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Notes

Temperature spectra of zircon crystallization in plutonic rocks

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ABSTRACT

The Ti-in-zircon thermometer is a potentially powerful new petrological tool, but conclusions drawn from such data are meaningful only to the extent that the underlying interpretational framework is sound. In the case of interpretation of detrital zircon crystallization temperature spectra, it has been assumed that comparisons can be made with potential host rocks based on calculated bulk zircon saturation thermometry. We show by calculation that most igneous rocks formed at high temperature ($>750^\circ\text{C}$) will yield Ti-in-zircon temperatures ($T_{\text{Ti}}^{\text{zir}}$) well above the wet granite solidus. This prediction is borne out by results from the Dala igneous complex, southeastern Tibet, which show a 300°C range in $T_{\text{Ti}}^{\text{zir}}$ beginning $>100^\circ\text{C}$ above the calculated bulk zircon saturation temperature. Thus the dominant $T_{\text{Ti}}^{\text{zir}}$ peak of >4 Ga zircons at $\sim 680^\circ\text{C}$ implies a wet, anatectic magma source rather than an origin in intermediate and mafic magmas. Given that preservation and analytical effects select against, or obscure recognition of, zircons formed at low temperature, the best explanation for the low Hadean $T_{\text{Ti}}^{\text{zir}}$ peak is that it reflects derivation from rocks that experienced prograde melting conditions under near-water-saturated conditions.

Keywords: zircon, crystallization, saturation, Ti thermometer, tonalite, Jack Hills.

INTRODUCTION

The advent of the Ti-in-zircon thermometer (Watson and Harrison, 2005; Watson et al., 2006) prompted its immediate application to petrological problems as well as ongoing tests of its validity (e.g., Bea et al., 2006; Lowery Claiborne et al., 2006; Valley et al., 2006; Nutman, 2006; Coogan and Hinton, 2006; Baldwin et al., 2007). Most of these reports acknowledge a relationship between zircon crystallization and the interplay of temperature and melt chemistry in controlling zircon solubility. However, the assumption that saturation thermometry is a benchmark for comparison with the crystallization thermometer has not been tested. Here we review the background of both types of zircon thermometry and combine them in a simple model that predicts the crystallization temperature of zircon in cooling magmas. The model results, borne out by a geologic example, show that the zircon saturation temperature ($T_{\text{sat}}^{\text{zir}}$) can significantly underestimate the onset temperature of zircon crystallization. This result has implications to the interpretation of detrital zircon spectra that bear on the nature of Hadean Earth.

ZIRCON SATURATION TEMPERATURE

By the early 1970s, U-Pb geochronologists had recognized that granitoids often contained “inherited” zircon (Grauert and Hofmann,

1973). Whether assumed to reflect entrained source material or late-stage xenocrysts, it was generally assumed that inherited zircon was a disequilibrium phenomenon. Watson and Harrison (1983) undertook synthesis experiments that showed zircon solubility in calc-alkaline magmas to be a function of the zirconium concentration of the melt ($[\text{Zr}]$), temperature (T), and magma composition. With regard to the latter, they adopted the compositional parameter $M = [(K + Na + 2Ca)/(Al \cdot Si)]$ as a proxy for the thermodynamic and melt structural effects believed to control zircon solubility (a_{SiO_2} , alkali/alumina index). Harrison and Watson (1983) undertook zircon dissolution experiments in a granitic melt, which provided both “reversal” confirmation of the solubility data obtained from crystallization experiments and Zr diffusion coefficients (D_{Zr}). These latter results showed a wide range of D_{Zr} depending on water content, but in general, “wet” felsic melts are characterized by D_{Zr} sufficient to dissolve small zircons on short time scales relative to those for the generation and transport of crustal magmas (Harrison and Watson, 1983; Watson, 1996). Thus inherited zircons are generally interpreted as evidence that the host magma was saturated in zircon during melting. Watson and Harrison (1984) proposed that their model could be used as a thermometer in those cases where the bulk $[\text{Zr}]$ of the melt was known and the amount of

restitic zircon could be estimated. Subsequently, $T_{\text{sat}}^{\text{zir}}$ has grown to be a widely used thermometer, as evidenced by the over one thousand citations the above papers have collectively received.

ZIRCON CRYSTALLIZATION TEMPERATURE

In the same way that the amount of Zr dissolved in the host melt can be used as a thermometer, the concentration of trace elements partitioned into zircon can be used to estimate temperature if the melt abundance is known. Analysis of synthesis experiments and natural assemblages in the temperature range 1450 – 590°C have shown that Ti is a potential zircon crystallization thermometer, provided a_{TiO_2} can be estimated (Watson and Harrison, 2005; Watson et al., 2006) and the presence of quartz can be assumed (Ferry and Watson, 2006). Fu et al. (2005) speculated that Ti content in zircon could be reset under granulite-facies metamorphism, but experimental data show that Ti diffusion is vanishingly slow (Cherniak and Watson, 2006).

The first application of the Ti-in-zircon thermometer ($T_{\text{Ti}}^{\text{zir}}$) was to Hadean zircons from Jack Hills, Western Australia (Compston and Pidgeon, 1986). Their oxygen isotopes have been interpreted as indicating that the source rocks of ca. 4.3 Ga magmas formed in the presence of water near Earth’s surface (e.g., Mojzsis et al., 2001), and other data (Harrison et al.,

2005) suggest a surface environment and petrogenetic processes more similar to the present day than the long-standing paradigm of an arid and continental-crust-free early Earth. Watson and Harrison (2005, 2006) measured Ti in 136 zircons ranging from 3.91 to 4.35 Ga, the vast majority of $T_{\text{Ti}}^{\text{zir}}$ plotting in a normal distribution (Fig. 1; see Table DR1¹). Excluding the >750 °C outliers (13% of results) yields an average temperature of 683 ± 26 °C (1σ).

A limitation in applying this thermometer to detrital zircons is the unknown Ti activity of the parent magma. Unless co-crystallization with rutile is known, $T_{\text{Ti}}^{\text{zir}}$ is a minimum estimate. Watson and Harrison (2005) argued that a_{TiO_2} is largely restricted to between ~0.6 and 1 in igneous rocks, as the general nature of evolving magmas leads to high a_{TiO_2} prior to zircon saturation. Thus for Hadean zircons of magmatic origin, it would be a rare case in which zircon formed in the absence of a Ti-rich phase (e.g., rutile, ilmenite, titanite), thus generally restricting a_{TiO_2} to ≥ 0.6 . In this case, calculated temperatures in the range 650 to 700 °C would be underestimated by ~40–50 °C. It has since come to light that this underestimate may be entirely compensated by a_{SiO_2} somewhat below unity (Ferry and Watson, 2006).

Thus the Hadean $T_{\text{Ti}}^{\text{zir}}$ spectrum was interpreted by Watson and Harrison (2005) as indicating that the zircons were dominantly sourced from crustal melts under conditions ranging from wet, minimum melting to vapor-absent anatexis. Kimberlites and mafic igneous complexes were ruled out as significant contributors due to their low U concentrations and/or higher expected crystallization temperatures.

It was subsequently argued that the low-temperature Hadean peak (Fig. 1) could be derived from zircons originating in mafic magmas (Valley et al., 2006; Coogan and Hinton, 2006) or reflect zircon saturation at low temperatures in rocks of the tonalite-trondhjemite-granodiorite suite (Nutman, 2006; Glikson, 2006). Glikson (2006) proposed that Hadean zircons could have originated in tonalite-trondhjemite-granodiorites that formed at high temperatures but did not crystallize zircon until near-eutectic temperatures were reached, and thus “zircon-poor tonalite-trondhjemite-granodiorites would be underrepresented in the detrital zircon population.” Similarly, Nutman (2006) argued on the basis of calculated $T_{\text{sat}}^{\text{zir}}$ for granitoids of intermediate composition that high-temperature melts do not crystallize zircon until

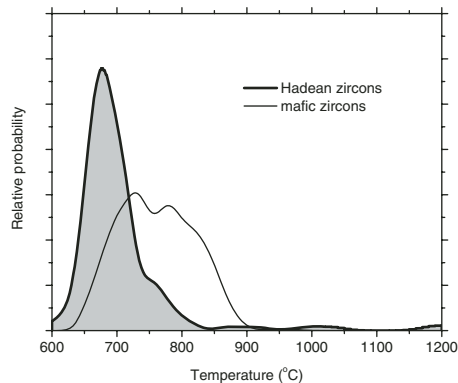


Figure 1. Probability plot of apparent zircon crystallization temperature. Results for 136 Hadean zircons from Jack Hills, Western Australia (Watson and Harrison, 2005, 2006) (Table DR1; see footnote 1) are shown by the heavy curve with gray infill. The distribution for 231 zircons from mafic rocks, digitized from data presented by Valley et al. (2006), is shown by the thin curve. Both spectra were produced using absolute errors, which vary as a function of temperature (see Table DR1).

they cool to temperatures near that of minimum melting (i.e., zircons from both wet tonalite and minimum melts yield similarly low $T_{\text{Ti}}^{\text{zir}}$).

We question the assumption that the expected temperature for zircons crystallizing from granitoids of intermediate composition is that indicated by $T_{\text{sat}}^{\text{zir}}$. Specifically, in a cooling, crystallizing magma system, modal phase growth prior to zircon saturation drives up the melt [Zr] while at the same time diminishing its capacity to dissolve zircon (i.e., by lowering M). Thus $T_{\text{sat}}^{\text{zir}}$ calculated from bulk rock chemistry could significantly underestimate the onset temperature of zircon crystallization.

ZIRCON CRYSTALLIZATION TEMPERATURE SPECTRA

It is clear that the timing of zircon crystallization and the level of saturation bear critically upon how the zircon crystallization temperatures should be interpreted. Phase equilibria in the system tonalite-peridotite- H_2O help to illustrate the basic principles involved. Carroll and Wyllie (1989, 1990) determined the liquidus phase relations in a system in which small amounts of peridotite were added to a tonalite with $M = 1.9$ (composition 101) between 850 and 1100 °C at 15 kbar. They measured major element glass compositions with 2.4%–5.2% water for mixtures of pure tonalite and 5% or 10% peridotite. Figure 2 shows the Carroll and Wyllie (1989, 1990) glass compositions plotted as a function of temperature. Regression of the array in Figure 2 yields the relationship $M = 0.5 + 0.0013 \times T$ (°C), which is used to predict melt composition as a function of tem-

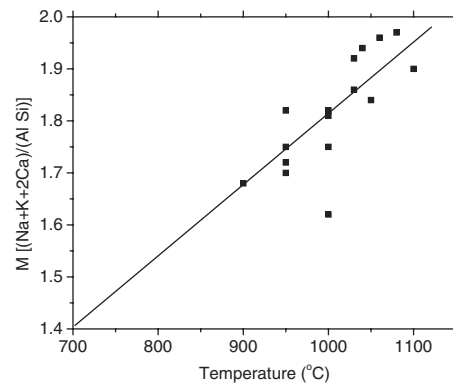


Figure 2. Plot of glass compositions from Carroll and Wyllie (1989, 1990) in terms of M versus temperature (850 °C datum omitted). A similar relationship is obtained from tonalite experiments only.

perature. Note that if early-formed mafic crystals are removed as cumulates, this relationship will underestimate M at a given temperature. However, since most tonalites likely form by vapor-absent partial melting of amphibolite at substantially lower temperatures (900–1000 °C; Rutter and Wyllie, 1988), the impact of this effect on our calculation is expected to be small.

Guided by the Carroll and Wyllie (1990) phase diagram, we approximated the melt crystallization sequence between 1100 and 700 °C as the function shown in Figure 3. To determine the progression of zircon crystallization, we have assumed a conservative [Zr] of 150 ppm (Condie, 1993). Using this value, a molten rock of the composition of tonalite 101 yields a model $T_{\text{sat}}^{\text{zir}} = 748$ °C.

The calculation begins at 1100 °C with a magma characterized by $M = 1.9$ containing only negligible crystals. Although a portion of

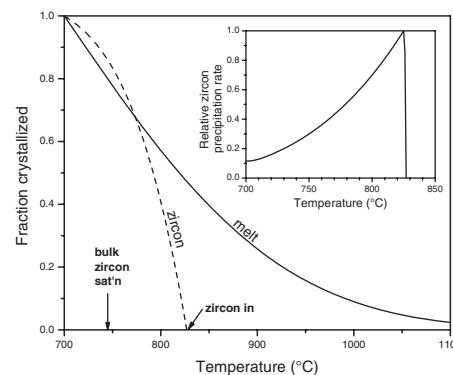


Figure 3. Assumed crystallization sequence for intermediate granitoid magma cooling from 1100 °C (solid curve). The cumulative growth of zircon growth (dashed line) indicates onset of zircon crystallization at 827 °C, or ~80 °C hotter than the calculated zircon saturation temperature. Zircon growth rate shown in the inset.

¹GSA Data Repository item 2007157, Hadean $T_{\text{Ti}}^{\text{zir}}$ (Table DR1), $T_{\text{sat}}^{\text{zir}}$ for Dala plutons (Table DR2), and $T_{\text{Ti}}^{\text{zir}}$ for Dala zircons (Table DR3), 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.

Zr would be expected to be taken up by crystallizing mafic phases, we've assumed for simplicity that no Zr partitions into modal phases. This is compensated for by our low value of initial [Zr]. By 827 °C, when crystallization is nearly half complete, M has dropped to 1.6 and the melt becomes saturated in zircon (at 285 ppm Zr). At this point, zircon begins to crystallize and the rate of precipitation decreases as temperature and melt [Zr] fall (inset in Fig. 3). By 760 °C, the magma is ~75% crystallized ($M = 1.5$) while [Zr] has dropped to 128 ppm. Crystallization is complete by 700 °C.

The predicted distribution of $T_{\text{Ti}}^{\text{zir}}$ (Fig. 3) is characterized by a monotonic decrease from the onset of crystallization, which begins ~80 °C higher than $T_{\text{sat}}^{\text{zir}}$. The shape and position of this curve is relatively insensitive to input parameters. For example, changing bulk [Zr] by ± 30 ppm only shifts the onset temperature by ± 11 °C. A linear increase of modal phase crystallization with temperature (as predicted by MELTS; Asimow and Ghiorso, 1998) increases the onset temperature of saturation by ~30 °C. In the expected case where the magma forms well below 1100 °C (Rutter and Wyllie, 1988), the shape of the crystallization spectrum is not appreciably changed provided that, as suggested by the phase diagram, substantial modal phase crystallization has occurred prior to ~830 °C.

Strictly speaking, Figure 3 depicts the zircon temperature spectrum for the case where a_{SiO_2} and a_{TiO_2} are both ~1 or have similar subunity values (Ferry and Watson, 2006). The former is unlikely but the latter approximation is probable for many magmas of intermediate composition. Pending discussion of our geologic example below, we interpret Figure 3 as indicating that at least half the $T_{\text{Ti}}^{\text{zir}}$ values in a tonalite could be $> T_{\text{sat}}^{\text{zir}}$.

For comparison with this calculation, we have measured $T_{\text{Ti}}^{\text{zir}}$ on zircons from the 44 ± 1 Ma Dala igneous complex, a suite of monzodiorite to granodiorite plutons in southeastern Tibet (Aikman et al., 2005). Seven samples ranging from 62% to 72% SiO_2 yield an average $T_{\text{sat}}^{\text{zir}} = 760 \pm 10$ °C (Table DR2). Fifty Ti analyses yield a 300 °C range in $T_{\text{Ti}}^{\text{zir}}$ beginning at 877 °C (Table DR3). The probability plot (Fig. 4A) shows that nearly half the calculated temperatures are $> T_{\text{sat}}^{\text{zir}}$ ($T_{\text{ave}} = 731$ °C). The relationship between $\log(\text{Th}/\text{U})$ and crystallization temperature is shown in Figure 4B. That close to half the apparent temperatures yield values above $T_{\text{sat}}^{\text{zir}}$, and by as much as 100 °C, confirms our prediction that a broad and elevated $T_{\text{Ti}}^{\text{zir}}$ spectrum is diagnostic of a magma cooling from high temperature. Moreover, this supports our view that subunity values of a_{SiO_2} and a_{TiO_2} have acted in a broadly compensatory fashion during the crystallization of the Dala igneous complex.

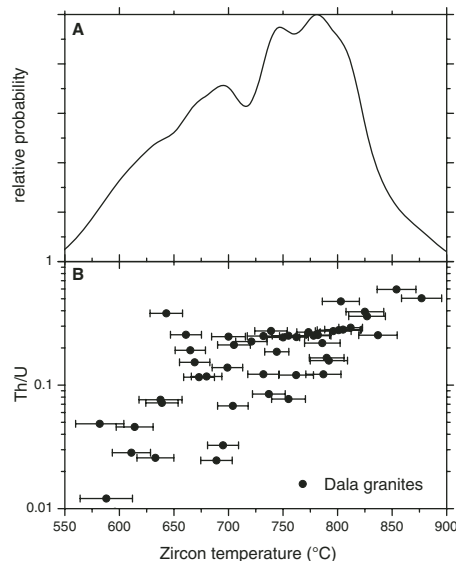


Figure 4. A: Relative probability plot of 50 $T_{\text{Ti}}^{\text{zir}}$ data points from the Dala igneous complex, southeastern Tibet. B: Plot showing the variation of Th/U with $T_{\text{Ti}}^{\text{zir}}$, interpreted to reflect the higher U contents of zircons formed at low temperature and lower Th due to co-crystallization of monazite.

DISCUSSION

Our calculation (Fig. 3) and empirical results (Fig. 4) indicate that $T_{\text{sat}}^{\text{zir}}$ is not an accurate predictor of the onset of zircon crystallization in an initially zircon-undersaturated magma. Rather, it appears that modal phase growth and decreasing M combine to produce a broad temperature distribution with zircon saturation initiated at substantially higher (50–100 °C) temperatures than that estimated from $T_{\text{sat}}^{\text{zir}}$. Lowery Claiborne et al. (2006) present further evidence of a broad range of crystallization temperatures beginning well above $T_{\text{sat}}^{\text{zir}}$.

Interpretation of the >4 Ga detrital $T_{\text{Ti}}^{\text{zir}}$ spectrum in terms of Hadean environments requires an understanding of how preservation effects and sampling artifacts can distort the record. For example, it is known that detrital zircon preservation is inversely proportional to U and Th contents, as radiation-damaged grains will tend not to survive erosion and sedimentary transport (Fedó et al., 2003). Thus we take issue with the view that tonalite-trondhjemite-granodiorites are zircon-poor and thus underrepresented in detrital zircon populations (Glikson, 2006) for two reasons. The first is that tonalites are Zr-rich (150–210 ppm; <http://earthref.org/GERM/>) relative to anatectic granitoids (~50 ppm; Vidal et al., 1982) and thus have the potential to crystallize abundant zircon. The second is that zircons formed at low temperature typically contain higher U and Th relative to grains formed at higher temperatures (e.g., Lowery Claiborne et al., 2006). We thus conclude that preservation

effects will tend to reduce the appearance of zircons formed at low temperatures (~700 °C) relative to much of the tonalite-trondhjemite-granodiorite and mafic spectra. Add to this that unseen, nm-scale, Ti-rich mineral inclusions can create spuriously high $T_{\text{Ti}}^{\text{zir}}$, and the distribution in Figure 1 appears all the more remarkable for the dominant ~680 °C peak.

Valley et al. (2006) reported $T_{\text{Ti}}^{\text{zir}}$ for 231 zircons from mafic rocks ranging from 650 to 950 °C with an average of 761 ± 57 °C (Fig. 1). They argued that overlap with the Hadean distribution refutes the claim that the ~680 °C Hadean peak necessarily reflects near-water-saturated granitoid melting. However, comparison of probability density functions shows that their distribution has much greater width and higher central tendency than that of the Hadean zircons (Fig. 1). Wilcoxon and Kolmogorov-Smirnov tests indicate that both the form and median value of the mafic distribution are distinct from that of the Hadean population with a remarkable degree of statistical significance (i.e., $p = 10^{-23}$), thus rendering the Valley et al. (2006) hypothesis untenable.

Coogan and Hinton (2006) reported Ti in 15 mid-oceanic-ridge basalt (MORB) gabbro zircons yielding an average $T_{\text{Ti}}^{\text{zir}}$ of 756 ± 34 °C. They similarly concluded that the small overlap with the Jack Hills distribution leaves open the possibility that the Hadean zircons grew from a melt produced by basalt differentiation. In addition to the remarks in the previous paragraph, which apply equally well to these data, we note that the order of magnitude lower average [U] in their MORB zircons relative to Hadean grains (i.e., 40 versus 400 ppm; Coogan and Hinton, 2006; Cavosie et al., 2004) clearly marks them as being derived from a distinctively different, low-U source. Coogan and Hinton (2006) speculated that Hadean zircon temperatures could be underestimated if a_{TiO_2} were ~0.5 rather than 1, but as all their samples contain ilmenite, they are certain to have had subunity a_{TiO_2} during zircon crystallization.

The distribution of $T_{\text{Ti}}^{\text{zir}}$ from mafic rocks (Valley et al., 2006; Coogan and Hinton, 2006) is palpably different from >4 Ga zircons. Thus it is highly improbable that the Hadean distribution (Fig. 1) could have been derived from the mafic zircon spectrum without operation of a sorting mechanism that preferentially excludes zircons formed at temperatures greater than 700–750 °C—the opposite of what could be expected due to preservation effects.

As a result of our calculation and its confirmation from a geologic example, as well as the indisputable differences with the mafic zircon distribution, we conclude that the vast majority of Hadean zircons could not be plausibly derived from slowly cooled mafic or intermediate magmas. As for their volcanic equivalents,

this is an even less likely environment for the creation of low-temperature zircons destined for detrital deposits, as volcanism will tend to truncate the tail of a $T_{\text{Ti}}^{\text{zir}}$ spectrum at the eruption temperature.

Given the above arguments, the simplest explanation for the dominant low-temperature Hadean peak is that it reflects prograde melting under conditions at or near water saturation. In effect, as soon as the source reached anatectic conditions, the majority of melt fertility was lost in the presence of excess water. That no subsequent peaks clearly correspond to higher-temperature vapor-absent melting equilibria supports this conclusion. A test of the prograde versus retrograde thermal history hypotheses is possible by further detailed examination of natural zircon crystallization temperature spectra and high-resolution imaging of Ti in Hadean zircons to assess whether a broad or narrow spectrum of crystallization temperatures are characteristic of these ancient grains.

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