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3 Redox evolution of silicic magmas: insights from
4 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 (2x4 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 $\text{Ce}^{4+}/\Sigma\text{Ce}$, with core regions that range from ~0.4 to 0.6 $\text{Ce}^{4+}/\Sigma\text{Ce}$ (i.e., ~40-60 % Ce^{4+}), while zircon rims range from ~0.7 to 1.0 $\text{Ce}^{4+}/\Sigma\text{Ce}$ (i.e., ~70-100 % Ce^{4+}). Repeat analysis on an individual point suggest, on average, a $\text{Ce}^{4+}/\Sigma\text{Ce}$ 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 $\text{Ce}^{4+}/\Sigma\text{Ce}$ 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 coupled with XANES spectra for Bishop Tuff samples reveal that different sectors yield notably different $\text{Ce}^{4+}/\Sigma\text{Ce}$, 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 $\text{Ce}^{4+}/\Sigma\text{Ce}$. 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_{O_2}), 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, 1990; 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_{O_2} -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 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 Ce/Ce^* (the normalized excess of Ce when compared to neighboring rare earth elements La and Pr; i.e., $[Ce]_N/\sqrt{La_N \times Pr_N}$) 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, 1992; Thomas et al., 2002).

The use of zircon as an f_{O_2} 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_{O_2} 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_{O_2} or disequilibrium partitioning cannot be ruled out, a large component of the accuracy of this f_{O_2} 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; Takahashi et al., 2000b; Berry et al., 2004; Berry et al., 2008; King et al., 2013). In principle, f_{O_2} 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 meters from x-ray source. The x-ray beam was focused using Kirkpatrick-Baez silicon mirrors onto an optically fluorescent standard 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 ($V^0 - 5465 \text{ eV}$) 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: CeSiO₄; 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" height 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 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 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 CeSiO_4 LCFs on Bishop Tuff zircons show 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 technique. Efforts were also made to correct for over absorption on Bishop zircons, despite very low Ce concentrations (20-100 ppm). Comparison of LCF data from absorption corrected and uncorrected Bishop Tuff zircons, yield virtually identical results and is therefore not considered further (i.e., <0.1% change in calculated Ce^{4+}).

The normalized spectral data were reduced in two general ways to calculate Ce valence. The first method used peak fitting with multiple Lorentzian lines to model spectral features. This approach is advantageous because it ascribes electron transitions

of valence orbitals to absorption energies in the XANES region, thereby proposing a physical explanation for the absorption features observed (Soldatov et al., 1994). Depending on the model used, this method may have numerous free parameters that can be varied to fit the unknown spectra. The second method involved the use of a linear combination of standard compounds of known valence. For this method, standard Ce valence end-members are mixed in the XANES fitting region and then combined to model unknown spectra. The XANES fitting region ranges from -20 eV to +30 eV where the reference energy is the Ce L_3 edge (5723 eV). This method is advantageous because natural Ce valence end-member spectra are used to model Ce valence in unknowns, and, in principle, the fitting method is simpler because there is only one free parameter. The spectra were reduced using both methods (a comparison can be found in the supplementary information); the results and discussion incorporate only the linear combination method (e.g., King et al., 2013). This technique was chosen because it is the simpler of the two possibilities and involves the fewest free parameters (and therefore the fewest assumptions) for the fitting procedure.

2.3 Valence standard selection for linear combination fitting

The linear combination method requires trivalent and tetravalent end-member standard spectra to calculate $\text{Ce}^{4+}/\Sigma\text{Ce}$ of unknowns; the candidates for this study are found in Figure 1. The Ce^{3+} standards display a pronounced pre-edge at 5727.7 eV, corresponding to the $2p\text{-}5d\text{ }^04f^1$ transition (Fig. 1a). The XANES peak height intensity in the normalized absorption spectra from Ce^{3+} compounds varies from 3.46 to 5.14 normalized units across the standards used here (e.g., CeCl_3 vs. CePO_4). This

demonstrates the necessity for appropriate standards when calculating valence ratios for linear combination fitting. Here, $\text{Ce}^{3+}\text{PO}_4$ was chosen to model Ce^{3+} in zircon because P is hypothesized (albeit somewhat speculatively) to be a dominant mechanism of Y^{3+} , Sc^{3+} , and REE^{3+} incorporation into zircon (e.g., Hoskin and Schaltegger, 2003).

Spectra from tetravalent Ce compounds show features dominated by absorption white lines at ~ 5732 and ~ 5739 eV (Bianconi et al., 1987; Soldatov et al., 1994; Takahashi et al., 2000a,b), and exist at higher energies than the $\text{Ce}^{3+} L_3$ white line. These respective absorption features correspond to the $2p-d^0 4f^0$ and $2p-5d^0 4f^0 \underline{L}$ energy transitions, where, $\underline{L}$ represents an energy transition involving a neighboring ligand hole (i.e., where an electron is transferred from an oxygen $2p$ shell to the Ce $4f$ shell). Previous studies also demonstrate that the relative intensity of the two Ce^{4+} XANES features may vary as a function of crystal structure (Bianconi et al., 1987); for example, see CeO_2 vs. $\text{Ce}(\text{SO}_4)_2$ in Figure 1b. The Ce^{4+} compound CeSiO_4 explored here yields a spectrum very similar to other reported tetravalent cerium compounds (Bianconi et al., 1987; Soldatov et al., 1994; Takahashi et al., 2000a,b) in that two dominant absorption features are seen at 5731.7 and 5739.0 eV (Fig. 1). This compound was ultimately chosen to model the spectra of unknowns because Schlüter et al. (2009) demonstrated that CeSiO_4 is isostructural with zircon.

2.4 Electron microprobe and LA-ICP-MS microanalysis.

Because it has been suggested that radiation damage alters primary Ce valence, U and Th contents were measured for Bishop Tuff zircons with the Cameca SX100 electron microprobe at Rensselaer Polytechnic Institute with a focused beam. X-rays were

simultaneously counted from U M_α and Th M_α using four PET spectrometers (two for each element). The beam current ranged from 20 to 60 nA, with the count times adjusted for the different currents such that the limits of detection were ~230 and ~200 ppm for Th and U, respectively. Cathodoluminescence imaging was conducted with a Gatan monoCL3 attached to the SX100 electron microprobe with a 15 kV accelerating voltage, a beam current of 5-10 nA, and a focused beam. Zircons were then analyzed with the RPI laser-ablation ICP-MS with the specific goal of obtaining Ce concentrations, Ce anomalies and Ti concentrations. This system consists of a Bruker 820-MS (formerly Varian) quadrupole mass spectrometer outfitted with a Photon Machines 193 nm excimer laser. All data were reduced using the Iolite v2.3 software package (Woodhead et al. 2007; Paton et al., 2010). A laser spot size of 30 μm was used with a mass table consisting of ^{29}Si , ^{49}Ti , ^{57}Fe , ^{91}Zr , ^{139}La , ^{140}Ce , and ^{141}Pr . The fluence ranged from 5.6-9 J/cm^2 with the laser pulse rate set at 10 Hz. A He carrier gas, with a flow rate of 0.7 liters per minute, was used in the sample chamber. Dwell times for individual masses were 50, 400, 100, 100, 1000, 100, and 400 ms for ^{29}Si , ^{49}Ti , ^{57}Fe , ^{91}Zr , ^{139}La , ^{140}Ce , and ^{141}Pr respectively. Analytical locations were first prioritized on the basis of lack of inclusions, as judged from backscattered-electron and reflected- and transmitted-light imagery. The second priority was to select grain regions that corresponded to the analytical locations of XANES measurements. Laser ablation occurred for ~25 of the total 100-120 second sampling time, and detection limits for Ti, Fe, La, Ce, Pr were ~0.5, 4, 0.002, 0.007, and 0.003 ppm, respectively. Silicon-29 was used as an internal standard, and concentrations were standardized against NIST612 glass (Pearce et al., 2007). Intermittent analyses were made on a chip of a zircon grain from the Kuehl Lake pegmatite, which is believed

to be from the same locality as the well-studied zircon standard 91500 (Wiedenbeck et al., 2004; Fu et al., 2008; Reid et al., 2011). The results from this grain compare very well to 91500 analyses reported in other studies (e.g., Reid et al. 2011); these data can be found in supplementary Table 2.

3 Results

Figure 2 shows the analytical locations of XANES measurements and subsequent LA-ICP-MS spots for the six zircons studied. Two XANES areas are represented on the CL image. The smaller $\sim 4\ \mu\text{m}$ spot corresponds to the surface region intersected by the incident x-ray beam. The x-rays also penetrate into the sample; this is represented by the $\sim 15\ \mu\text{m}$ long oval that reflects the 45° geometry of the incident beam. The approximate size of this oval was determined in two ways. First, the position and size of the x-ray beam during zircon analysis is aided by zircon fluorescence during data collection, and also provides a crude means for estimating the x-ray analytical volume in zircon for comparison with theoretical calculations. The dashed ovals in Figure 2 represent the maximum observed size of fluorescence during an analysis. Second, the inherent x-ray penetration depth in zircon that can be calculated from the mean density ($4.65\ \text{g/cm}^3$) and an x-ray energy that approximates the Ce L_3 edge (5723 eV). Models from Hephaestus software (version 0.8.056, Ravel and Newville, 2005) indicate an absorption length of $10.4\ \mu\text{m}$; i.e., the length at which about 63% of the incident photons have been absorbed, similar to the observed fluorescence of the x-ray beam at 45° .

3.1 Ce⁴⁺/ΣCe in zircon

A linear combination of Ce³⁺PO₄ and Ce⁴⁺SiO₄ spectra were used to model mixed-valance spectra for each unknown. Figure 3 shows an example of the data reduction procedure for unknown BT-03_line_06. Figure 3a represents the raw unreduced spectrum without normalization of the pre- and post edge (the regions of normalization are indicated on the figure). The shaded regions in Figure 3b represent the pre-edge and post-edge counts region. The shaded regions were also used to normalize the intensity of the post-edge minus the pre-edge to one (e.g. Fig 3c). For each spectrum, the selection of these shaded regions remained broadly consistent during data reduction. In order to ensure proper normalization of spectra and to minimize the chi-squared (χ^2) distribution of the fit. The pre-edge region was fit using a linear function, with input parameters set at energies generally between -71 (± 4) and -21 (± 6) eV of the Ce L_3 edge (5723 eV). The post-edge region was normalized against a second order polynomial, using an energy range of +77 (± 20) and +185 (± 34) eV from the Ce edge. The pre- and post-edge normalization fitting parameters were selected at these energies across all measured spectra in order to ensure normalization produces overlapping and consistent spectra in both the XANES (the region of interest) and EXAFS region. Figure 3d shows the standard CePO₄ and CeSiO₄ spectra that are linearly combined to yield the model spectrum for the unknown; in this case, the mixed-valence model spectrum is 64% Ce⁴⁺. All data reduced in this fashion are summarized in Table 1 where the pre- and post-edge average counts before normalization, Ce⁴⁺/ΣCe values, and χ^2 distributions are reported. Cerium concentrations based on the difference in unnormalized post- and pre-edge x-ray counts are also reported; section 3.2 and 3.3 discuss this calculation in detail.

306 The results indicate that zircon $\text{Ce}^{4+}/\Sigma\text{Ce}$ ranges from ~ 0.4 to 1 ± 0.05 [i.e., $\sim 40\%$
307 to $100\% \text{Ce}^{4+}$], and potential sources of errors are were investigated in three ways. The
308 first involves a comparison of replicate analyses on the exact same spot of Bishop Tuff
309 zircons. The data reduction procedure was conducted for each spectra; a comparison of
310 the results resulted in calculated valence differences of $\sim 1\text{-}5\%$. The second involves
311 multiple analyses of synthetic zircons with ~ 12 and 1400 ppm Ce from similar grain
312 locations, followed by a comparison of the reproducibility of replicate analysis of the
313 same grain location. Note that this reproducibly test is essentially identical to the first; it
314 was conducted because the Ce concentrations of experimental samples can be controlled.
315 The synthetic zircon with only 12 ppm of Ce is considered a more extreme case because
316 the natural samples explored here typically have 40 ppm Ce or more (but see BT-06).
317 Valence reproducibility for the synthetic samples was on the order of 5% (2σ). And
318 finally, because zircon is anisotropic and the incident x-ray beam is polarized, the spectra
319 of single crystals might vary as a function of grain orientation (Tailby et al., 2011a).
320 Since the BT grains are demonstrably heterogeneous, a large ($\sim 1 \times 4$ mm) synthetic flux-
321 grown zircon (after the technique described in Hanchar et al., 2001) was chosen for this
322 test. This sample was chosen because it offers the best opportunity to replicate the same
323 spot location during grain rotations, and this grain was found to be homogenous in Ce
324 valence after systematic valence traverses across the grain. In addition, due to its size,
325 this grain was easy to orientate along a crystallographic axis, and Ce concentrations in
326 this flux-formed grain were broadly equivalent, albeit higher than BT grains (see Table
327 1). Figure 4 shows the results of a series of 45° rotations; relatively modest changes in
328 the spectra do suggest a small orientation effect, though the calculated $\% \text{Ce}^{4+}$ 2 sigma

standard deviation for all rotations is 2%. Given that spot to spot reproducibility is on the order of ~5%, there is no evidence to support the premise that grain orientation influences the recorded valence measurements, and this is not considered further. These three tests provide the rationale for the ~5% (2σ) spot to spot reproducibility (internal error) reported in Table 1.

The χ^2 values are, on average ~2 (Table 1; a larger residual in the fit corresponds to a higher χ^2). Given the low concentration of Ce in zircon and the intrinsic noise this introduces to the spectra, this χ^2 suggests that standard compounds are appropriate for this study. The linear combination fit results also show there is no systematic fitting error; χ^2 does not correlate with $\text{Ce}^{4+}/\Sigma\text{Ce}$, suggesting that any error in this technique is intrinsic to the choice of standards. In other words, the choice of standards may result in under/overestimation of $\text{Ce}^{4+}/\Sigma\text{Ce}$ if standard intensity is too high or low or if valence mixing is not linear, but this does not cause any systematic error intrinsic to the fitting technique as a function of $\text{Ce}^{4+}/\Sigma\text{Ce}$. While future changes in the choice of standards may improve the quality of the linear combination fit (influencing the external error), it is unlikely that qualitative trends in Ce valence reported here will change because of the small internal errors observed here.

As shown in the transmitted light (TL) and CL images (Fig. 2) there are numerous inclusions in zircon, most notably apatite. Apatite XANES analyses were used in an attempt to determine Ce valence, and characterize the x-ray signature or intensity from the mineral. Figure 4 presents Ce^{4+} vs. the average counts, which correlates with concentration (post-edge - pre-edge e.g.; see Fig. 3a). Solid diamonds in Figure 4 represent analyses of apatite inclusions; due to the small size, the apatite inclusions

include Ce valence contribution from the host zircon, and are therefore not considered "clean" analyses. High counts from apatite-bearing regions, however, are consistent with the general expectation that apatites contain higher Ce contents than zircon (Watson and Green, 1981; Trail et al., 2012). The zircon array seen on the left of the graph shows analytical spots from domains that are free of any detectable signal from apatite inclusions (Fig. 4).

3.2 LA-ICP-MS results

Light-REE chondrite normalized data are presented in Table 2 for the annotated analytical spots of the transmitted light image; the trace element data can be found in supplementary Table 2. Cerium anomalies ($Ce_n/\sqrt{La_n \times Pr_n}$) range from ~20 to 460 (average = 64) and the calculated oxygen fugacity from data presented here is ~ FMQ+2.4 (Trail et al., 2011, 2012), with an average crystallization temperature of 706 ± 66 °C (2σ) (assuming a uniform titania activity of 0.53; Thomas et al. 2010). Temperatures are in agreement with the results of Watson et al. (2006) and Reid et al. (2011) who analyzed zircons by ion microprobe from the same mineral separates (733 ± 28 and 711 ± 28 °C, respectively). Transmitted light images are annotated with LA-ICP-MS spot locations; an 'X' indicates that an inclusion was encountered during ablation, and is therefore not considered further (Fig. 2).

3.3 Estimating Ce concentration of XANES analytical locations.

During the synchrotron session, no *a priori* attempt was made to correlate the post-edge minus the "background" pre-edge counts of XANES measurements with Ce

concentration. In principle, such correlations are possible from x-ray counts, if samples of known Ce contents are also analyzed by XANES. Since the working distance of the fluorescence detector remained fixed throughout the analytical session, the counts above background from the absorption event are broadly comparable, and can be utilized to estimate a concentration with an independent concentration constraint. The LA-ICP-MS data collected after the synchrotron session were used for this purpose; XANES analyses that fall within the $\sim 30\ \mu\text{m}$ ablated regions were pooled, averaged, and plotted against the calculated concentration. Even though the ablated analytical volume exceeds that of the XANES measurements, the average counts above background and the ppm Ce obtained by LA-ICP-MS yield a good correlation (Fig. 6). The data were fit to a linear equation, forced through the origin (the fit intersects the origin within error even without this constraint), and the result is used to estimate the Ce concentrations of the other XANES data that lacked correlative trace element measurements. While this is only an estimate of the true concentration, it is utilized in the discussion to explore trends in the data.

4 Discussion

A main impetus for undertaking this study was to explore whether Ce XANES spectra from zircon can be utilized to estimate the redox state and evolution of a silicic melt. Valence measurements of glasses offer a snapshot of melt oxidation state but minerals that incorporate polyvalent elements during crystallization offer an opportunity to investigate the f_{O_2} evolution over the time interval of crystal growth. While an experimental calibration does not exist in which a direct measurement of Ce^{4+} in zircon has been determined as a function of oxygen fugacity, in principle, higher $\text{Ce}^{4+}/\Sigma\text{Ce}$

value should reflect more oxidizing conditions; visual inspection of the normalized spectra for BT-03_line [spots 01 to 08] show a very clear (qualitative) trend towards more oxidizing conditions from core to rim (Fig. 7; see end-member standards in Figure 1 for comparison).

Quantitatively, four zircons (BT-02 [spots 01 to 03], BT-03_line [spots 01 to 08], BT-04 [spots 01 to 03]; BT-05 [spots 01 to 03]; Table 1) were analyzed from crystal core to rim within a common sector (sectoral variations in $\text{Ce}^{4+}/\Sigma\text{Ce}$ are discussed in section 4.4). Sectors in BT-06, which also has the largest aspect ratio of zircons explored here, were ambiguous and are therefore not considered here. Core-to-rim Ce concentration and $\text{Ce}^{4+}/\Sigma\text{Ce}$ variation are shown in Figures 8a,b. These grains broadly trend from higher Ce core contents (~70 ppm), to lower Ce contents near the rim (~30-50 ppm), which may be related to trace element depletion of the melt due to crystallization of LREE-bearing phases. Apatite and allanite, for example, are also present in the Bishop Tuff, and they would have contributed to melt depletion of REEs. The assimilation of less evolved material (with lower Ce contents) could also explain this observation (Simon et al. 2014). The exception is BT-05, which has Ce contents that decrease from 40 ppm to 24 ppm; if trace element depletion of the melt is responsible for the monotonic decrease in Ce contents, from core to rim, then BT-05 might have nucleated at a later time relative to the other three grains. A detailed traverse on zircon crystal BT-03 reveals that the proportion of Ce^{4+} progressively increases from ~40% in the core to ~75% near the rim of the crystal. In zircon crystal BT-04, 44% of the Ce analyzed in core is Ce^{4+} , whereas the rim is 98%. If zircon rims are assumed to be the best representation of the melt state prior to eruption, then the simplest interpretation of these data is that the melt became

progressively more oxidized from the time of zircon saturation up to the point of eruption. Note that in the case of BT-05 the grain yields a $\text{Ce}^{4+}/\Sigma\text{Ce}$ interior domain values of 0.97 to 0.98 and the rim is 1.00, but this considered to be unresolvable given the estimated errors on the measurements. For comparison, the two oxide $T-f_{\text{O}_2}$ data of Hildreth, (1977) and Hildreth and Wilson, (2007) indicate that the melt became progressively more reduced (relative to an oxygen fugacity buffer curve) at lower temperatures (Fig. 8c). These data do not agree with the qualitative $\text{Ce}^{4+}/\Sigma\text{Ce}$ trend observed for the zircons, and therefore some explanation is required.

Recently, Ghiorso and Gualda (2013) conducted a thermodynamic analysis to test f_{O_2} - T and [titania activity]- T systematics of the Fe-Ti oxides. They estimated T and f_{O_2} from the compositions of 729 volcanic Fe-Ti oxide pairs in compositions from dacitic to rhyolitic, including the Bishop Tuff. These workers concluded that rocks containing Fe-Ti oxides with negative $T-f_{\text{O}_2}$ trends (i.e., Fe-Ti oxide data that trend towards more oxidizing conditions relative to an f_{O_2} buffer curve with lower temperature) are consistent with crystallization driving compositions towards higher f_{O_2} at lower temperatures. In other words, rocks that contain Fe-Ti oxides with negative $T-f_{\text{O}_2}$ trends have oxide compositions that agree with theoretical melt activity-composition relations, which suggests that the Fe-Ti oxides were in equilibrium with the melt, and therefore the oxides record intensive parameters of the melt. In contrast, volcanic systems with Fe-Ti oxides that have *positive* $T-f_{\text{O}_2}$ trends (i.e., Fe-Ti oxide data that trend towards more reducing conditions relative to an f_{O_2} buffer curve with lower temperature) □ like Figure 8c □ are inconsistent with thermodynamic expectations based on plausible melt activity-composition relations. The positively correlated $T-f_{\text{O}_2}$ trends observed for Bishop Tuff

Fe-Ti oxides are opposite to theoretical expectations and support previous interpretations of open system behavior or non-contemporaneous/disequilibrium growth of the two oxide pairs (Lindsley et al., 1990; Ghiorso and Evans, 2008; Ghiorso and Gualda, 2013).

Ghiorso and Gualda (2013) concluded that the Fe-Ti oxides in volcanic systems with positively sloping $T-f_{O_2}$ trends probably do not reflect pre-eruptive conditions. In support of Ghiorso and Gualda's (2013) conclusions, the core-to-rim increase in $Ce^{4+}/\Sigma Ce$ of Bishop Tuff zircons suggests that f_{O_2} of the Bishop magmatic system increased during zircon growth. This result is not completely unexpected because other studies have shown that T and f_{O_2} estimates based the Fe-Ti oxides of volcanic rocks are sometimes not accurate (Lindsley et al., 1990; Frost and Lindsley, 1991; Frost and Lindsley, 1992; Lindsley et al., 1991; Ghiorso and Sack, 1991; Ghiorso and Evans, 2008; Thomas and Watson, 2012; Ghiorso and Gualda, 2013). While the XANES data are consistent with progressively more oxidizing conditions as zircon crystallization proceeds, a suite of other possibilities needs to be explored (sec. 4.1 - 4.5).

4.1 Temperature effect of measured $Ce^{4+}/\Sigma Ce$ of zircon

Trail et al. (2011, 2012) showed that zircon Ce anomalies of synthetic f_{O_2} -buffered experiments increase with decreasing temperature, which was attributed to a relative increase in compatibility of Ce^{4+} relative to other trivalent LREEs as a function of $1/T$, implying that zircon $Ce^{4+}/\Sigma Ce$ varies with oxygen fugacity *and* temperature. In other words, zircon may incorporate a progressively larger percentage of Ce^{4+} during cooling, even if cooling occurs along a fixed f_{O_2} buffer curve such as Ni-NiO. A clear decoupling of changes in temperature/ f_{O_2} , and the resulting effect of Ce valence in zircon

cannot be evaluated further until zircon/melt partitioning of Ce^{4+} as a function of temperature is well established; even at an f_{O_2} greater than that imposed by the magnetite-hematite buffer, a large percentage of the Ce^{3+} is still present in hydrous silicic melts (Trail et al., 2012). Moreover, changes in the *melt* $\text{Ce}^{4+}/\Sigma\text{Ce}$ vs. T along a constant f_{O_2} buffer curve (e.g. Ni-NiO), cannot be ruled out; increases in $\text{Ce}^{4+}/\Sigma\text{Ce}$ at lower temperatures have been reported in silicate melts (Paul and Douglas, 1965). That said, zircon data reported here record a large range of Ce valence values, ranging from ~0.4 to 1 $\text{Ce}^{4+}/\Sigma\text{Ce}$, even though zircon crystallization probably occurred over a relatively restricted temperature range of ~70 °C or less (Watson and Harrison, 1983; Ferry and Watson, 2007; Boehnke et al., 2013). This is also reinforced by the relatively restricted LA-ICP-MS Ti-in-zircon crystallization temperature reported here (706 ± 66 °C, 2σ) and the 711 ± 28 °C (2σ) temperature calculated from ion microprobe data originally presented by Reid et al. (2011).

4.2 Inherited cores and secular changes in $\text{Ce}^{4+}/\Sigma\text{Ce}$ of zircon.

The dissolution of zircon in felsic magmas is believed to be relatively sluggish, and the presence of inherited cores in silicic melts well established (e.g., Williams, 1992; Vavra et al., 1996; Watson, 1996). In other words, if core to rim analytical traverses include some volume of inherited core and overgrowth, then changes in Ce valence may not be related to the f_{O_2} evolution in the Bishop melt, but instead Ce valence differences between inherited and primary crystallization domains that exist within a single zircon grain. The CL images of BT-03 and BT-04 reveal a small central domain that could be an inherited core (Figure 2).

In a TIMS study of Bishop Tuff zircons conducted by Crowley et al. (2007), however, it was noted that there is no age relationship between the presence of central "core" domains and the absence of these domains, arguing against the ubiquitous presence of inherited zircon cores. These data were used to conclude that zircons crystallized at 767.1 ka over a very restricted time interval (0.9 ka), with the exception of two grains that yield ages older by 6 and 12 ka that may be related to the pre-eruptive magma residence time. While the accuracy of these results have been the subject of debate (e.g, Simon et al. 2014), this is in large part due to corrections associated with zircon U-Th disequilibrium of the entire sample set. In other words, a systematic shift of these ages by ~90 ka does not drastically change the restricted time interval of zircon growth reported in Crowley et al. (2007).

On the other hand, ion microprobe data yield two separate age peaks; one age peak is interpreted to represent zircon growth immediately prior to the eruption, and the other is suggested to correspond to the age of magma residence (Simon and Reid, 2005). The difference between the two age peaks range from 10s of thousands to ~100 thousand years, depending on the eruptive sequence (e.g. Simon and Reid, 2005), although it is rare to find both ages represented in a single crystal (e.g. Simon et al. 2014). While the exact timing of the magma residence is still unresolved, available data suggest that inherited cores are unlikely for zircons investigated here or for those of the other BT eruptive sequences.

4.3 Radiation damage and valence alteration in zircon

Based on the analysis of zircon samples from two Cretaceous granitoid rocks, Takahashi et al. (2003) speculated that radioactive decay of U (and Th) in zircon was responsible for the diminished abundance of Ce^{4+} when compared to estimates made based on the Ce anomaly. A zircon aliquot (~50 grains) from the Yamanaka granodiorite (112.0 ± 5.6 Ma) with Ce, U, and Th contents of 99.1, 142, and 125 ppm, respectively were analyzed by XANES using a beam size on the order of 1×1 mm. Assuming no inclusions were analyzed, only 18% of the Ce in the zircon was tetravalent. The Habu granodiorite (85.9 ± 1.7 Ma) zircon aliquot had Ce, U, and Th concentrations of 28.6, 641, and 216 ppm, respectively. However, in this sample 91% of the Ce was tetravalent. While the Yamanaka granodiorite zircons are older, the crystals also contain Ce contents lower by a factor of ~3 and U contents higher by a factor of ~4.5. If radiation damage is the dominant factor influencing the abundance of trivalent Ce in zircon, than the Habu granodiorite should be more reduced than Yamanaka, but the opposite is observed. Thus, these data are not internally constant with a simple mechanism of Ce^{4+} reduction caused by radiation damage.

That said, the possibility of radiation damage and valence alteration in zircon is returned to here for the much younger Bishop Tuff samples (767.1 ka) in part because these samples have been found to have higher U and Th contents (e.g., Reid et al. 2011). Similar to the observation of Takahashi et al. (2003), Ce^{4+} percentages calculated based on Ce anomalies (>90%; Table 2) exceeds almost all the direct valence measurements made by XANES. Thorium and U contents were collected by electron microprobe for 26 locations proximal to Ce valence measurements. Uranium concentrations range from the limit of detection (~200 ppm) to 5300 ppm, and Th contents range from 300 to 5800 ppm

(see supplementary Table 2). Importantly, there is no relationship whatsoever between radiation dosage (derived from U and Th contents) and the Ce valence of correlative grain locations. This observation argues against radiation damage as the dominant source of Ce^{3+} in the zircon. For comparison, time integrated dosages for the BT samples are (on average) about 2 orders of magnitude less than the Habu and Yamanaka zircon samples. And finally, the acicular BT-06 contained no detectable U but yielded a significant component of Ce^{3+} percentages (28% to 48%, $n = 9$). The mismatch between Ce anomaly-based Ce^{4+} calculations and the XANES-based Ce^{4+} calculations in zircon is broadly consistent with recent results; there is strong evidence that the lattice strain model most likely overestimates the partitioning of Ce^{4+} into zircon when compared to XANES measurements (Burnham and Berry, 2014).

4.4 $\text{Ce}^{4+}/\Sigma\text{Ce}$ of different zircon sectors

Up until now, it has been implicitly assumed that REE partitioning in Bishop Tuff zircons occurred under equilibrium conditions. While this may be true for some elements, CL images presented here reveal that some zircons are sector-zoned and display bright and dark sectors; this phenomenon is caused by differences in the compatibility of one or more elements in the near-surface regions of different growth facets (e.g., Watson and Liang, 1995). Discussion of disequilibrium phenomena of crystal in the BT is not new; for instance, Evans and Bachmann (2013) discovered that orthopyroxene and clinopyroxene are not in equilibrium with other Fe- and Mg-bearing phases. As the trivalent REEs (Dy and Pr in particular; Hancher et al., 2001) are generally attributed to the CL-active signal observed in most zircons, the differences in "brightness" is most likely due to differences in rare earth element contents. This also

confirmed by and electron microprobe x-ray maps of a Bishop zircon (e.g., see supplementary Figure 2).

While elemental concentration variation across sectors with different growth surfaces is well-known and documented in a number of minerals, there has been no demonstration that this phenomenon extends to a decoupling of polyvalent element incorporation between the different sectors. Rakovan et al. (2001) speculated that Eu^{2+} and Eu^{3+} decouple among sectors in apatite based on REE concentrations, but XANES measurements from this study were made on powdered samples, meaning that sectoral information was not preserved. This possibility is explored here for Ce in zircon; Figure 9 shows traces of contemporaneous growth regions across different sectors that also contain XANES analyses. Grains BT-02 and BT-04 demonstrate that sectors record different Ce valence from contemporaneous growth bands of adjacent sectors. The $\text{Ce}^{4+}/\square \text{Ce}$ values of zircon grain BT-02 changes from 0.46 to 0.78, and BT-04 changes from 0.49 to 0.65 from the bright to the dark sector, respectively. In addition, XANES analyses of BT-03 were obtained for opposite sectors of crystallographically equivalent surfaces; these data yield virtually identical $\text{Ce}^{4+}/\square \text{Ce}$ values (0.73, 0.77 vs. 0.76). Both of these observations are consistent with the hypothesis that Ce^{4+} and Ce^{3+} can be fractionated across sectors due to near-surface kinetic control during growth, which means that some measurements of $\text{Ce}^{4+}/\square \text{Ce}$ zircon values will be influenced by the mineral growth surface.

4.5 Melt composition

It is well known that major elements like $\text{Fe}^{3+}/\text{Fe}^{2+}$ vary as a function of melt redox state *and* melt composition (e.g., Sack et al., 1980; Carmichael and Ghiorso, 1990), and the same appears to be generally true of polyvalent trace elements such as Ce (Paul and Douglas, 1965; Schreiber et al., 1980; Thomas et al., 2002; Trail et al., 2012; Burnham and Berry, 2014). Chemical analyses of melt inclusions indicate that the Bishop Tuff is compositionally-zoned, especially for minor, trace element, and Hf/Nd/Sr isotopic ratios (Hildreth and Wilson, 2007; Simon et al., 2014). It is the major elements, however, that are expected to influence the redox equilibria of polyvalent elements at a constant oxygen fugacity (e.g., Schreiber et al., 1994). The BT consists predominantly of ash and pumice clasts of high silica rhyolite (~73-79%), but there are very rare pumice clasts that extend to a compositional range down to dacite/andesite, with SiO_2 contents near 57% (Hildreth and Wilson, 2007). The major element compositions of quartz melt inclusions from diverse units are very similar, with SiO_2 contents that typically range from 75 to 79% (Anderson et al., 2000; Schmitt and Simon 2004). If the above data are broadly assumed to be representative, then the majority of BT zircon likely saturated and grew in melts with ~73-79% SiO_2 (e.g., zircons do not saturate in mafic melts; Boehnke et al. 2013). While this is broadly restricted, it is not known at this time how ~5% changes in SiO_2 content (or other major elements) could change Ce valence at a constant oxygen fugacity.

5. Concluding remarks and observations

The high spatial resolution XANES technique makes it ideally suited for interrogating changes in element redox state during mineral growth. This technique has

great potential in future studies where glasses are absent or the primary redox equilibria of glass is suspect due to post-growth alteration; the redox state of glasses may even be altered during the XANES measurements themselves (e.g., Ferreira et al., 2013). New studies also suggest that, under certain circumstances, the two-oxide f_{O_2} sensor may not record primary redox equilibria of a magma, but instead may be caused by kinetic processes that occur during the quench (Ghiorso and Gualda, 2013). Given that zircon is among the most robust minerals and recorders of melt evolution, XANES measurements – conducted to investigate the speciation of Ce in zircon – indicate that: (i) $Ce^{4+}/\square Ce$ ranges from 0.40 to nearly 1(± 0.05); and (ii) zircon core to rim $Ce^{4+}/\square Ce$ values broadly trend to higher values. Notwithstanding the interpretations explored in the discussion, the most reasonable explanation for these data at this time is that the Bishop Tuff magma actually did become more oxidizing during zircon crystallization. Because zircons record mixed Ce valence in modern terrestrial settings, this opens up the possibility that such ratios may be correlated with oxygen fugacity. Results presented here also indicate that different zircon growth sectors, or more specifically domains within a crystal that grew at the same time, may record different $Ce^{4+}/\square Ce$ values. While this does imply that the kinetics of zircon growth influence the measured valence, it also suggests that zircon is capable of preserving Ce valence under certain conditions. If the observed $Ce^{4+}/\square Ce$ values were imprinted after zircon growth, the observed inter-sectoral variation becomes difficult to explain. Put another way, the variation in $Ce^{4+}/\square Ce$ implies that the valence state of Ce is not readily equilibrated or reset throughout the crystal, so long as the structure of zircon can be assumed to be broadly similar from sector to sector.

These results also lay the preliminary groundwork for interpretation of more complex data from the geological record that could be used to understand the redox evolution of modern and ancient magmas in great detail within a single crystal (Tailby et al., 2011b). However, it should be emphasized that only 6 grains were analyzed from a single pumice sample, which represents a very small sample set given the chemical diversity observed in BT samples. Future studies may take advantage of *both* the elemental and valence evolution that were observed here, as these changes in Ce concentration/valence could yield new information about the evolving melt and oxygen fugacity prior to eruption. If Ce valence were combined with high precision age measurements, this may enable a direct assessment of secular changes in magma oxidation state that occur over small time intervals during magma residence or just prior to eruption.

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Figure captions

Figure 1: Normalized Ce L_3 edge x-ray absorption spectra for Ce standard compounds of known valence. The exact normalization procedure for standards and unknowns is presented in sec. 3.1 and Figure 3. Normalized spectra were vertically offset by 0.5 units for easier visual comparison. All data were collected in this study, with the exception of $\text{Ce}(\text{SO}_4)_2$, which is after Bianconi et al. (1987). Standard measurements were made in transmission mode, with the exception of $\text{Ce}^{4+}\text{SiO}_4$ (idealized formula), which was measured in fluorescence mode. **(a)** Standard Ce^{3+} compounds. Note that Ce^{3+} standards display a single, pronounced XANES feature at 5727.7 eV corresponding to the $2p-4f^15d$ transition. CePO_4 was chosen as the Ce^{3+} end member, where Ce is in 9-fold coordination. **(b)** Standard Ce^{4+} compounds. The Ce^{4+} standards display doublets in the

XANES region at 5731.7 and 5739 eV, which correspond to $2p-4f^05d^0L$ and $2p-4f^05d^0$ transitions respectively. $CeSiO_4$ was chosen as the Ce^{4+} end member, where Ce is believed to be in 10-fold coordination because of its similarity to zircon.

Figure 2. Cathodoluminescence (CL) and transmitted light images of analyzed zircon grains (scale bars are 50 μm). Ovals in the CL images represent the maximum luminescence spot size from XANES analysis ($\sim 15 \mu m$; see supplementary Figure 3), while the smaller circle represents the estimated x-ray spot size at the crystal surface ($\sim 2 \times 4 \mu m$). Numerical values adjacent to XANES analytical ovals indicate the analytical spot number (Table 1). Solid circles and squares in transmitted light images represent the analytical location of LA-ICP-MS spots (Table 2).

Figure 3: Measured and model x-ray absorption spectra for zircon analysis BT-03_line_06. **(a)** Raw spectrum, prior to pre- and post edge normalization. **(b)** Raw data after pre- and post edge normalization, but prior to normalization of the intensity. The pre- and post-edge count average are reported for every spectra in Table 1. **(c)** Normalized XANES spectrum; note also the change in horizontal scaling. **(d)** Model spectrum produced from a linear combination of the two end-member Ce^{3+} and Ce^{4+} standard spectra (Fig. 1). The residual is the difference in the model spectrum subtracted from the normalized spectra in (b).

Figure 4: Orientation scans of a large $\sim 1 \times 4$ mm flux-grown zircon (Table 2; Flux-03). The rotation angle and the calculated Ce valence is given next to each spectrum. The

inset image shows the "rotation angle" of 0° , and also identifies the direction of the incident beam, which intersects the sample at 45° . Different orientations lead to changes in the calculated % Ce^{4+} of $<5\%$.

Figure 5: $\text{Ce}^{4+}/\square \text{Ce}$ verses average counts (post-edge – pre-edge; see Table 1) for Bishop zircons and apatite inclusions. $\text{Ce}^{4+}/\Sigma\text{Ce}$ was determined by linear combination fits of CeSiO_4 and CePO_4 . Open circles represent zircon analytical spots; the black diamonds represent apatite inclusion analytical spots, which represent a mixture of Ce valence from apatite and zircon. Zircon analysis carried out proximal to apatite inclusions are indicated in the enclosed dashed field. See section 3.1 for a discussion on error estimates.

Figure 6: Average XANES counts (post-edge – pre-edge) plotted against Ce contents of zircons, in ppm. The error bars (2σ) represents the standard deviations of pooled XANES analyses that are correlated to the same LA-ICP-MS spot, the latter of which has a lower spatial resolution. The error bars also propagate errors associated with changes in I_0 over the course of the analytical session. The plot and equation in this figure are used to estimate the concentrations of XANES spots analyzed on zircon grains that were not accessible by LA-ICP-MS. Note that this "calibration" will vary from session to session depending on x-ray flux, beam conditions, and proximity of the detector to the sample.

Figure 7. BT03 showing the normalized spectra of BTline01-08 (see Table 1) which were all collected at the same orientation; qualitative changes are clearly visible in the spectra, with a larger % Ce^{4+} near the rim.

Figure 8. Redox trends of the BT. **(a)** Zircon Ce contents (see Fig. 6 for calculation) and **(b)** $\text{Ce}^{4+}/\Sigma\text{Ce}$ of core to rim traverses showing that Ce is generally more oxidized near zircon rims. The data plotted are from individual zircon sectors because sectors belonging to different crystallographic faces are suspected to partition Ce^{3+} and Ce^{4+} differently (see sec 4.4. for details). **(c)** Temperature-oxygen fugacity (f_{O_2}) calculations of magnetite-ilmenite crystals from the Ig2E unit of the Bishop Tuff, after Hildreth (1977), and Hildreth and Wilson (2007). Oxide data indicate a decrease in oxygen fugacity with decreasing temperature. Data are shown with reference to common solid state oxygen buffers Ni-NiO (NNO) and $\text{FeSiO}_4\text{-Fe}_3\text{O}_4\text{-SiO}_2$ (FMQ) (O'Neill, 1987; O'Neill and Pownceby, 1993).

Figure 9: XANES analytical spots from common growth zones in sector-zoned zircons. The outlined regions, drawn in relation to XANES measurements, represent areas of contemporaneous growth and demonstrate that the zircon growth face can influence Ce valence measurements (BT-02, BT-04). BT-03 shows that opposing sectors with the same mineral growth face yield virtually identical Ce valence, further suggesting the results of BT-02, BT-04 are related to anisotropic surface decoupling of Ce^{3+} and Ce^{4+} . The concentrations reported here are estimated after Figure 6.

Figure 01

Figure 02

Figure 03

Figure 04

Figure 05

Figure 06

Figure 07

Figure 08

BT-02 (1) $\text{Ce}^{4+}/\Sigma\text{Ce} = 0.70$
(50 ppm Ce)

(5) $\text{Ce}^{4+}/\Sigma\text{Ce} = 0.46$;
(65 ppm Ce)

BT-03 (1) $\text{Ce}^{4+}/\Sigma\text{Ce} = 0.73$; (51 ppm Ce)
(2) $\text{Ce}^{4+}/\Sigma\text{Ce} = 0.77$; (51 ppm Ce)

(5) $\text{Ce}^{4+}/\Sigma\text{Ce} = 0.76$;
(63 ppm Ce)

BT-04

(5) $\text{Ce}^{4+}/\Sigma\text{Ce} = 0.49$;
(37 ppm Ce)

(6) $\text{Ce}^{4+}/\Sigma\text{Ce} = 0.65$; (77 ppm Ce)

Table 1: XANES data and calculated $\text{Ce}^{4+}/\Sigma\text{Ce}$, by linear combination.

Grain	Spot ^a	pre-edge counts (5650-5700 eV)	post-edge counts (5800- 5850 eV)	average counts (peak- bgd)	$\text{Ce}^{4+}/\Sigma\text{Ce}$	2σ	χ^2	[Ce] (ppm) ^b	[Ce] (ppm) est. ^c	Comments
BT-01	1	7.02E-04	5.20E-03	4.50E-03	0.78	0.05	1.41		50	
BT-01	2	7.03E-04	4.08E-03	3.38E-03	0.70	0.05	0.67		37	
BT-01	3	8.56E-04	5.36E-03	4.51E-03	0.76	0.01	1.08		50	
BT-01	4	8.42E-04	5.21E-03	4.37E-03	0.77	0.01	3.14		48	
BT-02	1	9.10E-04	5.46E-03	4.55E-03	0.70	0.05	1.02	57	50	RIM REGION
BT-02	2	9.17E-04	6.75E-03	5.83E-03	0.74	0.05	1.39	57	64	
BT-02	3	9.73E-04	7.39E-03	6.42E-03	0.58	0.05	0.94		71	CORE REGION
BT-02	4	1.32E-03	1.55E-02	1.42E-02	0.35	0.05	1.32		157	proximal to inclusion
BT-02	5	9.27E-04	6.82E-03	5.90E-03	0.46	0.05	1.08		65	
BT-03	1	8.81E-04	5.51E-03	4.63E-03	0.73	0.07	4.35		51	
BT-03	2	9.03E-04	5.52E-03	4.61E-03	0.78	0.07	2.39		51	
BT-03	3	7.28E-04	5.29E-03	4.56E-03	0.57	0.05	1.14		50	
BT-03	4	1.17E-03	8.31E-03	7.14E-03	0.67	0.05	1.62	83	79	
BT-03	5	8.62E-04	6.60E-03	5.74E-03	0.76	0.05	1.24	83	63	
BT-03	6	7.38E-04	5.33E-03	4.59E-03	0.72	0.05	1.10		51	
BT-03	inc	6.04E-03	1.19E-01	1.13E-01	0.40	0.05	1.85		1245	inclusion
BT-03_line	1	1.05E-03	5.84E-03	4.79E-03	0.76	0.05	1.06		53	RIM REGION
BT-03_line	2	9.29E-04	6.13E-03	5.20E-03	0.78	0.05	1.26		57	
BT-03_line	3	8.50E-04	6.23E-03	5.38E-03	0.77	0.05	1.82		59	
BT-03_line	4	8.90E-04	6.12E-03	5.23E-03	0.75	0.05	1.50		58	
BT-03_line	5	8.27E-04	5.83E-03	5.00E-03	0.72	0.05	1.08		55	
BT-03_line	6	7.37E-04	5.50E-03	4.76E-03	0.64	0.05	0.60	38	53	
BT-03_line	7	7.46E-04	5.33E-03	4.58E-03	0.55	0.05	0.85	38	51	
BT-03_line	8	8.26E-04	7.21E-03	6.38E-03	0.43	0.05	1.52	38	70	CORE REGION
BT-03_line	9	1.09E-03	1.33E-02	1.22E-02	0.44	0.05	2.55		134	proximal to inclusion
BT-03_line	10	1.54E-03	2.40E-02	2.25E-02	0.41	0.05	2.29		248	proximal to inclusion
BT-04	1	7.57E-04	3.36E-03	2.60E-03	0.98	0.05	4.84	37	29	RIM REGION
BT-04	2	7.75E-04	5.50E-03	4.72E-03	0.57	0.05	2.39	37	52	
BT-04	3	6.89E-04	6.66E-03	5.97E-03	0.44	0.05	0.96		66	CORE REGION
BT-04	4	7.44E-04	6.59E-03	5.85E-03	0.41	0.05	1.13		65	
BT-04	5	6.93E-04	4.04E-03	3.35E-03	0.49	0.05	1.27		37	
BT-04	6	8.30E-04	7.77E-03	6.94E-03	0.65	0.05	0.79		77	
BT-04	7	6.83E-04	5.94E-03	5.25E-03	0.52	0.05	0.96		58	