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Zircon saturation re-revisited

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ABSTRACT

Improvements in experimental, analytical and computational methodologies together with published studies yielding seemingly contradictory results prompted us to return to the determination of zircon stability in the range of felsic to intermediate melts expected in continental environments. We (re-)analyzed both the run products from the zircon crystallization study of Watson and Harrison (1983) and a new style of zircon dissolution experiments (up to 25 kbar) using a large radius ion microprobe to constrain a refined zircon solubility model. The new data yield broadly similar patterns as before when arrayed for temperature and confirm that the parameter M [$=(\mathrm{Na}+\mathrm{K}+2\mathrm{Ca})/(\mathrm{Al}\cdot\mathrm{Si})$] is an appropriate compositional proxy for the chemical interactions through which zircon is dissolved. We used a Bayesian approach to optimize the calculation of the coefficients in the zircon solution model, which is given by:

$$\ln\ D_{\mathrm{Zr}}=(10108\pm32)/T(\mathrm{K})-(1.16\pm0.15)(M-1)-(1.48\pm0.09)$$

where D_{Zr} is the distribution coefficient of Zr between zircon and melt and the errors are at one sigma. Sensitivity tests indicate that temperature and composition are the two dominant controls on zircon solubility in crustal melts with no observable effects due to pressure (up to 25 kbar) or variable water content. Comparison of the down-temperature extrapolation with natural examples confirms the validity of the model at ca. 700 °C.

1. Introduction

The recognition in the early 1980s that accessory minerals (e.g., zircon, monazite and apatite) are the principal hosts in the continents for geochemically important trace elements such as U, Th, and REE (Fourcade and Allegre, 1981; Gromet and Silver, 1983; Harrison et al., 1986) inspired experimental studies into their stability in crustal melts (Harrison and Watson, 1983; Watson and Harrison, 1983; Harrison and Watson, 1984; Rapp and Watson, 1985).

Because of its near ubiquitous presence in continental rocks and key role as a U–Pb chronometer, the solubility of zircon in a variety of melt compositions was the first to be extensively investigated (Watson, 1979; Dickinson and Hess, 1982; Harrison and Watson, 1983; Watson and Harrison, 1983). Watson and Harrison (1983) undertook experiments in which zircon was crystallized from seed ZrO_2 under hydrothermal conditions from mixtures of five glasses ranging from felsic to mafic in composition. Electron microprobe analysis (EPMA) of glass portions of the run products showed that zircon solubility in crustal magmas was a simple function of temperature, Zr content and composition. Notably, the parameter M [$=(\mathrm{Na}+\mathrm{K}+2\mathrm{Ca})/(\mathrm{Al}\cdot\mathrm{Si})$] was shown to be a good compositional proxy for the mechanism of zircon solution (note that M is calculated by obtaining the molar amounts of each component, renormalizing, and then obtaining the ratio). Their summary model for zircon solubility was given by

$$\ln D_{\mathrm{Zr}}=\frac{12900}{T(K)}-0.85\cdot(M-1)-3.80 \tag{1}$$

where $\ln D_{\mathrm{Zr}}$ is the distribution coefficient determined by ratioing the zirconium abundance [Zr] for zircon (i.e., [Zr] = 500,000 ppm) and melt (in ppm).

Harrison and Watson (1983) undertook zircon dissolution experiments that provided reversal confirmation of the crystallization studies, at least for the anhydrous case. It was found that zircon is relatively insoluble in anatectic melts. For example, a minimum melt at ca. 700 °C was found to dissolve only ~40 ppm zircon, corresponding to about one-fifth of the average Zr concentration in the crust (e.g., Rudnick and Gao, 2003).

The results of these experiments have been widely used to predict the occurrence of zircon in crustal magmas and to estimate the peak temperature experienced by magmatic rocks (i.e., accessory mineral thermometry; Watson and Harrison, 1984a,b). However limitations in both the analytical and experimental approaches restricted the resolution of the model. From the experimental perspective, many crystallization run products were complex mixtures of micron-sized crystals, glass and bubbles. This made electron microprobe analysis problematic as it was difficult to avoid overlapping the electron

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beam onto adjacent crystals and secondary fluorescence effects could contribute signal from adjacent nm-scale zircons undetected in micrographs. This can be seen in Fig. 1, a Zr ion image of one of the original run products showing abundant, tiny neoformed zircons (bright spots within the Zr-saturated glass). The above effects contributed to overall poor precisions for temperatures below ~900 °C (e.g., data at 750 °C could have ±100% uncertainty). Furthermore, subsequent published studies of zircon solubility in similar melt compositions yielded results that appeared somewhat at variance with that of Watson and Harrison (1983). Baker et al. (2002) found Zr dissolved at levels about one-third of that measured by Watson and Harrison (1983). They attributed this discrepancy to the higher f_{O_2} in their experiments which produced higher concentrations of Fe^{3+} which acted as a network former, thus reducing zircon solubility (and, effectively, M). Ellison and Hess (1986) examined Zr solubility in anhydrous melts at 1400 °C and 1 atm and found that the model of Watson and Harrison (1983) overpredicted their results by about 40%. Keppler (1993) examined the effect of halogens on granitic melt structure under similar conditions as that of Watson and Harrison (1983) and found similar Zr solubilities to theirs in halogen-free melts. However, solubility rose quasi-geometrically when ≥2% F was added. More recently, Rubatto and Hermann (2007) measured Zr solubility in peraluminous melts at 20 kbar and reported Zr concentrations ~40% lower than that of Watson and Harrison (1983) for the same temperature and composition. They attributed this difference to a previously undocumented pressure effect. Thus we have returned to this investigation 30 years later with a view to using an improved experimental design along with the superior sensitivity of a high resolution ion microprobe and improved computational methods to re-examine zircon solubility in crustal melts as a function of temperature, composition, and pressure.

2. Methods

2.1. Experimental approach

Most of the experiments reported by Watson and Harrison (1983) involved nucleation and growth of zircon from pre-synthesized ZrO_2-bearing glasses, followed by the measurement of Zr concentration in the quenched glass to determine the saturation level. This strategy was generally successful, but it also created analytical challenges because of the high nucleation density of zircon and its tendency to form small, needle-like crystals (Fig. 1). The 1983 study also included a few high-temperature reversal experiments in which large zircon slabs were partially dissolved in the melt. In this case, the Zr saturation level was estimated from the diffusion profile in the quenched glass near the dissolving zircon. The value of [Zr] at the zircon/glass interface – obtained by fitting the diffusion profile – was taken as the saturation concentration (see also Harrison and Watson, 1983). Although indirect, this approach offers the advantage of providing a clear field of quenched melt (free of small zircons) to analyze for Zr.

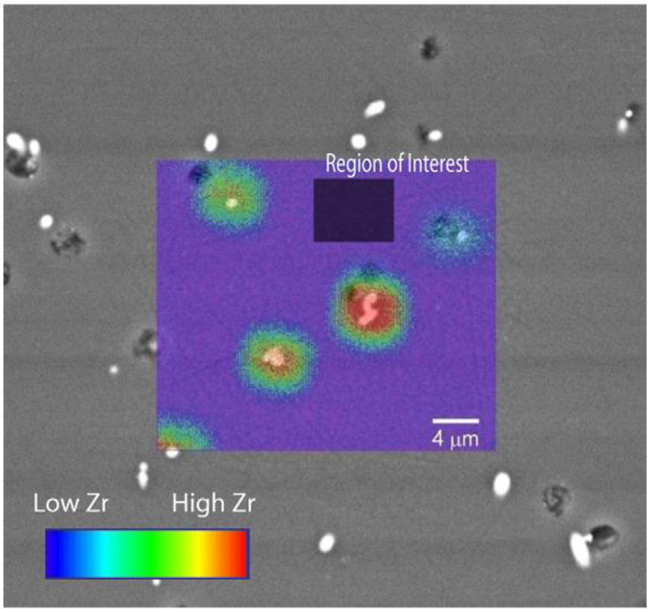

Fig. 1. Scanning ion image of a run product from Watson and Harrison (1983) superimposed on the BSE image. The bright areas are neoformed zircons whereas the shaded region is the area from which the saturation concentration is calculated ([Zr] = 367 ppm). The diffuse appearance of the ion-imaged zircon is not an effect of diffusion but rather due to the beam diameter (~3 μm).

In the 1983 studies, the partial dissolution method yielded good information at 1200–1400 °C but the prospects for obtaining data at temperatures approaching those relevant to natural systems were considered poor because Zr diffusion in silicic melts is slow (Harrison and Watson, 1983), and the resulting Zr profiles against a dissolving zircon slab would be too short for accurate characterization with available instruments. In the present study, we adopted a conceptually similar dissolution approach (to avoid the problem of myriad small crystals), but instead of immersing a large slab of zircon in the melt of interest, we equilibrated small, interstitial melt pools (10–20 μm dia.) with a surrounding matrix of crushed zircon.

2.2. Starting materials

In keeping with the general strategy used by Watson and Harrison (1983), five starting compositions were prepared to yield a range of crustal melt compositions when heated under pressure in the presence of zircon. The nominal bulk compositions range from mafic tonalite to rhyolite (Table 1; note that these do not represent actual melt compositions because crystalline phases in addition to zircon and glass were present in most run products; see Table 2). These five compositions were prepared from reagent-grade oxides and natural minerals, including $CaSiO_3$, Mg_2SiO_4, FeO, TiO_2, Al_2O_3, microcline and albite (all purchased from Alfa Aesar). These components were pre-mixed to yield compositions deficient in SiO_2 and Al_2O_3 so the latter oxides could be "topped up" as silicic acid and $Al(OH)_3$ to set the amount of H_2O contained in the mixtures (silicic acid contains 12.3 wt.% H_2O [quantified repeatedly by LOI]; gibbsite contains 34.6 wt.%). Introduction of H_2O in this manner made it possible to accurately regulate the bulk H_2O content of the non-zircon portion of the experimental charges at 5.9 ± 0.2 wt.%. The oxide/mineral mixtures were ground in agate under alcohol and dried at room temperature before use.

Additionally, four relatively mafic compositions were prepared in order to evaluate zircon solubility in such systems at near-liquidus temperatures under dry conditions. These consisted of a natural N-MORB, a synthetic tonalite, a synthetic high-alumina basalt, and a natural basaltic

Table 1
Anhydrous compositions of starting materials used in this study. These compositions were prepared by weighing $CaSiO_3$, Mg_2SiO_4, FeO, TiO_2, Al_2O_3, microcline, albite, silicic acid and $Al(OH)_3$ in appropriate portions to yield the rock-forming oxides shown plus 6 wt.% H_2O. See text for discussion.

Oxide	LCO	B	C	TN	BTC
SiO_2	77.0	73.7	70.2	61.9	65.8
TiO_2	0.1	0.3	0.5	0.8	0.8
Al_2O_3	13.1	13.5	13.9	16.9	18.6
FeO	0.7	1.8	2.9	5.8	4.8
MgO	0.1	1.1	2.2	3.0	1.6
CaO	0.5	1.7	3.1	5.7	2.8
Na_2O	3.7	3.6	3.5	3.9	1.7
K_2O	4.8	4.3	3.7	2.0	3.8
Total	100.0	100.0	100.0	100.0	99.9