material. The basis of their proposal is a careful experimental study which shows that olivine becomes neutrally bouyant in a melt representative of upper mantle composition at about 80 kbars. This experimental observation has led them to propose that the high Mg/Si ratio in the upper mantle results from mixing into the upper mantle of up to 30% olivine after solidification of a terrestrial magma ocean. This olivine crystallized from a magma ocean which was initially continuous in depth and formed a neutrally bouyant septum dividing the molten outer part of the Earth into two separated oceans. The result is a homogeneous upper mantle with a Mg/Si ratio greater than found in any class of chondritic meteorite except, possibly, the C3V chondrites (Palme and Nickel [31]). Their concept is shown schematically in Fig. 3, taken from Agee and Walker [30].

This novel proposal may be tested against olivine/melt partition coefficients for elements present in the upper mantle in chondritic ratios, following the approach of Kato et al. [24–26] for Mg-perovskite/melt and majorite garnet/melt pairs. Recall that Sc and Sm are present in chondritic ratios at chondritic abundance levels. Nickel and Co are present in chondritic ratios at about 20% of chondritic abundance levels. Iridium and Au are present in chondritic ratios at about 0.7% of chondritic abundance levels. As shall be demonstrated below, the elements in a given pair appear to have sufficiently different partition coefficients that their chondritic ratios may be used to limit possible olivine addition into the upper mantle.

Partition Coefficients

The partitioning of Sc, Sm, Ni, Co, Ir, and Au between olivine and melt at pressures corresponding to neutral buoyancy of olivine has not been investigated experimentally. We are currently undertaking an experimental program to measure mineral/melt partition coefficients for Ni, Co, Sc, and La (as a surrogate for Sm) at 1800 °C and 75 kbars, and mineral/melt partition coefficients for Ir and Au at 1300 °C and one bar (it is technically too difficult to attempt such measurements at high pressures at present). Detailed results of these studies are not yet available, and it is necessary to turn to literature data for appropriate numerical values.

Olivine/melt partition coefficients for Sc and Sm are not currently available at the pressure and temperature of interest. Lindstrom [32] quotes a Sc partition coefficient of 0.37 in the temperature range 1112 °C to 1134 °C at 1 bar, while McKay and Weill [33] quote a value of 0.27 at 1240 °C and 1 bar. It is unclear if this decrease is solely the result of higher temperature. For the purposes of calculation a value of $D(\mathrm{SC}) = 0.3$ will be used. Samarium is an incompatible element in olivine, and a value of $D(\mathrm{Sm}) = 0.02$ will be used.

Figure 4 summarizes olivine/melt partition coefficient data for Ni and Co. It is based on the review by Irving [34], and includes the recent experimental results of Seifert et al. [35]. Partition coefficients obtained at pressures up to 20 kbars are included in the envelopes of values. The range of values labeled 50 kbar represents olivine/melt partition coefficients for Ni from unpublished analyses in our laboratory of a run on KLB-1 kindly provided by E. Takahashi. It is clear that a wide range of olivine/melt partition coefficients is possible for both Ni and Co. It is also clear that the Ni partition coefficient is always higher than the Co partition coefficient. Exact values appropriate for about 80 kbars for use in model calculations are uncertain at present. Based on preliminary results of experiments at 75 kbars and 1800 °C conducted by our group (McFarlane et al., unpublished data), partition coefficient values based on extrapolations to 1800 °C in Fig. 4 appear to be the best choice.

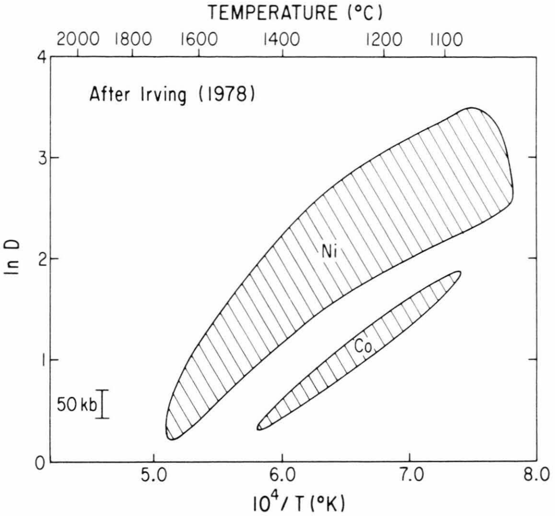

Fig. 4. Olivine/melt partition coefficients for Ni and Co. The shaded areas encompass the range of values summarized by Irving [34], and include the more recent results of Seifert et al. [35]. Included within the envelopes are experiments at pressures up to 20 kbars. Note that D(Ni) is always greater than D(Co). The range of values labeled 50 kbar represents olivine/melt partition coefficients for Ni from an experiment on natural KLB-1 kindly provided by E. Takahashi.

Olivine/melt partition coefficients for Ir and Au are also unavailable at the pressure and temperature of interest. Thus, estimates from one bar must also be used for these elements. Reliable experimental determinations are sparse. An upper limit for the diopside/melt partition coefficient for Au of 0.2 has been obtained in this laboratory at 1300 °C (unpublished results). A lower limit at 1300 °C for the olivine/melt partition coefficient for Ir of 7 was reported by Malvin et al. [36]. Burgmann et al. [37] report that Ir has an olivine/melt partition coefficient of about 2 and that Au is "moderately incompatible", based on modeling olivine fractionation in a komatiite flow. These authors were able to match Au fractionation trends using an olivine/melt partition coefficient of zero. Again, exact values for use in modeling at appropriate temperatures and pressures are uncertain, and examples will be used for purposes of illustration.

Discussion

Modeling the addition of olivine into the upper mantle following accumulation of an olivine septum requires certain assumptions.

1. Olivine will crystallize from a magma ocean over a range of tempertures, pressures, and fractions solidified. For the purposes of this calculation, we will assume that olivine equilibrates with magma at 80 kbars, and will calculate the composition of olivine at fractions of liquid remaining of 0.9 and 0.8.
2. The trace element content of the magma ocean at the time of olivine crystallization is unknown. It is assumed for the purposes of this calculation that the magma ocean had chondritic ratios of Sc/Sm, Ni/Co, and Ir/Au. Certainly prior segregation of metal will have fractionated the ratios of the siderophile elements. However, it seems unlikely that addition of olivine to the upper mantle would return ratios of these elements to the chondritic values observed today. Thus, we will assume that chondritic ratios were established without specifying a mechanism. Since, in practice, calculations carry the concentrations of elements as C_0, it is simple matter to replace the assumption of chondritic abundances with alternative values.
3. We will assume that the upper mantle to which olivine is being added is, on average, chondritic in relative and absolute abundances of these elements, recognizing that this assumption is unlikely to be correct in detail. Again, it seems unlikely that addition of olivine would return an upper mantle which initially had nonchondritic ratios of Sc/Sm, Ni/Co, and Ir/Au to chondritic ratios of these and other elements. As with assumption 2 above, it is a trivial matter to substitute alternative values.

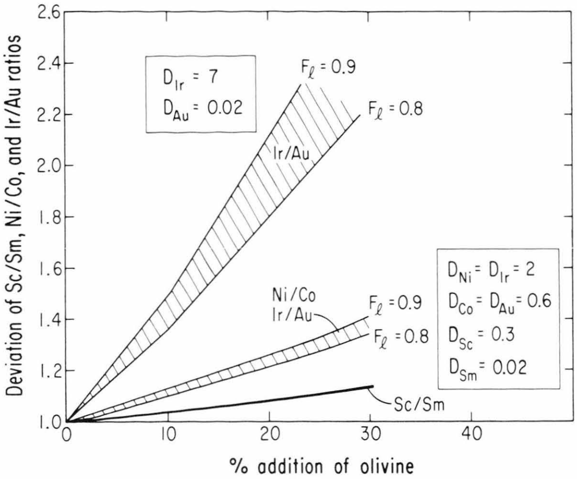

Fig. 5. Deviation of Sc/Sm, Ni/Co, and Ir/Au ratios in the upper mantle from initial values in a magma ocean as a result of addition of olivine into the upper mantle. $F_l = 0.9$ and $F_l = 0.8$ refer to the fractions of liquid remaining in the magma ocean at the time of olivine crystallization. Addition of enough olivine to raise the Mg/Si ratio of the upper mantle from thje CI value to the presently observed value (about 30%) would cause significant deviations of the ratios of the other element pairs from CI values, if the magma ocean had CI values.

Figure 5 summarizes the results of calculations employing the above assumptions and the partition coefficients discussed in the previous section. For convenience of calculation and display, we have assumed that $D(\mathrm{Ni}) = D(\mathrm{Ir}) = 2$, $D(\mathrm{Co}) = D(\mathrm{Au}) = 0.6$, $D(Sc) = 0.3$, and $D(\mathrm{Sm}) = 0.02$. The calculations are insensitive ot the value of $D(\mathrm{Sm})$ and any other partition coefficient of comparably small value. For the former set of partition coefficients and the assumptions above, Fig. 5 shows that addition of 30% olivine into the upper mantle raises ratios of two of the three element pairs by 30%–40% above chondritic ratios. If Ir is more compatible than assumed and Au is less compatible, then Ir/Au ratios will deviate still further from chondritic ratios. In the other example plotted on Fig. 5, where $D(\mathrm{Ir}) = 7$ and $D(\mathrm{Au}) = 0.02$, the Ir/Au ratio deviates by more than 200% from the chondritic value.

The uncertainties in the appropriate value of partition coefficients, coupled with the simplifying assumptions made to for the purposes of calculation, preclude firm statements concerning the expected values of elemental ratios following addition of olivine to the upper mantle. Nevertheless, the examples given in Fig. 5 suggest that conclusions drawn concerning addition of olivine to the upper mantle may be relatively robust. It seems difficult to avoid the conclusion that addition of enough olivine to the upper mantle to yield a Mg/Si ratio significantly higher than values observed in the chondritic meteorites will also yield nonchondritic ratios of lithophile, moderately siderophile, and highly siderophile elements, and these nonchondritic ratios are not observed in the upper mantle of the Earth today.

Summary and Conclusions

Details of the accretion of the Earth are uncertain, but it seems difficult to avoid the conclusion that the Earth should have been substantially molten during and immediately following accretion. If the Moon formed as a result of a giant impact, the Earth may even have been partially vaporized. Crystallization of the resultant magma ocean might be expected to result in segregation of minerals from melt, the development a of layered structure, and the fractionation of ratios of certain element pairs from chondritic values. These conclusions are based on analogies with terrestrial layered intrusions and with the results of an apparent magma ocean on the Moon. Paradoxically, ratios of element pairs such as Sc/Sm, Ni/Co, and Ir/Au inferred for the upper mantle of the Earth appear to be chondritic, contrary to prediction. The suggestion that the high Mg/Si ratio relative to chondritic meteorites inferred for the upper mantle of the Earth is the result of addition of olivine into the upper mantle following segregation from a terrestrial magma ocean likewise would be expected to yield nonchondritic ratios of these element pairs.

One conclusion which is consistent with these observations is that the Earth was never significantly melted. This conclusion requires reevaluation of our models of accretion. In particular, it seems difficult to make the Moon in a giant impact. It also raise questions concerning why the much smaller Moon apparently did melt significantly. An alternative possibility is that the Earth did melt substantially but, in the ensuing magma ocean stage, crystals remained entrained in magma and did not fractionate elemental ratios from their original values (Tonks and Melosh [38]). This possibility would resolve the paradox by eliminating the mechanism for fractionation, but would leave the high Mg/Si ratio of the upper mantle as a primordial feature of the upper mantle. The upper mantle constitutes only about 32% of the volume of the mantle and 21% of the volume of the planet. If the Earth was substantially molten, a significant fraction of the lower mantle must also have been molten. Thus, the high Mg/Si ratio of the upper mantle is presumably representative of the bulk silicate fraction of the Earth. Unless Si was removed into the core under very reducing conditions, raising the bulk silicate Mg/Si ratio, the material accreting to the Earth differed in composition from the chondritic meteorites. If the chondritic meteorites are indeed from the asteroid belt, as is generally assumed, then the accretional process was such that mixing between 1 AU and 2–4 AU did not occur.

Acknowledgements

The author thanks Heinrich Wänke for pointing out the possibility that the Sc/Sm ratio inferred for the upper mantle of the Earth may also be used to constrain the primordial fractionation of the Earth. E. Takahashi kindly provided a charge of natural KLB-1 run at 50 kbars and 1900 °C. Discussions with and reviews by C. Capobianco, D. Malvin, L. McFarlane, W. F. McDonough, and an anonymous reviewer are appreciated. This work was supported by NSF grant EAR 86-18266.

[1] R. J. Greenberg, J. F. Wacker, W. K. Hartmann, and C. R. Chapmann, Icarus **35,** 1 (1978).
[2] G. W. Wetherill, Science **288,** 877 (1985).
[3] M. J. Drake, W. V. Boynton, and D. P. Blanchard, EOS **68,** 111 (1987).
[4] V. S. Safranov, Moscow: Nauka. Transl. Israel Program for Scientific Translations. NASA TT F-677 (1972).
[5] W. Benz, W. L. Slattery, and A. G. W. Cameron, Icarus **66,** 515 (1986).
[6] W. Benz, W. L. Slattery, and A. G. W. Cameron, Icarus **71,** 30 (1987).
[7] W. Benz,. A. G. W. Cameron, and H. J. Melosh, Icarus (in press) (1989).
[8] J. Gradie and E. F. Tedesco, Science **216,** 1405 (1982).
[9] T. M. Donahue and J. B. Pollack, in: Venus (Hunten et al., eds.), University of Arizona Press, Tucson 1983, pp. 1003–1036.
[10] A. H. Treiman, M. J. Drake, M.-J. Janssens, R. Wolf, and M. Ebihara, Geochim. Cosmochim. Acta **50,** 1071 (1986).
[11] D. J. Stevenson, Science **214,** 611 (1981).
[12] M. E. Kipp and H. J. Melosh, Lunar and Planet. Sci. **17,** 420 (1986).
[13] M. E. Kipp and H. J. Melosh, Lunar and Planet. Sci. **18,** 491 (1987).
[14] P. H. Warren, Ann. Rev. Earth Planet. Sci. **13,** 201 (1985).
[15] C. J. Hostetler and M. J. Drake, Proc. Lunar Planet. Sci. Conf. 11th, **1980,** p. 1915.
[16] E. Takahashi, J. Geophys. Res. **91,** 9367 (1986).
[17] E. Ito and E. Takahashi, Nature **328,** 514 (1987).
[18] D. Walker, Contrib. Mineral Petrol. **92,** 3093 (1986).
[19] E. Jagoutz, H. Palme, H. Baddenhausen, K. Blum, M. Cendales, G. Dreibus, B. Spettel, V. Lorenz, and W. Wänke, Proc. Lunar Planet. Sci. Conf. 10th, **1979,** p. 2031.
[20] C.-L. Chou, D. M. Shaw, and J. M. Crocket, Proc. Lunar Planet. Sci. Conf. 13th, J. Geophys. Res. **88,** A 509 (1983).
[21] H. Wänke, Phil. Trans. Roy. Soc. London **A 303,** 287 (1981).
[22] R. Brett, Geochim. Cosmochim. Acta **48,** 1183 (1984).

[23] J. H. Jones and M. J. Drake, Nature London **322,** 221 (1986).

[24] T. Kato, T. Irifune, and A. E. Ringwood, Geophys. Res. Lett. **14,** 546 (1987).

[25] T. Kato, A. E. Ringwood, and T. Irifune, Earth and Planet. Sci. Lett. **89,** 123 (1988).

[26] T. Kato, A. E. Ringwood, and T. Irifune, Earth and Planet. Sci. Lett. **90,** 65 (1988).

[27] D. Walker and C. Agee, Earth and Planet. Sci. Lett. (in press) (1989).

[28] E. Ohtani, J. Moriyama, and I. Kawabe, Chem. Geol. **70,** 147 (1988).

[29] G. W. Kallemeyn and J. T. Wasson, Geochim. Cosmochim. Acta **45,** 1217 (1981).

[30] C. B. Agee and D. Walker, Earth and Planet. Sci. Lett. **90,** 144 (1988).

[31] H. Palme and K. G. Nickel, Geochim. Cosmochim. Acta **49,** 2123 (1986).

[32] D. J. Lindstrom, Ph.D. dissertation, University of Oregon 1976.

[33] G. A. McKay and D. F. Weill,. Proc. Lunar Sci. Conf. 7th, **1977,** p. 2339.

[34] A. J. Irving, Geochim. Cosmochim. Acta **42,** 743 (1978).

[35] S. Seifert, H. St. C. O'Neill, and G. Brey, Geochim. Cosmochim. Acta **52,** 603 (1988).

[36] D. J. Malvin, M. J. Drake, T. M. Benjamin, C. J. Duffy, M. Hollander, and P. S. Z. Rogers, Lunar Planet. Sci. **17,** 514 (1986).

[37] G. E. Brügmann, N. T. Arndt, A. W. Hofmann, and H. J. Tobschall, Geochim. Cosmochim. Acta **51,** 2159 (1987).

[38] W. B. Tonks and H. J. Melosh, Lunar Planet Sci. **20,** 1124 (1989).

[39] H. E. Newsom and S. R. Taylor, Nature London **338,** 29 (1989).

[40] A. E. Ringwood, Origin of the Earth and Moon, Springer, New York 1979.