

# The Hadean Crust: Evidence from >4 Ga Zircons

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## Key Words

continental crust growth, Jack Hills, Waterworld, detrital

## Abstract

A review of continental growth models leaves open the possibilities that Earth during the Hadean Eon (~4.5–4.0 Ga) was characterized by massive early crust or essentially none at all. Without support from the rock record, our understanding of pre-Archean continental crust must largely come from investigating Hadean detrital zircons. We know that these ancient zircons yield relatively low crystallization temperatures and some are enriched in heavy oxygen, contain inclusions similar to modern crustal processes, and show evidence of silicate differentiation at ~4.5 Ga. These observations are interpreted to reflect an early terrestrial hydrosphere, early felsic crust in which granitoids were produced and later weathered under high water activity conditions, and even the possible existence of plate boundary interactions—in strong contrast to the traditional view of an uninhabitable, hellish world. Possible scenarios are explored with a view to reconciling this growing but fragmentary record with our knowledge of conditions then extant in the inner solar system.

## INTRODUCTION

The Earth's bimodal hypsometry is a seemingly unique characteristic of our planet, and one that is a fundamental response to the operation of modern plate tectonics. Although overlaps occur, the division of crust into continental and oceanic varieties in terms of thickness, elevation, composition, density, kinematics, and age is clear. There is widespread agreement that partial melting of the mantle to produce magma enriched in incompatible elements is the ultimate source of continental crust, but the exact mechanisms responsible for this conversion are subject to debate. In the plate tectonic paradigm, the oceanic crust plays an intermediate role in this process, but again, its exact role is the subject of continued investigation.

The growth history of continental crust has special significance because it provides a stable raft for the preservation of the geologic record; thus, the literature is replete with attempts to constrain its birth and growth history (e.g., Rubey 1951, Hurley et al. 1962, Engel 1963, Hurley & Rand 1969, Moorbath 1975, Veizer & Jansen 1979, Taylor & McLennan 1985, Condie 2005). Although the crustal dichotomy is generally thought to be required to create a persistent surface scum, some (e.g., Warren 1989) take the view that continental crust is simply that which has long-term survivability in the lithosphere, whether felsic or otherwise. This review begins with an examination of growth models for the continental crust and an evaluation of their underlying constraints. It is concluded that current knowledge is consistent with a broad range of continental crust growth histories, including models that have previously been seen as infeasible. The results of recent investigations of Hadean zircons are then reviewed and possible scenarios are explored that appear to best explain our still fragmentary knowledge of this important early chapter of Earth history.

## THE FIRST ~70 MILLION YEARS

It is generally agreed that by 4.55 Ga, the Earth had largely accreted from planetesimals of broadly chondritic composition that formed between ~0.8 and 2 AU (Chambers 2004). Despite the lack of direct evidence for a collision shortly thereafter with a Mars-sized object, and some evidence that appears inconsistent (e.g., Wiechert et al. 2001; cf. Pahlevan & Stevenson 2007), there is also widespread agreement that the Moon formed by such a process (Canup 2004). The importance of whether this collision scenario to form the Moon occurred rests with the thermal and compositional consequences of a  $\sim 10^{32}$  J collision. Such an event would surely have vaporized a large portion of both impactor and target and melted the rest of the combined system, although little volatile loss would occur if temperatures were sufficiently high (i.e.,  $\geq 6000$  K; Genda & Abe 2005, Abe 2007). Independent of this Moon-forming scenario, the energy associated with assembly of the Earth and core formation would likely create a thermal structure conducive to formation of a magma ocean (Righter & Drake 1999). The timing of core formation—and thus an upper bound on the formation age of the metal-poor Moon—is not well known. An upper limit of ~150 Ma is derived from the single-stage  $^{207}\text{Pb}/^{206}\text{Pb}$  evolution of the most primitive known galena (Pidgeon 1978) and  $^{182}\text{Hf}$ - $^{182}\text{W}$  model ages that range from 20 to ~150 Ma (e.g., Lee & Halliday 1995, Jacobsen 2005, Touboul et al. 2007, Halliday 2008), depending on the assumed value of Hf/W in the silicate Earth (or Moon) and on poorly constrained aspects of W isotope equilibration during the hypothesized giant impact.

Timing constraints on terrestrial magma ocean history (or histories) are even less well understood. Indeed, geochemical evidence requiring that such an event occurred is almost entirely lacking (e.g., Righter & Drake 1999). The consensus view of terrestrial magma ocean crystallization is that solidification proceeded from the bottom up, driving such initially vigorous convection

such that the lower mantle (>28 GPa) crystallized within  $10^3$  years (Solomatov 2007). Calculations suggest that the remaining mantle would have been largely solid within  $10^5$  to  $10^7$  years, depending on volatile content (Elkins-Tanton 2008). Although a steam atmosphere would slow this process, the generally short timescales expected suggest that serial magma oceans, perhaps punctuated by clement conditions, were possible on earliest Earth (Elkins-Tanton 2008). Estimates of the depth of the last terrestrial magma ocean, based on apparent equilibration depths of moderately siderophile elements (e.g., Rubie et al. 2003, Elkins-Tanton et al. 2007) and geodynamic considerations (e.g., Solomatov 2000), range from relatively shallow to the core-mantle boundary. This range reflects, in part, the generally weak pressure dependence of siderophile element partitioning and uncertain extensive parameters (e.g.,  $f_{O_2}$ ).

Many possible permutations involving magma oceans and large impactors are consistent with what we actually know, but some proposed histories (e.g., Halliday 2008, Allegre et al. 2008) are contradicted by the Hadean zircon record. While the oldest direct evidence of terrestrial crust formation is in the presence of 4.38 Ga zircons, its existence can be inferred as early as 4.50 Ga from Lu-Hf data (Harrison et al. 2008), thus restricting the core formation/giant impactor/magma ocean phase to within  $\sim 70$  Ma of the formation of calcium- and aluminum-rich inclusions (CAIs) at  $4567.0 \pm 0.7$  Ma (Krot et al. 2005).

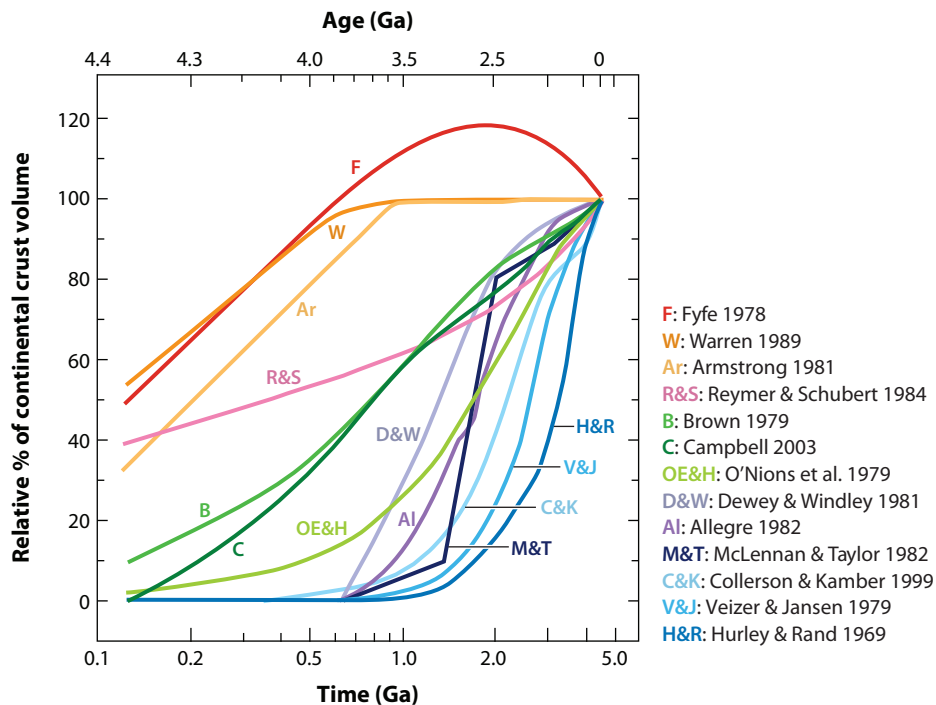
## EVIDENCE FOR EARLY SILICATE DIFFERENTIATION

In seeming contradiction to the widespread agreement that an early terrestrial magma ocean was inevitable, it was, until recently, widely assumed that the silicate Earth remained largely undifferentiated until  $\sim 4$  Ga. This began to change when investigations of early Archean rocks from West Greenland (Boyet et al. 2003, Caro et al. 2003) revealed distinctive  $^{142}\text{Nd}$  variations from which an early Hadean mantle fractionation event was inferred. With some assumptions as to the Sm/Nd ratios of key terrestrial reservoirs, coupled  $^{142,143}\text{Nd}/^{144}\text{Nd}$  systematics suggest a major differentiation of the silicate Earth within  $\sim 150$  Ma of planetary accretion (Caro et al. 2003). To explain the apparent lack of covariance of Nd and Hf isotopes in  $\sim 3.7$  Ga West Greenland gneisses, Caro et al. (2005) proposed a multi-stage model involving melt segregation from a crystallizing magma ocean, with Ca-perovskite playing a key role in fractionating the two isotopic systems.

Chondrites show a  $\sim 20$  ppm defect in  $^{142}\text{Nd}$  relative to the observable silicate Earth (Boyet & Carlson 2005, 2006). The restricted range of Sm/Nd in terrestrial reservoirs and the short (103 Ma) half-life of  $^{146}\text{Sm}$  imply either that Earth's inferred superchondritic terrestrial Sm/Nd formed globally within 30 Ma of accretion (i.e., by 4.53 Ga; Boyet & Carlson 2005), or that the Earth inherited Sm-Nd that was fractionated at the  $\sim 5\%$  level by solar nebula processes (Caro et al. 2008b). Correlated  $^{142,143}\text{Nd}/^{144}\text{Nd}$  variations in rocks from northern Canada (O'Neil et al. 2008) appear to record a mantle fractionation event that produced an incompatible-element-enriched reservoir at  $\sim 4.3$  Ga. Independent of these arguments, and as discussed later, Lu-Hf data from zircons as old as 4.37 Ga reveal unradiogenic compositions that require their source to have been sequestered in a low Lu/Hf (i.e., differentiated, crustal-type) environment as early as 4.5 Ga (Harrison et al. 2008).

## CONTINENTAL GROWTH MODELS

A long-standing view of continental crust growth is that it began to form after  $\sim 4$  Ga and progressively grew to the present (e.g., Moorbath 1975; Veizer & Jansen 1979; McLennan & Taylor 1982, 1991; Taylor & McLennan 1985) (**Figure 1**). This view largely reflects the absence of a  $>4$  Ga rock record, the apparent distribution of age provinces, and the broadly systematic



**Figure 1**

Schematic continental crust growth histories showing the diversity of proposed models, which range from early continent formation to growth histories entirely restricted to post-Hadean time. Modified with permission from Warren (1989).

<4 Ga evolution of depleted mantle  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  (e.g., McCulloch & Bennett 1993, Bowring & Williams 1999, Vervoort & Blichert-Toft 1999). The observation of some early Nd (Galer & Goldstein 1991) and Hf (Blichert-Toft & Arndt 1999, Blichert-Toft et al. 2004) isotopic heterogeneities leaves open the possibility of earlier global fractionations and sustained the minority view that continental crust was present during the Hadean Eon (e.g., Armstrong 1981, 1991; Reymer & Schubert 1984; Bowring & Housh 1995), which comprises the first ~600 Ma of Earth history (**Figure 1**). In the latter scenarios, a lack of evidence of earlier chemical depletions (whether due to a magma ocean or to development of basaltic or continental crust) reflects subsequent remixing of isotopic heterogeneities.

It is fair to say that the delayed, slow continental growth model (Veizer & Jansen 1979, McLennan & Taylor 1991, McCulloch & Bennett 1993) has been generally accepted by geochemists for 30 years. Although the existence of Hadean zircons has been known for nearly as long (Froude et al. 1983, Compston & Pidgeon 1986), they have been seen more as curiosities than helpful in understanding the origin of continental crust (e.g., Taylor & McLennan 1985, Galer & Goldstein 1991, McCulloch & Bennett 1993). Supporters of the slow growth paradigm point to the distribution of age provinces and the absence of >4 Ga crust, Archean-Proterozoic sediment REE patterns, the lack of fractionation of the Nd/Hf isotopic systems, the uniformity of Ce/Pb in basalts throughout time, Nb-U-Th systematics in mantle-derived rocks, and the implausibility of making early felsic crust. However, the evidence marshaled against the early formation of continental crust is far from compelling.

Compilations of model mantle extraction ages from exposed continental crust (e.g., McCulloch & Bennett 1993) tend to yield peaks at 2.7 Ga, 1.9 Ga, 1.2 Ga, and <0.4 Ga, arguably reflecting supercontinent assembly (Condie 2000). However, this approach is limited by sampling artifacts (e.g., glacially scoured bedrock exposures in developed nations actively engaged in minerals exploration can be overrepresented), irregular or poor exposure, and sampling limitations (i.e., 99%+ of the volume of continental crust has yet to be radiometrically dated). Although such data provide a lower bound on continental growth, they are often interpreted in terms of the rate of continental addition with time (e.g., Taylor & McLennan 1985) rather than the record of crustal preservation. Morgan (1985, 1989) noted that the anomalously low K, Th, and U contents seen in Archean rocks suggests that high-heat-production crust was preferentially recycled during subsequent orogenies. In this interpretation, the extent of exposed Archean crust is only a fraction of what existed prior to 2.5 Ga. Whether its mass was substantially greater than today is unknown.

Distinct differences in chemistry between fine-grained Archean and Proterozoic sediments have been interpreted as indicating that >2.5 Ga upper crust was substantially more mafic and less abundant than <2.5 Ga upper crust (Taylor & McLennan 1985). However, fine-grained Archean sediments are largely derived from greenstone belts where they represent material eroded from island arcs built on ocean floor. Thus, this observation may represent an environmental, as opposed to temporal, difference. Furthermore, higher ratios of incompatible to compatible elements (e.g., Th/Sc) in post-Archean sediments may reflect lesser vertical mixing in compositionally stratified crust rather than a fundamentally different crustal composition. Regardless, inferences regarding crustal volume drawn from trace element data are without basis; there is simply no definable relationship between sediment chemistry and continental growth.

Patchett et al. (1984) argued that because zircon-rich turbiditic sands have much lower Lu/Hf than superchondritic pelagic sediments, the broad coherence between the Nd and Hf isotopic systems in mantle-derived rocks is evidence that continental sediment has not been substantially subducted over geologic time. Armstrong (1991) counterargued that subduction of the mix of sediments characteristic of the ocean floor today would retain the mantle Nd-Hf array.

Modern mid-ocean ridge basalts (MORB) and oceanic island basalts (OIB) show uniformity in incompatible trace element ratios (e.g., Ce/Pb; Hofmann et al. 1986), while mafic volcanics appear to increase in Nb/U (and Nb/Th) through time (Sylvester et al. 1997, Collerson & Kamber 1999, Campbell 2003). Thus, secular variations in ratios of Nb-U-Th have been used to estimate the fraction of continental crust extracted from the mantle over time. The basis of this approach is that, while Nb, U, and Th are equally incompatible during mantle melting, they are fractionated in the processes of continental crust formation such that Nb/U of the continental crust, primitive, and depleted mantle are today  $\sim 10$ ,  $\sim 30$ , and  $\sim 50$ , respectively. Thus, documenting an Archean basalt with Nb/U  $\approx 50$  could be evidence that a similar magnitude of continental crust existed then as today. This approach, however, supports diverse conclusions. Although Collerson & Kamber (1999) concluded that growth of the continental crust mostly occurred since Archean time, with less than 20% of the present mass of continental crust present at 3.1 Ga, Campbell (2003) estimated that 70% of the continental crust had been extracted by  $\sim 3.1$  Ga. This disparity appears to reflect the vagaries in the way in which trace element ratios of ancient rocks are averaged (see Condie 2003). In any case, trace element ratios retain no clear or convincing record of the state of continental extraction prior to the beginning of the rock record at  $\sim 4$  Ga.

A widespread view is that the Earth could not have grown an early anorthositic crust similar to that which developed on the Moon because plagioclase is negatively buoyant in hydrous silicate melts (Condie 1982, Taylor 1982, Taylor & McLennan 1985; cf. Shaw 1976). However, Warren (1989) showed that even calcic plagioclase floats atop magmas with water contents greatly in excess of those present in upper mantle magmas.

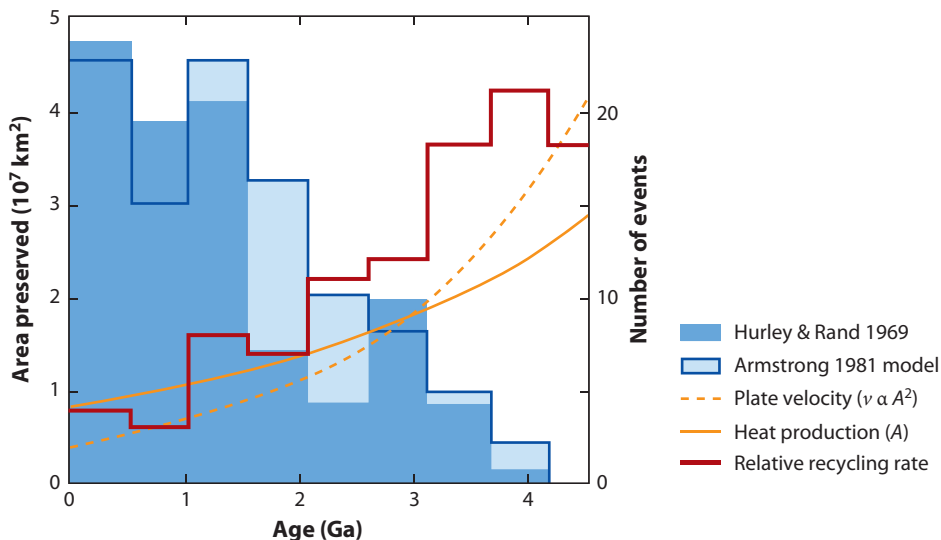
At the other extreme of this debate, advocates for massive early continental growth point to early silicate differentiation in other planets, continental free board, and the relationship between rates of arc magma production relative to sediment subduction to support their viewpoint. Armstrong (1981) emphasized that, like all other terrestrial bodies, Earth must have immediately differentiated into relatively constant-volume core, depleted mantle, enriched crust, and fluid reservoirs. Others have argued that, unlike Mercury, Mars, and the Moon, which developed primary crusts, exceptional circumstances (see earlier arguments; Smith 1981, Taylor & McLennan 1985) prevented this on Earth.

Assuming that the oceans maintained a constant volume over the past 3 Ga, the semicontinuous geologic record of shallow water sedimentation on stable cratons has been taken as evidence that sea level has not significantly deviated from the present base level of erosion. This is referred to as “constant continental freeboard.” In detail, however, such an inference is complicated by the isostatic response to changing thermal conditions in the mantle, the unknown thickness of oceanic crust in the distant past, whether plate tectonics operated in the past, and the role of mantle plumes in the ancient Earth (Eriksson 1999). Despite the many assumptions and uncertainties, there is general agreement that the thickness and areal extent of continents has been relatively constant since the Late Archean (Armstrong 1981, Taylor & McLennan 1985). Schubert & Reymmer (1985) argued that, because the mantle cools over time, mid-ocean ridges would have diminished in volume and thus constant freeboard implies some continental growth since  $\sim 3$  Ga. Armstrong (1991) countered that the diminishing volume of mid-ocean ridge would be compensated for by the subsidence of continental lithosphere as a result of its thickening ( $\sim 40$  km) over the past 2.5 Ga. In the author’s view, the present constraints are essentially equally supportive of the full range of continental growth models since  $\sim 3$  Ga and freeboard arguments provide no quantitative constraints on earlier histories.

The crux of the recycling model is that additions to the continental crust over time have been compensated by the recycling of similar amounts of continental material back into the mantle, mostly via sediment subduction. An appealing aspect of the model is that today the Earth appears to be in such a balance. A generation ago, estimates of sediment subduction rates were typically a fraction of a  $\text{km}^3 \text{ year}^{-1}$  (Dewey & Windley 1981, Reymmer & Schubert 1984, Taylor & McLennan 1985), and others ruled out the possibility of this process operating altogether (e.g., Moorbath 1976). It now seems irrefutable from geochemical data (Pb-Nd-Hf isotopes and the presence of  $^{10}\text{Be}$  in arc volcanics; Armstrong 1968, DePaolo 1983, Tera et al. 1986) and seismic imaging of accretionary arcs (e.g., Vannucchi et al. 2003) that significant amounts of continental sediment are being subducted into the mantle. Scholl and von Huene (2007) estimate that a minimum of  $\sim 3 \text{ km}^3 \text{ year}^{-1}$  of continental crust is introduced into the mantle via subduction processes. Other mechanisms, such as crustal delamination or continental subduction, would only add to this figure. Their estimate implies that a volume of continental crust equal to the present mass ( $\sim 6 \times 10^9 \text{ km}^3$ ) has been removed from the surface of Earth since 2.5 Ga. Estimates of magmatic additions at arcs long hovered at approximately  $1 \text{ km}^3 \text{ year}^{-1}$  (Condie 2005), but recent estimates range up to  $\sim 5 \text{ km}^3 \text{ year}^{-1}$  (Scholl and von Huene 2007).

The discussion above is intended to emphasize only that our present knowledge of continental additions and losses is consistent with planet’s continental crust budget being in steady state. Armstrong (1981) recognized that, even if this were the case, the present magnitude of recycling would be insufficient to remove surface vestiges of once widespread Hadean continental crust (**Figure 2**). He instead proposed that the rate of crustal recycling scales according to the square of the internal heat generation (i.e.,  $\sim 10$  times faster at 4.2 Ga than today)—a relationship supported by geodynamic models (e.g., Davies 2002)—and his model achieved a good fit with what was then taken to be the age distribution of continents (**Figure 2**). A limitation of Armstrong’s (1981)





**Figure 2**

Numerical recycling model showing predictions of Armstrong's 1981 model compared with preserved age provinces of Hurley and Rand (1969). (More recent compilations show a peak at  $\sim 2.6$  Ga; e.g., McCulloch & Bennett 1993.) Heat production ( $A$ ) with time is shown by the solid curve. The relative recycling rate, shown by the red staircase line, is qualitatively similar to the change in the square of the terrestrial heat generation (*dashed curve*), argued to be linearly related to plate velocity ( $v$ ). Modified with permission from Armstrong (1981).

model is that mantle-crust recycling was implemented via a Monte Carlo approach with no spatial dependence (i.e., mantle-crust box reservoirs were randomly accessed and mixed). Thus it remains an open question whether a physically plausible model in which recycling is restricted to mantle-crust interfaces could explain today's seeming absence of pre-Archean crust.

In summary, the rock record contains no clear evidence with which to constrain the magnitude, or even existence, of Hadean continental crust. Isotopic data (e.g., Sr-Nd isotopes of basalts) once thought to support rapid growth at  $\sim 2.7$  Ga (e.g., Taylor & McLennan 1985) are recognized as equally consistent with constant volume continental crust (DePaolo 1983). Even if there were a reliable method with which to estimate continental growth from the rock record, the possibility of crust-mantle recycling removes the ability to use such a relationship to predict crustal mass prior to 4 Ga.

A possible constraint on the magnitude of early felsic crust comes from the contrast between terrestrial and chondrite  $^{142}\text{Nd}/^{144}\text{Nd}$  (Boyett & Carlson 2006). If this effect is due to development of a superchondritic Sm/Nd reservoir at  $\sim 4.53$  Ga, as described earlier, the restricted range of Sm/Nd observed in terrestrial rocks limits early formed continental crust to only about a quarter of such a light-rare-earth-enriched (LREE) reservoir (Harrison et al. 2008).

## MAKING FELSIC CRUST AT 4.5 BILLION YEARS

Models of crustal growth on early Earth mostly favor mafic over felsic compositions, largely owing to the perceived lack of a viable mechanism to produce stable continental-type crust (i.e., plagioclase doesn't float on hydrous magmas and basaltic crust founders on a peridotitic liquid). The first parenthetical objection is, as already noted, unfounded, and the second may depend on the nature

of the terminal magma ocean phase. Given the relatively short durations estimated for magma ocean crystallization ( $10^3$ – $10^7$  years), the Earth may have experienced multiple such episodes. Forming an early felsic crust during solidification of molten primitive mantle is inhibited by the stabilization of garnet at depths greater than  $\sim 250$  km, which removes the feldspar component from the magma, leading to a mafic solute. However, a shallow magma ocean (e.g.,  $\leq 250$  km) crystallizing olivine at its base produces a light, polymerized melt that, upon ascent to shallow depths, rapidly nucleates feldspar (Morse 1986). This potentially results in rapid crystallization of tonalitic, network-rich, high viscosity liquids that could coalesce into rockbergs of stable, felsic crust.

Melting experiments using a primitive mantle composition in the CaO-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system at 6.5 GPa and 1850°C (Asahara & Ohtani 2001) yield liquids with up to 52%  $\text{SiO}_2$ . Zou and Harrison (2007) used the MELTS algorithm (Ghiorso & Sack 1995) to model the compositional change of such a magma during ascent to the near surface. Magmas rapidly evolve during crystallization to produce hydrous (1–2%  $\text{H}_2\text{O}$ ), tonalitic (57%  $\text{SiO}_2$ ) melts at 950 to 1000°C. At the surface, such a proto-crust would likely migrate to downwelling loci where they could be stabilized by locally cooler conditions. As the base of this crust heats up in response to shutdown of the descending cell, felsic liquids produced would tend to ascend diapirically, creating a self-stabilizing feedback.

The intent of this discussion is not to advocate a particular process but to instead suggest that formation of tonalitic crust almost immediately following Earth formation is possible. While no direct evidence of continental crust this old is offered, data derived from Hadean zircons (Harrison et al. 2008) are perhaps best explained by the presence at 4.5 Ga of a chemical component that has more in common with continental crust than any other known geochemical reservoir (e.g., very low Lu/Hf).

## EVIDENCE FROM HADEAN JACK HILLS ZIRCONS

In the absence of a rock record older than 4 Ga, our understanding of Hadean Earth has remained highly speculative (e.g., Smith 1981, Shirey et al. 2008). Although we can presume that the Hadean Earth experienced an intense impact flux, was characterized by approximately three times higher radioactive heating, and had roughly the same bulk chemistry as today, the only thing we know for certain is that it produced and somehow preserved the mineral zircon ( $\text{ZrSiO}_4$ ). Despite its compositional simplicity, many questions regarding the nature of the first  $\sim 600$  Ma years of Earth history can be addressed by detailed examination of Hadean zircons.

Hadean zircons have been found in numerous locations, but the best known occurrences are in the Mt. Narryer and Jack Hills regions of Western Australia (Froude et al. 1983, Compston & Pidgeon 1986). Zircon xenocrysts of Hadean age have also been identified in orthogneisses from Western Australia (Nelson et al. 2000), West Greenland (Mojzsis & Harrison 2001), and Northern Canada (Iizuka et al. 2006) but are not as abundant and thus have not been as intensively studied as the detrital grains from Western Australia.

The zircon-bearing rocks in the Jack Hills form part of a thick ( $>2$  km) series of fan delta deposits in a fault-bounded cratonic margin that were subsequently metamorphosed at  $\sim 3.1$  Ga to upper greenschist and amphibolite facies (Maas et al. 1992, Spaggiari et al. 2007). Most investigations of ancient zircon sampled heavy mineral-rich quartz-pebble conglomerates from a restricted locality in the Erawondoo region of the Jack Hills where they were first documented (Compston & Pidgeon 1986). Zircons are extracted from these rocks using separatory methods based on the zircons' high density and low magnetic susceptibility. Hand picked grains are mounted in epoxy, polished, and analyzed for  $^{207}\text{Pb}/^{206}\text{Pb}$  age, usually with an ion microprobe but laser ablation



inductively coupled plasma mass spectrometry (ICPMS) methods have also been used (e.g., Crowley et al. 2005). The ~3% of the analyzed grains that are older than 4 Ga are then characterized for U-Pb age. Jack Hills detrital zircons all show a characteristic bimodal distribution with peaks close to 3.3 and 4.1 Ga (Compston & Pidgeon 1986, Maas et al. 1992, Amelin 1998, Amelin et al. 1999, Mojzsis et al. 2001, Cavosie et al. 2004, Trail et al. 2007).

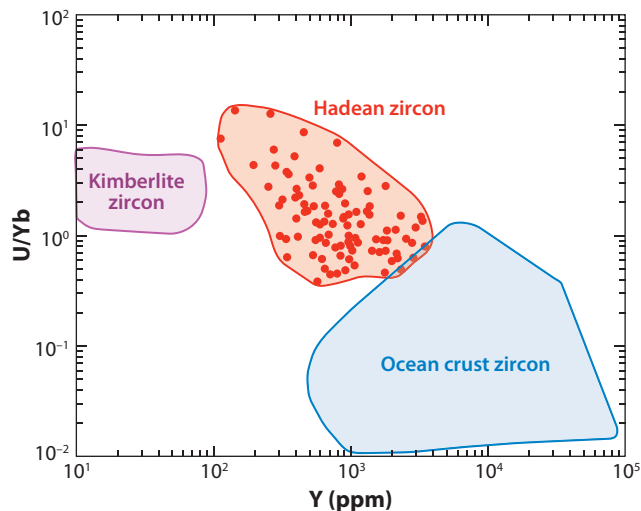
Hadean zircons, especially those from Jack Hills, have been analyzed by numerous methods to characterize oxygen isotope compositions (e.g., Mojzsis et al. 2001, Peck et al. 2001, Cavosie et al. 2005, Trail et al. 2007, Harrison et al. 2008), Xe isotopes (Turner et al. 2004, 2007), crystallization temperatures via Ti abundances (Watson & Harrison 2005, Harrison et al. 2007, Harrison & Schmitt 2007, Fu et al. 2008), Lu-Hf (Amelin et al. 1999; Harrison et al. 2005, 2008; Blichert-Toft & Albarède 2008), Sm-Nd (Amelin 2004, Caro et al. 2008a), Li isotopes (Ushikubo et al. 2008), and trace elements (e.g., Maas & McCulloch 1991, Peck et al. 2001), and have been characterized for mineral inclusions (Maas et al. 1992, Cavosie et al. 2004, Trail et al. 2004, Menneken et al. 2007, Hopkins et al. 2008). Results of these studies provide unique, if fragmentary, insights into the physical and chemical conditions on early Earth from which inferences regarding planetary evolution are beginning to emerge.

## SOURCE OF HADEAN JACK HILLS ZIRCONS

Due to zircon's inherent resistance to alteration by weathering, dissolution, shock, and diffusive exchange, and its enrichment in U and Th relative to daughter product Pb (Hanchar & Hoskin 2003), it has long been regarded as the premier crustal geochronometer. While highly valued in that role, the trace element and isotopic compositions of zircon have also recently become recognized as valuable probes of environmental conditions experienced during crystallization. Even in cases where zircon has been removed from its original rock context, such as detrital grains in clastic rocks, trace element and isotopic signatures can yield important information regarding source conditions because these records are often undisturbed.

Although zircon is dominantly a mineral of the continental crust, its formation is not restricted to that environment nor, for that matter, to Earth (e.g., Ireland & Wlotzka 1992). However, zircons of continental affinity can be readily distinguished from those derived from the mantle or oceanic crust by trace element characteristics and much lower crystallization temperatures (Grimes et al. 2007, Hellebrand et al. 2007; cf. Coogan & Hinton 2006) (**Figure 3**). Lunar and meteoritic zircons can be distinguished from terrestrial counterparts by their rare-earth-element (REE) signature (e.g., lack of a Ce anomaly; Hoskin & Schaltegger 2003). Furthermore, apparent crystallization temperatures for lunar zircons range from 900 to 1100°C (Taylor et al. 2008) in contrast to terrestrial Hadean zircons, which are restricted to 600 to 780°C (Watson & Harrison 2005, Harrison et al. 2007, Fu et al. 2008). Unlike meteoritic zircons, Hadean Jack Hills zircons array along the terrestrial-lunar oxygen isotope fraction line (M. Chaussidon, unpublished data). No extraterrestrial zircons have been recognized from the Jack Hills or any other terrestrial locality. Instead, the studied Hadean zircons appear to be derived exclusively from continental lithologies on Earth. Furthermore, textural characteristics of Hadean zircons from Jack Hills (e.g., growth zoning, inclusion mineralogy) indicate that virtually all are derived from igneous sources (e.g., Cavosie et al. 2004, Hopkins et al. 2008).

Now that the remarkably refractory nature and resistance to diffusive exchange of zircon (Cherniak & Watson 2003) have been emphasized, it is important to also note zircon's Achilles' heel. Zircon is sensitive to radiation damage and can degrade into metamict crystals consisting of heterogeneous microcrystalline zones encompassed by amorphous material (Ewing et al. 2003). Nature has, to some degree, already weeded out those grains most susceptible to metamictization



**Figure 3**

U/Yb versus Y plot that shows the distinctively different trace element signatures of zircons sourced from kimberlites and MORBs relative to Jack Hills zircons, which plot in the continental field. U is plotted using predecay U concentrations. Modified with permission from Grimes et al. (2007).

from detrital zircon populations as high U and Th grains are unlikely to survive sediment transport (e.g., Hadean Jack Hills zircons with initial U concentrations > 500 ppm are uncommon; Compston & Pidgeon 1986). Care must thus be taken to ensure that effects of postcrystallization alteration are not mistaken as primary features.

## THE HADEAN WATERWORLD HYPOTHESIS

Numerous studies summarized in this paper have interpreted a variety of Hadean Jack Hills zircon geochemical data to support the view that chemical weathering and sediment cycling were under way in the presence of liquid water within a few hundred million years of Earth's accretion. Although it may seem surprising that an anhydrous mineral can be used to argue for water on Hadean Earth, five lines of evidence have emerged that address this issue.

1. High  $\delta^{18}\text{O}$  in some zircons suggest that the magma from which the grains crystallized had a clay-rich protolith requiring that low-temperature hydrosphere-crust interactions had been occurring.
2. The inclusion mineralogy within zircons is consistent with their formation in hydrous meta- and peraluminous magmas, in the latter case implying both a surface origin of the protolith in the presence of liquid water and sedimentary cycling.
3. Zircon crystallization temperatures cluster near minimum melting conditions, indicating a narrow range of magmatic environments close to water saturation.
4. Pu/U variations in zircons with apparently concordant U-Pb and U-Xe ages are consistent with Pu-U fractionation occurring in aqueous fluids.
5. Negative  $\delta^7\text{Li}$  is interpreted to reflect zircon crystallization from crustal protoliths that had previously undergone intense chemical weathering.

## Oxygen Isotope Composition

In 2001, two independent groups simultaneously reported a heavy oxygen isotope signature in Hadean Jack Hills zircons and proposed that the protolith of these grains had contained  $^{18}\text{O}$ -enriched clay minerals, in turn implying that liquid water was present at or near the Earth's surface by  $\sim 4.3$  Ga (Mojzsis et al. 2001, Wilde et al. 2001). Although the datum that led Wilde et al. (2001) to this conclusion could not be reproduced (Cavosie et al. 2006), numerous follow-up measurements (e.g., Cavosie et al. 2005, Trail et al. 2007, Harrison et al. 2008) confirmed that a significant fraction of Hadean Jack Hills zircons contain  $^{18}\text{O}$  enrichments of 2 to 3‰ above the mantle zircon  $\delta^{18}\text{O}$  value of 5.3‰ (Valley et al. 1998). As the oxygen isotope fractionation between zircon and granitoid melt is approximately  $-2$ ‰ (Valley et al. 1994, Trail et al. 2008),  $\delta^{18}\text{O}$  values of the melt from which the zircons crystallized are inferred to be up to  $+9$ ‰.

Phanerozoic granitoids derived largely from orthogneiss protoliths (I types) tend to have  $\delta^{18}\text{O}$  below approximately  $+8$ ‰, whereas those derived by melting of clay-rich (i.e.,  $^{18}\text{O}$ -enriched) metasedimentary rocks (S types) have higher  $\delta^{18}\text{O}$  (O'Neil & Chappell 1977). Granitoids with  $\delta^{18}\text{O}$  values significantly less than 6‰ likely reflect hydrothermal interaction with meteoric water (Taylor & Sheppard 1986) rather than weathering. In general, S-type granitoids form by anatexis of metasediments enriched in  $^{18}\text{O}$ , compared with I-type granitoids that form directly or indirectly from arc processes. Jack Hills zircons enriched in  $\delta^{18}\text{O}$  thus provide evidence indicating the presence in the protolith of recycled crustal material that had interacted with liquid water under surface, or near surface, conditions (i.e., low temperature).

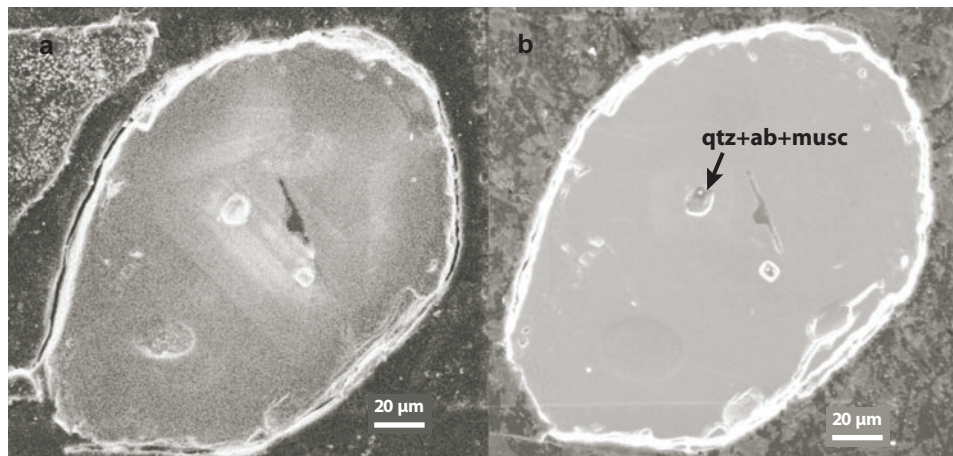
A limitation to this interpretation is the possibility of oxygen isotope exchange under hydrous conditions, even at postdepositional temperatures experienced by Jack Hills zircons (i.e.,  $\sim 450^\circ\text{C}$ ). For example, the characteristic diffusion distance for oxygen in zircon at  $500^\circ\text{C}$  for 1 Ma is  $\sim 1$   $\mu\text{m}$  (Watson & Cherniak 1997). Thus it is conceivable that oxygen isotope exchange during protracted thermal events could have introduced the heavy oxygen signature. This concern is somewhat mitigated by the relative unlikelihood of hydrothermal fluids being highly  $\delta^{18}\text{O}$  enriched, and the observed oxygen isotopic heterogeneity in Jack Hills zircons that indicates that isotopic equilibration did not occur.

## Hydrous, Peraluminous Inclusion Assemblages

It is perhaps misleading to have earlier stated that the only thing known about the Hadean Earth is that it contained the mineral zircon. Given that virtually every zircon contains mineral inclusions, it is, in effect, a microrock encapsulation system. Thus it is possible to infer some details about the chemistry of the host magma from which the zircon crystallized.

Examination of more than five hundred Hadean igneous zircons from Jack Hills, Western Australia reveals that the inclusion population includes quartz, muscovite, biotite, apatite, monazite, K-feldspar, albite, xenotime, rutile, chlorite, FeOOH, Ni-rich pyrite, thorite, amphibole, plagioclase, and diamond (Maas et al. 1992, Cavosie et al. 2004, Trail et al. 2004, Menneken et al. 2007, Hopkins et al. 2008). Potentially as interesting as the minerals present is the fact that garnet and  $\text{Al}_2\text{SiO}_5$  polymorphs have not yet been documented. In the most comprehensive study to date, Hopkins et al. (2008) examined more than four hundred Jack Hills zircons ranging in age from 4.01 to 4.27 Ga. They found that muscovite and quartz make up about two-thirds of the inclusion population and are closely associated with each another (**Figure 4**).

Mojzsis et al. (2001) noted the presence of hydrated mineral inclusions of broadly peraluminous character in the Hadean zircons (i.e., muscovite+quartz+biotite+K-feldspar+monazite) and suggested that this might also reflect the action of a Hadean hydrosphere. They reasoned



**Figure 4**

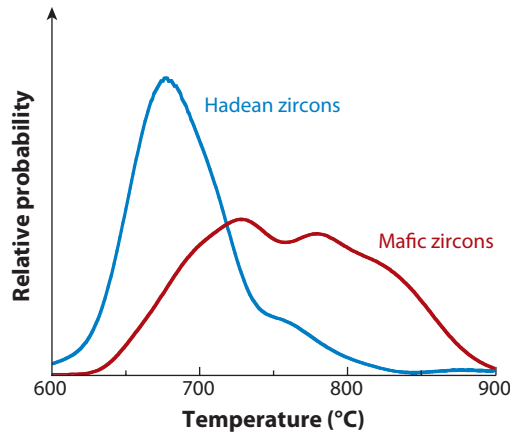
(a) Cathodoluminescence and (b) secondary electron micrographs of Jack Hills zircon RSES67\_3.2 ( $4.01 \pm 0.11$  Ga,  $693 \pm 15^\circ\text{C}$ ) containing an inclusion bearing coexisting quartz, feldspar, and muscovite.

that since the dominant Phanerozoic mechanism to create peraluminous granitoids is the melting of a pelitic protolith (White & Chappell 1977), the simplest explanation for the presence of this inclusion assemblage in Hadean zircons is that there was a terrestrial hydrosphere prior to  $\sim 4$  Ga. This reasoning implies that the Hadean oceans were salty: When granitoid rocks derived from partial melting of the mantle are exposed at the Earth's surface in the presence of water, feldspar (the most abundant mineral in the continental crust) breaks down to form aluminosilicate-rich clays and dissolved alkali and alkaline earth salts (e.g., chlorides of Na, K, and Ca). These components are separated when clays are deposited as shales and the latter remain in solution, ultimately contributing to ocean salinity. Subsequent anatexis of pelitic sediments produces S-type magmas with  $\text{Al}_2\text{O}_3 > \text{Na}_2\text{O} + \text{K}_2\text{O}$  (i.e., peraluminous). Although small amounts of peraluminous melts can also be generated by fractional crystallization of mantle-derived magmas, muscovite inclusion chemistry supports the view that the host magmas were dominantly metasedimentary rather than minor fractionates of mantle-derived systems (Hopkins et al. 2008).

### Zircon Thermometry

Because the abundance of a trace element partitioned between mineral and melt is temperature dependent, crystallization temperatures can, in principle, be estimated from knowing the concentration of that element in the solid phase if the magma is buffered at a known value. The advent of the Ti-in-zircon thermometer ( $T_{\text{Ti}}^{\text{zir}}$ ) permits zircon crystallization temperatures to be assessed provided the activities of quartz and rutile can be estimated (Watson & Harrison 2005, Watson et al. 2006, Ferry & Watson 2007). For example, in the case where zircon coexists with both quartz and rutile (i.e.,  $a_{\text{SiO}_2} \approx a_{\text{TiO}_2} \approx 1$ ), precise (e.g.,  $\pm 15^\circ\text{C}$ ) and accurate temperatures can routinely be determined. The diffusion of Ti in zircon is extremely sluggish under crustal conditions (Cherniak & Watson 2007) and thus the potential for re-equilibration of the thermometer is exceedingly low.

The Ti-in-zircon thermometer was first applied to Hadean Jack Hills zircons. Watson & Harrison (2005) measured Ti in zircons ranging in age from 3.91 to 4.35 Ga, most  $T_{\text{Ti}}^{\text{zir}}$  data defining a normal distribution (Figure 5). Excluding high-temperature outliers yielded an average



**Figure 5**

Probability plot of apparent zircon crystallization temperatures. Hadean zircons from Jack Hills, Western Australia (Watson & Harrison 2005) are shown by the blue curve, and zircons from mafic rocks (Valley et al. 2006, Fu et al. 2008) are indicated by the red curve. These spectra are distinctively different and preclude the Hadean zircons from being dominantly derived from mafic rocks.

temperature of  $682 \pm 26^\circ\text{C}$  ( $1\sigma$ ). However, a limitation in applying this thermometer to detrital zircons is the unknown  $a_{\text{TiO}_2}$  of the parent magma. Unless co-crystallization with rutile is known,  $T_{\text{Ti}}^{\text{zir}}$  is a minimum estimate. Watson & Harrison (2005) argued that  $a_{\text{TiO}_2}$  is largely restricted to between  $\sim 0.5$  and 1 in igneous rocks as the general nature of evolving magmas leads to high  $a_{\text{TiO}_2}$  prior to zircon saturation. Thus, for Hadean zircons of magmatic origin, it would be unusual for zircon to form in the absence of a Ti-rich phase (e.g., rutile, ilmenite, titanite), thus generally restricting  $a_{\text{TiO}_2}$  to  $\geq 0.6$ . In this case, calculated temperatures in the range of 650 to 700°C would be underestimated by  $\sim 40$  to 50°C, although this may be entirely compensated by  $a_{\text{SiO}_2}$  somewhat below unity (Ferry & Watson 2007).

Watson & Harrison (2005) thus concluded that the tight cluster of Hadean zircon crystallization temperatures at  $680 \pm 25^\circ\text{C}$  reflects prograde melting under conditions at or near water saturation (e.g., Luth et al. 1964). That is, most melt fertility was lost in the presence of excess water as soon as the source melted to form a granitic liquid. That no subsequent peaks are seen that clearly correspond to higher-temperature vapor-absent melting equilibria supports this conclusion.

Several critiques of the Watson-Harrison hypothesis have appeared but essentially reflect two specific arguments: Hadean zircons (*a*) are potentially sourced from late-stage differentiates of mafic magmas (Coogan & Hinton 2006, Valley et al. 2006, Rollinson 2008) or (*b*) reflect low-temperature zircon saturation in tonalitic magmas (Glikson 2006, Nutman 2006). Harrison et al. (2007) addressed these concerns, pointing out, in the former case, that crystallization temperatures and trace element characteristics (also see Grimes et al. 2007, Hellebrand et al. 2007) of Hadean and mafic zircon populations are distinctively different, and that, in the latter case, assumptions made regarding the applicability of zircon saturation thermometry are flawed (i.e., unaltered tonalites are unlikely to be characterized by an average  $T_{\text{Ti}}^{\text{zir}}$  of  $< 700^\circ\text{C}$ ). Rollinson (2008) argued that the  $\delta^{18}\text{O}$  and trace element signatures in Hadean Jack Hills zircons were consistent with their origin in ophiolitic trondhjemites rather than continental crust, although the latter view appears to reflect an inappropriate comparison between measured U concentrations rather than those corrected for radioactive decay (see **Figure 3**). The origin of muscovite, a mineral uncharacteristic of trondhjemite but the most common inclusion in Jack Hills Hadean zircons (Hopkins et al. 2008), was not addressed.



There is a preservation effect in detrital zircon populations that could influence the measured temperature spectrum, but it should only reduce the appearance of grains formed at low ( $\sim 700^\circ\text{C}$ ) temperatures. This is because the generally higher U and Th contents of zircons formed at lower temperatures preferentially lead to metamictization and then disintegration during sedimentary transport (Harrison et al. 2007). Lastly, high-resolution imaging of Ti in Hadean zircons (Harrison & Schmitt 2007) revealed that concentrations corresponding to temperatures above  $\sim 780^\circ\text{C}$  are typically associated with cracks and other crystal imperfections and thus are spurious.

## Xenon Isotopes

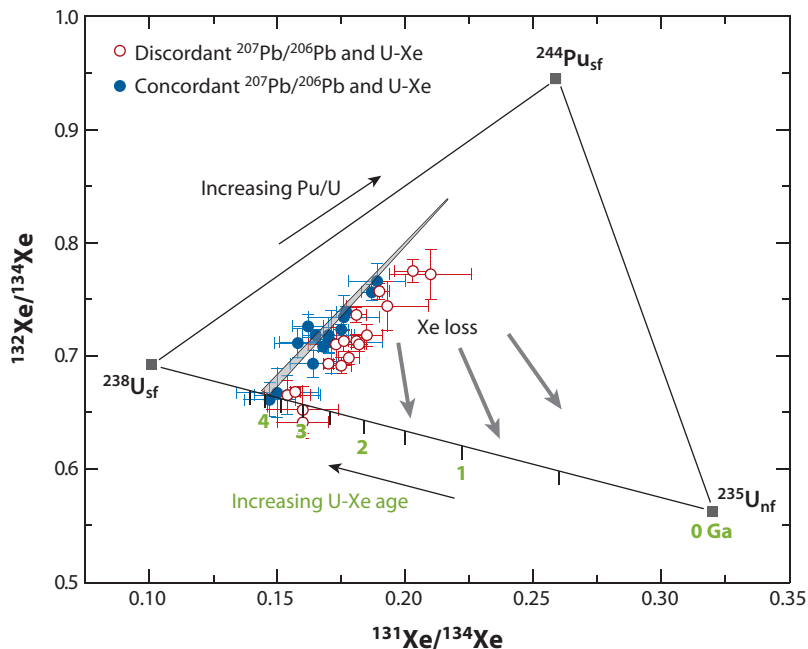
The meteorite record reveals that  $^{244}\text{Pu}$  was present in the early solar system with an initial abundance of  $\sim 1/100$  that of U (Ozima & Podosek 2002). However, its use as a geochemical tracer is restricted by its relatively short half-life ( $t_{1/2} = 82$  Ma);  $^{244}\text{Pu}$  was essentially extinct when the oldest known terrestrial rock formed at 4 Ga (Bowring & Williams 1999). Knowledge of the initial terrestrial Pu/U would be of great value as, for example, a nonchondritic Pu/U would require an unspecified cosmochemical process to have separated these two actinides. This has potentially important implications for early Earth. For example, models of volatile transport within the mantle and the origin and evolution of the atmosphere are largely derived from xenon isotopic data (Ozima & Podosek 2002, Pepin & Porcelli 2006).

As the only known relics of the Earth's earliest crust, analysis of Xe in Hadean zircons offers a way to determine terrestrial Pu/U ratios and potentially investigate Pu geochemistry during early crust forming events. Since these ancient zircons are detrital and of unknown provenance, it is essential that individual grains be analyzed. Turner et al. (2004) discovered the first evidence of extinct terrestrial  $^{244}\text{Pu}$  in individual 4.15–4.22 Ga Jack Hills zircons using the uniquely sensitive RELAX mass spectrometer (each zircon may contain as few as  $10^4$  atoms of Xe) (Gilmour et al. 1994). These measurements yielded initial Pu/U ratios ranging from chondritic ( $\sim 0.01$ ) to essentially zero. The latter results were first interpreted to be due to Xe loss during later metamorphism. This assumption was tested by irradiating 3.98–4.16 Ga zircons with thermal neutrons to generate Xe from  $^{235}\text{U}$  neutron fission in order to determine Pu/U simultaneously with U-Xe apparent ages (note that  $^{131}\text{Xe}/^{134}\text{Xe}$  and  $^{132}\text{Xe}/^{134}\text{Xe}$  can be used to calculate the relative contributions from  $^{244}\text{Pu}$ ,  $^{238}\text{U}$  spontaneous fission, and  $^{235}\text{U}$  neutron fission). Results comparing U-Pb and U-Xe ages on a ternary diagram (**Figure 6**) show varying degrees of Xe loss, but about a third of the zircons yield  $^{207}\text{Pb}/^{206}\text{Pb}$  and U-Xe ages that are concordant within uncertainty (Turner et al. 2007). However, Pu/U of these concordant zircons also range from chondritic to zero, allowing the possibility that Pu and U were fractionated from one another in crustal environments during the Hadean.

Although these are preliminary results, they raise the question: What conditions would be required for Pu and U to be substantially mobile with respect to each other during the Hadean? The magmatic behaviors of  $\text{U}^{+4}$  and  $\text{Pu}^{+4}$  are not well known, but they appear to behave coherently in silicate melts (Smith et al. 2003), consistent with their similar ionic radii (see Hoskin & Schaltegger 2003). Thus magmatic processes seem unlikely to be the source of large U-Pu fractionations.

In aqueous solution, uranium is essentially insoluble in the 4+ state, but greatly increases solubility when oxidized to the 6+ state (Langmuir 1978). The oxidation states of plutonium (3+ through 7+) also affect its behavior in solution, but all species have low solubilities relative to  $\text{U}^{6+}$ . Although  $\text{Pu}^{4+}$  is somewhat soluble across a range of pH, it reacts quickly with mineral surfaces to form essentially insoluble  $\text{Pu}^{3+}$  (Kersting et al. 1999). Thus a viable candidate to separate Pu and U appears to be aqueous fluids under appropriate redox conditions. How oxidizing would such fluids have to be? For illustration, note that the stability boundary separating  $\text{U}^{4+}$  from  $\text{U}^{6+}$  in





**Figure 6**

Plot of  $^{131}\text{Xe}/^{134}\text{Xe}$  and  $^{132}\text{Xe}/^{134}\text{Xe}$  for neutron irradiated Jack Hills zircons (modified from Turner et al. 2007). Data shown as blue circles have U-Xe and  $^{207}\text{Pb}/^{206}\text{Pb}$  ages that are within error, whereas data shown as red open circles are clearly discordant. Although Xe loss trajectories can be complex, the observation of concordant data spanning the Pu/U range from zero to chondritic ( $\sim 0.01$ ) is suggestive of Pu-U fractionation in aqueous fluids.

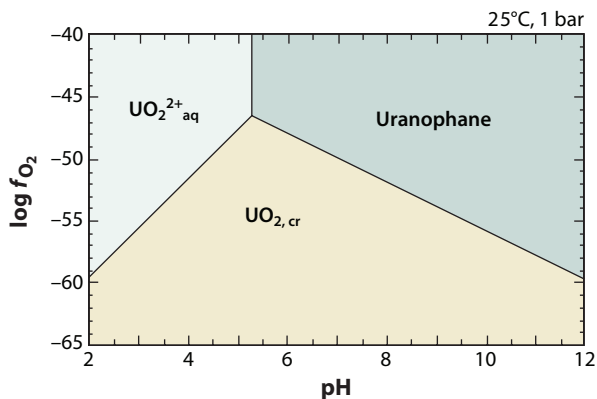
fluids containing dilute concentrations of  $\text{Ca}^{+2}$  and  $\text{SiO}_2$  in solution at  $25^\circ\text{C}$  and 1 bar (Figure 7) is at an  $f_{\text{O}_2}$  of  $10^{-50}$  for a pH of five. Thus, the apparent early fractionation of U from Pu need not have involved strongly oxidizing solutions. The large variations in Pu/U seen in Hadean granitoid zircons could well reflect the interaction of their protoliths with water-rich fluids expected under early Earth conditions.

## Li Isotopes

Isotopic analyses of Hadean Jack Hills zircons show  $\delta^7\text{Li}$ , ranging from  $-19$  to  $+13\%$  (Ushikubo et al. 2008). The highly negative values may reflect zircon crystallization from a source that experienced intense weathering. This would then place the crustal protolith at the Earth's surface at some point in its history. A limitation of this interpretation is that  $\text{Li}^+$  diffuses readily in silicate minerals, even at relatively low temperatures (e.g., Giletti & Shanahan 1997) and thus could have exchanged with species such as  $\text{H}^+$  during metamorphism. Were this the case, the measured isotopic compositions could reflect postdepositional alteration in the host quartzite rather than an intrinsic property of the zircon's protolith.

## EVIDENCE OF HADEAN CRUST AT 4.5 Ga

Studies of initial  $^{176}\text{Hf}/^{177}\text{Hf}$  in  $>4$  Ga detrital Jack Hills zircons show large deviations in  $\epsilon_{\text{Hf}(T)}$  from bulk silicate Earth (Kinny et al. 1991; Amelin et al. 1999; Harrison et al. 2005, 2008;



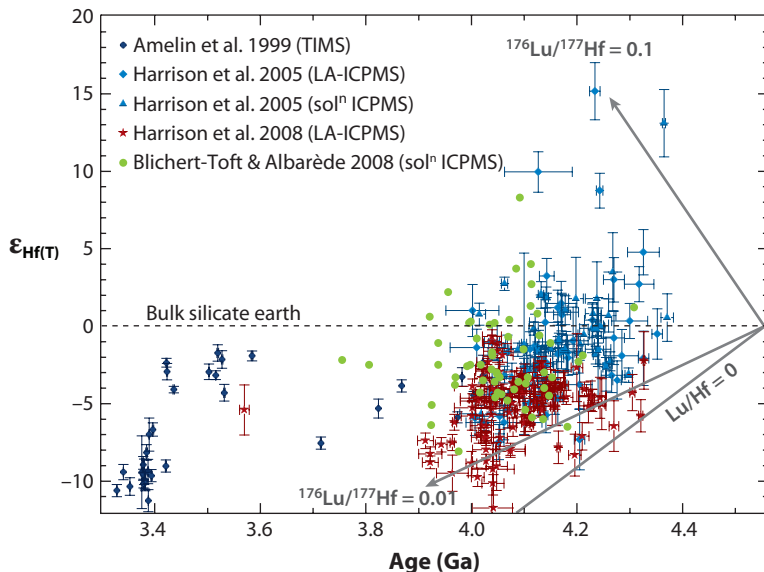
**Figure 7**

Activity versus pH plot showing stability relationships at 25°C and 1 bar in several oxidation-reduction systems, assuming  $a_{\text{Ca}^{2+}} = 10^{-3}$ ,  $a_{\text{SiO}_2(\text{aq})} = 10^{-4}$ , and  $a_j$  (other aqueous ions) =  $10^{-6}$ . Uranophane =  $\text{Ca}(\text{UO}_2)_2(\text{SiO}_3\text{OH})_2 \cdot 5\text{H}_2\text{O}$ . Note that under these conditions, the uranyl ion (i.e.,  $\text{U}^{+6}$ ) forms at remarkably low  $f_{\text{O}_2}$  (Dimitri Sverjensky, personal communication). Thus, the apparent early fractionation of U from Pu need not have involved strongly oxidizing solutions.

Blichert-Toft & Albarède 2008) that have been interpreted to reflect an early major differentiation of the silicate Earth (**Figure 8**). In attempts to quantify this, Blichert-Toft & Albarède (2008) and Harrison et al. (2008) undertook Monte Carlo modeling of these data by associating  $\epsilon_{\text{Hf}}$  with  $^{176}\text{Lu}/^{177}\text{Hf}$  obtained by random sampling of a function derived by compiling Lu/Hf from volcanic rocks. The peak in this distribution (Lu/Hf  $\approx 0.01$ ) is characteristic of the average ratio in the tonalite-trondhjemite-granodiorite (TTG) suite (Condie 1993). Although assuming extraction from a depleted mantle composition rather than a chondritic uniform reservoir (CHUR) increases the average extraction age, the overall results are consistent with the formation of crust occurring essentially continuously since 4.5 Ga. To underscore this, a subset of the data of Harrison et al. (2008) yields  $\epsilon_{\text{Hf}}$  within uncertainty of the solar system initial ratio (Bouvier et al. 2008), requiring that the zircon protoliths had been removed from a CHUR by 4.5 Ga (cf. Allegre et al. 2008).

Harrison et al. (2005) also reported several Hadean Jack Hills zircons with positive  $\epsilon_{\text{Hf}}$ , including one as high as +15, which they interpreted as evidence that a significant volume of mantle had been depleted to form an enriched reservoir—possibly continental crust. In a larger follow-up study, however, Harrison et al. (2008) did not observe any Hadean Jack Hills zircons with positive  $\epsilon_{\text{Hf}}$ . Blichert-Toft & Albarède (2008) did report additional positive values, but it remains possible that calculation artifacts in their bulk analysis approach, as opposed to the more spatially selective laser ablation method, are responsible. Indeed, nonlinear calculation artifacts (Harrison et al. 2005) are of real concern in estimating  $\epsilon_{\text{Hf}}$  for ancient zircons.

The most robust aspect of this growing data set (**Figure 8**) is the cluster of results along a line corresponding to a Lu/Hf  $\approx 0.01$ , a value characteristic of continental crust. Extrapolation of this trend yields a present-day  $\epsilon_{\text{Hf(T)}}$  of approximately  $-100$ , which is substantially lower than the most negative value yet seen (Vervoort & Blichert-Toft 1999). Indeed, the early Archean record shows only  $\sim 8 \epsilon$  variation in  $^{176}\text{Hf}/^{177}\text{Hf}$  centered about the bulk Earth Lu/Hf. Harrison et al. (2005) inferred this to reflect a  $\sim 150$  Ma timescale of crust-mantle recycling and mantle mixing during the Hadean. This estimate is consistent with subsequent numerical simulations of early Earth convection scenarios (Coltice & Schmalzl 2006). The continental trend may also bear on



**Figure 8**

Plot of  $\epsilon_{\text{Hf}(T)}$  versus age for more than 300 Lu-Hf measurements on zircons with  $^{207}\text{Pb}/^{206}\text{Pb}$  ages up to 4.36 Ga. Data from Blichert-Toft & Albarède (2008) (*green circles*) are bulk  $^{207}\text{Pb}/^{206}\text{Pb}$  ages corrected for common Pb, assuming  $\text{Th}/\text{U} = 1$  and concordancy between the U/Pb and Th/Pb systems with  $\epsilon_{\text{Hf}}$  corrected to 4.1 Ga. Gray lines emerging at 4.56 Ga are trajectories showing Hf isotope evolution for  $^{176}\text{Lu}/^{177}\text{Hf}$  values of 0, 0.01, and 0.1.

the question of whether the bulk Earth is characterized by superchondritic Sm/Nd. Caro et al. (2008b) proposed a bulk Earth  $^{147}\text{Sm}/^{143}\text{Nd}$  value of 0.206, or  $\sim 5\%$  higher than chondritic. As the scaling between Lu/Hf and Sm/Nd for planetary processes is approximately a factor of two, this would imply a bulk Earth  $^{176}\text{Lu}/^{177}\text{Hf}$  of  $\sim 0.37$ , which would make both the continental trend and the  $\epsilon_{\text{Hf}}$  values within uncertainty of the solar system initial ratio increasingly difficult to explain.

## EVIDENCE OF HADEAN PLATE BOUNDARY INTERACTIONS

The question of when plate tectonics began is highly contentious, with contemporary estimates ranging from 3.8 Ga to as recently as 1 Ga (see Rollinson 2007 and references therein). This extraordinary span in part reflects the contrasting criteria used for recognizing continuous subduction processes in the geologic record. For example, although trace evidence of ophiolites may extend back to  $\sim 3.7$  Ga (Furnes et al. 2007), this rock suite has a generally short ( $\sim 500$  Ma) erosional lifetime (e.g., the Cenozoic Indo-Asian suture has already lost ophiolite exposure over  $>80\%$  of its length; Yin & Harrison 2000). Blueschists and other accretionary rocks fare no better (Veizer & Mackenzie 2003). Thus the requirement of observing preserved sections of these transitory assemblages as evidence of plate tectonics by definition limits its recognition to rocks that are  $\leq 1$  Ga (Veizer & Jansen 1985). A few geodynamic models were proposed that push back the onset of plate tectonic behavior to  $\sim 3.5$  Ga (see Rollinson 2007 and references therein), but there was until recently little support for pre-Archean plate tectonics.

The traditional view has run along the following lines. Archaean komatiites indicate a mantle potential temperature of  $\sim 1650^\circ\text{C}$  (Green et al. 1975), reflecting high radioactive heat production in a still hot, young Earth. Such high temperatures in a fertile mantle would result in thick

(>40 km), fast-spreading oceanic crust (McKenzie & Bickle 1988) that in turn resists subduction (Davies 1992). If subduction does occur, high intrinsic Hadean heat production leads to trench lock, followed by development of a global magma ocean (Sleep 2000). Thus Hadean plate tectonics was widely viewed as unlikely.

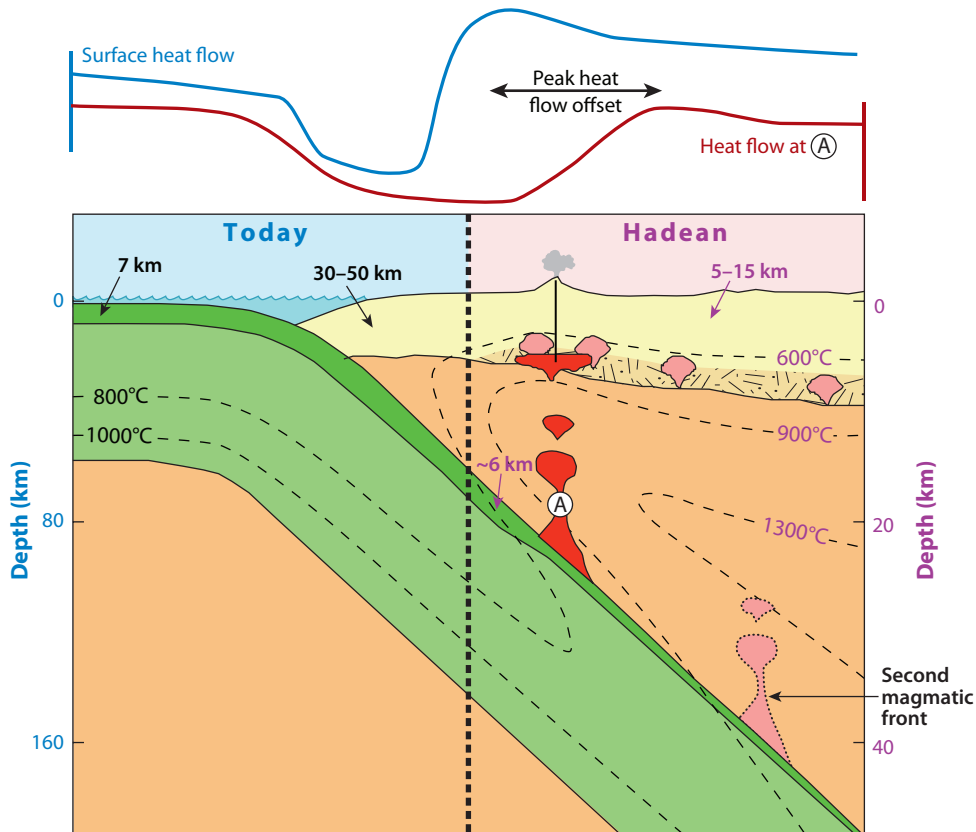
In light of the possibility of an early ( $\geq 4.5$  Ga) mantle depletion, Davies (2006) reexamined the possibility of plate-like behavior in the early Earth using advanced numerical methods that permit the simulation of more vigorous convection than did earlier models. High mantle potential temperatures in an initial depleted upper mantle enhances the density separation of enriched subducting oceanic crust, driving even greater upper mantle depletion that results in thin (4–6 km), highly subductable oceanic crust (Davies 2006). Other authors advocate the view that komatiites represent low ( $\sim 1450^\circ\text{C}$ ) melting temperatures under water-rich conditions (Grove & Parman 2004) or that unconventional scaling relationships between Earth's heat loss and mantle temperature imply that the Hadean heat flux was similar to today (Korenaga 2003). Thus, the emerging view is more supportive of a range of Hadean geodynamic regimes, including subduction, although direct evidence has been lacking. However, Hadean zircons bear witness to environmental conditions that suggest the possibility of plate boundary magmatism at that time.

As previously noted, the Hadean zircon inclusion population is dominated by muscovite and quartz, restricting zircon crystallization to broadly peraluminous magmas at  $>4$  kbars and  $<800^\circ\text{C}$ . Thermobarometric analyses of 4.02 to 4.19 Ga inclusion-bearing zircons further constrain magmatic conditions to  $\sim 700^\circ\text{C}$  and  $\sim 7$  kbars (Hopkins et al. 2008), implying an average geotherm of  $\sim 35^\circ\text{C km}^{-1}$ . This corresponds to a near surface ( $\leq 40$  km) heat flow similar to the global average today (Pollack et al. 1993) and is substantially less than that inferred for global heat flow during both the Archean (150–200  $\text{mW m}^{-2}$ , Bickle 1978, Lambert 1981, Abbott & Hoffman 1984) and Hadean (200–250  $\text{mW m}^{-2}$ , Smith 1981; 160–400  $\text{mW m}^{-2}$ , Sleep 2000).

Because radioactive heat generation was approximately three times greater at 4.1 Ga than present, and the Earth is generally thought to have cooled by 50 to  $100^\circ\text{C Ga}^{-1}$  (Turcotte & Schubert 2002, Bedini et al. 2004; cf. Korenaga 2003), it is difficult to conceive that Hadean global heat flow was less than approximately three times higher than the  $\sim 80 \text{ mW m}^{-2}$  observed today. The only magmatic environment currently characterized by heat flow of  $\sim 1/3$  the global average is where subducting oceanic lithosphere refrigerates the overlying wedge as it descends into the mantle (e.g., Pollack et al. 1993) (**Figure 9**). Given that the inclusion mineralogy of  $>4$  Ga zircons points toward their origin in hydrous,  $\text{SiO}_2$ -saturated, meta- and peraluminous melts similar to the two distinctive types of convergent margin magmas observed today (i.e., arc-type andesites and Himalayan-type leucogranites), these results are most simply interpreted as evidence that the zircons crystallized in an underthrust environment close to or at water saturation.

## SUMMARY AND FUTURE WORK

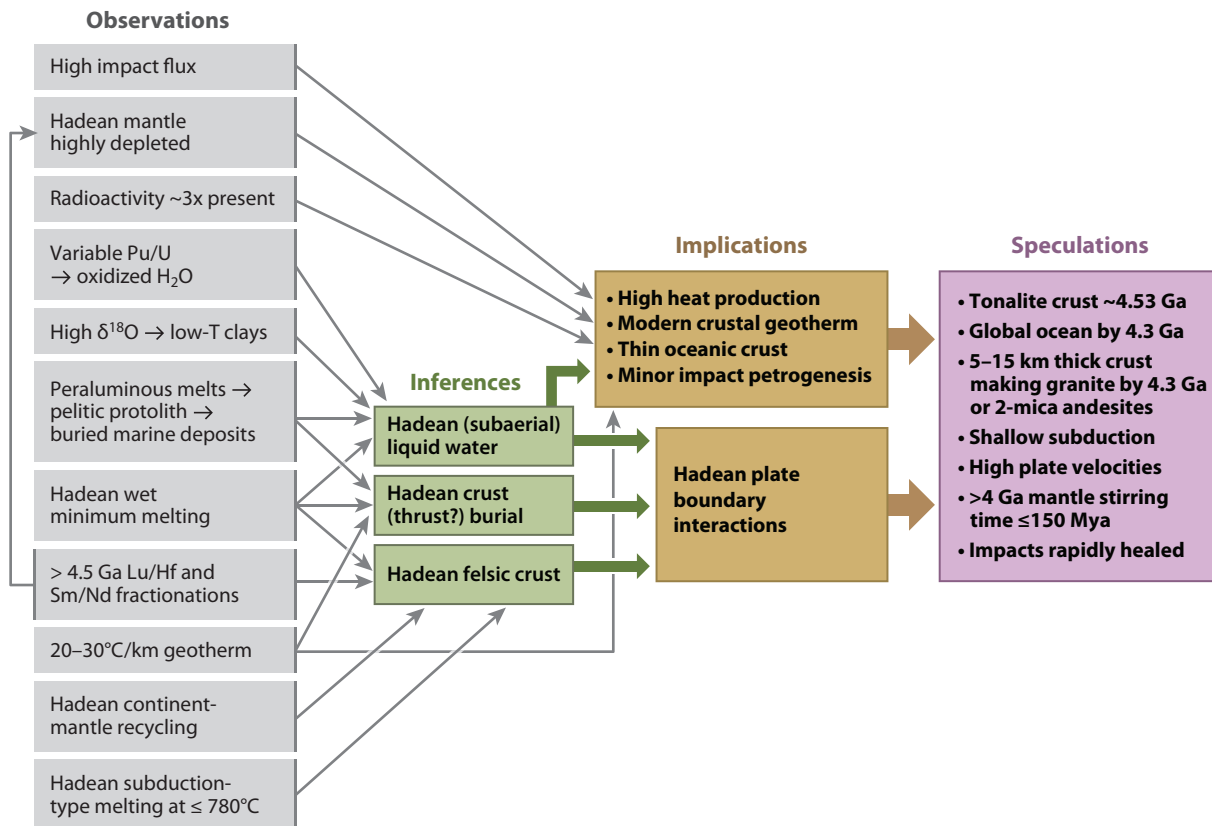
Although six visits to the Moon lasting only a total of two weeks returned specimens as old as 4.4 Ga, modern geochronology has failed to clearly document a single terrestrial rock significantly older than 4.0 Ga. This makes sense from the perspective of comparative planetology; the Moon is a relatively small, dead satellite, whereas the Earth is characterized by a globally dynamic regime that continuously destroys evidence of its past. This reasoning, however, has not always extended to consideration of the growth history of Earth's crust. The absence of continental crust  $>4$  Ga has often been taken as evidence that it didn't exist. A review of continental growth models suggests that the full range of evolutionary histories remains open for the Hadean Eon, from massive early crustal development to its near absence. Thus, we need to look elsewhere for traces of this inscrutable epoch.



**Figure 9**

Model of plate boundary interactions today (*left*) and during the Hadean (*right*) showing the refrigerating effects of underthrusting in both cases. Note that melting at *A* today corresponds to  $\sim 1100^{\circ}\text{C}$  at 70 km ( $\sim 15^{\circ}\text{C km}^{-1}$ ) and  $\sim 700^{\circ}\text{C}$  and 20 km for the Hadean ( $\sim 35^{\circ}\text{C km}^{-1}$ ). Both represent heat flow that is approximately one-third of the expected global averages. Relative surface heat flow is represented at the top of the figure and specifically for *A* at the bottom. Note that although surface heat flow in the magmatic arc is high (due to magmatic advection of heat), it is much lower at the source of melting. Thus the  $\sim 30^{\circ}\text{C km}^{-1}$  estimated Hadean geotherm implies magmatism in an underthrust environment—possibly analogous to modern subduction. The dotted melting region shows location of the second magmatic front, which appears absent in the Hadean zircon temperature spectrum (i.e., no temperature peaks are associated with the dehydration melting associated with muscovite, biotite, or amphibole breakdown).

Examination of Hadean detrital zircons yields a host of clues about environmental conditions prior to 4 Ga, ranging from the relatively unambiguous to the speculative. These observations, shown as oval balloons in **Figure 10**, have led to several inferences: felsic crust, subaerial liquid water, and thrust burial. When taken in context with the high expected Hadean heat production and impact flux, the simplest picture that emerges is that the planet was behaving much as it does today, with bimodal crustal blocks interacting destructively at their boundaries. If such interactions are not responsible for producing both kinds of convergent-margin magmas under high-water activities in an anomalously low geothermal gradient environment during the Hadean, it isn't obvious what substantially different mechanisms could be invoked. That said, although this evidence is internally consistent, it is almost entirely indirect and open to alternate interpretations.



**Figure 10**

Flow chart showing observations (*gray*) derived from analytical and sample characterization studies of Hadean Jack Hills zircons. These data lead to the following three inferences: a Hadean hydrosphere, continental crust, and underthrusting. Together these suggest the existence of Hadean plate boundary interactions. Speculations based on this possibility are shown in the purple box.

Given that Hadean zircons are our only sample of the first ~600 Ma of Earth history, how can we test these ideas? Some of the hypotheses proposed for the origin of Hadean zircons can be tested by coupled δ<sup>18</sup>O, Pu/U, Lu-Hf,  $T_{zir}$ , REE, etc. measurements on individual grains; e.g., the Hadean Waterworld hypothesis suggests correlations between δ<sup>18</sup>O and Pu/U. As we move away from the discovery and technique development phase, many more such measurements will certainly be undertaken. A further opportunity is to greatly expand the search for Hadean detrital/inherited zircons in Archean quartzites and orthogneisses. Twenty-five years ago it seemed inconceivable that we might find terrestrial fragments significantly older than 4 Ga (e.g., Schärer & Allègre 1985), but we now know of five locations on the planet with zircons at least this old and many much older. Concerns that the ancient detrital zircons are unrepresentative of Hadean Earth would potentially be transcended by discovery of numerous geographically dispersed sites. Indeed, where, one might ask, are all the zircons expected to have formed at >800°C by impact processes (Watson & Harrison 2005)? The absence of such a population signals either a profound sampling problem or a tantalizing hint of a history much different than previously supposed.

Lastly, as virtually all researchers agree that life could not have emerged until there was water at or near the Earth's surface, a significant implication arising from study of the Hadean zircons



is that our planet may have been habitable as much as 600 million years earlier than previously suggested (Mojzsis et al. 1996). Indeed, recent estimates for the time of molecular divergence among archaeobacteria are consistent with ages as old as 4.1 Ga (Battistuzzi et al. 2004), allowing the possibility that the Hadean supported the cradle of life on our planet.

## DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

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## Errata

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