1 REVISION 2

2	Titanium diffusion profiles and melt inclusion chemistry and morphology in quartz from
3	the Tshirege Member of the Bandelier Tuff
4	JOSEPH R. BORO ¹ , JOHN A. WOLFF ¹ , OWEN K. NEILL ² , ARRON R. STEINER ¹ ,
5	AND FRANK C. RAMOS ³
6	¹ School of the Environment, Washington State University, Pullman, WA 99163, USA
7	² School of Earth and Environmental Sciences, University of Michigan, Ann Arbor, MI 48109, USA
8	³ Department of Geological Sciences, New Mexico State University, Las Cruces, NM 88003, USA
9	
10	Keywords: caldera, cathodoluminescence, diffusion, inclusion, melt, quartz, tuff, volcano
11	
12	ABSTRACT
13	Many rhyolites contain quartz crystals with relatively Ti-rich rims and Ti-poor cores,
14	with a sharp interface between zones, attributed to partial dissolution followed by overgrowth
15	following a heating event due to mafic recharge of the system. Quartz crystals in the
16	compositionally zoned, high-silica rhyolite Tshirege Member of the Bandelier Tuff, erupted at
17	1.26 Ma from the Valles caldera, New Mexico, show a range in zoning styles with Ti-rich rims
18	becoming more abundant upwards in the ignimbrite sheet among progressively less evolved
19	magma compositions. Here we compare times between quartz overgrowth and eruption obtained
20	by applying Ti diffusion coefficients to Ti concentration profiles in Tshirege Member quartz
21	crystals with those from cathodoluminescence (CL) brightness profiles, and show that
22	panchromatic CL provides only a crude proxy for Ti in quartz in this unit. Titanium
23	concentrations are measured to detection limits of \sim 1.2 ppm with small analytical errors (<5%)

24 using MAN backgrounds, blank corrections, and oblique corrected transects to resolve diffusionrelaxed zone boundaries as thin as $\sim 10 \,\mu\text{m}$. Timescales derived from Ti profiles using the widely 25 applied Ti-in-quartz diffusion coefficients of Cherniak et al. (2007) range from 60 to 10,000 26 years, suggesting heating and mobilization events at different times prior to the eruption. 27 However, use of the newer Ti diffusivities reported by Jollands et al. (2020) yields timescales up 28 to three orders of magnitude longer, including results that are geologically unreasonable for the 29 Bandelier system. We suggest that assumptions commonly made in diffusion modeling, 30 specifically about the form of the Ti zoning profile prior to diffusive relaxation, may be invalid. 31 32 Melt inclusions in the Ti-poor cores of late-erupted quartz are chemically akin to early erupted melt compositions, while adhering and groundmass glasses more closely reflect the 33 composition of the host pumice. Heating and mobilization events identified from quartz Ti 34 zoning are thus linked to overall compositional zoning of the tuff, which may have been 35 produced by repeated episodes of melting of a crystal cumulate cognate to the early-erupted, 36 evolved rhyolite. Quartz-hosted melt inclusion faceting suggests the development of a crystal 37 much over a minimum time frame of 1,000 - 10,000 years prior to recharge events that produced 38 the eruptible Tshirege magma. 39

40

41

INTRODUCTION

Diffusion modeling of element concentration profiles in crystals is a fruitful way of extracting timescales of processes occurring at elevated temperatures in geologic systems. The approach relies on some assumptions, such as starting conditions for the diffusion episode and that the concentration profiles being modeled are indeed the result of ionic diffusion. In studies of volcanic systems, diffusion profiles can help determine residence times of crystals in magma

47 based on compositional zoning of the minerals of interest. Diffusion modeling can also be used to determine the time elapsed between an identifiable event in the history of a crystal (e.g., 48 overgrowth on a resorption surface) and eruption (Costa and Dungan, 2005; Morgan and Blake, 49 2006; Wark et al., 2007; Costa et al., 2008; Till et al., 2015). Timescales deduced from the 50 diffusive blurring of an overgrowth boundary can provide insights on how magma systems 51 respond to disturbance, such as rejuvenation and heating by magmatic recharge, shortly before 52 an eruption. This approach has yielded estimates of short activation timescales (<1 year – 1000 53 years) preceding past catastrophic silicic caldera-forming 'super-eruptions' (Wark et al., 2007; 54 55 Matthews et al., 2012; Till et al., 2015; Gualda and Sutton, 2016; Cooper et al., 2017). Smaller, much more frequent eruptions may also have activation timescales of < 1 year, for example 56 Calbuco volcano, 2015 (Arzilli et al., 2019). 57

In rhyolitic volcanic systems, quartz is an attractive and widely-used target for diffusion 58 modeling because quartz crystals are usually large and of effectively constant major element 59 composition. Trace element substitutions, particularly that of Ti⁴⁺ for tetrahedral Si⁴⁺ in the 60 quartz structure (Götze, 2012; Leeman et al., 2012), result in enhanced cathodoluminescence 61 (CL) brightness that in principle allows easy identification of trace cation concentration zoning, 62 and because the behavior of Ti in quartz is well-studied. Peppard et al. (2001) provided the first 63 detailed description of CL zoning in quartz from a high-silica rhyolite (the Bishop Tuff). Wark 64 and Watson (2006) calibrated Ti-in-quartz as a geothermometer, while Cherniak et al. (2007) 65 66 reported results for the diffusion coefficient of Ti (D_{Ti}) in quartz. These studies spawned a significant literature linking Ti-in-quartz variations, CL zoning, and magmatic temperature to 67 68 estimates of crystal residence timescales and the rejuvenation of large stagnant silicic magma 69 bodies to an eruptible state, as well as new calibrations of the Ti-in-quartz (TitaniQ) thermometer

70	(Hayden and Watson, 2007; Wark et al., 2007; Shane et al., 2008; Campbell et al., 2009; Thomas
71	et al., 2010; Gualda et al., 2012; Huang and Audétat, 2012; Matthews et al., 2012; Thomas and
72	Watson, 2012; Wilson et al., 2012; Wilcock et al., 2013; Gualda and Sutton, 2016; Pamukcu et
73	al., 2015; Seitz et al., 2016; Cooper et al., 2017). The temperature sensitivity of D_{Ti} requires
74	accurate knowledge of temperature during the diffusion episode in order to extract timescales
75	from modeled diffusion profiles, placing demands on geothermometry. Also, the application of
76	the Ti-in-quartz geothermometer requires precise knowledge of the activity of Ti in the melt in
77	equilibrium with the quartz, a parameter which is not always well constrained (Huang and
78	Audétat, 2012; Matthews et al., 2012; Thomas and Watson, 2012; Wilson et al., 2012).
79	Much of the interest in using Ti-in-quartz diffusion to estimate silicic magma
80	rejuvenation timescales stems from the geologically short durations that result from applying the
81	diffusivities of Cherniak et al. (2007) to observed Ti zoning profiles, with implications for
82	eruption prediction in regions of silicic volcanism. The estimated durations rely on the
83	assumption of an initial step-function zone boundary separating quartz interiors from rims grown
84	following a heating and resorption event (Wark et al., 2007), and range from hundreds of years
85	down to less than a year (Wark et al., 2007; Gualda et al., 2012; Wilcock et al., 2013; Seitz et al.,
86	2016; Gualda and Sutton, 2016). The shorter durations are supported by cation diffusion
87	estimates from other minerals in some cases, for example feldspar (Till et al., 2015) and
88	pyroxene Chamberlain et al., 2014a). However, U-Th-Pb geochronology of zircon grains from
89	silicic systems typically yields times of $10^4 - 10^5$ years, thought to record a long history of
90	magma body growth and evolution prior to destabilizing events leading to eruption (e.g. Reid
91	and Vasquez, 2017). Now, recent experiments on Ti-in-quartz diffusivity by Jollands et al.
92	(2020) yield much slower diffusion rates than proposed by Cherniak et al. (2007), and lead to

timescales for the preservation of Ti zoning profiles in quartz that are more consistent with those
derived from geochronology. Thus, the status of Ti zoning in quartz as a recorder of events

95 immediately preceding eruption is thrown into question.

In addition to zoning recorded in quartz during crystal growth, melt may become trapped as melt inclusions (MI; Fig. 1); MI are generally thought to record the liquid composition at the time of crystal growth (Lowenstern and Mahood 1991; Dunbar and Hervig 1992; Bacon et al. 1992) and are often abundant in quartz phenocrysts from rhyolites. These can then be used to make interpretations about the growth history of the quartz, and petrogenetic relations within the magma body.

This study examines measured Ti profiles in quartz phenocrysts from the Bandelier Tuff, 102 Valles caldera, NM, USA, and compares Ti zoning with MI chemistry. Using finite-difference 103 diffusion modeling procedures (Costa et al., 2008), the results are applied to estimating crystal 104 residence times between initiation of overgrowth following a crystal resorption event and 105 eruptive quenching, assuming diffusional relaxation of Ti in quartz crystals from an initial step 106 function distribution. Melt inclusions hosted within those crystals are used to determine the 107 petrogenetic history of the quartz. Wilcock et al. (2013) provide a detailed dataset on the CL and 108 Ti zoning in quartz from the Tshirege Member. This study expands on those data with higher 109 spatial resolution and MI chemistry. 110

- 111
- 112

GEOLOGICAL AND PETROLOGICAL BACKGROUND

The ~400 km³ Tshirege (upper) Member of the Bandelier Tuff erupted to form the Valles
caldera, Jemez Mountains, NM, USA at 1.26 Ma (Bailey et al., 1969; Phillips et al., 2007;
Gardner et al., 2010; Goff et al., 2014) and has been the subject of several petrological and

116 volcanological studies (Smith and Bailey, 1966; Self et al., 1986, 1996; Balsley, 1988; Warshaw and Smith, 1988; Caress, 1996; Stimac, 1996; Warren et al., 2007; Wilcock et al., 2013; Goff et 117 al., 2014; Wolff et al., 2015). It is strongly compositionally zoned from early-erupted high-silica 118 rhyolite to late-erupted low-silica rhyolite, with complex compositional variations in the last-119 erupted tuff (Smith and Bailey, 1966; Balsley, 1988; Goff et al., 2014; Boro, 2019). The 120 Tshirege Member event was preceded by eruption of the similarly-sized, chemically-zoned high-121 silica rhyolite Otowi (lower) Member of the Bandelier Tuff at ~1.60 Ma, which formed a caldera 122 now largely overprinted by the later eruption (Goff et al., 2011, 2014; Wolff and Ramos, 2014). 123 124 During the \sim 340,000 y interval between the two caldera-forming events, several minor eruptions produced the Valle Toledo Member rhyolite domes and pyroclastic flow and fallout deposits of 125 the Cerro Toledo Formation (Gardner et al., 2010). 126 The Tshirege Member consists of a widespread plinian fallout unit, the Tsankawi Pumice 127

Bed, overlain by non- to densely welded ignimbrite, emplaced by numerous pyroclastic density 128 currents (Bailey et al., 1969; Self et al., 1986, 1996). The ignimbrites are divided into mappable 129 units, recognized over a wide area and designated Qbt1 through Qbt5 in ascending order; some 130 numbered units are additionally subdivided (Warren et al., 2007; Goff et al., 2014). All units 131 contain a range of compositions shown by bulk chemical analysis of single pumices and bulk 132 tuff, representing magmas at different degrees of evolution (Balsley, 1988; Self et al., 1996; 133 Warren et al., 2007; Goff et al., 2014). The Tshirege Member consists of volumetrically 134 135 dominant high-silica rhyolite (75–79% SiO₂), low-silica rhyolite (73–75% SiO₂), and hornblende dacite with 67–71% SiO₂ (Bailey et al., 1969; Self et al., 1996; Stimac, 1996; Boro, 2019). The 136 137 dacite occurs as pumice clasts scattered through most of the Tshirege Member, and may 138 represent the recharge event that triggered the Tshirege eruption (Stimac, 1996; Goff et al., 2014;

139 Boro et al., 2020). Goff et al. (2014) also identify an additional component of andesite in lateerupted units. Despite the overall zoned character of the Tshirege Member, there is wide 140 variation in pumice composition at any one stratigraphic level (Self et al., 1996). Several 141 processes, such as overturn driven by gas exsolution or thermal disturbance before eruption 142 (Bachmann and Bergantz, 2006; Burgisser and Bergantz, 2011), extraction effects during 143 eruption (Blake and Ivey, 1986a,b; Trial et al., 1992), or non-sequential deposition of the 144 different magmatic components (Torres et al., 1996; Branney and Kokelaar, 2002) may limit, 145 scramble or obscure the record of zoning in the final deposits. Hence, we find the abundances of 146 147 incompatible elements in single pumice clasts to be the most useful indicators of degree of magmatic evolution and hence likely vertical position in the pre-eruptive magma body, assuming 148 them as proxies for melt H₂O contents and hence densities. This assumption is supported by H₂O 149 contents of melt inclusions in quartz and feldspar (Dunbar and Hervig, 1992). 150

151

152 Tshirege Pumice

Whole-pumice chemistry (Fig. 2) shows three distinct rhyolites were present in the 153 Tshirege magma body at the time of eruption (Boro, 2019): two high-silica rhyolites, one 154 enriched in incompatible trace elements (99-173 ppm Nb, 25-41ppm Th: HSR-e) and one 155 relatively depleted in those elements (44-74 ppm Nb, 14-21 ppm Th: HSR-d), and a low-silica 156 rhyolite (26–42 ppm Nb, 10–14 ppm Th: LSR). Quartz grains analyzed in this study were 157 158 extracted from these three compositional groups of rhyolite pumice. The HSR-e is representative of the Tsankawi Pumice Bed and the lowermost part of Qbt1, and the HSR-d corresponds to the 159 later-erupted Units Qbt2 and Qbt3 of Warren et al (2007). One additional sample, 88-1, is a 160

161	hornblende dacite pumice containing quartz scavenged from rhyolite, which is texturally
162	identical to the quartz in the rest of the rhyolite and so has been included in this study.
163	Quartz crystals in the Tshirege Member are frequently zoned when viewed in CL (Fig. 1).
164	The style of zoning varies, but is dominantly 'reverse' in character, where crystal cores appear
165	dark (lower Ti, consistent with more evolved melt or lower temperature) and rims appear bright
166	in CL (higher Ti). Wilcock et al. (2013) describe three different CL zoning types in the Tshirege
167	quartz: (1) reverse zoning, with varying sharpness of the boundary between CL-dark core and
168	CL-bright rim; (2) normal zoning with a bright core and dark rim; and (3) crystals that are
169	completely non-zoned. The full range of zoning styles and statistical analyses of their
170	distribution in the Tshirege Member is described by Wilcock et al. (2013) and our study finds a
171	similar distribution (Fig. 1). For the diffusion modeling portion of this study, we focus on
172	crystals with sharp reverse zoning boundaries, which were extracted from whole pumices
173	collected from the sub-unit Qbt3.

174

DATA ACQUISITION

We analyzed oriented quartz grain separates, cut normal to the c axis, from the Tshirege 175 Member. Grain mounts were made using >500 µm size-fraction crystal separates. Titanium 176 concentrations in quartz were measured by wavelength-dispersive electron probe microanalysis. 177 Measurements were made on a JEOL JXA-8500F field emission electron microprobe located in 178 the Peter Hooper GeoAnalytical Lab at Washington State University, using an accelerating 179 180 potential of 20kV, a beam current of 400nA, and a spot size of 2-10 µm, following the procedures described by Donovan et al. (2016) for analysis of trace elements in simple matrices 181 such as SiO₂. To summarize, measured peak X-ray intensities were corrected for continuum 182 intensity using the mean atomic number (MAN) method of Donovan and Tingle (1996), and then 183

blank corrected using the procedure of Donovan et al. (2011) to eliminate systematic errors in
accuracy resulting from background artifacts. Quartz crystals from Herkimer, NY, with Ti
concentrations of <30 ppb (Kohn and Northrup, 2009; Kidder et al., 2013) were used as a blank
standard. Several mounts of Herkimer quartz were prepared, so that blank standards and
unknowns could be carbon coated together prior to analysis to minimize differences in coating
thickness between blank standards and unknowns.

190 We acquired data for a cumulative time of 18 minutes using three spectrometers.

191 Titanium concentration profiles were measured with 4 or 8 µm spacing between analysis spots.

192 Measurement of [Ti] in this manner allows for detection limits of <2 ppm and analytical

precision (based on counting statistics) of <5% (2-sigma) for each individual measurement. This

194 combination of spot size and uncertainty is comparable to those obtained using synchotron XRF

on similar samples (Matthews et al., 2012; Gualda and Sutton, 2016), but with improved (i.e.,

196 shallower) depth averaging.

Measurements were made either on grain mounts, using quartz crystals separated from 197 the rock matrix, or in thin sections on areas far enough from adhering Ti-bearing glass or Ti-rich 198 phases, to avoid artifacts from continuum fluorescence (cf. Fournelle 2007). To minimize effects 199 arising from obliquely or randomly oriented zone boundaries and off-center sections (Shea et al., 200 2015), crystals were mounted such that profiles were measured normal to the c axis across the 201 broadest part of quartz bipyramids (Fig. 1). Titanium concentration profiles ranged in length 202 203 from 200-400 µm and multiple profiles were acquired on some grains to test for heterogeneity along CL brightness boundaries. Additionally, some profiles oblique to zone boundaries were 204 acquired and then trigonometrically corrected to obtain higher resolution across boundaries with 205 206 small diffusional relaxation widths. Modeling of the effects of continuum fluorescence across the

boundaries between low- and high-Ti zones within the quartz crystal using PENEPMA (Llovet
and Salvat, 2016) suggests that any effects of secondary fluorescence of the higher-Ti zone
across the boundary are negligible (~1 ppm or less). All profiles, their model times, explanation
of oblique profiles, and a comparison of multiple profiles on single crystals can be found in the
supplementary data file.

Grayscale CL images were obtained using a Gatan MiniCL cathodoluminescence
detector mounted on the WSU JEOL JXA-8500F using a 50 nA beam current, 10 kV, and 60
second capture time producing images with an effective image resolution of 1 µm, with constant
contrast and brightness settings. ImageJ software was used to produce grayscale intensity graphs
along EPMA transect lines. Under these conditions the grayscale intensities are considered
internally consistent.

Titanium concentrations were also measured in a subset of quartz crystals by laser 218 ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) to confirm the accuracy of 219 EPMA measurements. The LA-ICP-MS measurements were performed on zones in quartz 220 crystals that were uniformly CL-bright or CL-dark, where EPMA measurements yielded uniform 221 Ti concentrations. Data were collected using a Teledyne Analyte Excite Excimer 193 nm laser 222 ablation system attached to a Finnigan Element2 ICP-MS. A 20 µm spot size was used with 7 223 J/cm^2 beam energy, and counts collected for 30 seconds along transects that ran parallel to 224 crystal faces and zone boundaries, staying within the zones defined by CL imaging. Calibration 225 226 was achieved using NIST-612 and BCR-G glasses, plus a well-characterized internal standard quartz with 9 ppm Ti. Results of LA-ICP-MS and EPMA measurements of Ti are 227 228 indistinguishable within analytical uncertainty (Table 1).

229	Melt inclusions in quartz and external glasses in the HSR-e, HSR-d, and LSR samples
230	were analyzed for Ti, Zn, Rb, Sr, Y, Zr, Nb, Cs, Ba, REEs, Hf, Ta, Pb, Th, and U using LA-ICP-
231	MS. Some additional thin sections with exposed quartz melt inclusions were also analyzed. A
232	New Wave UP-213 laser was used for ablation with a 20 Hz rep rate and laser power from 3-3.5
233	J/cm ² . Ablations were analyzed using a sampling rate of every ~ 0.9 sec with an Agilent 7700
234	Series quadrupole mass spectrometer. Laser track widths varied from 12-30 μ m depending on
235	available glass and melt inclusion sizes. Inclusions $<50 \ \mu m$ in diameter were avoided. Data were
236	normalized to NIST-610 using ²⁸ Si or ²⁹ Si as an internal reference.
237	Whole-pumice clasts were analyzed for major, minor and trace elements in the Peter
238	Hooper GeoAnalytical Lab at Washington State University by X-ray fluorescence and
239	inductively coupled plasma mass spectrometry (methods and procedures described at
240	https://environment.wsu.edu/facilities/geoanalytical-lab/technical-notes/).
241	
242	
243	
244	RESULTS
245	Cathodoluminescence
246	CL grayscale images were obtained for >50 quartz crystals. Titanium concentration
247	profiles plus CL grayscale profiles were obtained for 20 quartz crystals from samples taken at
248	several stratigraphic heights within the Tshirege Member. Generally, CL zoning can be split into
249	three types (Fig. 1): 1. Non-zoned; 2. Reversely zoned; 3. Complex. In cases where there were
250	multiple zones (e.g., Fig. 1, panel 1, 3, and 5), the outermost zone boundary was used for
251	diffusion modeling.

252

253 Glass trace element chemistry and melt inclusion faceting

254 Trace-element abundances in glasses are somewhat bimodal, similar to the distribution of whole-pumice compositions, but do not always reflect the bulk chemistry of the clast from which 255 they were extracted (Fig. 3; full trace element glass data can be found in the supplementary data 256 file). Melt inclusions in quartz from HSR-e plot with glasses adhering to quartz crystals and 257 groundmass glass remote from crystals in thin section (collectively referred to as "external 258 glasses") from those samples. Melt inclusions from Ti-poor quartz cores in the HSR-d and LSR 259 plot with HSR-e glasses, whereas MIs that plot with HSR-d and LSR external glasses are found 260 in CL-bright rims of crystals or in crystals that show no zoning in the HSR-d or LSR. Some MIs 261 262 fill a gap between the two groups of data and may have trapped a liquid composition that is not represented by whole-pumice data or groundmass glass data. 263

Melt inclusions occur as faceted and non-faceted forms. Faceting in melt inclusions 264 occurs as an initially round inclusion attempts to acquire a negative crystal form, accomplished 265 through lateral diffusion of silica along the edges of the inclusion (see Fig. 3 in Gualda et al., 266 2012; supplementary file). The time that an inclusion takes to go from non-faceted to faceted is 267 positively correlated with the size of the inclusion and negatively correlated with temperature. 268 Melt inclusions in the Tshirege quartz vary from almost perfectly round to strongly 269 270 faceted (Fig. 4). Inclusions have been assigned a faceting strength (FS) value from 0 = unfaceted, spherical inclusion to 2 = strongly faceted, negative bipyramidal crystal shape (Fig. 4d). Facet 271 strength is assigned by visual inspection of facets; the requirements for a melt inclusion to fit into 272 273 any individual category are outlined in Figure 4e. Although there is some subjectivity around \sim FS = 1.0, 0 and 0.5 are very different from 1.5 and 2. In crystals that contain multiple facets 274

with different FS values, higher FS values are found towards the core of the crystal (Fig. 5).

276 Barium and Sr, compatible elements in rhyolite, are correlated with the degree of faceting, where

- no melt inclusions above FS = 1 have Ba above ~15 ppm; FS = <1 have Ba of 5–66 ppm, with
- unfaceted HSR-e inclusions having the highest Ba and Sr (Fig. 4a).

Highly incompatible elements (e.g., Nb and Th) show positive correlations among all

glasses (Fig. 3a). On most bivariate plots, external glasses and MIs from HSR-e pumices plot

together while glasses and MIs from the HSR-d and LSR pumices plot together (Fig. 3b, c);

some HSR-d and LSR MIs plot with HSR-e external glasses and MIs. Figure 3-d shows Rb/Sr vs

Ba/Nb and a field of strongly faceted melt inclusions. This field contains all melt inclusions with

a FS \geq 1 and none with FS < 1. Generally, when faceted and unfaceted inclusions occur together

in the same crystal, strongly faceted inclusions occur in the cores of crystals, where weakly or

unfaceted inclusions occur in the rims. MIs plotting with external glasses from LSR and HSR-d

pumices are only found in CL-bright rims and are unfaceted. The strongly faceted MIs have

clearly formed from a move evolved liquid.

Faceted inclusions with a FS = 2 are 50-125 μ m in radius, suggesting FS = 2 inclusions were trapped and stored in quartz for a time on the order of at least >1,000-10,000 years (Gualda et al., 2012) assuming an average storage temperature of 750 °C. Once an inclusion is strongly faceted, no further changes occur, so these are minimum times. Some of the largest (r = 150 μ m) faceted melt inclusions in the Tsankawi pumice (700 °C) may have taken on the order of 10⁴ years to develop (see supplementary data file for faceting times vs MI radius at different temperatures, Fig. A2).

296

297 [Ti] vs. CL grayscale intensity

298	In Figure 6, four representative Ti concentration profiles measured across CL brightness
299	boundaries are plotted with CL grayscale intensity, shown as 3 μ m pixel averages, together with
300	estimated times for development of each type of profile assuming an initial step function (next
301	section). The complete set of profiles are given in the supplementary file. Resolution of Ti data at
302	the effective spot size of 2 μ m does not allow for accurate modeling of diffusional boundaries
303	thinner than $\sim 16~\mu m$ (corresponding to $\sim \!\! 200$ years diffusive relaxation at 750 °C using
304	diffusivity coefficients from Cherniak et al., 2007) because 4-5 points are needed to define a
305	diffusion sigmoid; however in each case the Ti slope is less steep than this limit (Fig. 6). In
306	some cases, oblique corrected profiles allow for resolution of diffusional boundaries $<16 \ \mu m$ (see
307	supplementary file, sample 119-4). Usually (Fig. 6, Table 2) the CL grayscale profile is
308	'sharper', i.e. closer to a step function, than the Ti profile; in a few cases they are
309	indistinguishable within uncertainty, and in two cases the Ti profile is steeper than CL grayscale,
310	albeit still overlapping within uncertainty. To illustrate the effects of the different profiles on
311	calculated timescale estimates (see Modeled diffusion relaxation times below), in Fig. 6 we
312	compare results from CL grayscale and Ti profiles at a fixed $T = 750$ °C; estimates may differ by
313	more than an order of magnitude. We now attempt to additionally estimate diffusion times from
314	Ti profiles using temperatures derived from thermometry.

315 Estimation of temperature

Due to the generally high activation energies associated with cation diffusion in silicate minerals, timescales calculated from diffusion profiles are very sensitive to temperature (e.g., Cherniak et al., 2007). For example, a ΔT of ~50 °C, which is similar to the error range (i.e. ±25 °C) arising from calibration and microprobe data uncertainty for many mineral geothermometers, may result in an order of magnitude change in calculated relaxation time. It is therefore

321 necessary to constrain temperature during diffusive relaxation as closely as possible. The Tshirege Member contains magnetite and sporadic ilmenite, but we did not find any pairs that 322 pass the equilibrium test of Bacon and Hirschmann (1988). The first-erupted parts of both the 323 Otowi and Tshirege Members of the Bandelier Tuff (respectively, the Guaje and Tsankawi 324 Pumice Beds) have compositions that are close to haplogranite, are homogeneous, exhibit the 325 least textural evidence for internal disequilibrium within their respective members, and plot very 326 near the minimum in Q-Ab-Or at 2 kb H₂O saturation pressure (Wilcock et al., 2013; Wolff and 327 Ramos, 2014), consistent with a magma temperature close to 700 °C (Tuttle and Bowen, 1958) 328 329 and the measured H₂O contents of melt inclusions (Dunbar and Hervig, 1992). Warshaw and Smith (1988) give a temperature of 697 °C for the Tsankawi magma, based on an early version 330 of the QUILF thermometer (Andersen and Lindsley, 1988), but do not report uncertainties. 331 Wilcock et al. (2013) review several lines of evidence for storage depth of the Tshirege magma 332 and conclude that a pressure of 200 ± 50 MPa is most appropriate. We concur and assume this 333 pressure and a temperature of 700 °C for the Tsankawi Pumice magma. 334 The TitaniQ thermometer (Wark and Watson, 2006, equation 1 below; Thomas et al., 335 2010, equation 2 below; Huang and Audétat, 2012, equation 3 below), which relies on the 336 temperature dependence of [Ti] in quartz, can be applied to quartz grains chosen for diffusion 337 modeling, thus avoiding the potential problem in applying temperatures estimated from other 338 mineral phases in high-silica rhyolites that may not be in equilibrium with quartz (Evans and 339 340 Bachmann, 2013; Evans et al., 2016):

341
$$T(^{\circ}C) = \frac{-3765\pm24}{\log\left(\frac{x_{Ti}^{qtz}}{a_{TiO_2}}\right) - 5.69\pm0.02} - 273 \tag{1}$$

342

$$RT \ln X_{\text{TiO}_2}^{\text{quartz}} = -(60952 \pm 3177) + (1.520 \pm 0.39) * T(K) - (1741 \pm 63) * P(kbar) + RT \ln a_{TiO_2}$$

343

344

$$\log \text{Ti}(\text{ppm}) = -0.27943 * \frac{10^4}{T} - 660.53 * \frac{P^{0.35}}{T} + 5.6459$$
(3)

In each case, the thermometer is experimentally calibrated for melts saturated with rutile, 345 hence $a(TiO_2)_{melt} = 1$; the chief difficulty in its application therefore lies in the estimation of 346 $a(TiO_2)_{melt}$ because the vast majority of volcanic silicate liquids are not rutile-saturated. Hayden 347 and Watson (2007) provide a method for estimating $a(TiO_2)_{melt}$ based on rutile saturation as a 348 function of melt composition and temperature; however this is only calibrated at 1 GPa, at which 349 pressure rutile solubility is likely less than at the mid- to upper-crustal storage depths of most 350 rhyolites (Thomas and Watson, 2012). Rhyolite-MELTS (Gualda et al., 2012) calculates 351 $a(TiO_2)_{melt}$ but the values for the exceptionally Ti-poor glasses of the Tshirege Member are 352 extremely low ($\sim 10^{-5}$), yielding unreasonably high temperatures. 353

Instead, we have calculated $a(TiO_2)_{melt}$ for the Tshirege Member by 'internally 354 calibrating' to an assumed temperature of 700 °C for the first-erupted Tsankawi pumice, and 355 setting $a(TiO_2)_{melt}$ to a value of 0.34, which yields 700 °C for the average compositions of 356 Tsankawi quartz (~22.5 ppm Ti) using Eqn. (1). The same result is obtained from the Huang and 357 Audétat (2012) calibration (Eqn. 3) using this $a(TiO_2)_{melt}$ if P is set to 263 MPa. The high-358 pressure Thomas et al. (2010) calibration (Eqn. 2) requires a different a(TiO₂)_{melt} of 0.0775, and 359 was not used here. The Tsankawi-derived $a(TiO_2)_{melt}$ value is then treated in two ways. In the 360 361 first approach, $a(TiO_2)$ is assumed constant throughout the Tshirege Member high-silica rhyolite magma. This assumption can be justified on the basis that titanomagnetite is a ubiquitous, if 362 trace, phenocryst phase (Warren et al., 2007) and hence may buffer $a(TiO_2)_{melt}$. However, it is 363 unclear whether or not quartz and titanomagnetite were co-precipitating phases, or whether 364 titanomagnetite compositions or abundances may have changed during quartz growth, an issue 365

(2)

366	that has led to conflicting interpretations of temperature estimates for the Bishop Tuff, a similar
367	voluminous high-silica rhyolite eruption (Evans and Bachmann, 2013; Gualda and Ghiorso,
368	2013; Evans et al., 2016; Jolles and Lange, 2019). Therefore, when estimating $a(TiO_2)_{melt}$ for the
369	Tshirege Member magmas, buffering cannot be assumed. Instead, the $a(TiO_2)_{melt}$ value of 0.34 is
370	used to calculate an effective TiO_2 activity coefficient for measured TiO_2 in Tsankawi glasses,
371	which is then applied to compositions of glasses in contact with quartz rims throughout the
372	Tshirege Member. The assumption of constant $\gamma(TiO_2)_{melt}$, where γ denotes the activity
373	coefficient, is justified by the essentially constant major-element composition of Tshirege high-
374	silica rhyolite.
375	Modeled diffusion relaxation times (next section) are calculated using three different
376	temperature assumptions: (i) constant temperature of 750 °C (Fig. 6); (ii) temperature estimated
377	using the Wark and Watson (2006) and Huang and Audétat (2012) calibrations at 263 MPa,
378	assuming constant $a(TiO_2)_{melt}$; (iii) temperature estimated using the Wark and Watson (2006)
379	and Huang and Audétat (2012) calibrations at 263 MPa, and applying calculated $\gamma(TiO_2)_{melt}$ to Ti
380	contents of glasses adhering to quartz crystals to estimate $a(TiO_2)_{melt}$. In cases (ii) and (iii), the
381	temperature calculated from the rim composition of the quartz is assumed to apply to diffusion at
382	the inner boundary of the rim.
383	

384 Modeled diffusion relaxation times

We use the 1-D finite difference diffusion method (Costa et al., 2008, equation 4 below), to model Ti diffusion in quartz as a function of time and distance of travel in the lattice:

387
$$C_{i,j+1} = C_{i,j} + \left(\frac{D\Delta t (C_{i+1,j} - 2C_{i,j} + C_{i-1,j})}{\Delta x^2}\right)$$
(4)

Where: $C_{i,i}$ = the concentration at the current lattice location; $C_{i,i+1}$ = the concentration at the 388 current lattice location one time step forward; $C_{i+1,i}$ = the concentration one lattice step towards 389 the diffusion zone; $C_{i-1,i}$ = the concentration one lattice step away from the diffusion zone; D = 390 diffusion coefficient for the diffusing species in lattice of interest; Δt = change in time for one 391 step in the model; $\Delta x =$ step size. Boundary conditions for the high and low steps at time = 0 392 were set as the average [Ti] outside of the diffusive relaxation zone, where data formed a plateau, 393 or in cases where data did not form a good plateau, the boundary condition was set to a best fit 394 395 line through boundary data.

The diffusion coefficient of Ti in quartz parallel to the *c* axis is not well established and we use the two current published values given by (Cherniak et al., 2007, equation 5; Jollands et al., 2020, equation 6):

399
$$D_{\text{Ti}} = 7 \times 10^{-8} \exp(-273 \pm 12 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ sec}^{-1}$$
 (5)

400

401
$$log_{10}D_{\text{Ti}} = -8.3 \pm 0.4 - [311 \pm 12 \text{ kJ mol}^{-1}/(2.303RT)] \text{ m}^2 \text{ sec}^{-1}$$
 (6)

402 Where: D_{Ti} = diffusion coefficient of Ti in quartz, R is the universal gas constant and T is 403 absolute temperature. Cherniak et al. (2007) provide seven additional experiments measuring Ti diffusion in quartz normal to c, with little anisotropy apparent. Regression of those experiments 404 405 over the temperature range 750 - 1101 °C gives an Arrhenius relation that yields results indistinguishable from Eqn (5), which we use here and suggests that Ti-diffusion parallel or 406 perpendicular to *c*-axes is similar. Errors for the CL and Ti profiles at constant temperatures are 407 calculated from the inherent error in the D_{Ti} which, when applied to these data, lead to large (40-408 60%) errors of modeled times. In Table 2, uncertainties of diffusion times for the Ti profiles 409 calculated using temperatures from TitaniQ that arise from fitting sigmoids to the data are 410

reported separately. The very different diffusivities from Cherniak et al. (2007) and Jollands et
al. (2020) result in diffusion timescales that are systematically offset by an average of two orders
of magnitude (Figure 6; Tables 2 and 3); the implications of these results are outlined in the **Discussion** section below.

In most cases, Ti diffusive relaxation times calculated from CL grayscale profiles are 415 shorter than those calculated from Ti data using the same D_{Ti} , by up to an order of magnitude 416 (Table 2, Fig. 6). In some cases the two profiles yield identical results within error. Previous 417 authors have presented discrepant CL grayscale and Ti concentration data, consistent with our 418 findings (e.g., Fig. 9 of Matthews et al., 2012), but have discounted the significance for 419 calculated timescales. We also note that, overall, grayscale profiles are smoother than those for 420 Ti concentrations from the same crystal (Fig. 6), resulting in many cases in decreased, but 421 perhaps less realistic, calculated uncertainties associated with timescales (Table 2). Furthermore, 422 while spectroscopic measurements of quartz CL emissions at specific wavelengths, such as ~454 423 nm, are very well correlated with Ti contents (MacRae et al., 2013, 2018), greyscale CL is not a 424 reliable proxy for Ti concentration. For many panchromatic CL detectors, the collection optics 425 accept light from a wide variety of angles, and therefore light from adjacent areas, which are still 426 emitting from the initial electron bombardment, or light transmitted through the sample and 427 scattered off of microcracks in the sample, which may be included in a CL measurement that is 428 supposed to represent only the CL emitted from an individual pixel (MacRae et al., 2013). Also, 429 430 as described by Leeman et al. (2012) and MacRae et al. (2018), greyscale intensities include not only CL from Ti dopants, but also from the intrinsic CL produced by quartz, by crystallographic 431 defects, by aluminum dopants, and by non-bridging oxygen holes in the crystal structure. In fact, 432 433 certain CL emissions from quartz, such as those from non-bridging oxygen holes, are actually

434	inversely correlated with Ti contents (see Fig. 4 of Leeman et al., 2012). Therefore, the diffusion
435	profiles used for the modeling presented here are based on the Ti concentrations measured by
436	EPMA; profiles based on CL intensity are not considered.

- 437
- 438

DISCUSSION

439 Titanium concentrations in rims of zoned quartz are invariably higher than those in Tsankawi quartz, hence estimated temperatures are always higher. Assuming 700 °C for the 440 441 Tsankawi, the average temperature (excluding dacite 88-1) for quartz rims in pumice clasts with 64 – 73 ppm Nb is 774 ± 14 °C ($a(TiO_2)$ method) or 740 ± 17 °C ($\gamma(TiO_2)$ method). This 442 reinforces the qualitative value of the TitaniQ thermometer, but the difficulties associated with 443 444 $a(TiO_2)$ estimation somewhat negate its quantitative value as a thermometer applicable to rhyolites (see also Wilson et al., 2012). The majority of rhyolites with high magmatic H₂O 445 contents erupt at temperatures between 700 and 800 °C, so the temperature estimates in Table 2 446 are reasonable but hardly surprising. 447

Sample 88-1 is a hornblende dacite pumice containing quartz texturally indistinguishable 448 from that in the high-silica rhyolite (Fig. 1); the quartz is thought to have been incorporated as 449 dacite mixed with rhyolite immediately prior to the eruption (Stimac, 1996; Boro et al., 2020). 450 The quartz rim compositions yield temperatures of 799–825 °C, consistent with 797 ± 17 °C 451 452 from amphibole thermometry (Boro et al., 2020). Despite the higher temperature, this quartz crystal produces one of the longest modeled Ti diffusion times (see 750 °C Ti model-time 453 column, Table 2), and hosts a FS = 2 melt inclusion in the CL-dark core, supporting a long 454 455 storage time for this crystal.

456	There is a large discrepancy between the widely-used values of D_{Ti} in quartz of Cherniak
457	et al. (2007), and the recent estimate of Jollands et al. (2020); compare eqns (5) and (6). Use of
458	eqn. (5) has produced estimates of short timescales for quartz regrowth (Matthews et al., 2012;
459	Till et al., 2015; Gualda and Sutton, 2016; Cooper et al., 2017), although in some cases these
460	timescales are supported by other methods (e.g., Chamberlain et al., 2014a). In the case of the
461	Tshirege Member, the Jollands et al. (2020) diffusivities yield modeled diffusion times of
462	chemical relaxation across growth boundaries in quartz up to 10^7 years (Table 3), which is
463	geologically unreasonable for this system; we take the 360 k.y. time between the Otowi and
464	Tshirege eruptions as the maximum geologically reasonable timescale for crystal growth likely
465	to be recorded in the Tshirege Member. Most of the estimates in Table 3 are longer.
466	Therefore, if the Jollands et al. (2020) diffusion coefficients (Eqn. 6) are preferred, the
467	assumption of an initial step-function Ti concentration profile may be invalid, and the profiles in
468	Fig. 6 are partly inherited from crystal growth. In this case the initial condition is not
469	constrained. Although diffusion sigmoids can be fit to all cases, in detail both the CL and Ti
470	concentration profiles show numerous minor reversals and irregularities on either side of the
471	zone boundary. Commonly, a thin peak in Ti or Cl brightness occurs of the high-Ti side of the
472	boundary (Fig. 6; supplemental data). These variations may be due to changes in crystal growth
473	rate (Huang and Audétat, 2012). However, the major CL dark core – CL light rim boundary
474	often truncates earlier zoning in the crystal core, so is not solely a result of changes in growth
475	rate but is the product of an episode of resorption followed by regrowth. The presence of
476	unfaceted melt inclusions in many crystals, including some of the CL-bright crystal rims, limits
477	their residence at magmatic temperature to less than $\sim 2 \times 10^4$ years (supplementary data), using
478	the faceting time estimation of Gualda et al. (2012; their eqn. 9). In addition to the overall

chronology of the Bandelier system, this also militates against the timescales estimated using
Eqn. (6), and assuming an initial step function, having any geological meaning.

If the Cherniak et al. (2007) diffusion coefficients (eqn. 5) are preferred, the results 481 suggest that an event or events involving reheating of the system occurred over a range between 482 <100 and >1,000 years (order of magnitude) prior to eruption, generally consistent with melt 483 inclusion faceting times. These events preceded recharge by the dacite, which may have acted as 484 the trigger for the eruption (Stimac, 1996; Goff et al., 2014; Boro et al., 2020) on a shorter 485 timescale. Some quartz crystals (Fig. 1) have rounded edges and appear to have gone through an 486 487 additional resorption event, truncating existing zoning patterns, without subsequent growth of new quartz prior to the eruption, so the calculated times in Table 2 may reflect a sequence of 488 events cascading towards the caldera-forming eruption. 489

The reasons for the large contrast between fast and slow diffusivities estimated by 490 Cherniak et al. (2007) and Jollands et al. (2020) respectively is unclear. Each study uses a 491 experimentally similar method of exposing quartz to a powdered source of TiO₂ followed by 492 depth profiling, with the major differences being that Cherniak et al. (2007) used a 99.9% pure 493 TiO₂ source for Ti and Jollands et al. (2020) used a Ti-doped SiO₂ powder with [Ti] of ~100 494 ppm. Jollands et al. (2020) were unable to reproduce the results of Cherniak et al. (2007) using a 495 pure TiO₂ source due to degradation of the quartz crystal surface during a one-hour annealing 496 with a pure rutile powder, making subsequent depth profiling using SIMS unfeasible. Jollands et 497 498 al. (2020) speculate that Ti may have more than one diffusion mechanism in quartz, with the faster mechanism effectively absent at the low Ti concentrations of their experiments (see their 499 supplemental file p. 10), and therefore, by implication, in the majority of natural cases. The 500

question of which diffusivities are more correct has significant implications for understanding
the dynamics and timescales for silicic magma systems. Our study does not resolve this question.

505

504

IMPLICATIONS

505 Compositional zoning of the Tshirege Member magma

506 Most quartz cores from HSR-d pumice have near-constant and low Ti contents,

indistinguishable from non-zoned quartz in HSR-e Tsankawi pumice. The MIs hosted by these 507 cores are typically faceted and have trace element abundances similar to HSR-e pumice, whereas 508 the occasional MIs in the Ti-rich rims of quartz from HSR-d pumice have HSR-d chemistry and 509 are non- or weakly faceted (Fig. 5). These observations link overall bulk zoning in the Tshirege 510 511 Member to melt inclusion chemistry (Figs. 2, 3), quartz growth, and quartz residence time. The most evolved, first-erupted melt compositions (HSR-e chemistry) and low-Ti quartz existed 512 before the less evolved, late-erupted melt (HSR-d and LSR chemistries) and high-Ti quartz 513 developed in the erupted portion of the system. This is consistent with a simple model of 514 crystallization, cumulate formation, and subsequent melting and remobilization of the cumulate 515 to create a compositionally zoned magma body (Wolff et al., 2015, 2020). In this model, which 516 is an extension of the 'mush model' (Bachmann and Bergantz, 2004; Hildreth, 2004), the quartz-517 feldspar cumulate pile beneath a cognate crystal-poor melt lens is heated and remobilized by 518 519 recharge, with little mass contribution from the recharge magma (Wark et al., 2007; Wolff and Ramos, 2014). The result is a relatively water-poor rhyolite, of higher density and with lower 520 incompatible element concentrations than the initial rhyolite melt lens. The new melt, with a 521 522 cargo of crystals inherited from the cumulate pile, pools beneath the initial melt lens to form a thicker, compositionally zoned body of eruptible magma. The lack of quartz zoning in HSR-e 523

samples suggests an enriched liquid lens that was shut off from the thermal and chemical effects
of invading recharge magmas, likely shielded by a crystal mush that was melted and mobilized to
form the HSR-d magma.

527 Figure 7 depicts four stages in the development of zoning in the Tshirege system: a. Initial state of the system is an accumulating crystal mush overlain by a lens of 528 magma, which is highly enriched in incompatible trace elements, and depleted in 529 compatible trace elements – especially those which strongly partition into sanidine 530 (i.e., Sr and Ba). This system is producing quartz crystals that trap melt from the 531 evolved body and settle to contribute to the mush. 532 b. The mush is around 70% crystallinity with correspondingly lower bulk water content 533 then the melt and consists of crystals with melt inclusions. Storage for 1,000-10,000 534 years allows for faceting of melt inclusions. 535 c. Recharge magma, underplating and intruding the crystal mush column, acts as a 536 heating element and may also add H₂O to the system from second boiling, loosening 537 the mechanically locked mush (Boro, 2019), causing quartz crystals to partially 538 resorb. Simultaneous melting of feldspar adds Ba and Sr to the melt. Crystals resume 539 growing. 540

d. Quartz crystals regrow as they find a new equilibrium at higher temperatures forming
CL-bright rims with higher Ti concentrations, and capture the recharge event with
unfaceted melt inclusions enriched in Ba and Sr. Continued recharge of the system
mobilizes the mush and overpressure triggers the eruption.

545

546 Eruption forecasting

An important application of petrologic study of past eruptions is to draw links between 547 548 events recorded in crystals and melts, particularly those interpreted as destabilizing to the 549 system, and monitoring signals that might be detected at the surface in the run-up to a future eruption (Blundy and Cashman, 2008). Studies using the Cherniak et al. (2007) Ti-in-quartz 550 551 diffusion coefficients (e.g., Gualda and Sutton, 2016; Cooper et al., 2017) have emphasized short timescales of crystal regrowth and residence following recharge events prior to a supereruption. 552 In the case of the Tshirege Member, the events recorded in quartz would imply multiple 553 disturbances over $\sim 10^3$ years prior to eruption, culminating in the intrusion of dacite magma into 554 the system, the probable immediate trigger for the eruption (Goff et al., 2014; Boro et al., 2020). 555 If recharge events can be detected at the surface (e.g., inflation, seismicity, increased gas flux), it 556 is unclear how the critical eruption trigger could be identified, but a series of events over a long 557 term might indicate destabilization of a static magma body. The new diffusion coefficients of 558 Jollands et al. (2020) immediately throw all the short timescale estimates derived by previous 559 workers from Ti (or CL) profiles in quartz into question. Jollands et al. (2020) note that the 560 longer timescales of $10^{5\pm1}$ v they calculate for guartz residence and growth in the Bishop Tuff are 561 consistent with the durations of magma reservoir assembly derived from zircon U-Th-Pb dating 562 and other methods. We may note that both short and long timescales for the Bishop Tuff - Long 563 Valley system are currently supported by other methods: short times ($<10^2$ years. Wark et al., 564 565 2007, using the Cherniak et al., 2007 diffusivities) are supported by diffusion-based estimates from other phases (Chamberlain et al., 2014a) and long times ($\sim 10^5$ years, Jollands et al., 2020, 566 using their diffusivities) by radioisotope studies of zircon (Coath and Reid, 2000; Simon and 567 Reid, 2005; Chamberlain et al., 2014b). Regardless of which Ti diffusivities are correct, an 568

569	overall picture of silicic systems being established over $\sim 10^5$ years or longer, and subject to
570	multiple disturbances such as recharge which ultimately lead to eruption, seems robust; the
571	question that remains is what exactly quartz is telling us about this history.
572	Our results from the Tshirege Member suggest that the longer Ti-in-quartz duration
573	estimates may be incorrect, not necessarily because the diffusivity experiments are flawed, but
574	more probably because the assumption of an initial sharp Ti-zone boundary in quartz is invalid.
575	The agreement of shorter times obtained using the diffusivity value published by Cherniak et al.
576	(2007) with melt-faceting times is also notable. We conclude that, without constraints on initial
577	conditions, Ti profiles in quartz shed no light on the timescales for destabilization and
578	mobilization of rhyolitic magma bodies preparatory to eruption until this current discrepancy is
579	sufficiently addressed.
580	
581	ACKNOWLEDGEMENTS
582	This work was funded by NSF EAR-0810306 and Washington State University. We thank Tom
583	Shea, Ren Thompson, Fraser Goff, Steve Self and the late Jamie Gardner for discussion, Will
584	Nachlas for providing the Herkimer quartz crystals, and Scott Boroughs, Charles Knaack, Ashley
585	Steiner, Suzy Krahn and Kamilla Fellah for assistance in field and laboratory. The paper was
586	improved thanks to reviews by an anonymous reviewer and Fabio Arzilli.
587	

588

REFERENCES CITED

- Anderson, D.J., Lindsley, D.H. (1988) Internally consistent solution models for Fe-Mg-Mn-Ti
 oxides; Fe-Ti oxides. American Mineralogist 73, 714-726.
- 591 Arzilli et al. 2019. The unexpected explosive sub-Plinian eruption of Calbuco volcano
- 592 (22–23 April 2015; southern Chile): Triggering mechanism implications. Journal of
- 593 Volcanology and Geothermal Research 378 (2019): 35-50.
- Bachmann, O., Bergantz, G.W. (2004) On the Origin of Crystal-poor Rhyolites: Extracted from
 Batholithic Crystal Mushes. Journal of Petrology 45-8, 1565-1582.
- 596 Bachmann, O., Bergantz, G.W. (2006) Gas percolation in upper-crustal silicic crystal mushes as
- 597 a mechanism for upward heat advection and rejuvenation of near-solidus magma bodies.
- Journal of Volcanology and Geothermal Research, 149, 85-102.
- Bacon, C.R. and Hirschmann, M.M. (1988) Mg/Mn partitioning as a test for equilibrium between
 coexisting Fe-Ti oxides. American Mineralogist, 73, 57–61.
- Bacon, C.R., Newman, S., Stopler, E.M. (1992) Water, CO2, Cl, and F in melt inclusions in
 phenocrysts from three Holocene explosive eruptions, Crater Lake, Oregon. American
 Mineralogist, 77(9-10), 1021-1030.
- Bailey, R.A., Smith, R.L. and Ross, C.S. (1969) Stratigraphic nomenclature of volcanic rocks in
 the Jemez Mountains, New Mexico. U.S. Geological Survey Bulletin, 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. M.S. thesis, University of Texasat Arlington, 188 p.
- Blake, S., Ivey, G.N. (1986a) Magma-mixing and the dynamics of withdrawal from stratified
 reservoirs. Journal of Volcanology and Geothermal Research, 27, 153-178.
- Blake, S., Ivey, G.N. (1986b) Density and viscosity gradients in zoned magma chambers, and
- their influence withdrawal dynamics. Journal of Volcanology and Geothermal Research, 30,201-230.
- Blundy, J., Cashman, K. (2008) Petrologic Reconstruction of Magmatic System Variables and
 Processes. Reviews in Mineralogy and Geochemistry 69, 179-239.

- Boro, J.R. (2019) Recharge and mobilization of crystal mush to produce and erupt a zoned
- 617 magma chamber the Tshirege Member of the Bandelier Tuff, Valles caldera, New Mexico,

618 USA: Ph.D. dissertation, Washington State University.

Boro, J.R., Wolff, J.A. and Neill, O.K. (2020) Anatomy of a recharge magma: Hornblende dacite

pumice from the rhyolitic Tshirege Member of the Bandelier Tuff, Valles caldera, New

621 Mexico, USA. Submitted to Contributions to Mineralogy and Petrology.

- Branney, M.J. and Kokelaar, P. (2002) Pyroclastic Density Currents and the Sedimentation of
 Ignimbrites. Geological Society. Geological Society Memoir, 27, 143 pp.
- Burgisser, A., Bergantz, G.W. (2011). A rapid mechanism to remobilize and homogenize highly
 crystalline magma bodies. Nature, 471, 212-215.

626 Campbell, M.E., Hanson, J.B., Minarik, W.G., and Stix, J. (2009) Thermal history of the

Bandelier magmatic system: evidence for magmatic injection and recharge at 1.61 Ma as

revealed by cathodoluminescence and titanium geothermometry. Journal of Geology, 117,
469–485.

630 Caress, M.E. (1996) Zonation of alkali feldspar compositions in the Tshirege Member of the

Bandelier Tuff in Pueblo Canyon, near Los Alamos, New Mexico. New Mexico Geological
Society, 47th Field Conference Guidebook, 275–283.

633 Chamberlain, K.J., Morgan, D.J., and Wilson, C.J.N. (2014a) Timescales of mixing and

mobilisation in the Bishop Tuff magma body: perspectives from diffusion chronometry.

- 635 Contributions to Mineralogy and Petrology, 168:1034, 24 pp.
- 636 Chamberlain, K.J., Wilson, C.J.N., Wooden, J.L., Charlier, B.L.A., and Ireland, T.R. (2014b)
- New perspectives on the Bishop Tuff from zircon textures, ages and trace elements. Journal
 of Petrology, 55, 395–426.
- Cherniak, D.J., Watson, E.B, and Wark., D.A. (2007) Ti diffusion in quartz. Chemical Geology,
 236, 65–74.
- 641 Cooper, G.F., Morgan, D.J., and Wilson, C.J.N. (2017) Rapid assembly and rejuvenation of a
- large silicic magmatic system: insights from mineral diffusive profiles in the Kidnappers and
 Rocky Hill deposits, New Zealand. Earth and Planetary Science Letters, 473, 1–13.
- 644 Costa, F. and Dungan M.A. (2005) Short timescales of magmatic assimilation from diffusion
- 645 modelling of multiple elements in olivine. Geology, 33, 837–840.

- 646 Costa, F., Dohmen, R., and Chakraborty, S. (2008) Time scales of magmatic processes from
- modeling the zoning patterns of crystals. Reviews in Mineralogy and Geochemistry, 69, 545–
 594.
- Donovan, J.J., Lowers, H.A., and Rusk, B.G. (2011) Improved electron probe microanalysis of
 trace elements in guartz. American Mineralogist, 96, 274–282.
- Donovan, J.J., Singer, J.W. and Armstrong, J.T. (2016). A new EPMA method for fast trace
 element analysis in simple matrices. American Mineralogist, 101, 1839–1853.
- Donovan, J.J., Tingle, T.N., 1996. An improved mean atomic number background correction for
 quantitative microanalysis. J. Microsc. Soc. Am. 2, 1-7.
- 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. Journal of Geophysical Research, 97, 15,151-15,170.

- Evans, B.W. and Bachmann, O. (2013) Implications of equilibrium and disequilibrium among
 crystal phases in the Bishop Tuff. American Mineralogist, 98, 271–274.
- Evans, B.W., Hildreth, W., Bachmann, O., and Scaillet, B. (2016) In defense of magnetite-

ilmenite thermometry in the Bishop Tuff and its implication for gradients in silicic magma
 reservoirs. American Mineralogist, 101, 469–482.

- Fournelle, J.F. (2007) The Problem of Secondary Fluorescence in EPMA in the Application of
 the Ti-in-Zircon Geothermometer and the Utility of PENEPMA Monte Carlo Program.
- 665 Microscopy and Microanalysis, 13(S02), 1390-1391. doi: 10.1017/S1431927607079354
- Gardner, J.N., Goff, F., Kelley, S.A. and Jacobs, E. (2010) Rhyolites and associated deposits of
 the Valles-Toledo caldera complex. New Mexico Geology, 32, 3–18.
- 668 Goff, F., Gardner, J.N., Reneau, S.L., Kelley, S.A., Kempter, K.A., and Lawrence, J.R. (2011)

Geologic map of the Valles caldera, Jemez Mountains, New Mexico. New Mexico Bureau of
Geology and Mineral Resources Geologic Map, 79, scale 1:50,000.

- 671 Goff, F., Warren, R.G., Goff, C.J., and Dunbar, N. (2014) Eruption of reverse-zoned upper
- Tshirege member, Bandelier Tuff from centralized vents within Valles caldera, New Mexico.
- Journal of Volcanology and Geothermal Research, 276, 82–104.
- Götze, J. (2012) Application of cathodoluminescence microscopy and spectroscopy in
- 675 geosciences. Microscopy and Microanalysis, 18, 1270–1284.
- Gualda, A.R.G, Sutton, S.R. (2016) The Year Leading to a Supereruption. PLoS ONE 11, 18pp.

- Gualda, G.A.R, Pamukcu, A.S., Ghiorso, M.S., Anderson, A.T Jr., Sutton, S.R., Rivers, M.L.
- 678 (2012) Timescales of Quartz Crystallization and the Longevity of the Bishop Giant Magma679 Body. PLoS ONE 7(5).
- Gualda, G.A.R. and Ghiorso, M.S. (2013) The Bishop Tuff giant magma body: an alternative to
 the standard model. Contributions to Mineralogy and Petrology, 166, 755–775.
- 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 and Planetary Science Letters, 258,
 561–568.
- Hildreth, W. (2004) Volcanological perspectives on Long Valley, Mammoth Mountain, and
 Mono Craters: several contiguous but discrete systems. Journal of Volcanology and
- 687 Geothermal Research 136, 169-198.
- Huang, R. and Audétat, A. (2012) The titanium-in-quartz (TitaniQ) thermombarometer: a critical
 examination and re-calibration. Geochimica et Cosmochimica Acta, 84, 75–89.
- Jollands, M.C., Bloch, E., and Müntener, O. (2020) New Ti-in-quartz diffusivities reconcile
- natural Ti zoning with time scales and temperatures of upper crustal magma reservoirs.
 Geology 48, doi:10.1130/G47238.1
- Jolles, J.S.R. and Lange, R.A. (2019) High-resolution Fe-Ti oxide thermometry applied to
- single-clast pumices from the Bishop Tuff: a re-examination of compositional variations in
- 695 phenocryst phases with temperature. Contributions to Mineralogy and Petrology 174:70, 43
- 696 pp.
- 697 Kidder, S., J.-P. Avouac and Y.-C. Chan (2013), Application of titanium-in-quartz
- thermobarometry to greenschist facies veins and recrystal-lized quartzites in the Hsuehshan
 range, Taiwan, Solid Earth, 4(1), 1–21, doi:10.5194/se-4-1-2013
- Kohn MJ, Northrup CJ. 2009. Taking mylonites' temperature. Geology 37(1), 47–50
- Leeman, W.P., MacRae, C.M., Wilson, N.C., Torpy, A., Lee, C.-T.A., Student, J.J., Thomas,
- J.B., and Vicenzi, E/P. (2012) A study of cathodoluminescence and trace element
- compositional zoning in natural quartz from volcanic rocks: mapping titanium content in
 quartz. Microscopy and Microanalysis, 18, 1322–1341.
- Llovet, X., and Salvat, F. (2016) PENEPMA: a Monte Carlo programme for the simulation of X-
- ray emission in EPMA. IOP Conf. Ser.: Mater. Sci. Eng.109012009

- Lowenstern, J.B., Mahood, G.A. (1991) New data on magmatic H2O contents of pantellerites,
- with implications for petrogenesis and eruptive dynamics at Pantelleria. Bulletin of Volc. 57-1, 78-83.
- MacRae, C.M., Wilson, N.C., Torpy, A. (2013) Hyperspectral cathodoluminescence. Mineralogy
 & Petrology 107, 429-440. Doi: 10.1007/s00710-013-0272-8
- 712 MacRae, C.M., Wilson, N.C., Torpy, A., and Delle Piane, C. (2018) Soft X-ray and
- cathodoluminescence measurement, optimization and analysis at liquid nitrogen
- temperatures. IOP Conference Series: Materials Science and Engineering, Volume 304, Issue
 1, pp. 012010 (2018).
- Matthews, N.E., Huber, C., Pyle, D.M., and Smith, V.V. (2012) Timescales of magma recharge
 of large silicic systems from Ti diffusion in quartz. Journal of Petrology, 53, 1385–1416.
- Morgan, D.J. and Blake, S. (2006) Magmatic residence times of zoned phenocrysts: introduction
- and application of the binary element diffusion modeling (BEDM) technique. Contributions
 to Mineralogy and Petrology, 151, 58–70.
- Pamukcu, A.S., Ghiorso, M.S., Gualda, G.A. (2016) High-Ti, bright-CL rims in volcanic quartz:
 a result of very rapid growth. Contributions to Mineralogy and Petrology 172, 9pp.
- Peppard, B.T, Steele, I.M., Davis, A.M., Wallace, P.J., Anderson, A.T. (2001) Zoned quartz
 phenocrysts from the rhyolitic Bishop Tuff. American Mineralogist 86(9), 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 contraints on the duration of resurgence at the Valles caldera, New Mexico. Journal of Geophysical Research, 112, B08201, 15 p.
- Reid, M.R. and Vasquez, J.A. (2017) Fitful and protracted assembly leading to a giant eruption,
 Youngest Toba Tuff, Indonesia. Geochemistry, Geophysics, Geosystems 18, 156–177.
- 730 Seitz, S., Putlitz, B., Baumgartner, L.P., Escrig, S., Meibom, A., and Bouvier, A.-S. (2016) Short
- magmatic residence times of quartz phenocrysts in Patagonian rhyolites associate dwith
- Gondwana breakup. Geology, 44, 67–70.
- 733 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
- structure. Journal of Geophysical Research, 91, 1779–1798.

- 736 Self, S., Heiken, G., Sykes, M.L., Wohletz, K., Fisher, R.V., and Dethier, D.P. (1996) Field
- excursions to the Jemez Mountains, New Mexico. Bulletin of the New Mexico Bureau ofGeology and Mineral Resources, 134, 72 pp.
- 739 Shane, P., Smith, V.C., Narin, I. (2008) Millennial timescale resolution of rhyolite magma
- recharge at Tarawera volcano: insights from quartz chemistry and melt inclusions.
- Contributions to Mineralogy and Petrology 156, 397-411.
- Shea, T., Costa, F., Krimer, D., and Hammer, J.E. (2015) Accuracy of timescales retrieved from
 diffusion modeling in olivine: a 3D perspective. American Mineralogist, 100, 2026–2042.
- Simon, J.L. and Reid, M.R. (2005) The pace of rhyolite differentiation and storage in an
- 'archetypa' silicic magma system, Long Valley, California. Earth and Planetary Science
 Letters, 235, 123–140.
- Smith, R.L. and Bailey, R.A. (1966) The Bandelier Tuff a study of ash-flow eruption cycles
 from zoned magma chambers. Bulletin Volcanologique, 29, 83–104.
- Stimac, J.A. (1996) Hornblende-dacite pumice in the Tshirege member of the the Bandelier Tuff:
 Implications for magma chamber and eruptive processes. New Mexico Geological Society,
 47th Field Conference Guidebook, 269–274.
- Thomas, J.B. and Watson, E.B. (2012) Application of the Ti-in-quartz thermobarometer to rutilefree systems. Reply to: a comment on: 'TitaniQ under pressure: the effect of pressure and
 temperature on the solubility of Ti in quartz' by Thomas et al. Contributions to Mineralogy
 and Petrology, 164, 369–374.
- Thomas, J.B., Watson, E.B., Spear, F.S., Shemella, P.T., Nayak, S.K., and Lanzirotti, A. (2010)
 TitaniQ under pressure: the effect of pressure and temperature on the solubility of Ti in
 quartz. Contributions to Mineralogy and Petrology, 160, 743–759.
- Till, C.B., Vasqez, J.A. and Boyce, J.W. (2015) Months between rejuvenation and volcanic
 eruption at Yellowstone caldera, Wyoming. Geology, 43, 695–698.
- 761 Torres, R.C., Self, S. and Martinez, M.M.L. (1996) Secondary pyroclastic flows from the June
- 762 15, 1991, ignimbrite of Mount Pinatubo. In C.G. Newhall, R.S. Punongbayan, eds., Fire and
- 763 Mud: eruptions and lahars of Mount Pinatubo, Philippines. Philippine Institute of
- Volcanology and Seismology and University of Washington Press, pp. 665–678.
- 765 Trial, A.F., Spera, F.J., Greer, J. and Yuen, D.A. (1992) Simulations of magma withdrawal from
- compositionally zoned bodies. Journal of Geophysical Research, 97, 6713–6733.

- Tuttle, O.F. and Bowen, N.L. (1958) Origin of granite in the light of experimental studies in the
- system NaAlSi₃O₈-KAlSi₃O₈-SiO₂-H₂O. Geological Society of America Memoir, 74, 153 pp.
- Wark, D.A. and Watson, E.B. (2006) TitaniQ: a titanium-in-quartz geothermometer.

Contributions to Mineralogy and Petrology, 152, 743–754.

- 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.
- 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: New Mexico Geological Society, 58th Field Conference Guidebook,
- 776 316–332.
- Warshaw, C.M. and Smith, R.L. (1988) Pyroxenes and fayalites in the Bandelier Tuff, New
 Mexico: temperatures and comparison with other rhyolites. American Mineralogist, 73,
 1025–1037.
- Wilcock, J., Goff, F., Minarik, W.G., and Stix, J. (2013) Magmatic rewcharge during the
 formation and resurgence of the Valles calderam New Mexico, USA: evidence from quartz
 compositional zoning and geothermometry. Journal of Petrology, 54, 635–664.
- Wilson, C.J.N., Seward, T.M., Allan, A.S.R., Charlier, B.L.A. and Bello, L. (2012) A comment
- on: 'TitaniQ under pressure: the effect of pressure and temperature on the siolubility of Ti in
 quartz', by Jay B. Thomas, E. Bruce Watson, Frank S. Spear, Philip Shemella, Saroj K.
- Nayak and Antonio Lanzirotti. Contributions to Mineralogy and Petrology, 164, 359–368.
- 787 Wolff, J.A. and Ramos, F.C. (2014) Processes in caldera-forming high-silica rhyolite magma:
- Rb-Sr and Pb isotope systematics of the Otowi Member of the Bandelier Tuff, Valles
 Caldera, New Mexico, USA. Journal of Petrology, 55, 345–375.

Wolff, J.A., Ellis, B.S., Ramos, F.C., Starkel, W.A., Boroughs, S., Olin, P.H. and Bachmann, O.

- 791 (2015) Remelting of cumulates as a process for producing chemical zoing in silicic tuffs: a
- comparison of cool, wet and hot, dry rhyolitic magma systems. Lithos, 236–237, 275–286.
- Wolff, J.A., Forni, F., Ellis, B.S. and Szymanowski, D. (2020) Europium and barium
- enrichments in compositionally zoned felsic tuffs: A smoking gun for the origin of chemical
 and physical gradients by cumulate melting. Earth and Planetary Science Letters 540:116251,
- 796

12 pp.

797

798 FIGURE CAPTIONS

FIGURE 1. Cathodoluminescence grayscale images of representative quartz crystals from four
 different samples of the Tshirege Member, Bandelier Tuff, arranged in stratigraphic order. Note
 increasing complexity of CL-zoning upwards through the Tshirege Member. Crystallized melt
 inclusions appear bright; glassy inclusions are near-black.

FIGURE 2. Concentrations of Th and Nb in whole pumices plotted for the Tshirege Member.

Notice the bimodal distribution of the high-silica rhyolite magmas, allowing distinction of three

magma types (enriched high-silica rhyolite, HSR-e; depleted high-silica rhyolite HSR-d, and

806 low-silica rhyolite, LSR; see also Table 4).

FIGURE 3. Trace element variations among Tshirege glasses; EG = external glass, MI = melt
inclusion. a. Th vs. Nb; b. La vs. Hf; c. Hf/La vs Rb. d. Rb/Sr vs Ba/La, with faceted inclusions
identified – see text.

FIGURE 4. a. Faceting strength (FS) vs Ba concentration; explanation of FS given in text. b. Crystal containing melt inclusions with FS = 0 and 0.5. c. FS = 1 and 1.5. d. FS = 2. Note that not all crystals exhibit all FS values. e. Sketch comparison of FS categories and qualifications for any given FS value.

FIGURE 5. Back-scatter electron image of a quartz crystal from HSR-d pumice hosting four
melt inclusions (light gray). White numbers indicate FS rating; each inclusion is labeled with Ba
and Sr concentrations. Gray dashed line shows interpreted original crystal boundary, before
regrowth event. Note elevated Ba and Sr in the low FS inclusions in the interpreted rim. This
crystal has no CL zoning.

819	FIGURE 6. Titanium concentration and CL grayscale intensity profiles of four representative
820	quartz crystals from the Tshirege (158-3, 88-1, 151-3, and 90-1) with modeled diffusion curves
821	([Ti]: solid black lines; CL: dashed grey lines), calculated from eqns. (4) – (6). Error bars for [Ti]
822	points are smaller than symbol size. Transect data are cropped to the diffusional relaxation zone;
823	full transects can be found in supplementary data. CL grayscale images and transect locations are
824	included for each sample *OC = oblique corrected transect; explanation in supplementary data
825	file. C = diffusion times calculated using D_{Ti} from Cherniak et al. (2007); J = diffusion times
826	calculated using D_{Ti} from Jollands et al. (2020).
827	
828	FIGURE 7. A simplified four stage model showing the development of the CL zoning and melt
829	inclusion chemistry for the Tshirege magmas. a. Initial stage: accumulation of crystals, some
830	with melt inclusions depleted in compatible trace elements. b. Mature high-crystallinity mush;
831	ongoing faceting of melt inclusions on a \sim 1,000-10,000 year timescale. c. More primitive
832	magma starts to recharge the system with heating and possible release of volatiles, causing
833	resorption of quartz and feldspar. d. Quartz grows at higher temperatures trapping melt
834	inclusions with higher concentrations of compatible trace elements (i.e., Ba and Sr). Eventually,
835	the system overpressurizes to the point of eruption.

836

837 TABLES

Table 1. LA-ICP-MS and EPMA data for selected samples.

Table 2. Data from diffusion modeling results and titanium in quartz thermometry results using D_{Ti} from Cherniak et al. (2007) "Nb (ppm)" is the concentration of Nb in the host pumice.

- 841 **Table 3.** Data from diffusion modeling results and titanium in quartz thermometry results using
- 842 D_{Ti} from Jollands et al. (2020).
- **Table 4.** XRF analyses of whole pumice clasts from which quartz crystals were sampled and
- analyzed (Table 2). Sample 9 is from the Tsankawi Pumice and quartz-glass data from this
- sample were used to calibrate a_{TiO_2} for TitaniQ.

Sample:	LA-ICPMS (ppm)	WDS average (ppm)
Cores:		
158-3	$26.8 \pm \ 1.3$	24.7 ± 1.5
151-1	28.7 ± 2.5	$29.5 \pm 1.0 $
104-5	$30.8 \pm 2.4 $	32.7 ± 1.1
151-3	35.8 ± 2.8	$34.5 \pm 0.9 $
Rims:		
158-3	44.4 ± 2.2	42.4 ± 1.1
151-1	44.7 ± 3.1	$48.4 \pm 0.7 $
104-5	48.2 ± 2.8	51.1 ± 1.7
151-3	45.7 ± 3.6	46.3 ± 1.3

Table 1	: L	A-IC	CPMS	vs	WDS-	-EMP	Af	for	[Ti]	in	quartz

Errors reported in 1σ

Table 2: Diffusion Modeling Results

Sample	<u>CL Model time</u>			<u>[Ti] mod</u>	[Ti] model time			Model times <i>a</i> (TiO ₂)			<u>Model times $\gamma(TiO_2)$</u>		
<u>Tshirege</u>	time (years)	eri	ror ^a	time (years)	err	or ^a	time (years)	error ^b	T used (°C)	time (years)	error ^b	T used (°C)	<u>(ppm)</u>
88-1	2060	+824	-1236	10400	+4160	-6000	980	± 95	825	2200	± 275	799	37
151-3°	520	+208	-312	<520	+208	-312	<525	± 90	748	<780	± 140	727	64
151-1°	300	+120	-180	920	+368	-552	930	± 180	748	2300	± 300	727	64
104-4-2	180	+72	-108	240	+96	-144	<155	± 60	778	<490	± 220	731	65
104-5-1	160	+64	-96	<190	+76	-114	<185	± 80	752	<780	± 600	703	65
104-5-2				<270	+108	-162	<265	± 120	752	<900	± 600	703	65
141-1-1	400	+160	-240	2000	+800	-1200	1150	± 250	786	2000	± 550	748	68
141-2-1				<400	+160	-240	<150	± 60	786	<300	± 100	758	68
141-2-2	120	+48	-72	<180	+72	-108	<90	± 60	786	<160	± 90	758	68
119-3	600	+240	-360	900	+360	-560	250	± 40	783	480	± 90	762	69
119-4-OC				150	+60	-90	60	±15	783	105	± 20	762	69
158-3	120	+48	-72	1200	+480	-180	610	± 120	778	2300	±300	724	68
90-1	55	+22	-33	<280	+120	-45	<140	± 40	773	<265	± 55	753	73
90-1-OC				210	+88	-132	115	± 20	773	170	± 25	753	73
90-3	100	+40	-60	<1100	+440	-660	<650	± 105	783	<1050	± 215	753	73
90-3-OC				180	+72	-108	150	± 20	783	175	± 15	753	73
90-4	640	+248	-372	800	+96	-36	410	± 75	775	980	± 115	742	73

First two columns are calculated using 750°C to allow for comparison of the two profiles.

^aErrors arising from the error on the diffusion coefficient (Cherniak et al., 2007), calculated at a fixed T = 750 °C.

^bErrors from fitting diffusion sigmoid to data; errors from uncertainty of diffusion coefficient not included.

°No glass Ti contents measured; average Tshirege glass Ti concentration used for temperature estimation.

OC = oblique corrected transect. See supplemental data for explanation of oblique correction

Sample	Mod	imes <i>a</i> (TiC	D ₂)		Model times γ(TiO₂)					
	Model Time (years)		error	T used (°C)	Model Time (years)		error	T used (°C)		
88-1	1.1E+06	±	9.9E+03	825	5.65E+06	±	8.5E+04	799		
151-3	<3.1E+05	±	9.9E+03	748	<6.95E+05	±	2.2E+04	727		
151-1	9.9E+05	±	8.9E+03	748	6.18E+06	±	1.0E+05	727		
104-4-2	<2.66E+04	\pm	3.6E+04	778	<2.72E+05	±	5.4E+04	731		
104-5-1	<3.80E+04	±	3.9E+03	752	6.95E+05	±	4.1E+05	703		
104-5-2	<7.85E+04	±	7.0E+03	752	<9.28E+05	±	4.1E+05	703		
141-1-1	1.52E+06	±	1.6E+04	786	4.66E+06	±	3.4E+05	748		
141-2-1	<2.49E+04	±	7.0E+04	786	<1.01E+05	±	1.1E+04	758		
141-2-2	<8.86E+03	±	3.9E+03	786	<2.83E+04	±	8.9E+03	758		
119-3	6.98E+04	±	3.9E+03	783	2.61E+05	±	8.9E+03	762		
119 - 4-OC	3.91E+03	±	7.3E+02	783	1.21E+04	±	4.2E+02	762		
158-3	4.23E+05	±	2.4E+02	778	6.18E+06	±	1.0E+05	724		
90-1	<2.16E+04	±	1.6E+04	773	<7.85E+04	±	3.3E+03	753		
90-1-OC	1.45E+04	±	1.7E+03	773	3.20E+04	±	6.7E+02	753		
90-3	<4.81E+05	±	4.2E+02	783	<1.27E+06	±	1.0E+05	753		
90-3-OC	2.48E+05	±	2.2E+03	783	3.40E+05	±	2.4E+02	753		
90-4	1.90E+05	±	4.2E+02	775	1.10E+06	±	2.4E+02	742		

Table 3: Diffusion modeling results

Diffusional relaxation times calculated using D_{Ti} of Jollands et al. (2020).

Errors listed are from fitting of the diffusion sigmoid to data.

Major and minor elements (wt%)									
<u>Sample</u>	<u>88</u>	<u>90</u>	<u>104</u>	<u>119</u>	<u>141</u>	<u>151</u>	<u>158</u>	<u>9</u>	
SiO ₂	69.58	78.57	74.69	78.44	78.96	79.07	79.82	75.70	
TiO ₂	0.42	0.08	0.08	0.07	0.08	0.07	0.09	0.09	
Al_2O_3	15.87	12.21	11.83	11.70	11.40	11.45	11.44	13.53	
FeO*	3.30	1.36	1.33	1.19	1.26	1.18	1.38	1.85	
MnO	0.06	0.05	0.04	0.05	0.05	0.05	0.05	0.09	
MgO	0.98	0.01	0.15	0.13	0.05	0.16	0.02	0.11	
CaO	2.44	0.37	1.23	0.77	0.41	0.70	0.26	0.36	
Na ₂ O	3.59	2.67	3.18	2.90	2.96	2.87	2.58	3.07	
K ₂ O	3.64	4.67	7.43	4.71	4.82	4.43	4.34	5.18	
P_2O_5	0.13	0.01	0.03	0.04	0.02	0.03	0.02	0.02	
Trace ele	ments (ppm)							
Zn	109	77	74	74	73	76	72	152	
Ga	24	24	21	22	22	22	22	29	
Rb	112	158	133	151	147	142	144	273	
Sr	323	9	40	19	21	28	7	30	
Y	53	72	91	65	70	60	58	183	
Zr	268	213	198	204	213	199	223	289	
Nb	37	73	65	69	68	64	68	153	
Ba	559	93	70	67	49	52	52	64	
La	63	69	62	61	69	63	62	67	
Ce	101	118	112	112	117	118	118	120	
Nd	46	53	53	49	49	48	45	54	
Pb	463	43	111	28	50	38	92	63	
Th	15	22	20	22	21	20	22	38	

Table 4: Whole Pumice Analyses

.....

 ${}^{a}FeO = Fe_{Total}$

Major oxides normalized to a volatile-free basis















Figure 5





For simplicity, this diagram only draws quartz phenocrysts; crystals not to scale.

Figure 7