Guilherme A.R. Gualda¹, Ayla S. Pamukcu¹, Lily L. Claiborne¹, and Mark L. Rivers²,³
¹Department of Earth & Environmental Sciences, Vanderbilt University, Station B35-1805, Nashville, Tennessee 37235, USA
²Department of the Geophysical Sciences, University of Chicago, 5734 S. Ellis Avenue, Chicago, Illinois 60637, USA
³Center for Advanced Radiation Sources, University of Chicago, 9700 S. Cass Avenue, Argonne, Illinois 60439, USA

ABSTRACT

Accessory minerals preserve important records of the evolution of magmatic systems, but study of their textures and contact relations is hindered by the lack of suitable methods for characterization. We show here that differential absorption X-ray tomography can be used to yield three-dimensional maps of selected elements, particularly Zr and rare earth elements (REE), making it possible to qualitatively and quantitatively document the textures of zircon and REE minerals in situ and in three dimensions. We apply this method to pumice from the Peach Spring Tuff (Nevada, Arizona, California) and Mount St. Helens (Washington State) and present a few illustrative examples of the kinds of data that can be extracted using elemental and conventional tomographic data. Particularly when combined with compositional and age data, the ability to visualize and document accessory minerals in three dimensions and in textural context opens exciting new possibilities for the study of accessory minerals and the rocks that contain them.

INTRODUCTION

Textures of igneous rocks preserve invaluable information on the nucleation and growth history of crystals and bubbles from the melt, and therefore on the evolution of volcanic and plutonic magmatic systems (for reviews, see Marsh, 2007; Hersum and Marsh, 2007). While the qualitative study of igneous textures is at least as old as the optical microscope, quantitative investigation of igneous textures is a relatively recent development (e.g., Marsh, 1988, 1998; Cashman and Marsh, 1988; Cashman, 1988, 1993; Jerram et al., 1996, 2003; Jerram and Cheadle, 2000, among many others).

Much progress has been made in obtaining quantitative textural information from two-dimensional slices of rocks observed using optical and electron microscopy (e.g., Sahagian and Proussevitch, 1998; Higgins, 2000, 2006; Morgan and Jerram, 2006). However, employing techniques that allow direct imaging of materials in three dimensions is a highly preferable approach (for a review, see Jerram and Higgins, 2007), and X-ray tomography is now a mature technique that allows quantification of relevant textural parameters of rocks (e.g., Rivers et al., 1999; Stock, 1999, 2008, 2009; Ketcham and Carlson, 2001; Sutton et al., 2002; Ketcham, 2005a, 2005b; Gualda and Rivers, 2006; Jerram and Higgins, 2007; Baker et al., 2010).

Over the past several years, we have been using X-ray tomography to characterize pumice from the Bishop Tuff (Gualda et al., 2004; Gualda, 2007; Gualda and Anderson, 2007; Gualda and Ghiorso, 2007). Our goal is to better understand the crystallization history of the Bishop giant magma body, which fed the supereruption that formed the Long Valley Caldera ca. 760 ka (see Hildreth, 2004, for a review). Pumice is an ideal material to be studied using X-ray tomography, given that crystals are usually isolated from each other and surrounded by a porous matrix of vesiculated glass that yields significantly lower attenuation than crystals.

In the first part of this series (Gualda and Rivers, 2006), we utilized the shapes of large crystals and expected attenuation coefficients for the main phases present to successfully obtain quantitative textural information on six different phases in Bishop Tuff pumice clasts, i.e., Fe-Ti oxides (mostly magnetite), biotite, sanidine, quartz (plus minor plagioclase), glass, and vesicles. In that study, we were limited to crystals larger than ~35 µm due to the relatively large voxel sizes in the tomograms available (8.5 µm/voxel). By combining tomograms at four resolutions (spanning the range 2.5–17 µm/voxel), we are now able to quantify textures of crystals over two orders of magnitude in size (10–1000 µm), as demonstrated in Part 2 in Pamukcu and Gualda (2010), revealing significant information on the pre-eruptive and syn-eruptive evolution of the Bishop magma body (Gualda et al., 2007).

Despite these significant advances, the quantification of accessory phases using X-ray tomography has remained impractical. Accessory minerals (e.g., zircon, rare earth element [REE] bearing phases such as allanite and monazite,apatite) are important reservoirs of elements present in trace quantities in magmas that, despite their small size and relative scarcity, uniquely record the history of magmatic evolution. In this contribution we present a method that permits quantification of certain accessory phases, notably zircon and REE-rich phases such as allanite, chevkinite, and monazite. The method is based on the generation of three-dimensional (3D) elemental maps using differential absorption X-ray tomography (Flannery et al., 1987).

The method is limited to synchrotron-based systems in which monochromatic radiation can be selected, and takes advantage of the high spatial resolution achievable in these systems. We present here the principles of the method, as well as some examples of its application to pumice from the Peach Spring Tuff (Nevada, Arizona, California; Young and Brennan, 1974; Glazner et al., 1986; Nielson et al., 1990; Ferguson, 2008) and from Mount St Helens (Washington State; see Lipman and Mullineaux, 1981; Sherrod et al., 2008). The examples show that zircon and REE-rich phases such as allanite (žchevkinite) and titanite can be identified and quantified with relative ease. This allows not only the derivation of crystal size distributions, but also permits determination of textural and contact relationships between these and other phases present, opening new possibilities for the study of these accessories.
METHOD

X-ray tomograms are reconstructed from series of radiographs taken at varying angular positions. They consist of 3D maps of the linear attenuation coefficient, which depends upon the chemical composition and density of the volume element (i.e., voxel) (see Rivers et al., 1999; Sutton et al., 2002; Ketcham and Carlson, 2001; Stock, 1999, 2008, 2009). For a known chemical composition, density, and X-ray energy, the linear attenuation coefficient can be obtained from the mass attenuation coefficient for each constituent element. These mass attenuation coefficients are well known (Chantler et al., 2003).

Mass attenuation for any pure element is a generally smooth function of incident radiation energy, with significant discontinuities at very specific energies (Fig. 1; see Stock, 2009). The energies at which discontinuities occur, so called absorption edges, are the energies necessary to remove electrons in specific shells from the atom. Below the absorption edge (i.e., at energies lower than the transition), photons are not energetic enough to remove electrons in a particular shell; above the edge (i.e., at energies higher than the transition), however, electrons in this shell can be removed by incident photons, such that there is a significant increase in attenuation, causing the observed discontinuities (Stock, 2009). A similar behavior is observed for any chemical compound or mixture as the sum of the absorption edges of the various elements present in the substance (Fig. 2; see Stock, 2009).

Differential absorption tomography makes use of these discontinuities in attenuation to produce 3D elemental maps. Due to the smooth variations in attenuation with energy, if two

Figure 1. Variation of mass attenuation coefficient as a function of X-ray energy for selected elements relevant for silicic rocks. Note that mass attenuation coefficient decreases smoothly with increasing energy, except near absorption edges. Relevant absorption edges for the elements of interest are indicated. Note that absorption edges for Na K (1.07 keV), Mg K (1.31 keV), Al K (1.56 keV), and Si K (1.84 keV) occur at energies lower than the K K-edge. Data from Chantler et al. (2003).

Figure 2. Variation of mass attenuation coefficient as a function of X-ray energy for selected minerals (or end members) commonly present in silicic rocks. The mass attenuation for each phase is the combination of the effect of the various elements present in it. As such, phases will show large jumps in attenuation near the absorption edges of its major constituents (e.g., Zr in zircon, Ce in allanite, Fe in magnetite, Ca and Ti in titanite). Major minerals shown for comparison are listed as “Others” and include, in increasing order of attenuation: albite, quartz, anorthite, clinopyroxene (hedenbergite end member), and biotite (annite end member). Calculated using data in Figure 1 (from Chantler et al., 2003) following method described by Hubbell and Seltzer (2004; see also equation 2).
tomograms are taken at slightly different energies (e.g., separated by <0.5 keV), the contrast in attenuation for most elements is minimal. However, if these two tomograms are taken at energies that are just below and just above the absorption edge of a particular chemical element, absorption by this element will be quite different. Consequently, the difference in absorption between the two tomograms is essentially due to the presence of that particular element in the material. The magnitude of the difference in attenuation is proportional to the abundance of the element, such that contrast in images created by subtracting below-edge tomograms from above-edge tomograms reflects the abundance of the element in consideration.

This effect can be easily seen by comparing slices of tomograms of pumice taken above and below the Ce edge (Fig. 3) and the Zr edge (Fig. 4). The attenuation coefficient measured for most voxels is very similar in the above-edge (Figs. 3A and 4A) and below-edge (Figs. 3B and 4B) slices, with the exception of the Ce-rich and Zr-rich crystals, which show a large contrast in attenuation. Due to this contrast, these crystals are easily observed in images calculated as the difference between above-edge and below-edge slices (Figs. 3C and 4C). Note that the Ce maps obtained (Fig. 3) reveal two REE-rich phases, one with significantly more Ce than the other (see following for more details). Appropriate combination of above-edge and below-edge images into different color channels permits the generation of false-color images that clearly show where the phases of interest are located relative to the other phases in the sample (Figs. 3D and 4D).

In selecting elements suitable for differential absorption tomography, one important consideration is the energy of the absorption edges of elements of potential interest. Tomography reconstructions require that a significant proportion (i.e., >20%; see Stock, 2009) of the incident radiation be transmitted through the material. Transmittance decays exponentially with distance traveled (i.e., thickness), according to the Beer-Lambert law (Chantler et al., 2003):

$$\frac{I}{I_0} = \exp\left(-\frac{\mu}{\rho} x\right) = \exp(-\alpha x),$$

where $I/I_0$ is the ratio of transmitted to incident radiation, $x$ is distance traveled through the material, $\mu$ is the linear attenuation coefficient (in units of 1/length), $\rho$ is the density of the material, and $\alpha = \mu/\rho$ is the mass attenuation coefficient (in units of length$^2$/mass). Consequently, the maximum sample diameter that can be imaged at a particular energy depends strongly on the attenuation coefficient of the material at that energy. In other words, an elemental tomogram of a particular element can only be generated for samples that are small
enough so as to permit transmittance of at least 20% of the incident radiation at the absorption edge of that element.

As an example, we consider the attenuation of pumice, which can be calculated as a combination of the attenuation by its main constituents: quartz, feldspars, glass, and air (see Fig. 2). The attenuation of each constituent is calculated from the elemental mass attenuation coefficients using the relation (e.g., Hubbell and Seltzer, 2004)

\[ \alpha = \sum w_i \alpha_i, \]

where \( w_i \) is the fraction by weight of the \( i \)th atomic constituent, and the \( \alpha_i \) values are from Chantler et al. (2003) for the energy of interest.

By assuming the relative abundance of these phases in rhyolitic pumice (e.g., as obtained by Gualda and Rivers, 2006), we calculate the expected attenuation coefficient of bulk pumice at energies of absorption edges of several elements of interest (Fig. 5). Note that the elements shown in Figure 5 are major constituents (i.e., are present in abundances of several to tens of weight percent of the material) of one or more phases in pumice: Ce in REE-rich minerals, Zr in zircon, Fe in mafic minerals and Fe-Ti oxides, Ti in Fe-Ti oxides and titanite, and Ca in plagioclase, some mafic minerals, notably augite and hornblende, and important accessories such as titanite and apatite. Note also that other major elements in pumice phases, specifically K, Si, Al, Mg, and Na, all have their most energetic absorption edges at energies lower than Ca K-edge (see Table 1). What is apparent from Figure 5 is the strong effect of the absorption edge energy on the maximum thickness of pumice that can be imaged using differential absorption tomography. Only for absorption edges in excess of ~15 keV does the maximum sample size exceed 1 mm. Note that this value is for a material with large porosity (i.e., >60%) and density ~1 g/cm³; for a nonporous material with equivalent mass attenuation coefficient, the maximum thickness would be a factor of 2–3 smaller.

X-ray tomography is usually limited to resolutions of ~1 µm due to the use of visible light imaging of X-ray scintillators and phase contrast effects (Stock, 1999, 2008, 2009), such that features several micrometers across can ordinarily be identified and quantified (see Gualda and Rivers, 2006; Pamukcu and Gualda, 2010). As a result, a minimum sample size of ~1 mm is usually necessary for quantitative textural studies (see Gualda, 2006; Stock, 2008, 2009), making it impractical to employ differential absorption tomography to yield elemental maps for most major (low Z) elements in pumice. Many high-Z elements (e.g., Rb, Sr, Ba; see Table 1) would yield large enough minimum sample sizes; however, most of these elements are dispersed within major phases in pumice and other rocks, in concentrations that do not exceed tens to hundreds of parts per million, below the current practical detection limit of the technique. As a result, elements that stand out as prominent possibilities are Zr and REE, which possess the appropriate combination of high abundance in select phases in rocks and relatively high absorption edge energy, yielding suitable maximum sample sizes. This
Figure 5. Ratio of incident to transmitted X-ray intensity ($I/I_0$) versus sample thickness (i.e., distance traveled; see text) plot for energies corresponding to the absorption edges of key elements. Values indicated are the thicknesses (in mm) that yield 20% transmittance for the various energies considered. Calculated for a silicic rock with density ~1 g/cm$^3$ using mass attenuation coefficients of the elements from Chantler et al. (2003). Note that only for Zr and Ce K-edges can the sample size be larger than 1 mm as usually needed to study crystal size distributions in rocks. Other elements (e.g., Rb, Sr, Ba; see Table 1) have absorption edges at energies suitable for imaging millimeter- to centimeter-sized samples, but they are dispersed in minerals at trace element concentrations, below the current detection limit of differential absorption tomography.

is particularly fortunate, as zircon and REE-rich phases preserve remarkable records of magmatic evolution (e.g., Lipin and McKay, 1989; Hanchar and Hoskin, 2003; Harley and Kelly, 2007, and references therein). Additional possibilities include Hf, Pb, U, and Th (see Table 1), which are often concentrated in accessory minerals at suitable levels.

APPLICATIONS

We present here preliminary results obtained using the method outlined above to study zircon- and REE-rich minerals in pumice from the Peach Spring Tuff and from Mount St. Helens. This work is part of our ongoing effort to use accessory minerals to understand the evolution of shallow silicic magmatic systems (Claiborne et al., 2010; Miller et al., 2009; Pamukcu et al., 2009). The goal here is to demonstrate the applicability of the method and show the kinds of information and results that can be obtained using differential absorption tomography. In-depth discussions of the petrologic implications of our results are beyond the scope of this contribution, and will be discussed in subsequent publications.

Analytical Details

Tomography data were collected on the bending magnet beamline at the GeoSoilEnviroCARS sector at the Advanced Photon Source (APS), Argonne National Laboratory. Details on the experimental setup and general analytical procedure were described elsewhere (Rivers et al., 1999; Sutton et al., 2002; Gualda and Rivers, 2006).

For each pumice clast studied, cylinders of three sizes were cut using pliers and tweezers: ~10, 5, and 2.5 mm diameter; cylinder heights are about twice their diameter. In order to fully image these cylinders, stacks of tomograms were acquired and later patched together using IDL routines developed by us (part of the package ‘vol_tools’; Rivers and Gualda, 2009; also available at http://people.vanderbilt.edu/~g.gualda/vol_tools.htm). For simplicity, we will hereafter refer to a stack of tomograms simply as a tomogram.

For each cylinder, 5 tomograms were obtained: (1) 100 eV above Zr K-edge, (2) 100 eV below Zr K-edge, (3) 100 eV above Ce K-edge, (4) 100 eV below Ce K-edge, (5) at the ideal energy for each sample, usually in the range 20–25 keV, depending on the size and density of the sample. Tomograms 1–4 were taken with 2 × 2 binning of the pixels in the CCD (charge-coupled device) detector (i.e., 1 pixel in the resulting image is the combination of 4 pixels in the detector), to allow for short acquisition times. This results in tomograms with voxel sizes of ~18, 9, and 4.5 µm in each linear dimension for the cylinder diameters listed above (Pamukcu and Gualda, 2010). These tomograms are each reconstructed from series of 720 projections spaced 0.25° from one another, with counting times per projection usually between 0.1 and 1.5 s depending on the energy used and the size of the sample. All four tomograms can be typically acquired in ~1 h. Tomograms 5 were obtained with the CCD detector unbinned, yielding a factor of 2 improvement in resolution, with resulting voxel sizes of ~9, 4.5, and 2.25 µm for the cylinder sizes employed. These tomograms are reconstructed from 900 projections with 0.20° steps, with typical counting times per projection between 1 and 2 s. Because the CCD detector is unbinned and a larger number of projections...
is needed to reconstruct these tomograms, total acquisition times for these are 4–5 times longer than for tomograms 1–4, such that a single tomogram 5 can be acquired in ~1 h.

Tomograms were reconstructed using “tomo_display” (Rivers and Gualda, 2009; also available at http://cars9.uchicago.edu/software/idl/tomography.html). Image processing was performed using ‘vol_tools’ (Rivers and Gualda, 2009) and ‘Blob3D’ (Ketcham, 2005a), following the methods described in detail in Part 1 by Gualda and Rivers (2006). Data from various resolutions were combined using the procedure described in Part 2 by Pamukcu and Gualda (2010).

Peach Spring Tuff

The Peach Spring Tuff (Young and Brennan, 1974) is a large rhyolitic deposit formed ca. 18.5 Ma (Nielson et al., 1990) by a supereruption that ejected at least 640 km$^3$ of magma (Buesch, 1992), giving rise to very extensive deposits that span much of southern Nevada, northwestern Arizona, and southeastern California. The Peach Spring Tuff is an important stratigraphic marker in a region of complex geology and deformation (Glazner et al., 1986; Faulds et al., 2001; Varga et al., 2004), and its physical volcanology has been studied in some detail (Buesch and Valentine, 1986; Valentine et al., 1989; Buesch, 1992). We are currently detailing the petrology of the Peach Spring magma body. The Peach Spring Tuff is distinctive in that accessory minerals, particularly titanite, are abundant (Fig. 6). This offers an outstanding opportunity to study in detail the evolution of this magmatic system using its accessory mineralogy.

The presence of zircon (ZrSiO$_4$), titanite [(Ca, light REE)TiSiO$_5$; also known as sphene], allanite [(light REE, Ca)$_2$(Al, Fe)$_3$(SiO$_4$)$_3$(OH)], and possibly chevkinite [(light REE, Ca)$_4$(Fe, Ti)$_3$Si$_2$O$_{12}$] as small but relatively abundant crystals makes Peach Spring pumice particularly suitable for study using Zr and Ce 3D elemental mapping via differential absorption tomography. In the formulas above, light REE (LREE) refers in particular to La, Ce, Pr, and Nd; the most abundant of these is Ce, justifying the choice of Ce over other LREE for elemental mapping.

Data presented here are for samples collected from the outflow sheet exposed in the city of Kingman (Arizona), and come from a poorly welded horizon of Peach Spring Tuff that unconformably overlies cinder deposits (global positioning system, GPS coordinates N35.19, W114.04).

Inspection of elemental tomograms (Fig. 7) shows that (1) zircon crystals can be easily detected in the reconstructed tomograms, and (2) that titanite and allanite ± chevkinite are present in these samples. The results of this study will be published in a forthcoming paper, but data presented here are for samples collected from the outflow sheet exposed in the city of Kingman (Arizona), and come from a poorly welded horizon of Peach Spring Tuff that unconformably overlies cinder deposits (global positioning system, GPS coordinates N35.19, W114.04).

Figure 6. Photomicrograph of pumice clast from Peach Spring, showing examples of accessory minerals observed in thin section, as indicated. Note wedge-shaped habit of titanite, irregular shape of allanite, and round and blocky shapes of magnetite. Wedge-shaped titanite and round magnetite are seen in tomograms. Plane-polarized illumination. Scale bar corresponds to 1000 µm.

Figure 7. (A) Tomographic slice through pumice clast from Peach Spring Tuff. Brightness increases with mean atomic number and density (similar to backscattered electron images); region depicted in B–D is shown by dotted rectangle. (B) Zr differential absorption map showing zircon crystals. (C) Ce differential absorption map showing allanite ± chevkinite (bright round crystal) and titanite (dull wedge-shaped crystals). (D) Regions assigned to accessory phases based on Zr map (zircon), Ce map (allanite ± chevkinite), and tomogram obtained at ideal energy (titanite). Titanite shown in yellow, zircon in blue, allanite ± chevkinite in red. Note how zircon crystals are included in titanite and in contact with allanite ± chevkinite. Bars are 500 µm long.
identified (see Fig. 7B), and (2) two distinct Ce-rich mineral phases are present, one particularly rich in Ce and another with relatively low but detectable Ce abundances (Fig. 7C); we identify the phase with higher Ce as allanite (± chevkinite), and the phase with lower Ce as titanite. Superposition of the information from elemental maps onto tomograms obtained at the ideal energy (tomogram 5 as described above) using color channels makes it possible to locate these minerals in textural context (Fig. 7D).

What is remarkable is that textural features such as clustering, crystal shapes, and contact relationships can be easily observed. It is quite clear that zircon crystals appear as inclusions or in contact with the REE-rich phases (Fig. 7D). These features can be observed in a much more compelling way by using 3D renderings of the minerals of interest (Fig. 8; generated using ‘vol_tools’; Rivers and Gualda, 2009). The striking observation made possible by the tomographic data is that zircon crystals (blue in Fig. 8) form clusters of >10 crystals (see Fig. 8B), which are included or partly embedded within titanite (yellow in Fig. 8A) and to a lesser extent magnetite (green in Fig. 8A) crystals (titanite and magnetite have been omitted from Fig. 8B for clarity); note that zircon crystals are dispersed throughout the volume of the titanite crystals. Similarly, the allanite (± chevkinite) crystals have zircon crystals attached to them (Fig. 8). It is interesting that the titanite and magnetite crystals appear to impinge onto one another, forming clusters of a few partly intergrown grains. Some isolated zircon crystals are also observed, but they correspond to a very small fraction of all zircon present. These considerations suggest that the clustering is primary, i.e., formed during crystallization; however, the pockets of titanite + magnetite + zircon and magnetite + allanite + zircon (Fig. 8) correspond to regions with significant local enrichment in Fe, Ti, Zr, and LREE when compared to the glassy matrix, and the mechanism responsible for the generation of these enriched regions is not immediately clear. This recognition of at least two zircon populations is critical, as it has important implications for the interpretation of compositional data on zircon and allanite crystals obtained via microanalysis. These features are difficult to explain, because (1) there are no long range forces that can cause attraction of crystals after they have crystallized; (2) even if zircon, allanite, titanite, and magnetite crystals can be brought to close proximity, surface attachment forces between solids in a fluid are rather weak (in contrast with bubble-solid forces; see Gualda and Ghiorso, 2007), such that crystals would tend to detach easily; and (3) it is possible that titanite, magnetite, and allanite growth cause development of a Zr-enriched boundary layer that triggers zircon crystallization (see Bacon, 1989); however, this mechanism cannot readily explain the clustering of titanite and magnetite crystals. While the origin of these features is uncertain at this point, the method we propose here provides the tools to observe, quantify, and possibly explain these features.

Using the elemental tomograms, it is possible to derive crystal size distributions for the identified phases using image processing (Fig. 9; see Ketcham, 2005a; Gualda and Rivers, 2006; Pamukcu et al., 2009); in fact, image processing of the elemental tomograms is much simpler than of regular tomograms, due to the presence of only one or two phases in the elemental tomograms, as opposed to more than eight in regular tomograms. Combining tomograms obtained...
at various resolutions (following Pamukcu and Gualda, 2010) leads to zircon, allanite (± chevkinite), titanite, and magnetite size distributions for crystals larger than ~20 µm. While zircon size distributions can be derived using acid dissolution of bulk pumice or rock (e.g., Bindef, 2003), size distribution determinations for REE-rich minerals are entirely lacking. Furthermore, acid dissolution is limited by loss of small crystals during processing; in situ determination of size distributions with minimal sample processing is thus a much preferred approach, and the size of crystals that can be quantified is determined only by the resolution of available tomograms. At least in principle, it should be possible to derive size distributions for crystals at least as small as ~5 µm. In addition, combination of information from elemental maps and from regular tomograms allows the qualitative and quantitative characterization of textures of a variety of accessory minerals present, in a manner that is untenable using other techniques.

Mount St. Helens

Mount St. Helens is a classic arc stratovolcano in the central Cascades of Washington State. After 300 ka of episodic eruptive activity (Clyne et al., 2008), 2 very recent periods of activity beginning with the unprecedented lateral blast of 18 May 1980 have sparked great interest in the volcanic history and petrology of magmatism at this volcano (for reviews, see Lipman and Mullineaux, 1981; Sherrod et al., 2008). We are currently detailing the history of the Mount St. Helens plumbing system by exploring the ages and compositions of zircon crystals from pumice and lava that span the entire eruptive history (Claiborne et al., 2010).

Zircon crystals being studied are separated through classic crushing, sieving, and heavy liquid separation. Two populations of zircon crystals are found in crystal concentrates from pumice: (1) crystals fully surrounded by glass (Fig. 10A), interpreted to have been in contact with melt at the time of eruption; and (2) crystals lacking surrounding glass (Fig. 10B), potentially included in other minerals and not in contact with melt at the time of eruption. It is particularly important to understand these contact relations in order to accurately interpret geochemical and geochronologic data being gathered from the outermost grain surfaces (Claiborne et al., 2009). However, due to our crushing and sieving of the material, the potential for substantial loss of zircon crystals during processing, and the scarcity of zircon in Mount St. Helens lava and pumice, it is difficult to study the textures of zircon and contact relations with other minerals using our concentrates or conventional thin sections. Mount St. Helens pumice is, however, an ideal material to be studied using the method presented here.

The samples studied here are Yn pumice, erupted at 3.4 ka in one of the most voluminous eruptions in the history of the volcano (Mullineaux, 1996). The samples used here were collected from beneath the modern pumice plain on the north flank of Mount St. Helens (GPS coordinates N46.28, W122.11).

While zircon is scarce in pumice from Mount St. Helens and a few to no crystals may be found in any particular thin section, zircons are readily identified in elemental tomograms, and >40 zircon crystals were identified in Zr tomograms of a single ~2 cm³ pumice piece. Inspection of false-color overlays of Zr tomograms onto regular tomograms (Fig. 11) clearly demonstrates the presence of zircon crystals both isolated in the glass (Figs. 11A, 11B) and as inclusions in other minerals (Figs. 11C, 11D). This information significantly affects our interpretation of geochemical and geochronologic data gathered from zircon surfaces, by allowing us to divide crystals into two groups: (1) those in contact with melt, with surfaces that can potentially record the composition and age of the magma near the time of eruption; and (2) those isolated from the melt at the time of eruption, with surfaces that document exclusively earlier stages of the magmatic history. This distinction makes it easier to explain the range of ages sometimes recorded in zircon surfaces (Claiborne et al., 2009). Not only do the tomographic data con-
clusively establish the existence of these two zircon populations, but they also allow quantification of the relative abundance of these two populations and permit determination of separate crystal size distributions for each, which may provide important clues to the origin and evolution of zircon populations. Furthermore, use of the Zr tomograms makes it possible to evaluate the total zircon budget of Mount St. Helens pumice, overcoming one of the main shortcomings of the zircon concentration procedures we currently use and helping us to better understand zircon saturation systematics in Mount St. Helens magmas.

CONCLUSIONS

In this contribution we demonstrate how differential absorption X-ray tomography can be used to qualitatively and quantitatively study the textures of Zr-rich and REE-rich accessory minerals in rocks, particularly pumice. The method takes advantage of the large jumps in X-ray attenuation near absorption edges to generate 3D elemental maps for selected elements. One of the key limitations of the method is a strong dependence of the maximum sample diameter on the incident radiation energy. Because absorption edges for most major elements in silicate rocks occur at relatively low energies (e.g., <5 keV), only submillimetric samples can be imaged close to the absorption edges of these elements. Many elements with higher atomic number have absorption edges at energies suitable to image samples up to a few millimeters in diameter; however, most of these elements are dispersed in major minerals, in concentrations that are below the current detection limit of the technique. Zirconium and REE are remarkable exceptions, being major components of certain accessory minerals, and having absorption edges at energies suitable for imaging samples up to ~1 cm in diameter. This is particularly fortunate, given that zircon and REE minerals preserve rich records of magmatic evolution, and textural information can be combined with compositional and age information to unravel magmatic processes and histories.

We demonstrate the feasibility of the method, and illustrate the kinds of data that can be gathered using pumice from the Peach Spring Tuff and Mount St. Helens. Several factors make the use of 3D elemental maps particularly interesting for studies of accessory minerals.

1. Textures and contact relationships between accessory minerals can be documented in three dimensions, in unprecedented level of detail, as beautifully exemplified by the presence of numerous zircon crystals included in titanite in Peach Spring pumice.

2. Different populations of accessory minerals can be recognized and studied in textural context (i.e., before extraction of crystals from the host); this is particularly true given that the number of crystals included in a small rock chip is many times larger than the number of crystals present in a conventional thin section, allowing for much better characterization of their textures.

3. Crystal size distributions can be readily obtained, providing information on the crystal nucleation and growth histories, with important implications for the interpretation of compositional data on accessory minerals.

4. Complete characterization of accessory mineral crystal populations including crystals <10 µm permits evaluation of the total abundance of these phases, with implications for the total budgets of important elements such as Zr and REE.

Given the remarkable record of magmatic evolution preserved in accessory minerals, particularly in zircon and REE-rich minerals, the method presented here offers exciting new possibilities for their study, and is likely to promote better understanding of the processes leading to their origin and the origin of the rocks that contain them.

Figure 10. Photomicrographs of zircon crystals hand-picked from heavy mineral separates; sample is a pumice clast from Mount St. Helens. Crystals are immersed in refractive index oil and imaged using plane-polarized light; bars correspond to 100 µm. (A) Zircon crystals fully surrounded by vesiculated glass, interpreted to have been in contact with melt at the time of eruption. (B) Glass-free zircon crystals, presumably inclusions in other minerals that were isolated from melt since time of entrapment.
Figure 11. Tomographic slices through pumice clast from Mount St. Helens. All frames are false color images (R—above Zr edge, G—below Zr edge, B—above Zr edge), and zircon crystals appear pink. (A, B) Slices showing zircon crystals fully embedded within vesiculated glass; these crystals were clearly in contact with melt at the time of eruption. After laboratory processing, they retain the glass adhered to their surfaces (see Fig. 10A). (C, D) Slices showing zircon crystals fully embedded within mineral phases (in this case, feldspars); these crystals were isolated from the melt after entrapment. Recognition of these two populations is critical to properly interpret the results obtained by dating the outermost layers of zircon crystals (Claiborne et al., 2009). Bar is 300 µm long and applies to all images.

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