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Redox evolution of silicic magmas: Insights from XANES measurements of Ce valence in Bishop Tuff zircons

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ABSTRACT

The potential for zircon to record continuous and evolving magmatic redox conditions is investigated by quantifying Ce valence in natural and synthetic crystals by X-ray Absorption Near Edge Structure (XANES). Valence was determined at high spatial resolution (2 × 4 μm) by analysis of the Ce L_3 edge for synthetic zircons and crystals from the Bishop Tuff Ig2E sequence; analyses included both core-to-rim and cross-sector measurements. Core-to-rim zonation among natural grains reveals a systematic increase in $Ce^{4+}/\Sigma Ce$, with core regions that range from ~0.4 to 0.6 $Ce^{4+}/\Sigma Ce$ (i.e., ~40–60% Ce^{4+}), while zircon rims range from ~0.7 to 1.0 $Ce^{4+}/\Sigma Ce$ (i.e., ~70–100% Ce^{4+}). Repeat analysis on an individual point suggests, on average, a $Ce^{4+}/\Sigma Ce$ reproducibility at the 5% level or less. Changes in spectral features with grain orientation were also investigated by rotating and analyzing synthetic zircons every 45°. This resulted in changes to the calculated Ce valence of <5%, which is much smaller than the range observed in natural samples. The core-to-rim increase in $Ce^{4+}/\Sigma Ce$ of Bishop Tuff samples may indicate a continuous crystal-melt evolution to more oxidizing conditions prior to eruption, but this cannot be uniquely decoupled from other effects that may influence Ce valence in zircon, which potentially include temperature changes or kinetic processes related to the mineral growth surface. Cathodoluminescence imaging couples with XANES spectra for Bishop Tuff samples reveal that different sectors yield notably different $Ce^{4+}/\Sigma Ce$, implying anisotropic decoupling of Ce^{3+} and Ce^{4+} in the zircon near-surface during crystallization. Broadly correlative (albeit with lower spatial resolution) Ti-thermometry and light rare earth element LA-ICP-MS data are also reported for zircon grains; there is no correlation between measured Ce anomalies and $Ce^{4+}/\Sigma Ce$. Cerium valence measurements of zircon may be able to constrain magma redox evolution with time, without relying on the nearly ubiquitous low concentrations of La and Pr, which are classically used to calculate Ce anomalies.

1. Introduction

The redox evolution of pre-eruptive melts in silicic, volatile-rich systems has been well studied in samples spanning Earth history. This evolution is often explored through chemical analysis of magnetite–ilmenite pairs, which provide information on both temperature and oxygen fugacity (f_{O2}), provided that contemporaneous crystallization and retention of primary mineral chemistry can be assumed. Since the calibration of the two-oxide technique ~50 years ago (Buddington, and Lindsley, 1964), the method has been revised repeatedly (e.g., Andersen and Lindsley, 1988; Ghiorso and Sack, 1991; Ghiorso and Evans, 2008) and utilized extensively for investigating the evolution of pre-eruptive silicic melts (Hildreth, 1977; Hildreth and Wilson, 2007; Ghiorso and Evans, 2008). The Bishop Tuff (BT) arguably represents the best studied two-oxide example within a highly silicic volcanic system. If magnetite–ilmenite composition preserves primary pre-eruption chemistry, then BT data indicate a continuous f_{O2}-temperature trend from an oxygen fugacity of NNO + 0.5 at 825 °C to an oxygen fugacity equal to NNO − 0.5 at 680 °C (Ghiorso and Evans, 2008). Put simply, the two-oxide BT data indicates that the melt became more reduced with progressive cooling and crystallization — provided the oxides have not been variably subject to sub-solidus or quenching phenomena (Bacon and Hirschmann, 1988; Ghiorso and Gualda, 2013).

Recent trace element studies involving partitioning of redox-sensitive elements into zircon demonstrate that the mineral may be used to constrain magma oxidation state. The experimental work of Trail et al. (2011, 2012) and Burnham and Berry (2012) for example, has shown that the intensity of a zircon Ce anomaly or

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Ce/Ce* (the normalized excess of Ce when compared to neighboring rare earth elements La and Pr; i.e., $[\mathrm{Ce}]_N/\sqrt{\mathrm{La}_N \times \mathrm{Pr}_N}$) is related to magma oxygen fugacity. This is because Ce^{4+} is more compatible in the zircon lattice compared to Ce^{3+}, such that more oxidized magmas – which contain a higher percentage of Ce^{4+} – show higher Ce concentrations in zircons and a correspondingly larger Ce anomaly. In this regard, it is widely assumed that a larger Ce anomaly implies a larger percentage of Ce^{4+} in the zircon crystal (e.g., Hinton and Upton, 1991; Thomas et al., 2002).

The use of zircon as an f_{O2} sensor is worth investigating and expanding upon because the mineral's physical and chemical robustness has been well-established (e.g, Cherniak et al., 1997), making it a particularly powerful geochemical indicator among highly silicic melts that readily produce zircon. Individual zircon sample sets yield apparent oxygen fugacities that have intra-sample standard deviations that can vary by a few log units (Trail et al., 2011, 2012). For instance, estimating the f_{O2} of the Bishop Tuff magma with zircon Ce anomalies yields a value of NNO $+ 2.5[\pm 3.1]$ (Trail et al., 2012). While real variations in f_{O2} or disequilibrium partitioning cannot be ruled out, a large component of the accuracy of this f_{O2} calculation is based on accurate determination of La, Ce, and Pr contents. Because the light rare earth elements (LREEs) of zircon are generally very incompatible in zircon, and may have concentrations <1 ppm, precise measurements can represent an analytical challenge (e.g., Hanchar and van Westrenen, 2007). Furthermore, zircon Ce anomalies are generally calculated assuming that no Ce anomaly exists in the melt at any point during zircon saturation. While this assumption appears to be generally valid (Trail et al., 2011), any pre-existing Ce anomaly in the melt will influence the zircon Ce anomaly, and therefore any corresponding oxygen fugacity calculation (Trail et al., 2012). Given these uncertainties and assumptions, other concentration-independent analytical methods are warranted as they may contribute to our understanding of how polyvalent elements (e.g., Ce and Eu) are incorporated into zircon, and they may ultimately lead to a more precise determination of oxygen fugacity in the environment.

X-ray Absorption Near Edge Structure (XANES) spectroscopy is a high spatial resolution technique that can measure in-situ valence states of redox-sensitive elements at low concentrations (Takahashi et al., 2000a, 2000b; Berry et al., 2004, 2008; King et al., 2013). In principle, f_{O2} information (that is, direct determination of Ce valence in zircon) can be determined independent of REE concentrations, as long as Ce contents are high enough to obtain meaningful spectra. Previous studies by Takahashi et al. (2003) and King et al. (2013) have demonstrated that Ce valence can be determined directly when the element exists at trace or minor levels within zircon and other minerals. In this study, the first high spatial resolution measurements of Ce valence in Bishop Tuff zircons are presented, including analysis of multiple domains within individual crystals.

2. Methods

In preparation for analytical work, zircons from the IG2Ea sequence from the Chalfant Valley pumice quarry were separated following standard heavy mineral separation techniques. Prior to sample processing, the pumice clast had an even color and did not contain lithic fragments and was composed mostly of glass, quartz, and feldspar. Zircons were mounted in an epoxy disk, polished to expose the core regions, and finished with 0.3 μm alumina paste. In an effort to limit any potential damage or change in valence within zircon grains, no electron microprobe or x-ray imaging was carried out on zircon grains prior to synchrotron analysis. The grains reported here are from the same aliquot used by Watson et al. (2006) for the Ti-in-zircon thermometer calibration and some grains from this aliquot were analyzed for trace element contents (including Ti) by Reid et al. (2011).

2.1. Synchrotron techniques

Cerium L_3 edge XANES spectra were collected at Beamline 13 ID-E (GSECARS), at the 7 GeV Advanced Photon Source, Argonne National Laboratory (IL, USA). The incident x-ray energy was selected using a cryogenically-cooled Si (111) double crystal monochromator at 25 m from x-ray source. The x-ray beam was focused using Kirkpatrick–Baez silicon mirrors onto an optically fluorescent standard $\mathrm{CdWO_4}$ phosphor plate. The position of this visible beam on an optical microscope camera was used to define the plane where the x-ray beam and optical microscope were coincident, permitting direct control of beam position for all subsequent zircon analyses. Prior to analysis of unknowns, the incident x-ray energy was calibrated on the first derivative peak of a vanadium metal foil standard ($\mathrm{V}^0 - 5465$ eV) and no energy drift was detected throughout the analytical session, typically lasting 8 or more hours.

Each spectrum was divided into three separate regions with different energy steps. The pre-edge region (5643 to 5708 eV) was measured using 5 eV energy steps, the XANES region (5708 to 5753 eV) was measured with 0.5 eV steps, and the post-edge region (5753 to 5967 eV) was measured with 0.1 Å^{-1} steps (i.e., 2.1–6.0 eV steps with increasing energy).

Two methods were used to collect spectra. First, high concentration finely-ground powders of Ce standard compounds of known valence were analyzed in transmission mode. Powders were mounted perpendicular to the x-ray beam, with the sample linearly arranged in the x-ray beam between ion chambers to measure the x-ray flux before and after the sample. All the standards, with the exception of stetindite (ideal formula: $\mathrm{CeSiO_4}$; Schlüter et al., 2009), were analyzed using this approach (Fig. 1). Most unknowns and the stetindite standard (long-needle-like habit) were analyzed in fluorescence mode. These measurements were conducted with the sample orientated at 45° to the incident x-ray beam, and 45° to the fluorescence detector, such that the incident beam and detector array are at 90°. Fluorescence x-rays from the Ce L_α line were counted with four-element Vortex-ME4 silicon drift detector (SII NanoTechnology Inc.), and individual detector counts from a common analytical spot were merged with equal weighting, with care to monitor any potential error within an individual detector or significant variance across the detector array.

2.2. XANES data reduction method

Spectra were processed to resolve Ce valence using the Athena software package (version 0.9.20, Ravel and Newville, 2005). First, standard and unknown spectra were normalized so that the "pre-edge" and the "post-edge" heights yield an energy step of unity, thereby removing the concentration dependence of the absorption features. Background subtraction over the pre-edge energy region used a linear function regressed to raw spectra, and the post-edge region was regressed with a cubic polynomial. Visual inspection of the pre-edge and post-edge lines, with particular focus on spectral consistency of post-edge energies of normalized spectra, ensured the input parameters in Athena are optimal for normalization over the prescribed region.

The only high concentration Ce standard compound analyzed on the fluorescence detector was $\mathrm{CeSiO_4}$, and as such, this phase represents the only material that requires correction for over absorption (i.e., saturation effects related to resonant and non-resonant absorption about the Ce L_3 edge). Measured $\mathrm{CeSiO_4}$ spectra were corrected using the Fluo algorithm in Athena software (version 0.9.20, Ravel and Newville, 2005) which resulted in a slight increase in peak amplitude. Comparison of absorption-corrected and uncorrected $\mathrm{CeSiO_4}$ LCFs on Bishop Tuff zircons shows there is an average 6% change ($R^2 = 0.95$), indicating that while peak height attenuation may show some change during over absorption, the relative peak height of Ce^{4+} vs. Ce^{3+} compounds is by far the most important parameter for the LCF fitting