Trace element chemistry of zircons from oceanic crust: A method for distinguishing detrital zircon provenance

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ABSTRACT

We present newly acquired trace element compositions for more than 300 zircon grains in 36 gabbros formed at the slow-spreading Mid-Atlantic and Southwest Indian Ridges. Rare earth element patterns for zircon from modern oceanic crust completely overlap with those for zircon crystallized in continental granitoids. However, plots of U versus Yb and U/Yb versus Hf or Y discriminate zircons crystallized in oceanic crust from continental zircon, and provide a relatively robust method for distinguishing zircons from these environments. Approximately 80% of the modern ocean crust zircons are distinct from the field defined by more than 1700 continental zircons from Archean and Phanerozoic samples. These discrimination diagrams provide a new tool for fingerprinting ocean crust zircons derived from reservoirs like that of modern mid-ocean ridge basalt (MORB) in both modern and ancient detrital zircon populations. Hadean detrital zircons previously reported from the Acasta Gneiss, Canada, and the Narryer Gneiss terrane, Western Australia, plot in the continental granitoid field, supporting hypotheses that at least some Hadean detrital zircons crystallized in continental crust forming magmas and not from a reservoir like modern MORB.

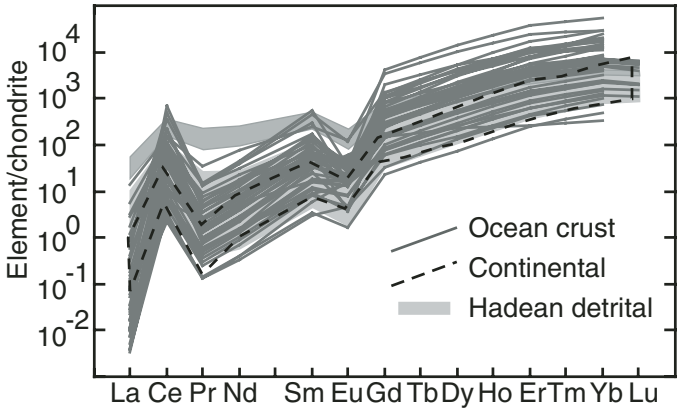

Figure 1. Rare earth element concentrations for ocean crust zircon normalized to C1 chondrite (McDonough and Sun, 1995). Hadean zircon data are from Maas et al. (1992), Wilde et al. (2001), Peck et al. (2001), and Crowley et al. (2005). Dashed field represents zircons from continental rocks (diorite to aplite) in Boggy Plains zoned pluton (Hoskin and Ireland, 2000).

Keywords: detrital zircon, trace elements, provenance, mid-ocean ridge, Hadean.

INTRODUCTION

Zircon ($ZrSiO_4$) is a common accessory mineral found throughout the geologic record in igneous, metamorphic, and clastic sedimentary rocks. Because zircon grains may undergo multiple episodes of sedimentation, magmatism, and/or metamorphism while retaining age and chemical information, numerous investigations have focused on relating the trace element geochemistry of zircon with provenance (e.g., Hoskin and Ireland, 2000; Belousova et al., 2002). Determining the provenance of detrital zircons is of interest in both modern and ancient sedimentary settings, where sources may be poorly defined. Unfortunately, distinction of source rock composition using zircon geochemistry is complicated, as indicated by the overlap in the rare earth element (REE) concentration of zircons from most rocks types (Fig. 1).

The robust nature of zircon is illustrated by the existence of detrital grains from Western Australia dated as older than 4.0 Ga (e.g., Compston and Pidgeon, 1986; Maas et al., 1992; Wilde et al., 2001; Crowley et al., 2005), despite the lack of rocks recognized from the first 550 m.y. of the Earth's history. These grains provide much of the limited direct data regarding the geochemical evolution of the early Earth crust. A granitic 'continental' source has been inferred for some Hadean detrital zircons based on their REE chemistry (Maas et al., 1992; Peck et al., 2001; Lizuka et al., 2006), evolved mineral inclusions such as quartz (Maas et al., 1992; Wilde et al., 2001), isotopic compositions (e.g., Peck et al., 2001; Valley et al., 2005; Harrison et al., 2005), and consistently low crystallization temperatures (Watson and Harrison, 2005). However, zircons recovered from modern mid-ocean ridges have been used to argue that Hadean detrital zircons cannot be distinguished from grains formed in differentiated basaltic crust based on REE composition and crystallization temperatures (Coogan and Hinton, 2006).

Although zircon traditionally has not been thought of as an abundant accessory mineral in mafic rocks, it has been recognized in gabbroic rocks exposed at the fast-spreading East Pacific Rise (Gillis et al., 1993), the slow- and ultra-slow-spreading Mid-Atlantic (MAR) and Southwest Indian (SWIR) Ridges (e.g., Cannat et al., 1995; John et al., 2004; Grimes et al., 2005; Coogan and Hinton, 2006), and plutonic rocks from ophiolites (e.g., Mukasa and Ludden, 1987). Here we compare the trace element chemistry for a large suite of zircon derived from modern in situ oceanic crust with zircons derived from both island and continental arcs. In doing so, we show that most ocean crust zircons can be distinguished from those formed in Archean to Phanerozoic continental settings.

SAMPLES AND ANALYTICAL METHODS

We present trace element data from 388 secondary ion mass spectrometry (SIMS) analyses on more than 300 zircon grains from 36 gabbros. These samples were collected from young oceanic crust along the MAR and SWIR (GSA Data Repository Fig. DR1[1]) by submersible and dredge, and in Ocean Drilling Program (ODP) bore holes 1270C, 1270D, 1271B,

[1]GSA Data Repository item 2007159, analytical procedures, Table DR1 (representative trace element data for ocean crust zircons), Figure DR1 (sample locations), Figure DR2 (zircon images), and Figure DR3 (supplemental geochemical plots for ocean crust zircon), is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

and 1275D, Integrated Ocean Drilling Program (IODP) hole U1309D, and ODP hole 735B. Host-rock compositions range from 49 wt% SiO_2 in oxide-bearing gabbro (JR 31 12–68; Coogan et al., 2001) to 69 wt% SiO_2 in tonalite dikelets (ODP209 1275D 31R2 piece 4f; Kelemen et al., 2004). Zircons from altered gabbroic veins cutting peridotite have also been analyzed (holes 1270C and 1270D). Zircon occurs with the greatest abundance (yields in crushed samples range from 10 to >1000 grains/kg of rock) in quartz diorite to tonalite dikes and oxide- and/or amphibole-bearing gabbro, and may contain inclusions of apatite-group minerals, quartz, xenotime, and monazite. Euhedral to anhedral zircons from 5 µm to >1.5 mm long are noted in thin section; 50–250-µm-long euhedral grains with concentric and sector zoning patterns are typical (Fig. DR2).

For comparison with the ocean crust zircon suite, we present trace element compositions of nine zircon grains from lower mid-crustal quartz diorite to tonalite dikes collected from the Jurassic Talkeetna terrane, Alaska. The Talkeetna arc is a mafic and ultramafic crustal section interpreted as part of the crust and upper mantle of an accreted intraoceanic island arc (Kelemen et al., 2003).

Trace element analyses of zircons collected along the MAR at 30ºN and the SWIR were performed using the sensitive high-resolution ion microprobe (SHRIMP-RG) located at the U.S. Geological Survey–Stanford Ion Probe Laboratory (Mazdab and Wooden, 2006). Zircons from the MAR collected at 15º20'N and the Talkeetna arc were analyzed using the Cameca IMS 3f SIMS at the Woods Hole Oceanographic Institute. Analytical procedures and SIMS trace element data for representative samples are in the GSA Data Repository (see footnote 1).

RESULTS

Trace Elements in Ocean Crust Zircon

The REE patterns for zircons recovered from in situ oceanic crust and continental granitoids, as well as Hadean detrital grains, show complete overlap on REE diagrams, including a subset of light (L) REE-enriched Hadean zircons (Fig. 1). In terms of primary igneous zircon, only kimberlites and carbonatites host zircons with consistently unique REE patterns (e.g., Hoskin and Ireland, 2000).

In contrast to REE diagrams, plots of U versus Yb and U/Yb ratio versus Hf and Y (Fig. 2), as well as Th versus Yb and Th/Yb ratio versus Hf, Y, and P (Fig. DR3; see footnote 1), show more distinct fields for zircons crystallized in ocean gabbros, continental granitoids, and kimberlites. The absolute concentrations of U, Th, and Yb may show large variations (to an order of magnitude) in an individual zircon and suites of zircon from the same rock; however, covariation of these elements is generally observed (Fig. 2A). Average U/Yb ratios for zircons from different settings are disparate, and increase from ocean gabbros (0.18) to continental granitoids (1.07) and kimberlites (2.1). The variation in ratios reflects the variation in average whole-rock U/Yb ratios for mid-ocean ridge basalt (MORB) lavas (0.01–0.1; Klein, 2003), bulk continental crust (0.7; Rudnick and Gao, 2003), and kimberlites (~4–6; Farmer, 2003).

Zircons from the Talkeetna arc are distinct from ocean crust zircons, and largely overlap the continental granitoid field (Fig. 2). However, some ocean island arc lavas exhibit significant overlap in whole-rock composition with MORB (Fig. 3). Thus we hypothesize that ocean island arcs could crystallize zircon that would plot in the ocean crust zircon field. We anticipate that zircon from other magmas with U/Yb ratios similar to MORB, such as continental flood basalts or ocean island basalts, might also overlap the field defined by ocean crust zircon. Additional analytical data for zircon from these environments are needed to evaluate these possibilities.

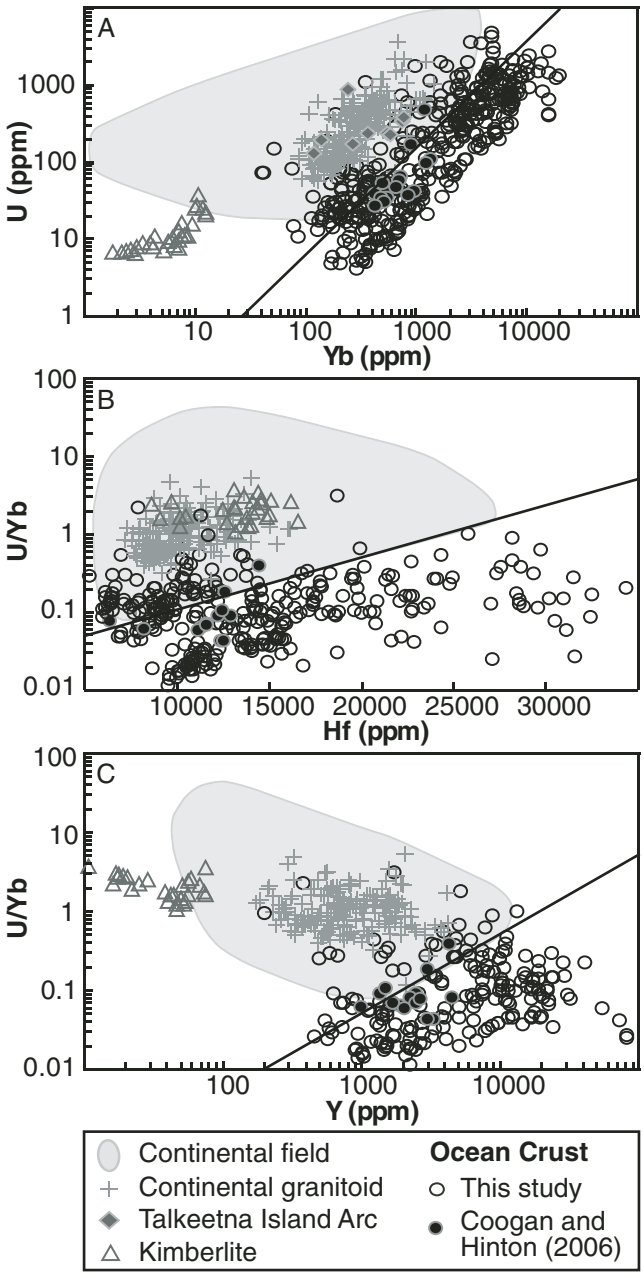

Figure 2. Geochemical discriminant diagrams for zircon. Plots include data reported here for ocean crust zircon (A, B: n = 388; C: n = 252) and Talkeetna (n = 9), and for zircon reported in literature from granitoid intrusions (n = 251) from northern Chile (Ballard et al., 2002) and eastern Australia (Belousova et al., 2006), kimberlites (n = 28; Belousova et al., 1998), and oceanic crust (n = 15; Coogan and Hinton, 2006). Shaded field represents >1500 analyses of Phanerozoic and Archean continental zircon performed by the U.S Geological Survey-Stanford SHRIMP-RG facility, and includes Phanerozoic and Archean zircon. Lower boundary of continental field is highlighted by solid line on each diagram and indicates upper limit for zircons that are unambiguously ocean crustal in origin (further discussion in Data Repository; see footnote 1). End points for lines: U vs. Yb (25, 1), (20000, 10000); U/Yb vs. Hf (5000, 0.05), (35000, 5); U/Yb vs. Y (200, 0.01), (100000, 5).

DISCUSSION

The similarity in REE patterns for igneous zircon from diverse source rocks is largely explained by the compatibility of REEs in the zircon lattice. Contraction of the trivalent lanthanide REEs with increasing atomic number results in the heavier REEs having ionic radii (0.985 Å for $^{VIII}Yb^{3+}$) closer to that of $^{VIII}Zr^{4+}$ (0.84 Å), leading to preferential incorporation over the lighter REEs (ionic radius of $^{VIII}La^{3+}$ = 1.16 Å). The relative difference in compatibility results in heavy (H) REE-enriched, LREE-depleted patterns characteristic of igneous zircon (e.g., Hoskin and Ireland, 2000). Also, because Zr and Si are tetravalent, sub-

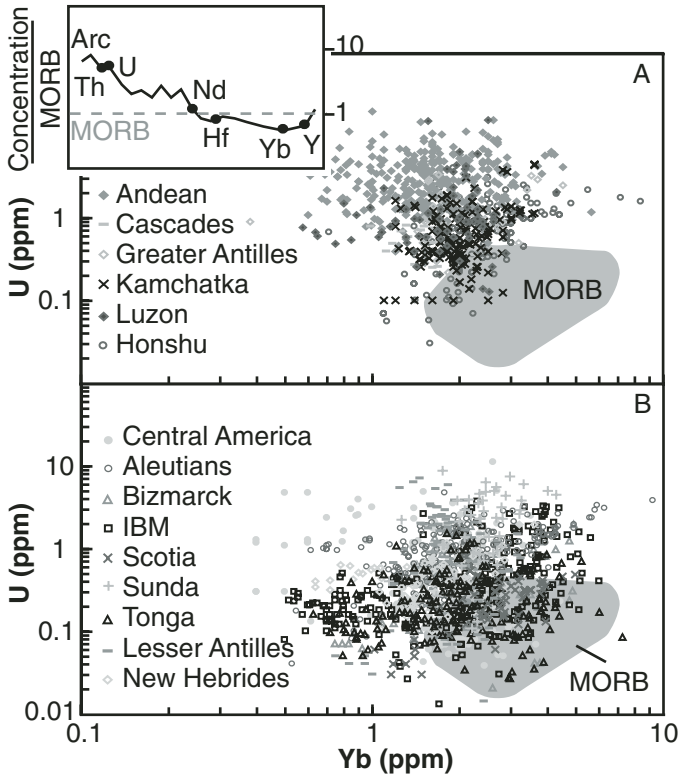

Figure 3. U and Yb compositions for mid-ocean ridge basalt (MORB) vs. (A) continental arc, and (B) island-arc magmas. MORB field defined by data compiled from Petrological Database of the Ocean Floor (www.petdb.org, October 2006). Arc data are from Kelemen et al. (2003). Inset: Schematic spider-diagram showing trace element concentrations of typical arc magma normalized to MORB (see text).

stitution of trivalent REEs into the Zr site results in a charge deficiency, and requires either an accompanying charge-compensating cation in the tetrahedral site (most commonly P^{5+}), or another substitution.

The tetravalent cations Hf, U, and Th are also common in zircon. These elements are incorporated by simple substitution for Zr (i.e., $Hf^{4+} = Zr^{4+}$; Hoskin and Schaltegger, 2003) and do not require additional substitutions for charge balance. Hafnium is highly compatible in zircon due to equivalent charge and similar ionic radius (0.83 Å) to $^{VIII}Zr^{4+}$ and often occurs at the weight percent level in zircon. The ^{VIII}Uranium and ^{VIII}Th are larger (1.0 and 1.04 Å, respectively), and therefore less compatible than Hf. Mineral/melt partition coefficients for U and Yb in zircon (254 and 278, respectively; Bea et al., 1994) indicate that they have nearly equivalent compatibility.

In contrast to their behavior in zircon, U and Yb exhibit disparate compatibility in magmatic systems, as illustrated in Figure 3 (inset). The U and Th concentrations are enriched in arc magmas (and the continental crust) relative to MORB, whereas HREEs (i.e., Yb) as well as Hf and Y can be slightly depleted in arc magmas. The affinity zircon has for U, Yb, and other HREEs permits these elements to be incorporated into zircon such that the U/Yb ratio of zircon will reflect that of the melt at the time of crystallization. Additional phases crystallizing with zircon (e.g., titanite, monazite, xenotime) likely compete for U and Yb, resulting in changing U/Yb ratios during zircon growth. As a result, the U/Yb and Th/Yb ratios can vary within an individual sample, although typically by much less than one order of magnitude. Despite this variation U/Yb ratios provide an effective method for determining zircon provenance, and when plotted against another HREE, Hf, Y, or P, allow discrimination of >80% of analyzed ocean crust zircons from the continental zircon field (Fig. 2). Because of overlap in composition between fields for zircon from different settings, we emphasize the need to evaluate data representative of a population, rather than an individual grain, in order to accurately assess provenance.

The observed enrichment of U, Th, and other large ion lithophile elements in arc magmas may result in part from the incorporation of subducted sediment, remelting of subducted ocean crust or lower arc crust, and slab-derived fluids that preferentially mobilize U, Th, and LREEs relative to HREEs (see Kelemen et al., 2003). Therefore, the geochemical signature of arc magmas and associated zircon reflects several processes of crust production, whereas MORB represents only melt generated by upwelling asthenospheric mantle.

IMPLICATIONS FOR DETRITAL ZIRCON STUDIES

The discriminant diagrams proposed here provide a robust method for distinguishing modern zircons crystallized in either continental or oceanic crust. The low U/Yb ratio characteristic of modern ocean crust zircons is inherited from depleted mantle-sourced host magmas, and is distinct from known continental zircons of all ages. Recent Nd and Hf isotope studies suggest that silicate differentiation and evolution of a depleted mantle reservoir could have occurred very soon (<150 m.y.) after the Earth was initially formed (e.g., Caro et al., 2003; Harrison et al., 2005). If a MORB-like reservoir existed during the Hadean, our discrimination diagrams provide a method for investigating the provenance of even the most ancient zircon grains.

Hadean detrital zircons recovered from Archean metasedimentary rocks exposed in the Narryer Gneiss terrane, as well as a 4.2 Ga zircon xenocryst from a 3.9 Ga granite in the Acasta Gneiss, plot predominately in the U/Yb versus Hf (and Y) field of more modern continental zircon; based on available data they are clearly distinct from the field of modern ocean crust zircon (Fig. 4). Oxygen isotope studies have shown that numerous Hadean detrital zircons exhibit $\delta^{18}O$ values elevated ($\delta^{18}O$ = 6.3‰–7.5‰; e.g., Peck et al., 2001; Cavosie et al., 2006) above values

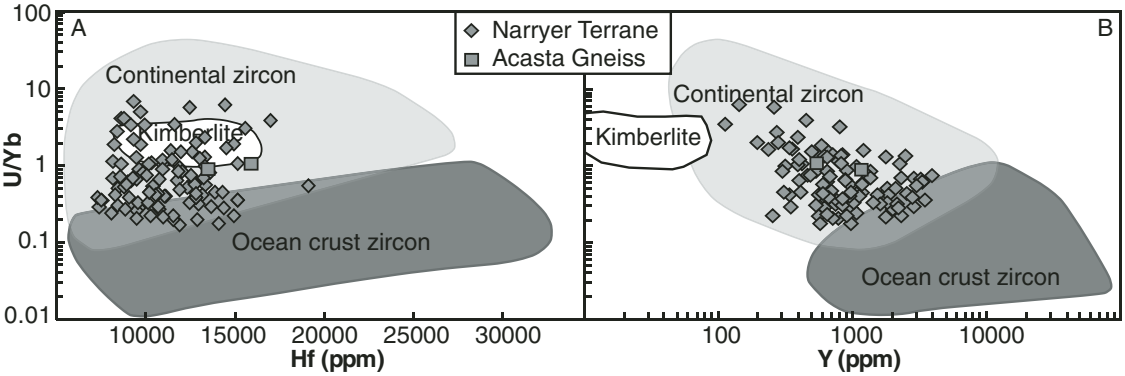

Figure 4. Discriminant diagrams with continental and ocean crust zircon fields defined using data points in Figure 2. Hadean detrital zircons (older than 3.9 Ga) from Narryer Gneiss terrane (n = 83; Maas et al., 1992; Crowley et al., 2005; Cavosie et al., 2006), and Acasta Gneiss (n = 2; Lizuka et al., 2006) are included. All U concentrations presented are present-day values. Initial U concentrations would be higher (~2× for Hadean zircons), thereby shifting original U/Yb ratio of older grains away from modern mid-ocean ridge basalt field, decreasing observed overlap.

for zircon in equilibrium with mantle (5.3‰ ± 0.3‰; e.g., Valley et al., 2005). These elevated values are interpreted to indicate a magmatic source that involved recycling of a protolith that had undergone low-temperature hydrothermal alteration (e.g., Valley et al., 2005), consistent with the onset of crustal growth, weathering, and recycling processes. Our results support interpretations that continental crust–forming processes were active by ~150 m.y. after the Earth's accretion, and show that currently analyzed Hadean detrital zircons are not consistent with crystallization from differentiated basalt derived from a depleted mantle reservoir like that of modern MORB.

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