Do the trace element compositions of detrital zircons require Hadean continental crust?

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ABSTRACT

The trace element compositions of Hadean zircons have been used in two ways to argue for the existence of Hadean continental crust. One argument is based on low crystallization temperatures of Hadean zircons that have been determined using a novel geothermometer based on the Ti content of zircons in equilibrium with rutile. The second argument is based on using the trace element abundances in zircons to calculate their parental melt compositions, especially the rare earth elements. Here we demonstrate that zircons that grow from a melt formed by basalt differentiation at modern mid-ocean ridges cannot be unambiguously distinguished from Hadean zircons on either of these grounds. Thus, we conclude that the trace element compositions of Hadean zircons are permissive of models that do not include the generation of continental crust in the Hadean.

Keywords: Hadean, mid-ocean ridge, zircon, continental crust.

INTRODUCTION

Models for the thermal and chemical evolution of Earth require information about the initial conditions and early differentiation processes. Because no rocks older than ca. 4.03 Ga are known (Bowring and Williams, 1999), the early geochemical evolution of the Earth is difficult to determine directly. Whether the lack of older rocks is because no continental crust formed prior to this or none is preserved is debated (e.g., see discussion in Armstrong, 1991). The only Earth materials that can be shown to have been preserved from this period are detrital zircons (e.g., Maas et al., 1992; Wilde et al., 2001), and these have been studied extensively.

Hadean (older than 4 Ga) detrital zircons have been found in ca. 3 Ga metasediments from Mount Narryer and Jack Hills in Australia (Compston and Pidgeon, 1986; Maas et al., 1992; Wilde et al., 2001). Zircons with U-Pb ages from 3.0 to 4.4 Ga (Wilde et al., 2001) have been found and their trace element and isotopic compositions have been used to infer the conditions under which they formed (Compston and Pidgeon, 1986; Maas et al., 1992; Amelin et al., 1999; Wilde et al., 2001; Mojzsis et al., 2001; Cavosie et al., 2005; Watson and Harrison, 2005; Harrison et al., 2005).

On the basis of trace element abundances, such as rare earth element (REE) patterns, and mineral inclusions, including quartz, in the zircons it has been suggested that these zircons crystallized from a granitic melt derived from continental crust (Maas et al., 1992; Wilde et al., 2001). Oxygen isotope ratios in some of these zircons are elevated over those expected for zircon in equilibrium with mantle melts. This observation has been used to argue that these zircons crystallized from a magma that must have contained recycled material that had interacted at low temperatures with water (Wilde et al., 2001; Peck et al., 2001; Mojzsis et al., 2001; Valley et al., 2002; Cavosie et al., 2005). Watson and Harrison (2005) developed a Ti-in-zircon thermometer and used this to show that Hadean zircons formed at low temperatures (~700 °C). Based on this low temperature, they suggested that the melt from which these zircons crystallized was generated by wet melting of continental crust.

HADEAN EARTH DIFFERENTIATION

Many lines of evidence suggest that the interior of the silicate Earth was hotter shortly after accretion than it is now. Impact heating, radioactive decay of both long- and short-lived isotopes, and potential energy release during core formation all led to the Earth being substantially hotter initially (Solomon, 1980; Pollack, 1997). Extensive mantle degassing, which requires magmatism, is thought to have occurred early, based on noble gas systematics. This early degassing has been interpreted to require much more active mantle convection during Earth's early evolution than at present (Yokochi and Marty, 2005).

Evidence for very early differentiation of the Earth into enriched and depleted reservoirs has been published. Differences in ^{142}Nd/^{144}Nd between Earth and chondritic meteorites suggest that an enriched reservoir must have formed within ~30 m.y. of Earth's accretion and remained unsampled since (Boyet and Carlson, 2005). A wide range of ^{176}Hf /^{177}Hf ratios in Hadean detrital zircons also apparently requires a high degree of differentiation of the sources to have occurred within <150 m.y. of Earth's accretion (Harrison et al., 2005). These data suggest that crystal-melt separation (partial melting and partial crystallization) created enriched and depleted reservoirs very early in Earth's history. However, these data cannot distinguish between magma ocean crystallization, basaltic crust generation, or continental crust generation (e.g., Caro et al., 2005).

Evidence for a long-term depletion of the mantle source that could be complementary to continental crust extraction has been searched for using Nd and Hf isotopes. The age-corrected Hf isotopic signatures of 3 Ga and younger zircons mostly are above those expected from a chondritic reservoir (Patchett et al., 1981), indicating a source that was depleted in Hf relative to Lu. The existence of both subchondritic and suprachondritic ^{143}Nd/^{144}Nd in Archean gneisses and volcanics also apparently requires the existence of enriched and depleted regions early in Earth history (e.g., Galer and Goldstein, 1991). However, whether this enriched reservoir was continental crust of a similar mass to that of the current continents (e.g., Armstrong, 1991), or was basalt directly derived from mantle melting (e.g., Galer and Goldstein, 1991), remains unclear.

In summary, there is clear evidence that crystal-melt separation led to the generation of enriched and depleted regions of the silicate earth from very early in Earth's history. The question remains whether a substantial portion of the enriched material was continental crust similar to that of the present day, requiring a multistage differentiation process and a hydrosphere (Campbell and Taylor, 1983), or was basaltic in bulk composition (e.g., Galer and Goldstein, 1991; Kamber et al., 2005). Because the existence of continental crust this early in Earth's history would have significant implications for both the Hadean Earth and subsequent Earth evolution, it is critical that models of Hadean continental crust are tested vigorously. Here we test the hypothesis that the trace element composition, and in partic-

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ular the crystallization temperatures, of Hadean zircons can be used to demonstrate that these crystallized from magmas generated within continental crust. We do this by comparing the compositions of zircons from modern lower oceanic crust, which formed from basalt differentiation, with the compositions of Hadean detrital zircons. We use samples from the modern oceanic crust because this is the simplest example of basalt differentiation available, but we do not suggest that Hadean zircons formed at spreading centers.

ANALYTICAL METHODS

Ion microprobe analyses were made at the Edinburgh Ion Microprobe Facility using a 5 nA $^{16}O^{-}$ primary ion beam of 15 keV impact energy. Secondary ions were measured using energy filtering (100–140 eV energy range) to reduce molecular interferences. REE analysis protocols were described in Hinton and Upton (1991). Titanium was measured on the ^{50}Ti peak, although the ^{49}Ti peak is equally clear of any molecular ions. In some runs both ^{50}Ti and ^{49}Ti were analyzed; no difference (within error) was observed. Potential overlaps of ^{50}Cr and ^{50}V were checked and shown to be negligible. Molecular interferences on this peak are estimated to be <0.1 ppm (see GSA Data Repository Table DR1[1]).

SAMPLE SUITE

We analyzed 15 zircons from 5 samples of oceanic gabbros from the modern oceanic crust. The samples we studied came from both fast- and slow-spreading ridges. Three samples formed at the fast-spreading East Pacific Rise and were sampled from Hess Deep in the equatorial Pacific. Sample 147–894G-9R3 70–76, recovered by Ocean Drilling Program (ODP) drilling on the intrarift ridge (Gillis et al., 1993), was studied by Gillis (1996), who analyzed the REE content of zircon in this sample and obtained results similar to ours, except for higher La concentrations. Samples NZ 10–14 and Alvin 3369–1431 were recovered by submersible (Hekinian et al., 1993; Karson et al., 2002) from the North Scarp of the Hess Deep. All of these samples contain plagioclase + amphibole + ilmenite + magnetite ± clinopyroxene ± quartz ± apatite. We also studied two samples from slow-spreading ridges. Sample 153 923A 8R2 13–19 is a felsic vein drilled by ODP Leg 153 from near the Mid-Atlantic Ridge (Cannat et al., 1995). It consists of plagioclase with minor orthopyroxene + ilmenite + magnetite + quartz + amphibole + titanite. Sample 6K–458–5 is an oxide-gabbronorite from the Atlantis Bank massif on the Southwest Indian Ridge (Kinoshita and Dick, 2001) and contains plagioclase + clinopyroxene + olivine + orthopyroxene + ilmenite + magnetite. The lithologies represented by these samples are characteristic of evolved oceanic plutonic rocks from the oceanic crust. The zircons analyzed are generally subhedral with straight grain boundaries and are 50–200 μm long. Exceptions are zircons in sample 153 923A 8R2 13–19 126, which are anhedral and as long as 300 μm, and in sample NZ 10–14 zircons, which are subeuhedral and as long as 1 mm.

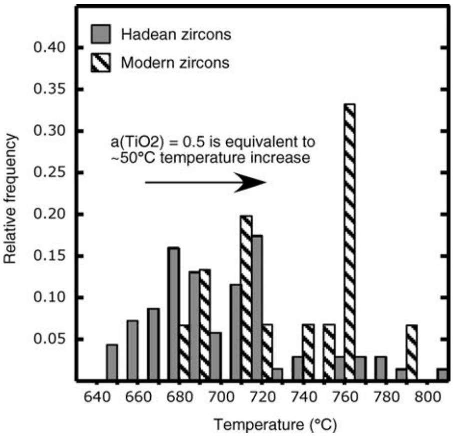

Figure 1. Comparison of zircon crystallization temperatures determined using Ti-in-zircon thermometer (Watson and Harrison, 2005) for Hadean zircons and zircons from modern lower oceanic crust. Arrow shows approximate increase in temperature if $a(TiO_2)$ is 0.5 rather than 1 (a is activity). Because primitive mantle had higher Zr/Ti than the mid-oceanic-ridge basalt (MORB) source, Hadean mantle melts may have had higher Zr/Ti and thus potentially lower Ti concentrations at zircon saturation, meaning that their temperatures are more likely to be underestimated than MORB zircons. Relative frequency is number of zircons with a given temperature range divided by total number of zircons analyzed.

RESULTS

Titanium-in-Zircon Thermometry

Watson and Harrison (2005) published a geothermometer based on the titanium content of zircon in equilibrium with rutile (i.e., where the activity of $TiO_2 = 1$) calibrated over an extremely wide temperature range (~900 °C), using both experimental and empirical data. When applied to Hadean zircons this thermometer gives crystallization temperatures between 644 °C and 801 °C, with most data <740 °C (Fig. 1; Watson and Harrison, 2005). Using the same thermometer, Ti concentrations in zircons from modern mid-ocean ridge plutonics give crystallization temperatures between 690 and 790 °C (Fig. 1), although Grimes et al. (2005) reported higher temperature in abstract form. The overlap between these temperature ranges demonstrates that the crystallization temperatures of Hadean zircons cannot be used to prove that they did not grow from a melt produced by basalt differentiation. Further, there is no systematic difference in zircon crystallization temperature between fast- and slow-spreading ridges (Table DR1; see footnote 1); i.e., no special conditions are required for basalt differentiation to lead to zircon crystallization at these temperatures.

The direct comparison of the Ti-in-zircon temperatures (Fig. 1) assumes that the activity of TiO_2, $a(TiO_2)$, was the same in both the Hadean and modern mid-ocean ridge systems and that the absolute temperatures require rutile saturation. Systematic differences in the activity of TiO_2 between these environments would lead to systematic differences between temperatures derived from this thermometer; if $a(TiO_2)$ was <1 during zircon crystallization, then the calculated temperatures are underestimates (Watson and Harrison, 2005). Ryerson and Watson (1987) and Watson and Harrison (1983) showed that the same factors that lead to a high activity coefficient for Ti in a melt lead to a high activity coefficient for Zr (see Watson and Harrison, 2005). On this basis, Watson and Harrison (2005) argued that most zircon-saturated melts have $a(TiO_2) > 0.5$, which will lead to zircon crystallization temperatures being underestimated by <60 °C.

If the activity coefficients for Ti and Zr in a melt are controlled by the same factors, then the Ti/Zr ratio of a melt should control $a(TiO_2)$ at zircon saturation. Present-day mid-ocean ridge basalts (MORB) have much higher Ti/Zr (~100; Sun and McDonough, 1989) than either melts of a primitive mantle composition or bulk continental crust (~30; Rudnick and Gao, 2003). This suggests that melts derived from either of these latter sources would have a lower $a(TiO_2)$ at zircon saturation than MORB. In turn, this means that temperatures derived from Ti-in-zircon thermometry will be underestimated more in these rocks than in differentiated MORB. On the basis of this argument, and the coexistence of ilmenite with zircon in all the modern samples we analyzed, any difference in $a(TiO_2)$ between the Hadean and MORB systems during zircon growth will tend to increase the calculated crystallization temperature of the Hadean zircons more than the mid-ocean ridge ones. This further supports the conclusion that Ti-in-zircon thermometry cannot unambiguously differentiate Hadean zircons from zir-

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[1] GSA Data Repository item 2006130, Table DR1, trace element composition of zircons from oceanic plutonic rocks, is available online at www.geosociety.org/pubs/ft2006.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

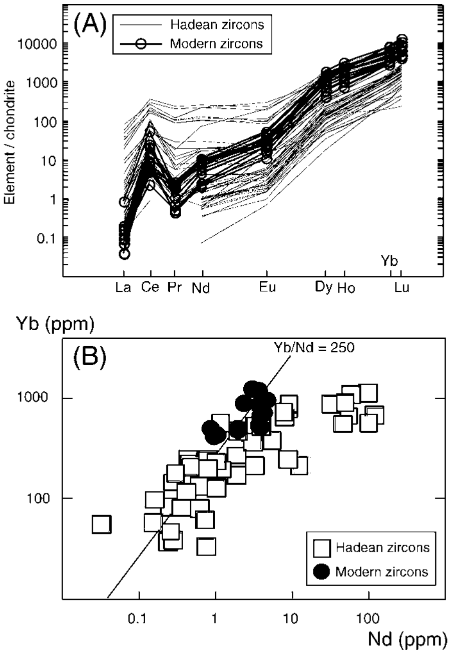

Figure 2. Comparison of rare earth element (REE) patterns of Hadean zircons and zircons from modern lower oceanic crust. Note the similarity in middle to heavy REE slope in most data (see inset). Hadean data are from Maas et al. (1992), Peck et al. (2001), and Wilde et al. (2001), and are exclusively for zircons with U-Pb ages older than 3.9 Ga.

cons that formed as the result of basalt differentiation.

Trace Element Abundances in Zircons

The REE concentrations and patterns in Hadean zircons have also been used to support models that they crystallized from melts derived from continental crust (Maas et al., 1992; Wilde et al., 2001; Peck et al., 2001). In Figure 2 we compare the REE abundances in zircons older than 4 Ga and in zircons from modern oceanic crust. The patterns observed are similar and the Nd/Yb ratio is almost identical in all but a subset of light (L) REE–enriched Hadean zircons. This is despite the fact that Nd/Yb is approximately five times higher in the bulk continental crust than in MORB. We suspect that the LREE-enriched subset of Hadean zircons can be explained by either minor inclusions, analytical problems (e.g., Maas et al., 1992), hydrothermal alteration, or by changes related to coupled substitution rather than differences in parental melt composition. Whitehouse and Kamber (2002) discussed several mechanisms of producing high apparent distribution coefficients for LREE in zircon, such as lattice distortion due to coupled substitution and microinclusions of LREE-enriched phases such as monazite, xenotime, or apatite (see also Hinton and Upton, 1991). Hoskin (2005) discussed the formation of LREE-enriched zircons through hydrothermal alteration and suggested that this can explain both the elevated $\delta^{18}O$ and LREE-enriched compositions of some Hadean zircons.

DISCUSSION

New trace element data for zircons hosted in samples from the modern lower oceanic crust demonstrate that neither REE nor Ti abundances can be used to unambiguously distinguish between Hadean zircons and zircons formed from basalt differentiation. Thus, these data cannot be used as evidence for the existence of continental crust during the Hadean. Because radiogenic isotopes cannot be used to infer the major element composition of isotopically enriched and depleted regions, these data cannot demonstrate the existence of Hadean continental crust. The final piece of evidence most commonly used to argue for Hadean continental crust is the O isotopic composition of Hadean zircons. We do not enter into the debate about whether these have been reset (e.g., Hoskin, 2005) or whether the fractionation factors are known well enough to predict the parental magma composition (Krylov et al., 2002; Valley et al., 2003); rather, we propose a model to develop $\delta^{18}O$-enriched magmas in the Hadean without continental crust or low-temperature oceans (<200 °C; Valley et al., 2002).

The oxygen isotope ratios in Hadean detrital zircons range from 4.6‰ to 15‰ (Mojzsis et al., 2001; Wilde et al., 2001; Cavosie et al., 2005). Cavosie et al. (2005, p. 663) suggested that all magmatic values are within the smaller range 5.3‰–7.3‰, with higher and lower values reflecting subsolidus modifications; however, they concurred with the earlier studies in interpreting the higher $\delta^{18}O$ values (between 6.3‰ and 7.3‰) as requiring that "the protoliths of the magmas these zircons crystallised in were altered by low temperature interaction with liquid water near Earth's surface" and that they formed in continental crust. Here we propose an alternative hypothesis to explain these data.

The composition of the early atmosphere is uncertain. It would almost certainly have contained large proportions of Earth's H and C, but in what form is unclear (H_2O, CH_4, H_2, CO, CO_2). Here we consider the widely proposed model of a CO_2-rich early atmosphere (e.g., Liu, 2004; Sleep et al., 2001) because: (1) there is growing evidence that early core formation left an oxidized mantle that would degas CO_2 during volcanism (e.g., Wade and Wood, 2005); (2) it has been suggested that reduced C species in the atmosphere would be oxidized to CO_2 by OH radicals produced by water vapor photolysis (Kasting et al., 1983); and (3) CO_2-rich atmospheres are observed on Venus and Mars.

Assuming a CO_2-rich Hadean atmosphere, we follow Sleep et al. (2001) in considering the carbonation of a basaltic Hadean crust that would be required to draw down this CO_2. If all of Earth's CO_2 were degassed the atmosphere would have a partial pressure of CO_2 of ~215 bar; under these conditions weathering and hydrothermal alteration of a basaltic crust would form carbonates (calcite, dolomite, siderite, magnesite; Sleep et al., 2001). A strong greenhouse atmosphere, high radiogenic heat production, extensive volcanism, and massive bombardment would have led to extensive weathering and hydrothermal alteration near Earth's surface. The formation of carbonates would lead to a greater increase in the $\delta^{18}O$ of the rock than the formation of hydrous silicates at the same temperature. The long-term demise of such a CO_2-rich atmosphere requires the removal of CO_2 from the atmosphere by these kinds of reactions (Sleep et al., 2001). Thus, if a CO_2-rich atmosphere ever existed on Earth, then the formation of carbonated basalts appears inevitable. Assimilation of these carbonated rocks by basaltic magmas would lead to increases in magma $\delta^{18}O$, a process that would probably be enhanced by the steep Hadean geotherm (Kamber et al., 2005). Zircons that crystallize from the differentiation products of these basalts would then be $\delta^{18}O$ enriched and would have the trace element chemistry of the Hadean zircons.

In summary we conclude that there is no unambiguous evidence for continental crust older than that found in the 4.03 Ga Acasta Gneiss (Bowring and Williams, 1999). The trace element compositions of detrital Hadean zircons could have been generated during differentiation of a basaltic melt, for example, above a mantle upwelling. Elevated $\delta^{18}O$ in these zircons can be explained by the melts that crystallized these magmas containing a component that was either altered at low temperatures by water (e.g., Valley et al., 2002) or at higher temperature by a CO_2-rich atmosphere. We do not claim to demonstrate here that Hadean zircons crystallized from differentiated basalt, we simply question whether the data exist to discount this hypothesis; the answer appears to be no.

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