

ARTICLES

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 1.61 Ma, and the second emplaced the Upper Bandelier Tuff (UBT) at 1.22–1.26 Ma. During the time between the LBT and the UBT, the much smaller-scale Cerro Toledo Rhyolite (CTR) was sporadically erupted. Quartz crystals from these stages of activity were imaged with cathodoluminescence microscopy, and growth zones in certain quartzes, due to varying Ti content, were revealed. Crystallization temperatures were obtained with a titanium-in-quartz geothermometer. The LBT quartzes are unzoned, with temperatures clustering between 660° and 715°C when a calculated a_{TiO_2} 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 in LBT crystals require that pervasive melting affected the LBT magma chamber at some point before 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, whereby new magma mixed vigorously with leftover magma and high-temperature rims crystallized around low-temperature restitic quartz cores. Thermal data for the rest of the CTR record the continuing cooling and evolution of this mixture of magma, while results for the culminating UBT reveal generally unzoned quartz crystals with a roughly constant temperature of 685°–725°C. Altogether, these results present an unprecedented glimpse into the thermal history of the Bandelier magma system, as well as strong evidence concerning the timing and overall importance of magmatic injections in silicic magma systems.

Online enhancement: appendix table.

Introduction

The Valles caldera, located in north-central New Mexico (fig. 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 that has shaped our understanding of cataclysmic silicic magmatism.

Two episodes of large-scale silicic volcanism, in-

cluding caldera collapse, have occurred at the Valles complex during the past 1.6 Ma. The first produced the 1.61-Ma Lower Bandelier Tuff and formed the Toledo caldera; the second erupted the 1.22–1.26-Ma Upper Bandelier Tuff (Spell et al. 1996; Phillips et al. 2007) and led to the collapse of the Valles caldera at a location nearly coincident with that of the earlier Toledo caldera (Self et al. 1986). In addition, several smaller lava dome, plinian, and ignimbrite eruptions, collectively termed the Cerro Toledo Rhyolite, occurred between the two caldera-

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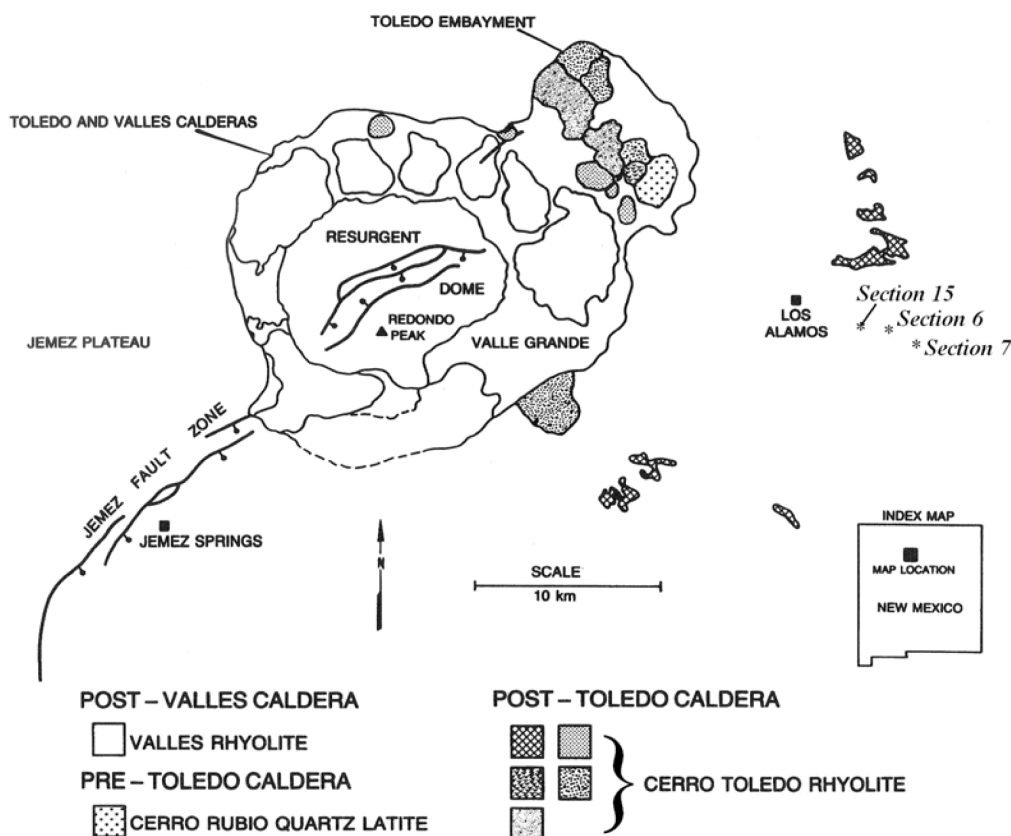


Figure 1. Simplified map of the Valles caldera complex, showing the locations of the Cerro Toledo Rhyolite erupted products and the three sections (6, 7, and 15) sampled for this study. Modified from Stix and Gorton (1993).

forming events (Heiken et al. 1986). This unusual combination of events offers a rare window into the development and evolution of a magmatic system that has undergone multiple caldera-forming events.

In this study, we examine growth zones in quartz crystals from the Bandelier Tuff and the intervening Cerro Toledo Rhyolite that are revealed by cathodoluminescence (CL) imaging of individual 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 its temperature of crystallization (Wark and Spear 2005; Wark and Watson 2006). Using a new titanium-in-quartz geothermometer based on this relationship (Wark and Watson 2006), we have calculated the crystallization temperatures 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 in which magma injection caused substantial crystal resorption throughout the magma chamber, thus becoming intimately related to the inception of caldera-forming eruptions. These processes, in turn, may have caused the destabilization and subsequent catastrophic evacuation of the magma chamber. In addition, 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 inter-

mediate 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 recently erupted products of the JVF. 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, according to Spell et al. (1996), or 1.256 ± 0.010 Ma, according to Phillips et al. (2007). The eruptions of the LBT and the UBT led to the formation of the Toledo and Valles calderas, respectively (fig. 1; Smith and Bailey 1968; Heiken et al. 1990).

The LBT is made up of the plinian Guaje 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 that blankets the underlying topography (Kuentz 1986). The deposits of this bed are massive to well bedded and 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). On the basis of 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 (Kuentz 1986; Self et al. 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 nonwelded nature of the LBT ignimbrite also promoted the relatively rapid erosion of this member (Kuentz 1986). The crystal content of the LBT reaches 19% (Kuentz 1986). The LBT ignimbrite is up to 800 m thick inside the caldera, as determined by drilling by Union Oil, and

varies from 0 to 120 m thick outside the caldera (Nielson and Hulen 1984; Kite 1985; Kuentz 1986). Outside the caldera, 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 tephras erupted sporadically during the 352–383-k.yr. time span between the eruptions of the LBT and the UBT (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 was essentially continuous 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 before the eruption of the UBT (Spell et al. 1996). The CTR was erupted from the Toledo caldera and the Toledo embayment, and outcrops of these tephras are generally restricted to locations such as canyons northeast of Los Alamos (Heiken et al. 1986).

The UBT comprises the plinian Tsankawi Pumice Bed and the Tshirege ignimbrite units. The total erupted volume of the UBT is approximately 250 km^3 DRE (Self and Lipman 1989), and it covers more than 1300 km^2 , with the 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 before column collapse and the production of large-scale pyroclastic flows. The vent location for the plinian eruption has been interpreted to be at the current location of resurgent doming, while the site of the Valles caldera is nearly coincident with that of the previous Toledo caldera (Heiken et al. 1986; 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). Trace-element studies of the UBT, unlike those of the LBT, do not reveal a simple fractional crystallization evolution. According to Balsley (1988), the magma composition was initially similar to the LBT's but experienced some fraction of either mixing or assimilation.

Methodology

Sample Collection. Samples were collected from the LBT (units G-1 and 7-7), the CTR (units 7-8, 15-8, 15-9, 15-11, and 6-8), and the UBT (units 6-12 and Alpha). All these units were described by Stix (1989), except for Alpha, which was sampled from unit 3t of the UBT ignimbrite (Warren et al. 2007). Ages of these units (Spell et al. 1996) and their locations within the stratigraphic sequence are shown 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 μm were handpicked and mounted in epoxy on 1-inch grain mounts, which were then polished and carbon coated for cathodoluminescence imaging.

Cathodoluminescence Imaging. Cathodoluminescence (CL) electron microscopy reveals the presence of zonations in certain quartz crystals (Pepard et al. 2001). The origin of CL zonations in quartz is thought to be variations in titanium incorporated into the SiO_2 crystal structure (Wark et al. 2007). The CL zones are imaged in two dimensions but are in actuality three-dimensional within the quartz grain. This fact, 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 (fig. 3) were obtained at the Université du Québec à Montréal with 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 s per picture. Scans were conducted at accelerating voltages of 15, 20, and 30 kV. Scans performed at the 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 A1, available in the online edition or from the *Journal of Geology* office). The instrument used was a NewWave UP-213 Laser Ablation System coupled to a PerkinElmer/SCIEX ELAN 6100 DRCplus ICP-MS. Ablations were usually conducted as line scans at

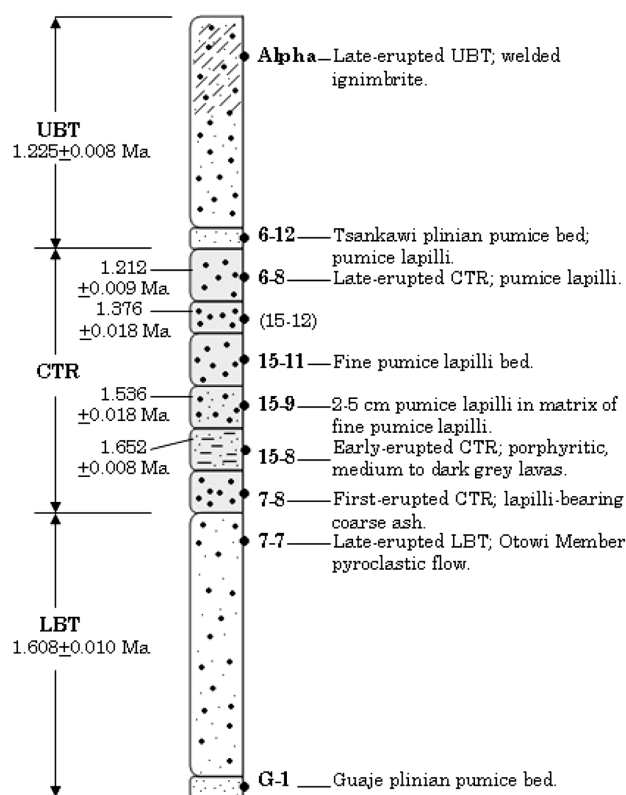


Figure 2. Simplified stratigraphic section of the Banderlier Tuff and the Cerro Toledo Rhyolite, showing only units relevant to our study. All units, except for Alpha, were defined and first described by Stix (1989). Dates are from Spell et al. (1996), and the age of unit 15-12 is shown to provide a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

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 with 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 of the LA-ICP-MS, as calculated by Glitter, 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 the %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

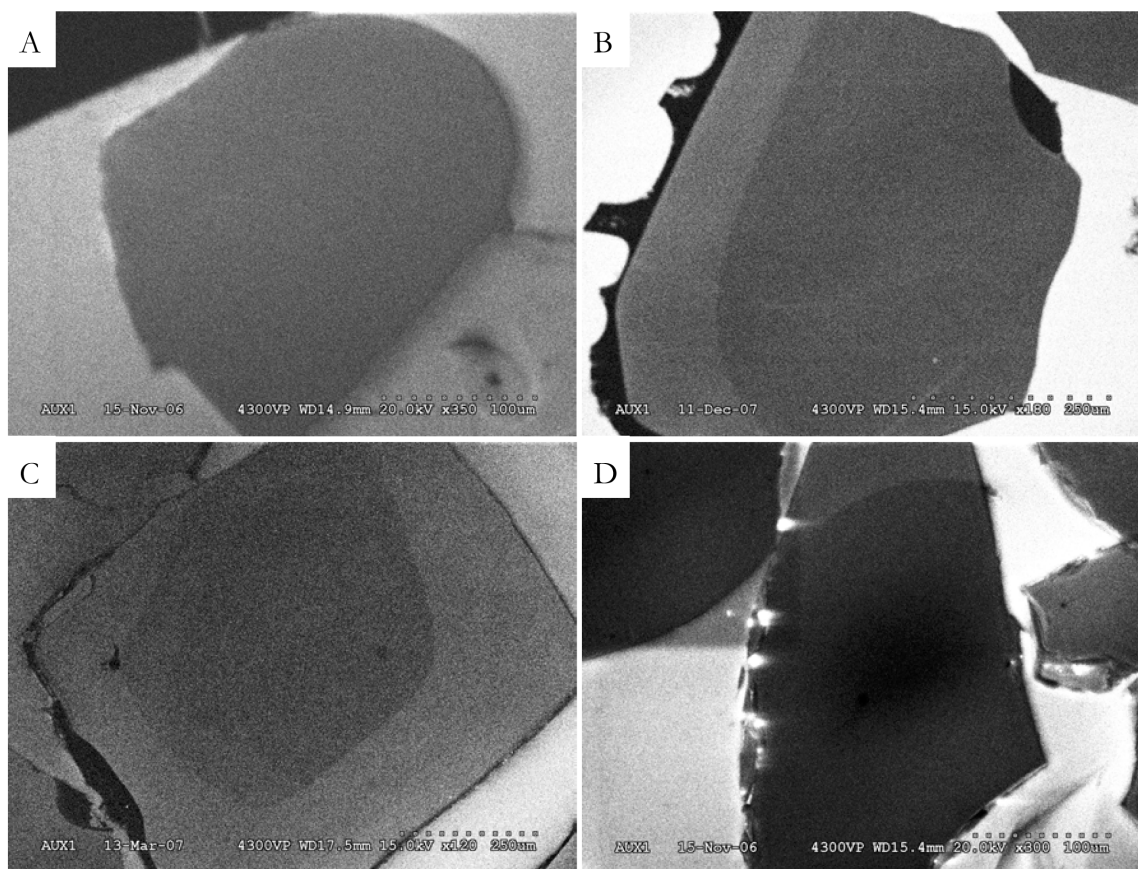


Figure 3. Images of quartz grains from cathodoluminescence imaging. *A*, Grain 2, unit G-1; note the very rounded appearance of the unbroken edge, typical of grains from this unit and ascribed to crystal resorption. *B*, Grain 26, unit 7-8. *C*, Grain 7, unit 15-8. *D*, Grain 27, unit 15-8; diffuse transition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

concentrations is not generally available, and use of the NIST 610–614 glasses as standards is ill advised because of 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, California, was used as a standard; the minor Zr content contributes insignificant counts at mass 48. Estimated total analytical accuracy is better than 10% at low TiO_2 concentrations and approaches 5% at higher TiO_2 concentrations. These estimates are based on comparisons between TiO_2 concentrations determined via LA-ICP-MS and those from electron microprobe analysis (EMPA) and secondary ion mass spectrometry (SIMS; Wark and Watson 2006).

Two isotopes of Ti, ^{48}Ti and ^{49}Ti , were measured during our LA-ICP-MS analyses. Because of 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 . The concentrations obtained for ^{48}Ti were therefore of higher precision than those for ^{49}Ti . However, relative precision for ^{48}Ti and ^{49}Ti differed significantly only when the count rates for ^{49}Ti descended to very low levels, below approximately 80 counts/s (which occurred only in certain samples with less than ~40 ppm Ti). Count rates for ^{49}Ti typically range from 100 to 1000 counts/s (~30–80 ppm) and tend 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). Because concen-

trations of Ti in igneous and metamorphic quartz phenocrysts are relatively high, generally ranging from 1 to >100 ppm (Wark and Watson 2006), they may be easily and precisely measured by microbeam techniques such as EMPA, SIMS, and 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 and Watson 2006; Wark et al. 2007). Using experimental data, Wark and Watson (2006) derived an equation describing the relationship between the temperature of crystallization and the concentration of Ti in quartz:

$$T(K) = \frac{-3765}{\log(X_{\text{Ti}}/a_{\text{TiO}_2}) - 5.69}.$$

The principal unknown in this relationship is the activity of titania (a_{TiO_2}). Assuming Henrian behavior, $a_{\text{TiO}_2} = \lambda X_{\text{Ti}}$, 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 $a_{\text{TiO}_2} = 1$. The lack of rutile indicates that $0 < a_{\text{TiO}_2} < 1$. Lowering a_{TiO_2} 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_{TiO_2} set to 1.0.

The activity of titania is the most difficult parameter to constrain. An extensive search was made for the presence of rutile in our samples. Several grains of quartz and sanidine were observed to contain needlelike inclusions of a brown mineral phase. When analyzed by electron microprobe, this phase was identified as chevkinite, a mineral enriched in light rare earth elements. No direct evidence was found for the presence of rutile in our samples. We thus conclude that $a_{\text{TiO}_2} < 1.0$.

Hayden and Watson (2007) determined an expected a_{TiO_2} range of $0.5 \leq a_{\text{TiO}_2} \leq 0.6$ for a large silicic system. In work on the Long Valley caldera, Wark et al. (2007) used $a_{\text{TiO}_2} = 0.6$ for the titanium-in-quartz temperature calculations. This value was based on calculations using iron-titanium oxides.

As proposed by Wark and Watson (2006), an a_{TiO_2} value for the Bandelier system was determined by using ferrohedenbergite-fayalite pairs from the Bandelier Tuff (Warshaw and Smith 1988) or magnetite-ilmenite pairs from the CTR (Stix and Gorton 1990). An a_{TiO_2} value of approximately 0.4 was calculated through the following steps. Temperature estimates for four different units (one from the

LBT, two from the CTR, and one from the UBT) were determined with the aforementioned geothermometers (table 1). The Ti content of quartzes in each unit, except those with notable core and rim zonations, was then calculated by averaging all analyses performed in each unit. Quartz crystals zoned with respect to Ti content were found in several units. In these well-zoned cases, only the Ti analyses performed on outer rims and on high-temperature grains were averaged, as these were deemed to be the only types of quartz that crystallized from the magmatic conditions prevalent at the time of their eruption. With the average Ti content, as well as the temperature estimate from the other geothermometers, for each unit in the titanium-in-quartz formula (Wark and Watson 2006), the remaining variable, a_{TiO_2} , was calculated as

$$10^{[\log X_{\text{Ti}} + (3765/T(K)) - 5.69]} = a_{\text{TiO}_2}$$

for the unit, where X_{Ti} is the unit average. An a_{TiO_2} value of ~0.4 was found using both sets of data (table 1). This conformity indicates that 0.4 is most likely a reasonably accurate estimate for a_{TiO_2} in the Bandelier system and the best estimate currently available. Temperatures were thus calculated using $a_{\text{TiO}_2} = 0.4$. Table A1 shows all of our results, and temperatures calculated using two other a_{TiO_2} values are shown for comparison: $a_{\text{TiO}_2} = 0.6$, which is both the a_{TiO_2} value chosen for the Bishop Tuff (Wark et al. 2007) and the highest value of a_{TiO_2} obtained in our calculations in table 1 ($a_{\text{TiO}_2} = 0.57$), and $a_{\text{TiO}_2} = 1.0$, which yields the lowest possible temperatures.

In the absence of mineral activity monitors, the activity of titania in the melt can also be estimated from the concentration of TiO_2 in the glass scaled to the concentration required to saturate rutile. In addition to the concentration of TiO_2 , the major-element composition of the melt must be known, as well as its temperature (Hayden and Watson 2007).

Dunbar and Hervig (1992) give compositions, including TiO_2 , for melt inclusions from LBT phenocrysts that correspond to our units G-1 (plinian) and 7-7 (ignimbrite). Hayden and Watson's (2007) melt composition parameter FM from the major elements is estimated to be 1.61 for the plinian samples and 1.60–1.65 for the ignimbrites of the LBT. TiO_2 concentrations in glass from quartz and feldspar hosts are relatively constant at approximately 300 ppm for most of the units, ranging from 265 to 320 ppm. Two LBT samples from near the top of the ignimbrite (BB-027 and BB-030) give

Table 1. Determination of the Activity of TiO_2 in the Bandelier System

Unit	Unit location ^a	Temperature estimate (K)	Average Ti of sampled quartzes in unit (ppm)	a_{TiO_2}	a_{TiO_2} per unit
G-1 ^b	LBT	969	22.30	.35	.35
15-8 ^c (lower estimate)	CTR	1056	69.75 ^d	.52	
15-8 ^c	CTR	1086	69.75 ^d	.42	.43 ± .09
15-8 ^c (upper estimate)	CTR	1116	69.75 ^d	.34	
15-11 ^c (lower estimate)	CTR	1010	43.79	.48	
15-11 ^c	CTR	1050	43.79	.34	.36 ± .12
15-11 ^c (upper estimate)	CTR	1090	43.79	.25	
6-12 ^b	UBT	970	36.60	.57	.57
Average					.43

^a CTR = Cerro Toledo Rhyolite; LBT = Lower Bandelier Tuff; UBT = Upper Bandelier Tuff.

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

^c Temperature estimates obtained by Stix and Gorton (1990) from magnetite-ilmenite pairs. Upper and lower estimates reflect the given error range for the temperatures, that is, 1086 ± 30 K for unit 15-8 and 1050 ± 40 K for unit 15-11.

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

higher TiO_2 concentrations of 414 and 443 ppm, respectively. One melt inclusion from BB-030 gives an extreme value of 637 ppm.

If the ferrohedenbergite-fayalite temperature estimate for the G-1 plinian unit of 696°C is used (Warshaw and Smith 1988; table 1), rutile should saturate at 475 ppm (Hayden and Watson 2007), suggesting an a_{TiO_2} of 0.65. This activity is similar to that estimated for other silicic systems (Hayden and Watson 2007; Wark et al. 2007).

The higher temperature of unit 15-8 from the CTR, estimated with magnetite-ilmenite pairs (813°C ; Stix and Gorton 1990; table 1), increases the solubility of TiO_2 to 1893 ppm. For this unit, the FM parameter is 1.71, while the Ti content in the matrix glass is 760 ppm (Stix 1989). The calculated a_{TiO_2} then becomes 0.40. This estimate is similar to those calculated in table 1 by equating temperature estimates from mineral pairs and titanium-in-quartz.

The key question, then, is whether this represents an actual change in the activity of titania between the start and the end of the LBT sequence. Dunbar and Hervig (1992) explain the increase in TiO_2 and other trace elements in inclusions of their samples BB-027 and BB-030 as resulting from compositional mixing of a second silicic magma intruded into the LBT magma. The increased TiO_2 concentrations, however, represent a decrease in a_{TiO_2} due to the concurrent increase in temperature. Unless the two magmas were at similar temperatures, heating would be the initial major effect because the thermal diffusivities were higher than the material diffusivities. The entire increase in melt TiO_2 concentration could be the result of mineral dissolution and increased melt TiO_2 solubility at

higher temperatures, as emphasized in Data Repository item DR3 of Wark et al. (2007).

Without further evidence, we assume that a_{TiO_2} was constant near 0.4, on the basis of the agreement of temperature changes calculated from both mineral pair and titanium-in-quartz thermometers. Furthermore, the activity of titania is assumed to be constant throughout the evolution of the system, again because of the similarity of the calculated values of a_{TiO_2} for the four units from the LBT, the CTR, and the UBT (table 1), which include samples originating from both preinjection and post-injection magma chamber conditions, as discussed below. The TiO_2 activity is also assumed to be constant throughout each of the various units at any given time.

Although the chosen value of a_{TiO_2} for this system as a whole will affect the absolute values of the temperatures calculated, the relative temperature differences within each unit are constant, assuming constant a_{TiO_2} within each individual unit. We can state with some confidence that a_{TiO_2} never reached a value of 1, because rutile crystals were not found during our analyses.

Results

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

Table A1 and figure 4 show the Ti concentration results and corresponding temperatures, as calculated by Wark and Watson's (2006) geothermome-

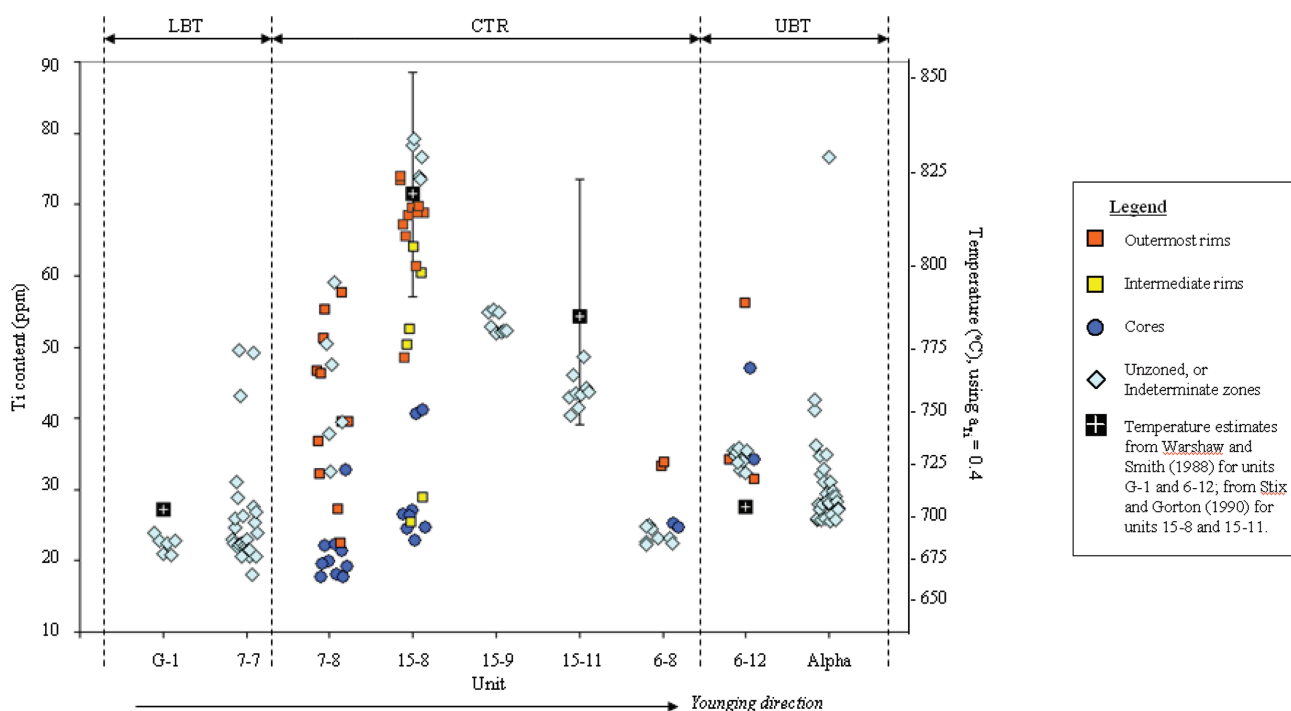


Figure 4. Titanium content of all sampled quartz crystals and corresponding temperatures of crystallization calculated with the Ti-in-quartz geothermometer described by Wark and Watson (2006). All temperatures were calculated using $a_{\text{TiO}_2} = 0.4$. Results are shown in table A1, available in the online edition or from the *Journal of Geology* office, 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).

ter, for each LA-ICP-MS analysis performed on quartz grains from 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 that could be imaged in one CL picture without significant mirror distortion are named by reference to the corresponding CL image. Larger crystals were given nonnumeric names and are represented by a collage of CL images.

Unit G-1. Unit G-1 is the Guaje pumice fall unit representing the onset of the LBT eruptive event. Ti concentrations are remarkably consistent, with a measured range from 20.8 to 23.9 ppm. The calculated temperatures reflect the consistent Ti concentrations, with temperatures ranging from 674° to 689°C at $a_{\text{TiO}_2} = 0.4$. No zoning was noted under CL imaging in any of the quartz crystals analyzed (fig. 3A).

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 (fig. 2). Pumice 7-7C has consistent Ti concentrations, with the exception of one analyzed grain. One analysis from crystal 13 shows a Ti concentration of ~49 ppm, more than double the average of ~24 ppm for pumice 7-7C. The rest of the analyses from pumice 7-7C are reasonably consistent, ranging from 18 to 28 ppm Ti, with a corresponding temperature range of 660°–705°C ($a_{\text{TiO}_2} = 0.4$). 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° to 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, ranging from 22 to 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 visible zoning under CL imaging. Two groups of unzoned quartz crystals have emerged. The majority of analyses show remarkable consistency and a mean Ti concentration of 26 ppm. The second, minor group is also fairly consistent, with concentrations of 43, 49, and 50 ppm.

Unit 7-8. Unit 7-8 represents the first erupted tephra of the CTR after the emplacement of the LBT ignimbrite (fig. 2). A majority of the quartz grains analyzed from this unit display at least some CL-visible zonations (e.g., fig. 3B), with cores being invariably darker than the corresponding rims. Two major types of zonation are apparent. In the first type, small differences in CL-visible contrast and Ti content are noted between the core and the 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 to 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: 22–37 ppm, or 682°–737°C. Finally, of the two grains that 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° and 796°C.

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

Of the nine clear cores, seven 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° and 827°C. In three crystals intermediate zones are seen, with variable Ti con-

tents and thus temperatures. Of particular note is crystal 27 (fig. 3D). 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 that 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 to 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 because of the paucity of quartz in samples from this unit. Neither grain shows any visible CL zoning, and the two have remarkably consistent Ti contents, ranging from 52 to 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 consistent Ti concentrations and no notable CL zoning. The LA-ICP-MS analyses show a range in Ti concentrations from ~40 to 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 CTR units before the UBT eruption. Three quartz crystals were successfully imaged for CL and measured for Ti. One of these, crystal 55, shows a distinct darker core with a lighter rim. The Ti measurements of the darker core correspond very closely to 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 (crystal 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 from unit

3t. Only one slightly zoned grain, crystal 51, was noted. Although we were unable to cleanly analyze the rim segment because of its thinness, an LA-ICP-MS sample spot on the zone boundary reveals Ti levels consistent with those of the other quartz crystals from this unit. There are three apparently anomalous analyses in Alpha, one of which, from crystal Michelle, appears to be an outlier, possibly because of contamination of a crack by epoxy, a thin grain that 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 to 36 ppm and a corresponding temperature range from 697° to 735°C.

In summary, several trends emerge from our results (fig. 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 CTR, 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 6-8 CTR unit 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 the CTR (fig. 4) have been calculated from ferrohedenbergite-fayalite (Warshaw and Smith 1988) and magnetite-ilmenite pairs (Stix and Gorton 1990), respectively. Thermal history is a parameter that is crucial to the accurate modeling and overall understanding of the nature of magma chambers, as well as to the timing and nature of potential injections of fresh magma into these systems. On the basis of 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 before the LBT caldera-forming eruption. Injection of new magma likely continued

during the LBT eruption but ceased shortly after the end of the eruption.

Nature of the Preinjection LBT Magma Chamber. Although some properties of the preinjection 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 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; fig. 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). One model, based on isotopic data and the principle of magma-country rock chemical exchange, suggests that the LBT magma chamber was composed of a country rock-bounding crystal carapace surrounding a center of aphanitic melt (Wolff et al. 1999, 2002). It has also been proposed that the chamber underwent turbulent convection just before eruption (e.g., Kuentz 1986).

Our thermal data, however, paint a different picture of the preinjection magma chamber: relatively cool, possibly highly crystalline, viscous, and stagnant (fig. 5A). This chamber would be unlikely to convect vigorously or to comprise a vast aphanitic zone. Our temperatures from units G-1 and 7-7 generally cluster between 660° and 717°C. These temperatures are grouped around the ~700°C solidus for the ternary minimum in the Ab-Or-Q system (Tuttle and Bowen 1958), at an approximate P_{H_2O} of 100–200 MPa for the system (Kuentz 1986). 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 was close to solidus conditions. Thus, a magma chamber at these temperatures was 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). A temperature gradient of at most 50°–60°C was present in the chamber, offering no clear evidence that the LBT magma chamber was strongly zoned in a thermal sense.

Given sufficient time, the Ti contained within quartz crystals will diffuse from areas of higher Ti

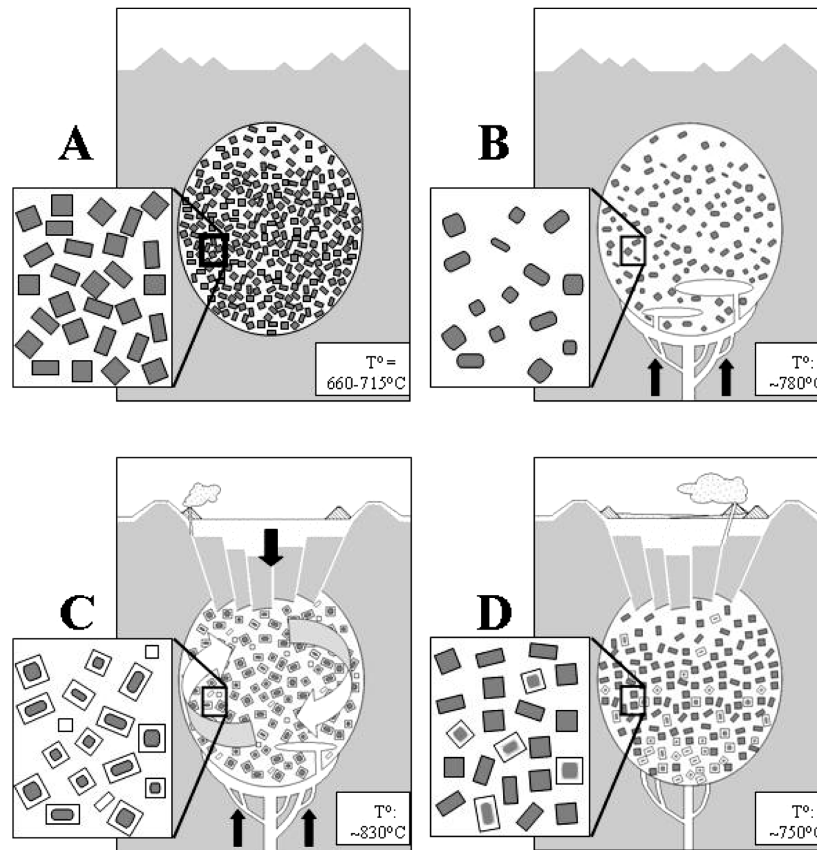


Figure 5. Schematic cartoon showing the different stages of the evolution of the Lower Bandelier magmatic system. *A*, Preinjection Lower Bandelier Tuff (LBT) magma chamber. At near-solidus temperatures, the chamber is highly crystalline and probably stagnant. *B*, Injection into the LBT chamber. Injection 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 state as well as the release of volatiles, may have triggered the LBT eruption at 1.61 Ma. *C*, Caldera collapse phase and early Cerro Toledo Rhyolite (CTR) postcollapse phase. The 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 that in *A*.

concentration to areas of lower Ti concentration. Thus, after a sufficient 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. (2007):

$$D = 7 \times 10^{-8} \exp\left(\frac{-273 \text{ kJ mol}^{-1}}{RT}\right) \text{ m}^2 \text{ s}^{-1}.$$

Thus, Ti diffusivity depends exclusively on temperature T and increases significantly with increas-

ing 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 A1), would take ~ 240 k.yr. to diffuse $50 \mu\text{m}$ (the approximate width of thin zones visible in quartz grains of unit 15-8). This means that, had any of the quartz grains

of unit G-1 been zoned originally, these phenocrysts would have theoretically become unzoned to their currently visible state via Ti diffusion had they resided in the magma chamber for at least ~250 k.yr. It is important to stress that our temperature results for unit G-1 and for the bulk of unit 7-7 reflect not the temperatures of these units at the time of their eruption but rather their temperatures during crystallization in the relatively cool regime of the preinjection 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 propose that an injection of fresh magma at the base of the magma chamber raised the chamber's temperature to above solidus levels, leading to substantial and widespread melting throughout the chamber (fig. 5B). We also suggest that evidence of this injection is present in the few outlier temperature results from unit 7-7, ranging from 757° to 774°C, which are significantly hotter than the main cluster of results (fig. 4). Recent experimental work on silicic magmatic systems that 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 2009).

After the initial magma injection into the system or the emplacement of magma at the base of the chamber, heat was added to 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. Bachmann and Bergantz (2006) propose that gas percolation may play a role in the reheating of large silicic systems, although an unrealistic total amount of volatiles would be required for gas percolation alone to account for the reheating of the entire Bandelier magma chamber. While many crystals from the 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 move the system from a state of crystallization to one of resorption. After the period of resorption, quartz crystal growth appears to have resumed for certain crystals of the LBT (unit 7-7). However, we suggest that high-temperature quartz grains or rims are not com-

monly found in the LBT because the caldera-forming eruption occurred before conditions in most of the magma chamber could switch back from favoring quartz resorption (hot) to favoring quartz crystallization (cooler). It should be noted that the higher temperatures found in unit 7-7 were not obtained from visibly zoned grains. We do not attribute any particular significance to the lack of zoning in these cases. It is possible that these grains represent only broken fragments of grains that were zoned when whole or that when crystallization resumed, conditions were such that new crystal nucleation was favored over crystallization on relict grains. 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).

As the sharp boundaries visible in zoned grains of unit 15-8 are <10 μm thick, Ti in quartz grains of this unit had time to diffuse only roughly 10 μm at temperatures on the order of 830°C (table A1) before being erupted (e.g., Wark and Watson 2006). Ti diffusion over a distance of 10 μm at 830°C will occur in only ~100 yr. In other words, the zoned quartz grains from unit 15-8 were probably erupted only ~100 yr, at most, after they crystallized their high-Ti rims. This calculation implies that the injection of magma that led to the formation of the bright, sharply defined rims on the majority of quartz grains from units 7-8 and 15-8 was followed very quickly by their eruption.

Hence, our data place the timing of the initial injection at just before the LBT caldera-forming eruption, early enough to allow for extensive crystal resorption but not sufficiently long to allow the magma chamber to cool to a point that widespread quartz crystallization might resume. Moreover, the injection must have occurred not long before eruption, because 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°C). Using 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 the two magmas shared a common origin or source material, with the newly

injected magma simply being less fractionated. Stix and Gorton (1993) also proposed, on the basis of trace elements, that the new magma was rhyolitic in composition. The presence of small amounts of dacitic erupted products in both the LBT and the UBT suggests that magma of a more primitive composition may have played a role as well.

Hervig and Dunbar (1992) collected compositional data from melt inclusions found within quartz, sanidine, and pyroxene phenocrysts and matrix glass from the LBT. They found that while major-element chemistry did not vary appreciably throughout the sampling, some trace elements did. In particular, two distinct clusters of Ti content were identified: ~300 and ~600 ppm. Hervig and Dunbar (1992) postulated that the melt inclusions of these clusters originated from different melts: an older, Ti-poor magma and a relatively new, recently injected, Ti-rich magma. Although it may appear improbable that two populations of melt inclusions with very different Ti contents may have crystallized from magmas with very similar a_{TiO_2} values, it is important to note that at constant a_{TiO_2} , melt inclusions will contain a greater amount of Ti when crystallizing at higher temperatures, much like quartz. Hence, at constant a_{TiO_2} , a hotter magma will contain higher concentrations of Ti. Thus, assuming constant a_{TiO_2} throughout Bandelier time, as our data indicate, the Hervig and Dunbar (1992) data set supports the view that the injected magma was considerably hotter than the resident magma. The CTR contains magnetite and ilmenite (Stix and Gorton 1990), suggesting that the a_{TiO_2} was buffered by these Ti-bearing phases. As illustrated by Wark and Watson (2006), increases in temperature result in increased dissolution of Ti-rich phases and, consequently, an increase in the Ti content of the melt. Thus, the Ti content of the melt was dependent on temperature in the buffered Bandelier magma system. Furthermore, this data set also indicates that some crystallization had indeed resumed in the LBT magma chamber after the injection, because a large number of Ti-rich melt inclusions (presumably from the newly injected melt) were identified in their samples. Hervig and Dunbar (1992) noted that only some of the sanidine phenocrysts they analyzed showed trace-element enrichment toward their edges. Thus, crystallization may have resumed in certain parts of the magma chamber only before its eruption. Finally, Hervig and Dunbar (1992) found no high-Ti melt inclusions in the LBT plinian unit, consistent with the paucity of high-Ti quartz identified in the LBT plinian in our study.

LBT Eruption. The injection of hot new magma would have altered the conditions within the

magma chamber in several ways. It would have introduced a volume of magma that 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 transformation of a potentially large volume of material from the solid to the liquid state; (2) a significant decrease in the viscosity of the magma due to the hotter temperatures and the presence of fewer and smaller crystals; and (3) the dissolution of silicate minerals. The first consequence could have generated additional pressure within the system. The second would have facilitated evacuation of the magma by causing it to become more fluid and thus more mobile. Finally, the third consequence would lead to the dilution of the initial dissolved H_2O content of the interstitial melts, as would be expected from the melting of anhydrous minerals.

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 plinian Guaje 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 preeruptive magmatic chemical zonation within the LBT ignimbrite (Kuentz 1986). Our results indicate that a significant thermal gradient (i.e., 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 that proceeded to cool and evolve. Thermal evidence of the hot injection is visible in the rimmed quartzes of units 7-8 and 15-8, which were the first-erupted units of the CTR. In fact, the emplacement of these two units occurred so soon after the LBT eruption that their ages are indistinguishable (Spell et al. 1996). The fact that the highest recorded temperatures of the CTR are found within grains of unit 15-8 (fig. 4) suggests that the injection of substantial amounts of new, hot melt into the system did not continue long after the eruption of

this unit, because the chamber subsequently exhibits a gradual cooling trend.

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, rounded contacts indicate that the rims grew after a period of crystal dissolution caused by immersion of the core of the grain into a higher-temperature regime. 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 lighter rim. Gradational zoning is rare but present, almost exclusively in unit 15-8, and is invariably lighter toward the exterior of the grain (fig. 3D). Although this pattern could be caused by progressive heating of the magma chamber, a more likely cause would be the gradual sinking of the grain toward the lower, hotter part of the magma chamber via crystal settling. By contrast, the sharp contact that is typically observed between cores and rims is indicative of the relatively abrupt heating of the grain due to the injection of new, hot magma. The sharp nature of the contacts visible between the cores and the 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 (fig. 4). These cores are thus presumed to be restite 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 quartz 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 also may have generated the heterogeneity we see in rim temperatures from unit 7-8. Turbu-

lent mixing can result in pockets of the chamber that 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 quartz grains 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, explaining the evolution noted by Stix and Gorton (1993) in the later-erupted CTR units and the UBT. The restitic quartz cores of units 7-8 and 15-8 represent evidence of 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 (fig. 4).

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 before 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. Ti diffusion also explains why no zoned crystals from the early stages of the CTR remain in the later CTR samples. Any zoned quartzes that formed after the LBT caldera collapse (i.e., from units 7-8 or 15-8), remaining as restitic grains in a magma chamber at a conservatively estimated temperature of 830°C, would

have undergone diffusion and reequilibration in only ~2 k.yr. These crystals would therefore no longer appear zoned in later-erupted CTR units.

Temperatures from the initial plinian fall deposit of the UBT (unit 6-12) are concentrated at the hotter end of the main cluster of temperature results for the main-stage ignimbrite of the UBT (~730°C; fig. 4). The slightly hotter nature of the UBT, in comparison to the LBT, may have contributed to 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 that zoned quartz crystals were erupted in post-caldera collapse time, as we see in the LBT.

Comparison with Another Large Silicic System: The Bishop Tuff. Wark et al. (2007) utilized CL-visible zonations in quartz phenocrysts and the TitaniQ geothermometer (Wark and Watson 2006) to document the thermal history of the 0.76-Ma Bishop Tuff, erupted from the Long Valley caldera. Although a detailed comparison between the Banderlier 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; Hildreth and Wilson 2007; Wark et al. 2007). Three types of CL zoning were noted in the Bishop Tuff: (1) weakly zoned cores and high-Ti, CL-bright rims, typical of most late-erupted and some middle-erupted products; (2) weakly zoned cores and low-Ti, CL-dark rims, found in early and middle deposits; and (3) no CL intensity differences from core to rim. It should be noted that the higher dwell times for the CL images of quartz in Peppard et al. (2001) permitted the capture of higher-resolution pictures. In particular, this allowed the imaging of individual growth rings within distinct CL zones; thus, several concentric growth rings were visible within both the dark cores and the lighter rims of zoned grains. Coupling this 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 on the relatively high CO₂ concentrations in melt inclusions near rims of late-erupted quartz and the evidence of 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 LBT; the great majority of zoned crystals were found in the basal CTR. 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 timing 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 likely that magma recharge played a significant role during the histories of caldera-forming eruptions at both the Long Valley and Valles calderas.

Conclusions

The analysis of quartz crystal zoning has provided unique insight into the thermal history of the Banderlier magma system. Cathodoluminescence imaging of sampled quartz grains, combined with titanium-in-quartz geothermometry, reveals a relatively isothermal magma chamber before the eruption of the LBT, 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 before its eruption. An injection of magma then occurred shortly before caldera collapse, raising the chamber temperature by at least ~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 CTR

quartz crystals are commonly zoned; these grains invariably reveal cold (685°–700°C) cores and hotter (by ~100°C) rims, while unzoned grains are uniformly of high temperatures. The common presence of restitic quartz cores in these units, which were crystallized during the colder chamber conditions of the preinjection LBT system, reveals that a significant amount of magma remained in the chamber after 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 because of turbulent mixing induced by caldera subsidence (Kennedy et al. 2008).

Through the thermal history of the LBT and CTR events, we are able to obtain glimpses into the long-term evolution of a magma chamber, from cool precaldera conditions, through mixing and mingling of resident and new magmas immediately before and/or during caldera formation, to a gradually cooler and more uniform chamber in postcaldera time. We do not see strong thermal evidence of continued large-scale magma injections throughout the CTR. Although the plinian unit of the UBT has a higher temperature than late-erupted CTR mag-

mas, our results show no clear evidence of an injection before the UBT eruption. Further investigation into the thermal history of the postcaldera rhyolites of the Valles caldera, erupted after the UBT event, would shed important light on this subject.

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REFERENCES CITED

- Aldrich, M. J., and Laughlin, A. W. 1984. A model for the tectonic development of the southeastern Colorado Plateau boundary. *J. Geophys. Res.* 89:10,207–10,218.
- Bachmann, O., and Bergantz, G. W. 2006. Gas percolation in upper-crustal silicic crystal mushes as a mechanism for upward heat advection and rejuvenation of near-solidus magma bodies. *J. Volcanol. Geotherm. Res.* 149:85–102.
- Bailey, R. A., Smith, R. L., and Ross, C. S. 1969. Stratigraphic nomenclature of volcanic rocks in the Jemez Mountains, New Mexico. *U.S. Geol. Surv. Bull.* 1274-P:1–19.
- Balsley, S. D. 1988. The petrology and geochemistry of the Tshirege Member of the Bandelier Tuff, Jemez Mountains Volcanic Field, New Mexico, U.S.A. MS thesis, University of Texas, Arlington.
- Cherniak, D. J., Watson, E. B., and Wark, D. A. 2007. Ti diffusion in quartz. *Chem. Geol.* 236:65–74.
- Dunbar, N. W., and Hervig, R. L. 1992. Volatile and trace element composition of melt inclusions from the Lower Bandelier Tuff: implications for magma chamber processes and eruptive style. *J. Geophys. Res.* 97:15,151–15,170.
- Gardner, J. N. 1985. Tectonic and petrologic evolution of the Keres Group: implications for the development of the Jemez Volcanic Field, New Mexico. PhD dissertation, University of California, Davis.
- Gardner, J. N., Goff, F., Garcia, S., and Hagan, R. C. 1986. Stratigraphic relations and lithologic variations in the Jemez volcanic field, New Mexico. *J. Geophys. Res.* 91:1763–1778.
- Girard, G., and Stix, J. 2009. Buoyant replenishments in silicic magma reservoirs: experimental approach and implications for magma dynamics, crystal mush remobilization and eruption. *J. Geophys. Res.* (forthcoming), doi:10.1029/2008JB005791.
- Goff, F., Gardner, J. N., Baldrige, W. S., Hulen, J. B., Nielson, D. L., Vaniman, D., Heiken, G., Dungan, M. A., and Broxton, D. 1989. Excursion 17B: volcanic and hydrothermal evolution of Valles caldera and Jemez volcanic field. *In* Chapin, C. E., and Zidek, J., eds. Field excursions to volcanic terranes in the western United States. Vol. I. Southern Rocky Mountain region. N.M. Bur. Mines Min. Res. Mem. 46:381–434.
- Hayden, L. A., and Watson, E. B. 2007. Rutile saturation in hydrous siliceous melts and its bearing on Ti-thermometry of quartz and zircon. *Earth Planet. Sci. Lett.* 258:561–568.
- Heiken, G., Goff, F., Gardner, J. N., Baldrige, W. S., Hulen, J. B., Nielsen, D. T., and Vaniman, D. 1990. The Valles/Toledo caldera complex, Jemez volcanic field, New Mexico. *Annu. Rev. Earth Planet. Sci.* 18:27–53.
- Heiken, G., Goff, F., Stix, J., Tamanyu, S., Shafiqullah, M., Garcia, S., and Hagan, R. 1986. Intracaldera volcanic activity, Toledo caldera and embayment, Jemez Mountains, New Mexico. *J. Geophys. Res.* 91:1799–1815.
- Hervig, R. L., and Dunbar, N. W. 1992. Cause of chemical

- zoning in the Bishop (California) and Bandelier (New Mexico) magma chambers. *Earth Planet. Sci. Lett.* 111:97–108.
- Hildreth, W. 1979. The Bishop Tuff: evidence for the origin of compositional zonation in silicic magma chambers. *Geol. Soc. Am. Spec. Pap.* 180:43–75.
- Hildreth, W., and Wilson, C. J. N. 2007. Compositional zoning of the Bishop Tuff. *J. Petrol.* 48:951–999.
- Kennedy, B. M.; Jellinek, A. M.; and Stix, J. 2008. Coupled caldera subsidence and stirring inferred from analogue models. *Nat. Geosci.* 1:385–389.
- Kite, W. M. 1985. Caldera-forming eruption sequences and facies variations in the Bandelier Tuff, central New Mexico. MS thesis, Arizona State University, Tempe.
- Kuentz, D. C. 1986. The Otowi Member of the Bandelier Tuff: a study of the petrology, petrography, and geochemistry of an explosive silicic eruption, Jemez Mountains, New Mexico. MS thesis, University of Texas, Arlington.
- Minarik, W. G. 2006. Titanium thermometry in zircon and quartz using LA-ICP-MS. GAC-MAC (Geological Association of Canada–Mineralogical Association of Canada) Annual Meeting Abstracts 31:102–103.
- Nielson, D. L., and Hulen, J. B. 1984. Internal geology and evolution of the Redondo dome, Valles caldera, New Mexico. *J. Geophys. Res.* 89:8695–8713.
- Peppard, B. T.; Steele, I. M.; Davis, A. M.; Wallace, P. J.; and Anderson, A. T. 2001. Zoned quartz phenocrysts from the rhyolitic Bishop Tuff. *Am. Mineral.* 86:1034–1052.
- Phillips, E. H.; Goff, F.; Kyle, P. R.; McIntosh, W. C.; Dunbar, N. W.; and Gardner, J. N. 2007. The $^{40}\text{Ar}/^{39}\text{Ar}$ age constraints on the duration of resurgence at the Valles caldera, New Mexico. *J. Geophys. Res.* 112: B08201, doi:10.1029/2006JB004511.
- Self, S.; Goff, F.; Gardner, J. N.; Wright, J. V.; and Kite, W. 1986. Explosive rhyolitic volcanism in the Jemez Mountains: vent locations, caldera development and relation to regional structures. *J. Geophys. Res.* 91: 1779–1798.
- Self, S., and Lipman, P. W., eds. 1989. Large ignimbrites and caldera-forming eruptions. Workshop handbook, IAVCEI (International Association of Volcanology and Chemistry of the Earth's Interior) Working Group on Explosive Volcanism and Its Products, Field Workshop 11WA (Santa Fe, NM, June 15–24, 1989).
- Smith, R. L., and Bailey, R. A. 1966. The Bandelier Tuff: a study of ash-flow eruption cycles from zoned magma chambers. *Bull. Volcanol.* 29:83–103.
- . 1968. Resurgent cauldrons. *Geol. Soc. Am. Mem.* 116:613–662.
- Spell, T. L.; Harrison, T. M.; and Wolff, J. A. 1990. $^{40}\text{Ar}/^{39}\text{Ar}$ dating of the Bandelier Tuffs and San Diego Canyon ignimbrites, Jemez Mountains, New Mexico: temporal constraints on magmatic evolution. *J. Volcanol. Geotherm. Res.* 43:175–193.
- Spell, T. L.; McDougall, I.; and Doulgeris, A. P. 1996. Cerro Toledo Rhyolite, Jemez Volcanic Field, New Mexico: $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of eruptions between two caldera-forming events. *Geol. Soc. Am. Bull.* 108: 1549–1566.
- Stix, J. 1989. Physical and chemical fractionation processes in subaerial and subaqueous pyroclastic rocks. PhD dissertation, University of Toronto.
- Stix, J., and Gorton, M. P. 1990. Changes in silicic melt structure between the two Bandelier caldera-forming eruptions, New Mexico, USA: evidence from zirconium and light rare earth elements. *J. Petrol.* 31:1261–1283.
- . 1993. Replenishment and crystallization in epicontinental silicic magma chambers: evidence from the Bandelier magma system. *J. Volcanol. Geotherm. Res.* 55:201–215.
- Turbeville, B. N., and Self, S. 1988. San Diego Canyon ignimbrites: pre-Bandelier Tuff explosive rhyolitic volcanism in the Jemez Mountains, New Mexico. *J. Geophys. Res.* 93:6148–6156.
- Tuttle, O. F., and Bowen, N. L. 1958. Origin of granite in the light of experimental studies in the system $\text{NaAlSi}_3\text{O}_8\text{--KAlSi}_3\text{O}_8\text{--SiO}_2\text{--H}_2\text{O}$. *Geol. Soc. Am. Mem.* 74:1–153.
- Wark, D. A.; Hildreth, W.; Spear, F. S.; Cherniak, D. J.; and Watson, E. B. 2007. Pre-eruption recharge of the Bishop magma system. *Geology* 35:235–238.
- Wark, D. A., and Spear, F. S. 2005. Ti in quartz: cathodoluminescence and thermometry. *Geochim. Cosmochim. Acta* 69(suppl. 1):A592.
- Wark, D. A., and Watson, E. B. 2006. TitaniQ: a titanium-in-quartz geothermometer. *Contrib. Mineral. Petrol.* 152:743–754.
- Warren, R. G.; Goff, F.; Kluk, E. C.; and Budahn, J. R. 2007. Petrography, chemistry, and mineral compositions for subunits of the Tshirege Member, Bandelier Tuff within the Valles caldera and Pajarito Plateau. In Kues, B. S.; Kelley, S. A.; and Lueth, V. W., eds. *Geology of the Jemez Region II. 58th Field Conference Guidebook*. Socorro, New Mexico Geological Society, p. 316–332.
- Warshaw, C. M., and Smith, R. L. 1988. Pyroxenes and fayalites in the Bandelier Tuff, New Mexico; temperatures and comparison with other rhyolites. *Am. Mineral.* 73:1025–1037.
- Wolff, J. A.; Balsley, S. D.; and Gregory, R. T. 2002. Oxygen isotope disequilibrium between quartz and sanidine from the Bandelier Tuff, New Mexico, consistent with a short residence time of phenocrysts in rhyolitic magma. *J. Volcanol. Geotherm. Res.* 116:119–135.
- Wolff, J. A., and Gardner, J. N. 1995. Is the Valles caldera entering a new cycle of activity? *Geology* 23:411–414.
- Wolff, J. A.; Ramos, F. C.; and Davidson, J. P. 1999. Sr isotope disequilibrium during differentiation of the Bandelier Tuff: constraints on the crystallization of a large rhyolitic magma chamber. *Geology* 27:495–498.