Rare earth element chemistry of zircon and its use as a provenance indicator

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ABSTRACT

Sedimentary mineral assemblages commonly contain detrital zircon crystals as part of the heavy-mineral fraction. Age spectra determined by U-Pb isotopic analysis of single zircon crystals within a sample may directly image the age composition—but not the chemical composition—of the source region. Rare earth element (REE) abundances have been measured for zircons from a range of common crustal igneous rock types from different tectonic environments, as well as kimberlite, carbonatite, and high-grade metamorphic rocks, to assess the potential of using zircon REE characteristics to infer the rock types present in sediment source regions. Except for zircon with probable mantle affinities, zircon REE abundances and normalized patterns show little intersample and intrasample variation. To evaluate the actual variation in detrital zircon REE composition in a true sediment of mixed provenance, zircons from a sandstone sample from the Statfjord Formation (North Sea) were analyzed. Despite a provenance including high-grade metasediment and granitoids and a range in zircon age of 2.82 b.y., the zircon REEs exhibit a narrow abundance range with no systematic differences in pattern shape. These evidences show zircon REE patterns and abundances are generally not useful as indicators of provenance.

Keywords: provenance, rare earths, trace elements, zircon.

INTRODUCTION

Sediments and sedimentary rocks, in recording past erosion and deposition, provide a record of tectonic activity. Zircon is an often studied component of detrital assemblages because it may withstand mechanical and chemical breakdown over billions of years. Another important characteristic is that zircon crystallizes with an extremely high U/Pb ratio and retains the daughter products of U and Th radioactive decay so that the array and frequency of U-Th-Pb ages measured on detrital zircon populations yields information about the ages of crustal elements in the source region and the elastic pathway (Roback and Walker, 1995; Machado et al., 1996; Ireland et al., 1998; Sicombe, 1999).

A potentially powerful complement to the chronology and typology (Dabard et al., 1996) of detrital zircon would be the identification of source-rock lithology by using zircon trace element composition. The populations of zircon crystals within a sediment or sedimentary rock could then potentially be used to determine both the ages and rock types in the source region. This dual approach of assessing zircon isotope and trace element chemistry would have enormous potential in determining sediment provenance, and its applications to studies of, for example, uplift and erosion, tectonics, and magma genesis.

BACKGROUND PRINCIPLES AND CONSIDERATIONS

Any mineral phase will indicate its whole-rock source if (1) the mineral composition can be related to a melt composition by the appropriate use of mineral/melt partition coefficients ($K_d$ values); (2) the mineral preserves elemental ratios that are also retained in the whole rock; or (3) chemical features of a mineral can be distinguished and systematically related to the rock type of origin.

Successful application of $K_d$ values to igneous minerals for the purpose of provenance tracing relies upon knowing the $K_d$ values under a range of magmatic conditions, accurate measurement of the elemental abundances, and the validity of assumptions that (1) the mineral was saturated in the melt at the liquidus and (2) equilibrium mineral/melt partitioning was attained. Satura
tion calculations for zircon (Watson and Harrison, 1983) and modeling of co-genetic rock suites reveal that zircon is only likely to be a liquids phase in felsic melts and in some intermediate igneous compositions. Zircon found in mafic and many intermediate rocks probably grew in trapped melt pools, far from the liquidus. The assumption of equilibrium element trace partitioning between zircon and melt in most cases is probably invalid because surface enrichment and growth entrapment (i.e., disequilibrium partitioning) of the rare earth elements (REEs, including Y) and other elements is inevitable (Watson, 1996). Moreover, recent experimental studies reveal that REE partitioning into zircon is not a simple function of REE$^{3+}$ ionic radii, but is greatly affected by structural strain by the REE as well as charge-balancing elements at both the Zr and Si lattice sites (Hanchar et al., 2000; Finch et al., 2000).

Using a different approach (that of 3 in the previous list), Heaman et al. (1990) showed that the trace element abundances of zircon from different rock types may cluster into discrete groupings on Harker-style discrimination plots. However, for the five rock groupings of Heaman et al. (1990) there is no clear discrimination on the basis of Lu, Sc, Th/U, or Lu/Sm alone, and only partial discrimination based on reported Hf abundances. Other previous and subsequently published zircon trace element analyses do not conform to the chemical discriminants of Heaman et al. (1990) (e.g., Muraili et al., 1983; Hinton and Upton, 1991; Ireland and Wlotzka, 1992; Barbe
ey et al., 1995; Belousova et al., 1998; Hoskin, 1998). Heaman et al. (1990) conceded that if zircon is to become widely used as a tracer, studies must be made of changes in zircon composition as a function of changes in lithology and degree of fractional crystallization.

Here we present microprobe SIMS (secondary ion mass spectrometry) and laser ablation ICP-MS (inductively coupled plasma/mass spectrometry) analyses of well-characterized zircon populations to assess the efficacy of zircon REE abundances and patterns as a provenance indicator. Raw data were normalized against NIST SRM 610. Reproducibility of elemental abundances was monitored by analysis of Mud Tank carbonatite and Boggy Plain zoned pluton zircon by both analytical techniques. Full analytical details are given elsewhere. The results are tested by combined in situ U-Pb and REE analysis of single detrital zircons from a petroleum-well sandstone sample from the Brent Field, northern North Sea.

RESULTS

To assess changes to the REE abundances and patterns of zircon that crystallized within a magma undergoing fractional crystallization, zircon populations from six whole-rock samples

3GSA Data Repository item 200068, Table 1, 1, Analysis techniques and data (ppm) for analyzed zircon in Figure 1, is available on request from Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, editing@geosociety.org, or at www.geosociety.org/pubs/ft2000.htm.

Data Repository item 200068 contains additional material related to this article.

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from the Boggy Plain zoned pluton, Australia, were analyzed. The pluton is concentrically zoned with olivine-bearing diorite on the margin, ranging through granodiorite, adamellite, to aplite, and the abundance range measured for a single population completely or significantly overlaps the range for all other populations. This result is illustrated in Figure 1A, in which chondrite-normalized REE patterns for zircon from the diorite and aplite zones are plotted; sets of zircon REE patterns from four samples from the granodiorite and adamellite zones fall within the same abundance range and are omitted for clarity.

Accessory-mineral assemblages in mafic igneous rocks may include zircon. A 2 kg sample of the Blind Gabbro, Australia, yielded in excess of 1000, 50–250-μm-long subhedral zircon crystals. The zircon REE pattern (Fig. 1B) has a shape similar to that for zircon from the Boggy Plain zoned pluton, but abundance levels of the light REEs (La–Nd) and middle REEs (Sm–Tb) are slightly higher. In contrast to Blind Gabbro, which may have formed above a subduction zone (Miller and Gray, 1996), the mafic igneous charnockite of Ufs Island, East Antarctica, represents an orogenic magma that probably formed by melting of thickened crust (Young and Black, 1991). Zircons in this rock exhibit REE patterns that parallel the range defined by Blind Gabbro zircon (Fig. 1B), but have lower abundances that largely overlap with zircon from the Boggy Plain zoned pluton.

The heavy REE (Dy–Lu) patterns of zircon from Blind Gabbro and Mawson igneous charnockite have a slight concave-down curvature. This is exhibited also for igneous zircon from a metamorphosed gabbroic ophiolite (Fig. 1C) on the island of Syros, Greece (Baldwin, 1996). There is considerable overlap of REE abundances for zircon from the ophiolite sample with zircon from an ophiolitic plagiogranite sample (from Manilla, Australia; Aitchison and Ireland, 1995), which does not have heavy REE curvature, suggesting that curvature in zircon heavy REE patterns from mafic rocks (Figs. 1B and 1C) may be due to heavy REE depletion of melt by crystallization of phases such as clinopyroxene and orthopyroxene. Plagiogranite zircons in this study have small Eu anomalies (Eu/Eu* averages 0.90).

Samples from kimberlite and carbonatite are included in this survey (Fig. 1D), although detritus from such rocks will be minor constituents in most sediments, and most probably absent. Large zircon crystals (to 1 cm) from kimberlites at Jwaneng, Botswana, are heavy REE enriched but much less so than for other igneous zircons (Figs. 1A–1C). The heavy REE pattern is approximately flat ([Yb/Gd]N = 0.8–1.4). These REE characteristics are observed for other African kimberlitic zircons (Belousova et al., 1998), and the near-flat heavy REE patterns are characteristic of zircon from the mantle-derived MARID (mica- amphibole-rutile-ilmenite-diopside) suite ([Yb/Gd]N = 1.3–3.7; Hoskin, 1998). Zircon from the Mud Tank carbonatite complex, Australia, occurs as megacrysts, sometimes >30 cm long. Fragments of a centimeter-sized zircon crystal were analyzed by Hanchar and Hoskin (1998) and have an REE pattern similar to that of Jwaneng kimberlite zircon, although the heavy REE pattern is steeper ([Yb/Gd]N = 7.2–9.7; Fig. 1D). Neither zircon from the Jwaneng kimberlite or the Mud Tank carbonatite have significant Eu anomalies (Eu/Eu* > 0.59). Although the Mud Tank carbonatite was emplaced at mid-crustal levels, the zircon REE pattern may indicate mantle affinities or reflect crystal growth under extremely high water and fluorine fugacities (Currie et al., 1992).

We separated 10 small (~30 μm), anhedral zircon crystals from a slab of carbonatite from the central carbonatite-bearing area of the Phalaborwa Complex, South Africa. The zircons contain numerous opaque inclusions, and only one good analysis was obtained (Fig. 1D). The REE characteristics of this zircon resemble REE patterns from silicic whole-rock samples and contrast with zircon REE patterns from the Mud Tank carbonatite. It is possible that the Phal-
aborwa zircons formed in silica-rich selvedges within the carbonatite magma or were derived from silicate magma that is believed to have mixed with the carbonatite (Eriksson, 1989). Zircon can form by a variety of different processes in rocks undergoing metamorphism, for example, by net-transfer reactions, or solid-state recrystallization, or in low-volume anatectic melts. Schaltegger et al. (1999) documented zircon grown in the presence of aqueous fluids and anatetic melts in high-grade metamorphic rocks from the Vosges Mountains, eastern France. Despite some variation in zircon REE patterns for different rock samples, they found that zircon formed by these different processes has near-identical REE abundances and patterns (Schaltegger et al., 1999, their Fig. 7). The typical REE pattern and range measured by these workers are shown in Figure 1E. Superimposed are REE patterns measured for metamorphic zircon SL1 from the gem gravels of Sri Lanka and metamorphic zircon from granulites of the Georgetown region, north Queensland, Australia. The north Queensland zircons are characterized by nearly flat light REE patterns (Sm/LaN = 1.3–8.2) and atypical steepness from Gd to Er ([Er/Gd]N = 11–34) relative to other zircon REE patterns. These characteristics are related to the process of formation by solid-state recrystallization of protolith zircon. Partial solid-state recrystallization has been shown to produce flatter light REE patterns and steep heavy REE patterns, and to leave a “memory” of the preexisting chemistry and zoning of the protolith zircons (Hoskin and Black, 2000). The REE patterns of metamorphic zircon from Sri Lanka and France overlap in pattern shape and abundance range and are generally indistinguishable from zircon from silicic crustal igneous rocks (Figs. 1A–1C).

To evaluate the actual variation in detrital zircon REE composition in a real sediment, zircons from a sandstone from the North Sea were analyzed. The sandstone is from the Statfjord Formation (Zone A) and was sampled at 3011 m downhole in Brent Field well 211/29-6 located on the seafloor between Scotland and Norway. Evidence from Sm-Nd isotopes, paleo-current data, heavy-mineral assemblages, detrital-garnet composition, and detrital-zircon U-Pb isotope spectra indicate that the source region of this sample comprised high-grade metasediment and Caledonian granites (Morton, 1992; Dulland et al., 1995; Morton and Berge, 1995; Morton et al., 1996). The REE abundances for concordant detrital zircon from each of the three main age groups identified by Morton et al. (1996) were analyzed (Fig. 1F). Despite different crustal elements in the source region and an age range of 2.82 b.y., for the zircons we analyzed, there are no systematic differences for zircon REE chemistry within or between the age groupings. This result cannot be attributed to a chemically homogenous source region or derivation of detritus from a single source, but confirms the apparent monotonous REE patterns and abundances in zircon derived from a range of common crustal rock types (Figs. 1A–1C and 1E).

Other trace elements were also measured for zircons in Figure 1. The Zr/Hf ratio is highest for zircon from Jwaneng kimberlite (Zr/Hf = 75–168) and Phalaborwa carbonatite (Zr/Hf = 253). All other zircon populations have Zr/Hf values that range across and near the chondritic value of 37. Apart from high Zr/Hf values in kimberlite and carbonatite, there are no systematic differences between other zircon populations according to source-rock composition. Phosphorus values range considerably; the lowest abundances were measured for zircon from Mawson igneous charnockite (31–77 ppm), Manilla plagiozinite (24–59 ppm), and Mud Tank carbonatite (55–61 ppm). These values are well within the 20–110 ppm range that Belousova et al. (1998) considered to be distinctive for kimberlitic zircons.

Geochronologists have recognized for some time that there is variation in the zircon Th/U elemental ratio, and have used this as a first-order discriminant between igneous and metamorphic zircon (e.g., Ahrens et al., 1967; Williams et al., 1996). Metamorphic zircons in this study (Fig. 1E) have Th/U ratios of 0.01–0.08, whereas zircons of igneous origin (Figs. 1A–1D) range from 0.16 to 2.37. Values greater than Th/U = 1 are uncommon for most igneous zircons; typical values are within the range 0.4–1.0. Due to order of magnitude range in Th/U ratio often found in single zircon populations, we consider the Th/U ratio to be of limited use as a discriminant.

CONTROLS ON ZIRCON REE CHARACTERISTICS

Although recognizing minor differences between some zircon populations, we have demonstrated that the REE chemistry of zircon from a wide range of crustal rock types and tectonic settings exhibit remarkable similarity. From a North Sea sediment sample of known provenance, we have shown that zircon REE patterns and abundances are not generally useful as indicators of provenance.

A similar conclusion was reached by Maas et al. (1992) in their attempt to determine the provenance of Earth’s oldest-known zircons, and by Sawka (1988), who documented zircon REE uniformity across the McMurray Meadows pluton of the Sierra Nevada, United States. There are at least two possible explanations for the apparent monotonous zircon REE characteristics. First, the composition of most silicate melts at the point of zircon saturation can be considered as broadly “granitic.” This is true even for trapped intercumulus melt in mafic granitoids, which will evolve toward a granitic composition and perhaps zircon saturation by in situ fractionation. It may be that the REE chemistries of these granitic melts are sufficiently similar to impart REE characteristics to crystallizing zircon that are not significantly different from zircons from a sample with different whole-rock chemistries. However, this is unlikely because the REE chemistry of granitic melts differs depending upon a range of factors, including ambient intensity parameters and crystallization history.

A second explanation for the similarity of zircon REE abundances may relate to lattice strain and charge-balance requirements for REE substitution into the zircon lattice. Incorporation of REEs into the zircon structure is thought to be dominated by the xenotime coupled substitution mechanism (Speer, 1982): (Y + REE)3+ + P5+ = Zr4+ + Si4+. Although this mechanism has been shown to have strain-related limits (Hancher et al., 2000; Finch et al., 2000). A limit on the amount of light REE3+ substitution for Zr4+ is due to strain at the Si site and may partly explain (in addition to ionic radii) why La–Nd abundances for all zircons in Figure 1 typically range between 10–1 and 10–2 times chondrite abundance despite many having grown in melt with strong light REE enrichment (e.g., Jwaneng kimberlite and Mud Tank carbonatite). The heavy REEs have smaller ionic radii that more closely match that of Zr4+; incorporation of these elements in zircon is potentially limited by strain at the Si site by incorporation of charge compensating P5+. This limit is not reached for most zircon populations in Figure 1 because the mole percent (mol%) of REE exceeds that of P (the xenotime substitution mechanism requires the mol% ratio of REE to P to be unity). This observation suggests that other substitution mechanisms are operating to charge balance the REE, probably in addition to the xenotime mechanism. For zircon from the Boggy Plain zoned pluton, xenotime-type mechanisms involving minor abundances of interstitial cations are believed to provide charge balance for REE in excess of P (Hoskin et al., 2000). Other mechanisms may involve coupled substitution of Nb, Ta, and the REEs at the Zr site, although abundances of Nb and Ta in zircon are typically very low (<10 ppm).

It is possible that heavy REE abundances for most zircon populations in Figure 1 are retarded by the lack of sufficient P5+ substitution into the mineral lattice, but that further heavy REE substitution is possible by other mechanisms, yet these also are limited by lattice strain. The combined effect of these restricted substitution mechanisms for REE incorporation in zircon is the imposition of REE characteristics that are similar for populations derived from different whole-rock sources.

CONCLUSIONS

Results from this study demonstrate that the REE chemistry of zircons from a wide range of crustal rock types and tectonic settings exhibit remarkable similarity, and therefore zircon chemistry is not generally useful as an indicator of sedi-
ment or inherited zircon provenance. An exception to this conclusion is zircon with mantle affinities (kimberlite, MARID suite, and perhaps the Mud Tank carbonatite), which have REE-P mol% ratios of 1:1, lower REE abundances, and flatter normalized patterns compared to crustal zircon populations. However, in addition to age data, important provenance information might be obtained by investigation of the occurrence and chemistry of inclusions hosted by detrital zircon.

REFERENCES CITED


