



Hydrogen incorporation and charge balance in natural zircon

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Abstract

The water and trace element contents of natural igneous zircons were determined to constrain the mechanism of hydrogen incorporation. The low radiation-damage zircons were derived from Fe–Ti oxide gabbros from the Vema Fracture Zone (11°N, Mid-Atlantic Ridge). They contain up to 1212 ppmw H₂O, 1.9 wt.% Y₂O₃ and 0.6 wt.% P₂O₅ and are generally strongly zoned. REE + Y are partially charge-balanced by P (Y, REE³⁺ + P⁵⁺ = Zr⁴⁺ + Si⁴⁺), but a large REE excess is present. On an atomic basis, this excess is closely approximated by the amount of H present in the zircons. We therefore conclude that H is incorporated by a charge-balance mechanism (H⁺ + REE³⁺ = Zr⁴⁺). This interpretation is consistent with FTIR data of the Vema zircons, which shows a strongly polarised main absorption band at ca. 3100 cm⁻¹, similar to experimentally grown Lu-doped hydrous zircon. The size of this 3100 cm⁻¹ band scales with H and REE contents. Apart from a small overlapping band at 3200 cm⁻¹, no other absorption bands are visible, indicating that a hydrogrossular-type exchange mechanism does not appear to be operating in these zircons. Because of charge-balanced uptake of H, P and REE in zircon, the partitioning of these elements into zircon is dependent on each of their concentrations. For instance, $D_{\text{zrc/melt}}^{\text{REE}}$ increases with increasing H and P contents of the melt, whereas $D_{\text{zrc/melt}}^{\text{H}}$ increases with increasing REE content but decreases with increasing P content. In addition, H–P–REE systematics of sector zoning indicate kinetic effects may play an important role. Hence, using H in zircon to determine the water content of melts is problematic, and REE partitioning studies need to take into account P and H₂O contents of the melt.

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1. INTRODUCTION

The amount of water in nominally anhydrous minerals (NAMs, minerals without water in their structural formulae) has received great interest, as NAMs may hold most of the Earth's water budget, their water content has significant effect on mineral and rock properties such as mechanical strength and electrical conductivity, and play a role in global

geodynamics, such as the location of mantle discontinuities and depth of mantle melting (Smyth, 1987; Jacobsen, 2006; Kohlstedt, 2006; Ohtani and Litasov, 2006; Regenauer-Lieb, 2006). In igneous rocks, the water content of NAMs may be used to reconstruct magma water contents (e.g., Kohn and Grant, 2006). The mechanism by which water (or hydroxyl) is incorporated in minerals is essential for understanding and evaluating these processes. Water uptake is often related to vacancy substitution, i.e., crystal defects (Smyth, 2006), but incorporation of other trace elements can play an essential role (e.g., Berry et al., 2005).

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Zircon is a common accessory mineral and one of the most versatile geological tools, with applications ranging from U–Pb dating of igneous, metamorphic rocks and sediments, trace element contents to determine rock paragenesis and evolution, whereas oxygen, hafnium and lithium isotope studies can provide information about the genetic environment of ancient rocks (e.g., [Wilde et al., 2001](#); [Cavosie et al., 2005, 2011](#); [Trail et al., 2007](#); [Harrison et al., 2008](#); [Ushikubo et al., 2008](#)). In addition, trace elements such as REE can be used to determine the oxidation state of magmas, whereas Ti-thermometry may provide information about zircon crystallisation temperature ([Ferry and Watson, 2007](#); [Trail et al., 2007, 2012](#); [Grimes et al., 2009](#); [Burnham and Berry, 2012](#)).

In contrast, the water content of zircon has received relatively little attention, perhaps due to the low abundance of zircon and, as a result, its limited effect on water budgets of Earth's reservoirs, as well as the likelihood of the presence secondary H due to radiation damage of zircons. The limited data so far suggests low water contents of <0.01 wt.% in most natural zircons ([Woodhead et al., 1991b](#); [Bell et al., 2004](#)). Larger amounts of water (up to 16.6%; [Fronzel, 1953](#); [Coleman and Erd, 1961](#)) can be present in metamict zircon, but this is a result of a secondary process related to destruction of the crystal structure by radiation damage due to the presence of radioactive elements such as U and Th ([Aines and Rossman, 1986](#); [Woodhead et al., 1991b](#); [Nasdala et al., 2001](#)). Trace elements may play a dominant role in the uptake of water in zircon, as charge imbalance in zircon (REE exceeding P) is common ([Speer, 1980](#)) and incorporation of Al, Fe, Mg and Li has been proposed to provide charge balance ([Hanchar et al., 2001](#); [Hoskin and Schaltegger, 2003](#)). However, charge balance could also be attained by the presence of hydrogen (e.g., [Woodhead et al., 1991b](#); [Hinton et al., 2003](#); [Trail et al., 2011](#)), but no study exploring this relation for natural zircon yet exists.

Here we present a detailed study of water and trace element contents of natural, non-metamict zircons to constrain the mechanism of water incorporation into zircon, to determine whether water plays a role in maintaining charge balance, and to investigate if water contents of igneous zircons may be used to reconstruct the water content of host magmas.

1.1. Sample suite

Zircons were separated from Fe–Ti oxide gabbros from oceanic crust exposed at the Vema Lithospheric Section (VLS) at 11°N on the Mid-Atlantic Ridge ([Auzende et al., 1988](#); [Brunelli et al., 2006](#); [Lissenberg et al., 2009](#)). This suite of zircons is ideally suited for this study as they are primary magmatic zircons from a well-constrained magma source, have young ages (ca. 14 Ma) and have therefore suffered negligible radiation damage $D\alpha < 10^{18}$ α decay events/g ([Murakami et al., 1991](#)), and show a range of trace element zoning features, such as normal, oscillatory and sector zoning ([Lissenberg et al., 2009](#)).

The VLS is exposed along the southern wall of the transverse ridge of the Vema Fracture Zone, which rises from 5100 to 450 m below sea level. It exposes a full section of

mantle peridotites, lower crustal gabbros and basaltic upper crust formed along the Mid-Atlantic Ridge ([Auzende et al., 1988, 1989](#); [Bonatti et al., 2003, 2005](#)). The studied samples were collected by submersible craft and by dredging along a section of the VLS centred around 42°30'W and ca. 4–5000 m depth ([Table 1](#)). The gabbros commonly contain Fe–Ti oxides, indicating extensive differentiation.

Here we present data from nine zircon grains and grain fragments from four samples ([Table 1](#)). This is a subset of a larger study ([Lissenberg et al., 2009](#); in preparation). Zircons range in size from 75 to 500 μm and generally show a subhedral to euhedral prismatic habit. Many show complex zoning patterns, but do not have xenocrystic cores and appear to have a continuous magmatic growth history. Some zircons show signs of resorption and later overgrowth ([Figs. 1 and 2](#)). These features are discussed in more detail in [Section 3.1](#).

2. ANALYTICAL TECHNIQUES

2.1. Imaging and chemical maps (EPMA)

X-ray distribution maps were acquired with the JEOL JXA-8500F field-emission electron probe micro-analyzer at the University of Hawaii, using the following analytical conditions: 15 keV accelerating potential, 100 nA probe current and focused beam, 50 ms dwell time per pixel, a step size of 0.5–1.5 μm using a stage with linear encoders, and a resolution of individual maps of 250–550 pixels in X by 350–1000 pixels in Y. The Y-L α distribution maps shown in [Figs. 1 and 2](#) are based on combining the counts collected simultaneously on three or four spectrometers (1 PETH crystal with a Xe-sealed detector, 1 PETH crystal with gasflow detector, 1–2 PETJ with gasflow detector).

2.2. Trace elements (SIMS)

Trace elements were measured by ion microprobe (Secondary Ion Mass Spectrometry, SIMS) using a Cameca 4f monocollector instrument at the Edinburgh Ion Microprobe Facility. A beam of $^{16}\text{O}^-$ was accelerated to 14.5 kV and impacted onto gold-coated samples. Two beam currents were used depending on the size of the area to be analysed: a 10 nA beam resulting in a sputtered area of ca. 20 μm diameter and a 2.5 nA beam resulting in a sputtered area of ca. 10 μm . High energy (120 ± 20 eV) secondary ions were extracted and accelerated into the mass spectrometer and counted using an electron multiplier. The instrument was operated in low mass resolution mode.

The following isotopes were measured: ^{30}Si , ^{31}P , ^{40}Ca , ^{49}Ti , ^{89}Y , ^{138}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{149}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{161}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{171}Yb , ^{175}Lu , ^{178}Hf , ^{232}Th , ^{238}U . In addition mass 130.5 was measured to determine the electron multiplier background signal and mass 134 ($^{90}\text{Zr}^{28}\text{Si}^{16}\text{O}$) to allow correction of the ZrSiO interferences on Ba, La, Ce and Pr. Each analysis consisted of six cycles (sweeps through the mass spectrum). Counting times ranged from 2 s for major elements to 20 s for the lowest abundance isotopes (^{149}Sm , ^{151}Eu) for a total analysis time of 948 s (excluding waiting times while cycling the magnet).

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