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Abstract: The rhyolitic Valles Caldera complex, New Mexico, is one of the type examples of resurgent calderas, and has experienced two well-studied caldera-forming eruptions. The first formed the Lower Bandelier Tuff (LBT) at 1.608 ± 0.010 Ma, and the second emplaced the Upper Bandelier Tuff (UBT) at 1.225 ± 0.008 Ma. During the time between the LBT and UBT, the much smaller-scale Cerro Toledo Rhyolite (CTR) was sporadically erupted. Quartz crystals from these stages of activity were imaged using cathodoluminescence (CL) microscopy, and growth zones in certain quartzes, due to varying Ti content, were revealed. Using a titanium-in-quartz geothermometer, crystallization temperatures were obtained. LBT quartzes are unzoned, with temperatures clustering between 660-715°C when a calculated aTi of 0.4 is applied to the system. These near-solidus temperatures imply that the LBT magma chamber was highly crystalline at one point. However, the low crystal content and the widespread presence of resorption features on LBT

crystals require that pervasive melting affected the LBT magma chamber at some point prior to eruption. This melting is hypothesized to result from a hot magmatic injection into the system, with the injection also being a likely trigger of the cataclysmic LBT volcanism. The earliest erupted CTR units contain many zoned quartz crystals. Inner zones are usually rounded and invariably reveal cold (~660-700oC) cores and hot (~750-825oC) rims. We interpret these results as thermal evidence of magmatic recharge, where new magma mixed vigorously with leftover magma, and high-temperature rims crystallized around low-temperature restitic quartz cores. Thermal results for the rest of the CTR record the continuing cooling and evolution of this mixture of magma. These results present an unprecedented glimpse into the thermal history of the Bandelier magma system, as well as strong evidence for the timing and overall importance of magmatic injections in silicic magma systems.

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**Thermal History of the Bandelier Magmatic System:
Evidence for Magmatic Injection and Recharge at 1.61 Ma as Revealed by
Cathodoluminescence and Titanium Geothermometry**

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ABSTRACT

The rhyolitic Valles Caldera complex, New Mexico, is one of the type examples of resurgent calderas, and has experienced two well-studied caldera-forming eruptions. The first formed the Lower Bandelier Tuff (LBT) at 1.608 ± 0.010 Ma, and the second emplaced the Upper Bandelier Tuff (UBT) at 1.225 ± 0.008 Ma. During the time between the LBT and UBT, the much smaller-scale Cerro Toledo Rhyolite (CTR) was sporadically erupted. Quartz crystals from these stages of activity were imaged using cathodoluminescence (CL) microscopy, and growth zones in certain quartzes, due to varying Ti content, were revealed. Using a titanium-in-quartz geothermometer, crystallization temperatures were obtained. LBT quartzes are unzoned, with temperatures clustering between 660-715°C when a calculated a_{Ti} of 0.4 is applied to the system. These near-solidus temperatures imply that the LBT magma chamber was highly crystalline at one point. However, the low crystal content and the widespread presence of resorption features on LBT crystals require that pervasive melting affected the LBT magma chamber at some point prior to eruption. This melting is hypothesized to result from a hot magmatic injection into the system, with the injection also being a likely trigger of the cataclysmic LBT volcanism. The earliest erupted CTR units contain many zoned quartz crystals. Inner zones are usually rounded and invariably reveal cold (~ 660 -700°C) cores and hot (~ 750 -825°C) rims. We interpret these results as thermal evidence of magmatic recharge, where new magma mixed vigorously with leftover magma, and high-temperature rims crystallized around low-temperature resorptic quartz cores. Thermal results for the rest of the CTR record the continuing cooling and evolution of this mixture of magma. These results present an unprecedented glimpse into the thermal history of the

Bandelier magma system, as well as strong evidence for the timing and overall importance of magmatic injections in silicic magma systems

Introduction

Valles Caldera, located in north-central New Mexico (Figure 1), has often been referred to as the type example of a resurgent caldera. Early caldera collapse models were developed through the study of this system (e.g. Smith and Bailey, 1968), work which has shaped our understanding of cataclysmic silicic magmatism.

Two episodes of large-scale silicic volcanism, including caldera collapse, occurred at the Valles complex during the past 1.6 Ma. The first produced the 1.61 Ma Lower Bandelier Tuff and formed Toledo caldera; the second erupted the 1.22 Ma Upper Bandelier Tuff (Spell et al., 1996) and led to the collapse of Valles caldera at a location nearly coincident with the earlier Toledo caldera (Self et al., 1986). Additionally, several smaller lava dome, plinian and ignimbrite eruptions, termed the Cerro Toledo Rhyolite, were erupted from the system between the two caldera-forming events (Heiken et al., 1986). This unusual combination of events offers a rare window into the development and evolution of a magmatic system which has undergone multiple caldera-forming events.

In this study, we examine growth zones in quartz crystals from the Bandelier Tuff and intervening Cerro Toledo Rhyolite that are revealed by cathodoluminescence (CL) imaging of individual quartz crystals (Peppard et al., 2001). It has recently been shown that the intensity of the different CL zones in quartz crystals is directly related to their Ti content, and that the Ti content of quartz can in turn be related to the quartz's temperature of crystallization (Wark and Spear, 2005; Wark and Watson, 2006). Using a new

titanium-in-quartz geothermometer based upon this relation (Wark and Watson, 2006), we have calculated the crystallization temperature of quartz grains and their various growth zones.

Our results shed light on the thermal history and evolution of the Bandelier magmatic system during and between the Toledo and Valles caldera-forming eruptions. In conjunction with previous research on the Bandelier system (e.g. Stix and Gorton, 1993), we propose a model of magma injection which is intimately related to the inception of caldera-forming eruptions, by causing substantial crystal resorption throughout the magma chamber. These processes in turn may have caused the destabilization and subsequent catastrophic eruption of the magma chamber. Additionally, our thermal data for the Cerro Toledo Rhyolite provide new insights into the inner workings of the system's magmatic recharge, which culminated in the eruption of the Upper Bandelier Tuff.

Geological Background

The Jemez Volcanic Field. The Jemez Volcanic Field (JVF) is a 2000 km³ complex located in north-central New Mexico, at the intersection of the northeast-trending Jemez lineament and the north trending Rio Grande rift (Smith and Bailey, 1968; Aldrich and Laughlin, 1984). The JVF has been volcanically active from 13 Ma to Recent times, and has been characterized by predominantly intermediate to mafic volcanism over most of its history (Gardner et al, 1986). The range of magmatic compositions observed in the JVF is ascribed to the interactions between two fundamental magma types: mantle-derived olivine tholeiite basalt and high-silica rhyolite from melted crust (Gardner, 1985; Gardner et al., 1986; Wolff and Gardner, 1995). The first eruptive products of the JVF

that appear genetically related to the Bandelier Tuff are the 4 Ma rhyolitic San Diego Canyon ignimbrites (Turbeville and Self, 1988). At about 1.8 Ma, high-silica rhyolitic ignimbrites, chemically very similar to the Bandelier Tuff, were erupted from the same locality as the later Valles caldera (Spell et al., 1990). These pre-Bandelier ignimbrites may have been derived from the same magma body as the Bandelier Tuff (Self et al., 1986).

The Bandelier Tuff and the Cerro Toledo Rhyolite. The Bandelier Tuff, a series of two large volume, high-silica rhyolite tephra and ignimbrites, is among the most recent erupted products of the Jemez Volcanic Field. The Bandelier Tuff comprises the Lower Bandelier Tuff (LBT), which was emplaced at 1.608 ± 0.010 Ma, and the Upper Bandelier Tuff (UBT), which was erupted at 1.225 ± 0.008 Ma (Spell et al., 1996). The eruptions of the LBT and UBT led to the formation of Toledo caldera and Valles caldera, respectively (Figure 1) (Smith and Bailey, 1968; Heiken et al., 1990).

The LBT is made up of the Guaje Plinian Pumice Bed and the Otowi ignimbrite units. The total erupted volume of the LBT is estimated at 400 km^3 DRE (Dense Rock Equivalent) (Self and Lipman, 1989). The Guaje Pumice Bed is a plinian pumice fall deposit which blankets the underlying topography (Kuentz, 1986). The deposits of this bed are massive to well-bedded, unconsolidated, and are made up of coarse, well-sorted, angular pumice clasts of an average size of 1-4 cm (Kuentz, 1986). The crystal content of the Guaje pumices ranges up to 17%, with vesicularity taken into account (Kuentz, 1986). Based upon isopach and maximum grain size isopleth maps, it is thought that the Guaje deposits were erupted from either a single central vent or multiple closely-spaced vents (Self et al., 1986; Kuentz, 1986). The LBT ignimbrites consist of surge beds and massive

ignimbrite dispersed in a radially symmetrical fashion around the caldera (Goff et al., 1989). The commonly non-welded nature of the LBT ignimbrite also promoted the relatively rapid erosion of this member (Kuentz, 1986). The crystal content of the LBT extends up to 19% (Kuentz, 1986). The LBT ignimbrite is up to 800 m thick inside the caldera, as determined by drilling by Union Oil Co., and varies from 0-120 m thick outside the caldera (Nielson and Hulen, 1984; Kite, 1985; Kuentz, 1986). The LBT ignimbrite commonly shows weak to no bedding and variable alteration, related to variations in precipitation (Kuentz, 1986). Pumices of dacitic composition are also occasionally found in the LBT (Kuentz, 1986).

The Cerro Toledo Rhyolite (CTR) is a series of high-silica rhyolite domes, lavas, and fallout and surge tephra that were erupted sporadically during the 383 ka timespan between the eruptions of the Lower and Upper Bandelier Tuffs (Heiken et al., 1986; Stix and Gorton, 1993; Spell et al., 1996). Ages obtained for the lowermost CTR and for the LBT are indistinguishable (Spell et al., 1996), suggesting that volcanism resumed almost immediately after the caldera-forming eruption of the LBT. Similarly, the ages obtained for the uppermost CTR and for the base of the UBT are identical, suggesting that volcanism was occurring immediately prior to the eruption of the UBT (Spell et al., 1996). The CTR was erupted from the Toledo caldera and the Toledo embayment, and outcrops of their deposits are restricted to locations such as canyons northeast of Los Alamos (Heiken et al., 1986).

The UBT comprises the Tsankawi Plinian Pumice Bed and the Tshirege ignimbrite units. The total erupted volume of the UBT is approximately 250 km³ DRE (Self and Lipman, 1989), and covers more than 1300 km², with Valles caldera at the

center (Smith and Bailey, 1966). The Tsankawi Pumice Bed (Bailey et al., 1969) represents the initial plinian fall of the Valles caldera-forming eruption. This fall unit is laterally extensive, representing the stage prior to column collapse and the production of large scale pyroclastic material. The vent location for the eruption column has been interpreted to be at the current location of resurgent doming, and the site of Valles caldera is nearly coincident with that of the previous Toledo caldera (Self et al., 1986). Total phenocryst content of the Tsankawi is approximately 5% (Smith and Bailey, 1966). Although high-silica rhyolite pumices are characteristic of the vast majority of the UBT, small amounts of dacite pumice are also found in the UBT plinian unit and ignimbrite (Balsley, 1988). The UBT ignimbrite is also more commonly welded than the LBT, and has a total crystal content of ~15-35% (Smith and Bailey, 1966). Unlike the LBT, trace element studies of the UBT do not reveal a simple fractional crystallization evolution. According to Balsley (1988), the magma composition was initially similar to the LBT, but experienced some fraction of either mixing or assimilation.

Methodology

Sample Collection. Samples were collected from units G-1, 7-7, 7-8, 15-8, 15-9, 15-11, 6-8, 6-12 and “Alpha” from the LBT, the Cerro Toledo Rhyolite and the UBT. All these units were described by Stix (1989), except for unit Alpha, which is located near the top of the UBT ignimbrite. Ages of these units (Spell et al., 1996), and their location within the stratigraphic sequence, are found in Figure 2.

Sample Preparation. A light crush was applied to samples, with care taken not to damage individual crystals. Quartz grains ranging in size from 63 to 250 microns were

handpicked and mounted in epoxy in 1-inch grain mounts, which were then carbon-coated for cathodoluminescence imaging.

Cathodoluminescence Imaging. Cathodoluminescence (CL) electron microscopy reveals zonations in quartz crystals (Peppard et al., 2001). The origin of CL zonations in quartz is thought to be due to variations in titanium incorporated into the SiO₂ crystal structure (Wark et al., 2004). The CL zones are imaged in two dimensions, but in actuality are three-dimensional in nature within the actual quartz grain. This, along with the broken nature of many quartz grains analyzed, may affect the visualization and interpretation of the zonations for some grains.

Digital CL pictures were obtained at the Université du Québec à Montréal (UQÀM) using a Hitachi S-4300SE/N (VP-SEM), with a CL lens attached. Pictures were obtained under vacuum with a total image scanning time of 200 seconds per picture. Scans were conducted at 15, 20 and 30 kV accelerating voltage. Scans performed at 30 kV accelerating voltage were found to yield the clearest images of grains which filled the image collection screen. However, when the grain did not fill the image collection screen, a significant amount of epoxy was visible. Epoxy emitted very strongly under CL relative to the quartz grains. When significant epoxy was visible, an accelerating voltage of 20 kV yielded the best results.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry. Titanium concentrations of selected quartz grains were obtained by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at McGill University (Table 1). The instrument used was a New-Wave UP-213 Laser Ablation System coupled to a

PerkinElmer/SCIEX ELAN 6100 DRCplus ICP-MS. Ablations were usually conducted as line-scans at 10 Hz, with a beam size of 60 μm , and 10 J/cm^2 laser fluence.

Background counts, signal selection interval and data reduction were performed using Glitter software. ^{29}Si was chosen as the ratioing isotope, and ^{27}Al and ^{43}Ca were monitored to reveal surface contamination or melt inclusions. Instrumental precision calculated by Glitter of the LA-ICP-MS was excellent. The Relative Standard Deviation (%RSD), which is defined as the standard deviation divided by the mean of the analyses, was below 4.0% and 7.5% for ^{29}Si and ^{48}Ti respectively, with %RSD of both typically hovering around 3-4%.

Accuracy of the determined concentrations depends in part on the choice of standards. A set of quartz standards with well-characterized titanium concentrations is not generally available, and use of the NIST 610-614 glasses as standards is ill-advised due to an isobaric calcium interference on mass 48 (the major titanium isotope), as well as a potential interference from $^{96}\text{Zr}^{++}$. Benitoite ($\text{BaTiSi}_3\text{O}_9$) has the advantage of being a calcium-free titanium silicate with limited compositional variation (Minarik, 2006). Hence gem-quality benitoite from New Idria, CA, was used as a standard; the minor Zr content contributes insignificant counts at mass 48.

Two isotopes of Ti were measured during our LA-ICP-MS analyses, ^{48}Ti and ^{49}Ti . Due to the much greater natural abundance of ^{48}Ti (73.8% vs. 5.5% for ^{49}Ti), the count rates for ^{48}Ti in each LA-ICP-MS analysis were much higher than those for ^{49}Ti . As such, the concentrations obtained for ^{48}Ti were of somewhat higher precision than those for ^{49}Ti . However, relative precision for ^{48}Ti and ^{49}Ti only differed significantly when the count rates for ^{49}Ti descended to very low levels, below approximately 80

counts/second (which only occurred in certain of the samples with less than ~40 ppm Ti). Count rates for ^{49}Ti typically range from 100-1000 counts/second (~30-80 ppm), tending to increase with increasing Ti content.

Titanium-in-Quartz Geothermometer. Titanium is one of many trace elements that may replace silicon in the mineral quartz (SiO_2). As the concentrations of Ti in igneous and metamorphic quartz phenocrysts are relatively high, generally ranging from 1 to over 100 ppm (Wark and Watson, 2006), they may be easily and precisely measured by microbeam techniques such as Electron Microprobe Analysis (EMPA), Secondary Ion Mass Spectrometry (SIMS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). The extent of Si replacement by Ti occurs in a temperature-dependent fashion, effectively rendering the concentration of Ti in quartz a geothermometer (Wark et al, 2004; Wark and Watson, 2006). Based upon experimental data, Wark and Watson (2006) derived an equation describing the relationship between the temperature of crystallization and the concentration of Ti in quartz:

$$T(\text{K}) = -3765 / [\log(X_{\text{Ti}}/a_{\text{Ti}}) - 5.69]$$

The principal unknown in this relationship is the activity of titanium (a_{Ti}). Assuming Henrian behavior, $a_{\text{Ti}} = \lambda * X_{\text{Ti}}$, where the activity coefficient λ is a constant and X_{Ti} is the concentration of Ti in quartz. The presence of rutile (TiO_2) intergrown within the quartz would signify that rutile was an equilibrium phase in the system in question, and therefore that $a_{\text{Ti}} = 1$. The lack of rutile indicates that $0 < a_{\text{Ti}} < 1$. Lowering a_{Ti} to a value below unity results in an increase in the calculated temperature. Thus, when the activity of Ti is unknown, one can calculate minimum temperatures of crystallization by employing the geothermometer with a_{Ti} set to 1.0.

The activity of titanium is the most difficult parameter to constrain. No rutile was identified in any of the samples used in this study, and thus $a_{\text{Ti}} < 1.0$. Hayden et al. (2005) determined an expected a_{Ti} range of $0.5 \leq a_{\text{Ti}} \leq 0.6$ for a large silicic system. In work on Long Valley caldera, Wark et al. (2007) used $a_{\text{Ti}} = 0.6$ for the titanium-in-quartz temperature calculations. This value was based upon calculations using iron-titanium oxides.

As proposed in Wark and Watson (2006), an a_{Ti} for the Bandelier system was determined independently using ferrohedenbergite-fayalite pairs from Warshaw and Smith (1988) and magnetite-ilmenite pairs from Stix and Gorton (1990) from the Bandelier and the CTR. Temperature estimates for four different units were determined with these geothermometers (Table 2). The Ti content of quartzes in each unit, except unit 15-8, was then calculated by averaging all analyses performed in each unit. For unit 15-8, only those analyses performed on outer rims and on high-temperature grains were averaged, as these were deemed to be representative of the magmatic conditions at this time. Using the average Ti content of our analyses from each unit in the titanium-in-quartz formula (Wark and Watson, 2006), the remaining variable, a_{Ti} , was calculated:

$$\frac{X_{\text{Ti}} (\text{unit average})}{10^{[-(T(K) + 5.69)/3765]}} = a_{\text{Ti}} (\text{for the unit})$$

An a_{Ti} value of ~ 0.4 (Table 2) was found using both sets of data. This conformity indicates that 0.4 is most likely a reasonably accurate estimate for a_{Ti} in the Bandelier system, and the best estimate currently available. Temperatures were thus calculated using $a_{\text{Ti}} = 0.4$. Table 1 shows all of our results, and temperatures calculated using a_{Ti} values of 0.6 and 1.0 (which yields minimum temperatures) are shown for comparison. The activity of titanium is assumed to be constant throughout the evolution of the system,

again based on the similarity of the calculated value of a_{Ti} for four different units from the CTR and LBT (Table 2). The Ti activity is also assumed to be constant throughout the various units at any given time.

It should be noted that although the chosen value for a_{Ti} in this system will affect the absolute values of the temperatures calculated, the relative differences in temperatures within each unit are immutable.

Results

Crystals from nine different units within the Bandelier Tuff and the Cerro Toledo Rhyolite were imaged with CL. LA-ICP-MS analyses were then conducted on selected crystals, with several analyses performed on each crystal.

Table 1 and Figure 4 show the Ti concentration results and corresponding temperatures, as calculated by Wark and Watson's (2006) geothermometer, for each LA-ICP-MS analysis performed on quartz grains, for units G-1, 7-7, 7-8, 15-8, 15-9, 15-11, 6-8, 6-12 and "Alpha" in order of increasing stratigraphic height. The location of each of these units within the eruptive sequence is illustrated in Figure 2.

Crystals which could be imaged in one CL picture without significant mirror distortion are named by the reference to the corresponding CL image. Larger crystals were given names and are represented by a collage of CL images.

Unit G-1. G-1 is the Guaje pumice fall unit representing the onset of the LBT eruptive event. Ti concentrations are remarkably consistent, with a range from 20.8-23.9 ppm measured. The calculated temperatures reflect the consistent Ti concentrations, with temperatures ranging from 674-689°C at $a_{\text{Ti}} = 0.4$. No zoning was noted under CL imaging in any of the quartz crystals analyzed (Figure 3 A).

Unit 7-7. Four pumices were analyzed from unit 7-7: C, X, Y and Z. These pumices were sampled from section 7 at the top of the LBT ignimbrite deposit (Figure 2). Pumice 7-7C has consistent Ti concentrations, with the exception of one grain analyzed. One analysis from crystal 13 shows a Ti concentration of ~49 ppm, more than double the pumices' average of ~24 ppm. The rest of the analyses from pumice 7-7C are reasonably consistent, ranging from 18-28 ppm Ti, with a corresponding temperature range of 660-705°C ($a_{\text{Ti}} = 0.4$). The anomalous value of 49 ppm Ti gives a temperature of 773°C. Three quartz grains were analyzed from pumice 7-7X. Two crystals show reasonable consistency, with a range of 22-31 ppm Ti, resulting in a temperature range from 680-717°C. Crystal 18 shows distinctly higher Ti concentrations throughout, with two analyses of 43 and 50 ppm Ti corresponding to 757 and 774°C, respectively. In pumice 7-7Y, only two grains were analyzed. Concentrations are quite consistent, with Ti concentrations ranging from 22-26 ppm Ti. The corresponding temperature range is 681-700°C. Three crystals were analyzed from pumice 7-7Z. They show high consistency, with a range of 21-23 ppm Ti, corresponding to a 674-685 °C temperature range.

In general, unit 7-7 pumices show no zoning visible under CL imaging. Aside from one anomalous quartz grain and one anomalous analysis in another grain, there is remarkable consistency and a mean Ti concentration of 26 ppm. The outliers themselves are fairly consistent, with concentrations of 43, 50 and 50 ppm.

Unit 7-8. Unit 7-8 represents the first erupted tephra of the Cerro Toledo Rhyolite following the emplacement of the LBT ignimbrite (Figure 2). A majority of the quartz grains analyzed from this unit display at least some CL-visible zonations (e.g. Figure 3 B), with cores being invariably darker than the corresponding rims. Two major types of

zonations are apparent. In the first type, a small difference in CL-visible contrast and Ti content are noted between the core and rim of the grain. In the second type, the cores and rims are better defined, with clear differences in Ti content observed. Rims of these grains invariably have higher Ti content than their corresponding cores. Analyzed cores yielded Ti concentrations ranging from 18-33 ppm, corresponding to temperatures of 658-724°C. Analyses of high-contrast rims (“type 2”) gave Ti contents of 40-59 ppm, or 746-796°C, while the low-contrast (“type 1”) rims had Ti concentrations similar to those obtained for the cores, of 22-37 ppm, or 682-737°C. Finally, of the two grains which show no visible CL zoning, grain #11 yielded Ti contents of 33, 38 and 50 ppm, while grain #20 gave elevated Ti concentrations of 48 and 59 ppm, and corresponding temperatures of 769°C and 796°C.

Unit 15-8. Many of the crystals analyzed from unit 15-8, which is stratigraphically above and erupted just following unit 7-8, display significant CL zoning. Of the 11 quartz grains examined, 9 show a distinct darker core to lighter rim pattern (e.g., Figure 3 C, D). In some cases, the darker core appears to become lighter in a gradational and concentric fashion, followed by a discrete lighter zone near the rim of the grain. The edges of the “cores” are generally quite rounded (Figure 3 C, D).

Of the 9 clear cores, 7 of them are very similar, with Ti ranging from 23 to 27 ppm, corresponding to temperatures of 684-702°C. The other two cores have Ti concentrations of approximately 40 ppm, corresponding to a temperature of 750°C, possibly indicating that the core of the crystal belongs in the intermediate zone. Clear, distinct outer rims exhibit a range of 61-74 ppm, corresponding to temperatures between 801-827 °C. On three crystals intermediate zones are seen, with variable Ti contents and

thus temperatures. Of particular note is crystal 27 (Figure 3 D). It clearly shows a gradational zoning pattern from the dark core, abruptly truncated by the appearance of a light zone. The core has a Ti concentration of 41 ppm, and analyses both just inward of the light zone and at the opposite edge of the crystal reveal that Ti concentrations increase to ~51 ppm, while the light zone at the rim has a significantly higher Ti content of ~70 ppm. The two crystals which show no zoning have Ti concentrations similar to those on the outermost rims of the other crystals (with the exception of the rim of crystal #13), ranging from 74-79 ppm. The corresponding temperature range is 826-836°C. The outer rim of crystal #13 has a Ti content of only 48 ppm, possibly because the original outermost rim of this crystal was not preserved.

Unit 15-9. Only two quartz grains from unit 15-9 were successfully analyzed, in part due to the paucity of quartz in samples from this unit. Neither grain shows any visible CL zoning, and both have remarkably consistent Ti contents, ranging from 52-55 ppm. These Ti concentrations correspond to a temperature range of 779-788°C.

Unit 15-11. The later erupted CTR unit 15-11 shows no notable CL zoning and consistent Ti concentrations. The LA-ICP-MS analyses show a range in Ti concentrations from ~40-49 ppm Ti throughout the unit. This corresponds to a temperature range of ~748-772°C.

Unit 6-8. Unit 6-8 is one of the last erupted CTR units before the UBT eruption. Three quartz crystals were successfully imaged for CL and measured for Ti. One of these, #55, shows a distinct darker core with a lighter rim. The Ti measurements of the darker core correspond very closely with the measurements of the other unzoned quartzes, with a

range of 22-25 ppm Ti and corresponding temperatures of 681-695°C. The lighter rim has a Ti concentration of approximately 33 ppm (727°C).

Unit 6-12. Unit 6-12 is the plinian unit of the UBT eruption. Only one quartz crystal from unit 6-12, #10, yielded zoning when imaged under CL. However, the zonations of this crystal appear to be somewhat discontinuous and diffuse, and the measured Ti concentrations of this crystal do not clearly correlate with CL brightness. The numerous melt inclusions in this crystal also may have affected the Ti measurements. In general, the quartzes of unit 6-12 are unzoned and have Ti concentrations ranging from 31 to 36 ppm, with a corresponding temperature range of 719-734°C.

Unit Alpha. Unit Alpha is a sample of the densely welded massive UBT ignimbrite. Only one slightly zoned grain, #51, was noted. Although we were unable to cleanly analyze the rim segment due to its thinness, an LA-ICP-MS sample spot on the zone boundary reveals Ti levels which are consistent with the other quartzs from this unit. There are three apparently anomalous analyses in Alpha, one of which, from crystal Michelle, appears to be an outlier, possibly due to contamination of a crack by epoxy, a thin grain which was contaminated, or a subsurface melt inclusion, which would be rich in Ti. The majority of unit Alpha analyses are fairly consistent, with a Ti range from 26-36 ppm, and a corresponding temperature range from 697-735°C.

In summary, several trends emerge from our results (Figure 4). The LBT units sampled (G-1 and 7-7) show consistently low Ti concentrations and temperatures, with the exception of a few analyses from unit 7-7. By contrast, units 7-8 and 15-8, from the earliest erupted CTR, reveal significant variation in temperature and quartz growth patterns. Within the crystals from these units are found unzoned high-temperature grains,

while zoned crystals invariably have low-temperature cores and higher-temperature rims, which are typically sharply defined. Subsequently, temperatures gradually decrease with time and crystals are principally unzoned throughout the later-erupted Cerro Toledo Rhyolite, as shown by units 15-9, 15-11 and 6-8. Quartz grains from the UBT units 6-12 and Alpha show a small increase in temperature relative to the earlier CTR units and a paucity of zoned grains.

Discussion

The results obtained here provide an unusual glimpse into the thermal history of the Valles magmatic system. Previous temperature estimates for a few units of the Bandelier Tuff and CTR (e.g., Warshaw and Smith, 1988; Stix and Gorton, 1990) (Figure 4) have been calculated from ferrohedenbergite-fayalite and magnetite-ilmenite pairs, respectively. Thermal history is a parameter which is crucial to the accurate modeling and overall understanding of the nature of magma chambers, as well as to the timing and nature of fresh magma potentially being injected into these systems. Based upon our thermal data, we propose that magma injection into the Bandelier system did indeed occur, and that the first substantial injection during Bandelier time took place immediately prior to the LBT caldera-forming eruption. Injection of new magma likely continued during the LBT eruption, but ceased around the end of the eruption.

Nature of the Pre-Injection LBT Magma Chamber. Although some properties of the pre-injection LBT magma chamber are well constrained, many questions remain. Melt inclusion work by Dunbar and Hervig (1992) yielded water contents of ~5% within the Guaje plinian pumice fall unit (representing the volatile-rich cap of the magma chamber)

and ~2-3% for the remainder of the LBT ignimbrite (the main body of the magma chamber). Temperature estimates of ~700°C were calculated for the Guaje pumice bed from ferrohedenbergite-fayalite pairs by Warshaw and Smith (1988) (Figure 4), with temperatures for the LBT ignimbrite likely hotter. Finally, crystal contents of up to ~17% and ~19% are found in unit G-1 and throughout the rest of the LBT ignimbrite, respectively (Kuentz, 1986). It has been proposed that the chamber was almost certainly undergoing vigorous turbulent convection prior to eruption (e.g. Kuentz, 1986).

Our thermal data, however, paint a different picture of the pre-injection magma chamber, one which was relatively cool, possibly highly crystalline, highly viscous and stagnant (Figure 5A). This chamber would be unlikely to convect vigorously. Our temperatures from units G-1 and 7-7 generally cluster between 660-717°C. These temperatures are grouped around the ~700°C solidus for the ternary minimum in the system Ab-Or-Q (Tuttle and Bowen, 1958), at an approximate P_{H_2O} of 1-2 kbar (Kuentz, 1986) for the system. Although the Ab-Or-Q system is an approximation for the Bandelier magma, we may conclude that a high-Si rhyolite system at these temperatures is close to solidus conditions. Thus, a magma chamber at these temperatures is most likely highly crystalline and not sufficiently fluid to allow vigorous convection. Our findings also indicate that the magma chamber was relatively isothermal, with little difference found between the temperatures of unit G-1 (674-689°C) and the main cluster of temperatures from unit 7-7 (660-717°C). Our results suggest that a temperature gradient of at most 50-60°C was present in the chamber, and offer no clear evidence that the LBT magma chamber was thermally zoned.

It is important to stress that our temperature results for unit G-1 and for the bulk of unit 7-7 do not reflect the temperatures of these units at the time of their eruption, but rather their temperatures during crystallization in the relatively cool regime of the pre-injection LBT chamber.

Initial Magma Injection. If the temperature of the LBT magma chamber had dropped to near-solidus conditions, why are the LBT deposits not highly crystalline? We believe that a new injection of fresh magma at the base of the magma chamber raised the chamber's temperature to above solidus levels, which consequently led to substantial and widespread melting throughout the chamber (Figure 5B). We also believe that evidence for this injection is present in the few outlier temperature results from unit 7-7, ranging from 757-774°C, that are significantly hotter than the main cluster of results (Figure 4). Recent experimental work on silicic magmatic systems which are both liquid and mushy shows that denser inputs will pond at the base of the chamber, while buoyant inputs will rise efficiently through both liquid and mush, entraining crystals (Girard and Stix, 2008).

Following the initial magma injection into the system, or the emplacement of magma at the base of the chamber, heat and volatiles were added into the stagnant magma chamber. We propose that this input of heat raised the temperature of almost the entire magma chamber to well above solidus levels, initiating magma chamber-wide crystal resorption. Although most crystals from LBT have been broken or shattered, resorption features are nevertheless very common. These features include rounding of both quartz and sanidine (which make up ~95% of the modal mineralogy), and the common presence of pockmarked surfaces on quartz crystals, which Kuentz (1986) thought may be due to resorption. This resorption is likely to have been triggered mainly

by an increase in temperature. At near-solidus conditions, an increase in temperature can easily move the system from a state of crystallization to one of resorption. Changes in volatile content, both CO_2 and H_2O , also can affect whether resorption is occurring in a given system. Higher H_2O contents have the effect of lowering the solidus in the system Ab-Or-Q (Tuttle and Bowen, 1958). CO_2 can have a similar effect, as $\text{H}_2\text{O} - \text{CO}_2$ fluid mixtures can significantly lower the solidus of granitic crystalline assemblages (e.g., Petersen and Newton, 1990). However, few data are available on H_2O and even less on CO_2 at Valles, so at this point temperature remains the most likely mechanism of resorption.

Following the period of resorption, quartz crystal growth appears to have resumed for certain crystals of the LBT (unit 7-7). But we suggest that high-temperature quartz grains or rims are not commonly found in the LBT because the caldera-forming eruption occurred before conditions in the magma chamber could switch back from favoring quartz resorption (hot) to favoring quartz crystallization (cooler). The resumption of high-temperature quartz growth in the lower parts of the magma chamber, rather than at the top (unit G-1), may be due to the greater volatile content in the cap of the magma chamber (Dunbar and Hervig, 1992).

Our data place the timing of the initial injection at just prior to the LBT caldera-forming eruption, at a time early enough to allow for extensive crystal resorption, but not sufficiently long to allow the magma chamber to cool to a point such that widespread quartz crystallization might resume. Moreover, the injection must have occurred not long before eruption, since diffusion of Ti from relatively Ti-rich zones to relatively Ti-poor zones in quartz would have occurred on longer timescales, blurring the contacts between

the zones. Importantly, we see very sharp zones. Little evidence as to the composition or exact nature of the initial injection of magma is obtainable from our data, only that it was relatively hot ($>830^{\circ}\text{C}$). Based upon chemical analyses of Bandelier samples, Hervig and Dunbar (1992) concluded that rhyolitic magma was mixed into the LBT magma chamber at a time soon before its eruption. This new magma was found to have similar major elements but distinct trace elements compared to the magma already resident in the chamber, suggesting that both magmas shared a common origin or source material, with the newly injected magma simply being less fractionated. Stix and Gorton (1993) also proposed that the new magma was rhyolitic in composition, based on trace elements. The presence of small amounts of dacitic erupted products in both the LBT and UBT suggests that magma of a more primitive composition may have played a role as well.

LBT Eruption. The injection of the hot new magma would have altered the conditions within the magma chamber in several ways. It would have introduced a volume of magma which increased pressure and caused crystal resorption by superheating and/or release of latent heat by crystallization of this new magma. The increase of mass and volume within the chamber due to magma replenishment may have overpressurized the LBT magma chamber, triggering its explosive eruption. The widespread crystal resorption would have the following consequences: 1) the release of volatiles contained in melt inclusions within the grains; 2) the transformation of a potentially large volume of material from the solid to the liquid state; and 3) a significantly lowered viscosity of the magma, due to the hotter temperatures and the presence of fewer and smaller crystals. The first two consequences could potentially have generated additional pressure within

the system. The third result, the lowered viscosity, would have facilitated evacuation of the magma by causing it to become more fluid, and thus more mobile.

During the onset of the LBT eruption, the volatile-rich cap of the LBT magma chamber is thought to have been discretely tapped, forming the Guaje plinian pumice bed. The lack of clear chemical stratification within the LBT ignimbrite has led some to conclude that the rest of the LBT magma chamber was subsequently tapped chaotically, obscuring the presence of any pre-eruptive magmatic chemical zonation within the LBT ignimbrite (Kuentz, 1986). Our results indicate that a significant magmatic thermal gradient, of greater than 60°C, is unlikely to have been present. Finally, the drop in overburden pressure caused by the eruption of the LBT may have promoted continued replenishment of new magma into the system (e.g., Stix and Gorton, 1993).

Magma Recharge and Mixing: Thermal History of the CTR. Magma recharge likely occurred mainly before and during the LBT eruption. This new magma proceeded to mix and/or mingle with the remains of the LBT magma chamber, creating a new hybrid magma which then proceeded to cool and evolve. Thermal evidence of the hot injection is visible in the rimmed quartzes of unit 7-8, which was the first erupted unit of the Cerro Toledo Rhyolite, and of unit 15-8, which was erupted soon after. In fact, the emplacement of these two units occurred so soon after the LBT eruption that their ages are indistinguishable (Spell et al., 1996).

A majority of the CL-imaged quartz grains of both units 7-8 and 15-8 are zoned, and these zoned grains invariably have darker, lower-temperature cores and brighter, higher-temperature outer rims. Boundaries between cores and rims are generally very sharp and commonly rounded. These sharp contacts indicate that the rims grew following

the immersion of the core of the grain into a higher-temperature regime following a period of crystal resorption and dissolution. The gradual transition of the core to a higher-temperature environment would, on the other hand, most likely be reflected by a gradational change from the darker core to a brighter rim. Gradational zoning is rare but present, almost exclusively in unit 15-8, and is invariably lighter towards the exterior of the grain (Figure 3D). Although this pattern could be caused by progressive heating of the magma chamber, a more likely scenario is the gradual sinking of the grain towards the lower, hotter part of the magma chamber via crystal settling. Evidence of this process may only be observable in unit 15-8 due to a high thermal gradient which was present in the chamber during magmatic recharge, in contrast to the relatively isothermal LBT magma chamber. The sharp nature of the contacts visible between the cores and rims of most zoned grains also indicates that little time elapsed between crystallization of the rims and eruption of the grains.

The core temperatures from units 7-8 and 15-8 correspond very closely to the bulk of LBT temperatures (Figure 4). These cores are thus presumed to be relict from the LBT magma chamber, with rims crystallized in the new, hotter regime due to the magmatic injections before, during and after caldera collapse. This implies that magma mixing and mingling occurred between the old and new magmas, resulting in hotter conditions throughout the magma chamber. Based on the abundance of colder cores in units 15-8 and 7-8, a considerable amount of magma failed to erupt and proceeded to mix with the new injection.

The new magma injection likely continued during caldera collapse. This cataclysmic eruption would have decreased the overlying pressure, thus allowing new

magma to enter the system. The mechanism of caldera collapse also likely facilitated the mixing of the two magmas. Experiments by Kennedy et al. (2008) have shown that a subsiding caldera block or blocks can efficiently stir and mix magmas in a magma chamber. This vigorous stirring of the magma chamber also may have generated the heterogeneity we see in rim temperatures from unit 7-8. Turbulent mixing can result in pockets of the chamber which are hotter than others. In unit 7-8, certain quartz crystals have rims with a range of temperatures, although all are hotter than the relatively homogeneous core temperatures.

Simple mixing of a strongly thermally zoned magma chamber could not have created the observed quartz zoning patterns without a new injection. In a magma chamber in which only stirring had occurred, both cold core/hot rim and hot core/cold rim combinations should be present. Such a pattern is never observed in quartzes from units 7-8 and 15-8.

Stix and Gorton (1993) proposed two distinct Rayleigh fractionation trends in the Bandelier magma system, suggesting that early-erupted CTR material may represent the tapping of a deeper, hotter part of the LBT magma. In accordance with a second hypothesis proposed by Stix and Gorton (1993) to explain these trends, we propose that the early CTR material represents a mixing trend between the LBT magma and the newly injected magma. This new mixed magma then proceeded to fractionate to explain the evolution noted by Stix and Gorton (1993) in the later-erupted CTR units and the UBT. The restitic cores of 7-8 and 15-8 represent evidence for mixing, while the progressively cooler temperatures of succeeding CTR units, as shown by our data, support the idea of fractionation and cooling during the time of CTR activity.

Later-erupted CTR and UBT. The later-erupted CTR units appear to record the tapping of an evolving magma body. The small volumes of these units indicate that only a small portion of the magma system was sampled during each event, presumably from the topmost part of the chamber. The temperature evolution that we observe indicates a gradually cooling system (Figure 4). Zoned grains are the exceptions during this period, perhaps caused by small-scale injections of hotter magma into the system during CTR time.

Temperatures from the initial plinian fall deposit of the UBT cluster around the hotter end of the temperature range found in the main-stage ignimbrite. The hotter nature of the UBT, in comparison to the LBT, may explain the greater degree of welding present in this deposit. No clear evidence of a trigger was found in this study, although further work on the post-UBT rhyolites is clearly warranted to explore the possibility of zoned quartz crystals being erupted in post-caldera collapse time, as we see in the LBT.

Diffusion of Ti in Quartz. Given sufficient time, the Ti contained within quartz crystals will diffuse from areas of higher Ti concentration to areas of lower Ti concentration. Thus, after a sufficiently long period of time, a crystal zoned in Ti concentration could theoretically become “unzoned.” Ti diffusion is described by the Arrhenius relationship of Cherniak et al. (2004):

$$D = 7 \times 10^{-8} \exp [(-273 \text{ kJ mol}^{-1}) / RT] \text{ m}^2 \text{ s}^{-1}$$

Thus, Ti diffusivity depends exclusively on temperature T and increases significantly with increasing temperature. From the diffusivity D , it is then possible to calculate the distance d over which Ti is likely to diffuse within a grain:

$$d = [4Dt]^{0.5}$$

where t is time (e.g. Wark and Watson, 2006). Ti in quartz phenocrysts of unit G-1, for example, at an average temperature of 682°C (Table 1), would take ~250 ka to diffuse 50 μm (the approximate width of thin zones visible in quartz grains of unit 15-8). Therefore, had any of the quartz grains of unit G-1 been zoned originally, these phenocrysts would have become unzoned to their presently visible state via Ti diffusion had they dwelled in the magma chamber for at least ~250 ka. This also signifies that any zoned crystals which formed following the LBT caldera collapse (i.e., in units 7-8 or 15-8), in a magma chamber at a conservatively estimated temperature of 830°C, would have undergone diffusion and re-equilibration in only ~3 ka. These crystals would therefore no longer appear zoned in later-erupted CTR units. Our observations are consistent with this hypothesis.

As the sharp boundaries visible in zoned grains of unit 15-8 are <10 μm thick, Ti in quartz grains of this unit only had time to diffuse roughly 10 μm at temperatures on the order of 830°C (Table 1) before being erupted (e.g., Wark and Watson, 2007). Ti diffusion over a distance of 10 μm at 830°C will occur in only ~100 years. In other words, the zoned quartz grains from unit 15-8 were probably erupted at most only ~100 years after they crystallized their high-Ti rims. This calculation implies that the injection of magma which led to the formation of the bright, sharply defined rims on many quartz grains from units 7-8 and 15-8 was followed very quickly by their eruption. The presence of sharply defined rims on certain quartz grains from later eruptions of the CTR may also indicate that magmatic recharge occurred as discrete pulses of new magma shortly prior to the eruption of each zoned quartz-bearing CTR unit. However, zoned

quartz crystals from these later-erupted CTR units are rare, suggesting that these potential new magma injections may have been very localized and/or of small volume.

Comparison to Another Large Silicic System: the Bishop Tuff. Wark et al. (2007)

utilized CL-visible zonations in quartz phenocrysts and the TitaniQ geothermometer to document the thermal history of the 0.76 Ma Bishop Tuff, erupted from Long Valley caldera. Although a detailed comparison between the Bandelier Tuff and the Bishop Tuff is beyond the scope of this work, a few significant similarities between our results and those of Wark et al. (2007) may be briefly highlighted. The Bishop Tuff is a chemically and thermally zoned sequence (Hildreth, 1979; Wark et al., 2007; Hildreth and Wilson, 2007). In the Bishop Tuff, quartz phenocrysts from all but early-erupted pumices display CL-visible zonations, with rims brighter than cores and with thickness and CL emission intensity increasing with the eruption sequence. Coupled with melt inclusion data from previous studies, Wark et al. (2007) concluded that their observations were best explained by the injection of hot, CO₂-rich mafic magma into the magmatic system several hundred years before the eruption of the Bishop Tuff. This explanation was based upon the relatively high CO₂ concentrations in melt inclusions near rims of late-erupted quartz, and the evidence for partial dissolution of quartz cores followed by new growth at higher temperatures. The mechanism proposed for this new growth of quartz is the reduction of H₂O activity in the system by the addition of CO₂. Recharge by mafic or silicic magma is proposed as a likely trigger of the 0.76 Ma caldera-forming eruption (Hildreth and Wilson, 2007; Wark et al., 2007).

Our results, and thus our conclusions, show some similarities and some differences with those for the Bishop Tuff. First, we found only a very small number of

zoned quartz phenocrysts within the Lower Bandelier Tuff; the great majority of zoned crystals were found in the basal Cerro Toledo Rhyolite. However, the same pattern of zoned crystals, invariably featuring hotter rims and cooler cores with a sharp boundary separating the two zones, is found in both systems. Thus, while the injection of new, possibly CO₂-rich and hotter magma may be documented in the quartz phenocrysts of both systems, the timings of these injections with respect to the caldera-forming eruptions, or the manner by which these injections affected the magma chamber, may differ. Magma recharge may have been a cause of the caldera-forming eruption at Long Valley, and likely played a similar role for the LBT caldera-forming eruption. Although many questions clearly remain unresolved, it is most likely that magma recharge played a significant role during the histories of caldera-forming eruptions at both Long Valley and Valles.

Conclusions

The analysis of quartz crystal zoning has provided unique insight into the thermal history of the Bandelier magma system. Cathodoluminescence imaging of sampled quartz grains, combined with titanium-in-quartz geothermometry, reveals a relatively isothermal magma chamber prior to the eruption of the Lower Bandelier Tuff, at temperatures in the vicinity of 660-715°C. These temperatures are near the solidus estimated for such a system, implying that the LBT chamber was highly crystalline at some point prior to its eruption. An injection of magma then occurred shortly before caldera collapse, raising the chamber temperature by ~100°C and triggering widespread crystal resorption. The ubiquitous presence of resorption features on crystals from the LBT and the low crystal content of the erupted products chronicle this injection into the system. Magma injection

is a likely trigger for the LBT cataclysmic volcanism. Large-scale magma recharge of the system probably continued during caldera formation, and possibly for a short period of time thereafter.

After the period of crystal resorption, crystallization of quartz continued, although at significantly higher temperatures. Early-erupted Cerro Toledo Rhyolite quartzes are commonly zoned; these grains invariably reveal cold (685-700°C) cores and hotter (by ~100°C) rims, while unzoned grains are uniformly high-temperature. The common presence of restitic quartz cores in these units, which were crystallized during the colder chamber conditions of the pre-injection LBT system, reveals that a significant amount of magma remained in the chamber following caldera formation. A reasonably large range of observed rim temperatures in early-erupted CTR units shows that the chamber was not thermally uniform during this time, possibly due to turbulent mixing induced by caldera subsidence.

Through the thermal history of LBT and CTR events, we are able to obtain glimpses into the long-term evolution of a magma chamber, from cool pre-caldera conditions, through mixing and mingling of new and restitic magmas immediately prior to and/or during caldera formation, to a gradually cooler and more uniform chamber in post-caldera time. We do not see strong thermal evidence of continued large-scale magma injections throughout the CTR. Although the plinian unit of the Upper Bandelier Tuff has a higher temperature than late-erupted CTR magmas, our results show no clear evidence for an injection preceding the UBT eruption. Further investigation into the thermal history of the post-caldera rhyolites of Valles caldera, erupted following the UBT event, would shed more light on this subject.

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FIGURE CAPTIONS

Figure 1: Simplified map of the Valles caldera complex, showing the locations of the Cerro Toledo Rhyolite erupted products, and the three sections (6, 7 and 15) sampled for this study. Modified from Stix and Gorton (1993).

Figure 2: Simplified stratigraphic section of the Bandelier Tuff and the Cerro Toledo Rhyolite, showing only those units relevant to our study. All units, except for unit Alpha, were defined and first described by Stix (1989). Dates are from Spell et al. (1996), and the age of unit 15-12 is shown to provide a better constraint for the age of unit 15-11. All dates are $^{40}\text{Ar}/^{39}\text{Ar}$ isochron ages, except for unit 15-8, which is a weighted mean average. Section is not to scale.

Figure 3: Images of quartz grains by cathodoluminescence imaging. A: grain #2, unit G-1; note the very rounded appearance of the unbroken edge, typical of grains from this unit, and ascribed to crystal resorption. B: grain #26, unit 7-8. C: grain #7, unit 15-8. D: grain #27, unit 15-8; diffuse transition visible between darkest innermost core and intermediate zone, possibly due to crystal settling. Images B, C and D represent typical examples of zoned quartz grains from the early erupted Cerro Toledo Rhyolites; all have darker cores and lighter rims, the cores exhibit rounding, and the outermost rims display sharp contacts with adjacent rims or cores.

Figure 4: Titanium content of all sampled quartzes, and corresponding temperatures of crystallization calculated with the Ti-in-quartz relationship described in Wark and Watson (2006). All temperatures calculated using $a_{\text{Ti}} = 0.4$. Results are shown in Table 1, and are here organized by unit in increasing stratigraphic order. Temperature

estimates using other geothermometers for four units from previous work are also shown for comparison (units G-1 and 6-12: Warshaw and Smith (1988); units 15-8 and 15-11: Stix and Gorton (1990)).

Figure 5: Schematic cartoon showing the different stages of the evolution of the Lower Bandelier magmatic system. A: Pre-injection LBT magma chamber. At near-solidus temperatures, the chamber is highly crystalline and probably stagnant. B: Injection into LBT chamber. Injection of new, relatively hot magma into the system results in significant and widespread crystal resorption. This melting, causing the transfer of a large volume of material from the solid to the liquid phase as well as the release of volatiles, may have triggered the LBT eruption at 1.61 Ma. C: Caldera collapse phase and early CTR post-collapse phase. LBT caldera collapse stirs remnant resident magma with new, relatively hot magma replenishing the system. Mixing and mingling are promoted by upwelling of less dense new magma, and by downward pressure exerted by collapse of the overlying caldera block or blocks. High-temperature rims grow over restitic, partially resorbed cores during and after mixing. D: Later-erupted CTR. System gradually cools, with limited or no magma injected into the system. New crystals grow at relatively low temperatures, and zoned grains from early CTR time are gradually unzoned by Ti diffusion. The chamber becomes more crystalline as it cools, gradually returning to a state similar to A above.

Table 1. Ti Contents of Sampled Quartz Grains from the Bandelier Tuff and Cerro Toledo Rhyolite and Corresponding Temperature Calculations

Unit and Grain #	Ti (ppm)	T (°C) with $a_{Ti}=0.4$	T (°C) with $a_{Ti}=0.6$	T (°C) with $a_{Ti}=1.0$	Zonation Analyzed
Unit G-1:					
# 2	23.94	689	648	600	unzoned
# 4	22.76	684	643	596	unzoned
	21.04	676	635	589	unzoned
# 6	22.46	682	642	595	unzoned
	20.75	674	634	588	unzoned
# 11	22.87	684	643	589	unzoned
<hr/>					
Averages:					
Unzoned	22.30	682	641	593	
<hr/>					
Unit 7-7:					
7-7 X					
“Wolf”	23.04	685	644	597	unzoned
	22.40	682	641	595	unzoned
	24.72	693	651	603	unzoned
	25.87	698	655	607	unzoned
“Island”	30.97	717	674	624	unzoned
	28.87	710	666	617	unzoned
	21.97	680	639	593	unzoned
	22.34	682	641	594	unzoned
# 18	49.50	774	725	669	unzoned
	43.19	757	709	656	unzoned
7-7 Y					
“Apophis”	22.53	683	642	595	unzoned
	26.36	700	657	609	unzoned
“Hathor”	22.09	681	640	593	unzoned
7-7 Z					
“Jack”	21.72	679	638	592	unzoned
	21.92	680	639	593	unzoned
“Man”	22.93	685	644	597	unzoned
	21.55	678	638	591	unzoned
	20.67	674	634	588	unzoned
# 23	21.45	678	637	591	unzoned
	20.66	674	634	588	unzoned
7-7 C					
# 10	18.02	660	621	576	unzoned
# 11	27.61	705	662	613	unzoned
# 13	49.11	773	724	669	unzoned
	25.31	695	653	605	unzoned
# 15	20.54	673	633	587	unzoned
	26.78	701	659	610	unzoned
	23.99	689	648	601	unzoned
<hr/>					
Averages:					
Unzoned	26.15	696	654	606	
<hr/>					

Unit 7-8:

# 1	17.62	658	619	574	core
	19.95	670	630	585	core
	46.65	766	718	663	rim
	46.16	765	717	662	rim
# 8	22.02	680	640	593	core
	32.68	724	679	629	core
	36.78	737	692	640	rim
	32.10	722	677	627	rim
# 9	19.43	667	628	582	core
	51.22	778	729	673	rim
	55.24	788	737	681	rim
# 11	50.41	776	727	671	unzoned
	37.90	741	695	643	unzoned
	32.52	723	679	628	unzoned
# 20	47.61	769	720	665	unzoned
	58.99	796	745	688	unzoned
# 23	22.35	682	641	594	core
	17.99	660	621	576	core
	27.26	703	661	612	rim
	22.41	682	641	595	rim
#25	21.41	677	637	591	core
	17.77	658	620	575	core
	39.53	746	700	647	rim+core (overlap)
#26	19.09	666	626	581	core
	57.62	793	742	685	rim
<hr/>					
Averages:					
Cores	21.03	674	634	588	
Rims	41.50	748	701	648	
Unzoned	45.49	761	713	659	
<hr/>					
Unit 15-8:					
March '07					
#7	73.34	826	772	711	rim
	73.91	827	773	712	rim
	27.05	702	660	611	core
#8	67.05	813	761	701	rim
	26.55	700	658	610	core
#13	48.43	771	722	667	rim
	24.68	692	651	603	core
#18	65.42	810	758	699	rim
	28.87	710	666	617	intermediate zone
	24.55	692	650	603	core
#21	68.47	816	763	704	rim
	60.32	799	748	690	intermediate zone
	26.21	699	657	608	core
	63.95	807	755	696	intermediate zone
	69.47	818	765	705	rim
December					
'06					
#20	78.28	835	780	719	unzoned
	79.11	836	782	720	unzoned
#22	25.38	695	654	606	intermediate zone
	22.87	684	643	596	core (with diffuse boundary)
	61.21	801	750	692	rim
#23	40.56	749	702	649	core

	68.78	817	764	704	rim
	68.82	817	764	704	rim
#26	73.9	827	773	712	unzoned
	73.58	826	772	712	unzoned
	76.58	832	777	716	unzoned
#27	52.53	781	732	675	intermediate zone
	41.06	750	704	651	core
	50.26	776	726	671	intermediate zone
	69.66	819	766	706	rim
<hr/>					
Averages:					
Cores	33.36	718	674	624	
Intermed.	46.89	761	714	659	
Rims	66.78	812	760	700	
Unzoned	76.29	831	777	716	
<hr/>					
Unit 15-9:					
#3	54.87	787	737	680	unzoned
	52.76	782	732	676	unzoned
	55.29	788	738	681	unzoned
#5	51.84	779	730	674	unzoned
	54.79	787	737	680	unzoned
	52.10	780	731	675	unzoned
	52.27	780	731	675	unzoned
	52.30	781	731	675	unzoned
<hr/>					
Averages:					
Unzoned	53.28	783	733	677	
<hr/>					
Unit 15-11:					
#3 *	42.87	756	708	655	unzoned
*	40.31	748	702	649	unzoned
*	46.11	765	717	662	unzoned
*	43.52	758	710	656	unzoned
*	41.48	752	705	652	unzoned
#6	43.38	757	710	656	unzoned
	48.71	772	723	668	unzoned
#9	44.15	759	712	658	unzoned
	43.60	758	710	657	unzoned
<hr/>					
Averages:					
Unzoned	43.79	758	711	657	
<hr/>					
Unit 6-8:					
#54	25.00	694	652	604	unzoned
	24.47	692	650	602	unzoned
	23.20	686	645	598	unzoned
#55	25.24	695	653	605	core
	24.64	692	651	603	core
	33.29	726	681	630	rim
	33.89	728	683	632	rim
#58 *	24.83	693	651	604	unzoned
#60 (*)	22.58	683	642	595	unzoned
(*)	22.24	681	641	594	unzoned
#61	23.15	686	644	597	unzoned
	22.52	683	642	595	unzoned
	22.52	683	642	595	unzoned

Averages:					
Cores	24.94	694	652	604	
Rims	33.59	727	682	631	
Unzoned	23.50	687	646	599	
Unit 6-12:					
#1	35.45	733	688	636	unzoned
	34.69	731	686	634	unzoned
#4	35.25	732	687	636	unzoned
	35.80	734	689	637	unzoned
	32.78	724	680	629	unzoned
#7	35.40	733	688	636	unzoned
	34.05	728	684	633	unzoned
#8	32.36	722	678	628	unzoned
	33.72	727	683	632	unzoned
#10	34.25	729	684	633	core
	47.01	767	719	664	core
	34.19	729	684	633	rim (low-contrast)
	56.08	790	739	682	rim (low-contrast)
	31.34	719	675	625	rim (low-contrast)
Averages:					
Cores	40.63	748	702	649	
Rims	40.54	746	699	647	
Unzoned	34.39	729	685	633	
Unit Alpha:					
#47	41.07	751	704	651	unzoned
	42.51	755	708	654	unzoned
	36.14	735	690	638	unzoned
#48	25.69	697	655	607	unzoned
	25.99	698	656	608	unzoned
	27.93	706	663	614	unzoned
	27.29	703	661	612	unzoned
#49	34.72	731	686	634	unzoned
	32.23	722	678	627	unzoned
#51	25.82	697	655	607	core
	27.99	706	663	614	core
	31.09	718	674	624	core+rim (overlap)
#52	32.96	725	680	629	unzoned
	25.91	698	656	607	unzoned
"Jonathan"	29.35	711	668	619	unzoned
	34.81	731	686	635	unzoned
	28.49	708	665	616	unzoned
	28.03	706	663	614	unzoned
	28.16	707	664	615	unzoned
"Bill"	31.13	718	674	624	low-contrast rim
					low-contrast
	25.64	697	655	606	intermediate zone
	26.53	700	658	610	core
	29.84	713	670	620	core
	29.13	711	667	618	core
"Michelle"	76.69	832	778	716	unzoned
	29.13	711	667	618	unzoned
	25.79	697	655	607	unzoned
	28.25	707	664	615	unzoned

	27.30	703	661	612	unzoned
	27.27	703	661	612	unzoned
<hr/>					
Averages:					
Cores	27.86	706	663	614	
Rims	31.11	718	674	624	
Intermed.	25.64	697	655	606	
Unzoned	32.53	720	676	626	

Notes: 1) Analyses with an asterisk (*) were performed on grains with faint growth zones visible, but without any appreciable change in CL tone from core to rim (and so technically CL-unzoned). 2) “Low-contrast” rims are similar, but still slightly different, in tone compared to the core.

Table 2. Determination of the Activity of Ti in the Bandelier System

Unit	Temperature estimate (K)	Average Ti of sampled quartzes of Unit (ppm)	a_{Ti}	a_{Ti} per unit
G-1 ¹	969	22.30	0.35	0.35
6-12 ¹	970	36.60	0.57	0.57
15-8 ² (lower estimate)	1056	69.75*	0.52	
15-8 ²	1086	69.75*	0.42	0,43 +/- 0,09
15-8 ² (upper estimate)	1116	69.75*	0.34	
15-11 ² (lower estimate)	1010	43.79	0.48	
15-11 ²	1050	43.79	0.34	0.36 +/- 0.12
15-11 ² (upper estimate)	1090	43.79	0.25	
Average				0.43

¹ Temperature estimates obtained from ferrohedenbergite-fayalite pairs, by Warshaw and Smith (1988).

² Temperature estimates obtained from magnetite-ilmenite pairs, by Stix and Gorton (1990). Upper and lower estimates reflect the given error range for the temperatures, i.e. 1086K $\pm$ 30K for unit 15-8, and 1050K $\pm$ 40K for unit 15-11.

* Listed Ti content for unit 15-8 is the average of all the analyses of both unzoned high-temperature quartz grains and of the outer rims of zoned quartz grains.

Figure 1

Figure 1.

Figure 2

Figure 2.

Figure 3

Figure 3.

Figure 4

Figure 4.

Figure 5

Figure 5.

14 May 2008

Professor Alfred T. Anderson, Jr.
Editor
The Journal of Geology
University of Chicago
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USA

Dear Fred,

I am pleased to submit the accompanying manuscript, "Thermal History of the Bandelier Magmatic System: Evidence for Magmatic Injection and Recharge at 1.61 Ma as Revealed by Cathodoluminescence and Titanium Geothermometry", by Michelle E. Campbell, Jonathan B. Hanson, William G. Minarik, and myself. I would be most grateful if you might consider this work for publication in the Journal of Geology. The manuscript is not being considered for publication elsewhere, and all authors have seen and approved the manuscript. Potential reviewers for the paper are:

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I believe the paper is an interesting study of how a large silicic magma chamber is replenished with new magma, triggering a caldera-forming eruption, as revealed by quartz geothermometry. If you require anything further, please don't hesitate to ask.

Kind regards,

John

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