

MECHANISMS OF EARTH DIFFERENTIATION: CONSEQUENCES FOR THE CHEMICAL STRUCTURE OF THE MANTLE

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Abstract. Compared to the mantles of the Moon and perhaps Mars, the Earth's mantle is much less differentiated chemically. Both the Moon and Mars appear to have undergone a major differentiation accompanying planet formation. The only clear signature of a similar event on the Earth is core formation. While this might imply that the Earth did not experience extensive melting and differentiation during planet formation, the higher pressures and temperatures present in the Earth could have led to a distinctly different chemical evolution for this initial differentiation. The most significant potential outcome of early differentiation on the Earth's mantle is formation of chemically distinct upper and lower mantles distinguished by Mg/Si higher and lower than chondritic, respectively. Plate tectonics on Earth provides a continuing mechanism for planet differentiation that forms crust at the expense of chemical differentiation of the mantle. Plate tectonics, however, also offers a mechanism to return the chemically distinct materials of the crust back into the mantle. Mixing of subducted crustal material into the mantle through the stirring provided by mantle convection can serve to negate the effects of crust forma-

tion on the chemical composition of the mantle. Similarly, mixing within the mantle could serve to destroy evidence of early differentiation, if such differentiation occurred on Earth. Completely efficient operation of the plate tectonic cycle would result in remixing of crust and differentiated mantle, with the end result being a homogenous mantle with composition identical to that of the bulk earth minus the materials segregated into the core. In part, this may explain the relatively undifferentiated nature of the Earth's mantle. Plate tectonics has not been completely efficient on Earth, however. Both oceanic and continental crust exist, and there is widespread evidence for chemical variability in the mantle. At least four chemically and isotopically distinct components are observed in mantle-derived rocks. The nature of these components points to the importance of crust formation and recycling in determining the chemical variability of the mantle. Mapping of the surface expression of chemical heterogeneity in the mantle is providing new views of the chemical structure of the mantle and the geodynamic processes that operate in the Earth's interior.

INTRODUCTION

The Earth is separated into chemically distinct layers of core, mantle, crust, hydrosphere, and atmosphere. The manner in which the Earth has accomplished this differentiation, and the end result, are quite different from that observed on two neighboring planetary objects, Mars and the Moon. Distinctions in the chemical evolution of the terrestrial planets appear to relate to differing balances between early global differentiation accompanying planet formation and continued differentiation, for example, through a long-lived mechanism such as the plate tectonic cycle on the Earth.

Plate tectonics on the Earth provides a mechanism for continuing chemical differentiation of the planet through melt production and segregation into

the crust. An equally important aspect of this process, however, is that it allows the chemically distinct materials of the crust and lithospheric mantle to be reinjected into the convecting mantle. The stirring provided by mantle convection can then serve to homogenize the products and residues of Earth differentiation. If this process were completely efficient, the mantle would be chemically homogeneous and equal in composition to its initial state. Plate tectonics on the Earth has not been this efficient. Some elements have been concentrated and stored in the core or in ancient portions of the continental crust, others have been transferred to the hydrosphere and atmosphere, and some light volatile elements have been lost to space. Nevertheless, several lines of evidence suggest that the Earth's mantle is much more homogeneous and gives a younger mean

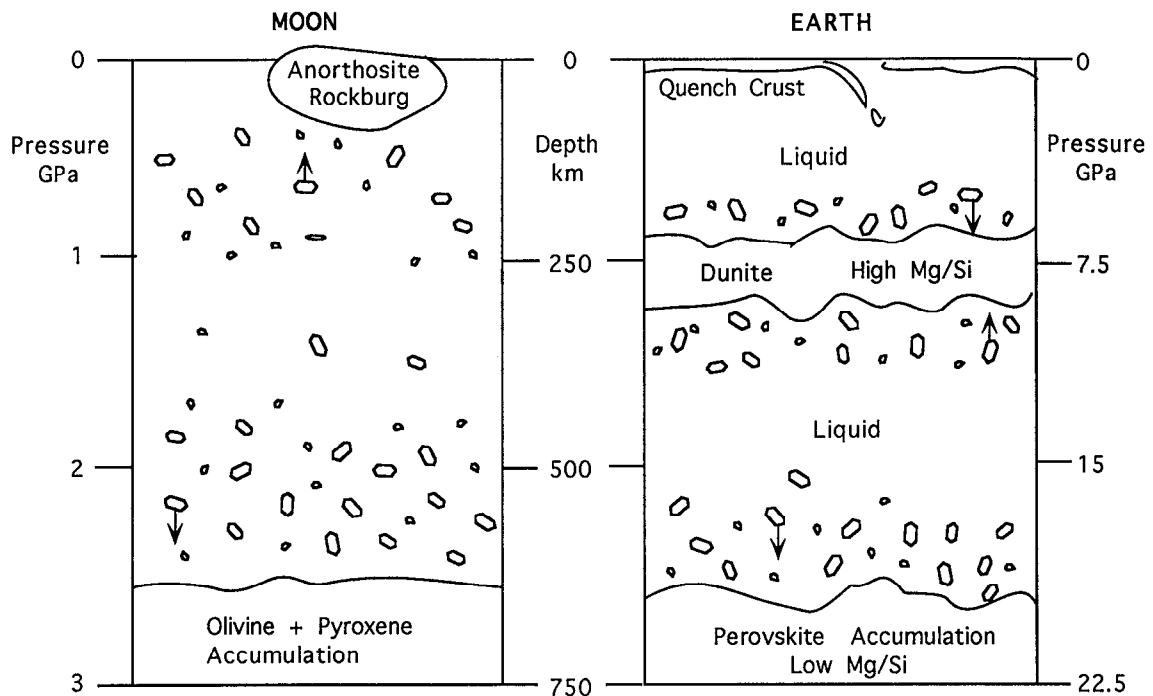


Figure 1. Examples of the differing chemical and physical evolution expected for crystallization of magma oceans on Earth and the Moon. Crystallizing phases and the relative density of magma and solid are controlled by the composition of the magma and by the pressure versus depth relation in these planetary objects. The lunar example is redrawn from Longhi [1980] and the terrestrial case is redrawn from Agee and Walker [1988].

age of differentiation than one would expect based on lunar or Martian analogs.

One of the keys to understanding the chemical structure of the Earth's interior is an accurate evaluation of the degree to which the plate tectonic cycle and the stirring of mantle convection have affected mantle composition. For example, how much of the observed chemical heterogeneity in the mantle is the result of imperfectly recycled subducted lithosphere? What is the lateral distribution of geochemical variation in the mantle, and what does this say about mantle circulation patterns? Is the mantle chemically and convectively layered, and if so, what are the compositional differences and the magnitude of mass transfer between layers? Are any of Earth's internal features determined by early global differentiation as opposed to continued operation of the plate tectonic cycle?

This paper will attempt a brief summary of current ideas on the chemical structure of the mantle by examining the processes that can create chemical heterogeneity and then compare the expected outcome of these differentiation processes with the observable characteristics of mantle geochemistry. While many questions remain on these topics, the emerging appreciation of the significance of differentiation during the high-energy early life of a planet and improved views of the geodynamic processes of the Earth's interior are providing fresh views of the chemical structure, his-

tory, and dynamics of the solid Earth. For a review of the mechanisms, nomenclature, and quantification for evaluating elemental and isotopic compositions, see the appendix.

DIFFERENTIATION ACCOMPANYING PLANET FORMATION

Evidence From Neighboring Planets

The Moon shows clear evidence for extreme chemical differentiation within 200 m.y. of its formation [Tera and Wasserburg, 1974; Nyquist et al., 1979; Carlson and Lugmair, 1988]. A widely accepted model for early lunar differentiation, the so-called magma ocean model, involves a starting condition where the Moon was largely or totally molten [Taylor and Jakes, 1974; Hubbard and Minear, 1975; Warren, 1985]. Upon cooling, fractional crystallization of the magma ocean formed a thick flotation crust of buoyant plagioclase overlying a lunar mantle composed of dense ferromagnesian minerals such as olivine and pyroxene [Longhi, 1980] (Figure 1). Similarly, early differentiation of Mars may be indicated by isotopic data [Jagoutz, 1991] for the SNC class of meteorites, named after the Shergotite, Nahklite, and Chassignite meteorite types that define this class, widely believed to derive from Mars.

Post magma ocean magmatic activity clearly has occurred on both the Moon and Mars. Nevertheless, key characteristics of the chemical separation of the silicate portion of these planetary objects appear to have been determined within the first 200 to 300 m.y. of their formation. In contrast, no rocks from this period of Earth history survive. More importantly, evidence for extensive igneous differentiation of our home planet during this interval is lacking. For example, while the mantle sources of both terrestrial mid-ocean ridge basalts (MORB) and lunar mare basalts show chemical and isotopic complementarity to the crusts that were extracted from their respective mantles (Figure 2), mare basalts give isotopic model ages for their source mantle that approach 4.5 Ga [Lugmair and Marti, 1978; Shih *et al.*, 1986], whereas MORB source model ages scatter widely in the range of 1 to 2 Ga [Church and Tatsumoto, 1975; Brooks *et al.*, 1976; Carlson *et al.*, 1978; Silver *et al.*, 1988] and probably represent open system continuing differentiation of the mantle [Galer and O'Nions, 1985] rather than a discrete terrestrial differentiation event.

Evidence for early, global differentiation of the silicate portion of the Moon and Mars provides an observable basis for the idea that large-scale or total melting is an expected result of the formation of the terrestrial planets. Energy sources for early planet-scale melting have appeared in abundance in the last few years. These include both the demonstration of the existence of short-lived radionuclides of major elements such as ^{26}Al [Lee *et al.*, 1977] (0.73-m.y. half-life) and ^{60}Fe [Shukolyukov and Lugmair, 1993] (1.49 m.y. half-life) in the early solar system and an emerging consensus from theoretical models that the latter stages of terrestrial planet formation are dominated by collisions between large, energetic planetesimals [Wetherill, 1990]. The most extreme example of this latter point is the model for formation of Earth's moon by collision between the proto-Earth and an object roughly the size of Mars [Hartmann and Davis, 1975; Boss and Peale, 1986; Benz *et al.*, 1987; Stevenson, 1987]. Besides ejecting enough material to form the Moon, an impact of this magnitude would deposit enough energy within the Earth to raise its temperature by 5000°K assuming complete conversion of the impact energy to heat [Stevenson, 1987]. Even conservative estimates of energy partitioning during such a collision predict that between 30 and 65% of the Earth would melt [Tonks and Melosh, 1993] depending on the preimpact temperatures of the colliding bodies (Figure 3).

Once a planet develops a global molten layer, convection within the magma ocean and radiation from the surface to space will ensure rapid cooling and crystallization [Hofmeister, 1983]. On relatively small objects like the Moon and Mars, crystallization will occur at low pressure and follow a path much like that of many layered mafic intrusions in the Earth's crust.

Gravitational sorting of the crystals will allow the dense ferromagnesian minerals to settle to the bottom of the molten layer, while plagioclase, which can be less dense than the liquid it crystallizes from, will float to the surface eventually to form the crust (Figure 1). Strong evidence for this differentiation scheme is provided by the anorthositic crust of the Moon and its chemical complement in the mantle that later served as the source of mare basalts [Taylor and Jakes, 1974] (Figure 2b). Spectral observations of Mercury imply a highly differentiated surface [Mitchell and Pater, 1993], and the evidence from the Martian (SNC) meteorites [Jagoutz, 1991] suggests an early crust-mantle differentiation event on Mars as well.

Early Terrestrial Differentiation?

Core formation. With one exception, similarly explicit evidence for this type of global differentiation is not evident on the Earth. The exception is core-mantle separation. Pb isotope data provide an "age of the Earth" in the 4.45- to 4.54-Ga range [Patterson, 1956; Manhès *et al.*, 1979]. This "age" dates a time of major U/Pb fractionation that took the $^{238}\text{U}/^{204}\text{Pb}$ of the Earth from a solar value of 0.1 to the bulk mantle value near 8. In addition to the loss (or noncondensation) of volatile Pb relative to refractory U during Earth formation, core separation could have increased the mantle's U/Pb if significant amounts of Pb were incorporated into the core. Based on the abundances of other chalcophile elements in the mantle, Azbel *et al.* [1993] suggest that core formation decreased the mantle Pb abundance by a factor of 0.4. Assuming that no U partitioned into the core, the model predicts that core formation increased the mantle's U/Pb by a factor of 3.6. This suggests that most of the change from solar to terrestrial U/Pb relates to the volatility of Pb rather than to core formation. Still, the factor of 3 to 4 increase in U/Pb caused by core formation should have left a readily observable imprint on the Pb isotopic evolution of the mantle if this increase occurred substantially (e.g., >100 m.y.) after Earth formation. Thus the near 4.5-Ga U-Pb age of the Earth suggests that separation of core from mantle occurred within the first 100 million years of Earth history.

Analysis of siderophile relative to lithophile element abundance variation in the mantle through time suggests that there has been little chemical exchange between mantle and core over most of Earth history [Newsom and Palme, 1984; Newsom *et al.*, 1986; Jochum *et al.*, 1993] (Figure 4, bottom). This is substantiated further by the observation that the mantle abundances of highly siderophile elements such as Ir, Re, and Os are in roughly chondritic proportions relative to one another and are not as low in concentration as expected for metallic core-silicate mantle equilibrium [Wänke *et al.*, 1984] (Figure 4, top). Both observations suggest incomplete chemical equilibrium

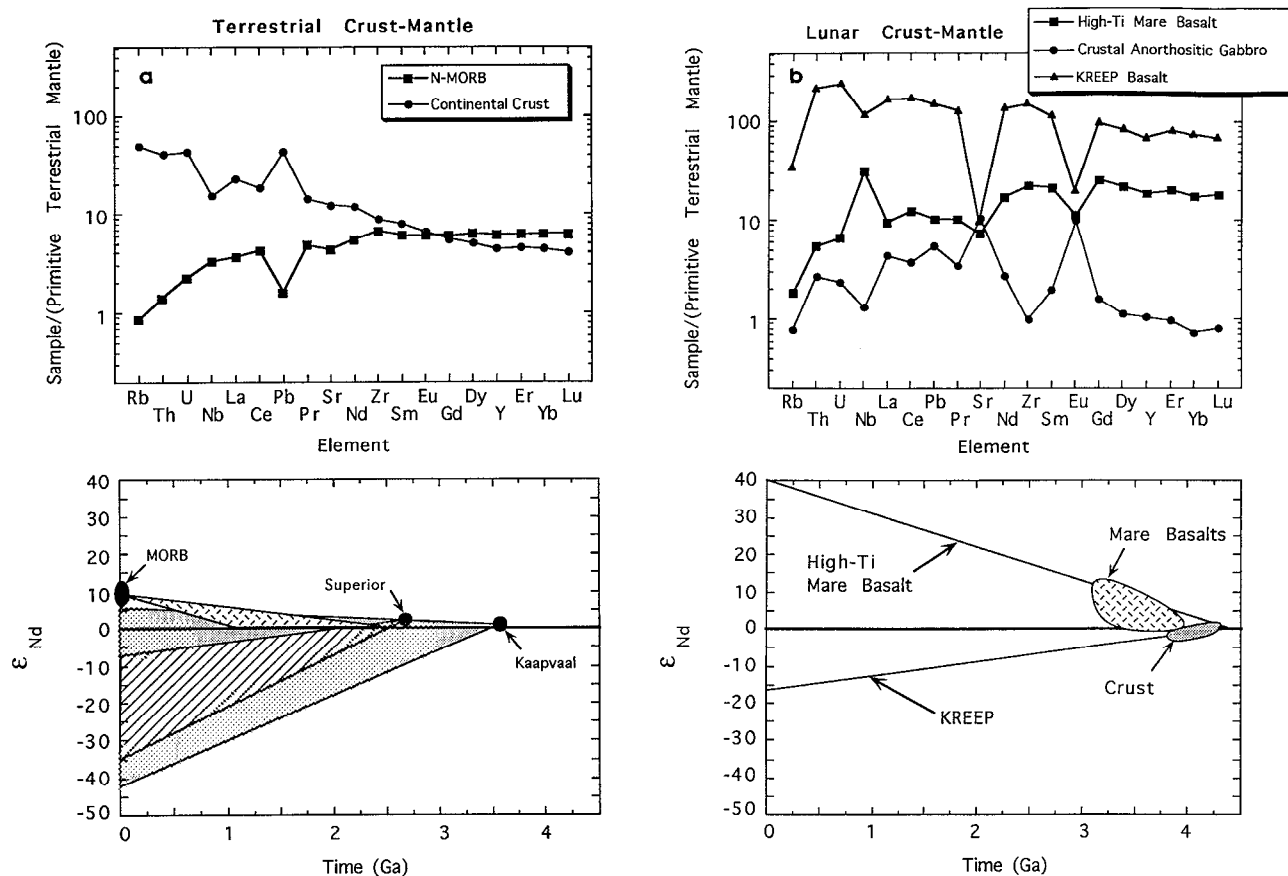


Figure 2. Incompatible lithophile element distribution in the crust and mantle of (a) Earth and (b) the Moon and its effect on Nd isotopic evolution. Elements are arranged in order of decreasing incompatibility during melting of peridotite [Hofmann, 1988]. Average continental crust abundances from Taylor and McLennan [1985], average normal mid-ocean ridge basalt (MORB) composition and primitive mantle normalizing values from Sun and McDonough [1989]. Mare basalt and anorthositic gabbro compositions from the Basaltic Volcanism Study Project [1981], potassium, rare earth element, and phosphorus-rich (KREEP) basalt composition from Warren and Wasson [1979]. The present day range in Nd isotopic composition of MORB is shown by the solid oval in Figure 2a. Evolution lines for Nd isotopic composition of the MORB source mantle, calculated using the measured Sm/Nd of primitive MORBs [Carlson et al., 1978], enclose the hatched triangle and can be seen to intersect the Nd isotopic composition of undifferentiated earth ($\epsilon_{Nd} = 0$) between 1.2 and 2.6 Ga. Examples of the range in initial Nd isotopic composition and subsequent evolution for a variety of crustal compositions in the Superior (dashed field) [Shirey and Hanson, 1986] and Kaapvaal (dotted field) [Carlson et al., 1983] cratons show the distinct Nd isotope evolution of generally light rare earth element (LREE) enriched (low Sm/Nd) crustal rocks in comparison to the LREE-depleted (high Sm/Nd) MORB. Figure 2b shows selected Nd isotope evolution lines for high-Ti mare basalts and KREEP basalts based on measured Nd isotopic compositions and Sm/Nd of these materials. The complementary evolution of the LREE-depleted source of high-Ti basalts toward positive ϵ_{Nd} and the evolution of LREE-enriched KREEP toward negative ϵ_{Nd} mirror the complementary evolution of terrestrial continental crust and MORB mantle, but the relatively young model differentiation ages of the MORB source contrast with the ancient ages obtained for both mare basalts [Lugmair and Marti, 1978; Nyquist et al., 1979] and for KREEP [Lugmair and Carlson, 1978].

between core and mantle. One explanation for this is that as much as 1 to 2% of the mass of the present Earth was added after core formation was complete and that this "late veneer" of material was mixed throughout the silicate portion of the planet but never interacted with the core [Wänke et al., 1984; Newsom, 1990]. Alternatively, if this late veneer were composed of strongly oxidized material, for example, carbona-

ceous chondrites, then metal segregation from this material may not have taken place, allowing its inventory of siderophile elements to mix into the mantle rather than segregate into the core [Schmitt et al., 1989]. An interesting implication of this model is that Earth's hydrosphere and atmosphere may derive in large part from this late accreting material, since the amount of water contained in 1% Earth mass of CI

chondrite is approximately equal to the mass of water in the Earth's crust [Dreibus and Wänke, 1987].

Intramantle and mantle-crust differentiation. While core-mantle separation appears to have been completed within 100 m.y. of Earth formation, evidence for similarly early global differentiation of the silicate earth is not so obvious. Why is this? Did the silicate earth not undergo a global melting episode during its formation? Were the products of this initial differentiation stirred back together by mantle convection? Are the results of this differentiation distinct from those observed on the Moon because of the difference in composition and physical (i.e., pressure and temperature) characteristics of the two objects?

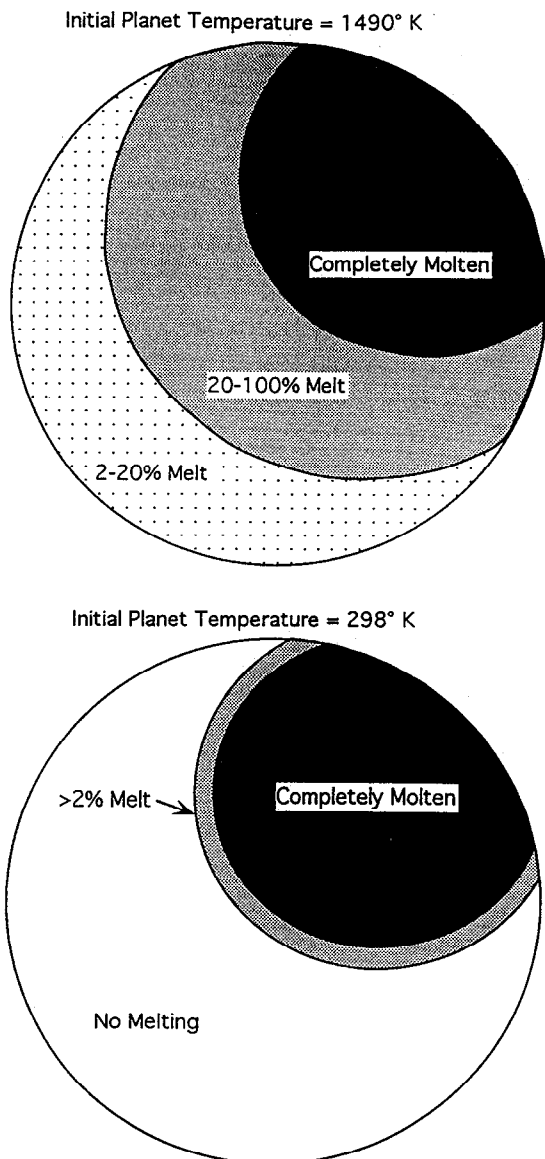


Figure 3. Illustration of the degree of melting expected for collision between the Earth and an object one-tenth the Earth mass. The amount of melting depends critically on the temperature of the Earth prior to impact. Figure redrawn from Tonks and Melosh [1993].

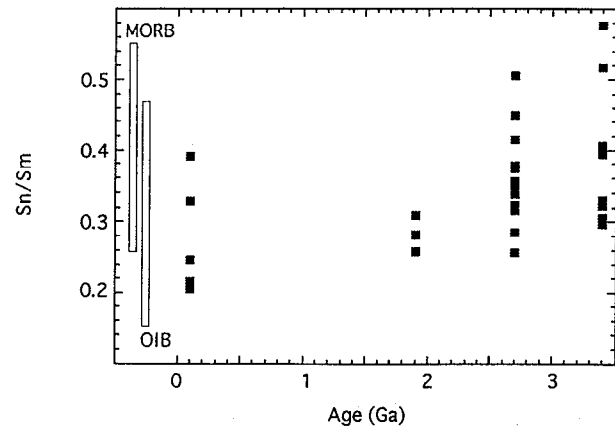
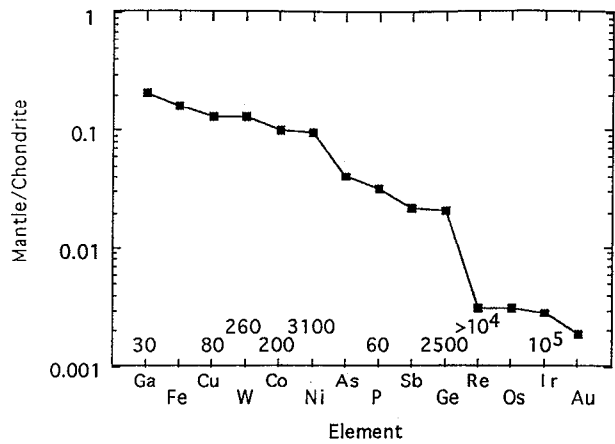


Figure 4. Siderophile element abundances in the upper mantle relative to chondritic abundances. (top) Numbers along abscissa are measured metal-silicate distribution coefficients for these elements. Data from Wänke *et al.* [1984]. (bottom) Invariant siderophile (Sn) to lithophile (Sm) element ratios in mantle-derived rocks of varying ages [Jochum *et al.*, 1993] implying that no elemental exchange between mantle and core has occurred over the 3.5-Gyr period recorded by these rocks. OIB, ocean island basalt.

The changing relative density of liquids and solids. Mafic/ultramafic liquids are sufficiently compressible to approach and eventually exceed the density of crystallizing mafic solids with increasing pressure [Stolper *et al.*, 1981; Agee and Walker, 1988, 1993; Miller *et al.*, 1991a, b]. Agee and Walker [1988] describe a model for magma ocean crystallization that explains the olivine-rich nature of Earth's upper mantle as the result of accumulation of olivine in the middle upper mantle, where it sinks from the low-pressure, low-density magma above and floats from the high-pressure, high-density magma below (Figure 1). Of some interest in this model is the effect a mid-ocean layer of solid crystals would have on the thermal evolution of the magma ocean. A terrestrial magma ocean 100 km deep would completely crystallize in under 2 m.y. if it formed a conductive upper boundary (i.e., crust) no more than 1 km thick [Hofmeister, 1983]. Presumably, a perched solid layer within the magma ocean would

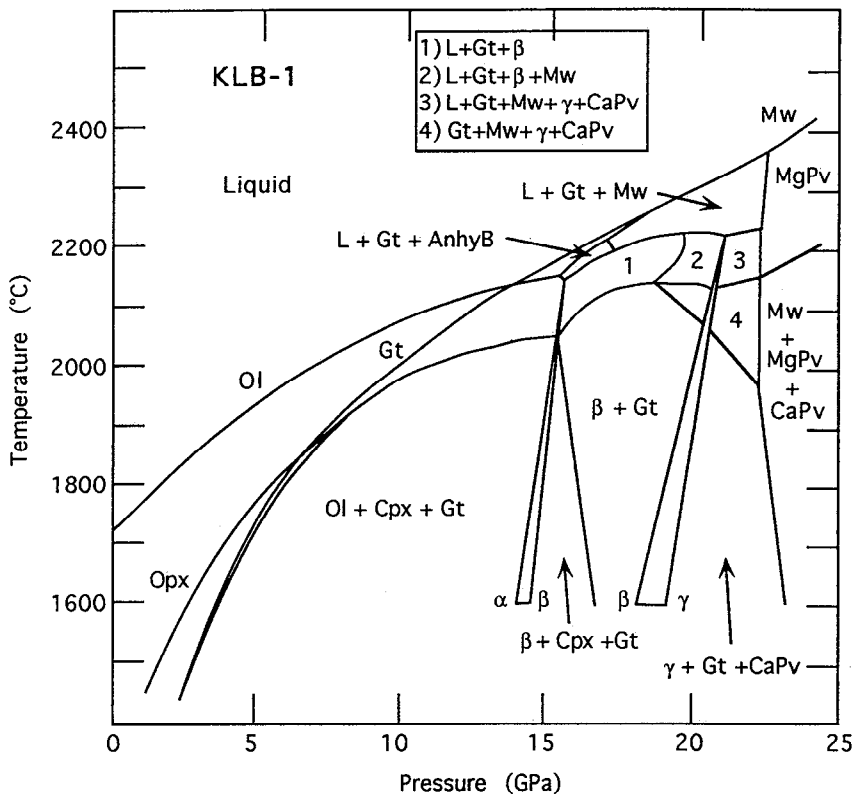


Figure 5. Phase diagram determined for peridotite KLB-1. Redrawn from Zhang and Herzberg [1994].

substantially impede heat transfer from below and hence delay crystallization of the magma below this layer [Nisbet and Walker, 1982]. If so, a liquid-solid density crossover could serve to retain substantial "primordial" heat within the Earth's interior and thus may provide a partial explanation for the continuing vigor of plate tectonics and surface magmatism on the Earth.

Why is the Earth's crust so small and so young?

The Earth's crust accounts for only 0.7% of the volume of the planet compared to a lunar crust that is some 10% of the volume of the Moon. The lunar crust is ancient (mostly >4.2 Ga), thick (>50 km), and rich in anorthosite, whereas the Earth's oceanic crust is thin (<7 km), transient (<200 m.y.), and basaltic. The Earth's continental crust is thicker (20–60 km) and more evolved in composition, but it covers only one quarter of the surface and was assembled over most of Earth history.

An early suggestion for these differences in crustal thickness on the Earth and Moon notes that while plagioclase is a stable crystallizing phase at low pressure, at higher pressure the stable aluminous phase is the dense mineral garnet [Ringwood, 1979]. Consequently, a crust thick enough to stabilize garnet at its base would no longer be gravitationally stable floating above a mantle composed of olivine and pyroxene. A garnet-rich crust would either delaminate its dense lower layers or experience wholesale subduction.

On the Moon, plagioclase is completely replaced by garnet only at depths greater than 700 km, whereas on

the Earth this transition induces a bottom boundary to the crust at about 40- to 60-km depth. Recent work on the crystallization paths of magmas at very high pressures indicates that garnet will be the liquidus phase at pressures of 14 to 22 GPa [Herzberg and Gasparik, 1991] (Figure 5). Should a terrestrial magma ocean have been present that was deep enough to allow garnet crystallization, fractionation of garnet could lead to a residual liquid too poor in Al and Ca to crystallize enough plagioclase to form a thick flotation crust.

Mantle Mg/Si: Nonchondritic Earth or global differentiation? Because of the different crystallizing mineralogy expected for a deep terrestrial magma ocean compared to a lunar magma ocean, the chemical fractionation caused by the crystallization of a terrestrial magma ocean could be quite different from the lunar example. With the development of multianvil, high-pressure experimental apparatus has come an explosion of attempts to determine melting relations of mantle compositions throughout the pressure and temperature range of the upper mantle [Ohtani *et al.*, 1986; Ito and Takahashi, 1987; Kato *et al.*, 1988; Herzberg *et al.*, 1990; Agee, 1993; Drake *et al.*, 1993]. That these experiments are difficult is indicated by the variability in results that have been obtained during the development of these procedures (Figure 6).

One goal of high-pressure experimental studies is to define whether the observationally determined composition of the upper mantle is that of the bulk silicate earth or is instead a product of global-scale differenti-

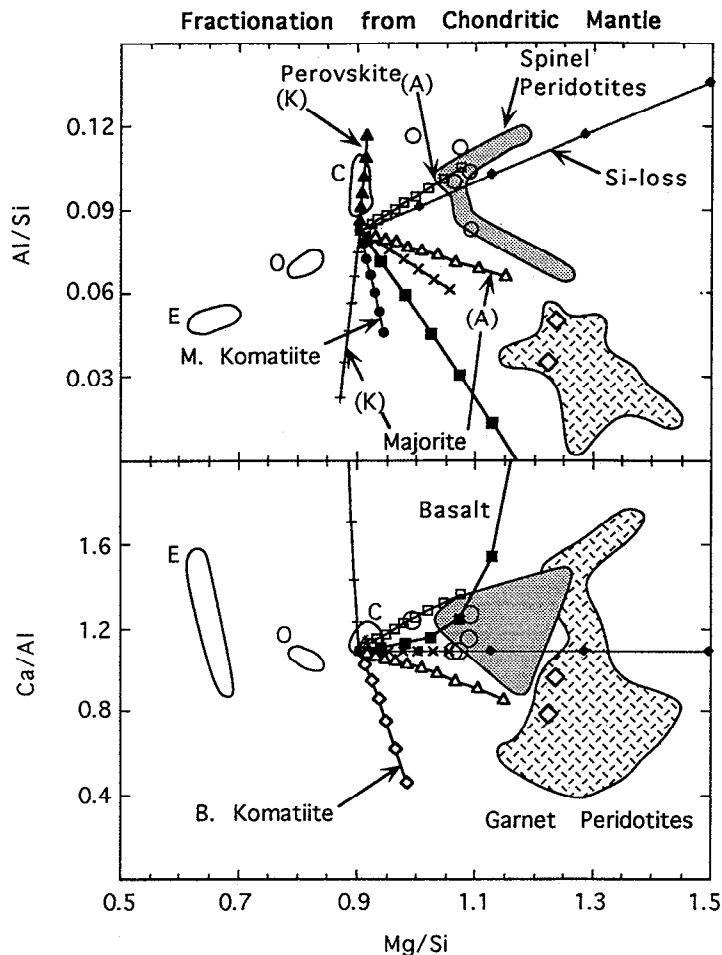


Figure 6. Effect on Mg, Al, Ca, and Si abundances of removing various mineral or melt compositions from a mantle initially of chondritic composition. Lines emanating from the C chondrite starting point reflect removal, in 5% by weight increments, of SiO_2 (Si-loss), basalt (Mauna Loa tholeiite HAW-11 from the *Basaltic Volcanism Study Project* [1981]), and both Al-rich (Munro Township [Arndt et al., 1977]) and Al-depleted (Barberton [Smith and Erlank, 1982]) komatiites. To illustrate the range in perovskite and majorite compositions reported from various high-pressure experiments, crystal fractionation paths are shown for the perovskites and majorites analyzed by Kato et al. [1988], the "K" paths, and from Agee [1993], the "A" paths. The line marked with "x" denotes the trend expected for olivine addition to a chondritic mantle [Agee and Walker, 1988]. Fields labeled E (enstatite), O (ordinary), and C (carbonaceous) enclose data for various types of chondritic meteorites [Jarosewich, 1990]. Spinel peridotite field encloses the data for fertile peridotite xenoliths studied by Jagoutz et al. [1979], while the garnet peridotite field shows the data for highly fractionated xenoliths from the Kaapvaal craton [Boyd and Mertzman, 1987]. Open circles show various estimates of primitive upper mantle composition [Jagoutz et al., 1979; Ringwood, 1979; Palme and Nickel, 1985; Hart and Zindler, 1986; Sun and McDonough, 1989]. The open diamonds in the garnet peridotite field are averages for spinel and garnet peridotite xenoliths [Maaloe and Aoki, 1977].

ation whose conjugate lies buried within the Earth. Of particular concern are the decidedly higher than chondritic Mg/Si [Jagoutz et al., 1979; Ringwood, 1979; Hart and Zindler, 1986] and the arguably higher than chondritic Ca/Al [Palme and Nickel, 1985] of proposed upper mantle compositions, since these elements are refractory lithophile elements that should be present in the silicate earth in roughly chondritic proportions.

One way out of this problem is to relax the requirement of a chondritic Mg/Si for the bulk earth. Different classes of chondritic meteorites define trends on plots of Al/Si and Ca/Al versus Mg/Si that are consistent with variable abundances of Si compared to these other, more refractory, major elements [Jagoutz et al., 1979; Jarosewich, 1990] (Figure 6). Estimates of upper mantle composition extend these trends to slightly higher Mg/Si than observed for chondrites. If the whole mantle is equal in composition to the upper mantle, the bulk silicate earth must then be deficient in Si by about 5 to 7% by weight compared to carbonaceous chondrite compositions. This silicon simply might not have condensed with the materials that formed the Earth [Ringwood, 1979], a possibility that is in line with many other observations that the Earth is depleted in volatile elements compared to chondrites [Wänke et al., 1984]. An interesting recent ob-

servaion is that the chondrules in ordinary chondrites have an average composition close to that of pyrolite [Herzberg and Zhang, 1994], which might suggest that the Mg/Si of the upper mantle was present in the planetesimals that formed the Earth.

An alternate explanation to Si volatilization is that some Si segregated into the core. If the whole mantle has lost 5 wt % SiO_2 to the core, the core SiO_2 concentration would be approximately 10%. This is within the range of Si solubility in Fe [Ringwood and Hibberston, 1991] as well as the concentration needed for a light element dilutant in order to match the observed density of the core. Nevertheless, by comparison with TiO_2 , which is more siderophilic than SiO_2 yet is present in roughly chondritic relative proportions in the upper mantle, Ringwood and Hibberston [1991] reject the possibility of substantial Si in the core.

Emerging from the results of high-pressure melting experiments of chondritic bulk compositions is the possibility that the Si-deficient upper mantle is the conjugate to a Si-enriched lower mantle. This conclusion is contentious and has its supporters [Herzberg et al., 1990; Agee, 1993] and detractors [Kato et al., 1988; Drake et al., 1993] who base their arguments on the results of different high-pressure experiments. Figure 6 illustrates the nature of this difference in opinion

by showing the evolution paths expected for fractionation of the range of majorite and perovskite compositions that have been observed in various experiments. The main point of argument is whether the liquidus majorite, magnesiowüstite, and perovskite that would crystallize from a melt with chondritic Mg/Si have the correct composition to produce the observed upper mantle Mg/Si, Al/Si, and Ca/Al, should these early crystallizing phases be accumulated preferentially into the lower mantle. In any event, upward of 40% crystallization of perovskite would be required to produce a residual liquid with upper mantle Mg/Si. Thus if this model is correct, the upper mantle would be the end product of extensive fractional crystallization of a terrestrial magma ocean.

Recent measurements of the thermoelastic properties of Mg-perovskite and magnesiowüstite and comparison of these properties with the seismically determined density and sound velocity in the lower mantle indicate that the lower mantle is more Si- and Fe-rich than the upper mantle [Knittle *et al.*, 1986; Bina and Silver, 1990; Stixrude *et al.*, 1992]. This provides support, from an independent line of evidence, for a chemical distinction between the upper and lower mantle.

Trace element constraints. While several mechanisms could lead to quite distinct chemical evolutionary paths for a terrestrial magma ocean, compared to the lunar example, any model invoking crystal accumulation must address the issue that the trace element composition of the present upper mantle does not bear a strong signature of any particular mineral. In fact, for a wide range of nonvolatile, nonsiderophile elements, model upper mantle compositions closely approximate chondritic compositions. Even the incompatible-element-depleted MORB source mantle shows an elemental fractionation pattern expected for a residue of shallow, clinopyroxene-dominated melting [Hofmann, 1988], not that expected for extensive fractionation of perovskite, magnesiowüstite, and majorite [Ringwood, 1991] (Figure 2a).

In an olivine accumulation model, such as the one proposed by Agee and Walker [1988], one might expect to see quite high Ni/Co in the upper mantle, since Ni is strongly concentrated in olivine while Co is not [McFarlane and Drake, 1990]. Instead, the upper mantle has a Ni/Co ratio very close to chondritic (Figure 4). Experimental studies investigating mineral melt distribution coefficients for a variety of elements in phases, such as majorite, magnesiowüstite and Mg-perovskite will constrain this problem further, but the general conclusion at this time is that any model invoking extensive fractional crystallization will be hard pressed to explain the wide variety of elements that are present in the upper mantle in roughly chondritic relative abundances [Kato *et al.*, 1988; McFarlane and Drake, 1990; McFarlane *et al.*, 1991, 1992; Drake *et al.*, 1993].

One way around this problem is the possibility that at the very high temperatures expected for a deep terrestrial magma ocean, elemental distribution coefficients between solid and liquid approach 1 for elements that do not form the major structural components of the mineral. In other words, with increasing temperature, minerals begin to lose their ability to discriminate between the elements they incorporate during crystallization. This suggestion was made originally on the basis of thermodynamic arguments [Murthy, 1991] that have been the target of much discussion [Jones *et al.*, 1992; Murthy, 1992; O'Neill, 1992], but the suggestion has spurred on several measurements of distribution coefficients at high pressure and temperature [Capobianco *et al.*, 1993; Walker *et al.*, 1993] directed both at magma ocean evolution and element partitioning between mantle and core. The early results from these experiments show significant temperature and pressure effects on element partitioning between metal and silicate liquids, with partition coefficients moving closer to 1 for many elements (Figure 7). The convergence is not universal for all elements in metal-silicate liquid partitioning, nor do high-temperature/pressure experiments show high-pressure silicate phases to be completely indifferent toward trace element partitioning [Drake *et al.*, 1993]. Consequently, the relatively unfractionated trace element abundances in the upper mantle will continue to be in conflict with models invoking extensive mineralogical layering of the mantle or even complete chemical equilibrium between core and mantle.

Model age information from radiogenic isotope systems. One long-standing problem with models for a major early terrestrial differentiation event is that isotopic model ages for various mantle and crustal components never suggest Hadean ages. The Pb-Pb pseudoisochrons for oceanic basalts range between 1 and 2.5 Ga, clustering around the 1.7-Ga trend defined by the northern hemisphere reference line of Hart [1984] (Figure 2a). The Rb-Sr [Brooks *et al.*, 1976] and Sm-Nd [Carlson *et al.*, 1978] model ages for MORB also are in the 1- to 2-Ga range. Whether these ages relate to any discrete differentiation event or instead reflect mantle mixing processes [Galer and O'Nions, 1985] is uncertain, but they provide no indication of an early (i.e., pre-4.0 Ga) differentiation of the silicate earth.

Some suggestions of early differentiation can be found in the isotopic record of the mantle, however. Besides the Pb-Pb age of the Earth discussed previously, excess ^{129}Xe found in MORB [Allègre *et al.*, 1983a] and recently in xenoliths from Samoa [Poreda and Farley, 1992] compared to atmospheric Xe suggests the presence of live ^{129}I (17-m.y. half-life) when the degassing of the MORB source occurred. If the ^{129}Xe excess is not from other than primordial sources of ^{129}I , such as U fission [Caffee and Hudson, 1987], then the presence of excess ^{129}Xe in MORB implies

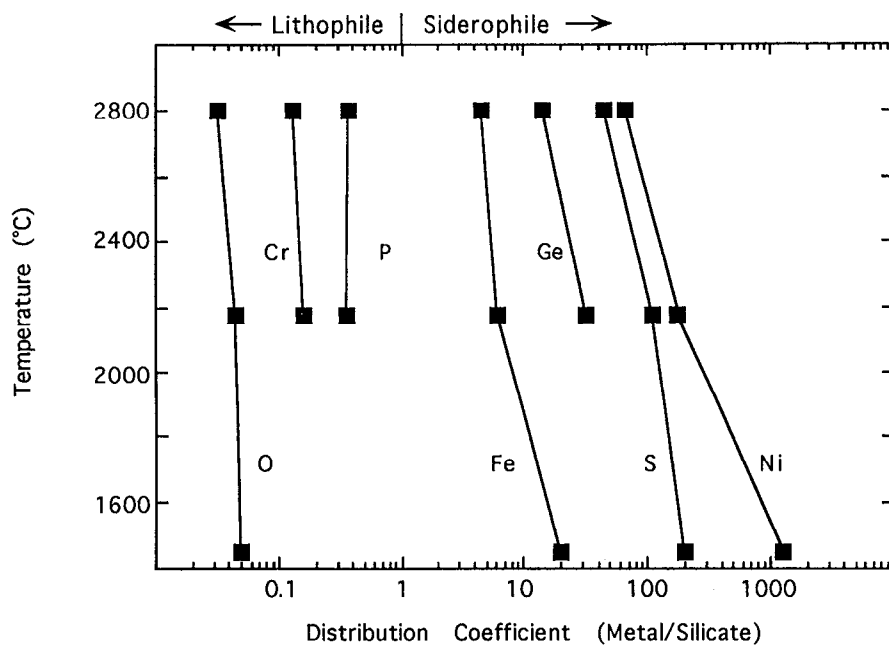


Figure 7. Effect of temperature on metal-silicate distribution coefficients. Figure redrawn from Walker *et al.* [1993].

that degassing of the MORB mantle occurred within the first ~50 m.y. of Earth history.

Another line of isotopic evidence for early differentiation comes from the observation that the oldest crustal rocks in every craton were derived from mantle sources with more radiogenic Nd than expected for the bulk earth; e.g., they have positive initial ϵ_{Nd} [Shirey and Hanson, 1986]. This suggests that an incompatible-element-depleted, MORB-like source formed in the mantle in the first few hundred million years of Earth history. Recent attempts to place stricter time constraints on this differentiation have searched for evidence of ^{142}Nd abundance anomalies derived from the decay of now extinct ^{146}Sm (103-m.y. half-life) [Bennet and McCulloch, 1992; Galer and Goldstein, 1992; Harper and Jacobsen, 1992]. With only one unconfirmed exception [Harper and Jacobsen, 1992], the measurements show no evidence for variations in ^{142}Nd abundance, indicating that the high Sm/Nd needed to evolve radiogenic excesses in ^{143}Nd in this source was not established in the first ~200 m.y. of Earth history, when ^{146}Sm was still present.

Overall, isotopic data for mantle-derived rocks do not require pre-4.0-Ga differentiation of the silicate earth. Instead, these data appear to reflect continuing differentiation processes that overprinted the signatures of early differentiation, if they were ever present.

PROCESSES FOR CONTINUING DIFFERENTIATION

Though based on sound theory and observations from comparative planetology, a major early differentiation of the silicate earth largely is conjectural. Evidence for continuing differentiation of the Earth's interior, however, is readily observable. The globe

encircling ocean ridge system annually produces approximately 17 km^3 of new basaltic crust [Turcotte and Schubert, 1982]. Eventual subduction of oceanic plates instigates convergent margin volcanism that adds $1.1 \text{ km}^3/\text{yr}$ of differentiated material to the Earth's crust [Reymer and Schubert, 1984]. Intraplate volcanism also is a significant contributor to crustal production, particularly if sporadic, but huge, eruptions associated with flood basalt provinces [Coffin and Eldholm, 1993] are included. Including oceanic plateaus, intraplate volcanism produces of the order of 1 to $1.5 \text{ km}^3/\text{yr}$ of crust [Schubert and Sandwell, 1989], a volume comparable to that produced through convergent margin volcanism.

Significant recent advances have been made in the understanding of the physical and chemical processes operating at ocean ridges [Klein and Langmuir, 1987; McKenzie and Bickle, 1988; Salters and Hart, 1989; Langmuir *et al.*, 1992; Spiegelman and McKenzie, 1992], island arcs [McCulloch and Gamble, 1991; Von Huene and Scholl, 1991; Davies and Stevenson, 1992], and large-volume intraplate volcanism [Richards *et al.*, 1989; Campbell and Griffiths, 1990; Carlson, 1991; Duncan and Richards, 1991; Coffin and Eldholm, 1992]. Discussion of the details of these processes is beyond the scope of this review. In effect, all serve to differentiate the Earth by transferring partial melts from the shallow mantle to the crust.

The mantle source of MORB has long been known to be depleted in incompatible elements [Engel *et al.*, 1965; Kay *et al.*, 1970]. This depletion often is modeled as the complement to the incompatible element enrichment of the continental crust [Jacobsen and Wasserburg, 1979; O'Nions *et al.*, 1979; Allègre *et al.*, 1983a, b]. Because of the high degree of enrichment of continental crust in the most incompatible elements (e.g.,

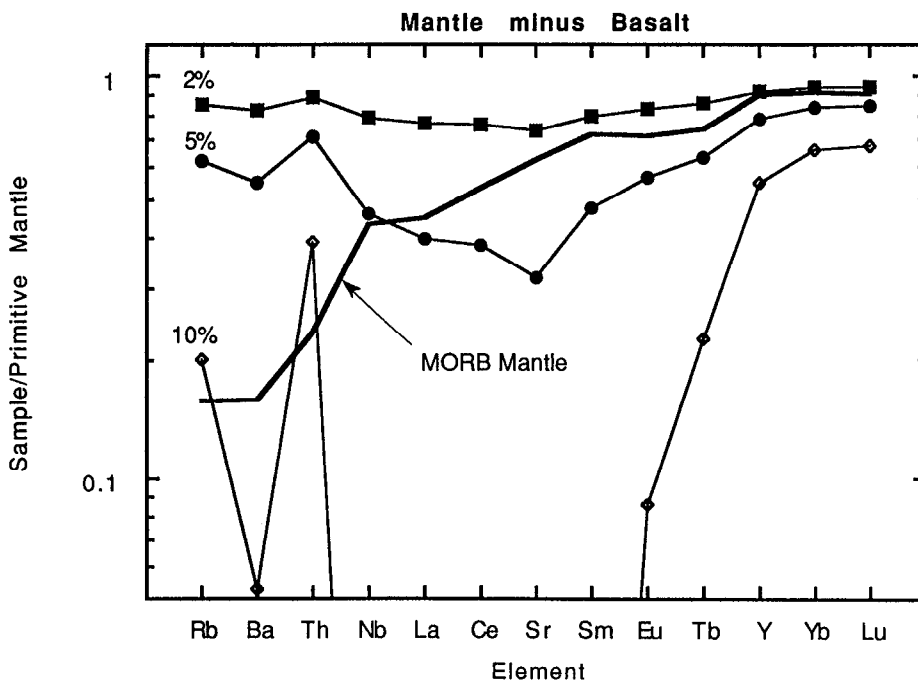


Figure 8. Incompatible lithophile element distributions caused by removal of basaltic melt from primitive mantle. For these calculations the trace element composition of basalt produced by melting primitive mantle is approximated by the composition of Mauna Loa tholeiite HAW-11 [Basaltic Volcanism Study Project, 1981]). The different curves represent different mass percentages (2%, 5%, and 10%) of basalt of constant composition removed from a given volume of mantle. They do not reflect differing degrees of partial melting to produce basalts of varying composition. Thick-lined curve shows composition of the MORB mantle.

Rb and Ba [Taylor and McLennan, 1985]), even the small volume of existing continental crust is capable of causing depletions of the magnitude seen in the MORB source in a considerable volume (i.e., more than a third) of the mantle. Because of its small volume, however, the continental crust is less effective in depleting the mantle in those elements not so highly concentrated in the crust, particularly major elements such as Al and Ca and the moderately incompatible elements. On the basis of simple mass balance calculations for the major elements, only a volume of mantle approximately the size of the continental lithospheric mantle, depleted to the degree observed in the continental mantle xenoliths [Jordan, 1979], is needed to balance the continental crust [Silver et al., 1988].

While the existing oceanic crust is small in volume, it is being produced at a considerable rate. If this crust, following subduction, remains isolated from mixing back into the mantle for substantial time periods, the quantity of basalt removed from the mantle at any given time could approach sufficient quantities to create significant incompatible element depletion in the residual mantle.

Chemical Consequences of Ocean Crust Production

For ocean crust production to have a net chemical effect on the mantle requires further processing of the crust-depleted lithospheric mantle package, since if mixed back together, these two components will sum to the starting composition. This additional processing can include alteration of the oceanic lithosphere by interaction and exchange with seawater [Hart and Staudigel, 1989], dehydration and/or melting of the subducting lithosphere at sites of convergent margin

volcanism [McCulloch and Gamble, 1991], and potentially delamination of crust from depleted lithosphere during passage of this package through the mantle convection system. The first two processes clearly do occur. The latter process largely is conjecture, but the consequences may have important implications for the structure of chemical heterogeneity in the mantle if the basaltic crust can be kept out of the general mantle circulation pattern for a significant amount of time [Carlson and Shirey, 1988; Chase and Patchett, 1988; Silver et al., 1988; Ringwood, 1990; Galer and Goldstein, 1991; McDonough, 1991].

The volume of basalt that may have been removed from the mantle can be constrained by the observed abundances of moderately incompatible elements in the MORB source. Figure 8 illustrates the effect of removing an approximately 10% partial melt of primitive mantle in varying amounts from the residual mantle. These calculations show that removal of roughly 2 to 5% of basalt from the mantle will leave a residue with concentrations of moderately incompatible elements (e.g., the rare earth elements (REE)) approximating those observed for the MORB source. The highly incompatible elements (e.g., Th, Ba, and Rb) in the MORB source are much more depleted than would be predicted for basalt removal alone, reflecting the importance of continental crust formation to the geochemical characteristics of the MORB source.

One way to resolve the relative roles of continental versus oceanic crust removal in the formation of the MORB source is to find elements that are not fractionated in the same manner or degree by continent and ocean crust formation. Continents clearly are enriched in Pb [Hofmann et al., 1986; Hofmann, 1988] and depleted in high field strength elements (HFSE, e.g.,

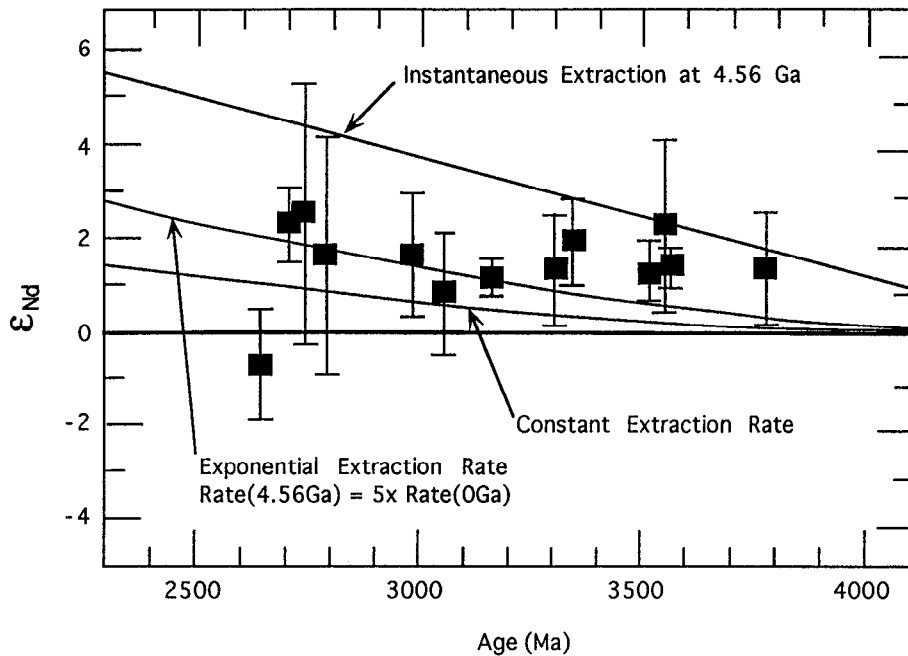


Figure 9. Effect of basalt removal on the Nd isotopic evolution of the residual mantle. Removal of 5% by weight basalt from a primitive mantle results in increased Sm/Nd and hence evolution toward positive ϵ_{Nd} in the residual mantle with time. The different curves result from different models for the rate of extraction of basalt. Data shown represent the average values and ranges observed in initial Nd isotopic compositions of Archean rocks [Shirey and Hanson, 1986].

Ti, Nb, and Ta) [Taylor and McLennan, 1985] compared to MORB and ocean island basalts (OIB) (Figure 2a). This leads to Nb/U and Ce/Pb in MORB and OIB that are greater, and in continental crust lower, than expected for the bulk silicate earth [Hofmann et al., 1986]. The Nb, Ta, and Ti, however, appear to be anomalously depleted in both the MORB source mantle and continental crust compared to their expected abundance in the bulk earth [Saunders et al., 1988; McDonough, 1991]. Through melt-fluid transfer in subduction zones, subducted basaltic oceanic crust may become preferentially enriched in Ti, Nb, and Ta compared to the more fluid soluble elements (e.g., Ba and Rb) as these more mobile elements leave the subducted crust and migrate into the overlying mantle wedge and, from there, arc magmas. Removal of roughly 2% of the mass of the mantle in the form of such subduction-processed basaltic oceanic crust could explain the abundance distribution of Ti, Nb, and Ta [McDonough, 1991] and provide further support for the idea that basaltic oceanic crust removal contributes to defining the geochemical characteristics of the MORB source mantle.

An interesting aspect of the basalt removal model will be its effect on the isotopic evolution of the residual mantle, particularly on the Nd isotopic system [Carlson and Shirey, 1988; Chase and Patchett, 1988; Galer and Goldstein, 1991]. Melt removal will leave a residual mantle with Sm/Nd greater than chondritic and thus will cause the residual mantle to grow toward more radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ (e.g., positive ϵ_{Nd}) with time compared to a chondritic bulk silicate earth model. The MORB mantle shows the outcome of this effect by its high positive (+8 to +12) ϵ_{Nd} , as do many of the oldest mantle-derived rocks from Archean cra-

tions [Shirey and Hanson, 1986] (Figure 9). Because of the limited natural fractionation between the neighboring rare earth elements Sm and Nd, and the 106-Ga half-life of ^{147}Sm , the positive ϵ_{Nd} of Archean crustal rocks implies that their mantle source was depleted in incompatible elements well before their formation. This observation can be explained by invoking the presence of pre-Archean continental crust [Jacobsen, 1988]. However, this explanation requires complete destruction of the ancient crust in spite of the tendency of buoyant, water-rich, continental materials to return rapidly to the surface if subducted into the mantle. An alternate explanation is that this early incompatible element depletion of the mantle was caused by extraction of basaltic crust [Chase and Patchett, 1988; Galer and Goldstein, 1991]. Figure 9 illustrates that extraction of 5% basalt from the mantle will cause the residual mantle to evolve along Nd isotopic trajectories that mimic those of the Archean data set depending on the timing of extraction of this crust.

What then is the net effect of basalt extraction on the chemical structure of the mantle? The loss of 2 to 5% by weight of basalt is not sufficient to explain first-order features of mantle composition such as its high Mg/Si, although basalt removal might contribute to the greater than chondritic Ca/Al proposed for the upper mantle [Palme and Nickel, 1985] and the lower Al/Si that typifies model mantle compositions constructed on petrologic grounds [Ringwood, 1979] rather than on cosmochemical abundance arguments [Jagoutz et al., 1979; Hart and Zindler, 1986]. Basalt extraction alone cannot explain the severe depletion of the MORB source in the highly incompatible elements, such as Rb, Ba, and Pb. The additional influence of convergent margin processes in selectively enriching

these elements in arc magmas and the continental crust is required in order to explain the very low concentrations of these elements in the MORB source. Where the effect of basalt extraction would be most significant is on the abundance of the moderately incompatible trace elements and the radiometric isotope systems based on them, e.g., Sm-Nd and Lu-Hf.

The effect of basalt segregation could become significant for the major element composition of portions of the mantle if a sufficient amount of basalt can be concentrated into a relatively small volume of mantle. For example, extraction of 5% basalt from the upper 400 km of the mantle would produce about 6×10^{25} g of basalt, approximately 35% of that formed at ocean ridges over all of Earth history if oceanic crust production was constant and equal to the present rate. If added to the whole lower mantle, this mass of basalt would have a minor effect on the major element composition of the lower mantle. If instead this mass of basalt were concentrated into smaller layers of the mantle, such as the transition zone between 400- and 670-km depth or in the D" layer just above the core, the effect on the composition of these layers would be significant, since this mass of basalt is 18% of the mass of the transition zone and 26% of the mass of the D" layer. In essence, it would turn these layers into "piclogite," a hypothetical rock type between peridotite and basalt in composition [Anderson and Bass, 1986]. Piclogite formed by the addition of basalt to fertile mantle, however, will have enhanced incompatible element abundances, well above those of the source of MORB, and thus cannot serve as the source of MORB [Anderson, 1983]. Instead, a piclogite- or megalith-rich [Ringwood, 1991] transition zone could serve as a source of some of the incompatible-element-enriched components seen in ocean island volcanism.

Fate of Oceanic Lithosphere

A key question in mantle geochemistry and geodynamics is the ultimate fate of subducted oceanic crust. Earthquakes along the Wadati-Benioff zone that define the trace of plate subduction into the upper mantle cease at depths no greater than the 670-km seismic discontinuity separating upper and lower mantle [Isacks and Molnar, 1971]. This observation has been known for decades, but the issue of whether slabs continue aseismically past the 670-km discontinuity into the lower mantle has not been resolved. Recent high-resolution seismic tomographic images of subduction zones show that some subducting slabs "bounce off" the 670-km discontinuity and accumulate in the upper mantle [van der Hilst et al., 1991; Fukao et al., 1992] while others continue as visible high-seismic-velocity anomalies well into the lower mantle [van der Hilst et al., 1991].

A type of layered convection known as penetrative convection [Silver et al., 1988] occurs when there is only a small (approximately 2 to 6%) compositionally

induced density difference between layers. In this situation the density difference between layers impedes general mass exchange but allows the passage of material that exceeds the density difference between layers. If the Earth's mantle operates in the penetrative convection mode, then mass exchange between upper and lower mantle might be restricted only to the anomalously cold, dense, subducting slabs and the anomalously hot material in mantle plumes, should these plumes originate in the lower mantle. Evidence that this might be a proper description of the geodynamics of the mantle comes from the observation of occasional slab penetration [van der Hilst et al., 1991] and from recent determinations of the density of model upper mantle compositions in comparison to the seismically determined density of the lower mantle [Knittle et al., 1986; Stixrude et al., 1992].

An additional factor affecting the fate of subducted plates is their changing density relative to surrounding materials as they descend into the mantle. This issue has been addressed in considerable detail by Ringwood [1991] and Irifune and Ringwood [1993], and the following discussion presents conclusions derived from this work. At ocean ridges, both basaltic crust and basalt-depleted mantle residue are less dense than underlying fertile peridotite and hence are buoyantly stable (Figure 10). As the basaltic crust descends following subduction, the mineralogical transformation from basalt to eclogite occurs at a relatively shallow depth (~60 km) accompanied by a large density increase (basalt = 2.9 g/cm³, eclogite = 3.4 g/cm³) that enhances the density anomaly of the cold subducting slab relative to an upper mantle dominated by olivine. At 400-km depth, where olivine transforms to spinel structure, the oceanic crust will consist principally of garnet and stishovite and will remain denser than the surrounding peridotite. On approaching 650 km, however, the relatively high Ca and Al contents of the basalt stabilize garnet and hinder the transition to the denser perovskite phase that occurs in the surrounding peridotite. Consequently, between 650 and 750 km, subducting crust may be substantially less dense than its surroundings. If the temperature anomaly associated with the cool oceanic crust is not sufficiently large to overwhelm the mineralogically induced density difference, subduction will be impeded and the oceanic crust will tend to remain above 670 km, independent of a compositionally induced density difference between upper and lower mantle.

OBSERVATIONS ON MANTLE CHEMICAL HETEROGENEITY

Number of Components

Beginning in the late 1970s and early 1980s, the combined use of several isotope tracers applied to

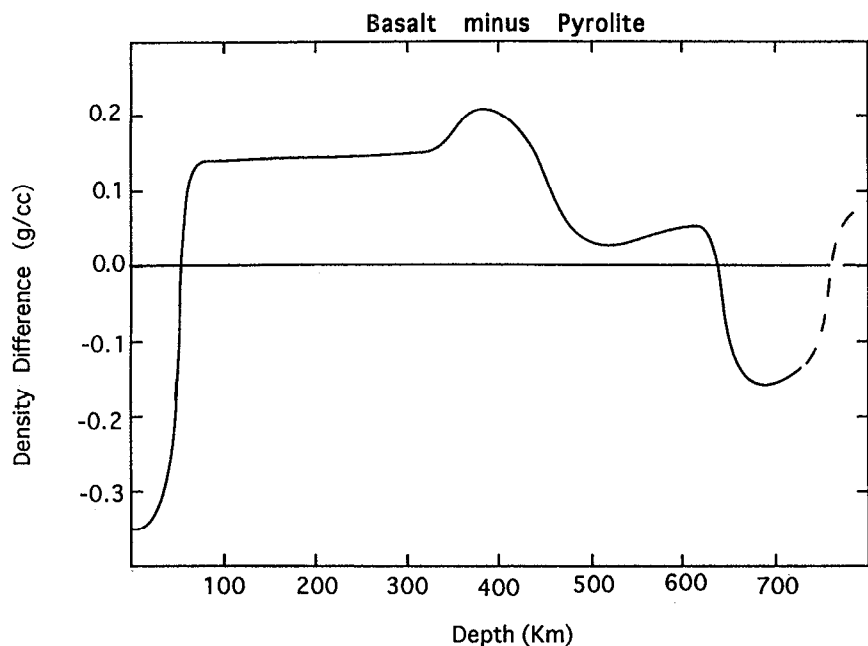


Figure 10. Density of basalt relative to pyrolite as a function of depth. Changes are caused primarily by pressure-induced mineralogical transformations in these compositionally distinct materials. Figure after *Irfune and Ringwood* [1993].

MORB and ocean island volcanism identified four isotopically distinct components within the suboceanic mantle [Zindler *et al.*, 1982; White, 1985; Zindler and Hart, 1986; Allègre *et al.*, 1987; Hart, 1988; Hart *et al.*, 1992]. Using the terminology of Zindler and Hart [1986], these four components are, the depleted MORB mantle (DMM), the source of most MORB; HIMU, distinguished in part by high $^{206}\text{Pb}/^{204}\text{Pb}$, a signature of high U/Pb ($\mu \equiv ^{238}\text{U}/^{204}\text{Pb}$), and two "enriched" mantle (EM) components, where "enriched" signifies $\epsilon_{\text{Nd}} < 0$, a sign of long-term light rare earth element (LREE) enrichment compared to bulk earth REE abundances. EM1 has relatively low $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ compared to EM2 which has intermediate $^{206}\text{Pb}/^{204}\text{Pb}$ (~ 18.8) and high $^{87}\text{Sr}/^{86}\text{Sr}$ (> 0.706) (Figure 11). Both EM components are distinguished by high $^{207}\text{Pb}/^{204}\text{Pb}$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$ compared to MORB.

An often discussed fifth component, undifferentiated mantle, does not appear to be reflected in the ocean island basalt record when data for several isotope systems in the same samples are considered simultaneously. The presence of high $^3\text{He}/^4\text{He}$ in some ocean islands is commonly taken to indicate a primitive, undegassed, mantle source [Craig and Lupton, 1976; Farley *et al.*, 1992]. The high $^3\text{He}/^4\text{He}$ component, however, appears to have radiogenic Pb [Farley *et al.*, 1992], with Sr and Nd isotopic compositions approaching DMM [Hart *et al.*, 1992; Graham *et al.*, 1993] and $^{20}\text{Ne}/^{22}\text{Ne}$, $^{40}\text{Ar}/^{36}\text{Ar}$, and $^{129}\text{Xe}/^{136}\text{Xe}$ higher than atmospheric values [Allègre *et al.*, 1983a; Poreda and Farley, 1992; Farley and Poreda, 1993], all of which suggest that the high $^3\text{He}/^4\text{He}$ component has experienced chemical differentiation and degassing at some point in Earth history. The high ^{129}Xe of this

component, possibly derived from decay of now extinct ^{129}I , may indicate that this outgassing occurred within 100 m.y. of Earth formation [Allègre *et al.*, 1983a; Poreda and Farley, 1992]. Alternatively, subduction of pelagic sediment rich in extraterrestrial dust that has high contents of ^3He and ^{20}Ne [Ozima *et al.*, 1984; Matsuda *et al.*, 1990; Nier *et al.*, 1990] could serve as a "recycled" source of solar rare gases in the mantle [Allègre *et al.*, 1993; Anderson, 1993]. In detail, however, there are many questions about the survivability of this cosmic rare-gas-rich component through subduction [Staudacher and Allègre, 1988; Hiyagon, 1994], as well as mass balance concerns regarding its ability to modify mantle He isotopic compositions [Allègre *et al.*, 1993].

The existence and uniqueness of these four end-member chemical and isotopic components in the mantle are now well documented [Allègre *et al.*, 1987; Hart, 1988]. What remains to be verified is the origin of the components and their relative and absolute locations in the mantle. Much progress on these issues has been made recently by including new isotopic (Ne [Farley and Poreda, 1993; Honda *et al.*, 1993], Os [Martin, 1991; Hauri and Hart, 1993; Reisberg *et al.*, 1993]) and chemical (Nb/U, Ce/Pb, Sn/Sm [Hofmann *et al.*, 1986; Jochum *et al.*, 1993]) tracers and by examining the geographic distribution of the components in comparison with mantle geophysical characteristics such as seismic velocity structure and the geoid [Hart, 1984; Castillo, 1988]. Another line of investigation makes use of the fact that the volcanic rocks on most ocean islands represent mixtures between two or more of these components. The hierarchy of the mixing relationship, coupled with models of

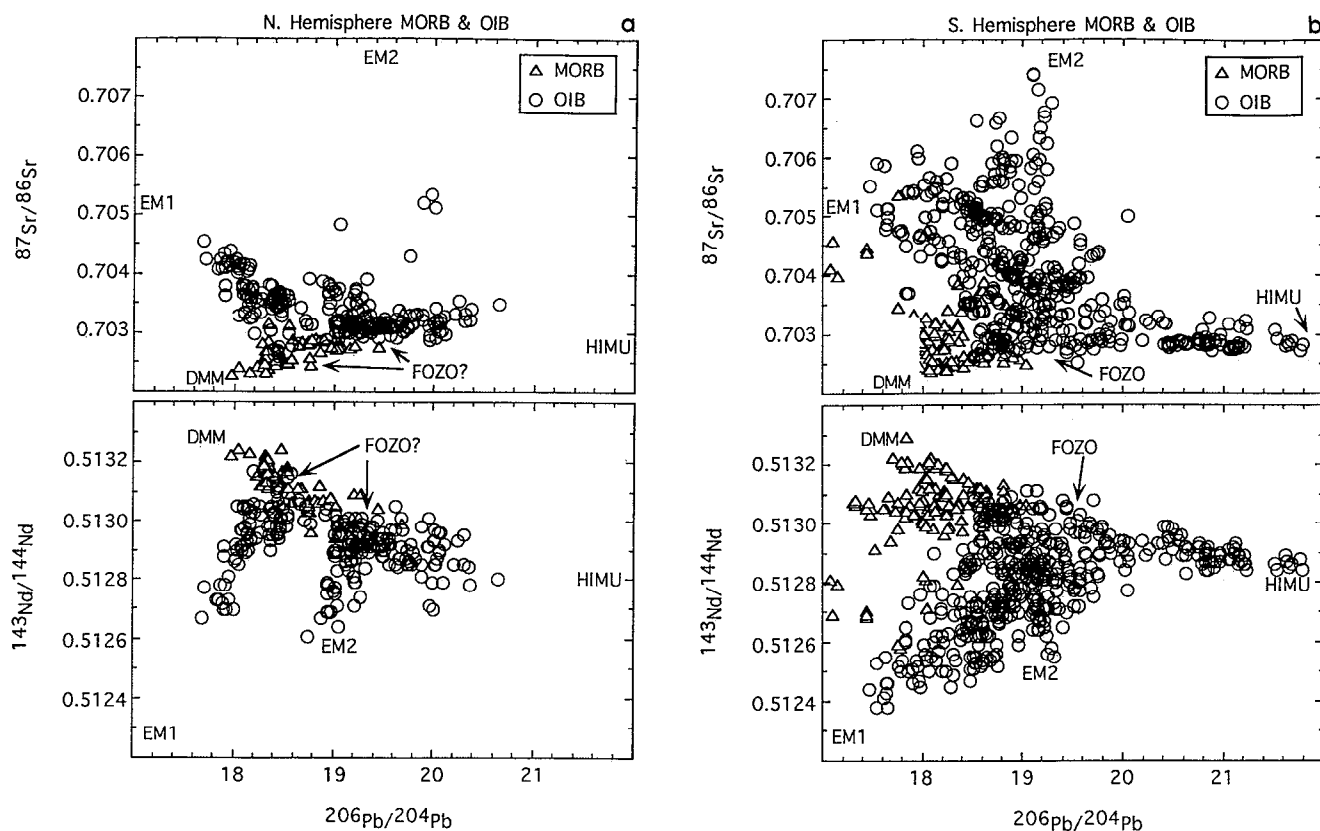


Figure 11. The Sr-Nd-Pb isotopic variation in MORB and ocean island basalts. Southern hemisphere MORB and OIB (Figure 11b) show extensive mixing between HIMU and a point, near depleted MORB mantle (DMM) but at slightly higher $^{87}\text{Sr}/^{86}\text{Sr}$ than DMM, on the DMM-EM1 connector. Trends for different OIB emanate toward enriched mantle (EM) components from a midpoint on the DMM-HIMU connector (focus zone, or FOZO [Hart *et al.*, 1992]). Northern hemisphere MORB and OIB (Figure 11a) show much more subdued influence of both HIMU and EM components. DMM-HIMU trends in the northern hemisphere suggest an end-member on the HIMU-EM2 (or -EM1) connector rather than pure HIMU. The EM2 mixing trend in the northern hemisphere, defined by samples from the Azores, points toward a “FOZO” composition consistent with that defined by southern hemisphere OIB. The EM1 trend in the northern hemisphere, however, emanates from a point closer to DMM than to the southern hemisphere FOZO.

mixing during flow in the mantle, can provide clues to the relative location of the components [Hart *et al.*, 1986, 1992; Hart, 1988; Graham *et al.*, 1993].

Compositional Characteristics

DMM is almost universally regarded as residual mantle that is the complement to the incompatible-element-rich continental crust. The residual nature of DMM is consistent with its Sr, Nd, and Hf isotopic composition, its general depletion in incompatible elements, and its rare gas isotopic compositions (e.g., radiogenic $^{21}\text{Ne}/^{22}\text{Ne}$ [Sarda *et al.*, 1988], $^{40}\text{Ar}/^{36}\text{Ar}$ [Sarda *et al.*, 1985], and $^{129}\text{Xe}/^{136}\text{Xe}$ [Allègre *et al.*, 1983a]) that suggest DMM is outgassed compared to

other mantle components. The preferential loss of some basaltic oceanic crust may account for the second-order trace element differences between DMM and the mantle residue from continent formation [McDonough, 1991].

Radiogenic isotope and trace element characteristics of HIMU lead to the suggestion that this component represents ancient basaltic oceanic crust subducted and imperfectly mixed into the mantle [Hofmann and White, 1982]. This mechanism of origin is shown most clearly by the radiogenic Pb and Os [Hauri and Hart, 1993; Reisberg *et al.*, 1993] defining HIMU coupled with the fact that certain trace element characteristics of HIMU, particularly Ba/Nb, Ce/Pb,

and Nb/U [Hofmann *et al.*, 1986; Weaver, 1991; Chauvel *et al.*, 1992], are within the range seen in all MORB but distinct from those of any continental material.

Both EM components have $^{143}\text{Nd}/^{144}\text{Nd}$ less than expected for a "chondritic" mantle. Thus both EM1 and EM2 have been enriched in incompatible elements over bulk silicate earth values at some stage in their evolution. Mechanisms proposed to explain this characteristic of the enriched end-members include mixing of subducted sediments with mantle peridotite [Hofmann and White, 1982] and intramantle metasomatism caused by the migration of small melt volumes in the mantle [Vollmer, 1983]. The EM2 component has fairly radiogenic Pb isotopic composition within the range of terrigenous sediments of continental origin [Zindler and Hart, 1986; Hart, 1988]. The EM1 component is less radiogenic in Pb but still within the range expected for old recycled pelagic sediments that are characterized by low U/Pb [Chauvel *et al.*, 1992]. Both EM components tend toward low, continental values of Nb/U and Ce/Pb [Devey *et al.*, 1990; Chauvel *et al.*, 1992], and both appear to have oxygen isotopic compositions ($\delta^{18}\text{O}$) slightly higher than found for MORB [Woodhead *et al.*, 1993]. While the Sr, Nd, and Pb isotopic compositions of the EM components could be explained by either sediment addition or mantle metasomatism, their high $\delta^{18}\text{O}$ and low Nb/U and Ce/Pb argue strongly in favor of a recycled sediment contribution.

Geographic Distributions

Within the general global occurrence of MORB derived from DMM sources, important chemical and isotopic variations can be observed at a variety of length scales. At the smallest scale, nearly the whole range in MORB chemical and isotopic composition has been observed over distances of tens of kilometers at fracture zones [Carlson *et al.*, 1978; Shirey *et al.*, 1987] and near-ridge seamounts [Zindler *et al.*, 1984]. Regions of the ocean ridge system, well displaced from hotspot influence, have been discovered that show the influence of the "enriched" components seen in OIB [Shirey *et al.*, 1987; Michael *et al.*, 1994]. The observations of chemical variability of MORB along normal ridge segments suggest a general "marble cake" style of chemical variation in the MORB mantle where small volumes of enriched material reside within a matrix of DMM [Allègre and Turcotte, 1986]. Along normal ridge segments, where melting, melt segregation, and magma chamber development may all serve to mix the melting products of enriched and DMM zones [Kenyon, 1990], relatively homogenous normal MORB is erupted. Where this melting and melt segregation regime is disturbed [Langmuir and Bender, 1984], such as at fracture zones and off the ridge axis, enriched veins may be sampled preferentially.

At larger spatial scales are the well-known zones, such as that south of Iceland [Schilling, 1973], of transitional chemical and isotopic composition where

"normal" ocean ridges approach hotspots. The most successful model explaining this scale of variation invokes a zone of mixing between DMM and enriched mantle components supplied to the hotspot by a mantle plume [Schilling, 1985]. Curiously, the gradual change in basalt isotopic and chemical characteristics observed south of Iceland is not symmetric about the hotspot. Basalts with typical DMM compositions occur immediately north of the Tjörnes fracture zone that forms the northern boundary of the Iceland Plateau [Mertz *et al.*, 1991]. This may reflect a southward directed flow of the plume material once it reaches the near surface [Mertz *et al.*, 1991]. Alternatively, this observation might provide information on the maximum size of the geochemical anomaly of the plume at depth. A chemical anomaly larger than the Iceland Plateau occurring below the flow perturbation caused, or reflected, by the Tjörnes fracture zone might be expected to be entrained in the flow to both sides of the fracture zone and thus appear in the volcanic products north of Iceland. A similar sharp break between geochemical "provinces" has been observed at the Australia–Antarctic discordance [Klein *et al.*, 1988] (Figure 12). In this case, rather than reflecting a plume boundary, the discordance may mark the upper mantle boundary separating convective flow in the sub-Pacific mantle from that in the geochemically distinctive Indian Ocean upper mantle [Klein *et al.*, 1988].

At still larger spatial scales is the distribution of enriched components at different hotspots and global-scale variations in MORB characteristics. With few but important exceptions, most ocean islands showing EM-type components occur in the southern hemisphere [Dupré and Allègre, 1983; Hart, 1984] (Figure 11). Similarly, MORB from the North Atlantic and from most of the East Pacific Rise are close in composition to end-member DMM, but South Atlantic MORB and particularly MORB from the Indian Ocean contain definite signatures of EM components. This band of enrichment in the southern hemisphere has been labeled the DUPAL anomaly [Hart, 1984].

Mixing Hierarchies

When viewed in multi-isotope space, the arrays defined by MORB and various ocean islands do not scatter randomly between the four-end-member components but tend to cluster along distinct two- and three-component mixtures involving different subsets of the components (Figure 11). Certain components commonly are coupled, which allows some sense of the order and degree to which these components are intermixed in the mantle. This "hierarchy" of mixing also provides input for geodynamic models of the processes of mixing and entrainment in both general convective and plume-specific flow in the mantle. S. R. Hart and coworkers [Hart *et al.*, 1986; Hart, 1988; Hart *et al.*, 1992] describe these features in great

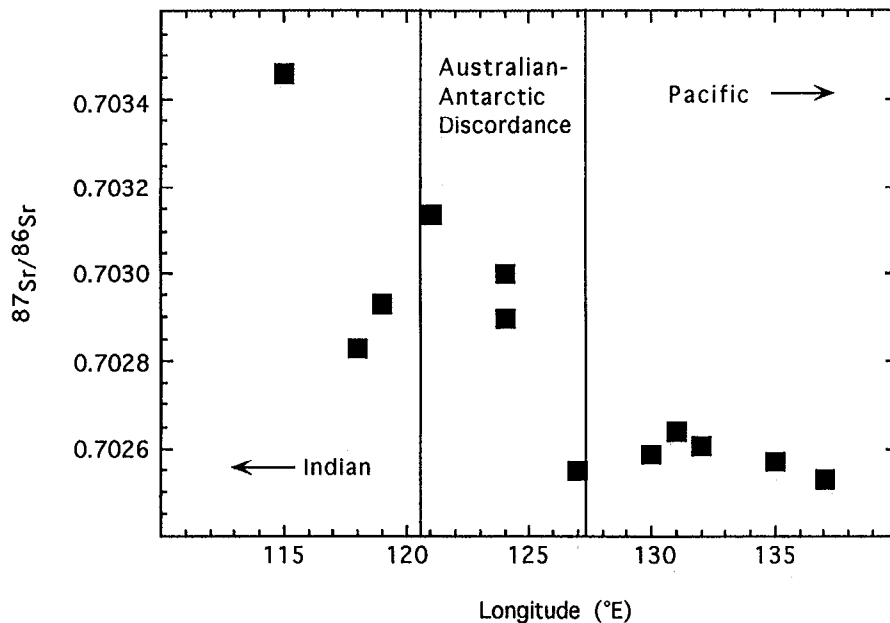


Figure 12. Sr isotopic variation across the Australian-Antarctic discordance showing the sharp boundary between the Pacific and Indian MORB chemical types. Figure redrawn from Klein *et al.* [1988].

detail, and most of the following discussion is derived from these studies.

MORB and several ocean islands fall on a DMM-HIMU connection without any indication of containing either EM component (Figure 11). Other islands emanate away from the DMM-HIMU trend in the direction of either EM1 or EM2. Of particular interest is that many of the mixing arrays emanate not from individual end-member components but from binary joins between two components [Hart *et al.*, 1986]. For example, several mixing arrays appear to point not directly toward DMM, but to a point on the DMM-HIMU join [Barling and Goldstein, 1990; Devey *et al.*, 1990] (Figure 11). This could reflect a “most common” mixture between DMM and HIMU that then mixes with enriched materials contributed from other regions in the mantle. Alternatively, the possibility exists for a discrete mantle component, called the “focus zone” (FOZO) of mixing arrays [Hart *et al.*, 1992], that lies wholly within the isotopic range described by DMM-HIMU-EM1-EM2. Data for southern hemisphere islands suggest a focus zone with $^{87}\text{Sr}/^{86}\text{Sr} \approx 0.7029$, $^{143}\text{Nd}/^{144}\text{Nd} \approx 0.5129$, $^{206}\text{Pb}/^{204}\text{Pb} \approx 19.5$. The northern hemisphere hotspots of Iceland and Hawaii suggest an isotopic focus zone with Pb isotopic composition ($^{206}\text{Pb}/^{204}\text{Pb} \approx 18.4$) within the DMM range (Figure 11a).

Ocean island basalts lying on mixing trajectories heading toward FOZO appear to have increasing $^3\text{He}/^4\text{He}$ in the direction of FOZO [Hart *et al.*, 1992; Graham *et al.*, 1993], although this observation is not universally accepted [Farley and Craig, 1992] primarily because of the limited number of He data for samples where Sr, Nd, and Pb isotopic compositions also have been measured. If valid, this observation would lend more credence to the idea that FOZO

indeed is a discrete component in the mantle and one that has not experienced the same degree of outgassing as have other mantle components. The radiogenic Nd and Pb and unradiogenic Sr of FOZO indicate that this component cannot be undifferentiated mantle, but the high $^3\text{He}/^4\text{He}$ is suggestive of a deep, nonrecycled, source for FOZO.

STRUCTURE OF CHEMICAL HETEROGENEITY

The limited occurrence of true DMM as a mixing end-member, and the almost complete lack of evidence for a “primordial” mantle component in the isotopic mixing arrays of ocean islands conflicts with the simple model of chemical variation in the mantle where an upper mantle of DMM composition overlies an undepleted, “primordial” lower mantle [Wasserburg and DePaolo, 1979]. Indeed, the limited occurrence of DMM in ocean island basalts, yet its ubiquitous occurrence along the global ocean ridge system poses an interesting question for mantle geodynamics. Where can the large-volume, globally distributed DMM source reside in the mantle and yet not be entrained as a mixing component in plumes supplying ocean island volcanism?

Most models conclude that DMM occupies the whole of the upper mantle. The minimum volume of the MORB reservoir is constrained by the volume of mantle that must have been depleted in incompatible elements to produce the continental crust [Jacobsen and Wasserburg, 1979; O’Nions *et al.*, 1979; Allègre *et al.*, 1983b, c]. Arguments for this placement include the observation that DMM MORB basalts appear wherever there is passive rifting of oceanic plates and continue to be the prime magmatic component even

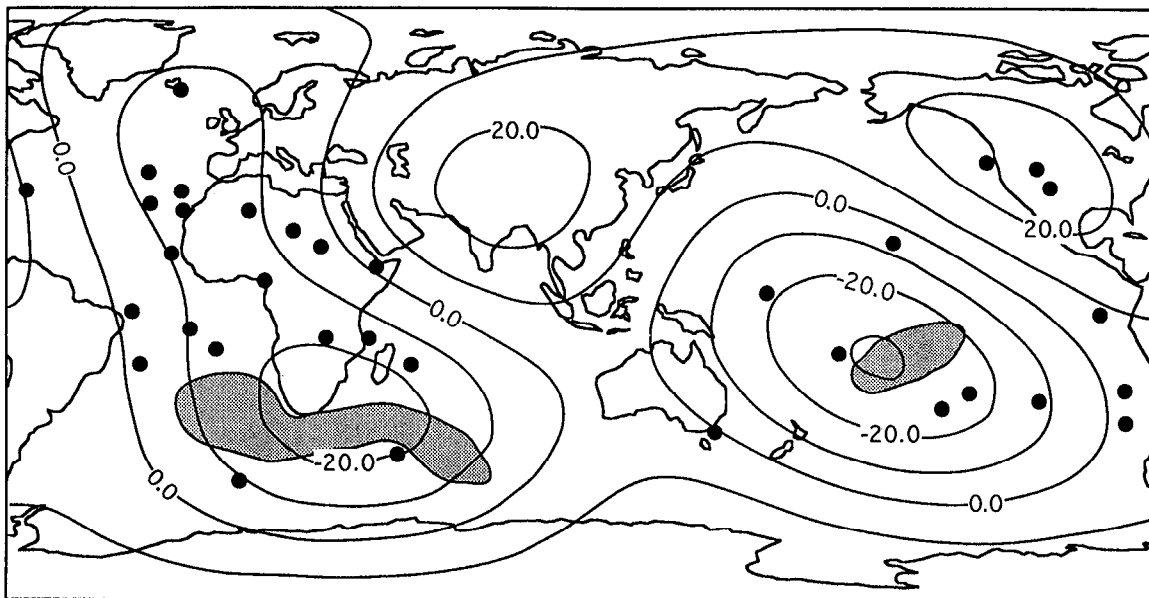


Figure 13. Contours of average lower mantle seismic velocity perturbations compared to location of hotspots (solid circles) and regions of DUPAL isotopic anomaly (shaded areas). Both DUPAL and hotspots tend to cluster in areas of slow seismic velocity in the lower mantle. Figure redrawn from *Castillo* [1988].

when ocean ridges “jump” considerable distances and reinitiate spreading in a new location. End-member DMM is rare to nonexistent in continental rift basalts, but volcanism on continents is susceptible to contamination from the continental lithospheric mantle and crust [Carlson, 1991]. When continental rifts develop to the point of becoming recognizable ocean basins, even as small as the Red Sea, DMM becomes the primary contributor to rift volcanism.

As seems typical of mantle structure models developed on the basis of geochemical arguments, both shallow and deep origins have been proposed for the DUPAL clustering of EM components in the southern hemisphere. The deep origin arguments note that the zones of maximum expression of the DUPAL anomaly correlate best with seismic wave velocity profiles just above the D'' layer at the base of the mantle [Castillo, 1988; Hart, 1988] (Figure 13). Hotspots are concentrated, and DUPAL maxima occur, over the seismically slowest portions of the lower mantle, suggesting that DUPAL is an expression of material rising in plumes originating at the core-mantle boundary. One of two occurrences of EM components in the northern hemisphere, the Azores hotspot, also occurs above a seismically slow patch at the D'' layer [Castillo, 1988]. Hawaii, the other occurrence of EM components in the northern hemisphere, is not situated above anomalously slow D'' mantle.

Another line of evidence for a core-mantle boundary source for plumes comes from a correlation of enhanced plume activity with characteristics of the Earth's magnetic field. Enhanced hotspot volcanic ac-

tivity may occur preferentially during “normal” polarity epochs [Moberly and Campbell, 1984], and periods of decreased pole reversal frequency seem to accompany major flood basalt events [Larson, 1991]. Flood basalts may reflect the arrival of plumes at the Earth's surface [Richards *et al.*, 1989; Campbell and Griffiths, 1990]. Correlation of plume activity with magnetic field reversals implies that heat transfer across the core-mantle boundary initiates a mantle plume and simultaneously alters the pattern of convective flow in the outer core thereby affecting magnetic field generation.

Arguments for a shallow origin for DUPAL point out that DUPAL maxima occur over zones of extensive Mesozoic subduction around Pangea [Anderson, 1982]. The spatial relation of DUPAL to subduction coupled with the observation that the EM components that define DUPAL may be subducted sediments [White, 1985; Weaver, 1991; Chauvel *et al.*, 1992] lend strength to the idea that DUPAL is a shallow feature that reflects contamination of the upper mantle by materials derived from subducting plates. If the DUPAL concentration of EM components originated at the core-mantle boundary, the EM components might be expected to show evidence of chemical interaction with the core. They do not [Newsom *et al.*, 1986; Jochum *et al.*, 1993].

A shallow origin for DUPAL gains additional strength from the observation that intraoceanic island arcs and back arc basins of the western Pacific also show a general enrichment in EM components on going from the northern hemisphere into the zone of

DUPAL maxima in the southwestern Pacific [*Stern*, 1982]. Identification of the mantle contribution to arc and back arc rocks always is complicated by the degree to which recently subducted material has affected the chemical and isotopic characteristics of these lavas. Nevertheless, there is no clear reason to expect a hemispherical variation in this parameter. Consequently, since the ultimate mantle source of arc magmas clearly must be the shallow upper mantle, and the source of back arc magmas probably is in the upper mantle, the fact that the DUPAL signature also is recorded in arcs and back arcs of the western Pacific suggests that DUPAL is indeed a feature of the chemical variation of the upper mantle.

An alternate arrangement of mantle components, promoted primarily by *Anderson* [1979, 1981], has DMM residing in the transition zone (400-km to 670-km depth) beneath a peridotitic upper mantle. In this model, the mixing hierarchies described above could be satisfied if ocean island basalt sources were in an upper mantle that consisted of "plum pudding" composed of a matrix of incompatible element depleted peridotite very slightly contaminated by high $^3\text{He}/^4\text{He}$ and radiogenic Pb from subducted sediment, the mixture comprising the FOZO component. The "plums" would represent contributions from various subducted materials (basaltic oceanic crust, HIMU; terrigenous sediment, EM2; continental lithospheric mantle or pelagic sediment, EM1). DMM thus would not be an important contributor to ocean island basalt mixing arrays. This model obviously conflicts with the evidence discussed above for placing DMM in the upper mantle and enriched hotspot components in the lower mantle. However, the recognition of FOZO, its importance as a mixing component in ocean island arrays, and the consequent removal of both "primordial undifferentiated" mantle and true DMM as components in most ocean island basalts provides a critical, as yet unsolved, problem in the dynamics of mantle mixing for models invoking plume penetration of an upper mantle dominated by DMM.

Given the current evidence, and this opportunity to present a personal opinion on the evidence, the most significant chemical signatures recorded in the mantle are the complementary relationships between incompatible element enrichment of the continental crust, the presumed siderophile element enrichment of the core, and the corresponding depletion of these elements in the mantle source of MORB. Thus the prime events affecting compositional variation in the solid Earth are early core formation followed by gradual segregation of continental crust to leave the mantle slightly depleted in incompatible elements. The "recycled" nature of all other mantle components expressed in OIB, with the possible exception of FOZO, reflects imperfections in the operation of the plate tectonic cycle in that these materials are subducted crustal materials that have not yet been sufficiently remixed

into the mantle to destroy their chemical and isotopic signature of crustal residence. Evidence, from geochemical arguments, for major chemical layering in the mantle is sketchy and equivocal. The data do not exclude chemical layering but require that the degree of convective isolation of the layers, if they exist, is sufficient to mask the contribution of chemically distinct material to surface volcanism. The nonrandom occurrence of "enriched" mantle, primarily in OIB volcanism, suggests some organization to the distribution of subducted crustal materials in the mantle. Whether this requires the different chemical components to be segregated into layers or reflects long-term organization of mantle convective patterns is unclear. An answer to this question remains a fundamental goal of mantle chemical geodynamics.

FUTURE PROSPECTS

Of particular importance in the near future will be further documentation of the validity of FOZO. Clear identification of FOZO requires complete isotopic data sets for mantle-derived rocks, since FOZO overlaps DMM in Sr and Nd isotopic composition and is distinguished only by its combination of unradiogenic Sr, radiogenic Nd, moderately radiogenic Pb, and perhaps high $^3\text{He}/^4\text{He}$. Additional measurements of rare gas isotopic composition in concert with Sr, Nd, and Pb isotopic composition and complete trace element analyses on the same samples will provide a better understanding of the degree to which rare gas and lithophile element variation are correlated in the mantle. In turn, this will help to further define the origin of the variety of chemical components observed in the mantle. Continued mapping of the geographic variation of these components may serve to better define their relative and absolute positions in the mantle as well as the mantle dynamics that cause the intermixture of components. Together with improved observational data of the mantle from seismology, a better understanding from mineral physics of the physical properties of earth materials at lower mantle pressures and temperatures, and the effectiveness of mixing caused by mantle convection, the geochemical characteristics of mantle-derived rocks can serve to define the chemical structure of the mantle and the nature of mantle dynamics.

APPENDIX

Tracing the Effects of Chemical Fractionation

Compositional variation within a planet arises because the crystalline, liquid, or gaseous phases present under varying pressure and temperature conditions preferentially include or exclude elements depending on the chemical behavior, ionic radius, and/or ioniza-

tion state of the element. When these phases separate from one another, for example by melt migration or degassing to the atmosphere, a chemical signature is imparted to both residue and product that can be used to decipher the nature of the event that caused the differentiation.

Consequently, the abundance patterns of elements in rocks, ocean water, or the atmosphere indicate the processes that were involved in their formation and in the formation and evolution of their host planet. These processes can include element transfer into the atmosphere because of the volatility of an element, or complete loss of that element from the planet either by direct loss to space from the top of the atmosphere or by noncondensation of the element from the solar nebula into the materials that accumulate to form the planet. The latter possibility is the most likely explanation for the lack of H- and He-dominated atmospheres on the terrestrial planets compared to the Jovian planets and also may explain the observed depletion of the Earth in moderately volatile elements like Na, K, Rb, Cl, Br, Zn, Pb, and F. The Moon often is referred to as volatile depleted compared to the Earth. This can be seen in the element abundance patterns shown in Figure 2b by the ubiquitous deficiency in volatile Rb compared to refractory Th in lunar rocks when normalized to primitive terrestrial mantle abundances. Segregation of a Fe core from a silicate mantle is another process that leaves behind a clear chemical signature in the residual mantle (Figure 4) of depletion in siderophile (preferentially partition into metal) and chalcophile (partition into sulfides) elements such as Fe, Ni, Co, Cu, Ga, P, Sn, W, Pb, and particularly the platinum group elements Pt, Pd, Ir, Au, Re, and Os.

The so-called incompatible, or lithophile, elements are those elements that preferentially partition into melts because they do not fit well into the crystal structures of the minerals that remain unmelted. Incompatible elements include the large-ion lithophile (LIL) elements like K, Rb, Cs, U, Th, Sr, Ba; the light rare earth elements (REE) like La, Ce, and Nd; and the high field strength elements (HFSE) that have high ionic charge, e.g., Nb, Ta, Zr, Hf, and Ti.

The compatibility or incompatibility of an element depends on the phases that are present during melting. For example, while the HFSE are incompatible during melting of an olivine + pyroxene lherzolite, if a phase such as rutile that concentrates HFSE is present, the HFSE may well stay with the melting residue. Similarly, chalcophile or siderophile elements will behave compatibly (i.e., preferentially concentrate in the residue of melting) when melting a source containing metal or sulfide but may be incompatible when no such phases are present. Crystallization of any particular phase will leave the residual liquid enriched or depleted in an element depending on whether or not the element is concentrated in the crystallizing mineral.

Thus crystallization of olivine from a mantle melt will cause the Mg and Ni content of the liquid to decrease because these elements are particularly concentrated in olivine. In this manner, each mineral that forms and fractionates during melt production, or crystallization of magma, will leave a chemical fingerprint in a differentiated melt or residue of melting.

Element concentrations in rocks often are shown as diagrams listing the elements according to some measure of their incompatibility (e.g., Figures 2 and 8), siderophility (Figure 3), or volatility to emphasize the process controlling the elemental fractionations observed in the sample. The element abundances are further normalized to the concentrations in some reference material such as a model of the "primitive mantle" or average mid-ocean ridge basalt (MORB) mantle composition. The element order shown in Figures 2 and 8 derives from the studies of A. W. Hofmann and coworkers [Hofmann, 1988] where the relative incompatibility of elements during the melting processes that created MORB and ocean island basalts were determined. If similar processes controlled all element partitioning on Earth, then the patterns shown on normalized incompatible element concentration diagrams like Figures 2 and 8 should be smooth and vary in curvature primarily as a function of the degree of partial melting. The fact that there are notable spikes in these figures, for example, the excess of Pb in the continental crust and the corresponding deficiency of Pb in the source of MORB (Figure 2a), indicates that the distribution of Pb between continent and oceanic mantle is controlled by processes other than melting at ocean ridges and oceanic hotspots. The clear candidate is melting in convergent margins, where the additional influence of fluids and subducted sediments is involved. Similarly, the large negative abundance anomalies in potassium, rare earth element, and phosphorous-rich (KREEP) lunar basalt (Figure 2b) suggest the removal of a mineral that preferentially concentrates these elements. This mineral is plagioclase.

Chemical Variability as Recorded in Radiometric Isotope Systems

The compositional changes that take place during planet formation, core segregation, or partial melting also affect the relative abundances of parent (radioactive) and daughter (stable decay product) elements in the radioactive decay systems. Thus any chemical process that fractionates U from Pb will result in a changing rate of growth of ^{207}Pb (from ^{235}U decay) and ^{206}Pb (from ^{238}U decay) compared to an unfractionated reservoir. If the chemical change occurs during a recent event, such as partial melting just prior to eruption of a lava, there will not be sufficient time for that lava to evolve a Pb isotopic composition distinct from its source material reflecting its new U/Pb. If the fractionation of U/Pb occurred sufficiently long ago, the change in U/Pb will result in a measurable difference

between the Pb isotopic composition of the melt and its source. This is the basis for the technique of radiometric age dating. However, whereas an isochron determined by isotopic measurements of minerals separated from a single rock dates the time of crystallization of the rock, isotopic variation in larger reservoirs within the Earth (e.g., continents versus oceanic mantle, Earth versus Moon, etc.) in principle can be used to date the time of chemical fractionation between these reservoirs [Faure, 1986]. In practice, this technique is compromised by multiple differentiation events and mixing between reservoirs, but no other technique provides time information comparable to radiogenic isotope systematics, and many first-order conclusions can be drawn from isotopic variation of He, Sr, Nd, Hf, Os, and Pb.

For radioactive systems based on refractory lithophile elements like the ^{147}Sm - ^{143}Nd and ^{176}Lu - ^{176}Hf systems, the undifferentiated bulk earth most likely has near-chondritic Sm/Nd and Lu/Hf because the abundance distribution of these elements will not be affected by volatile loss or core formation. Thus, undifferentiated earth materials today will have Nd and Hf isotopic compositions indistinguishable from chondrites. Processes that enrich incompatible elements will lower the Sm/Nd and Lu/Hf of the affected material because Nd and Hf are the more incompatible elements of these pairs. Over time, this will cause these enriched materials to become displaced toward lower $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$. To simplify presentation of these isotopic shifts, isotopic ratios of Nd and Hf in a sample often are normalized by dividing by the isotopic composition of an estimate of "average" chondrite, subtracting 1, and then multiplying by 10,000. The resulting relative difference, expressed as epsilon (ϵ), is then positive for those materials with $^{143}\text{Nd}/^{144}\text{Nd}$ or $^{176}\text{Hf}/^{177}\text{Hf}$ greater than chondritic and negative for those samples less than chondritic.

Because of the relative incompatibilities of Sm versus Nd and Lu versus Hf, positive ϵ_{Nd} and ϵ_{Hf} indicate long-term incompatible element depletion, while negative ϵ_{Nd} and ϵ_{Hf} signify incompatible element enrichment compared to "undifferentiated" material. This is illustrated in Figure 2a where the incompatible element enriched continental crust can be seen to evolve to negative ϵ_{Nd} with time while the incompatible element depleted source of MORB has evolved to positive ϵ_{Nd} . The general characteristics of the Nd isotopic differences between continent and MORB mantle are exactly what would be expected given the relative incompatible element abundances of these two reservoirs. The magnitude of the isotopic effects further indicates that the chemical differences between MORB mantle and continental crust have existed for at least a billion years, but not necessarily more than a couple of billion years because the trajectories of Nd isotope evolution cross that of undifferentiated mantle ($\epsilon_{\text{Nd}} = 0$) in the 1- to 3-Ga time interval. In contrast,

high-Ti mare basalts and KREEP have complementary Nd isotope evolution paths (Figure 2b) in accordance with their respective light rare earth element (LREE) depletion and enrichment, but the isotopic evolution lines of both high-Ti and KREEP basalt cross that of the undifferentiated Moon between 4.35 and 4.5 Ga, indicating the antiquity of the chemical differentiation between the sources of these two basalt types.

Other radiometric systems in common use involve at least one element of the pair that will be affected by volatile loss or core formation. Helium is a noble gas and hence extremely volatile, Rb and Pb are both moderately volatile, and Pb is chalcophile. Consequently, the Rb/Sr of the bulk earth is much lower and the U/He, Th/He, U/Pb, and Th/Pb of the Earth are much higher than solar values. Re and Os are both highly siderophile. While both are depleted in abundance in the mantle compared to chondrites, the Re/Os ratio of the mantle appears to be close to chondritic, the significance of which is discussed in the text. Thus in principle, the Rb-Sr, U-Th-Pb-He, and Re-Os decay systems can be used to investigate the timing of condensation of the parental materials of the Earth and core formation in addition to the effects of melting-induced chemical differentiation of the planet. The combined use of all of these systems on the same rock samples takes advantage of the differing chemical behavior of the elements involved and provides more definitive information on the nature of the processes involved in Earth differentiation.

ACKNOWLEDGMENTS Two anonymous reviewers provided highly detailed and constructive reviews that (hopefully) significantly improved the scope and accuracy of this manuscript and from which I personally learned much. I thank these reviewers for their detailed reading of this rather long and winding contribution. Stan Hart allowed use of his complete MORB-OIB isotope data file for which I am grateful.

Thomas Torgersen was the editor responsible for this paper. He wishes to thank two anonymous technical reviewers and one anonymous cross-disciplinary referee.

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