The Geological Society of America
Special Paper 440
2008

A review of the isotopic and trace element evidence for mantle and crustal processes in the Hadean and Archean: Implications for the onset of plate tectonic subduction

Steven B. Shirey*
Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road NW, Washington, D.C. 20015, USA

Balz S. Kamber*
Department of Earth Sciences, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

Martin J. Whitehouse*
Laboratory for Isotope Geology, Swedish Museum of Natural History, Box 50007, Stockholm S-105 05, Sweden

Paul A. Mueller*
Department of Geological Sciences, Box 112120-241, Williamson Hall, University of Florida, Gainesville, Florida 32611, USA

Asish R. Basu*
Earth and Environmental Sciences, 227 Hutchinson Hall, University of Rochester, Rochester, New York 14627, USA

ABSTRACT

Considerable geochemical evidence supports initiation of plate tectonics on Earth shortly after the end of the Hadean. Nb/Th and Th/U of mafic-ultramafic rocks from the depleted upper mantle began to change from 7 to 18.2 and 4.2 to 2.6 (respectively) at 3.6 Ga. This signals the appearance of subduction-altered slabs in general mantle circulation from subduction initiated by 3.9 Ga. Juvenile crustal rocks began to show derivation from progressively depleted mantle with typical igneous ε_{Nd}:ε_{Hf} = 1:2 after 3.6 Ga. Cratons with stable mantle keels that have subduction imprints began to appear by at least 3.5 Ga. These changes all suggest that extraction of continental crust by plate tectonic processes was progressively depleting the mantle from 3.6 Ga onwards. Neoarchean subduction appears largely analogous to present subduction except in being able to produce large cratons with thick mantle keels. The earliest Eoarchean juvenile rocks and Hadean zircons have isotopic compositions that reflect the integrated effects of separation of an early enriched reservoir and fractionation of Ca-silicate and Mg-silicate perovskite from the terrestrial magma oceans associated with Earth accretion and Moon formation, superposed on subsequent crustal processes. Hadean zircons most likely were derived from a continent-absent, mafic to ultramafic protocrust that was

*Corresponding author, Shirey: shirey@dtm.ciw.edu; Kamber: bkamber@laurentian.ca; Whitehouse: martin.whitehouse@nrm.se; Mueller: mueller@geology.ufl.edu; Basu: abasu@earth.rochester.edu

Shirey, S.B., Kamber, B.S., Whitehouse, M.J., Mueller, P.A., and Basu, A.R., 2008, A review of the isotopic and trace element evidence for mantle and crustal processes in the Hadean and Archean: Implications for the onset of plate tectonic subduction, *in* Condie, K.C., and Pease, V., eds., When Did Plate Tectonics Begin on Planet Earth?: Geological Society of America Special Paper 440, p. 1–29, doi: 10.1130/2008.2440(01). For permission to copy, contact editing@geosociety.org.

multiply remelted between 4.4 and 4.0 Ga under wet conditions to produce evolved felsic rocks. If the protocrust was produced by global mantle overturn at ca. 4.4 Ga, then the transition to plate tectonics resulted from radioactive decay-driven mantle heating. Alternatively, if the protocrust was produced by typical mantle convection, then the transition to plate tectonics resulted from cooling to the extent that large lithospheric plates stabilized.

Keywords: subduction, plate tectonics, mantle, crust, Hadean, Archean, radiogenic isotopes.

INTRODUCTION

The surface of Earth is composed of geodynamically stable continental cratons, orogenically active continental and oceanic margins, and freshly created ocean floor that compositionally reflects 4.5 billion years of geological evolution. While present plate tectonic processes (summed up as the "Wilson cycle"), driven by subduction and its consequent return flow, adequately explain much of the surface topography and composition of the crust and lithosphere, it is not known how plate tectonics in the Precambrian was different from today or even whether a particular time in Earth's geological history can be recognized as the time when plate tectonics started in its present form. The oceanic sedimentary record, the location of earthquake foci, and magnetic anomaly patterns on the ocean floor are the key evidence that show how plate tectonics operates today. The pre-Mesozoic record has been fragmentally compressed into the continents or reassimilated in to the mantle and is lost to simple, direct inspection or measurement. The isotope geochemistry of old continental and young oceanic rocks, however, can provide insight into the record of global lithospheric recycling in a manner that, if consistent with slab subduction and plume/ridge return flow, could reveal when plate tectonics began. Even for data obtained on recent igneous rocks, this isotopic record appears to date from earliest Earth history as a consequence of the continuity of Earth's tectonic activity, its global extent, and the ongoing nature of crustal differentiation. While these isotopic data will not directly correlate spatially with plate boundaries, they will record the time-integrated geochemical effects of plate tectonic processes. This manuscript reviews chiefly the isotopic evidence plus some supporting trace element evidence that relate specifically to the onset of plate tectonics on Earth.

EVIDENCE FOR PLATE TECTONICS FROM CRUST-MANTLE RECYCLING AND MANTLE DEPLETION

Mantle Heterogeneity and Its Implications for Early Earth

Melting at the linear volcanic chains that form at mid-ocean ridges and at the central volcanic complexes of oceanic islands provides a geochemical probe of upper-mantle and in some cases lower-mantle compositions. Radiogenic isotopic data of Pb and Sr for these zero-age basalts have long been known to display isotopic variations (heterogeneity) that can only be explained by isolation of their mantle sources for hundreds of millions to several billion years (e.g., Gast et al., 1964; Sun and Hanson, 1975a, 1975b; Sun, 1980). In the 1980s these variations were systematized into end-member mantle components or reservoirs (e.g., EMI, EMII, HIMU, DMM, FOZO; see Hofmann, 1997, 2003, for more recent reviews) to express their geochemical similarities and thus the combined petrogenetic histories of portions of mantle (e.g., Zindler and Hart, 1986). Implicit in these isotopic mantle reservoirs was the recycling of surface materials: pelagic sediments to explain EMI, continental sediments to explain EMII, and altered oceanic crust to explain HIMU (Hofmann and White, 1982; White and Hofmann, 1982; Zindler and Hart, 1986). Concurrently it was recognized that oceanic mantle isotopic compositions represented by both mid-ocean ridges and ocean islands are not truly randomly distributed geographically (Hart, 1984; Hawkesworth et al., 1986; Shirey et al., 1987) and in some cases define patterns that can be related to the opening of ocean basins and the movement of continental terranes with their attendant mantle keels (Hawkesworth et al., 1986; Luais and Hawkesworth, 2002). Continuing efforts have served to refine the identity of the end members by adding new isotopic systems (Hf and Os; Salters and Hart, 1991; Hauri and Hart, 1993), to clarify the extent of the compositional effects by pairing them with trace element and stable isotopic data (e.g., O; Eiler et al., 2000) and to better define the petrology of the recycled materials by using major elements (high-silica components; Hauri, 1996). The most viable current model to explain mantle heterogeneity focuses on the erosion of ancient continental mantle keel components and the subduction of oceanic lithosphere with its included volatiles, sediments, and seawater-altered peridotite and basalt. The basic subduction aspects of this geochemical model were presciently advocated by Ringwood (1991). More recent geophysical studies using tomographic inversion and shear wave splitting basically corroborate all aspects of this model: slab subduction into and through the transition zone (van der Hilst et al., 1997), deep-seated return flow in plumes (Montelli et al., 2004), and sublithospheric flow directed around mantle keels (Behn et al., 2004).

The isotopic expression of these processes is perhaps best illustrated using the Pb isotopic compositions of mid-oceanic-ridge and oceanic-island basalts (Fig. 1). The Pb paradoxes presented by these data have been discussed by numerous authors (e.g., Hofmann, 2003; Hart and Gaetani, 2006) and are not the

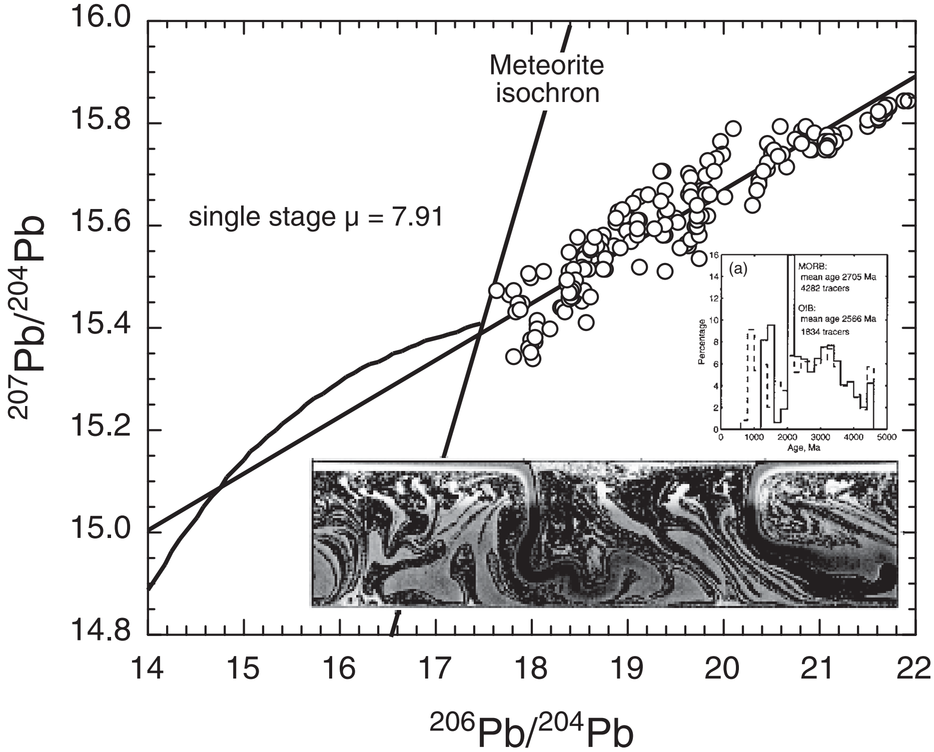

Figure 1. Representative worldwide ocean island basalt (OIB) common Pb isotope compositions (compilation of Murphy et al., 2003) relative to the positions of the meteorite isochron and a single-stage mantle evolution curve ($\mu = 7.91$). Note that a regression line through the OIB array has a slope corresponding to ca. 1.6–2.0 Ga and also intersects the single-stage growth curve at a similar date. Convection model after Davies (2002) in insets shows how old tracers would be distributed in the convecting upper mantle that will be sampled by MORB and OIB and could explain Mesoproterozoic ages.

subject of discussion here. What is of importance is the average 2 Ga slope of the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ array and the scatter of data within the array. This array represents the mixing of the many isolated mantle sources that were melted to generate these oceanic basalts. The parent radionuclide of ^{207}Pb, ^{235}U, has a short enough half-life that by 1.5 billion years ago roughly 75% of it had decayed. Thus, the bulk slope of the oceanic array and higher-angle excursions of subsets of data above this array have long been interpreted as reflecting a mixing history with portions of the mantle that inherited U/Pb variations from before the earliest Mesoproterozoic when more ^{235}U was actively decaying. Because the *average* slope of this array is Paleoproterozoic and because the array was at least partially derived from mantle sources with geologically recently established U/Pb variations (which are only capable of affecting $^{206}Pb/^{204}Pb$ variability), then it is most probable that these trends reflect mixing of end members of Mesoarchean, Eoarchean, or perhaps even Hadean ages. (Note that the International Commission on Stratigraphy [ICS] has revised the boundaries and nomenclature of the Precambrian to be Eoarchean >3600 Ma, Paleoarchean 3200–3600 Ma, Mesoarchean 2800–3200 Ma, Neoarchean 2500–2800 Ma, Paleoproterozoic 1600–2500 Ma, Mesoproterozoic 1000–1600 Ma, and Neoproterozoic 542–1000 Ma. See Gradstein et al., 2005. The term Hadean was left undefined but is widely accepted to refer to the time before Earth's oldest rocks, ca. >4000 Ma.)

The continents, though, provide a ready storehouse of Paleoarchean to Neoarchean material that could be recycled as sediment, and for this reason, there is always potential for recent incorporation of ancient, isolated continental crust or ancient incorporation of juvenile continental crust as the old mixing end members of the oceanic array. Detailed studies of the trace element and isotopic composition of oceanic basalts have shown though that continental material only appears in the EM signature found in a few oceanic-island basalts and some Indian Ocean MORBs (mid-oceanic-ridge basalts) (Hofmann, 1997, 2003; Rehkamper and Hofmann, 1997; Sims and DePaolo, 1997). Therefore, the chief cause of the apparent ancient ages on the Pb isotope array of oceanic basalts must be the recycling of altered oceanic lithosphere (and perhaps to a lesser degree, some continental lithosphere) into the upper mantle beginning at least in the Neoarchean to Paleoproterozoic. For these components, radiogenic ingrowth occurs during residence in the upper mantle before they are returned nearer to the surface to be sampled in the mantle sources of ocean islands and, in more diluted fashion, ocean ridges.

Geodynamic Aspects of Recycling

Accepting from the modern evidence in oceanic basalts that oceanic lithosphere recycling occurs and that it can carry older components at least to the transition zone, it is important for the question of plate tectonic initiation to understand just when in the Proterozoic, Archean, or Hadean recycling of the oceanic lithosphere started. The effect of this process over time is to produce a "marble-cake" mantle (Allegre and Turcotte, 1986), an idea that can be traced through the literature in discussions of veined oceanic mantle (Sun and Hanson, 1975b; Hanson, 1977), pyroxenite veins in orogenic lherzolite and harzburgite (Allegre and Turcotte, 1986), and the pyroxenitic-eclogitic component in oceanic-island basalts (Hirschmann and Stolper, 1996; Kogiso et al., 2003; Sobolev et al., 2005). Note, however, that in most samples of veined mantle, the veins have been interpreted as melt, not stretched lithosphere (e.g., Bodinier and Godard, 2003). Nonetheless, pyroxenitic components are thought to be ubiquitously distributed and are preferentially sampled by melting at low extents as shown by studies of posterosional volcanism at hot spots, off-axis seamounts (Zindler et al., 1984), and magmatism at propagating rifts.

Mantle convection calculations (Christensen and Hofmann, 1994; Davies, 2002; Huang and Davies, 2007) show that a small percentage of tracers as old as 3.6–4 Ga, when introduced from the top, do survive whole-mantle convection for nearly the age of Earth (Fig. 1, insets). These models roughly reproduce a Paleoproterozoic Pb-Pb age for the oceanic array, albeit one that can be too old to match its true 1.8 Ga age without starting the process later (Christensen and Hofmann, 1994; Davies, 2002) or reducing lower mantle viscosity (Davies, 2002). Recent three-dimensional models that involve rapid early mantle overturn, and that can be scaled to Earth, more closely approximate the 1.8 Ga age (Huang and Davies, 2007). Thus, the Pb-Pb array for modern oceanic rocks, the prime example of mantle heterogeneity, is consistent with recycling of oceanic lithosphere back into mantle convective flow by some mechanism perhaps as early as the Eoarchean. This process could be plate subduction, but the geochemical effects of recycling do not unambiguously demand this. Note, though, that this evidence is independent of the subduction signatures seen within continental rocks themselves, as discussed below.

The current mode by which Earth releases 90% of its deep-seated internal heat (from accretion, inner core crystallization, and radioactive decay) is through mantle convection coupled to hydrothermal circulation at the ocean ridges (Davies, 1999). Continents provide 24% of the surface heat, but this comes chiefly from decay of radionuclides in the crust. Only 12% of Earth's heat emanates from the lithospheric mantle beneath the continents because the lithospheric mantle has low heat production and it must move by conduction. So the effect of continents is to insulate the asthenospheric mantle beneath them (Gurnis, 1988; Lowman and Jarvis, 1999) and to limit the surface area over which the oceanic convective + hydrothermal heat-loss engine can operate. Recent work on the interaction of conduction and convection between ocean basins and continents (Lenardic et al., 2005; Lenardic, 2006) extrapolates these processes back through the Eoarchean and does not preclude extension into the Hadean. The percentage of surface area covered by continental crust had a minimal effect on global mantle heat flow and perhaps even contributed to its increase (Lenardic et al., 2005). Raising the internal temperature of the mantle with insulating continents would have increased convective velocities in the whole mantle because of the mantle's temperature-dependent viscosity. Earth's mantle is near its solidus, and too much early continental area would have triggered widespread mantle melting in the Eoarchean, for which there is no direct evidence (Lenardic, 2006). Thus, Lenardic et al. (2005) concludes that progressive growth of the continental crust (McCulloch and Bennett, 1994; Kramers and Tolstikhin, 1997; Collerson and Kamber, 1999) offers a better explanation for the heat loss mechanisms of the mantle through time than does the early formation of areally extensive early continental crust.

A corollary of the above arguments is that an oceanic-lithospheric, mantle-convective heat loss model may have been as applicable to the convecting mantle on early Earth as it is to today's mantle. Although the nature of convection in the Hadean is poorly understood (van Hunen et al., this volume) and depends critically on the heat distribution of Earth (e.g., whether there was a mantle overturn after the magma ocean that was generated by a Mars-sized impact; see Kamber, 2007; Kramers, 2007; and discussion below), the Eoarchean mantle would have eventually started to convect. When it did, the early existence of a global ocean (Marty and Yokochi, 2006; Kramers, 2007) means that heat transfer by hydrothermal circulation would have been as important then as it is today if not more so. It would have accompanied oceanic volcanism, and it would have altered the composition of oceanic lithosphere, which was likely to have been mostly composed of harzburgite, komatiite, and basalt (Takahashi and Brearley, 1990). It also would have been available for lowering the solidus of altered komatiite and basalt and for recycling into melting mantle sources. What is typically expected to have been different on Eoarchean to Hadean Earth was a hotter mantle, an atmosphere that was less oxidizing, and lithosphere that was bombarded more frequently by meteorites. A hotter mantle existed in the Archean because Earth is now and was then cooling, radioactive decay produced more heat in the past (Davies, 1999), and komatiite petrogenesis supports higher temperatures estimated to range from 100 °C (Grove and Parman, 2004) to 300 °C (Nisbet et al., 1993) hotter depending on source water content (Arndt et al., 1998). The atmosphere was less oxidizing because there is clear evidence for a rise in the oxygen content in the Proterozoic (e.g., Bekker et al., 2004). Meteorite bombardment was more frequent as shown by the lunar cratering record (e.g., Koeberl, 2006).

Another major difference expected between the Archean and younger Earth models would be the lack of topographically emergent stable continents of sizeable area because such continental masses only could have been preserved when they were developed concomitantly with thick, stable, depleted keels. Without extensive early sizeable continents then, the question of when plate tectonics started on Earth and its form can be reduced to the question of how the different conditions affected whether the style of lithosphere creation was at ridges and whether its destruction was in subduction zones or whether other geometries would be viable. While the isotopic data cannot directly constrain the tectonic form of oceanic lithosphere creation and destruction in the Eoarchean and Hadean, this paper will evaluate whether it is consistent with a plate tectonic mode for the oceanic regime. Since, in the absence of continents, an early basalt-capped, oceanic lithosphere would have entirely covered Earth, its stability and longevity become important considerations (see discussion below). Rheological modeling (Korenaga, 2006) and Pb isotopic data on the oldest sediments derived from basaltic precursors (Kamber, 2007) support a stable, near-surface, long-lived reservoir of basalt. The need to release Earth's heat by convection with hydrothermal circulation (Lenardic, 2006), however, seems critically limited by a stable, early depleted oceanic lithosphere (Davies, 2006). Though reconciling such contrasting models remains challenging, the continually evolving geochemical databases discussed below offer significant insight into the geodynamic evolution of Earth, including the initiation of plate tectonics.

Evolution of Depleted Mantle Trace Element Compositions

An important aim of trace element studies of ancient, mantle-derived rocks is to reconstruct the chemical evolution of the depleted mantle through time. In this regard, the most useful chemical elements are those that are heavily concentrated in continental crust, through the isolation of which the mantle becomes ultimately and severely depleted. It is important to remember that continental crust cannot form directly by mantle melting. Rather, the chemical inventory of modern arc-type continental crust reflects a step in a complex chain of processes beginning with the formation, alteration, and hydration of oceanic lithosphere. Eventual subduction, metamorphism, and associated devolatilization of such lithosphere leads to fluid-induced melting of the suprasubduction zone mantle (Tatsumi and Kogiso, 1997). The resulting melt undergoes differentiation and eventually forms sialic crust as well as ultramafic cumulates that are returned to the mantle (Muentener et al., 2001). This succession of processes ultimately imparts a characteristic geochemical fingerprint on continental crust. In a diagram where elements are arranged according to their relative incompatibility in mantle melting, it is evident (Fig. 2) that certain elements appear more concentrated than expected, while others are less abundant than could be expected from their incompatibility during upper-mantle, MORB-style melting (Hofmann, 1988). The most widely discussed element that is overenriched in arc-type crust is Pb (Miller et al., 1994), which shows a prominent positive spike in the N-MORB (normal mid-oceanic-ridge basalt) normalized trace element plot (Fig. 2). The most conspicuous group of elements that are less abundant than could be expected from their incompatibility are Ti, Nb, and Ta. A detailed discussion of how exactly the arc geochemical pattern develops is beyond the purpose of this treatment, but to a first order, the overly enriched elements are those that are particularly soluble in the metamorphic fluids expelled from the oceanic slab upon subduction, while the underabundant elements are much less fluid-soluble and are preferentially retained in the slab, mainly in Ti minerals.

It has been known for some time (Jochum et al., 1991) that the gradual depletion of highly incompatible elements of oppo-

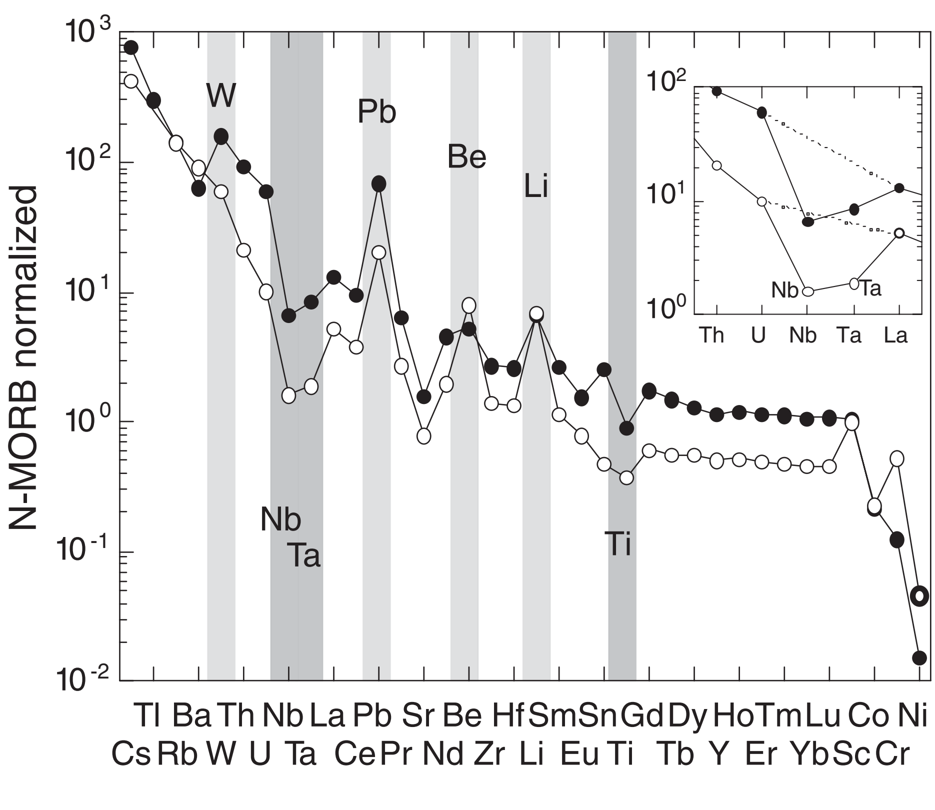

Figure 2. Full trace element patterns of modern continental sediment composite (solid circles; Kamber et al., 2005a) and average sediment from the 3.7 Ga Isua greenstone belt (open circles; Bolhar et al., 2004). Data are normalized to N-MORB (normal mid-ocean ridge basalt), and elements are arranged according to relative incompatibility (see Kamber et al., 2002, 2005a, for further information). In mid-ocean-ridge-style mantle melting, the liquid is most enriched for elements on the left-hand side of the plot and least enriched for the most compatible elements plotting at the very right. Note that this trend is also generally true for suprasubduction zone melting, leading to the pronounced exponentially decaying trend seen on this plot. However, suprasubduction zone melting is characterized by more complex processes that lead to the overenrichment of fluid-mobile elements (W, Pb, Be, and Li; highlighted with light gray backgrounds) and depletion in the refractory Nb, Ta, and Ti (highlighted with dark gray backgrounds). Importantly, the extent of the Nb deficit is greater than that of Ta, resulting in a characteristic positive step in the pattern highlighted on the inset of the figure. All these fingerprints of arc-type melting are already evident in the 3.7 Ga sediment composite.

site behavior during the fluid-induced melting that accompanies subduction (e.g., those that are conserved versus those that are fugitive during slab dehydration) could be used to reconstruct the amount of continental crust present through time. To accomplish this, two conditions must be met: that the crust form in a similar way as crust today and that fossil mantle melts be found that truthfully reflect the inventory of these elements in a rather uniformly depleted portion of the mantle. With respect to the first condition, there is excellent evidence from the trace element geochemistry of Eoarchean granitoids (Nutman et al., 1999; Kamber et al., 2002) and the oldest Eoarchean terrestrial clastic sediments (Bolhar et al., 2005) that the arc geochemical fingerprint was already established by 3.7–3.8 Ga. Remarkably, despite their long, complex geological histories, these Eoarchean rocks not only show the modern arc-characteristic depletion in the relatively immobile Ti-Nb-Ta (Fig. 2) but also display the overenrichment in the much less conservative elements Pb, Li, Be, and W. The consistency of this overenrichment with that seen in more immobile elements suggests that it is not due entirely to alteration. Indeed, the magnitude of the positive Pb spike is as large in Eoarchean sediment as in modern alluvial arc-dominated continental sediment (Fig. 2).

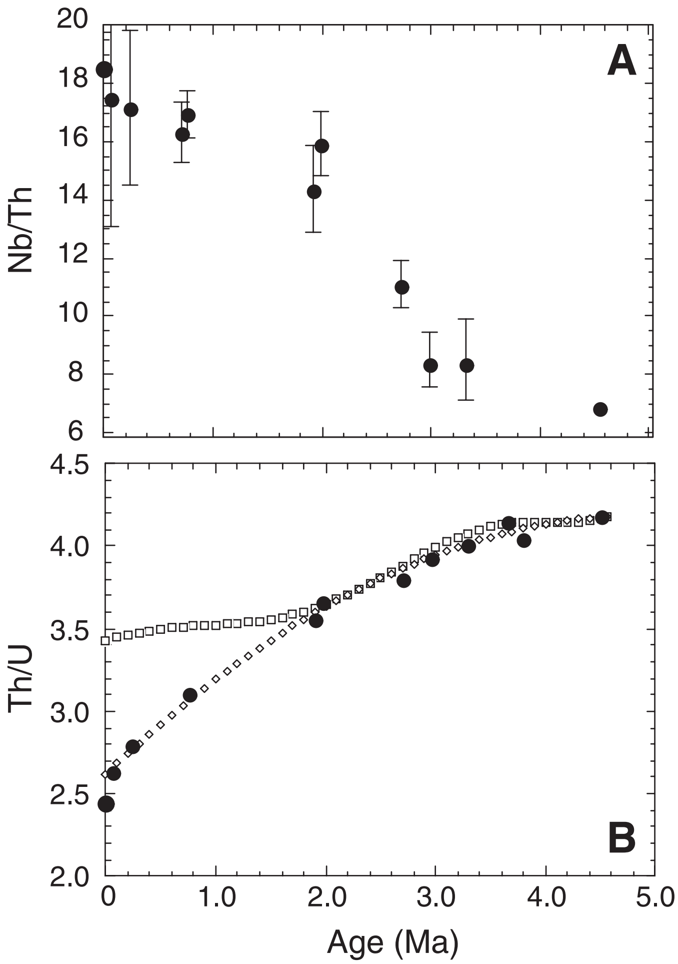

Figure 3. (A) Reconstruction of the depleted mantle Nb/Th (after Collerson and Kamber, 1999; see Kamber et al., 2003b, for chondritic values and input parameters). Note that the Hadean bulk silicate Earth Nb/Th is assumed to be slightly subchondritic due to either Nb incorporation into the core or Hadean silicate Earth differentiation. Importantly, the modern Nb/Th of the depleted mantle is more than twice as high as it was in the Paleoarchean. The increase in the ratio is due to extraction of continental crust. (B) Reconstruction of the depleted mantle Th/U (after Collerson and Kamber, 1999). Extraction of continental crust alone predicts a modern MORB Th/U of ~3.4 because the continental crust Th/U of ~4.5 is only slightly higher than chondrite (4.0–4.2). However, there is a marked deviation some time after 2.0 Ga, of the observed (solid black circles, from high-Mg basalts with juvenile Nd isotopes) from the modeled (open squares) trend due to formation of crust with constant Th/U. A better fit can be obtained (open diamonds) with preferential U recycling via subduction after the first significant atmospheric oxygenation at ca. 2.2 Ga.

In terms of the second condition, many studies have shown that chemically diverse mantle source areas have existed at least since the Neoarchean (Kerrich et al., 1999). For this reason, it is necessary to limit this type of trace element investigation to those basalts that can independently be shown to have been derived from the depleted portion of the mantle. ^{147}Sm-^{143}Nd isotope systematics are most commonly used as a screening tool to identify the purest melts from the most depleted mantle based on the most radiogenic initial $^{143}Nd/^{144}Nd$ composition (Collerson and Kamber, 1999).

In such basalts, the element pair Nb-Th (niobium-thorium) has proven very insightful for reconstruction of depleted mantle chemistry. Both elements are similarly and strongly incompatible (hence plotting close together and far to the left in Fig. 2) as well as relatively immobile during metamorphism and alteration. As a result, the ratio of Nb to Th in basalts of great geological antiquity reflects, to a first order, the Nb/Th in the depleted mantle melt source (Jochum et al., 1991). Figure 3A shows that the Nb/Th of modern MORB is substantially higher than that of chondritic meteorites. This increase in Nb/Th cannot be attributed to the earliest terrestrial mantle depletion event recorded by $^{146}Sm/^{142}Nd$ (see below) because it is not evident in early Precambrian basalts. Rather, the increase in the depleted mantle Nb/Th was initially slow (until ca. 2.9 Ga), then proceeded rapidly until ca. 1.8 Ga, since which time it has slowed again (Collerson and Kamber, 1999; Kamber et al., 2003b). The gradual sigmoidal increase in Nb/Th is readily explained by the progressively increasing separation of arc-type continental crust, with its relative Nb deficit and is prima facie evidence against the notion of constant continental volume (Armstrong, 1981; see below).

A related observation can be made by comparing the abundances of Nb and Ta. It can be seen in the inset of Figure 2 that although both elements are relatively depleted in average continental crust, Ta is noticeably less so. This is expressed in the positive slope from Nb to Ta (Fig. 2, inset) in the otherwise exponentially decaying trend of a typical continental trace element plot. This qualitative statement can be quantified via the Nb/Ta, which in continental crust is ~11 (Kamber et al., 2005b). This is 40% lower than in chondritic meteorites (~18; Münker et al., 2003). The exact properties of Nb and Ta that cause this effect during arc magmatism are a matter of ongoing debate, but what is beyond any doubt is that this process was operative in the Eoarchean, because the same rocks that show characteristic Pb, Li, Be, and W enrichment and Ti, Nb, and Ta depletion also show a strongly subchondritic Nb/Ta. In the case of the oldest known clastic metasedimentary rocks, the average Nb/Ta is indistinguishable within error from average continental crust. A bulk silicate Earth mass balance issue arises because the vast majority of mantle melts and continental rocks have Nb/Ta lower than chondrites. While some of the missing Nb probably was sequestered into the core (Wade and Wood, 2001), the relatively constant depleted mantle Nb/Ta through time (Kamber et al., 2003b) requires the long-term storage of eclogitic oceanic slabs in the mantle (Rudnick et al., 2000).

Another important ratio to define the evolution of the mantle is Th/U. Judging from the high incompatibility of these elements (Fig. 2) and the slightly higher incompatibility of Th, the extraction of continental crust from the mantle would be expected to lead to a very modest reduction of Th/U in the depleted mantle from the chondritic value of ~4.0–4.2 to ~3.75. Pb isotopic systematics of modern MORB allow an independent estimate of the time-integrated Th/U of ~3.4 for the depleted mantle (Kramers and Tolstikhin, 1997). However, the present-day measured MORB Th/U, both directly as concentrations and indirectly from U-series systematics (Galer and O'Nions, 1985), is 2.6, much lower than the time-integrated ratio. Furthermore, as the data on mafic to ultramafic rocks (Fig. 3B) (Collerson and Kamber, 1999) and the deep-seated parental magmas to kimberlites (Zartman and Richardson, 2005) show, the Th/U of the depleted upper mantle has been on a steady decline since ca. 3.6 Ga. This observation constitutes the second terrestrial Pb isotope paradox and is explained by preferential recycling of continental U at subduction zones (Elliott et al., 1999). This process, whereby oxidized U (+6) is lost during weathering and incorporated into oceanic sediment and hydrated oceanic lithosphere through valence reduction (+4) and returned to the mantle with subducting slabs, became progressively more effective as the atmosphere became more oxidizing by ca. 2.2 Ga (Fig. 3B) (Bekker et al., 2004). But it had evidently been developing since 3.6 Ga due to the slightly higher incompatibility of Th relative to U. Subduction is the chief mechanism responsible for the preferential recycling of U relative to Th into the mantle. Uranium recycling into the mantle is also the reason why it is not possible to directly estimate the continental crust volume versus time curve from Nb/U systematics (e.g., Sylvester et al., 1997). As pointed out by Collerson and Kamber (1999), the Nb/U of the MORB-source mantle was higher two billion years ago than it is today, not because more continental crust existed but because of U recycling.

Observations of depleted mantle Nb-Ta-Th-U systematics show that after the earliest mantle depletion events, recorded by ^{142}Nd/^{144}Nd (see below), gradual extraction and isolation of continental crust and continuous recycling of slabs of oceanic lithosphere progressively changed the abundances of these elements in the depleted mantle. Suprasubduction zone melting and slab subduction are the only known geological processes that are capable of separating these similarly incompatible elements in the recorded fashion. The near-chondritic Nb/Th of Eo- and Mesoarchean basalts with slightly superchondritic initial ^{143}Nd/^{144}Nd values clearly argues against a voluminous Eoarchean continental crust. It is important to realize that, unlike long-lived radiogenic tracers, Nb/Th would also record the temporary extraction of voluminous short-lived, juvenile continental crust, for which there is again no evidence. However, Nb/Th and Th/U place no constraints on the amount of oceanic lithosphere (including plateaus) that could have coexisted with nascent continental crust. Oceanic lithosphere is less visible to these element ratios, because it forms by processes that are not nearly as effective at discriminating between these elements. Nonetheless, it seems quite capable of recording the chemical effects in the mantle of the slab return flow, the main mechanism by which recycling is accomplished. Hence, while Nb-Th-Ta-U strongly argue for the initiation of subduction and the start of formation of continental crust at ca. 3.9 Ga (Kamber et al., 2002; and see below), the possibility remains that voluminous long-lived mafic crust existed during the earliest (pre–3.9 Ga) part of Earth history.

PLATE TECTONIC IMPLICATIONS OF ARCHEAN CRUSTAL EVOLUTION

Earliest Mantle Isotopic Signatures from Juvenile Crust

The "juvenile" component of Archean crust includes either those rocks that are derived directly from the mantle (e.g., komatiites, basalts, andesites, diorites) or those rocks that form from crustal sources rapidly enough (e.g., <50 m.y.) to be considered to come indirectly from the mantle (e.g., tonalities, trondhjemites, and some granodiorites whose isotopic systems do not reveal a prolonged continental crustal history). Collectively these rocks have long been used to track the evolution of the mantle in the Archean (e.g., Peterman, 1979) because they are the best ancient analogues to modern oceanic mantle-derived rocks. Many are recognized to have had suprachondritic initial isotopic compositions in the long-lived ^{147}Sm-^{143}Nd system (based on the decay of ^{147}Sm to ^{143}Nd) throughout the Neoarchean to the Paleoarchean (e.g., Shirey and Hanson, 1986; Shirey, 1991; Nägler and Kramers, 1998; Bennett, 2003). It is important to recognize that Sm-Nd isotopic data are obtained on whole rocks and that all the oldest terrestrial rocks are severely and multiply metamorphosed in the crust. This has led to a debate in the literature (e.g., Arndt and Goldstein, 1987; Moorbath et al., 1997; Bennett and Nutman, 1998; Kamber et al., 1998) on the ability of a whole rock to retain its igneous ^{147}Sm/^{144}Nd unchanged during metamorphic recrystallization and has cast doubt on the veracity of the highest ε_{Nd} measured, especially in the oldest rocks. Nonetheless, the Nd isotopic signatures of the oldest rocks clearly reflect a depleted origin, regardless of their absolute initial value. This has previously been interpreted as the result of earlier Hadean depletion events that resulted from the removal of an enriched (e.g., low-

Sm/Nd) component of oceanic (Carlson and Shirey, 1988; Chase and Patchett, 1988) or continental (Armstrong, 1981, 1991; McCulloch and Bennett, 1994; Harrison et al., 2005) crustal affinity. The timing of the prior depletion event(s), the extent of depletion, and the composition of the sequestered enriched components (continental versus oceanic) are important because they are keys to constraining the range of Hadean tectonic processes.

Additional insight into the nature of early mantle depletion processes has been gained from the documentation of variations in the Lu-Hf isotopic system (based on the decay of ^{176}Lu to ^{176}Hf) and in the short-lived ^{146}Sm-^{142}Nd system (based on the decay of ^{146}Sm to ^{142}Nd). The Lu-Hf system has the advantage of zircon as its chief host mineral. Zircon, besides being resistant to isotopic resetting, carries most of the Hf in a whole rock. With a low Lu/Hf, it has a measurable ^{176}Hf/^{177}Hf that requires little correction to establish the initial value, and can be dated independently with the U-Pb system (see detailed discussion below). The ^{146}Sm-^{142}Nd system has the advantage of being able to record time-averaged Sm/Nd that predates much later metamorphic impacts on Sm/Nd that lead to inaccurate initial ^{143}Nd/^{144}Nd. Initially, studies of Hf isotopes in zircons and whole rocks appeared to support the existence of the early depleted mantle reservoirs evident in the ^{147}Sm-^{143}Nd isotopic system from whole rocks. This is because they were compatible with systematic, early separation of continental and/or oceanic crustal components. For example, initial Hf isotopic composition of juvenile crustal rocks, expressed as ε_{Hf}, was about twice that seen with the Nd system (e.g., $\varepsilon_{Hf} \approx 2 \times \varepsilon_{Nd}$)—a value close to the slope of the modern Nd-Hf array (Vervoort et al., 1996; Vervoort and Blichert-Toft, 1999; Bennett, 2003). This simple picture was subject to the accuracy of the poorly determined ^{176}Lu decay constant. When the early Hf data are recalculated with the 4% lower decay constant proposed by Nir-El and Lavi (1998) and subsequently confirmed by others (Scherer et al., 2001; Söderlund et al., 2004; Amelin, 2005), the Hf-Nd correspondence disappeared for the oldest terrestrial rocks (cf. Bennett, 2003) because the recalculated initial Hf ratios were now much less radiogenic and thus much lower relative to Nd-based mantle evolution models (e.g., Kramers, 2001).

^{146}Sm-^{142}Nd isotope system studies aimed at constraining the timing of early mantle depletion also corroborated the creation of depleted reservoirs in the first 200 m.y. of Earth history, but suggested that they were sampled rarely and unevenly (McCulloch and Bennett, 1993; Bennett et al., 2007b; Caro et al., 2003, 2006; Boyet et al., 2003; Sharma and Chen, 2004) perhaps because of dilution of the depleted source signatures by mantle-mixing processes (e.g., Bennett et al., 2007b). The recent discovery (Fig. 4A) that all chondrites and most eucrites have an average 20 ppm lower ^{142}Nd/^{144}Nd than the average of all measured terrestrial igneous rocks (Boyet and Carlson, 2005, 2006; Andreasen and Sharma, 2006) suggests that if a chondritic model for Earth's composition at its accretion is valid (Bennett et al., 2007; Carlson et al., 2007), then an enriched component must have been removed from Earth's upper mantle before the production of any of the Hadean or Archean crust preserved today as rocks or zircons (Fig. 4B) (Boyet and Carlson, 2005, 2006). Taken together, both the refined ^{176}Lu decay constant and the meteorite ^{146}Sm-^{142}Nd data require that the Nd-Hf systematics and the identity of Neoarchean to Paleoarchean juvenile rocks be reconsidered for their Hadean tectonic implications.

Geochemically, the average depletion reflected in the initial ^{143}Nd/^{144}Nd isotopic compositions of Eoarchean to Paleoarchean juvenile crustal rocks of +2.5 (ε_{Nd}) is best explained by separating an early enriched reservoir (EER) from the newly accreted, still molten, mantle within the first 30 m.y. of Earth history. The lack of negative ε_{Nd} values reported for Eoarchean crustal rocks suggests this EER was not continental crust but rather enriched mafic to ultramafic material that was segregated at the base of the mantle (perhaps in the D″ layer) or in the lower mantle (Fig. 4) (Boyet and Carlson, 2005, 2006). In this model, the entire upper mantle would have contained both a 20 ppm average ^{142}Nd/^{144}Nd anomaly and an ε_{Nd} = +2.5 (250 ppm) ^{143}Nd/^{144}Nd anomaly resulting from evolution subsequent to the early separation of the EER. As such, it would be a viable source for all Hadean and Eoarchean juvenile crustal rocks.

The timing of the separation of the EER, its putative composition, and the formation of the Moon are closely connected (e.g. Boyet and Carlson, 2005) and important to constrain the composition of the Hadean mantle. Geochemical research on the Moon and Hadean Earth is active, and the understanding is evolving rapidly. Recent work on the Hf-W system in lunar metals shows a remarkable homogeneity and an ^{182}W/^{184}W isotopic composition identical to the Earth's mantle (Touboul et al., 2007). This shows that the Moon formed after core formation on the Earth, further strengthens the compositional similarities between the Moon and the Earth's silicate mantle, and indicates that the Moon must have formed after ^{182}Hf had decayed away, or 62 m.y. after formation of the Solar System (Brandon, 2007; Touboul et al., 2007). The oldest lunar samples (4.2–4.4 Ga) have similar suprachondritic signatures in both their initial ^{142}Nd/^{144}Nd and ^{143}Nd/^{144}Nd isotopic compositions (Boyet and Carlson, 2005), whereas younger lunar basalts (3.1–3.9 Ga) record chondritic initial ^{142}Nd/^{144}Nd, but both supra- and subchondritic initial ^{143}Nd/^{144}Nd values (Rankenburg et al., 2006). These datasets imply that lunar basalt sources were in equilibrium some 200 m.y. after formation of the Moon (Rankenburg et al., 2006). EER formation from the postaccretion terrestrial magma ocean better fits the lunar data (Boyet and Carlson, 2005; Rankenburg et al., 2006) chiefly because of the highly variable Nd isotopic compositions of differentiated lunar rocks and the newly refined later age for formation of the Moon, but it would require the EER to remain separated during the moon-forming, giant impact. Formation of an EER from the Moon-forming, giant-impact-generated magma ocean seems less feasible because of the extreme Sm/Nd required to explain subsequent terrestrial mantle compositions (Boyet and Carlson, 2005) and the requirement that it produce suprachondritic ^{142}Nd/^{144}Nd and ^{143}Nd/^{144}Nd in the oldest lunar rocks.

Nonetheless, the EER is modeled to be enriched in the light rare earth elements (LREEs) and depleted in the heavy rare earth

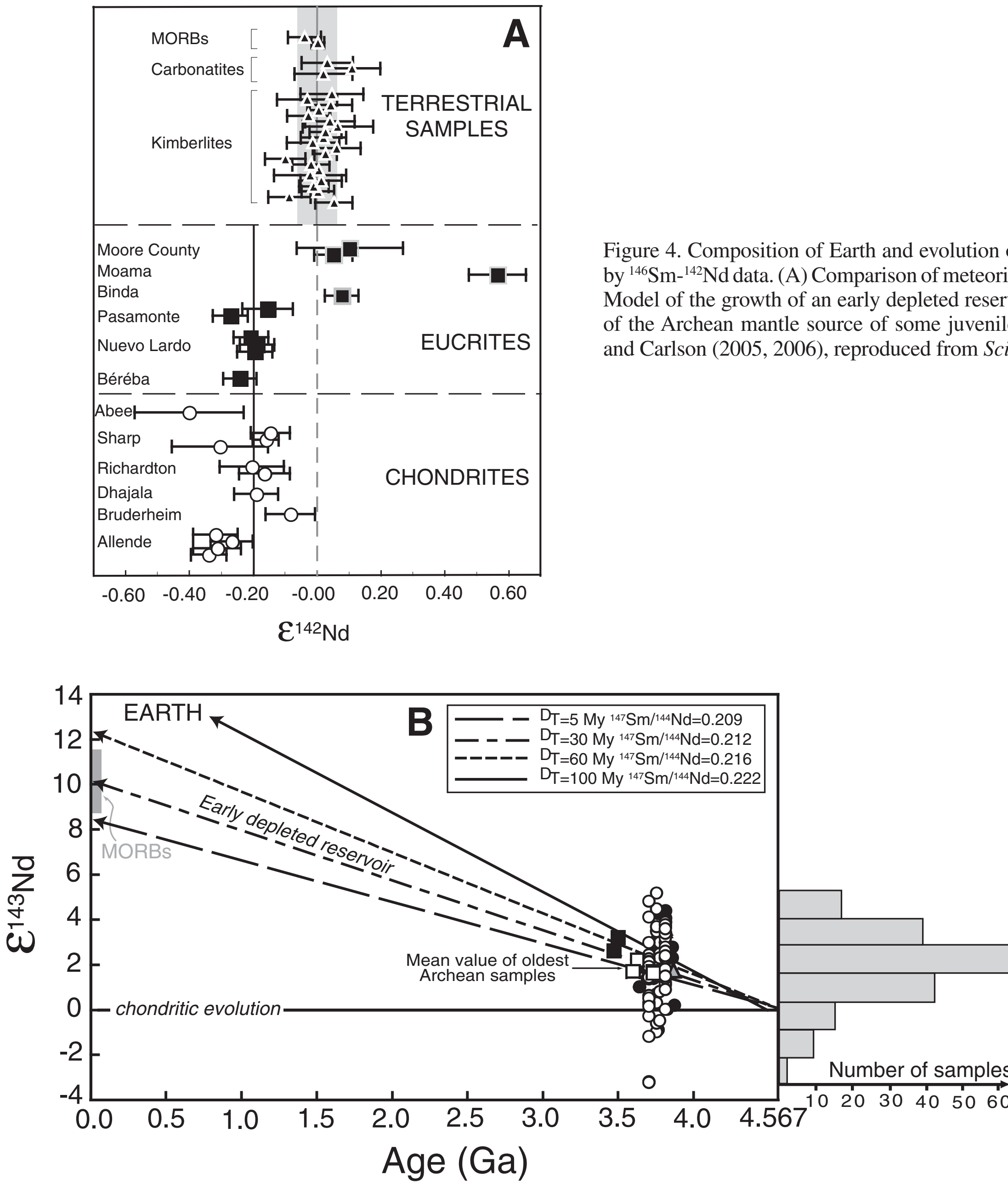

Figure 4. Composition of Earth and evolution of the mantle as constrained by ^{146}Sm-^{142}Nd data. (A) Comparison of meteorites to terrestrial samples. (B) Model of the growth of an early depleted reservoir to explain the depletion of the Archean mantle source of some juvenile crustal rocks. After Boyet and Carlson (2005, 2006), reproduced from *Science* with permission.

elements (HREEs), so its separation also leads to an upper mantle with a radiogenic Hf isotopic composition that grows to an ε_{HF} of +4 by 3 Ga. Thus, separation of the EER produces an early depleted reservoir that becomes the starting composition for the Hadean upper mantle and thus the base composition for the genesis of Archean juvenile crust. Excursions above and below in Nd and Hf isotopic composition are the isotopic signal that reflects the nature of the Hadean and Archean tectonic processes necessary to develop spatially separate geochemical reservoirs. Consequently, Eoarchean to Paleoarchean juvenile crustal rocks that have higher ε_{Nd} than the average mantle growth model (Figs. 4B and 5A) result from (1) isolated, extreme LREE depletions of mantle sources (e.g., McCulloch and Bennett, 1994) and/or (2) secondary metamorphic perturbations of their ^{147}Sm/^{144}Nd (Arndt and Goldstein, 1987), which leads to anomalously high calculated ^{143}Nd/^{144}Nd for a given age (Moorbath et al., 1997). Apparently juvenile crustal rocks with lower ε_{Nd}, i.e., below the average mantle evolution model, result from either separate LREE-enriched sources or a short, but discernable, involvement of some source component(s) with low-Sm/Nd material (e.g., not totally juvenile crust).

The extension of these arguments to include the Lu-Hf data from Hadean and Eoarchean rocks and zircons, however, requires a more complicated scenario. A canon of isotope geology and igneous petrogenesis is that melting processes producing basalts from the mantle or producing felsic rocks from mafic crust fractionate Sm/Nd and Lu/Hf in a corresponding way; the melts have low Sm/Nd and Lu/Hf and the residues have higher Sm/Nd and Lu/Hf, which evolve with time to higher ε_{Nd} and ε_{Hf} isotopic compositions. Another canon is that the fractionation is more extreme for crustal melting because the Sm/Nd and Lu/Hf in the felsic melts relative to the basalts are much lower than for the ultramafic to mafic melting that produces the original mafic crust. Ideally then, the Hf isotopic composition of whole rocks and especially zircons should be able to support the interpretations based on the $^{143}Nd/^{144}Nd$ isotopic data. But with recent revisions to the Lu decay constant (Nir-El and Lavi, 1998; Scherer et al., 2001; Söderlund et al., 2004; Amelin, 2005), Eoarchean to Paleoarchean juvenile crustal rocks do not appear to have been derived from a depleted mantle reservoir in the Lu-Hf isotopic system that corresponds to the depleted mantle required by the ^{147}Sm-^{144}Nd isotopic system (Figs. 5A and 5B). Rather, they derive from one that is chondritic to slightly LREE-enriched (e.g., $\varepsilon_{Hf} = 0$ to -4; Fig. 5B) (Bennett, 2003; Caro et al., 2005; Bennett et al., 2007; Kramers, 2007), thus violating the basic Nd-Hf canons (whole-rock Sm/Nd perturbations accompanying alteration notwithstanding; see discussion above) and presenting a major challenge for understanding tectonic and petrogenetic processes for early Earth.

On the basis of the evidence presented above, the formation of either basaltic or granitic protocrusts and their separation from the mantle should form residual upper-mantle reservoirs that on remelting produce rocks that have a positive ε_{Nd} and even more positive ε_{Hf}. Furthermore, the effects should be more pronounced if granitic crust was involved. Therefore, despite the existence of Hadean zircons, scenarios that invoke the Hadean formation and sequestering of volumetrically sizeable continental crust (e.g., Armstrong, 1981, 1991; Harrison et al., 2005) are inconsistent with the lack of Archean rocks derived from mantle reservoirs that had a high ε_{Hf} and a high ε_{Nd} (Figs. 5A, 5B, and 6). In addition, sizeable amounts of basaltic or granitic crustal components could not have been recycled into the upper-mantle sources of juvenile Archean crustal rocks because this process would have produced a similarly more negative ε_{Nd} (e.g., evidence of LREE-enriched crustal material) compared to ε_{Hf}, which again is not seen in the data. Therefore, the oldest Archean juvenile crustal rocks can be explained by the high-pressure segregation of a phase that fractionates Sm/Nd differently from Lu/Hf, such as Mg-silicate and Ca-silicate perovskite (Figs. 5A, 5B, and 6). Early work on Mg-silicate and Ca-silicate perovskite partitioning (Kato et al., 1988a, 1988b) showed that substantial fractionation (>10%) of either phase from a magma ocean would lead to nonchondritic trace element ratios for many elements unless the perovskite phases were homogenized by mantle convection (Kato et al., 1988b; Drake et al., 1993). More recent work corroborates this effect and sets a new limit for Ca-silicate perovskite fractionation of less than 8%–11% (Corgne et al., 2005; Liebske et al., 2005). Caro et al. (2005) recently recognized that even at these low percentages, Ca-silicate perovskite crystallization, in particular, substantially lowers the Lu/Hf while raising the Sm/Nd of the resulting melt. This could have produced a resultant mantle with chondritic or bulk silicate Earth ε_{Hf}, but suprachondritic or depleted ε_{Nd}. The likely magma ocean candidate in which such fractionation may have occurred was the one created by the Moon-forming giant impact (Canup and Asphaug, 2001), which occurred after the separation of the EER (but see uncertainties in timing of EER separation, discussed above).

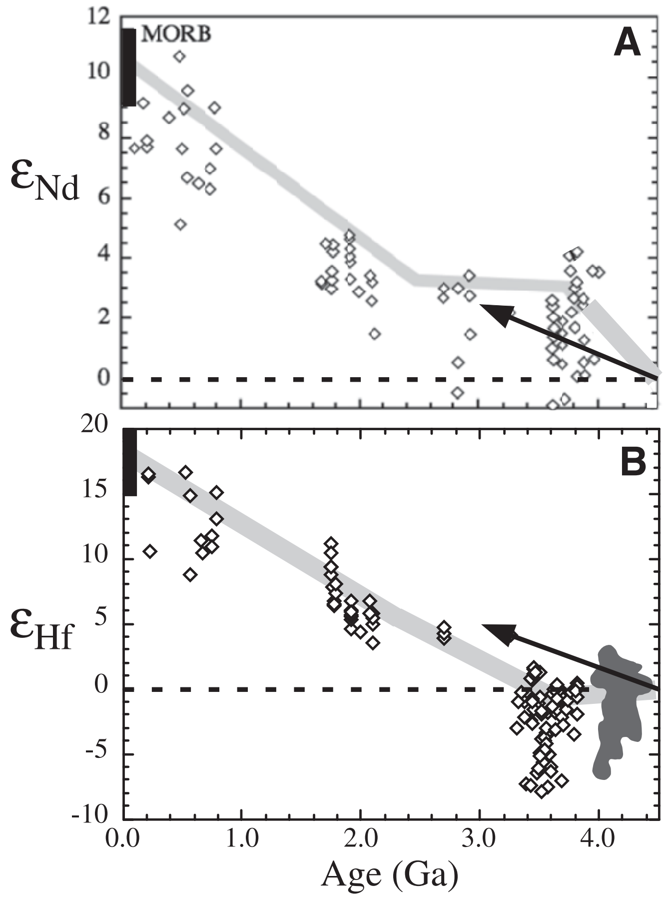

Figure 5. Nd isotopic composition (A) and Hf isotopic composition (B) of Archean to recent mantle-derived rocks and juvenile granitoids (both shown as open diamonds and the oldest samples on B containing some granitoids with older crustal components) versus age. Hadean zircons are the dark gray field in B. Range of MORB shown by black bars. Both A and B have been modified from Bennett (2003), Figures 1 and 3 therein (respectively), and the ε_{Hf} in B has been recalculated using the decay constant proposed by Scherer et al. (2001) and the chondritic composition for $^{176}Hf/^{177}Hf$ and $^{176}Lu/^{177}Hf$ given in Blichert-Toft and Albarede (1997). The dashed line represents chondritic evolution, the thick gray line the evolution of the mantle sources for juvenile rocks, and the arrow the growth of the early depleted reservoir (Boyet and Carlson, 2005). Primary data sources for Nd are Baadsgaard et al. (1986), Jacobsen and Dymek (1988), Collerson et al. (1991), Bennett et al. (1993), Bowring and Housh (1995), Moorbath et al. (1997), Vervoort and Blichert-Toft (1999), and the compilation of Shirey (1991). Primary data sources for Hf are Salters (1996), Amelin et al. (1999, 2000), Vervoort and Blichert-Toft (1999), and Harrison et al. (2005).

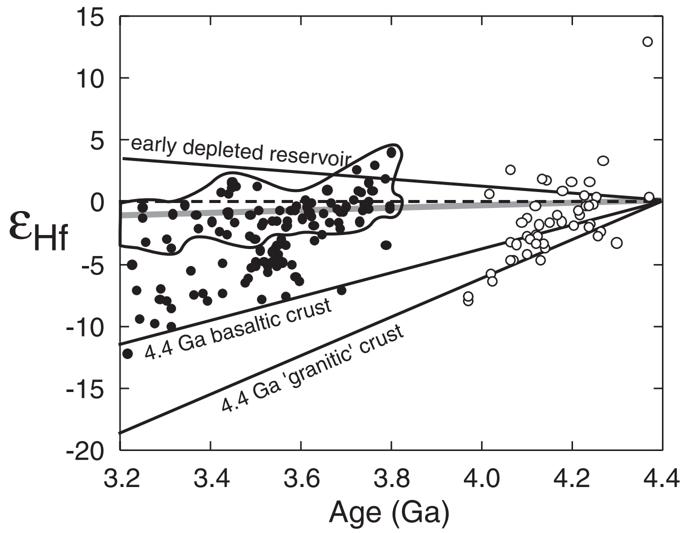

Figure 6. Initial Hf isotope systematics of Hadean and Eoarchean zircon after Kramers (2007) and Kamber (2007) with original data sources given in the caption to Figure 5. ε_{Hf} was calculated from a present-day chondritic $^{176}Hf/^{177}Hf$ of 0.282772 and $^{176}Lu/^{177}Hf$ of 0.0332 with a ^{176}Lu decay constant of 1.865×10^{-11} yr^{-1}. Early depleted reservoir evolution (separation at 4.5 Ga) after Boyet and Carlson (2005) projects to modern N-MORB Hf isotope composition. Two types of early Hadean (4.4 Ga) crustal reservoirs were modeled to separate from chondritic composition with $^{176}Lu/^{177}Hf$ of 0.021 (basaltic) and 0.012 ("granitic"). Note that all initial Hf isotope compositions of Eoarchean zircons from the Acasta, southern West Greenland, Barberton, North China, Yangtze, and the western Superior localities fall into the fields defined by the early depleted reservoir and the *mafic* Hadean crust. Also, the bulk of the depleted juvenile whole-rock data (inside balloon) straddles estimates of mantle evolution (gray line) following Ca-silicate and Mg-silicate perovskite fractionation from the magma ocean generated by the Mars-sized impact (Caro et al., 2005).

The Oldest Sialic Rocks: Evidence for the Transition to Plate Tectonics in the Archean

The only samples presently available to us from the Hadean eon are ancient detrital zircons preserved in substantially younger sedimentary rocks, key evidence from which is discussed below. Although there may be significant petrogenetic differences between the host rocks for the Hadean zircons and the first preserved terrestrial rocks from the Eoarchean, the latter may still be used to provide some clues about the nature of Earth's earliest tectonic regime and its transition to a style we might loosely term "plate tectonics." Particularly important among these earliest rocks are the extensive 3.6–3.8 Ga tonalite-trondhjemite-granodiorite gneisses and supracrustal rocks of southern West Greenland, the Pb isotopic systematics of which have been used to propose a single-plate model for the Hadean (Kamber et al., 2003a, 2005b). This approach is based on the much faster decay of ^{235}U compared to ^{238}U, which results in more rapid production of radiogenic ^{207}Pb relative to ^{206}Pb in early Earth, defining the characteristic shape of the $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ growth curve shown in Figure 7 (see also Stacey and Kramers, 1975; Kramers and Tolstikhin, 1997).

When plotted in this coordinate space, Eoarchean samples from southern West Greenland define a broad array between two ca. 3.7 Ga reference isochrons. The lower margin of this array is defined by 3.65–3.75 Ga tonalite-trondhjemite-granodiorite (Amîtsoq) gneisses from the Godthåbsfjord region, while the upper margin is defined by chemical sediments (banded iron formation and chert, as well as galenas) of the 3.7–3.8 Ga Isua greenstone belt. Clastic metasedimentary rocks from the Isua greenstone belt, together with some amphibolitic gneisses and ca. 3.8 Ga tonalite-trondhjemite-granodiorite gneisses from south of the Isua greenstone belt, scatter between these two boundaries. The lower trend intersects the Pb growth curve at essentially the same age as the age of the regression line itself, indicating that these rocks were derived from a typical mantle Pb isotope reservoir, which has evolved predictably to the present day. In contrast, appropriate age regression lines through other sample sets intersect the growth curve of this reservoir at ages that are unrealistically young. For example, in the case of >3.7 Ga banded iron formations and cherts, this intersection occurs at <3.4 Ga (Fig. 7). The more radiogenic (specifically, elevated ^{207}Pb) composition of these samples requires long-term (~500 m.y.) isolation of their Pb isotope source reservoir with a time-averaged μ ($^{238}U/^{204}Pb$ extrapolated from the present) value of 10.5, considerably higher than that typical of convecting mantle ($\mu \approx 8$).

In order to physically achieve this isolation in a reservoir that ultimately is accessible to surface weathering, Kamber et al. (2003a) proposed that this reservoir might have represented a stable crustal lid of basaltic composition that existed for most of the Hadean. In this case, earliest Earth could have been a single-plate planet without active convection and subduction processes (Kamber, 2007; Kramers, 2007). Additional supporting evidence for the crustal lid hypothesis comes from solar rare gas composition of the deep mantle sampled in plumes, which requires a prolonged period of surface exposure (Tolstikhin and Hofmann, 2005). The presence of a stagnant lid in the Hadean is by no means certain (e.g., Davies, 2006), and it would in any case be stable only in the absence of convection as a terrestrial heat loss mechanism. There is also the potential of impacts to break up the crust, and the crustal reprocessing evident in the Hadean zircon record must be explained. Both argue for some local recycling of the lid (see below). Nonetheless, if a stagnant lid occurred, the obvious implication would be that subduction tectonics, which in effect defines the tectonic regime of a multiple-plate planet, did not operate during the Hadean.

The Pb isotopic data provide further insights into the actual transition from a possible single-plate crustal lid to a multiple-plate

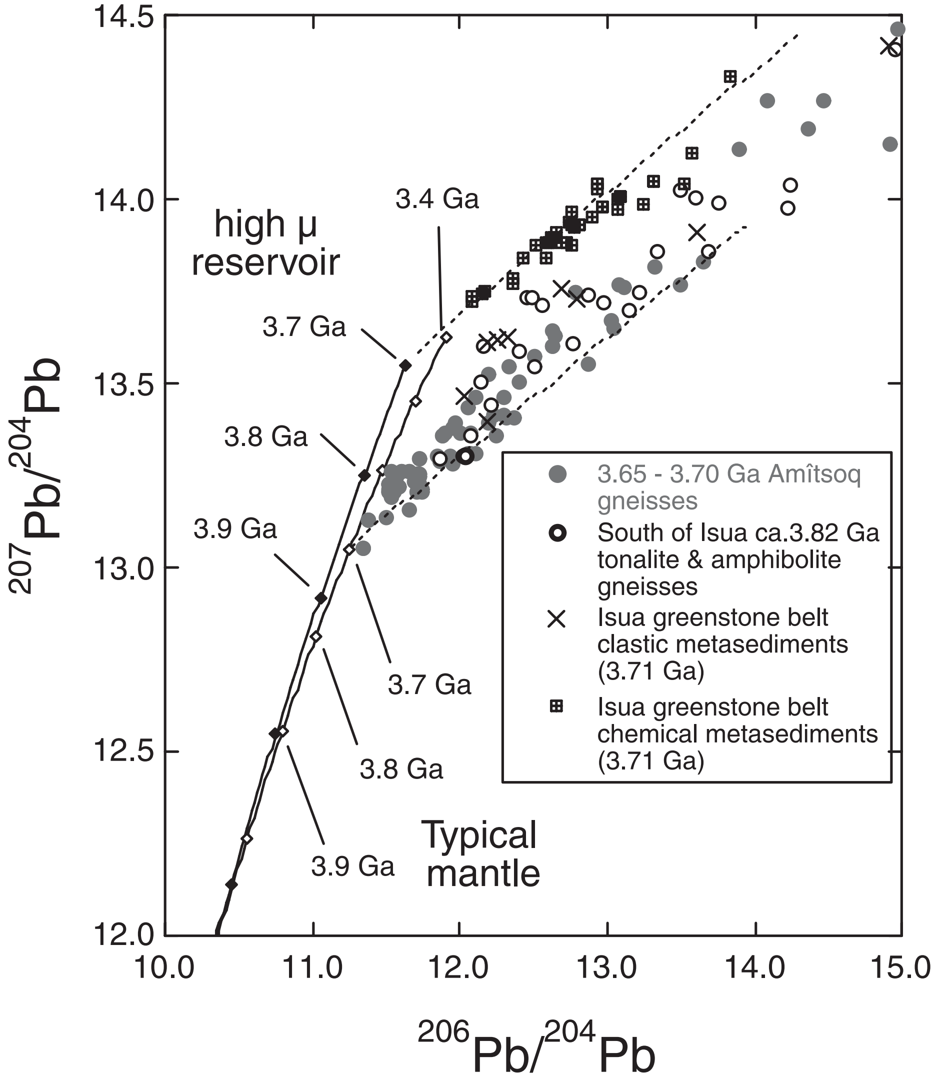

Figure 7. Pb isotope systematics of Eoarchean rocks of southern West Greenland (modified from Kamber et al., 2003a). A 3.65 Ga regression line through Godthabsfjord Amîtsoq gneisses intersects the typical mantle evolution curve (open diamonds; after Kramers and Tolstikhin, 1997) at the expected age of ca. 3.67 Ga. By contrast, 3.71 Ga chemical metasediments intersect the same mantle evolution line at a much younger, implausible date of <3.4 Ga, implying that their Pb had previously evolved in a high-U/Pb environment for several hundred million years. This is approximated with the "high-µ reservoir" growth curve (solid diamonds; see Kamber et al., 2003a, for details of growth curve). This required separation from the mantle at 4.3 Ga with a µ of 10.5. Eoarchean clastic metasediments incorporated Pb from both sources. Ca. 3.82 Ga tonalite and amphibolite gneisses from south of Isua also have an affinity with the high-µ reservoir.

system. Of particular significance are the ca. 3.8 Ga tonalite-trondhjemite-granodiorite (TTG) gneisses from south of Isua. Near this area, remnants of Earth's oldest ophiolite have been discovered (Furnes et al., 2007). More importantly, these rocks have typical trace element characteristics expected of magmatic rocks produced above a subduction zone (Kamber et al., 2002), such as enrichment in fluid-mobile incompatible elements (B, Li, Pb, U) and depletion in Nb and the heavy rare earth elements. These depletions can be explained by melting of garnet amphibolite (e.g., Foley, this volume). The TTGs also contain a Pb isotopic memory of the high-µ Hadean reservoir. This dichotomy can be explained if these earliest preserved TTGs represent some of the first true subduction-related rocks in which the fluid-mobile, but incompatible, element Pb was derived from the initial subduction and melting of the high-µ basaltic reservoir. If so, the inherent instability of the early basaltic crustal lid following initiation of global subduction would have resulted in its rapid recycling into the mantle within 100–150 m.y., so that no discernable isotopic trace of its former existence was imparted to the 3.65 Ga Amîtsoq TTG gneisses.

An inevitable consequence of voluminous TTG magmatism marking the onset of subduction tectonics between 3.75 and 3.65 Ga is the formation of cratonic nuclei capable of preserving some vestige of the Hadean crust. In this way, the high-µ signature developed during the lifetime of the Hadean crustal lid was tapped at a much later time and is evident in long-recognized (Oversby, 1975) high-µ cratons that are formed largely of Meso- to Neoarchean rocks, i.e., the North Atlantic, Slave, Wyoming, Yilgarn, and Zimbabwe cratons. In a similar way, physical relicts of the Hadean protocrust, most notably 4.0–4.4 Ga zircon from the Jack Hills, were eventually liberated by unroofing and erosion. The significance of these zircon grains for evolution of earliest Earth is the subject of great debate as discussed below.

Arc-Like Juvenile Crustal Growth Starting in the Mesoarchean-Paleoarchean

Nd and Hf isotopic data for rocks of direct mantle derivation and juvenile crustal rocks from the Mesoarchean onwards define a trend toward increasing ε_{Nd} and ε_{Hf} as the rocks get younger, culminating in isotopic compositions that approach the composition of modern MORB (Figs. 5A and 5B). During this time, the ε_{Nd} and ε_{HF} take on the roughly one-to-two correspondence expected from the normal igneous fractionation of $^{147}Sm/^{144}Nd$ versus $^{176}Lu/^{177}Hf$ during mantle and crustal melting. This suggests that crustal formation processes at the top of the mantle (e.g., low pressure and not associated with a magma ocean as hypothesized for the Hadean) are dominating the composition of the progressively depleting mantle. The complementary nature of the trace element composition of continental crust compared to the depletions estimated for the MORB source (Hofmann, 1988; Workman and Hart, 2005), the very survival of ancient continental crust in cratons, and the increasing areal accumulations of continental crust through time (Hurley and Rand, 1969) have long led to the idea that irreversible continental crustal extraction has caused a progressive depletion of the upper mantle through time that can be traced by changes in its isotopic compositions in the ^{147}Sm-^{143}Nd and Lu-Hf systems.

Nb/Th and Th/U of mantle-derived rocks (Figs. 3A and 3B) echo the beginning of this major, unidirectional change in mantle composition near the same time as, or perhaps slightly before, the change seen in the Nd-Hf isotopic curves. Nb versus Th is a compelling tracer of slab-wedge interaction in subduction zones, whereas U versus Th is a compelling tracer of preferential incorporation of U into the altered oceanic crustal slab (as discussed above). The Nb-Th-U data trace the injection of oceanic slabs into the deeper mantle circulation, and this is an important adjunct of the arc crustal growth process and a strong indicator of plate subduction. Thus the Nb-Th-U data support the onset of continental crustal growth by the conventional arc process in an entirely complementary way to the Nd-Hf curves; the former records the long-term effects of slab additions to the mantle, whereas the latter records the long-term effects of crustal melts extracted from the mantle.

Arc models of continental crustal growth have long been advocated by studies of Pb isotopes in crustal hydrothermal ore deposits (Stacey and Kramers, 1975; Zartman and Doe, 1981; Zartman and Haines, 1988) and rare earth elements in continental sediments (Taylor et al., 1981; Taylor and McLennan, 1995). The crust itself also carries a record of the onset of the arc process in the change of the common Pb isotopic composition of galena and feldspar during the Mesoproterozoic, which requires an increase in time-averaged U/Pb of the crustal sources of these low-U/Pb minerals (Stacey and Kramers, 1975; Tera, 1982, 2003). The Re-Os system is one radiogenic isotopic system that is a relatively poor recorder of this process. The high Os content of the mantle makes it much less sensitive to the Re increases resulting from the introduction of basaltic components added during slab recycling than the other isotope systems in which lithophile trace element daughter elements (e.g., Sr, Nd, Pb, and Hf) are greatly enriched in the crust relative to the mantle. This is perhaps the reason that return plume flow as seen in oceanic-island basalts only starts to show significant enrichments relative to the mantle after the Paleoproterozoic (Shirey and Walker, 1998) or Neoarchean (Bennett, 2003).

Nd and Hf isotopic data on the oldest Paleoarchean and Eoarchean rocks are difficult to interpret in the simple context of arc-growth/mantle-depletion/crustal-recycling models. The ε_{Nd} of the oldest juvenile rocks have long appeared extraordinarily high, which supported an apparent constancy of ε_{Nd} throughout the Mesoarchean (Fig. 5A). This feature in Nd isotopic data was ascribed (e.g., DePaolo, 1983; Chase and Patchett, 1988; McCulloch and Bennett, 1994) to inputs of crustal material with low Sm/Nd back into the depleted mantle in the period before the progressive rise in the ε_{Nd} of the depleted mantle after the Neoarchean. While such crustal recycling may have happened, the Nd isotopic data are no longer especially good evidence for it. Nd isotopic data are obtained on whole rocks, which can be subject to age uncertainties and to metamorphic perturbations of their Sm/Nd (see above). Both features can lead to anomalously high estimates of initial ε_{Nd}. The ε_{Nd} of +3 to +6 on 3.8 Ga rocks cannot be easily explained by the early separation of enriched material (whether it is continental crust or the EER) because the high Sm/Nd needed would lead to ultradepleted mantle reservoirs at younger ages, which are not seen. Furthermore, a similar constancy in the Mesoarchean of Nb/Th, Th/U, and the ratio of ε_{Hf} to ε_{Nd} is missing. This suggests that straightforward slab return flow into the general mantle circulation is likely not the cause of constant ε_{Nd} evolution in the Mesoarchean. For the late Neoarchean and after though, both the Nd and Hf evolution curves show an ever increasing positive ε_{Nd} and ε_{Hf} coupled with an increase in Nb/Th and decrease in Th/U. This occurs during and just postdating the addition of large volumes of continental crust on Earth. This temporal connection and the well-established complementary nature of the isotopic composition and trace element content of the continental crust to depleted upper mantle suggest that permanent extraction of continental crust progressively depleted the upper mantle since at least the Neoarchean.

Examples from Mesoarchean to Neoarchean Terranes

The arc model clearly is not the only way the continental crust has been hypothesized to form. Lateral accretion of oceanic plateaus (Boher et al., 1992), mantle plume upwellings (Hollings et al., 1999; Bedard, 2006; Fralick et al., this volume), subduction into differentiated oceanic plateaus (Benn and Moyen, this volume), large mantle overturns (Stein and Hofmann, 1994), and vertical differentiation due to density downwellings (Zegers and van Keken, 2001; Bedard, 2006; van Hunen et al., this volume) all have been suggested. Apparent Neoarchean crustal growth so rapid as to lead to "un-subduction-like" crustal growth rates (e.g., Reymer and Schubert, 1984) was taken as indirect justification for some of these nonsubduction crustal growth models. Since then, it has become clear that in some terranes, such as the western Superior province, these high growth rates resulted from incomplete sampling of magmatic rocks for the U-Pb zircon age record. More thorough sampling and dating reveals development of some Neoarchean continental crustal terranes over longer periods than previously inferred, approaching modern subduction rates.

So, at present, the arc model of crustal growth by plate tectonic processes is directly supported by observations of Mesoarchean to Neoarchean terranes (e.g., western Superior province, Canada; the Pilbara craton, Australia; the Dharwar craton, India; and the North Atlantic craton) that have geological evidence that they were formed by or closely associated with subduction or accretion by subduction (Krogstad et al., 1989; Smithies et al., 2005; Percival et al., 2006b; Polat et al., this volume; Wyman et al., this volume). The western Superior province in particular, provides the most striking such case. Geological/tectonic syntheses of the western Superior province (Card, 1990; Stott, 1997; Percival et al., 2004, 2006b; Pease et al., this volume) recognize three distinct terrane types that repeat in five linear crustal domains: (1) old remnants of continental crust, (2) oceanic domains, and (3) metasedimentary belts separating continental and oceanic domains (Fig. 8). The old remnants of continental crust were created chiefly in the Mesoarchean and must have existed independently as continental nuclei rafted into position in the Neoarchean entrained in younger oceanic lithosphere. Geological and geophysical observations strongly favor a plate tectonic model of building the western Superior province by operation of a southward-younging succession of subduction zones: (1) the presence of clear continental and oceanic domains indicating a Neoarchean plate tectonic Wilson cycle (Percival et al., 2006b); (2) juvenile mantle-derived magmas with source enrichments due to the introduction of fluids in the mantle wedge (Shirey and Hanson, 1984; Stern et al., 1989; Stern and Hanson, 1992); (3) calc-alkaline granitoid batholiths whose dimensions are comparable to those in modern continental arcs such as Sierra Nevada, Patagonia, and British Columbia (Percival et al., 2006b); (4) long strike-slip fault systems (Percival et al., 2006a) similar to those in California, British Columbia, and Alaska; and (5) shallowly dipping crustal and mantle seismic reflectors that trace relict subduction zones (van der Velden and Cook, 2005) and show fossil slabs preserved near the Moho (Musacchio et al., 2004). Attached to this subduction terrane is the most seismically well-defined mantle root of any craton (Grand, 1987; van der Lee and Nolet, 1997; Goes and van der Lee, 2002; van der Lee and Frederiksen, 2005).

Cratons such as the Superior province show that as far back as 3.1 Ga, plate tectonics strikingly similar to that operating on present-day Earth not only existed but resulted in a voluminous peak in global crustal production. This voluminous peak in crustal production ca. 2.7–2.9 Ga (McCulloch and Bennett, 1994; Condie, 1998) occurred as the mantle evolved to higher ε_{Nd}, ε_{Hf}, and Nb/Th (Figs. 3A, 5A, and 5B) from 2.8 Ga onwards. Presumably this change was made larger by the irreversibility of removing crust from the mantle and stabilizing it with depleted mantle keels. Nonetheless, the evidence that peaks in crustal production were produced by subduction seems to argue against plume models or mantle overturns (e.g., Stein and Hofmann, 1994) for direct production of large crustal volumes in the Mesoarchean because it is not evident how they would produce crustal rocks with clear subduction-like geochemical features.

ZIRCON CONSTRAINTS ON ARCHEAN CRUSTAL RECYCLING

Understanding the impact of crustal recycling on the development of the modern mantle and crustal reservoirs requires accurate descriptions of their Hadean and Eoarchean counterparts. As noted above, these relationships have been primarily explored using whole-rock abundances of isotopes in the U-Pb, Sm-Nd, Lu-Hf, and Rb-Sr systems in Archean rocks, which are susceptible to change during alteration and metamorphism leading to uncertainty when extrapolating observed parameters to initial parameters (e.g., Vervoort et al., 1996; Moorbath et al., 1997). More recently, however, direct measurements of the Hf, O, and trace element abundances in individual zircon grains have been used to provide additional constraints on the Hadean-Eoarchean crust-mantle system that are more robust than measurements in any whole-rock system (Vervoort et al., 1996; Amelin et al., 2000; Machado and Simonetti, 2001; Griffin et al., 2002; Zheng et al., 2004; Cavosie et al., 2005; Davis et al., 2005; Halpin et al., 2005; Harrison et al., 2005; Nemchin et al., 2006).

Trace Element and O Isotopic Systematics of Zircon

Studies of O isotopic and trace element variations in zircons have been interpreted to varying degrees to indicate the presence of differentiated, sialic crust and a liquid hydrosphere (e.g., Peck et al., 2001; Wilde et al., 2001; Cavosie et al., 2005) on Hadean Earth (see discussion below). Although the trace element abundances in individual zircons do not uniquely constrain the bulk composition of the rocks from which they were derived (e.g., Hoskin and Ireland, 2000; Whitehouse and Kamber, 2002; Coogan and Hinton, 2006), some of the most ancient zircons apparently retain primitive (mantle-like) O isotopic signatures (e.g., Cavosie et al., 2005; Nemchin et al., 2006). As noted by Valley et al. (2006), however, the retention of these relatively primitive ratios is best documented when O isotopic analyses can be spatially paired with U-Pb data (e.g., via ion probe). Using a spatially resolved data set helps reduce effects related to subsequent alteration and metamorphism, which can dilute the original signal via mixing at later times (e.g., Valley et al., 2006). The ability of individual zircons or specific domains within individual zircons to consistently preserve their original O isotopic composition in conjunction with zircon's well-established ability to preserve U-Pb isotopic systematics, despite even granulite facies metamorphism, provides important evidence that the Lu-Hf system in zircon can also preserve original signals especially in nonmetamict, low-U, low-Th zircons.

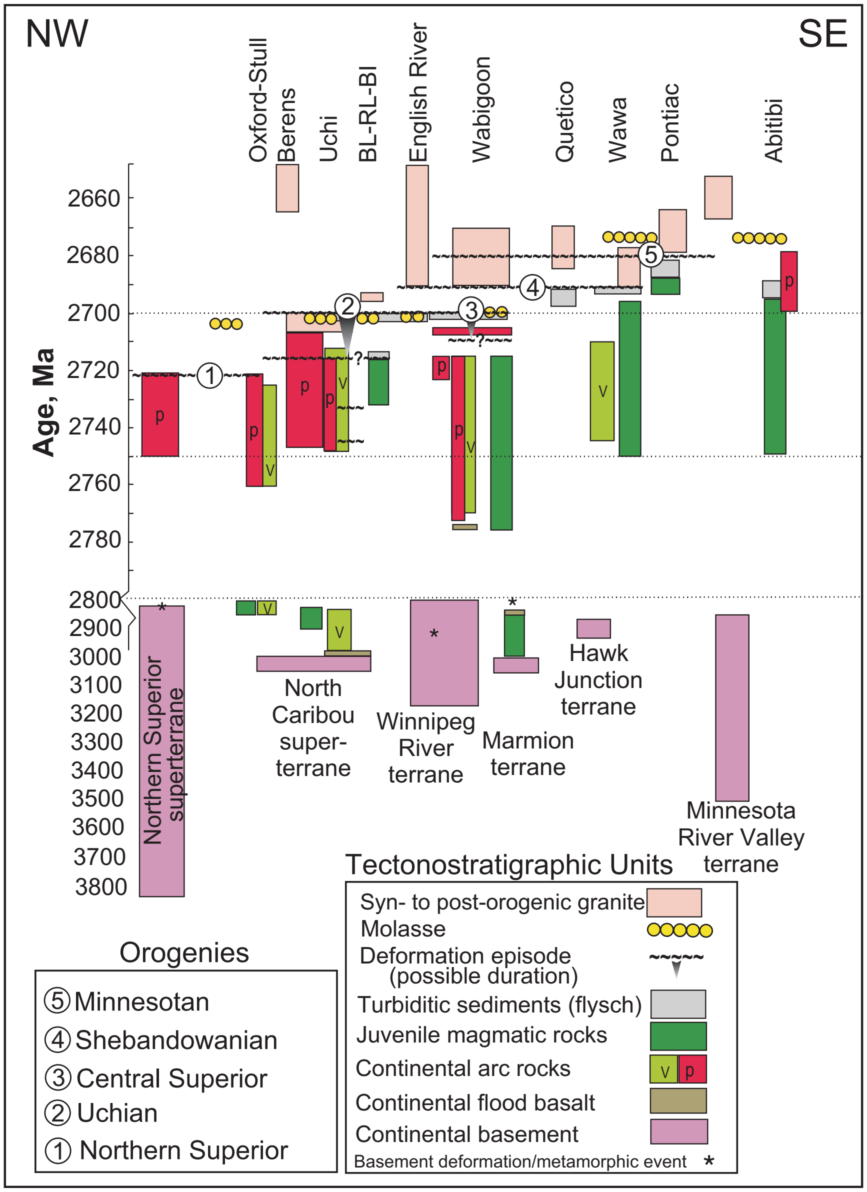

Figure 8. Repeating geomagmatic cycles of crustal evolution are evidence of subduction-accretion of the western Superior province, Canada, from oceanic and continental fragments (horizontally oriented names just above the legend). Vertically oriented names at top of figure designate the various terranes of the Superior province. Lithologic makeup of each terrane is shown directly under the terrane name. Note that the same sequence of tectonostratigraphic units is repeated five times at successively younger ages toward the southeast: continental arc rocks (v–volcanic, p—plutonic); juvenile magmatic rocks; sediments; and postorogenic granites. After Percival et al. (2006b), with permission of *Canadian Journal of Earth Sciences*.

Lu-Hf Systematics of Zircon and Their Utility in Studies of Crustal Recycling

While the whole-rock Sm-Nd system has been a staple of Archean crustal studies for many years, the Lu-Hf system (in zircon) is rapidly becoming recognized as at least a valuable complement to the traditional Sm-Nd measurements for a number of reasons: (1) The Lu-Hf system has a shorter half-life that provides better temporal resolution; (2) Hf (a high field strength element) is relatively immobile during metamorphic and/or metasomatic processes; (3) Hf can be readily measured in very robust mineral reservoirs characterized by both high Hf and low Lu/Hf (i.e., zircon and baddeleyite) with no chemical preparation in the case of laser ablation and smaller potential errors of extrapolation to initial values; (4) the concordancy of the U-Pb data for an individual zircon or part thereof can be used as a guide to the extent to which the Hf isotopic systematics in an individual zircon (or part of a zircon) have been disturbed; and (5) quartz-saturated mafic rocks may contain zircon or if undersaturated, baddeleyite, providing a significant advantage over extrapolating the relatively high and more readily disturbed whole-rock Sm/Nd over billions of years to obtain initial ratios for mafic compositions. This is particularly true for Archean rocks because the differences in isotopic composition between models for chondritic and depleted sources become progressively smaller with age, regardless of the parameters chosen (e.g., Patchett et al., 2004). Although these differences appear larger for the more rapidly decaying Lu-Hf system, it is still critically important to measure the Hf isotopic system in the most robust and carefully characterized reservoirs. Consequently, the Lu-Hf system in zircon offers a better opportunity to obtain reliable initial isotopic ratios throughout the Hadean and Eoarchean. This system, therefore, is better able to distinguish the extent of juvenile and recycled components in Archean crust even though zircons typically form in evolved, felsic magmas that may have incorporated Hf from preexisting crust.

Zircon Hf Evidence from the Oldest Zircons for Hf Isotopic Evolution in the Hadean and Eoarchean

At present there are only a limited number of studies in which U-Pb ages and Lu-Hf data have been reported for individual Eoarchean and Hadean zircons and even fewer that report O isotopic and trace element data for the same grains or parts thereof (e.g., Amelin et al., 1999; Cavosie et al., 2005; Harrison et al., 2005). Collectively these studies have focused on defining the extent of Hf isotopic variability by developing time-ε_{Hf} databases for individual rocks or regions. For example, Amelin et al. (2000), Harrison et al. (2005), Bennett et al. (2007a), and Griffin et al. (2004) have reported ε_{Hf} values for 2.5–4.3 Ga zircons from the Archean cratons of Australia. Reported values for ε_{Hf} at 4.2 Ga range from +15 to –7 and imply the early development of reservoirs both higher ($^{176}Lu/^{177}Hf > 0.1$) and lower ($^{176}Lu/^{177}Hf < 0.01$) than modern depleted mantle (~0.04) and continental crust (~0.01). The least extreme Hf compositions from the oldest Hadean zircons appear to derive from a range of sources that include those consistent with the upper mantle after global differentiation of the EER (Fig. 6; slightly positive ε_{Hf}), whereas the more extreme compositions may reflect not-yet-mixed, short-lived, depleted and enriched reservoirs (e.g., Kamber, 2007). Many other younger Hadean zircons must have been derived from enriched sources (negative ε_{Hf}; Fig. 6) (Harrison et al., 2005; Kramers, 2007). In the case of the zircon derived from the very depleted reservoir noted in Harrison et al. (2005), the extrapolated value exceeds the modern depleted mantle value by more than an order of magnitude. Assuming that the reported Hf values are correct for the depleted reservoir, this early, "ultradepleted" reservoir must have been severely and rapidly altered by recycling and mixing with less depleted or even enriched in order to produce the more moderate values that characterize the modern depleted mantle (e.g., Salters and Stracke, 2004).

Harrison et al. (2005) proposed that the mixing of an early ultradepleted reservoir occurred with the enriched reservoir represented by ε_{Hf} values <0, which these authors interpreted to be differentiated sialic crust based on Ti crystallization temperatures and felsic mineral inclusions found in some zircons. Though these arguments are strong with regard to the existence of a sialic crustal composition, they do not speak directly to the relative volumes of such materials in the Hadean, nor do they provide insight into how these sialic materials may have been recycled. In modern Earth, recycling of differentiated compositions is highly concentrated at convergent plate boundaries in which subduction of sialic detritus and/or tectonic erosion occurs. For either of these mechanisms to operate, however, much larger volumes of oceanic lithosphere are concomitantly recycled (e.g., Chase and Patchett, 1988). For Hadean Earth, we have no firm understanding of whether terrestrial geodynamics included plates, and if so, were plate boundary interactions similar to those of today? We do know, however, that differentiated rocks at mid-ocean ridges do produce zircon with some compositional similarities to zircons produced in convergent margin settings (e.g., Hoskin and Ireland, 2000; Coogan and Hinton, 2006), although several cycles of remelting may be needed to produce the closest similarities to continental zircons (Grimes et al., 2007).

A clear understanding of the geodynamic and geochemical implications of reported Hf isotopic compositions in Hadean zircons from Australia will ultimately require verification from other localities as well as evidence from other systems in ancient rocks that are consistent with these data (e.g., Kramers, 2007). To date, the very enriched and depleted reservoirs implied by the data of Harrison et al. (2005) have not been confirmed. Bennett et al. (2007), however, report $^{142-143}Nd/^{144}Nd$ from 3.6 to 3.9 Ga rocks from Greenland and Australia and $^{176}Hf/^{177}Hf$ from their zircons that show evidence for extraction from a reservoir with strong, early depletion in the Sm-Nd system, but with a chondritic signature in the Lu-Hf system (as recorded in zircon). A first-order mass balance between sialic crust and depleted mantle cannot account for this "discrepancy" and strongly suggests that a pairing of less fractionated mafic crust (e.g., stronger LREE fractionation than HREE fractionation) and depleted mantle may be more realistic for early Earth (Kramers, 2007). Dominance of a mafic differentiate rather than a sialic differentiate as the primary complement to the early depleted mantle would not, however, preclude the development of strongly LREE-depleted mantle sources, as seen in lunar samples. The (relatively) moderate $^{143}Nd/^{144}Nd$ and $^{176}Hf/^{177}Hf$ of the modern MORB source, the petrogenetically reasonable relationship between its Sm-Nd and Lu-Hf systems as evidenced by the Hf-Nd array of MORB (e.g., Vervoort and Blichert-Toft, 1999), and the lack of evidence from the mantle keels of ancient continental nuclei in the form of either xenoliths or younger magmatic rock compositions (see below), however, suggest that any ultradepleted reservoirs were short-lived. The formation of these depleted reservoirs, regardless of the degree of depletion, is undoubtedly tied to melt extraction. Whether this melt extraction occurred in a plate tectonic scenario (i.e., melting at ridges) or was related to formation of a magma ocean (Kramers, 2007) is not yet resolvable.

CONTINENTAL LITHOSPHERIC MANTLE WITH SUBDUCTION IMPRINTS

Continental cratons are hallmark features of Earth because of their high topographic surface, old geologic age, sialic composition, seismic stability, fast P-wave velocity, and high proportion of mineral deposits. Ancient cratonic regions also are characterized by lithospheric mantle keels that are similar in age to the overlying crust and are thought to stabilize cratons over time.

Thus the process of making ancient continental crust requires the production of a full continental lithospheric section (termed the "continental tectosphere" by Jordan, 1981) with an attendant mantle keel, in some cases more than 150 km thick. Although present subduction produces some depleted mantle, no modern subduction zone seems capable of depleting the mantle to the extent that it is seen in the Archean. Furthermore, Meso- to Neoarchean subduction terranes with mantle keels (see above) provide evidence from samples of the mantle keel itself (e.g., kimberlite-borne xenolith suites) that some variant of subduction was the key to forming continental cratons. These samples of peridotite, eclogite, and diamond are important to the debate on the onset of plate tectonics on Earth because they come from the only portion of the mantle isolated from plate tectonic convection since the Meso- to Neoarchean.

Evidence from Mantle Xenoliths

Recent reviews (Pearson et al., 2003; Carlson et al., 2005) cover the geochemical aspects of the two main types of xenoliths in kimberlites: peridotites (harzburgites, lherzolites, and wehrlites) and eclogites (the high-pressure metamorphic equivalent of basalt). Most studies have focused on the Kaapvaal craton of southern Africa, although detailed studies have been completed also on the Siberian, Tanzanian, and Slave cratons. Peridotites, although they make up the bulk of the continental mantle keel by volume (Schulze, 1989), carry ambiguous subduction signatures. They are characterized by strong depletion in melt components (e.g., Fe, Ca, Al) but also secondary enrichments in Si and the large ion lithophile trace elements. The latter is taken as primary evidence of the process of mantle metasomatism. The depletion is understood to be a primary feature of the peridotites due to high extents of melting and has been dated by Re-Os model age systematics (Carlson et al., 2005) as Neoarchean to Mesoarchean in the Kaapvaal. The depletion could be related to melting in the mantle wedge, especially if Archean subduction zones were hotter than and perhaps as wet as those today. Such differences, though, are not clear, as the debate over wet (subduction-related; Grove et al., 1999; Parman et al., 2004) versus dry (plume-related; Arndt et al., 1998) komatiites shows. Si enrichment in cratonic peridotites leads to high modal orthopyroxene contents (Boyd et al., 1997; Boyd, 1999) and has been linked to subduction through the partial melting of eclogite. Eclogites melt to form tonalitic magmas that react with the bulk peridotite, leaving it Si-enriched (e.g., Kelemen et al., 1998). In principle, large ion lithophile trace element enrichments in the peridotite would be a good indicator of subduction zone fluids except that they are nearly completely overprinted at much younger times by the high trace element content of the kimberlitic host magma. Although there are no direct age constraints on when Si enrichment occurs, it likely follows closely after the depletion for two reasons: This is when eclogite would be available to melt, and Si enrichment is not related to the very young trace element enrichments imparted by the host kimberlitic magma because kimberlites are silica-undersaturated. Thus, cratonic mantle peridotites carry evidence consistent with, but not requiring, Mesoarchean subduction.

On the other hand, eclogites do carry clear subduction signatures. The most direct of these signatures is oxygen isotopic composition. Eclogites from Roberts Victor were discovered in the 1970s to have both anomalously light and heavy $\delta^{18}O$ (MacGregor and Manton, 1986) similar to that seen in ophiolites. The recent summary of models for the formation of mantle eclogite (Pearson et al., 2003; Jacob, 2004) shows that this is a ubiquitous feature of mantle eclogites (Fig. 9). Eclogites, therefore, are not simply high-pressure magmas formed below or within the lithosphere, because temperatures at those depths would be in excess of 1100 °C and would not permit O isotopes to retain their low-temperature, fractionated compositions. Rather, eclogites carry a surface geochemical imprint of seawater alteration in the hydrothermal systems that interact with oceanic lithosphere to continental lithospheric mantle keel depths. Also consistent with the former residence of eclogite xenoliths at Earth's surface is the common occurrence of coesite and reduced carbon in the form of graphite or diamond. Eclogites, like the peridotites, are subject to infiltration from the host kimberlitic magma, thus requiring very careful treatment of clean mineral separates that can be used to reconstruct whole-rock compositions. Trace element contents of whole-rock eclogites reconstructed from their constituent minerals are roughly consistent with the patterns seen in basalt or gabbro from the depleted oceanic lithosphere (Jacob et al., 1994; Jacob, 2004). Radiogenic isotopes (U-Pb, Sm-Nd, and Re-Os) establish eclogite ages as Neoarchean to Mesoarchean (Jacob

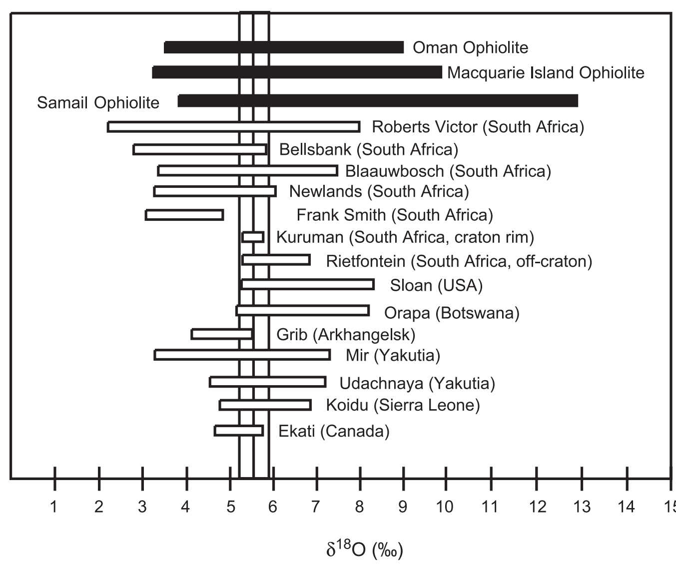

Figure 9. Oxygen isotopic composition ($\delta^{18}O$) of eclogite xenoliths (white bars) compared to that of ophiolites (black bars) and isotopically unaltered mantle (white vertical field). Note that most eclogite suites fall well outside the range for the mantle, similar to ophiolites, which is widely accepted as due to low-temperature seafloor alteration. After Jacob (2004), which cites the original data sources.

and Jagoutz, 1994; Pearson et al., 1995; Shirey et al., 2001; Barth et al., 2002; Menzies et al., 2003; Jacob, 2004), proving that they cannot be pieces of modern oceanic lithosphere and implying subduction by that time. Furthermore, the high Os and low Re content of eclogite xenoliths are typical of basaltic komatiites to komatiite rather than basalt (Shirey et al., 2001; Menzies et al., 2003). Komatiite or basaltic komatiite is an expected product of melting in a hotter mantle either at ridges (Takahashi and Brearley, 1990) or in plumes (Herzberg, 1999; Arndt, 2003), thus providing another link between eclogite and the Archean oceanic lithosphere.

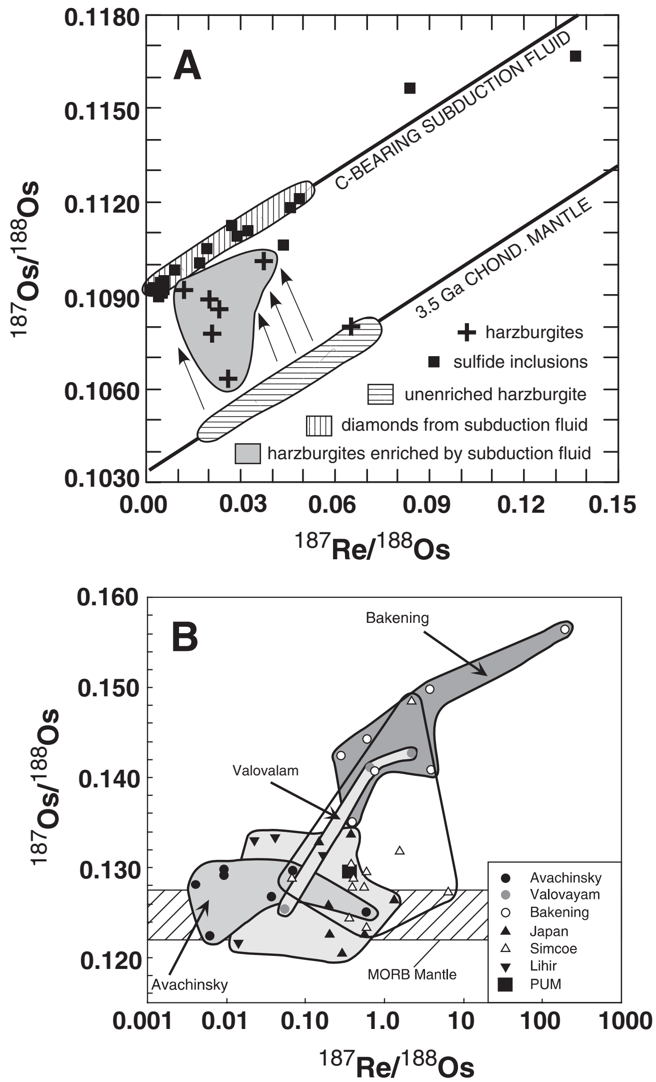

Figure 10. Comparison of Re-Os isotopic systematics for 3.52 Ga sulfide inclusions in diamonds and harzburgites from the Panda kimberlite pipe, Slave craton, Canada (A), versus recently erupted Kamchatka peridotites from the mantle wedge (B) (adapted from Widom et al., 2003; Westerlund et al., 2006). Horizontally ruled field and 3.5 Ga reference line in A show the expected position for harzburgites if they had chondritic Re-Os systematics. Note that only one harzburgite falls in this field; the other harzburgites have distinctly elevated Os isotopic compositions (within gray field) toward that of the diamonds that they host (vertically ruled field and reference line for C-bearing fluid). Kamchatka peridotites (Bakening, Valovalam, Avachinsky) and others from arc settings (Japan, Simcoe, Lihir) show similar enrichments in $^{187}Os/^{188}Os$ (PUM—primitive undepleted mantle).

Evidence from Diamonds and Their Inclusions

Macrodiamonds from the continental lithospheric mantle carry two types of inclusion suites that have been amenable to trace element and isotopic analysis: silicates (garnet, olivine, orthopyroxene, and clinopyroxene) and sulfides (pyrrhotite, pentlandite, or chalcopyrite). Silicate inclusions have been divided into p-type (peridotitic, including both harzburgitic and lherzolitic compositions) and e-type (eclogitic) parageneses based on garnet (Cr, Al) and pyroxene (Na, Mg, Fe) compositions, whereas sulfide inclusions have been subdivided into p-type versus e-type based on the Ni content of their sulfide. Sm-Nd and Rb-Sr isotopes from silicate inclusions from both suites have allowed dating of their diamond hosts (see review of Pearson and Shirey, 1999) as Archean (e.g., Richardson et al., 1984) or Proterozoic (e.g., Richardson, 1986; Richardson et al., 1990; Richardson and Harris, 1997). The Sm-Nd isotopic data on silicate inclusions have been difficult to relate directly to subduction either because the use of model age systematics assumes the extraction of their host from a chondritic mantle reservoir or because the Sm-Nd isochrons with negative initial ε_{Nd} compositions more typically reflect a lithospheric history of metasomatism with low-Sm/Nd fluids prior to diamond growth.

Sulfide inclusions analyzed for their Re-Os isotopic systematics provide much clearer age and petrogenetic links to subduction (Shirey et al., 2004). P-type sulfides have proven to be rare in the Kaapvaal craton. A remarkable suite of p-type sulfides from diamonds in the Panda kimberlite pipe, Slave craton, Canada, however, provides a Paleoarchean (3.52 Ga) isochron age and an elevated initial Os isotopic composition that is most readily explained by fluid enrichment in a mantle wedge (Fig. 10) (Westerlund et al., 2006). E-type sulfides from the Kimberley pool of the Kaapvaal craton show sources similarly enriched in Os isotopic composition that also are interpreted to reflect subduction-related enrichments (Richardson et al., 2001). Sulfur isotopic compositions of eclogitic sulfides from Orapa on the Zimbabwe craton show isotopically light values of $\delta^{34}S$ (Eldridge et al., 1991) and unusual Pb isotopic compositions (Rudnick et al., 1993) that have long been linked to low temperature, and thus implicate surficial sulfur. Mass-independent fractionations in $\Delta^{33}S$ (Farquhar et al., 2002a, 2002b) are further evidence that the sulfur was volcanogenic and obtained its distinctive mass-independent fractionation signature via photocatalyzed reactions in a low-pO_2 atmosphere that existed prior to 2.3 Ga (Farquhar et al., 2002a, 2002b). Subduction is by far the most plausible way to incorporate such sulfur. For the Kaapvaal craton in particular, an indirect but perhaps more extensive link to subduction is made by the association between diamondiferous eclogite xenoliths and eclogitic diamonds, the overlap in Neoarchean to Mesoarchean ages of both diamonds and eclogites, and the widespread occurrence across the craton of these sulfide inclusions (Shirey et al., 2001).

The trace element and isotopic compositions of macrodiamonds that host inclusions have been recently reviewed (Pearson et al., 2003). Briefly, macrodiamonds can be distinguished on the basis of the paragenesis of their inclusions as described above into peridotitic and eclogitic types. The p-type diamonds have C and N isotopic compositions centered roughly around mantle values ($\delta^{13}C$ = –6‰ to 0‰ and $\delta^{15}N$ = –10‰ to 0‰, except for one locality; see Fig. 11), whereas the e-type diamonds overlap these compositions but also carry a subpopulation that tails off to isotopically light carbon ($\delta^{13}C$ = –22‰) and heavy nitrogen ($\delta^{15}N$ = +7‰). The cause of these isotopic differences in carbon and nitrogen relative to the mantle is by no means clear, and it has been argued from mass balance considerations and the composition of isotopic end members that they result from intra-mantle fractionation (Cartigny et al., 1998, 2001). However, note that the position of some eclogitic diamonds in carbon and nitrogen composition is consistent with having incorporated some of the isotopic signatures of organic-rich sediments (Fig. 11) (Pearson et al., 2003).

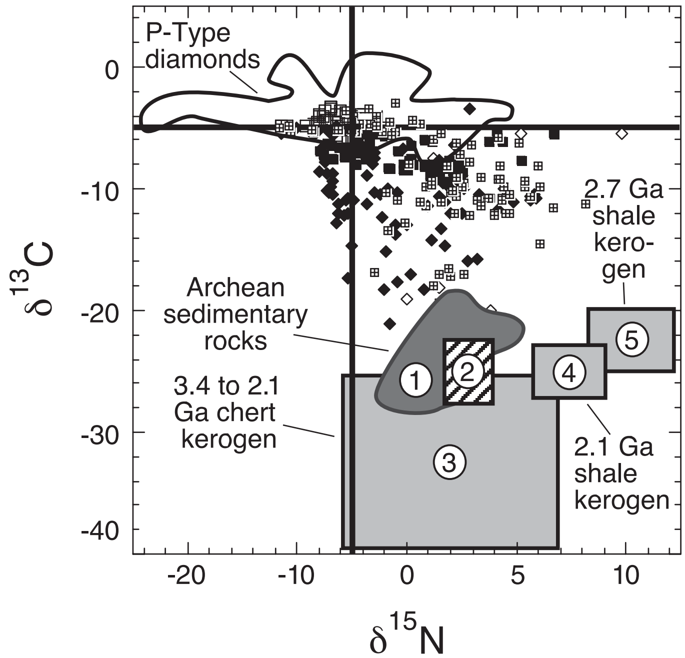

Figure 11. Carbon and nitrogen isotopic composition of macroscopic diamonds mined from kimberlite compared to the mantle (solid lines) and various supracrustal rocks and organic components. Separate symbols are e-type diamonds; p-type diamonds are within a field. Most of the diamond isotopic data are from the work of Cartigny (2005) with references as given in Pearson et al. (2003; see caption to Fig. 57 therein, after which this figure was modified). Composition of Precambrian and Phanerozoic sedimentary rocks (1) taken from Navon (1999) and the references therein. Modern subducting sediment compositions (2) from Sadofsky and Bebout (2004). Fields for 2.1–3.4 Ga chert kerogen (3), 2.1 Ga shale kerogen (4), and 2.7 Ga shale kerogen (5) estimated from the work of Jia and Kerrich (2004) and Marty and Dauphas (2003).

HADEAN AND ARCHEAN OCEANIC LITHOSPHERE-HYDROSPHERE: EVIDENCE FOR EARLY WATER

The presence of liquid water at the surface of early Earth is important in the plate tectonic debate because of water's role in producing silicic magmas typical of continents through wet melting of mantle peridotite and basaltic crust. Detailed consideration of the ultimate source of terrestrial water is beyond the scope of this paper. Furthermore, sources as diverse as chondrites, comets, hydrous planetesimals, hydrous minerals, and gas-absorbing grains recently have been proposed by the cosmochemical and astrophysical community (Abe et al., 2000; Morbidelli et al., 2000; Kramers, 2003; Drake, 2005; Marty and Yokochi, 2006). Experimental data on water solubility and partitioning in mantle minerals and various geophysical arguments and measurements in nominally anhydrous minerals indicate a bulk Earth (including its surface water) content of 350–500 ppm water (Marty and Yokochi, 2006). Consideration of this water originating from chondritic sources requires the early Earth water content to be much higher, as high as 50 times the current ocean masses of water (Abe et al., 2000). The current estimate of much lower bulk Earth water content is possible due to the water lost during terrestrial evolution and the Moon-forming event.

Recent high-precision ^{142}Nd measurements in primitive meteorites (Boyet and Carlson, 2005) indicate terrestrial differentiation within 30–40 m.y. after the solar system condensation event. It is interesting to speculate how much water was retained by Earth after the early differentiation episode and the Moon-forming event, although it is generally believed that some volatiles were added via asteroidal and interplanetary dust input during later accretion. The relative abundances of the radiogenic, nucleogenic, and fissiogenic noble gas isotopes and, in particular, the Xe isotope record as measured in present-day MORB and plume sources are consistent with extensive loss of volatiles in the first 100 m.y. after Earth formation. The Xe isotope constraints also imply that during the Hadean the rate of loss of volatile elements was at least one order of magnitude higher than at present (Yokochi and Marty, 2005). These data also imply that Hadean Earth was more thermally active.

Elevated $\delta^{18}O$ in excess of typical mantle values observed in 4.1–4.3 Ga detrital zircons in Western Australia (Mojzsis et al., 2001; Peck et al., 2001; Wilde et al., 2001) imply water-rock interaction in crustal processes at least as early as these well-dated zircon ages indicate. One of these studies (Mojzsis et al., 2001) suggested that the elevated values were evidence of generation of granitic melts in a suprasubduction zone environment and thus were evidence for plate tectonic processes analogous to those of the present day operating in the Hadean. Subsequent studies have cast doubt on the veracity of the elevated values in unambiguously magmatic, undisturbed zircon (Nemchin et al., 2006) and/or questioned whether the hydrous granite origin for such zircon is a necessary conclusion from O data (e.g., Whitehouse and Kamber, 2002; Coogan and Hinton, 2006). Alternative suggestions to explain the elevated $\delta^{18}O$ values include burial of hydrated metabasalts to depth by volcanic resurfacing (Kamber et al., 2005b) or fractionation resulting from carbonation of basalts in a CO_2-rich Hadean atmosphere (Coogan and Hinton, 2006).

In order to evaluate the possible existence of an early liquid water ocean on Earth, Kramers (2003, 2007) considered the relative abundances, with respect to carbonaceous chondrites, of the volatile elements H, C, N, Cl, Br, I, Ne, Ar, Kr, and Xe that are presently concentrated in the outer Earth reservoirs such as atmosphere, hydrosphere, and sediments, and concluded that their elevated abundances including overabundances of H and Cl are best explained by the presence of liquid water at the surface early in Earth history.

MAFIC-ULTRAMAFIC COMPOSITION OF THE EARLIEST RECYCLED CRUST

Consideration of the type of crust that was available to have been recycled on earliest Earth is critical to the debate on when plate tectonics started. It is central to whether we can say that plate tectonics operated from formation of the very first crust and constrains how early plate tectonics must have worked. Estimates for the composition of early crust range from silicic (e.g., granitic; Armstrong, 1981, 1991; Mojzsis et al., 2001; Harrison et al., 2005), to mafic-ultramafic (e.g., basaltic to komatiitic; Carlson and Shirey, 1988; Chase and Patchett, 1988; Takahashi and Brearley, 1990; Galer and Goldstein, 1991; Kamber, 2007; Kramers, 2007). A granitic crust implies differentiation, access of water to melt source regions, buoyancy, and a recycling mechanism such as erosion and sedimentation that can lead to entrainment of continental material into the oceanic lithosphere and eventually the mantle. A mafic to ultramafic crust implies direct mantle derivation, little first-stage differentiation, no necessary access of water to the mantle source, and a bulk recycling mechanism involving density such as lithospheric slabs or eclogitic blobs.

Armstrong (1981, 1991) was the main proponent of early, complete, and large-volume crustal differentiation and recycling. His model hinges on the continental freeboard argument of Wise (1974) extrapolated back into the Hadean, and on the mechanisms of continental erosion and sediment recycling at subduction zones, and it draws parallels to the early differentiation that occurred on the Moon and the terrestrial planets (Armstrong, 1981, 1991). Recent work on the oldest terrestrial zircons that show evidence of crustal reprocessing (e.g., Fig. 6) (Amelin et al., 2000; Harrison et al., 2005), rather cool magmatic temperatures (Watson and Harrison, 2005), and heavier-than-mantle $\delta^{18}O$ (Mojzsis et al., 2001, the arguments of Nemchin et al., 2006, above notwithstanding; Cavosie et al., 2005) has revived the idea of an early granitic crust and thus the early crustal growth models of Armstrong (e.g., Harrison et al., 2005). Because sediment subduction is inherent in the Armstrong model, its acceptance would argue that plate tectonics starts with the earliest differentiation of Earth, whereas its refutation would suggest plate tectonics starts at some later time. These questions are central to this volume.

While the separation of an early continental crust does explain some of the isotopic and geochemical features of the oldest zircons mentioned above, it is inconsistent with many features of Hadean-Eoarchean Earth and its juvenile rock record. Its key premise of continental freeboard (Wise, 1974) has dubious applicability to continents that had not been cratonized with thick mantle keels (e.g., the Hadean to Eoarchean). When freeboard arguments are reexamined, they preclude large volumes of continental crust in the Hadean and Archean (Hynes, 2001). As discussed in detail above ("Earliest Mantle Isotopic Signatures from Juvenile Crust"), separation of large volumes of continental crust would produce depletions in the Nd and Hf isotopic composition of the depleted mantle such that ε_{Hf} would be about twice ε_{Nd}. Uncertainties about the pristine nature of the Nd and Hf isotopic compositions on the earliest rocks aside, this relationship is not seen for earliest Earth but rather after the Paleoarchean (Figs. 5A and 5B). Erosion and sedimentation is not an effective way to recycle continental crust without the high elevations to speed erosion. Not only are high elevations unlikely in the Hadean, but they should have left larger amounts of residual Hadean crust preserved at the surface than the detrital zircons occurring in the few small outcrop belts that currently exist. Careful examination of the oldest sediments (3.5–3.8 Ga) shows that they only contain zircons that are 100–300 m.y. older than the deposition age and no Hadean zircons (Fig. 12) (Nutman, 2001). This pattern precludes widespread existence of voluminous continental crust. The continent age versus surface area map first published by Hurley and Rand (1969) shows *preserved* crust, not crustal growth. Armstrong was able to mimic the histogram of crustal age versus crustal area preserved by appealing to more rapid ocean-floor creation, subduction, and mantle mixing in the Archean—all driven by higher Archean temperatures (Armstrong, 1981). Because subduction is widely accepted as a process to form continental crust, it not clear from the Armstrong model how or why subduction should destroy crust in the Hadean yet create it from the Neoarchean onward. Finally, implicit in the mechanism of continental crustal recycling of Armstrong is the necessity to recycle much larger amounts of oceanic lithosphere to incorporate the sediment into the mantle. Thus, the idea of a voluminous early continental or granitic crust that was fully recycled is not tenable.

Instead, the early crust on Earth was likely to have been mostly mafic to ultramafic (e.g., Kamber, 2007; Kramers, 2007), and its melting and recycling must have dominated geochemical processes in the Hadean. The Hadean zircon record itself is consistent with this scenario and does not provide unequivocal evidence for a dominantly granitic crust. In addition to being found in continental rocks, zircon also occurs today in oceanic settings where silica-saturated to -oversaturated melts are produced from silica-undersaturated parents: pegmatitic patches or plagiogranites that crystallize within gabbros, dacites that form as extreme differentiates of mid-oceanic-ridge magma chambers, and rhyolites or trondhjemites generated by differentiation or melting of oceanic-island basalt. The last petrogenetic setting, where hydrothermally altered basalt can be buried to the depths of wet

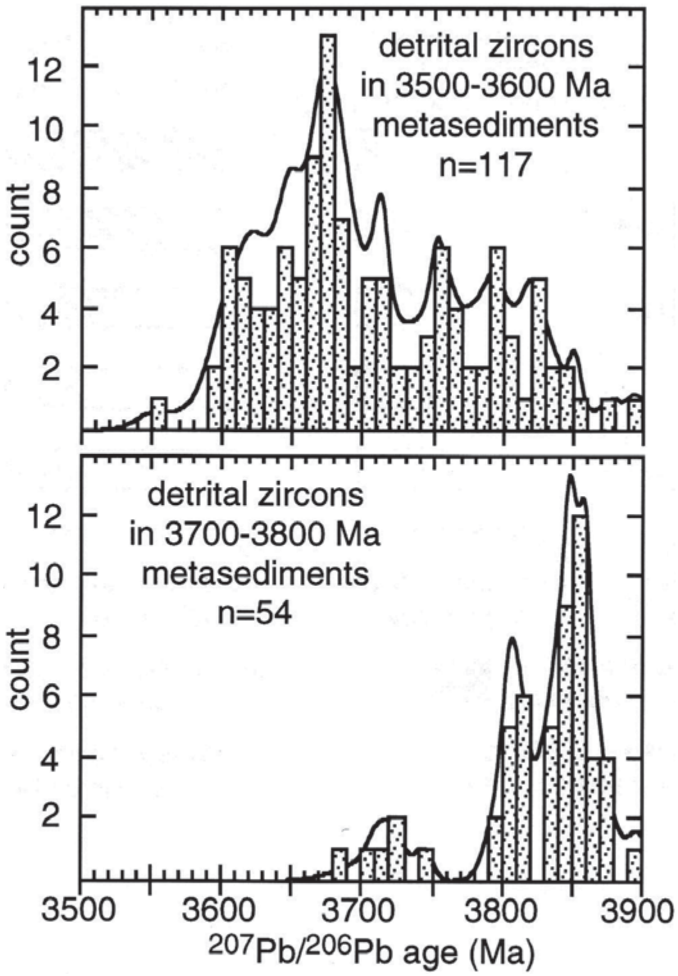

Figure 12. Histograms of detrital zircon in Mesoarchean sediments plotted versus ^{207}Pb/^{206}Pb age (with relative probability curves in background) showing a lack of grains older than 3.9 Ga. After Nutman (2001), with permission from *Precambrian Research*.

melting (e.g., Marsh et al., 1991) by the repeated addition of new basalt in shield-building stages, is interesting because it may be the most akin to Hadean conditions. The composition of some Hadean zircon does resemble the composition of modern oceanic zircons (Coogan and Hinton, 2006), and there is a population of least altered Hadean zircon that displays magmatic, mantle-like δ^{18}O (Nemchin et al., 2006). Many other Hadean zircons display inclusions of crustal minerals (e.g., quartz, K-feldspar) and much heavier δ^{18}O (Maas et al., 1992; Peck et al., 2001; Wilde et al., 2001; Cavosie et al., 2005), but these could have an explanation in the repeated remelting of newly formed silica-oversaturated parents, again under wet conditions. Thus, we interpret the Hadean zircon record chiefly as evidence of remelting of mafic to ultramafic crust under wet melting conditions that would have produced silica-oversaturated trondhjemitic to tonalitic melts from the first stage and ever more siliceous and granitic melts in subsequent stages. These nascent sialic components apparently lacked a well-developed, depleted mantle keel to preserve them and disaggregated rapidly, but remained near the surface to survive recycling. Such multiple processing could be areally restricted and shallow, leaving small terranes whose zircons were eventually collected into the restricted occurrences seen today. Each silica-oversaturated melt is a product of small degrees of partial melting, so rather than representing large volumes of granitic crust, the zircons may instead represent many tens to hundreds of times the volume of reprocessed mafic to ultramafic crust (e.g., Kamber, 2007). Thus these zircons reveal more about the hydrothermal/anatectic processes accompanying melting and alteration in the shallow lithosphere than about the early tectonic processes on Earth involving deeper portions of the upper mantle and clearly do not dictate continental crust as the dominant component of any EER.

ONSET OF PLATE SUBDUCTION AND CONTINENT FORMATION

Although this paper has focused chiefly on the isotopic data, the question of when plate tectonics started on Earth and its form require an integration of these data with additional evidence from geophysics, trace elements, and petrology. Taken together, the evidence produces a self-consistent model for Earth's geologic history and a specific starting point for plate tectonics at ca. 3.9 Ga. This is not inconsistent with specific terrane studies (e.g., Benn and Moyen, this volume; Polat et al., this volume), key lithological associations (e.g., Foley, this volume; Wyman et al., this volume), and geologic syntheses (e.g., Brown, this volume; Condie and Kröner, this volume; Pease et al., this volume) that have plate tectonics operating by the late Mesoarchean or Neoarchean. Rather, it is apparent from the global isotopic and trace element record that plate tectonics, even restricted in extent, likely started earlier. Prior to ca. 3.9 Ga, earliest Earth underwent global dynamic and differentiation processes that were not plate tectonic, but that need to be considered to interpret the later rock isotopic record's implications for the start of plate tectonics: the separation of the core, the deep sequestering of the EER and the consequent formation of the early depleted reservoir, the giant impact to form the Moon, and the formation of an impact-generated magma ocean from which some perovskite fractionated (Table 1). Magma oceans inevitably convect rapidly and cool quickly, so the mantle would have solidified and the oceans condensed back to liquid water within a few thousand to at most a few million years. Kramers (2007) has proposed that the magma ocean would have frozen along its solidus from the bottom of the lower mantle upward, leading to a solidus-determined mantle that would have been gravitationally unstable. A mantle overturn would have ensued, producing large volumes of mafic to ultramafic crust above a stable, nonconvecting mantle that led to a "quiescent" Hadean period (Kramers, 2007). After the quiescent period, the accumulated heat from perhaps 400 m.y. of radioactive decay would initiate convection where the thermal gradient was greatest—from the top down. Throughout the quiescent

TABLE 1. SUGGESTED SUMMARY OF EARLY EARTH EVENTS

Time (Ga)	Event	Evidence
4.57	Accretion	Short- and long-lived isotopic systems in meteorites
4.57–4.51	Core formation	Composition, Hf-W
	First magma ocean	Modeling, energetics
	Separation of early enriched reservoir (EER)	Sm-Nd, composition, Hf-W, Sm-Nd
4.51–4.4	Giant impact to form Moon	Composition, modeling
	Second magma ocean	Modeling
	Perovskite fractionation	Lu-Hf, Sm-Nd
	Mantle overturn?	Hypothesis
4.4–3.9	Oceanic lithosphere (noncontinental)	Hadean zircons, O, Lu-Hf
3.9	Onset of subduction, and first continental crust	Arc-like rocks, ophiolites
3.5	First mantle keels and permanent crust extraction	Nb-Th, Sm-Nd, samples
2.5–3.1	Terranes with direct subduction imprints	Preserved arcs, geophysics

Note: This table is compiled from the literature discussed in the text. Ages are meant to serve as guides, not firm boundaries, since future research will produce new age constraints. The short- and long-lived radioisotopic systems that have been applied to meteorites include: Al-Mg ($^{26}Al \rightarrow ^{26}Mg$), Mn-Cr ($^{53}Mn \rightarrow ^{53}Cr$), Pd-Ag ($^{107}Pd \rightarrow ^{107}Ag$), Rb-Sr ($^{87}Rb \rightarrow ^{87}Sr$), Sm-Nd ($^{146}Sm \rightarrow ^{142}Nd$; $^{147}Sm \rightarrow ^{143}Nd$), Lu-Hf ($^{176}Lu \rightarrow ^{176}Hf$), Hf-W($^{182}Hf \rightarrow ^{182}W$), U-Pb ($^{235}U \rightarrow ^{207}Pb$; $^{238}U \rightarrow ^{205}Pb$).

period, there would have been no continents and Earth's surface would have been dominated by some form of stable, nonconvecting, oceanic lithosphere (Kamber, 2007; Kramers, 2007). This model has the attractions of being able to rapidly remove an excess of terrestrial heat, of a long period where little new crust of any kind was produced, and of providing a surficial reservoir in which to store the high-U/Pb protoliths of the first Archean sediments (e.g., Fig. 7).

The stability of this earliest oceanic lithosphere, however, is an open question because whether Earth's mantle underwent such a convective overturn is not known. Also, it is unclear how a quiescent, stable oceanic lithosphere would have withstood the late, heavy meteorite bombardment or been able to produce Hadean zircons throughout the period from 4.4 to 4.0 Ga without being continually remelted. If, instead, there was no mantle overturn, a more "uniformitarian" scenario can be envisioned where the oceanic lithosphere was produced throughout the Hadean by rapid mantle convection occurring in both ridge and plume modes. Crustal differentiation occurred, producing the early zircon record, but it must have happened around dispersed and recyclable ocean islands or plateaus where water could access the thickening basaltic-komatiitic piles and produce silica-saturated, relatively low-temperature melting. Recycling of these terranes into the mantle would not have been complete because the mafic sources to the earliest sediments were prevented from recycling into the mantle and zircons crystallized from these silicic rocks survived. This period (4.3–3.9 Ga) would have been marked by convective vigor in the mantle and intense meteorite bombardment. Both processes worked to break up the lithosphere, preventing the differentiation from occurring long enough in one localized setting such that the mantle could not form a large enough mass of depleted keel to resist being recycled. Recycling did not occur by slab subduction, but by some other form that was density-driven from the bottom (e.g., Bedard, 2006). This period of dominant recycling would have included only nascent crustal differentiation; there would have been no continent formation or recognizable plate tectonics as marked by the slab subduction geometry observed today.

With the meteorite bombardment tailing off by 3.6 Ga, the oceanic lithosphere could have been maintained in large lithospheric plates with a long enough residence at the surface to cool and become slabs that could sink by subduction. This was the beginning of plate tectonics and the formation of continents. The sequestering of Nb, Ta, and Ti in subducting slabs and their anomalously lower abundance in arc rocks and continental crustal materials is the hallmark signature of slab subduction, modern plate tectonics, and continental growth by the subduction process. Ratios involving Nb in the depleted mantle from which crust was extracted clearly start to change at 3.5 Ga, signaling that the plate tectonic process already had started to make preservable continental crust. The presence of subduction imprints within the continental lithospheric mantle as far back as 3.5 Ga and within the crust as far back as 3.8 Ga support this model. Continental crust only began to be preserved on Paleoarchean to Mesoarchean Earth because deep mantle keels are more effectively produced in Archean subduction settings where water-fluxed, localized melting can achieve crustal differentiation, residue removal, a high degree of mantle depletion, and advective thickening.

The geophysical, isotopic, trace element, and petrologic synthesis presented here allows us to propose that plate tectonics started on Earth ca. 3.6–3.9 Ga and that it is marked by the onset of crustal preservation. It is important to identify what conditions changed in Hadean Earth to allow this change. In the quiescent Hadean model, it would have been the accumulation of radioactive heat in the cool-bottom, postoverturn, nonconvecting, mantle, which took some 400 m.y. to build up after the giant impact that formed the Moon. In the active "uniformitarian" Hadean model, a loss of heat would have, after 400 m.y., permitted silicic crust to begin to stabilize in large enough masses to serve as centers of crustal production and storage. In both models, termination of the late heavy meteorite bombardment would have permitted the survival of larger lithospheric plates than was possible before this time.

CONCLUSIONS

Regardless of initial conditions, diverse lines of evidence point to the start of plate tectonics on Earth shortly after the end of the Hadean. The present upper mantle retains old heterogeneities, some of which could date from subduction in the early Eoarchean, although some of them also could be Eoarchean material subducted more recently. Nb/Th and Th/U of well-characterized mafic to ultramafic rocks though time, representing good estimates of the depleted upper mantle, begin to change from initial values (Nb/Th = 7; Th/U = 4.2) at 3.6 Ga in a unidirectional fashion toward present values (Nb/Th = 18.2; Th/U = 2.6). This signals the appearance of subduction-altered slabs in general mantle circulation from subduction initiated at 3.9 Ga. Juvenile crustal rocks also begin to show that they were derived from progressively depleted mantle after 3.6 Ga from sources that have a typical igneous fractionation of ε_{Nd}:ε_{Hf} = 1:2. This, and the start of the appearance of cratons with stable mantle keels that have subduction imprints at 3.5 Ga, strongly suggest that continental crustal extraction was progressively depleting the mantle from 3.6 Ga onwards. By the Neoarchean, subduction had taken on an appearance similar to present subduction and was capable of producing large cratons with thick mantle keels.

The Hadean zircons precede the subduction processes evident in the earliest Eoarchean juvenile rocks. Their compositions are incompatible with derivation from a voluminous continental crust but instead reflect the integrated effects of separation of the EER and fractionation of Ca-silicate and Mg-silicate perovskite from the magma ocean generated by the Mars-sized impact. This requires the Hadean zircons to come from a continent-absent, mafic to ultramafic protocrust that was recycled in transitory, small-scale fashion that would not have reflected a global plate tectonic system. If the mafic-ultramafic protocrust was a product of a magma ocean overturn after the giant impact, then a stable, cool-bottom mantle might have resulted and the transition to plate tectonics could have been the result of mantle heating from radioactive decay. If, alternatively, the mafic-ultramafic protocrust was produced by traditional mantle convection with no global overturn, then the transition to plate tectonics might have marked the cooling of the mantle to the point where large lithospheric plates could have been formed on a global scale. Cessation of the late heavy meteorite bombardment also contributed to creating an environment that allowed lithospheric plates to stabilize.

ACKNOWLEDGMENTS

The careful editorial handling of Vicky Pease and Kent Condie is appreciated. Bob Stern, Alfred Kröner, and Kent Condie are thanked for originally convening the Penrose Conference "When Did Plate Tectonics Start?" in Lander, Wyoming, June 2006, which led to the review and synthesis presented here. The manuscript was improved by the careful reviews of Al Hofmann, Jan Kramers, and Erik Scherer. Discussions with Al Brandon, Rick Carlson, Janne Blichert-Toft, Vickie Bennett, and Jeff Vervoort were helpful in preparing the original text.

REFERENCES CITED

Abe, Y., Ohtani, E., Okuchi, T., Righter, K., and Drake, M.J., 2000, Water in the early Earth, *in* Righter, K., and Canup, R.M., eds., Origin of the Earth and Moon: Tucson, University of Arizona Press, p. 413–433.

Allegre, C.J., and Turcotte, D.L., 1986, Implications of a two-component marble-cake mantle: Nature, v. 323, p. 123–127, doi: 10.1038/323123a0.

Amelin, Y., 2005, Meteorite phosphates show constant ^{176}Lu decay rate since 4557 million years ago: Science, v. 310, p. 839–841, doi: 10.1126/science.1117919.

Amelin, Y., Lee, D.-C., Halliday, A.N., and Pidgeon, R.T., 1999, Nature of the Earth's earliest crust from hafnium isotopes in single detrital zircons: Nature, v. 399, p. 252–255, doi: 10.1038/20426.

Amelin, Y., Lee, D.C., and Halliday, A.N., 2000, Early-middle Archaean crustal evolution deduced from Lu-Hf and U-Pb isotopic studies of single zircon grains: Geochimica et Cosmochimica Acta, v. 64, p. 4205–4225, doi: 10.1016/S0016-7037(00)00493-2.

Andreasen, R., and Sharma, M., 2006, Solar nebula heterogeneity in p-process samarium and neodymium isotopes: Science, v. 314, p. 806–809, doi: 10.1126/science.1131708.

Armstrong, R.L., 1981, Radiogenic isotopes: The case for crustal recycling on a near-steady-state no-continental-growth Earth: Royal Society of London Philosophical Transactions, ser. A, v. 301, p. 443–472, doi: 10.1098/rsta.1981.0122.

Armstrong, R.L., 1991, The persistent myth of crustal growth: Australian Journal of Earth Sciences, v. 38, p. 613–630, doi: 10.1080/08120099108727995.

Arndt, N.T., 2003, Komatiites, kimberlites, and boninites: Journal of Geophysical Research, v. 108, no. B6, p. 2293, doi: 10.1029/2002JB002157.

Arndt, N.T., and Goldstein, S.L., 1987, Use and abuse of crust-formation ages: Geology, v. 15, p. 893–895, doi: 10.1130/0091-7613(1987)15<893:UAAOCA>2.0.CO;2.

Arndt, N.T., Ginibre, C., Chauvel, C., Albarede, F., Cheadle, M., Herzberg, C., Jenner, G., and Lahaye, Y., 1998, Were komatiites wet?: Geology, v. 26, p. 739–742, doi: 10.1130/0091-7613(1998)026<0739:WKW>2.3.CO;2.

Baadsgaard, H., Nutman, A.P., Rosing, M., Bridgwater, D., and Longstaffe, F.J., 1986, Alteration and metamorphism of Amitsoq gneisses from the Isukasia area, West Greenland: Recommendations for isotope studies of the early crust: Geochimica et Cosmochimica Acta, v. 50, p. 2165–2172, doi: 10.1016/0016-7037(86)90071-2.

Barth, M.G., Rudnick, R.L., Carlson, R.W., Horn, I., and McDonough, W.F., 2002, Re-Os and U-Pb geochronological constraints on the eclogite-tonalite connection in the Archean Man Shield, West Africa: Precambrian Research, v. 118, p. 267–283, doi: 10.1016/S0301-9268(02)00111-0.

Bedard, J.H., 2006, A catalytic delamination-driven model for coupled genesis of Archaean crust and sub-continental lithospheric mantle: Geochimica et Cosmochimica Acta, v. 70, p. 1188–1214, doi: 10.1016/j.gca.2005.11.008.

Behn, M.D., Conrad, C.P., and Silver, P.G., 2004, Detection of upper mantle flow associated with the African superplume: Earth and Planetary Science Letters, v. 224, p. 259–274, doi: 10.1016/j.epsl.2004.05.026.

Bekker, A., Holland, H.D., Wang, P.L., Rumble, D., Stein, H.J., Hannah, J.L., Coetzee, L.L., and Beukes, N.J., 2004, Dating the rise of atmospheric oxygen: Nature, v. 427, p. 117–120, doi: 10.1038/nature02260.

Benn, K., and Moyen, J.-F., 2008, this volume, The Late Archean Abitibi-Opatica terrane, Superior province: A modified oceanic plateau, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(09).

Bennett, V.C., 2003, Compositional evolution of the mantle, *in* Carlson, R.W., ed., Treatise on geochemistry, volume 2: The mantle: New York, Elsevier, p. 493–519.

Bennett, V.C., and Nutman, A.P., 1998, Extreme Nd isotope heterogeneity in the Early Archean—Fact or fiction? Case histories from northern Canada and West Greenland: Comment: Chemical Geology, v. 148, p. 213–217, doi: 10.1016/S0009-2541(98)00031-X.

Bennett, V.C., Nutman, A.P., and McCulloch, M.T., 1993, Nd isotopic evidence for transient, highly depleted mantle reservoirs in the early history of the Earth: Earth and Planetary Science Letters, v. 119, p. 299–317, doi: 10.1016/0012-821X(93)90140-5.

Bennett, V.C., Brandon, A.D., Heiss, J., and Nutman, A.P., 2007a, Coupled ^{142}Nd, ^{143}Nd, and ^{176}Hf isotopic data from 3.6–3.9 Ga rocks: New constraints on the timing and composition of early terrestrial chemical reservoirs: 38th Lunar Science Conference, Houston, Texas March 12–16.

Bennett, V.C., Brandon, A.D., and Nutman, A.P., 2007b, Coupled ^{142}Nd-^{143}Nd isotopic evidence for Hadean mantle dynamics: Science, v. 318, p. 1907–1909, doi:10.1126/science.1145928.

Blichert-Toft, J., and Albarede, F., 1997, The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system: Earth and Planetary Science Letters, v. 148, p. 243–258, doi: 10.1016/S0012-821X(97)00040-X.

Bodinier, J.-L., and Godard, M., 2003, Orogenic, ophiolitic, and abyssal peridotites, *in* Carlson, R.W., ed., Treatise on geochemistry, volume 2: The mantle: New York, Elsevier, p. 103–170.

Boher, M., Abouchami, W., Michard, A., Albarede, F., and Arndt, N.T., 1992, Crustal growth in West Africa at 2.1 Ga: Journal of Geophysical Research, v. 97, p. 345–369.

Bolhar, R., Kamber, B.S., Moorbath, S., Fedo, C.M., and Whitehouse, M.J., 2004, Characterisation of Early Archaean chemical sediments by trace element signatures: Earth and Planetary Science Letters, v. 222, p. 43–60, doi: 10.1016/j.epsl.2004.02.016.

Bolhar, R., Kamber, B.S., Moorbath, S., Whitehouse, M.J., and Collerson, K.D., 2005, Chemical characterization of Earth's most ancient clastic metasediments from the Isua Greenstone Belt, southern West Greenland: Geochimica et Cosmochimica Acta, v. 69, p. 1555–1573, doi: 10.1016/j.gca.2004.09.023.

Bowring, S.A., and Housh, T., 1995, The Earth's early evolution: Science, v. 269, p. 1535–1540, doi: 10.1126/science.7667634.

Boyd, F.R., 1999, The origin of cratonic peridotites: A major-element approach, *in* Snyder, G.A., et al., eds., Planetary petrology and geochemistry: The Lawrence A. Taylor 60th Birthday Volume: Columbia, Maryland, Bellwether Publishing, p. 5–14.

Boyd, F.R., Pokhilenko, N.P., Pearson, D.G., Mertzman, S.A., Sobolev, N.V., and Finger, L.W., 1997, Composition of the Siberian cratonic mantle: Evidence from Udachnaya peridotite xenoliths: Contributions to Mineralogy and Petrology, v. 128, p. 228–246, doi: 10.1007/s004100050305.

Boyet, M., and Carlson, R.W., 2005, ^{142}Nd evidence for early (>4.53 Ga) global differentiation of the silicate Earth: Science, v. 309, p. 576–581, doi: 10.1126/science.1113634.

Boyet, M., and Carlson, R.W., 2006, A new geochemical model for the Earth's mantle inferred from ^{146}Sm-^{142}Nd systematics: Earth and Planetary Science Letters, v. 250, p. 254–268, doi: 10.1016/j.epsl.2006.07.046.

Boyet, M., Blichert-Toft, J., Rosing, M., Storey, M., Telouk, P., and Albarede, F., 2003, ^{142}Nd evidence for early Earth differentiation: Earth and Planetary Science Letters, v. 214, p. 427–442, doi: 10.1016/S0012-821X(03)00423-0.

Brandon, A., 2007, Planetary science: A younger Moon: Nature, v. 450, p. 1169–1170, doi:10.1038/4501169a.

Brown, M., 2008, this volume, Characteristic thermal regimes of plate tectonics and their metamorphic imprint throughout Earth history: When did Earth first adopt a plate tectonics mode of behavior?, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(05).

Canup, R.M., and Asphaug, E., 2001, Origin of the Moon in a giant impact near the end of the Earth's formation: Nature, v. 412, p. 708–712, doi: 10.1038/35089010.

Card, K.D., 1990, A review of the Superior province of the Canadian Shield, a product of Archean accretion: Precambrian Research, v. 48, p. 99–156, doi: 10.1016/0301-9268(90)90059-Y.

Carlson, R.W., and Shirey, S.B., 1988, Magma oceans, ocean ridges, and continental crust: Relative roles in mantle differentiation: Lunar and Planetary Institute Contribution 681, p. 13–14.

Carlson, R.W., Pearson, D.G., and James, D.E., 2005, Physical, chemical and chronological characteristics of continental mantle: Reviews of Geophysics, v. 43, RG1001, doi: 10.1029/2004RG000156.

Carlson, R.W., Boyet, M., and Horan, M., 2007, Chondrite barium, neodymium, and samarium isotopic heterogeneity and early Earth differentiation: Science, v. 316, p. 1175–1178, doi:10.1126/science.1140189.

Caro, G., Bourdon, B., Birck, J.-L., and Moorbath, S., 2003, ^{146}Sm-^{142}Nd evidence from Isua metamorphosed sediments for early differentiation of the Earth's mantle: Nature, v. 423, p. 428–432, doi: 10.1038/nature01668.

Caro, G., Bourdon, B., Wood, B.J., and Corgne, A., 2005, Trace-element fractionation in Hadean mantle generated by melt segregation from a magma ocean: Nature, v. 436, p. 246–249, doi: 10.1038/nature03827.

Caro, G., Bourdon, B., Birck, J.L., and Moorbath, S., 2006, High-precision ^{142}Nd/^{144}Nd measurements in terrestrial rocks: Constraints on the early differentiation of the Earth's mantle: Geochimica et Cosmochimica Acta, v. 70, p. 164–191, doi: 10.1016/j.gca.2005.08.015.

Cartigny, P., 2005, Stable isotopes and the origin of diamond: Elements, v. 1, p. 79–84.

Cartigny, P., Harris, J.W., and Javoy, M., 1998, Eclogitic diamond formation at Jwaneng: No room for a recycled component: Science, v. 280, p. 1421–1424, doi: 10.1126/science.280.5368.1421.

Cartigny, P., Harris, J.W., and Javoy, M., 2001, Diamond genesis, mantle fractionations and mantle nitrogen content: A study of δ^{13}C-N concentrations in diamonds: Earth and Planetary Science Letters, v. 185, p. 85–98, doi: 10.1016/S0012-821X(00)00357-5.

Cavosie, A.J., Valley, J.W., and Wilde, S.A., 2005, Magmatic δ^{18}O in 4400–3900 Ma detrital zircons: A record of the alteration and recycling of crust in the Early Archean: Earth and Planetary Science Letters, v. 235, p. 663–681, doi: 10.1016/j.epsl.2005.04.028.

Chase, C.G., and Patchett, P.J., 1988, Stored mafic/ultramafic crust and Early Archean mantle depletion: Earth and Planetary Science Letters, v. 91, p. 66–72, doi: 10.1016/0012-821X(88)90151-3.

Christensen, U.R., and Hofmann, A.W., 1994, Segregation of subducted oceanic crust in the convecting mantle: Journal of Geophysical Research, v. 99, p. 19,867–19,884, doi: 10.1029/93JB03403.

Collerson, K.D., and Kamber, B.S., 1999, Evolution of the continents and the atmosphere inferred from Th-U-Nb systematics of the depleted mantle: Science, v. 283, p. 1519–1522, doi: 10.1126/science.283.5407.1519.

Collerson, K.D., Campbell, L.M., Weaver, B.L., and Palacz, Z.A., 1991, Evidence for extreme mantle fractionation in Early Archaean ultramafic rocks from northern Labrador: Nature, v. 349, p. 209–214, doi: 10.1038/349209a0.

Condie, K.C., 1998, Episodic continental growth and supercontinents: A mantle avalanche connection?: Earth and Planetary Science Letters, v. 163, p. 97–108, doi: 10.1016/S0012-821X(98)00178-2.

Condie, K.C., and Kröner, A., 2008, this volume, When did plate tectonics begin? Evidence from the geologic record, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(14).

Coogan, L.A., and Hinton, R.W., 2006, Do the trace element compositions of detrital zircons require Hadean continental crust?: Geology, v. 34, p. 633–636, doi: 10.1130/G22737.1.

Corgne, A., Liebske, C., Wood, B.J., Rubie, D.C., and Frost, D.J., 2005, Silicate perovskite-melt partitioning of trace elements and geochemical signature of a deep perovskitic reservoir: Geochimica et Cosmochimica Acta, v. 69, p. 485–496, doi: 10.1016/j.gca.2004.06.041.

Davies, G.F., 1999, Dynamic Earth: Cambridge, UK, Cambridge University Press, 458 p.

Davies, G.F., 2002, Stirring geochemistry in mantle convection models with stiff plates and slabs: Geochimica et Cosmochimica Acta, v. 66, p. 3125–3142, doi: 10.1016/S0016-7037(02)00915-8.

Davies, G.F., 2006, Gravitational depletion of the early Earth's upper mantle and the viability of early plate tectonics: Earth and Planetary Science Letters, v. 243, p. 376–382, doi: 10.1016/j.epsl.2006.01.053.

Davis, D.W., Amelin, Y., Nowell, G.M., and Parrish, R.R., 2005, Hf isotopes in zircon from the western Superior province, Canada: Implications for Archean crustal development and evolution of the depleted mantle reservoir: Precambrian Research, v. 140, p. 132–156, doi: 10.1016/j.precamres.2005.07.005.

Debaille, V., Brandon, A.D., Yin, Q.Z., and Jacobsen, B., 2007, Coupled ^{142}Nd-^{143}Nd evidence for a protracted magma ocean on Mars: Nature, v. 450, p. 525–528, doi:10.1038/nature06317.

DePaolo, D.J., 1983, The mean life of continents: Estimates of continent recycling rates from Nd and Hf isotopic data and implications for mantle structure: Geophysical Research Letters, v. 10, p. 705–708.

Drake, M.J., 2005, Origin of water in the terrestrial planets: Meteoritics and Planetary Science, v. 40, p. 519–527.

Drake, M.J., McFarlane, E.A., Gasparik, T., Rubie, D.C., and Agee, C.B., 1993, Mg-perovskite/silicate melt and majorite garnet/silicate melt partition coefficients in the system CaO-MgO-SiO_2 at high temperatures and pressures: Journal of Geophysical Research, v. 98, p. 5427–5431.

Eiler, J.M., Schiano, P., Kitchen, N., and Stolper, E.M., 2000, Oxygen-isotope evidence for recycled crust in the sources of mid-ocean-ridge basalts: Nature, v. 403, p. 530–534, doi: 10.1038/35000553.

Eldridge, C.S., Compston, W., Williams, I.S., Harris, J.W., and Bristow, J.W., 1991, Isotope evidence for the involvement of recycled sediments in diamond formation: Nature, v. 353, p. 649–653, doi: 10.1038/353649a0.

Elliott, T., Zindler, A., and Bourdon, B., 1999, Exploring the kappa conundrum: The role of recycling in the lead isotope evolution of the mantle: Earth and Planetary Science Letters, v. 169, p. 129–145, doi: 10.1016/S0012-821X(99)00077-1.

Farquhar, J., Wing, B., McKeegan, K.D., and Harris, J.W., 2002a, Insight into crust-mantle coupling from anomalous Δ^{33}S of sulfide inclusions in diamonds, *in* Abstracts of the 12th annual V.M. Goldschmidt conference: Geochimica et Cosmochimica Acta, v. 66, p. 225.

Farquhar, J., Wing, B.A., McKeegan, K.D., Harris, J.W., Cartigny, P., and Thiemens, M.H., 2002b, Mass-independent sulfur of inclusions in diamond and sulfur recycling on early Earth: Science, v. 298, p. 2369–2372, doi: 10.1126/science.1078617.

Foley, S., 2008, this volume, A trace element perspective on Archean crust formation and on the presence or absence of Archean subduction, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(02).

Fralick, P., Hollings, P., and King, D., 2008, this volume, Stratigraphy, geochemistry, and depositional environments of Mesoarchean sedimentary units in western Superior province: Implications for generation of early crust, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(04).

Furnes, H., de Wit, M.J., Staudigel, H., Rosing, M., and Muehlenbachs, K., 2007, A vestige of the Earth's oldest ophiolite: Science, v. 315, p. 1704–1707, doi: 10.1126/science.1139170.

Galer, S.J.G., and Goldstein, S.L., 1991, Early mantle differentiation and its thermal consequences: Geochimica et Cosmochimica Acta, v. 55, p. 227–239, doi: 10.1016/0016-7037(91)90413-Y.

Galer, S.J.G., and O'Nions, R.K., 1985, Residence time of uranium, thorium and lead in the mantle with implications for mantle convection: Nature, v. 316, p. 778–782, doi: 10.1038/316778a0.

Gast, P.W., Tilton, G.R., and Hedge, C., 1964, Isotopic composition of lead and strontium from Ascension and Gough islands: Science, v. 145, p. 1181–1185, doi: 10.1126/science.145.3637.1181.

Goes, S., and van der Lee, S., 2002, Thermal structure of the North American uppermost mantle inferred from seismic tomography: Journal of Geophysical Research, v. 107, no. B3, p. 2050, doi: 10.1029/2000JB000049.

Gradstein, F.M., Ogg, J.G., and Smith, A.G., 2005, A geologic scale 2004: New York, Cambridge University Press, 610 p.

Grand, S.P., 1987, Tomographic inversion for shear velocity beneath the North American plate: Journal of Geophysical Research, v. 92, p. 14,065–14,090.

Griffin, W.L., Wang, X., Jackson, S.E., Pearson, N.J., O'Reilly, S.Y., Xu, X., and Zhou, X., 2002, Zircon chemistry and magma mixing, SE China: In situ analysis of Hf isotopes, Tonglu and Pingtan igneous complexes, *in* Wiebe, R.A., ed., Magmatic processes: A special issue in honor of R.H. Vernon: 15th Australian Geological Convention, Sydney: Lithos, v. 61, p. 237–269.

Griffin, W.L., Belousova, E.A., Shee, S.R., Pearson, N.J., and O'Reilly, S.Y., 2004, Archean crustal evolution in the northern Yilgarn Craton: U-Pb and Hf-isotope evidence from detrital zircons, *in* Van Kranendonk, M.J., ed., Archaean tectonics, volume 2: 4th International Archean Symposium, Perth, Western Australia, Australia, September 24–28, 2001: Precambrian Research, v. 131, p. 231–282.

Grimes, C.B., John, B.E., Keleman, P.B., Mazdab, F.K., Wooden, J.L., Cheadle, M.J., Hanghøj, K., and Schwartz, J.J., 2007, Trace element chemistry of zircons from oceanic crust: A method for distinguishing detrital zircon provenance: Geology, v. 35, p. 643 646, doi:10.1130/G23603A.1.

Grove, T.L., and Parman, S.W., 2004, Thermal evolution of the Earth as recorded by komatiites: Earth and Planetary Science Letters, v. 219, p. 173–187, doi: 10.1016/S0012-821X(04)00002-0.

Grove, T.L., Parman, S.W., and Dann, J.C., 1999, Conditions of magma generation for Archean komatiites from the Barberton Mountain Land, South Africa: Geochemical Society Special Publication 6, p. 155–167.

Gurnis, M., 1988, Large-scale mantle convection and the aggregation and dispersal of supercontinents: Nature, v. 332, p. 695–699, doi: 10.1038/332695a0.

Halpin, J.A., Gerakiteys, C.L., Clarke, G.L., Belousova, E.A., and Griffin, W.L., 2005, In situ U-Pb geochronology and Hf isotope analyses of the Rayner Complex, East Antarctica: Contributions to Mineralogy and Petrology, v. 148, p. 689–706, doi: 10.1007/s00410-004-0627-6.

Hanson, G.N., 1977, Geochemical evolution of the suboceanic mantle: Geological Society [London] Journal, v. 134, p. 1–19.

Harrison, T.M., Blichert-Toft, J., Mueller, W., Albarede, F., Holden, P., and Mojzsis, S.J., 2005, Heterogeneous Hadean hafnium: Evidence of continental crust at 4.4 to 4.5 Ga: Science, v. 310, p. 1947–1950, doi: 10.1126/science.1117926.

Hart, S.R., 1984, A large-scale isotope anomaly in the Southern Hemisphere mantle: Nature, v. 309, p. 753–757, doi: 10.1038/309753a0.

Hart, S.R., and Gaetani, G.A., 2006, Mantle Pb paradoxes: The sulfide solution: Contributions to Mineralogy and Petrology, v. 152, p. 295–308, doi: 10.1007/s00410-006-0108-1.

Hauri, E.H., 1996, Major-element variability in the Hawaiian mantle plume: Nature, v. 382, p. 415–419, doi: 10.1038/382415a0.

Hauri, E.H., and Hart, S.R., 1993, Re-Os isotope systematics of HIMU and EMII oceanic island basalts from the South Pacific Ocean: Earth and Planetary Science Letters, v. 114, p. 353–371, doi: 10.1016/0012-821X(93)90036-9.

Hawkesworth, C.J., Mantovani, M.S.M., Taylor, P.N., and Palacz, Z., 1986, Evidence from the Parana of south Brazil for a continental contribution to Dupal basalts: Nature, v. 322, p. 356–359, doi: 10.1038/322356a0.

Hiess, J. Nutman, A.P., Bennett, V.C., and Holden, P., 2008, Ti-in-zircon thermometry applied to contrasting Archean metamorphic and igneous systems: Chemical Geology, v. 247, p. 323–338, doi:10.1016/j.chemgeo.2007.10.012.

Herzberg, C., 1999, Phase equilibrium constraints on the formation of cratonic mantle: Geochemical Society Special Publication 6, p. 241–257.

Hirschmann, M.M., and Stolper, E.M., 1996, A possible role for garnet pyroxenite in the origin of the "garnet signature" in MORB: Contributions to Mineralogy and Petrology, v. 124, p. 185–208, doi: 10.1007/s004100050184.

Hofmann, A.W., 1988, Chemical differentiation of the Earth: The relationship between mantle, continental crust, and oceanic crust: Earth and Planetary Science Letters, v. 90, p. 297–314, doi: 10.1016/0012-821X(88)90132-X.

Hofmann, A.W., 1997, Mantle geochemistry: The message from oceanic volcanism: Nature, v. 385, p. 219–229, doi: 10.1038/385219a0.

Hofmann, A.W., 2003, Sampling mantle heterogeneity through oceanic basalts: Isotopes and trace elements, *in* Carlson, R.W., ed., Treatise on geochemistry, volume 2: The mantle: New York, Elsevier, p. 61–101.

Hofmann, A.W., and White, W.M., 1982, Mantle plumes from ancient oceanic crust: Earth and Planetary Science Letters, v. 57, p. 421–436, doi: 10.1016/0012-821X(82)90161-3.

Hollings, P., Wyman, D., and Kerrich, R., 1999, Komatiite-basalt-rhyolite volcanic associations in northern Superior province greenstone belts: Significance of plume-arc interaction in the generation of the proto-continental Superior province: Lithos, v. 46, p. 137–161, doi: 10.1016/S0024-4937(98)00058-9.

Hoskin, P.W.O., and Ireland, T.R., 2000, Rare earth element chemistry of zircon and its use as a provenance indicator: Geology, v. 28, p. 627–630, doi: 10.1130/0091-7613(2000)28<627:REECOZ>2.0.CO;2.

Huang, J., and Davies, G.F., 2007, Stirring in three-dimensional mantle convection models and implications for geochemistry: Passive tracers: Geochemistry, Geophysics, Geosystems, v. 8, p. 17.

Hurley, P.M., and Rand, J.R., 1969, Pre-drift continental nuclei: Science, v. 164, p. 1229–1242, doi: 10.1126/science.164.3885.1229.

Hynes, A., 2001, Freeboard revisited: Continental growth, crustal thickness change and Earth's thermal efficiency: Earth and Planetary Science Letters, v. 185, p. 161–172, doi: 10.1016/S0012-821X(00)00368-X.

Jacob, D.E., 2004, Nature and origin of eclogite xenoliths from kimberlites, *in* Mitchell, R.H., et al., eds., 8th International Kimberlite Conference, Victoria, BC: Lithos, v. 77, p. 295–316.

Jacob, D.E., and Jagoutz, E., 1994, A diamond-graphite bearing eclogitic xenoliths from Roberts Victor (South Africa): Indication for petrogenesis from Pb-, Nd- and Sr-isotopes, *in* Meyer, H.O.A., and Leonardos, O.H., eds., Kimberlites, related rocks and mantle xenoliths: Proceedings of the Fifth Kimberlite Conference, CPRM, p. 304–317.
Jacob, D.E., Jagoutz, E., Lowry, D., Mattey, D., and Kudrjavtseva, G., 1994, Diamondiferous eclogites from Siberia: Remnants of Archean ocean crust: Geochimica et Cosmochimica Acta, v. 58, p. 5191–5207, doi: 10.1016/0016-7037(94)90304-2.
Jacobsen, S.B., and Dymek, R.F., 1988, Nd and Sr isotope systematics of clastic metasediments from Isua, West Greenland: Identification of pre–3.8 Ga differentiated crustal components: Journal of Geophysical Research, v. 93, p. 338–354.
Jia, Y., and Kerrich, R., 2004, Nitrogen 15–enriched Precambrian kerogen and hydrothermal systems: Geochemistry, Geophysics, Geosystems, v. 5, Q07005, doi: 10.1029/2004GC000716.
Jochum, K.P., Arndt, N.T., and Hofmann, A.W., 1991, Nb-Th-La in komatiites and basalts: Constraints on komatiite petrogenesis and mantle evolution: Earth and Planetary Science Letters, v. 107, p. 272–289, doi: 10.1016/0012-821X(91)90076-T.
Jordan, T.H., 1981, Continents as a chemical boundary layer: Royal Society of London Philosophical Transactions, ser. A, v. 301, p. 359–373.
Kamber, B.S., 2007, The enigma of the terrestrial protocrust: Evidence for its former existence and the importance of its complete disappearance, *in* Van Kranendonk, M.J., Smithies, H., and Bennett, V., eds., Earth's Oldest Rocks: Amsterdam, Elsevier, Developments in Precambrian Geology, v. 15, p. 75–89.
Kamber, B.S., Moorbath, S., and Whitehouse, M.J., 1998, Extreme Nd-isotope heterogeneity in the Early Archaean—fact or fiction? Case histories from northern Canada and West Greenland: Reply: Chemical Geology, v. 148, p. 219–224, doi: 10.1016/S0009-2541(98)00032-1.
Kamber, B.S., Ewart, A., Collerson, K.D., Bruce, M.C., and McDonald, G.D., 2002, Fluid-mobile trace element constraints on the role of slab melting and implications for Archaean crustal growth models: Contributions to Mineralogy and Petrology, v. 144, p. 38–56.
Kamber, B.S., Collerson, K.D., Moorbath, S., and Whitehouse, M.J., 2003a, Inheritance of Early Archaean Pb-isotope variability from long-lived Hadean protocrust: Contributions to Mineralogy and Petrology, v. 145, p. 25–46.
Kamber, B.S., Greig, A., Schoenberg, R., and Collerson, K.D., 2003b, A refined solution to Earth's hidden niobium: Implications for evolution of continental crust and depth of core formation: Precambrian Research, v. 126, p. 289–308, doi: 10.1016/S0301-9268(03)00100-1.
Kamber, B.S., Greig, A., and Collerson, K.D., 2005a, A new estimate for the composition of weathered young upper continental crust from alluvial sediments, Queensland, Australia: Geochimica et Cosmochimica Acta, v. 69, p. 1041–1058, doi: 10.1016/j.gca.2004.08.020.
Kamber, B.S., Whitehouse, M.J., Bolhar, R., and Moorbath, S., 2005b, Volcanic resurfacing and the early terrestrial crust: Zircon U-Pb and REE constraints from the Isua Greenstone Belt, southern West Greenland: Earth and Planetary Science Letters, v. 240, p. 276–290, doi: 10.1016/j.epsl.2005.09.037.
Kato, T., Ringwood, A.E., and Irifune, T., 1988a, Constraints on element partition coefficients between $MgSiO_3$ perovskite and liquid determined by direct measurements: Earth and Planetary Science Letters, v. 90, p. 65–68, doi: 10.1016/0012-821X(88)90111-2.
Kato, T., Ringwood, A.E., and Irifune, T., 1988b, Experimental determination of element partitioning between silicate perovskites, garnets and liquids: Constraints on early differentiation of the mantle: Earth and Planetary Science Letters, v. 89, p. 123–145, doi: 10.1016/0012-821X(88)90038-6.
Kelemen, P.B., Hart, S.R., and Bernstein, S., 1998, Silica enrichment in the continental upper mantle via melt/rock reaction: Earth and Planetary Science Letters, v. 164, p. 387–406, doi: 10.1016/S0012-821X(98)00233-7.
Kerrich, R., Polat, A., Wyman, D., and Hollings, P., 1999, Trace element systematics of Mg-, to Fe-tholeiitic basalt suites of the Superior province: Implications for Archean mantle reservoirs and greenstone belt genesis: Lithos, v. 46, p. 163–187, doi: 10.1016/S0024-4937(98)00059-0.
Koeberl, C., 2006, Impact processes on the early Earth: Elements, v. 2, p. 211–216.
Kogiso, T., Hirschmann, M.M., and Frost, D.J., 2003, High-pressure partial melting of garnet pyroxenite: Possible mafic lithologies in the source of ocean island basalts: Earth and Planetary Science Letters, v. 216, p. 603–617, doi: 10.1016/S0012-821X(03)00538-7.
Korenaga, J., 2006, Archean geodynamics and the thermal evolution of Earth, *in* Benn, K., et al., eds., Archean geodynamics and environments: American Geophysical Union Geophysical Monograph 164, p. 7–32.
Kramers, J., 2001, The smile of the Cheshire Cat: Science, v. 293, p. 619–620, doi: 10.1126/science.1063288.
Kramers, J.D., 2003, Volatile element abundance patterns and an early liquid water ocean on Earth, *in* Appel, P.W.U., et al., eds., Early Archean processes and the Isua greenstone belt, West Greenland: Isua multidisciplinary project workshop, Berlin, FDR, January 17–20, 2002: Precambrian Research, v. 126, p. 379–394.
Kramers, J.D., 2007, Hierarchical Earth accretion and the Hadean eon: Geological Society [London] Journal, v. 164, p. 3–17, doi: 10.1144/0016-76492006-028.
Kramers, J.D., and Tolstikhin, I.N., 1997, Two terrestrial lead isotope paradoxes, forward transport modelling, core formation and the history of the continental crust, *in* Hawkesworth, C., and Arndt, N.T., eds., Highlights of the Goldschmidt meeting, in honor of A.W. Hofmann: Goldschmidt meeting, Heidelberg, FRG, March 31–April 4, 1996: Lithos, v. 139, p. 75–110.
Krogstad, E.J., Balakrishnan, S., Mukhopadhyay, D.K., Rajamani, V., and Hanson, G.N., 1989, Plate tectonics 2.5 billion years ago: Evidence at Kolar, South India: Science, v. 243, p. 1337–1340.
Lenardic, A., 2006, Continental growth and the Archean paradox, *in* Benn, K., et al., eds., Archean geodynamics and environments: American Geophysical Union Geophysical Monograph 164, p. 33–45.
Lenardic, A., Moresi, L.N., Jellinek, A.M., and Manga, M., 2005, Continental insulation, mantle cooling, and the surface area of oceans and continents: Earth and Planetary Science Letters, v. 234, p. 317–333, doi: 10.1016/j.epsl.2005.01.038.
Liebske, C., Corgne, A., Frost, D.J., Rubie, D.C., and Wood, B.J., 2005, Compositional effects on element partitioning between Mg-silicate perovskite and silicate melts: Contributions to Mineralogy and Petrology, v. 149, p. 113–128, doi: 10.1007/s00410-004-0641-8.
Lowman, J.P., and Jarvis, G.T., 1999, Effects of mantle heat source distribution on supercontinent stability: Journal of Geophysical Research, v. 104, p. 12,733–12,747, doi: 10.1029/1999JB900108.
Luais, B., and Hawkesworth, C.J., 2002, Pb isotope variations in Archaean time and possible links to the sources of certain Mesozoic-Recent basalts, *in* Fowler, C.M.R., et al., eds., The early Earth: Physical, chemical and biological development: Geological Society [London] Special Publication 199, p. 105–124.
Maas, R., Kinny, P.D., Williams, I.S., Froude, D.O., and Compston, W., 1992, The Earth's oldest known crust: A geochronological and geochemical study of 3900–4200 Ma old detrital zircons from Mt. Narryer and Jack Hills, Western Australia: Geochimica et Cosmochimica Acta, v. 56, p. 1281–1300, doi: 10.1016/0016-7037(92)90062-N.
MacGregor, I.D., and Manton, W.I., 1986, Roberts Victor eclogites: Ancient oceanic crust: Journal of Geophysical Research, B, Solid Earth and Planets, v. 91, p. 14,063–14,079.
Machado, N., and Simonetti, A., 2001, U-Pb dating and Hf isotopic composition of zircon by laser ablation-MC-ICP-MS, *in* Sylvester, P.J., ed., Laser-ablation-ICPMS in the earth sciences: Principles and applications: Toronto, MAC Short Course Handbook, v. 29, p. 121–146.
Marsh, B.D., Gunnarsson, B., Congdon, R., and Carmody, R., 1991, Hawaiian basalt and Icelandic rhyolite: Indicators of differentiation and partial melting: International Journal of Earth Sciences, v. 80, p. 481–510.
Marty, B., and Dauphas, N., 2003, The nitrogen record of crust-mantle interaction and mantle convection from Archean to present: Earth and Planetary Science Letters, v. 206, p. 397–410, doi: 10.1016/S0012-821X(02)01108-1.
Marty, B., and Yokochi, R., 2006, Water in the early Earth: Water in nominally anhydrous minerals, in Keppler, H. and Smyth, J.R., ed., Water in Nominally Anhydrous Minerals: Reviews in Mineralogy and Geochemistry 62, p. 421–450.
McCulloch, M.T., and Bennett, V.C., 1993, Evolution of the early Earth: Constraints from ^{143}Nd-^{142}Nd isotopic systematics, *in* Campbell, I.H., Maruyama, S., and McCulloch, M.T., eds., The Evolving Earth: Lithos, v. 30, p. 237–255.
McCulloch, M.T., and Bennett, V.C., 1994, Progressive growth of the Earth's continental crust and depleted mantle: Geochemical constraints: Geochimica et Cosmochimica Acta, v. 58, p. 4717–4738, doi: 10.1016/0016-7037(94)90203-8.
Menzies, A.H., Carlson, R.W., Shirey, S.B., and Gurney, J.J., 2003, Re-Os systematics of diamond-bearing eclogites from Newlands kimberlite: Lithos, v. 71, p. 323–336, doi: 10.1016/S0024-4937(03)00119-1.

Miller, D.M., Goldstein, S.L., and Langmuir, C.H., 1994, Cerium/lead and lead isotope ratios in arc magmas and the enrichment of lead in the continents: Nature, v. 368, p. 514–520, doi: 10.1038/368514a0.

Mojzsis, S.J., Harrison, T.M., and Pidgeon, R.T., 2001, Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4300 Myr ago: Nature, v. 409, p. 178–181, doi: 10.1038/35051557.

Montelli, R., Nolet, G., Dahlen, F.A., Masters, G., Engdahl, E.R., and Hung, S.-H., 2004, Finite-frequency tomography reveals a variety of plumes in the mantle: Science, v. 303, p. 338–343, doi: 10.1126/science.1092485.

Moorbath, S., Whitehouse, M.J., and Kamber, B.S., 1997, Extreme Nd-isotope heterogeneity in the Early Archaean—Fact or fiction? Case histories from northern Canada and West Greenland: Chemical Geology, v. 135, p. 213–231, doi: 10.1016/S0009-2541(96)00117-9.

Morbidelli, A., Chambers, J., Lunine, J.I., Petit, J.M., Robert, F., Valsecchi, G.B., and Cyr, K.E., 2000, Source regions and timescales for the delivery of water to Earth: Meteoritics and Planetary Science, v. 35, p. 1309–1320.

Muentener, O., Keleman, P.B., and Grove, T.L., 2001, The role of H_2O during crystallization of primitive arc magmas under uppermost mantle conditions and genesis of igneous pyroxenites: An experimental study: Contributions to Mineralogy and Petrology, v. 141, p. 643–658.

Münker, C., Pfander, J.A., Weyer, S., Buchl, A., Kleine, T., and Mezger, K., 2003, Evolution of planetary cores and the Earth-Moon system from Nb/Ta systematics: Science, v. 301, p. 84–87, doi: 10.1126/science.1084662.

Murphy, D.T., Kamber, B.S., and Collerson, K.D., 2003, A refined solution to the first terrestrial Pb-isotope paradox: Journal of Petrology, v. 44, p. 39–53, doi: 10.1093/petrology/44.1.39.

Musacchio, G., White, D.J., Asudeh, I., and Thomson, C.J., 2004, Lithospheric structure and composition of the Archean western Superior province from seismic refraction/wide-angle reflection and gravity modeling: Journal of Geophysical Research, v. 109, B03304, doi: 10.1029/2003JB002427.

Nägler, T.F., and Kramers, J.D., 1998, Nd isotopic evolution of the upper mantle during the Precambrian: Models, data and the uncertainty of both: Precambrian Research, v. 91, p. 233–252, doi: 10.1016/S0301-9268(98)00051-5.

Navon, O., 1999, Diamond formation in the Earth's mantle, *in* Gurney, J.J., Pascoe, M.D., and Richardson, S.H. et al., eds., Proceedings of the 7th International Kimberlite Conference, p. 584–604.

Nemchin, A.A., Pidgeon, R.T., and Whitehouse, M.J., 2006, Re-evaluation of the origin and evolution of >4.2 Ga zircons from the Jack Hills metasedimentary rocks: Earth and Planetary Science Letters, v. 244, p. 218–233, doi: 10.1016/j.epsl.2006.01.054.

Nir-El, Y., and Lavi, N., 1998, Measurement of the half-life of ^{176}Lu: Applied Radiation and Isotopes, v. 49, p. 1653–1655, doi: 10.1016/S0969-8043(97)10007-0.

Nisbet, E.G., Cheadle, M.J., Arndt, N.T., and Bickle, M.J., 1993, Constraining the potential temperature of the Archaean mantle: A review of the evidence from komatiites, *in* Campbell, I.H., et al., eds., The evolving Earth: Lithos, v. 30, p. 291–307.

Nutman, A.P., 2001, On the scarcity of >3900 Ma detrital zircons in ≥3500 Ma metasediments: Precambrian Research, v. 105, p. 93–114, doi: 10.1016/S0301-9268(00)00106-6.

Nutman, A.P., Bennett, V.C., Friend, C.R.L., and Norman, M.D., 1999, Meta-igneous (non-gneissic) tonalites and quartz-diorites from an extensive ca. 3800 Ma terrain south of the Isua supracrustal belt, southern West Greenland: Constraints on early crust formation: Contributions to Mineralogy and Petrology, v. 137, p. 364–388, doi: 10.1007/s004100050556.

Oversby, V.M., 1975, Lead isotopic systematics and ages of Archaean acid intrusives in the Kalgoorlie-Norseman area, Western Australia: Geochimica et Cosmochimica Acta, v. 39, p. 1107–1125, doi: 10.1016/0016-7037(75)90053-8.

Parman, S.W., Grove, T.L., Dann, J.C., and de Wit, M.J., 2004, A subduction origin for komatiites and cratonic lithospheric mantle: South African Journal of Geology, v. 107, p. 107–118, doi: 10.2113/107.1-2.107.

Patchett, P.J., Vervoort, J.D., Soderlund, U., and Salters, V.J.M., 2004, Lu-Hf and Sm-Nd isotopic systematics in chondrites and their constraints on the Lu-Hf properties of the Earth: Earth and Planetary Science Letters, v. 222, p. 29–41, doi: 10.1016/j.epsl.2004.02.030.

Pearson, D.G., and Shirey, S.B., 1999, Isotopic dating of diamonds, *in* Lambert, D.D., and Ruiz, J., eds., Application of radiogenic isotopes to ore deposit research and exploration: Reviews in economic geology: Boulder, Colorado, Society of Economic Geologists, p. 143–171.

Pearson, D.G., Snyder, G.A., Shirey, S.B., Taylor, L.A., Carlson, R.W., and Sobolev, N.V., 1995, Archaean Re-Os age for Siberian eclogites and constraints on Archaean tectonics: Nature, v. 374, p. 711–713, doi: 10.1038/374711a0.

Pearson, D.G., Canil, D., and Shirey, S.B., 2003, Mantle samples included in volcanic rocks: Xenoliths and diamonds, *in* Carlson, R.W., ed., Treatise on geochemistry, volume 2: The mantle: New York, Elsevier, p. 171–277.

Pease, V., Percival, J., Smithies, H., Stevens, G., and Van Kranendonk, M., 2008, this volume, When did plate tectonics begin? Evidence from the orogenic record, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(10).

Peck, W.H., Valley, J.W., Wilde, S.A., and Graham, C.M., 2001, Oxygen isotope ratios and rare earth elements in 3.3 to 4.4 Ga zircons: Ion microprobe evidence for high δ^{18}O continental crust and oceans in the Early Archean: Geochimica et Cosmochimica Acta, v. 65, p. 4215–4229, doi: 10.1016/S0016-7037(01)00711-6.

Percival, J.A., McNicoll, V.J., Brown, J.L., Whalen, J.B., and Percival, J.A., 2004, Convergent margin tectonics, central Wabigoon subprovince, Superior province, Canada: Precambrian Research, v. 132, p. 213–244, doi: 10.1016/j.precamres.2003.12.016.

Percival, J.A., McNicoll, V., and Bailes, A.H., 2006a, Strike-slip juxtaposition of ca. 2.72 Ga juvenile arc and >2.98 Ga continent margin sequences and its implications for Archean terrane accretion, western Superior province, Canada: Canadian Journal of Earth Sciences, v. 43, p. 895–927, doi: 10.1139/E06-039.

Percival, J.A., Sanborn-Barrie, M., Skulski, T., Stott, G.M., Helmstaedt, H., and White, D.J., 2006b, Tectonic evolution of the western Superior province from NATMAP and lithoprobe studies: Canadian Journal of Earth Sciences, v. 43, p. 1085–1117, doi: 10.1139/E06-062.

Peterman, Z.E., 1979, Strontium isotope geochemistry of Late Archean to Late Cretaceous tonalites and trondhjemites, *in* Barker, F., ed., Tonalites, trondhjemites, and related rocks: IGCP Project 092: Amsterdam, Elsevier, p. 133–147.

Polat, A., Frei, R., Appel, P.W.U., Fryer, B., Dilek, Y., and Ordóñez-Calderón, J.C., 2008, this volume, An overview of the lithological and geochemical characteristics of the Mesoarchean (ca. 3075 Ma) Ivisaartoq greenstone belt, southern West Greenland, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(03).

Rankenburg, K., Brandon, A.D., and Neal, C.R., 2006, Neodymium isotope evidence for a chondritic composition for the Moon: Science, v. 312, p. 1369–1372, doi: 10.1126/science.1126114.

Rehkamper, M., and Hofmann, A.W., 1997, Recycled ocean crust and sediment in Indian Ocean MORB: Earth and Planetary Science Letters, v. 147, p. 93–106, doi: 10.1016/S0012-821X(97)00009-5.

Reymer, A., and Schubert, G., 1984, Phanerozoic addition rates to the continental crust and crustal growth: Tectonics, v. 3, p. 63–77.

Richardson, S.H., 1986, Latter-day origin of diamonds of eclogitic paragenesis: Nature, v. 322, p. 623–626, doi: 10.1038/322623a0.

Richardson, S.H., and Harris, J.W., 1997, Antiquity of peridotitic diamonds from the Siberian craton: Earth and Planetary Science Letters, v. 151, p. 271–277, doi: 10.1016/S0012-821X(97)81853-5.

Richardson, S.H., Gurney, J.J., Erlank, A.J., and Harris, J.W., 1984, Origin of diamonds in old enriched mantle: Nature, v. 310, p. 198–202, doi: 10.1038/310198a0.

Richardson, S.H., Erlank, A.J., Harris, J.W., and Hart, S.R., 1990, Eclogitic diamonds of Proterozoic age from Cretaceous kimberlites: Nature, v. 346, p. 54–56, doi: 10.1038/346054a0.

Richardson, S.H., Shirey, S.B., Harris, J.W., and Carlson, R.W., 2001, Archean subduction recorded by Re-Os isotopes in eclogitic sulfide inclusions in Kimberley diamonds: Earth and Planetary Science Letters, v. 191, p. 257–266, doi: 10.1016/S0012-821X(01)00419-8.

Ringwood, A.E., 1991, Phase transformations and their bearing on the constitution and dynamics of the mantle: Geochimica et Cosmochimica Acta, v. 55, p. 2083–2110, doi: 10.1016/0016-7037(91)90090-R.

Rudnick, R.L., Eldridge, C.S., and Bulanova, G.P., 1993, Diamond growth history from in situ measurement of Pb and S isotopic compositions of sulphide inclusions: Geology, v. 21, p. 13–16, doi: 10.1130/0091-7613(1993)021<0013:DGHFIS>2.3.CO;2.

Rudnick, R.L., Barth, M., Horn, I., and McDonough, W.F., 2000, Rutile-bearing refractory eclogites: Missing link between continents and depleted mantle: Science, v. 287, p. 278–281, doi: 10.1126/science.287.5451.278.

Sadofsky, S.J., and Bebout, G.E., 2004, Nitrogen geochemistry of subducting sediments: New results from the Izu-Bonin-Mariana margin and insights regarding global nitrogen subduction: Geochemistry, Geophysics, Geosystems, v. 5, doi: 10.1029/2003GC000543.

Salters, V.J.M., 1996, The generation of mid-ocean ridge basalts from the Hf and Nd isotope perspective: Earth and Planetary Science Letters, v. 141, p. 109–123, doi: 10.1016/0012-821X(96)00070-2.

Salters, V.J.M., and Hart, S.R., 1991, The mantle sources of ocean ridges, islands and arcs: The Hf-isotope connection: Earth and Planetary Science Letters, v. 104, p. 364–380, doi: 10.1016/0012-821X(91)90216-5.

Salters, V.J.M., and Stracke, A., 2004, Composition of the depleted mantle: Geochemistry, Geophysics, Geosystems, v. 5, Q05004, doi: 10.1029/2003GC000597.

Scherer, E., Muenker, C., and Mezger, K., 2001, Calibration of the lutetium-hafnium clock: Science, v. 293, p. 683–687, doi: 10.1126/science.1061372.

Schulze, D.J., 1989, Constraints on the abundance of eclogite in the upper mantle: Journal of Geophysical Research, v. 94, p. 4205–4212.

Sharma, M., and Chen, C., 2004, Neodymium isotope fractionation in the mass spectrometer and the issue of ^{142}Nd anomalies in Early Archean rocks, *in* Mojzsis, S.J., ed., The first billion years: Selected papers presented at the 13th V.M. Goldschmidt conference, Kurashiki, Japan, September 7–12, 2003: Precambrian Research, v. 135, p. 315–329.

Shirey, S.B., 1991, The Rb-Sr, Sm-Nd and Re-Os isotopic systems: A summary and comparison of their applications to the cosmochronology and geochronology of igneous rocks, *in* Heaman, L., and Ludden, J.N., eds., Short course handbook on application of radiogenic isotopic systems to problems in geology: Toronto, Mineralogical Association of Canada, p. 103–166.

Shirey, S.B., and Hanson, G.N., 1984, Mantle-derived Archaean monzodiorites and trachyandesites: Nature, v. 310, p. 222–224, doi: 10.1038/310222a0.

Shirey, S.B., and Hanson, G.N., 1986, Mantle heterogeneity and crustal recycling in Archean granite-greenstone belts: Evidence from Nd isotopes and trace elements in the Rainy Lake area, Superior province, Ontario, Canada: Geochimica et Cosmochimica Acta, v. 50, p. 2631–2651, doi: 10.1016/0016-7037(86)90215-2.

Shirey, S.B., and Walker, R.J., 1998, The Re-Os isotope system in cosmochemistry and high-temperature geochemistry: Annual Review of Earth and Planetary Sciences, v. 26, p. 423–500, doi: 10.1146/annurev.earth.26.1.423.

Shirey, S.B., Bender, J.F., and Langmuir, C.H., 1987, Three-component isotopic heterogeneity near the oceanographer transform, Mid-Atlantic Ridge: Nature, v. 325, p. 217–223, doi: 10.1038/325217a0.

Shirey, S.B., Carlson, R.W., Richardson, S.H., Menzies, A.H., Gurney, J.J., Pearson, D.G., Harris, J.W., and Wiechert, U., 2001, Archean emplacement of eclogitic components into the lithospheric mantle during formation of the Kaapvaal Craton: Geophysical Research Letters, v. 28, p. 2509–2512, doi: 10.1029/2000GL012589.

Shirey, S.B., Richardson, S.H., and Harris, J.W., 2004, Integrated models of diamond formation and craton evolution: Lithos, v. 77, p. 923–944, doi: 10.1016/j.lithos.2004.04.018.

Sims, K.W.W., and DePaolo, D.J., 1997, Inferences about magma sources from incompatible element concentration ratios in oceanic basalts: Geochimica et Cosmochimica Acta, v. 61, p. 765–784, doi: 10.1016/S0016-7037(96)00372-9.

Smithies, R.H., Champion, D.C., Van Kranendonk, M.J., Howard, H.M., and Hickman, A.H., 2005, Modern-style subduction processes in the Mesoarchaean: Geochemical evidence from the 3.12 Ga Whundo intra-oceanic arc: Earth and Planetary Science Letters, v. 231, p. 221–237, doi: 10.1016/j.epsl.2004.12.026.

Sobolev, A.V., Hofmann, A.W., Sobolev, S.V., and Nikogosian, I.K., 2005, An olivine-free mantle source of Hawaiian shield basalts: Nature, v. 434, p. 590–597, doi: 10.1038/nature03411.

Söderlund, U., Patchett, P.J., Vervoort, J.D., and Isachsen, C.E., 2004, The ^{176}Lu decay constant determined by Lu-Hf and U-Pb isotope systematics of Precambrian mafic intrusions: Earth and Planetary Science Letters, v. 219, p. 311–324, doi: 10.1016/S0012-821X(04)00012-3.

Stacey, J.S., and Kramers, J.D., 1975, Approximation of terrestrial lead isotope evolution by a two-stage model: Earth and Planetary Science Letters, v. 26, p. 207–221, doi: 10.1016/0012-821X(75)90088-6.

Stein, M., and Hofmann, A.W., 1994, Mantle plumes and episodic crustal growth: Nature, v. 372, p. 63–68, doi: 10.1038/372063a0.

Stern, R.A., and Hanson, G.N., 1992, Origin of Archean lamprophyre dykes, Superior province, Canada: Rare earth element and Nd-Sr isotopic evidence: Contributions to Mineralogy and Petrology, v. 111, p. 515–526, doi: 10.1007/BF00320906.

Stern, R.A., Hanson, G.N., and Shirey, S.B., 1989, Petrogenesis of mantle-derived, LILE-enriched Archean monzodiorites and trachyandesites (sanukitoids) in southwestern Superior province: Canadian Journal of Earth Sciences, v. 26, p. 1688–1712.

Stott, G.M., 1997, The Superior province, Canada, *in* de Wit, M.J., and Ashwal, L.D., eds., Greenstone belts: New York, Oxford, Clarendon Press, p. 480–557.

Sun, S.S., 1980, Lead isotopic study of young volcanic rocks from mid-ocean ridges, ocean islands, and island arcs: Royal Society of London Philosophical Transactions, v. 297, p. 409–445, doi: 10.1098/rsta.1980.0224.

Sun, S.S., and Hanson, G., 1975a, Evolution of the mantle: Geochemical evidence from alkali basalt: Geology, v. 3, p. 297–302, doi: 10.1130/0091-7613(1975)3<297:EOTMGE>2.0.CO;2.

Sun, S.S., and Hanson, G.N., 1975b, Origin of Ross Island basanitoids and limitations upon the heterogeneity of mantle sources for alkali basalts and nephelinites: Contributions to Mineralogy and Petrology, v. 52, p. 77–106, doi: 10.1007/BF00395006.

Sylvester, P.J., Campbell, I.H., and Bowyer, D.A., 1997, Niobium/uranium evidence for early formation of the continental crust: Science, v. 275, p. 521–523, doi: 10.1126/science.275.5299.521.

Takahashi, E., and Brearley, M., 1990, Speculations on the Archean mantle: Missing link between komatiite and depleted garnet peridotite, *in* Dingwell, D.B., ed., Special section on silicate melts and mantle petrogenesis (in memory of Christopher M. Scarfe): American Geophysical Union 1989 Spring Meeting Symposium on Silicate Melts and Mantle Petrogenesis, Baltimore, Maryland, May 8–12, 1989: Journal of Geophysical Research, v. 95, p. 15,941–15,954.

Tatsumi, Y., and Kogiso, T., 1997, Trace element transport during dehydration processes in the subducted oceanic crust, 2: Origin of chemical and physical characteristics in arc magmatism: Earth and Planetary Science Letters, v. 148, p. 207–221, doi: 10.1016/S0012-821X(97)00019-8.

Taylor, S.R., and McLennan, S.M., 1995, The geochemical evolution of the continental crust: Reviews of Geophysics, v. 33, p. 241–265, doi: 10.1029/95RG00262.

Taylor, S.R., McLennan, S.M., Armstrong, R.L., and Tarney, J., 1981, The composition and evolution of the continental crust: Rare earth element evidence from sedimentary rocks: Royal Society of London Philosophical Transactions, ser. A, v. 301, p. 381–399, doi: 10.1098/rsta.1981.0119.

Tera, F., 1982, An outline of Earth's evolution as inferred from lead isotopes: Yearbook of the Carnegie Institution of Washington, v. 81, p. 539–543.

Tera, F., 2003, A lead isotope method for the accurate dating of disturbed geologic systems: Numerical demonstrations, some applications and implications: Geochimica et Cosmochimica Acta, v. 67, p. 3687–3716, doi: 10.1016/S0016-7037(03)00132-7.

Tolstikhin, I., and Hofmann, A.W., 2005, Early crust on top of the Earth's core: Physics of the Earth and Planetary Interiors, v. 148, p. 109–130, doi: 10.1016/j.pepi.2004.05.011.

Touboul, M., Kleine, T., Bourdon, B., Palme, H., and Weiler, R., 2007, Late formation and prolonged differentiation of the Moon inferred from W isotopes in lumar metals: Nature, v. 450, p. 1206–1209, doi:10.1038/nature06428.

Valley, J.W., Cavosie, A.J., Fu, B., Peck, W.H., and Wilde, S.A., 2006, Comment on "Heterogeneous Hadean hafnium: Evidence of continental crust at 4.4 to 4.5 Ga": Science, v. 312, p. 1139, doi: 10.1126/science.1125301.

van der Hilst, R.D., Widiyantoro, S., and Engdahl, E.R., 1997, Evidence for deep mantle circulation from global tomography: Nature, v. 386, p. 578–584, doi: 10.1038/386578a0.

van der Lee, S., and Frederiksen, A., 2005, Surface wave tomography applied to the North American upper mantle: American Geophysical Union Geophysical Monograph 157, p. 67–80.

van der Lee, S., and Nolet, G., 1997, Upper mantle S-velocity structure of North America: Journal of Geophysical Research, v. 102, p. 22,815–22,838, doi: 10.1029/97JB01168.

van der Velden, A.J., and Cook, F.A., 2005, Relict subduction zones in Canada: Journal of Geophysical Research, v. 110, B08403, doi: 10.1029/2004JB003333.

van Hunen, J., van Keken, P.E., Hynes, A., and Davies, G.F., 2008, this volume, Tectonics of early Earth: Some geodynamic considerations, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(08).

Vervoort, J.D., and Blichert-Toft, J., 1999, Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time: Geochimica et Cosmochimica Acta, v. 63, p. 533–556, doi: 10.1016/S0016-7037(98)00274-9.

Vervoort, J.D., Patchett, P.J., Gehrels, G.E., and Nutman, A.P., 1996, Constraints on early Earth differentiation from hafnium and neodymium isotopes: Nature, v. 379, p. 624–627, doi: 10.1038/379624a0.

Wade, J., and Wood, B.J., 2001, The Earth's "missing" niobium may be in the core: Nature, v. 409, p. 75–78, doi: 10.1038/35051064.

Watson, E.B., and Harrison, T.M., 2005, Zircon thermometer reveals minimum melting conditions on earliest Earth: Science, v. 308, p. 841–844, doi: 10.1126/science.1110873.

Westerlund, K.J., Shirey, S.B., Richardson, S.H., Carlson, R.W., Gurney, J.J., and Harris, J.W., 2006, A subduction origin for Early Archean peridotitic diamonds and harzburgites from the Panda kimberlite, Slave craton: Implications from Re-Os isotope systematics: Contributions to Mineralogy and Petrology, v. 152, p. 275–294, doi: 10.1007/s00410-006-0101-8.

White, W.M., and Hofmann, A.W., 1982, Sr and Nd isotope geochemistry of oceanic basalts and mantle evolution: Nature, v. 296, p. 821–825, doi: 10.1038/296821a0.

Whitehouse, M.J., and Kamber, B.S., 2002, On the overabundance of light rare earth elements in terrestrial zircons and its implication for Earth's earliest magmatic differentiation: Earth and Planetary Science Letters, v. 204, p. 333–346, doi: 10.1016/S0012-821X(02)01000-2.

Widom, E., Kepezhinskas, P., Defant, M., Horan, M.F., Brandon, A.D., and Neal, C.R., 2003, The nature of metasomatism in the sub-arc mantle wedge: Evidence from Re-Os isotopes in Kamchatka peridotite xenoliths: Chemical Geology, v. 196, p. 283–306, doi: 10.1016/S0009-2541(02)00417-5.

Wilde, S.A., Valley, J.W., Peck, W.H., and Graham, C.M., 2001, Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago: Nature, v. 409, p. 175–178, doi: 10.1038/35051550.

Wise, D.U., 1974, Continental margins, freeboard and the volumes of continents and oceans through time, *in* Nairn, A.E.M., and Stehli, F.G., eds., The geology of continental margins: New York, Springer, p. 45–58.

Workman, R.K., and Hart, S.R., 2005, Major and trace element composition of the depleted MORB mantle (DMM): Earth and Planetary Science Letters, v. 231, p. 53–72, doi: 10.1016/j.epsl.2004.12.005.

Wyman, D.A., O'Neill, C., and Ayer, J.A., 2008, this volume, Evidence for modern-style subduction to 3.1 Ga: A plateau–adakite–gold (diamond) association, *in* Condie, K.C., and Pease, V., eds., When did plate tectonics begin on planet Earth?: Geological Society of America Special Paper 440, doi: 10.1130/2008.2440(06).

Yokochi, R., and Marty, B., 2005, Geochemical constraints on mantle dynamics in the Hadean: Earth and Planetary Science Letters, v. 238, p. 17–30, doi: 10.1016/j.epsl.2005.07.020.

Zartman, R.E., and Doe, B.R., 1981, Plumbotectonics—The model: Tectonophysics, v. 75, p. 125–162.

Zartman, R.E., and Haines, S., 1988, The plumbotectonic model for Pb isotopic systematics among major terrestrial reservoirs—A case for bi-directional transport: Geochimica et Cosmochimica Acta, v. 52, p. 1327–1339, doi: 10.1016/0016-7037(88)90204-9.

Zartman, R.E., and Richardson, S.H., 2005, Evidence from kimberlitic zircon for a decreasing mantle Th/U since the Archean: Chemical Geology, v. 220, p. 263–283, doi: 10.1016/j.chemgeo.2005.04.003.

Zegers, T.E., and van Keken, P.E., 2001, Middle Archean continent formation by crustal delamination: Geology, v. 29, p. 1083–1086, doi: 10.1130/0091-7613(2001)029<1083:MACFBC>2.0.CO;2.

Zheng, J., Griffin, W.L., O'Reilly, S.Y., Lu, F., Wang, C., Zhang, M., Wang, F., and Li, H., 2004, 3.6 Ga lower crust in central China: New evidence on the assembly of the North China Craton: Geology, v. 32, p. 229–232, doi: 10.1130/G20133.1.

Zindler, A., and Hart, S.R., 1986, Chemical geodynamics: Annual Review of Earth and Planetary Sciences, v. 14, p. 493–571, doi: 10.1146/annurev.ea.14.050186.002425.

Zindler, A., Staudigel, H., and Batiza, R., 1984, Isotope and trace element geochemistry of young Pacific seamounts: Implications for the scale of upper mantle heterogeneity: Earth and Planetary Science Letters, v. 70, p. 175–195, doi: 10.1016/0012-821X(84)90004-9.

Manuscript Accepted by the Society 14 August 2007

Printed in the USA