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Experimental zircon/melt and zircon/garnet trace element partitioning and implications for the geochronology of crustal rocks

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Abstract

Garnet is the most commonly used mineral in thermobarometry, whereas zircon is the most robust chronometer to date high-grade metamorphic rocks. To provide a basis for correlation of zircon and garnet growth, we determined experimentally the trace element partitioning between zircon, a hydrous granitic melt and garnet at 20 kbar and 800–1000 °C for P, Y, rare earth elements (REE), Zr, Hf, Th and U. In respect to melt, zircon preferentially incorporates all investigated elements apart from REE with atomic number lower than Sm. At this pressure and in the chosen composition, the distribution coefficient between zircon and melt ($D^{Zrn/Melt}$) for REE increases with increasing atomic number of the REE and with decreasing temperature. $D^{Zrn/Melt}_{Yb}$ is ~20 at 1000 °C, but more than an order of magnitude higher at 800 °C. The solubility of Zr in hydrous granitic melts buffered by zircon is about a factor of two lower at 20 kbar than what has been previously established for mid-crustal pressures. Large garnet produced in the experiments allowed determination of garnet/melt trace element partitioning ($D^{Grt/Melt}$) at temperatures of 800–1000 °C, conditions relevant for partial melting of crustal rocks. There is a systematic increase in $D^{Grt/Melt}_{REE}$ with decreasing temperature. Zircon contains significantly more heavy-REE than garnet at temperatures of 800–850 °C. Zircon/garnet partition coefficients of heavy-REE decrease with increasing temperature from $D^{Zrn/Melt}_{Lu}$ of 12 at 800 °C to 1.4 at 1000 °C. Middle-REE partitioning is close to unity for the whole investigated temperature range. Different empirically determined zircon/garnet partition coefficients from granulites and ultra-high temperature granulites can potentially be explained by the experimentally determined change of partitioning as a function of temperature. These data can assist in establishing equilibrium between garnet and zircon zones in natural rocks, and in the construction of detailed pressure–temperature–time paths in high-grade metamorphic rocks.

Keywords: Zircon; Garnet; Trace element partitioning; Experimental petrology; U–Pb geochronology

1. Introduction

Garnet and zircon are key minerals for the understanding of high-grade metamorphic processes and their chronology. Garnet is an indicator mineral of high-temperature and/or high-pressure metamorphism and is the main mineral used in thermobarometry. It is a common restitic phase during partial melting of crustal rocks and is an important sink for trace elements such as Y and the heavy rare earth elements (HREE) (e.g. Hickmott et al., 1987; Bea et al., 1994; Hermann, 2002; Otamendi et al., 2002; Rubatto and Hermann, 2003). HREE depletion of partial crustal melts is commonly used as evidence of restitic garnet in the source region (Otamendi and Patiño Douce, 2001). In contrast, zircon is one of the main accessory phases in crustal rocks.

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Because zircon contains significant amounts of Y, Zr, Hf, P, U, Th and middle-REE to heavy-REEs (e.g. Hinton and Upton, 1991), it is relevant for U–Pb geochronology and for trace element budgets during high-grade metamorphism and anatexis (Watson and Harrison, 1983; Bea et al., 1994; Hoskin et al., 2000; Linnen and Keppler, 2002; Hoskin and Schaltegger, 2003; Rubatto and Hermann, 2003).

In order to fully exploit the wealth of information from high-grade metamorphic rocks, it is therefore critical to correlate the growth of zircon with garnet growth. This would allow the age of accessory zircon to be related to metamorphic conditions and hence to construct robust temperature–pressure–time path for high-grade metamorphic rocks. Additionally, such a correlation would allow the monitoring of crustal anatexis using a major and an accessory phase. It is very difficult to relate zircon to garnet growth on the basis of textural relationships because of the extreme difference in size. However, there is mounting evidence that this correlation is possible on the basis of trace element compositions. Garnet and zircon both show strong HREE enrichment with respect to chondrite values and display highly variable REE patterns. On the basis of the trace element composition of garnet and zircon found in partially molten rocks, a number of studies have determined empirical partitioning (Rubatto, 2002; Hermann and Rubatto, 2003; Whitehouse and Platt, 2003; Hokada and Harley, 2004; Kelly and Harley, 2005; Buick et al., 2006; Rubatto et al., 2006). The results obtained from different studies are in apparent disagreement, particularly for the HREE. A first group of studies (Rubatto, 2002; Hermann and Rubatto, 2003; Rubatto and Hermann, 2003; Buick et al., 2006; Rubatto et al., 2006) focused on granulite-facies rocks that underwent partial melting and new zircon growth at temperatures around 800 °C and variable pressures (4–9 kbar). These studies agree in calculating zircon garnet partitioning for the HREE above unity, between 0.7–2.3 for Gd and increasing gradually to 6.3–24 for Lu. A similar trend with partitioning increasingly in favour of zircon across the HREE has been documented in eclogite-facies rocks that never reached melting ($T \sim 600$ °C and $P \sim 20$ kbar) and where metamorphic zircon likely formed by the interaction with fluids (Rubatto, 2002; Rubatto and Hermann, 2003). A second group of studies (Hokada and Harley, 2004; Kelly and Harley, 2005) dealt with zircon and garnet in Antarctic rocks that underwent ultra-high temperatures (UHT) up to 1100 °C at ~7 kbar. These studies concluded that the zircon/garnet partitioning is equally close to unity across the HREE, between 1.3 and 0.6 for elements from Gd to Lu. The work of Whitehouse and Platt (2003) investigated granulite facies rocks (750–800 °C and 8.5–9 kbar), and obtained zircon/garnet partitioning for the HREE close to unity.

In order to address the apparent disagreement of empirical data and to provide a basis for further correlation between zircon and garnet, we performed a series of piston-cylinder experiments at temperature conditions relevant for natural samples (temperature, T, between 800 and 1000 °C and pressure, P, of 20 kbar). The distribution of trace elements (P, Y, Zr, REE, Hf, Th and U) between garnet, zircon and a hydrous granitic melt were determined for a synthetic NKCFMASH system. A comprehensive set of garnet/melt, zircon/melt and zircon/garnet distribution coefficients was determined experimentally for the first time. The results permit an evaluation of the empirical data and explain some of the variations observed in nature.

2. Experimental and analytical techniques

2.1. Starting material

Different mechanisms have been proposed for the incorporation of REE in zircon, mainly involving P and H (e.g. Speer, 1982; Hinton et al., 2003; Hoskin and Schaltegger, 2003 and references therein; Spandler et al., 2004). Considering these constraints, we aimed at a starting material that contains water and moderate amounts of phosphorous. We avoided saturation of a phosphate phase because such a trace element-rich accessory phase would have interfered in the measurements of trace elements in the phases of interest. Because the melt composition is likely to play a role in partitioning, we have chosen a starting material with a granitic composition, so that the obtained results are relevant for crustal anatexis and granite formation. We have chosen a relatively high water content in the melt in order to suppress crystallization of phases other than garnet and zircon at the relatively low temperatures of the experiments.

In order to obtain a starting material homogeneous in Zr and trace elements, we produced first a zirconium- and phosphorus-free gel with the major elements Si, K, Na and all the other trace elements. About 2 wt.% ZrO_2 and 0.5 wt.% apatite was added and the mix was ground and melted to a glass at 1400 °C. Inspection by optical microscopy, secondary-electron microscope (SEM) imaging and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) revealed that the glass was homogenous. Aluminium was then added to the ground glass as $Al(OH)_3$, in order to have an