Earth and Planetary Science Letters 453 (2016) 260–266

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

# Magmatic oxygen fugacity estimated using zircon-melt partitioning of cerium

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ARTICLE INFO

*Article history:*
Received 7 January 2016
Received in revised form 4 August 2016
Accepted 8 August 2016
Available online 30 August 2016
Editor: M. Bickle

*Keywords:*
zircon
oxygen fugacity
magmas
cerium
Hadean

ABSTRACT

Using a newly-calibrated relation for cerium redox equilibria in silicate melts (Smythe and Brenan, 2015), and an internally-consistent model for zircon-melt partitioning of Ce, we provide a method to estimate the prevailing redox conditions during crystallization of zircon-saturated magmas. With this approach, oxygen fugacities were calculated for samples from the Bishop tuff (USA), Toba tuff (Indonesia) and the Nain plutonic suite (Canada), which typically agree with independent estimates within one log unit or better. With the success of reproducing the $fO_2$ of well-constrained igneous systems, we have applied our Ce-in-zircon oxygen barometer to estimating the redox state of Earth's earliest magmas. Using the composition of the Jack Hills Hadean zircons, combined with estimates of their parental magma composition, we determined the $fO_2$ during zircon crystallization to be between FMQ $-1.0$ to $+2.5$ (where FMQ is the fayalite–magnetite–quartz buffer). Of the parental magmas considered, Archean tonalite–trondhjemite–granodiorite (TTG) compositions yield zircon-melt partitioning most similar to well-constrained modern suites (e.g., Sano et al., 2002). Although broadly consistent with previous redox estimates from the Jack Hills zircons, our results provide a more precise determination of $fO_2$, narrowing the range for Hadean parental magmas by more than 8 orders of magnitude. Results suggest that relatively oxidized magmatic source regions, similar in oxidation state to that of 3.5 Ga komatiite suites, existed by ∼4.4 Ga.

## 1. Introduction

The mineral zircon incorporates a variety of trace elements during crystallization, including the rare-earth elements (REE), uranium, thorium, and titanium, which makes this phase particularly useful for tracing magma chemistry as well as for geochronometry and geothermometry (Hoskin and Schaltegger, 2003; Watson and Harrison, 2005). A nearly ubiquitous, but until recently underutilized, feature of terrestrial zircon (though generally lacking in lunar and meteoritic samples) is the anomalously high chondrite-normalized concentration of Ce relative to neighboring REEs. In most terrestrial magmas, Ce will exist in both 3+ and 4+ oxidation states (Trail et al., 2011, 2012; Burnham and Berry, 2012, 2014; Smythe and Brenan, 2015), so anomalous Ce concentrations in zircon result from the favored partitioning of $Ce^{4+}$ relative to $Ce^{3+}$ into the zircon structure; $Ce^{4+}$ is isovalent with, and a close match in ionic radius to $Zr^{4+}$ (Shannon, 1976). The change in Ce oxidation state in silicate melts can be expressed via the homogeneous reaction,

$$CeO_{3/2}^{melt} + \frac{1}{4}O_2^{melt} = CeO_2^{melt} \tag{1}$$

This implies that the relative proportions of $Ce^{3+}$ ($CeO_{3/2}$) and $Ce^{4+}$ ($CeO_2$) in a silicate melt will be a function of the oxygen fugacity ($fO_2$) of the system, and the magnitude of the resulting Ce anomaly in zircon will then be a record of the prevailing redox conditions during crystallization. In principle, it might be possible to measure the $Ce^{4+}/Ce^{3+}$ in zircon directly as an indicator of magma oxidation state. However, alpha recoil events during radioactive decay of U and Th induce structural changes in zircon (Trachenko et al., 2002), which allow for post-crystallization changes in $Ce^{4+}/Ce^{3+}$, making this approach unreliable. Instead, because the sluggish diffusion rates of 3+ and 4+ cations in zircon (Cherniak et al., 1997a, 1997b) prevent modification of absolute Ce concentrations, Ce anomalies produced during crystal growth potentially constitute a robust record of magma redox state.

Recently, Trail et al. (2011, 2012) provided an experimental calibration that relates the magnitude of the Ce anomaly in zircon, termed $(Ce/Ce^*)_D$ (in which $Ce^*$ is the estimated value for

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http://dx.doi.org/10.1016/j.epsl.2016.08.013

$D^{zircon/melt}_{Ce^{3+}}$), to $fO_2$ and temperature. Values of $(Ce/Ce^*)_D$ can be calculated from natural samples from knowledge of the bulk partition coefficient for Ce, combined with the estimated value for $D^{zircon/melt}_{Ce^{3+}}$ as interpolated from partition coefficients for the neighboring light REEs (LREEs), La and Pr. This approach is a valuable first step in exploiting the Ce anomaly as a redox sensor, but seems to yield relatively imprecise estimates for magma $fO_2$ (possible reasons for this are discussed later). As an alternative, we have taken the approach of Ballard et al. (2002), in which the concentration of Ce in zircon and melt, along with values of $D^{zircon/melt}_{Ce^{3+}}$ and $D^{zircon/melt}_{Ce^{4+}}$ are related to the mole fractions of $Ce^{4+}$($x^{melt}_{Ce^{4+}}$) and $Ce^{3+}$ ($x^{melt}_{Ce^{3+}}$) in the melt by the equality:

$$\left[\frac{x^{melt}_{Ce^{4+}}}{x^{melt}_{Ce^{3+}}}\right] = \left[\frac{\sum Ce_{zircon} - (\sum Ce_{melt} * D^{zircon/melt}_{Ce^{3+}})}{(\sum Ce_{melt} * D^{zircon/melt}_{Ce^{4+}}) - \sum Ce_{zircon}}\right] * 1.04877 \qquad (2)$$

where $\Sigma$Ce is the total concentration of Ce in zircon or melt, and the constant 1.04877 is the mole to wt% conversion factor. Using results from our previous work on the redox behavior of Ce in silicate melts (Smythe and Brenan, 2015), the relative proportions of $Ce^{4+}$ and $Ce^{3+}$ can be related to melt $fO_2$ through the equation:

$$\ln\left[\frac{x^{melt}_{Ce^{4+}}}{x^{melt}_{Ce^{3+}}}\right] = \frac{1}{4}\ln fO_2 + \frac{13136(\pm 591)}{T} - 2.064(\pm 0.011)\frac{\text{NBO}}{\text{T}} - 8.878(\pm 0.112)\cdot xH_2O - 8.955(\pm 0.091) \qquad (3)$$

where $T$ is in Kelvin and can be determined using the Ti-in-zircon thermometer (Ferry and Watson, 2007), NBO/T is the proportion of non-bridging oxygens to tetrahedrally coordinated cations (Virgo et al., 1980) calculated on an anhydrous basis (assuming all ferrous iron), and $xH_2O$ is the mole fraction of water dissolved in the melt. Zircon/melt partition coefficients for $Ce^{3+}$ ($D^{zircon/melt}_{Ce^{3+}}$) and $Ce^{4+}$ ($D^{zircon/melt}_{Ce^{4+}}$) can be calculated for individual zircon-melt pairs using the lattice strain model of Blundy and Wood (1994), and are constrained by the partition coefficients for the other REEs as well as Hf, Th, and U (as described below). In this communication, we demonstrate the accuracy of this new oxygen barometer through application to three zircon-saturated igneous suites whose redox state has been determined by independent methods. We then show how the method can be used to estimate the $fO_2$ during crystallization of magmas formed within 500 million years of terrestrial accretion, as represented by the Hadean-aged Jack Hills zircons.

## 2. Samples investigated

Samples investigated in this study were taken from three different localities for which $fO_2$ has been estimated previously, namely: the Bishop tuff (California), Toba tuff (Indonesia), and Umiakovik pluton (Nain plutonic suite, Labrador). Eruption of Bishop tuff occurred at 760 ka and the unit consists of several packages of fall deposits and ignimbrite. Samples of Bishop tuff were obtained from the Ig2E unit as defined by Wilson and Hildreth (1997), and consist of high-silica rhyolite pumices containing <5% crystal fragments, primarily of quartz, in a glassy matrix. Fourier transform infrared (FTIR) spectroscopy of melt inclusions in quartz have determined the $H_2O$ content of the pre-eruptive magma to be between 5.1 and 6.8 wt% (Anderson et al., 1989; Wallace et al., 1999). Oxygen fugacity and temperature for Bishop tuff samples, calculated from Fe–Ti-oxide thermobarometry, range from ΔFMQ of +0.5 to +2.0 and ~700 to 840 °C (Hildreth and Wilson, 2007). The Toba tuff sample is a potassic high-silica rhyolitic welded tuff that erupted at 74 ka, belonging to the youngest unit in the Toba volcanic package (YTT as defined by Chesner, 1998). The sample is primarily composed of ~25% crystal fragments (consisting of quartz, plagioclase, sanidine, and biotite) in a partially devitrified glass matrix. Oxygen fugacity and temperature for Toba tuff samples, also calculated from Fe–Ti-oxide thermobarometry, yielded ΔFMQ of 0 to +1.5 and 680 to 850 °C (Chesner, 1998). Melt inclusions analyzed by FTIR spectroscopy constrain the pre-eruptive $H_2O$ content of the Toba tuff to between 4.0 and 5.5 wt%. For the cases of Bishop tuff and Toba tuff, we adopt the higher value within each range of $H_2O$ content for the calculations. The sample from Umiakovik pluton (Geological Survey of Canada sample number EC87-86) is a pyroxene-bearing quartz monzodiorite that intruded Archean and Proterozoic gneisses 1311–1320 Ma (Emslie and Loveridge, 1992). The $fO_2$ and temperature of crystallization for the Umiakovik pluton, estimated by the intersection of isopleths defined by the hematite content of ilmenite and the ferric–ferrous ratio of biotite, range from ΔFMQ of −1 to −4 and 710 to 840 °C. The water content of the Umiakovik pluton magma is somewhat less straightforward to estimate, as primary melt inclusions have not been documented. Instead, the $fH_2O$ has been calculated, from biotite-melt phase relations, to be ~250 bars (Emslie and Stirling, 1993), equivalent to ~4.5 wt% $H_2O$.

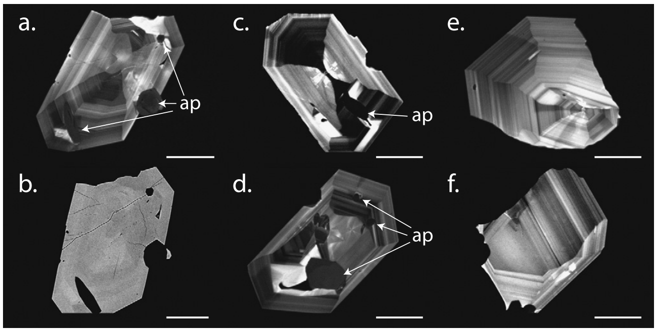

**Fig. 1.** Representative zircon textures from the Bishop tuff. Images a) and b) are CL and BSE images, respectively, of 12-BT2-9, c) through f) are CL images of 12-BT-1, 12-BT2-3, 12-BT2-4 5, 12-BT2-2, respectively. Prominent sector and oscillatory zoning are present in all zircons. Samples in a) and d) contain partially resorbed cores which appear bright in CL, and dark in BSE. Apatite (ap) inclusions are common and are found in most crystals. Scale bars = 50 μm.

Zircons obtained from Bishop tuff are clear, and generally have a prismatic crystal habit, ranging in size from ~50 to 200 μm. Inclusions of apatite were found in nearly all of the Bishop tuff zircons. Back-scattered electron (BSE) and cathodoluminescence (CL) images show relatively simple chemical zonation with sector zoning superimposed on oscillatory growth zoning (Fig. 1). Approximately half of the zircons from Bishop tuff contain cores with a relatively high CL response. Zircons from Toba tuff are clear, highly elongate prisms up to 300 μm in length with abundant apatite and melt inclusions (Fig. 2). From BSE and CL imaging, the Toba tuff zircons appear to have a relatively complex growth history, showing in some cases multiple episodes of growth and resorption. The outer domains in all Toba tuff zircons have oscillatory zoning occasionally with faint sector zoning. Umiakovik pluton zircons are typically 100 to 500 μm in size with tabular to prismatic morphologies (Fig. 3). Grains vary from colorless to pale brown and generally lack mineral inclusions. Imaging shows broad and oscillatory zoning in the outer domains of most samples, cored by regions with convolute zoning or lacking any internal structure suggesting recrystallization. Chemical analyses of all zircons were restricted to pristine regions with oscillatory growth zoning. Central domains interpreted to be regions of early growth were avoided.