Ti Concentrations in Zircon from the Boggy Plain Zoned Pluton; Implications for Zircon Petrology and Hadean Tectonics

Ryan B. Ickert*†; Ian S. Williams
Research School of Earth Sciences, The Australian National University, Canberra ACT, 0200, Australia
*Ryan.Ickert@ualberta.net, www.ualberta.ca/~ickert
†Current address: Canadian Centre for Isotopic Microanalysis, Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton AB, T6G 2E3, Canada

Summary
The Ti-in-zircon thermometer is employed in the zoned, high temperature (>1000°C) Boggy Plain Pluton. Measurements were made on zircon in rocks ranging in bulk compositions from gabbro to aplite. Apparent crystallization temperatures range from about 820-750°C (corrected for non-unity TiO_2 activity). There is no correlation of Ti concentrations with rock type. The distributions of apparent crystallization temperatures are compared with a simple forward model. The model captures broad characteristics of the distributions, but has important differences. These differences may be the result of either sampling bias and/or a non-monotonic P-T-X history of the magma chamber during zircon crystallization. Titanium concentrations are generally higher than those in the Hadean zircon suite from the Jack Hills of Western Australia.

Introduction
Zircon has become the mineral of choice for a wide range of geochemical techniques, including U-Pb dating, Lu-Hf tracer studies, $\delta^{18}O$ measurements, and trace element studies. With the development of the Ti-in-zircon thermometer (Watson and Harrison, 2005), an opportunity was presented to put this geochemical and geochronological information contained in zircon into a thermal context. Despite the usefulness of a thermometer that can be linked to other geochemical and isotopic information in zircon, there is much to learn about its behaviour in natural systems. In particular, the use of the Ti-in-zircon thermometer to extract information from "out of context" zircon (particularly detrital zircon) requires a better knowledge of how Ti-systematics in igneous zircon are influenced by magma-chamber processes.

The interpretation of Ti concentrations in Hadean zircon from Early Archean metasediments at Jack Hills, Western Australia is controversial (Watson and Harrison, 2005; Nutman, 2006; Fu et al., 2008). Watson and Harrison (2005) have argued that the clustering of Ti concentrations near 6 ppm (corresponding to a temperature near 700°C for unity α-TiO_2 and α-SiO_2) are best interpreted as reflecting an origin in ``…wet, minimum melts under prograde conditions'' (Harrison and Schmitt, 2007) and should be used as evidence that a cycle of crustal weathering and cycling, presumably similar to that occurring at the present day, was occurring as early as 4.3 Ga. Nutman (2006) has argued that the apparent zircon crystallization temperatures could plausibly represent cooling of initially hotter magmas and that the recorded temperatures cannot distinguish between cooling of zircon undersaturated magmas and low-temperature, water saturated melting.

The Boggy Plain Zoned Pluton (BPZP) provides an excellent natural laboratory to further test the Ti-in-zircon thermometer. The pluton is concentrically and continuously zoned from a two-pyroxene (±olivine) gabbro through granodiorite to a granite with an aplitic core. The minimum initial magmatic temperature is constrained by independent thermometry to > 1000°C and all phases contain zircon.

Methods

Zircon was extracted using standard heavy liquid and magnetic techniques and mounted in the large epoxy mount described by Ickert et al. (2008), along with reference zircon and brought to a fine polish. All crystals were documented in transmitted and reflected light and by secondary electron microscopy-cathodoluminescence. Prior to trace element analysis, zircon were dated by U-Pb using the ANU SHRIMP II according to the methods described by Williams (1998). After U-Pb analysis, the epoxy mounts were re-polished to remove the ca. 2μm deep sputtering craters.

Ti concentrations were determined on the ANU SHRIMP II multicollector using the methods described by Hiess et al. (2008). A ca. 25μm diameter O_2^- primary beam was employed to generate $^{49}Ti^+$ and $^{28}Si^{16}O^+$ secondary ions, which were collected simultaneously using a Faraday cup ($^{28}Si^{16}O^+$) and a continuous dynode electron multiplier ($^{49}Ti^+$). The average $^{49}Ti^+/^{28}Si^{16}O^+$ of ten, 10 second periods of data collection were converted to Ti concentrations by referencing to zircon SL13 (6.3 ppm Ti). Uncertainties on all analyses are better than 10% and over half are better than 5% (2σ).

Ti and Si Activity

The relationship between the Ti concentration (in ppm) and crystallization temperature is given by $Temp(K) = B/\log(Ti_{ppm}) + \log(\alpha SiO_2) - \log(\alpha TiO_2) - A$ (where *Temp* is in degrees Kelvin; *B* and *A* are constants, Ti_{ppm} is the Ti concentration of zircon, and αSiO_2 and αTiO_2 are the activities of SiO_2 and TiO_2, respectively. Quartz is present, so the αSiO_2 is constrained to a value of unity. TiO_2 activity is constrained by ilmenite – quartz – rutile – ferrosilite equilibria in the orthopyroxene, ilmenite and quartz bearing gabbroic phase. Using measured orthopyroxene and ilmenite compositions, a αTiO_2 of 0.74 was determined which is within the typical range for igneous rocks.

Results

SHRIMP U-Pb analyses reveal that a small component of zircon from the granodiorite through granite phases of the pluton contain inherited zircon, ranging in age from ca. 430 Ma, through ca. 1.0 Ga. There is no inheritance detected in the gabbroic phase. The aplitic phase contained a large proportion of zircon grains (>50% of those analyzed) that appear to be xenocrysts from the older, S-type, granite that partly encloses the Boggy Plain Pluton. Combining the results from three analytical sessions and 110 analytical spots yields the best estimate of the crystallization age of zircon in the Boggy Plain Pluton of 416.8±2.0 Ma (^{207}Pb-corrected $^{206}Pb/^{238}U$ age, 2σ). There is no correlation of apparent age with pluton phase.

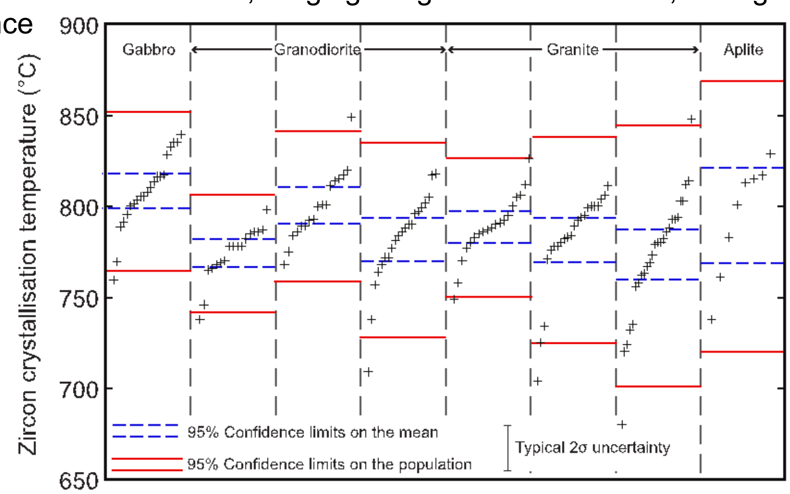

Figure 1: Results of Ti-in-zircon thermometry measurements. Each cross represents a single spot, and rocks are arranged from the outer, most mafic zone to the inner, most felsic zone.

Titanium concentrations mostly range from 8-15 ppm, corresponding to an apparent temperature range of 753-817°C (for an αTiO_2 = 0.74; Fig. 1). Apparent crystallization temperatures, for individual rocks, show scatter in excess of that which can be explained by analytical errors. In addition, there is no substantial change in apparent temperatures between different samples or phases of the pluton.

Discussion

Despite a wide range in bulk compositions and some variation in zircon morphology, zircon crystallization temperature distributions (ZCTDs) are very similar in each rock type (Fig. 2). If the residual melts that crystallized zircon mimic the rock bulk composition, the onset of zircon crystallization should differ by over 100°C. Instead, it is likely that the magmatic rocks are all related broadly to parental magmas of similar compositions and that compositional differences reflect the sorting of high temperature minerals (pyroxene, plagioclase) rather than fundamental differences in liquid composition.

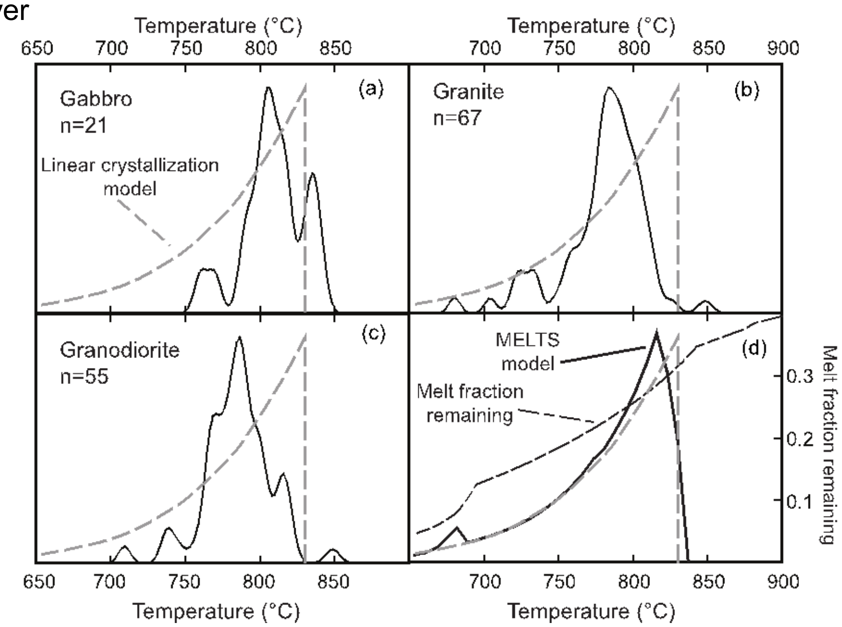

Figure 2: Results of Ti-in-zircon thermometry (a, b, c) compared to a model based on MELTS (d). The grey line labeled "linear crystallization model" in (a,b,c) is a smoothed version of the MELTS model in (d).

To test this hypothesis, zircon crystallization was simulated using MELTS (Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998) combined with the zircon saturation model of Watson and Harrison (1983). The results (Fig. 2) show that zircon crystallization does not occur until relatively late (at about a 30% melt fraction) in the cooling history of the Boggy Plain-type magma and that ZCTDs for a simple cooling and crystallizing system should have a characteristic "reverse exponential" shape to their distribution.

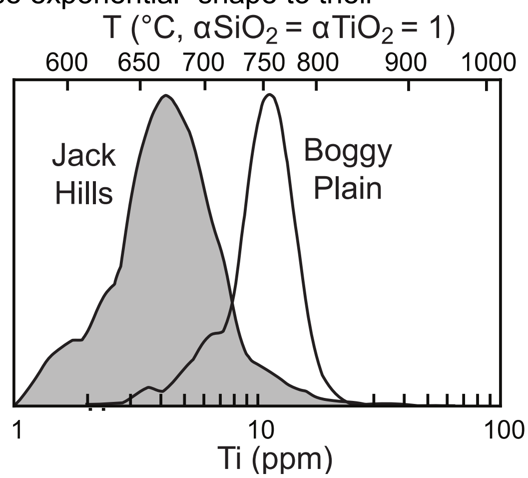

Figure 3: Ti concentrations in Boggy Plain zircon, compared to Ti concentrations in Jack Hills zircon (Harrison and Schmitt, 2007; Harrison et al., 2007; Trail et al., 2007; Fu et al., 2008).

Although the modeled distributions capture some of the broad characteristics of the true ZCTDs, such as the ranges of apparent zircon crystallization temperatures, the characteristic exponential shape is not apparent. Numerical experiments confirm that a low sampling density is not the cause. Multiple spots on single grains show that most zircon are zoned in Ti concentrations (most show an apparent cooling trend, as would be expected from growth during a cooling and crystallizing magma) therefore, sampling bias towards the mid-range Ti concentrations (as centres and edges of zircon are difficult to sample, and the finite probe size averages Ti-concentrations over a substantial portion of the grain) could, in part, be responsible. In addition, non-monotonic cooling or crystallization histories resulting from decompression of ascending magma, heating from new pulses of magma in the chamber, or even appearance of new minerals on the liquidus, can cause a ZCTD to depart from the exponential shape.

A comparison of the Ti concentrations in the Boggy Plain Pluton, an initially high temperature magma, with Hadean zircon from the Jack Hills of Western Australia (Fig. 3; Harrison and Schmitt, 2007; Harrison et al., 2007; Trail et al., 2007; Fu et al., 2008) shows that the distributions are distinct. However, the Boggy Plain zircon clearly crystallized well below the liquidus temperature of the host magma, and a similar magma with a much lower initial Zr concentration could precipitate zircon with Ti concentrations similar to those seen in the Jack Hills zircon.

Conclusions

1) Even in relatively simple magmatic systems, zircon crystallizes over a wide range in temperatures.

2) With a large enough sample set, zircon crystallization temperature distributions can be used to distinguish between models of zircon crystallization.

3) The Ti concentrations from the Boggy Plain Pluton are different from that of the Hadean detrital zircon but much lower than the liquidus temperature of the magma.

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