A glimpse into Augustine volcano's Pleistocene past: insight from the petrology of a massive rhyolite deposit

Patricia A. Nadeau^{1*}, James D. Webster¹, Charles W. Mandeville^{2,1}, Beth A. Goldoff¹, Nobumichi Shimizu³, Brian Monteleone³

¹ Department of Earth and Planetary Sciences, American Museum of Natural History, New York, NY 10024, USA

²Volcano Hazards Program, United States Geological Survey, Reston, VA 20192, USA

³Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

*Corresponding author: pnadeau@amnh.org, (p) 1-212-769-5314, (f) 1-212-769-5533

1 ABSTRACT

Activity at Augustine Volcano, Alaska, has been characterized by intermediate composition domes, flows, and tephras during the Holocene. Erosive lahars and pyroclastic flows associated with the 2006 eruption revealed large exposures of voluminous rhyolite pumice fall beneath glacial tills; the massive rhyolite deposit is evidence of anomalously large prehistoric eruptions. The rhyolite is petrologically and mineralogically different from more recent eruptive products, with abundant amphibole (calcic amphiboles and cummingtonite) and quartz. Three texturally and chemically distinct lithologies are present. Fe-Ti oxide equilibria suggest temperatures of $\sim 765^{\circ}\text{C}$ and oxygen fugacities of $\text{NNO}+1.5$. Melt inclusions indicate that magma representing the stratigraphically lowest lithology was crystallizing at ~ 260 MPa with a contemporary mixed $\text{H}_2\text{O}-\text{CO}_2$ fluid phase becoming progressively more H_2O -rich. Magma forming the other lithologies crystallized in the presence of this H_2O -dominated fluid, as demonstrated by the presence of cummingtonite and little to no CO_2 in melt inclusions. Amphibole and quartz-feldspar-melt equilibria models yield results indicating a range of crystallization pressures from ~ 400 MPa to ~ 175 MPa. Apatites and melt inclusions have lower chlorine contents than more recently erupted material at Augustine suggesting that the composition of Augustine's volatile phase has changed over time. Reheating textures in melt inclusions and phenocrysts, as well as the presence of xenocrysts of olivine and clinopyroxene containing mafic melt inclusions, signify the likelihood of mixing and/or mingling of magmas as an eruption trigger. The unique qualities of this Pleistocene rhyolite and the potential hazard of a similarly large eruption in modern times indicate that further study is warranted.

Keywords: Augustine Volcano; Alaska; rhyolite; melt inclusions; cummingtonite; volcanic hazards

2 INTRODUCTION

Volcanoes present a range of hazards, from localized lava flows to ash and gas clouds that can affect global climate. Alaskan volcanoes, in particular, despite many of them being quite remote, pose significant danger to passing aircraft. Volcanic ash from explosive eruptions is dangerous for aircraft; the glassy ash shards are ingested by the engines, melted, and subsequently deposited and solidified deeper in the engines, causing them to lose power.

Evaluation of volcanic hazards relies directly on evidence of previous activity at a given volcano. Careful monitoring of ongoing activity and rigorous examination of deposits from previous eruptions allow for consideration of the likelihood of certain types of future activity. Studies of past tephras and lavas can yield important information concerning magma flux, eruption volume, and eruption frequency (e.g., Newnham et al., 1999; Connor et al., 2001; Gamble et al., 2003), and even eruption intensity and column height (e.g., Gardner et al., 1998). In-depth studies of a deposit's petrology can inform of magma chamber processes that can lead to elevated levels of hazardous activity (e.g., Turner et al., 2008; Samaniego et al., 2011). A complete assessment of potential hazards, however, is contingent upon a thorough understanding of previous activity, but the older units of a volcanic record may eventually be obscured by younger deposits or eroded away, especially at latitudes subject to glaciation. As such, the history of some Alaskan volcanoes remains mostly unknown. Located in Cook Inlet, south of Anchorage, Alaska, Augustine Volcano has been largely resurfaced by material from relatively

recent eruptions. Aside from Jurassic non-volcanic sediments, pre-Holocene material is rare. Herein we present some of the first mineralogic and petrologic analyses of rocks from a large Pleistocene pumiceous fall deposit at Augustine Volcano, Alaska, the existence of which may bear on potential future hazards at the volcano.

3 AUGUSTINE VOLCANO

Augustine Volcano is a 1,252 m volcanic cone located approximately 290 km southwest of Anchorage, Alaska. The volcanic island, about 90 km² in area, lies in Kamishak Bay toward the southern end of Cook Inlet and is one of Alaska's most active volcanic systems (Waitt and Begét, 2009). Recent eruptions in 1976, 1986, and 2006 consisted of small explosions and extrusion of viscous lavas that collapsed into pyroclastic flows and lahars (Roman et al., 2006; Coombs et al., 2010). Older historical eruptions are associated with landslides involving large sectors of the volcano's summit, some of which may have generated tsunamis in Cook Inlet (Begét and Kienle, 1992; Waitt and Begét, 2009). Though Augustine Island itself is uninhabited, rendering lava flows and small landslides mostly inconsequential in terms of hazards to human life, Cook Inlet is home to ~15 oil platforms, numerous oil and gas pipelines, and freight ships traveling to the Port of Anchorage, all of which could potentially be affected by activity at Augustine. Many aviation routes cross Alaskan air space in the vicinity of Augustine and other nearby volcanoes; plumes from Augustine's 2006 eruption also led to the cancellation and diversion of numerous flights (Neal et al., 2010). Accordingly, an Augustine eruption larger than any in historic times would have serious consequences for the population and industries in the region.

Augustine's historical eruptions have been witnessed and studied since at least 1883 (e.g., Waitt and Begét, 2009) and have been particularly well-studied since the 1976 eruption (e.g., Johnston, 1979; Symonds et al., 1990; Holaske and Rose, 1991; Johnson et al., 1996; Roman et al., 2006; Power et al., 2010; De Angelis et al., 2013). Tephra and landslide deposits from prehistoric times have also been examined (e.g., Begét and Kienle, 1992; Tappen et al., 2009), with Waitt and Begét (2009) dating such deposits, including Plinian falls, back to 2,200 B.P. These relatively recent eruptions at Augustine volcano have typically involved intermediate composition products and a range of activities from dome extrusion and collapse to ash falls to pyroclastic flows to large-scale sector collapse. The primary mineralogy of erupted material for the past few thousand years has been fairly consistent, marked by the presence of plagioclase, orthopyroxene, clinopyroxene, and Fe-Ti oxides, along with variable, but small, amounts of olivine, amphibole, and rare quartz. Models for the storage system that fed Holocene eruptive activity invoke moderately shallow magma bodies and/or networks of dikes extending to depths of 5-6 km (Roman et al., 2006; Larsen et al., 2010), with geochemistry indicative of an immature volcanic plumbing system with no upper-crustal magma chamber (Johnson et al., 1996).

However, strikingly different deposits from earlier in Augustine's history do exist, including a Pleistocene water-rich, olivine-bearing basalt/basaltic-andesite (Zimmer, 2009; referred to as basalt for this study; Zimmer et al., 2010) and large silicic deposits dating as far back as ~26 ka (Coombs and Vazquez, 2014). A detailed Augustine stratigraphy was constructed by Wallace and Coombs (2013), including the preglacial rhyolitic pyroclastic unit in the oldest portion of the column. Such rhyolitic material on Augustine was previously recognized by Johnston (1979), Begét and Kienle (1992), and Waitt and Begét (2009; unit Pvr), though its petrology was not studied in-depth. As such, it is clear that the volcanological community does

not yet fully understand the evolution of the Augustine system. In order to better understand the magmatic system, as well as gain a fuller understanding of the size of its Pleistocene eruptions and potential current threats posed by the volcano, we must extend the knowledge of Augustine's behavior further into the past. With this in mind, we sampled portions of newly exposed rhyolite when conducting fieldwork in response to Augustine's 2006 eruption. Herein we describe the mineralogy, petrology, and geochemistry of the rhyolite, providing new data that we use to explore the storage conditions, evolution, and eruption of Augustine in the Pleistocene.

4 SAMPLE DESCRIPTIONS

Erosive lahars associated with the 2006 eruption created new exposures at Augustine, particularly to the south of the summit. Among the newly exposed deposits is a >30 m-thick coarse pumice fall (59.34320° N, 153.40005° W), which underlies ~8 m of glacial till and is likely the stratigraphically lowest known exposure of rhyolite on the island (Wallace and Coombs, 2013; M.L. Coombs, pers. comm.). The lower 6 m of the main deposit contain lithics 1-2 cm in diameter, while the upper 25 m of the fall are lithic-poor but contain pumice blocks up to 2 m in diameter. The majority of the unit is white pumice, with ~10 volume % denser gray banded pumices. Yellowed, slightly weathered pumices underlie the white pumice and comprise the base of the section.

Rhyolite has been observed multiple times on Augustine Island prior to the 2006 eruption and the exposure and collection of these samples (Johnston, 1979; Begét and Kienle, 1992; Waitt and Begét, 2009; Wallace and Coombs, 2013; Coombs and Vazquez, 2014). These have been described variably as pumice fall deposits, pyroclastic flow deposits, and bedded pumiceous

sands and were often found in close association with deposits of Pleistocene basalt. Bed thicknesses and block sizes are smaller than those we report here, but our sample site was only ~1 km from these other rhyolite exposures and may very well represent portions of the same deposit(s). Wallace and Coombs (2013) describe similar clast types (white-cream pumices and banded gray-cream pumices) to ours for the rhyolite at the base of their stratigraphic section of Augustine.

Our three samples from the newly-exposed section are informally named based on appearance and include: multiple small (<10 cm), rounded, and weathered pumices from the base of the unit (yellow pumice); a single large (~30 cm) angular pumice fragment from near the deposit top (white pumice); and a single gray, banded pumice (flow-banded pumice), also from closer to the top of the unit. The yellow pumices appear moderately vesicular, with white interiors and yellowed outer edges. The white pumice appears to be of a similar vesicularity and color to the interior of the yellow pumices, but occurs as a larger block. The flow-banded pumice is denser, with spatially variable but generally low vesicularity and color bands that range from medium gray to white. The yellow and white pumices are fairly crystal-poor, while the flow-banded sample includes a somewhat higher concentration of phenocrysts. Minerals identifiable in each of the three hand samples include feldspar, quartz, and amphibole.

5 METHODOLOGY

5.1 Sample preparation

Portions of the three pumice lithologies were crushed manually for further analysis; the white and flow-banded samples were from the single pumice blocks of each, while the yellow

pumice sample consisted of multiple small pumices combined. We then powdered small aliquots of each crushed sample for whole-rock analysis using an alumina ball mill. Subsequently, each powder was sealed in a gold capsule with water sufficient to support complete fusion without fluid saturating the melt and heated in an internally heated pressure vessel at the American Museum of Natural History (AMNH). The samples remained at ~1050 C and ~400 MPa for three days before quenching to glass over the course of tens of seconds. Glass chips were then extracted from the capsule, mounted in epoxy, and polished for analysis.

Phenocrysts for melt inclusion analysis were isolated from the coarser portion of the crushed sample by manually picking crystals under a microscope. We roughly divided the ferromagnesian phases from much of the matrix glass and the remainder of the phenocrysts with a Frantz magnetic separator. Quartz- and feldspar-picking was assisted by water flotation of pumiceous matrix glass fragments. We mounted all grains in epoxy on glass slides for polishing and microscopic identification of melt inclusions. Additional melt inclusions were present on the surfaces of polished thin sections.

We further separated residual powders with a magnet to isolate Fe-Ti oxides. Epoxy grain mounts were made for each pumice type, polished, and examined for intergrown magnetite-ilmenite pairs.

5.2 Analytical procedures

Compositional analyses of phenocrysts, melt inclusions, matrix glasses, and fused whole-rock glasses were performed at AMNH using a Cameca SX-100 electron microprobe (EMP). All measurements used wavelength dispersive spectrometry at 15 kV. We analyzed the glasses for SiO₂, Al₂O₃, Na₂O, K₂O, CaO, FeO, MgO, MnO, TiO₂, F, Cl, P₂O₅, and SO₂. Glass analyses

utilized a 5- μm spot at 10 nA for all elements, except Na_2O , FeO , K_2O , SiO_2 , and F, which we analyzed at 2 nA. To minimize sodium (and potassium, to a lesser extent) migration during analysis, matrix glass, fused glasses, and melt inclusions larger than $\sim 25\text{-}30\ \mu\text{m}$ were measured by moving the samples under the electron beam, and Na and K were also measured in the first analytical pass (i.e., the first exposure of the glass to the beam). For melt inclusions between 10 and $\sim 25\ \mu\text{m}$, we used the time-zero method of the Cameca software, wherein successive stationary measurements are made and decreasing counts extrapolated back to the initiation of measurement (Nielsen and Sigurdsson, 1981). We also performed trace element analyses (Ba, Sr, Zr) on the matrix of the flow-banded sample using the EMP with a 3- μm spot at 40 nA. All Fe-Ti oxide analyses included SiO_2 (to ensure no contamination from adjacent glass or silicate phenocrysts), Al_2O_3 , MgO , FeO , NiO , TiO_2 , V_2O_3 , Cr_2O_3 , and MnO ; some included CuO and SO_2 as well. We measured the Fe-Ti oxides with a 3- μm spot at 20 nA, while phenocrysts analyses involved a 5- μm spot at 10 nA. Most phenocrysts were analyzed for either the same array of components as glasses (melt inclusion hosts) or with Cr_2O_3 , BaO , and SrO substituted for P_2O_5 and SO_2 (non-hosts).

Melt inclusions in phenocrysts from all pumice types were consistently small ($< \sim 40\ \mu\text{m}$); accordingly, we deemed them inappropriate for double-polishing for Fourier Transform Infrared (FTIR) spectroscopy analysis. Instead, we analyzed the melt inclusions for H_2O and CO_2 via Secondary Ion Mass Spectrometry (SIMS) using a Cameca IMS 1280 ion microprobe at the Northeast National Ion Microprobe Facility (NENIMF) at the Woods Hole Oceanographic Institution (WHOI). Phenocrysts were mounted in epoxy, ground to expose melt inclusions, and polished. Phenocrysts were then removed from epoxy, pressed into indium (to reduce background C and H), and coated with a thin layer of gold. The primary beam comprised $^{133}\text{Cs}^{+1}$

ions with a current of ~400 pA, an acceleration of 10 kV focused and rastered over a 20x20 micron area. Secondary ions ($^{12}\text{C}^-$, $^{16}\text{O}^1\text{H}^-$, and $^{30}\text{Si}^-$) sputtered from the melt inclusions were extracted with a voltage potential of 10 kV, separated and measured with an ion counting electron multiplier. We used the $^{16}\text{O}^1\text{H}^-$ as a proxy for H_2O . In order to minimize contamination from extraneous C and OH from the sample surface, a 240-second pre-sputter was used, and a field aperture in the secondary column blocked the transmission of secondary ions from outside of 4-6 microns of the center of the crater. We counted transmitted ions for 10, 5, and 3 seconds per cycle, respectively for $^{12}\text{C}^-$, $^{16}\text{O}^1\text{H}^-$, and $^{30}\text{Si}^-$, over 10 cycles. Mean ratios of $^{16}\text{O}^1\text{H}/^{30}\text{Si}$ and $^{12}\text{C}/^{30}\text{Si}$ were measured for each melt inclusion and compared to ratios measured for rhyolitic standard glasses. Precision of measured ratios was typically less than $\pm 10\%$ error for $^{12}\text{C}/^{30}\text{Si}$ and less than $\pm 2\%$ for $^{16}\text{O}^1\text{H}/^{30}\text{Si}$. Standards included both natural (macusanite, Los Posos rhyolite) and synthetic (haplogranite) glasses with SiO_2 contents ranging from ~72-76 wt% and varied H_2O and CO_2 contents. We independently verified volatile contents of standard glasses using FTIR at AMNH. Standard deviations on repeat measurement of standard glasses were generally below 7% of the measured ratio and R^2 values for the linear fit calibration curves were 0.94 or better. A few melt inclusions yielded anomalously high values for C, a remnant of previous carbon coating for EMP analysis; we removed those measurements from the dataset.

Once we had collected EMP and SIMS data for matrix glass, melt inclusions, and various phenocrysts typed, we endeavored to utilize the compositions in a selection of appropriate geobarometers and geothermometers, discussed further below, to elucidate various magma chamber conditions.

Petrographic analysis of thin sections (3 sections per lithology) included documentation of matrix and phenocryst textures, which was supplemented by examination of hand samples and

an X-ray computed tomography scan of the flow-banded sample conducted on a GE Phoenix v|tome|x s 240 at AMNH. We also performed EMP x-ray mapping to determine modal mineralogy via image analysis. We collected thin section element x-ray maps of each lithology using a 1- μ m beam size at 20 nA, with a point spacing of 9 μ m and a dwell time of 7 ms. Maps were created for 10 elements (Na, Fe, Cl, Al, P, Mg, Si, S, Ca, and Ti) and tiles of each map were balanced and stitched together using Interactive Data Language (IDL) software to create full thin section maps for each element. Following creation of individual element maps, we imported files into the IDRISI Selva program (Eastman, 2012), which stacked the maps and classified each pixel as a mineral or other thin section component (e.g., epoxy, glass). An example of a resulting mineral map is shown in Figure 2. For detailed explanation of the algorithms used, see Appendix A.

6 RESULTS

6.1 Whole-rock characteristics

EMP results from measurements on the fused glasses indicate that the bulk of the unit, as represented by the white pumice, is rhyolite, at ~ 72.5 wt% SiO_2 (anhydrous). The yellow pumice is of similar composition at ~ 72 wt% SiO_2 and the flow-banded is slightly less silicic, falling into the dacite field with a SiO_2 content of just under 71 wt% (Figure 3). Alkali contents for all three lithologies are roughly equivalent at $\sim 5.5\%$ $\text{Na}_2\text{O} + \text{K}_2\text{O}$. Fused whole-rock glass analyses and matrix glass compositions are provided in Table 1. Matrix glass compositions are consistent between the three samples at ~ 76.6 wt% SiO_2 . Both whole-rock and matrix compositions are

similar to those reported by (Larsen et al., 2010) and Coombs and Vazquez (2014) for other Augustine rhyolite samples of 71-74 and 76-77 wt% SiO₂, respectively.

Image analysis of the three samples yields similar proportions of glass and phenocrysts for each, but with varying degrees of vesicularity, and with differences in proportions of individual phenocryst types (Table 2). The flow-banded pumice is most dense, at 35% vesicularity. The white pumice has the highest vesicularity, with roughly inverse proportions at 62% void space. The yellow pumice is intermediate, at 49% vesicles. Despite varying degrees of vesiculation, the solid portions of both the flow-banded and yellow pumices are 88% glass and 12% phenocrysts, nearly identical to the 89% and 11%, respectively, of the white pumice.

6.1.1 Pumice textures

Despite similar matrix compositions, texture varies between lithologies. Vesicle sizes in each lithology range from a few microns through the most common size of ~20-100 µm. The largest vesicles in the yellow pumice are on the order of a few millimeters, in the flow-banded one centimeter, and in the white a few centimeters. The white pumice exhibits the roundest, least-distorted vesicles, though bubble size and shape vary over the scale of a single thin section (Figure 4a). Some areas display much more apparent shearing than others. The yellow pumice, while still displaying rounded bubble margins, has far more deformed and collapsed vesicles than the white pumice (Figure 4b). Many portions of the thin section appear nearly vesicle-free, as bubbles have been stretched such that bubble walls have aligned and merged. As with the white pumice, deformation appears variable and some areas exhibit more rounded bubbles. The banding in the flow-banded pumice appears to be solely textural (Figure 4c), with identical matrix glass compositions for both the dense and vesicular bands. Less-dense areas exhibit rounded bubbles, similar to the texture of the white pumice, although with little to no apparent

shear. The most-deformed bubbles often occur along margins of the vesicular bands where they grade into denser material, and also around some phenocrysts. Rings of elongate vesicles appear to radiate from many phenocryst edges in contact with the more vesicular bands (Figure 4d). Phenocrysts completely enclosed by the vesicular bands display a circular halo of the elongate, radiating bubbles, while crystals on the borders between the vesicular and dense bands display the texture only on the crystal margin in contact with the vesicular band, similar to vesicle shadows noted in Toba ash (Rose and Chesner, 1987). Phenocrysts in dense bands do not exhibit that style of vesiculation. Denser areas appear to have a bimodal distribution of void sizes; small (micron-scale) angular voids and some small rounded vesicles occur throughout, but jagged-edged millimeter-scale voids also exist. Examination of the flow-banded sample at thin section scale indicates preferential alignment of elongate minerals. Often, though not exclusively, the large voids occur at the ends of the larger, elongate phenocrysts, akin in appearance to a metamorphic pressure shadow around a central porphyroblast (Figure 4e). In hand sample, these large voids in the dense bands appear to have a crumbly texture.

6.2 Mineralogy

Minerals found include plagioclase, quartz, amphibole, orthopyroxene, Fe-Ti oxides, and apatite, with trace amounts of zircon, anhydrite, sulfides, clinopyroxene, and olivine, largely the same as the dominant assemblage reported for rhyolite by Coombs and Vazquez (2014). Each lithology's phenocryst population is dominated by plagioclase, comprising ~9-10% or greater of the rock. Proportions of orthopyroxene and cummingtonite are roughly subequal in all samples at ~0.2-0.4%. Quartz is present at ~0.4% in the flow-banded and yellow pumices and at 0.7% in the white pumice. Magnetite ranges from 0.15-0.3% and ilmenite is <0.05% in all samples. Apatite is also a minor phase at ~0.08% in each pumice type. The largest variation between the samples

is manifested in the proportion of calcium-rich amphibole (magnesian-hornblende to tschermakitic pargasite). While these calcic amphiboles represent >1% of the phenocrysts in the flow-banded assemblage, only 0.35% of the white pumice's phenocrysts are calcic amphiboles. Such amphiboles are apparently absent in the yellow pumice, where cummingtonite seems to be the sole amphibole. Representative compositions of all minerals are shown in Table 3.

6.2.1 Plagioclase

The plagioclase displays a large range of textures in all three lithologies, as in recent eruptive products (Larsen et al., 2010), including unaltered, euhedral grains to rounded, sieve-textured grains (Figure 5). Plagioclase exhibits variable zoning, with some grains showing a clear oscillatory pattern, others non-oscillatory zonation, and still others displaying near-homogeneous composition. Many, but not all, crystals with high-Ca cores are rimmed with lower-Ca plagioclase. Phenocryst size ranges up to ~4 mm. Compositions in the three lithologies cover broad, but similar, ranges (Figure 6). The flow-banded pumice unit includes An₃₈ to An₈₇. The yellow pumice has a similar range, with An₄₀ to An₈₇. The white pumice has a smaller range, which spans from An₃₉ to An₈₀. Each lithology exhibits a bimodal distribution of compositions, with a lower-An peak centered roughly at An₄₆. The higher-Ca peak is less defined, with the yellow and flow-banded lithologies having a peak around An₇₀, while the white pumice's peak is around An₇₈. Given the lower crystallinity of the white pumice, however, a smaller sample size may bias the results. A possible subordinate third mode may also be present in all three pumice types around An₅₇, though it seems most apparent in the flow-banded and white lithologies. In terms of proportions, the flow-banded contains the most high-Ca plagioclase, while the white pumice contains the least. As a comparison, Augustine's 2006 eruption had a fairly consistent

plagioclase compositional distribution across lithologies, with a single dominant mode at An₅₄ and a range from An₄₅ to An₉₀ (Larsen et al., 2010).

6.2.2 Pyroxene

Orthopyroxenes are present and exhibit similar morphology in all three lithologies. Phenocrysts appear as subhedral grains up to ~1 mm in size. The orthopyroxenes are nearly uniform in composition across all samples. Flow-banded and white pumices contain hypersthene with compositions of Wo₁En₆₅₋₆₈Fs₃₁₋₃₄. The hypersthene of the yellow lithology exhibit a slightly larger compositional range at Wo₁En₆₄₋₇₀Fs₂₉₋₃₅. These compositions are nearly identical to other reported Augustine hypersthene with compositions of approximately Wo₂En₆₅Fs₃₂ from both the Pleistocene basalt and the 2006 eruptive products (Tappen et al., 2009; Larsen et al., 2010). Orthopyroxenes in all samples appear to be mostly unzoned, though a few in each pumice type show slight iron enrichment in the rims.

Clinopyroxene is apparently absent from all three pumice types, except one rounded diopside grain observed in the yellow pumice. With a composition of Wo₄₅En₄₇Fs₈, the clinopyroxene has a slightly more magnesium-rich composition than reported for pyroxenes of more recent Augustine eruptions (~Wo₄₄En₄₁Fs₁₅; Tappen et al., 2009; Larsen et al., 2010). It is consistent, however, with the magnesian end of the compositional range reported for the Pleistocene basalt (Tappen et al., 2009).

6.2.3 Amphibole

Amphiboles are rare in Augustine's recent eruption products (Tappen et al., 2009; Larsen et al., 2010; De Angelis et al., 2013), but the lithologies studied here each contain a significant proportion of amphiboles: 12%, 6%, and 3.5% of the total phenocryst assemblage of the flow-

353 banded, white, and yellow pumices, respectively. Unlike in many recently erupted amphiboles,
354 reaction rims are consistently absent from the Pleistocene phenocrysts and grain morphology
355 ranges from euhedral to broken to rounded subhedral grains, with possible resorption textures
356 (Figure 7). Amphiboles do not vary morphologically or texturally between lithologies and are
357 generally single crystals, sometimes intergrown with phenocrysts of another mineral. The
358 exception is one glomerophytic clot found within the white pumice sample composed of 26
359 partially intergrown magnesio-hornblendes and minor plagioclase, oxides, and glass (Figure 7c).

360 Two distinct populations of amphiboles exist in our samples: cummingtonites and a
361 higher-Ca and -Al group that ranges from magnesio-hornblende to tschermakitic pargasite
362 (calcic amphiboles) according to the classification of Leake et al. (1997). The calcic amphiboles
363 are apparently absent from the yellow pumice, while the flow-banded and white pumices contain
364 both types. Of the calcic amphiboles, tschermakitic pargasite is dominant in the flow-banded
365 pumice, while the white contains more magnesio-hornblendes. Some larger amphiboles in the
366 flow-banded pumice are zoned such that pargasitic cores are rimmed by magnesio-hornblende,
367 with higher Ca, Al, and Na in the cores and higher Si, Mn, and Fe in the rims. Others show no
368 zoning. Cummingtonites do not exhibit discernible zoning.

369 When compared compositionally to amphiboles of more recent eruptions (Figure 8), the
370 calcic amphiboles are generally richer in Al with slightly less Mg. Our higher-Al end of the
371 compositional range roughly overlaps with amphibole compositions reported for the Pleistocene
372 basalt (Daley, 1986) as well as from quenched mafic inclusions erupted in the 2006 andesites
373 (De Angelis et al., 2013). As compared to the one cummingtonite phenocryst measured by
374 Tappen et al. (2009), the cummingtonites in these rhyolitic deposits contain significantly less
375 Mg.

6.2.4 Quartz

Whereas quartz, like amphibole, is rare or absent in more recent Augustine eruptive products (Tappen et al., 2009; Waite and Begét, 2009; Larsen et al., 2010), it represents ~3-7% of the phenocrysts in the three studied samples. Grains are typically small (<0.5 mm) and appear subhedral to euhedral in thin sections (Figure 9) of all three lithologies, with dipyrimal stubby prisms of euhedral β -quartz as a common form. Quartz grains often contain larger melt inclusions than other host minerals, but such inclusions usually appear to have leaked along fractures in the phenocrysts.

6.2.5 Fe-Ti oxides

Both magnetite and ilmenite are present as phenocrysts in all samples, and also as inclusions in other phenocrysts. Magnetite grains are usually larger (up to ~1.5 mm in flow-banded and white pumices; slightly smaller in yellow pumice) than ilmenite grains (up to ~0.4 mm) and anhedral to subhedral, whereas ilmenites are subhedral to euhedral (Figure 10). In the flow-banded and white lithologies, magnetites tend to be anhedral and ilmenites euhedral, while the yellow pumice lithology contains more well-formed subhedral magnetites along with the euhedral ilmenites. Both oxide types appear unzoned. Exsolution lamellae are absent.

6.2.6 Other minerals

Apatite is present either as inclusions in other phenocrysts or as needle-like to stubby prisms, up to ~0.6 mm long, in the groundmass. In each case, they are often associated with oxides, usually magnetite. Apatites of the three lithologies have generally lower X_{Cl} and X_F , with a higher hydroxylapatite component, than apatites measured from more recent Augustine eruptions (Webster, unpublished data; Tappen et al., 2009). Apatites in the flow-banded lithology

are the most water-rich, with X_{OH} up to 0.66. Apatites from the yellow pumice have the smallest range of X_{OH} , with the highest value at only 0.54. All three lithologies have a minimum X_{OH} of approximately 0.34 (Figure 11).

One olivine grain was found in the white pumice. The grain was broken as a result of the crushing process, but unbroken edges appeared to exhibit scallop-edged resorption textures. The forsterite content (For_{85}) is similar to those reported in the material erupted from Augustine in 2006 (For_{84} ; Larsen et al., 2010) and to olivines from Augustine's Pleistocene basalt (For_{76} - For_{89} ; Daley, 1986; Zimmer et al., 2010).

We were able to identify both anhydrite and iron sulfide blebs as inclusions in phenocrysts. There was a single occurrence of anhydrite in a magnesio-hornblende within the white pumice sample, and rare sulfides were present in hypersthene in the yellow pumice. Additional minor sulfides were present as inclusions in magnetite in all three pumice types.

Trace zircons were also present as both inclusions in other minerals and in the matrix for all three lithologies. The zircons were small, generally $<25\ \mu m$.

6.3 Melt inclusion textures and chemistry

Plagioclase is the most common host for the melt inclusions in each of these deposits, but calcic amphibole, orthopyroxene, and quartz host inclusions as well. We did not find inclusions in any cummingtonites. Melt inclusions range from irregularly shaped inclusions in the voids of sieve-textured plagioclase to elongate inclusions along growth zones to typical ellipsoid shapes. We aimed to evaluate only the typical ellipsoidal type. The vast majority of inclusions contained shrinkage/vapor bubbles, and although the volume estimation of bubble to glass ratio is not entirely accurate following polishing to an intermediate level in the inclusion, we estimate that

most inclusions had a bubble to glass ratio from 1:10 to 1:20. However, some inclusions displaying an inverse crystal shape (e.g., Chaigneau et al., 1980) in quartz crystals did not have bubbles. Most melt inclusions were uniformly glassy with no daughter crystals, except for a few orthopyroxene crystals that contained small linear clusters of objects that were too small to identify as silicates, oxides, or bubbles.

Inclusions in all phases are quite small (most $<50\text{ }\mu\text{m}$, many $<25\text{ }\mu\text{m}$), leading to migration of Na in some EMP analyses of melt inclusion glass. We present full analyses of representative melt inclusions in Table 4. As only the Na analysis was found to be problematic, information on other elements are still valid and useful. Inclusion compositions cluster generally around the matrix glass composition on a TAS diagram (Figure 3), with some less evolved inclusions trending towards the bulk-rock composition. Inclusions from the olivine and clinopyroxene plot on roughly the same linear trend as the bulk-rock and the matrix compositions, but at much more primitive basaltic and basaltic-andesitic compositions, respectively. Inclusions falling significantly below the main cluster around the matrix glass compositions are those that have suffered Na-loss via migration during measurement.

6.4 Magma chamber conditions

We applied a variety of geochemical tools to elucidate various magma chamber conditions, including melt composition, temperature, pressure, and oxygen fugacity. While results from some methods are expected to disagree given that they represent different stages of the magma evolution (e.g., melt inclusion entrapment versus eruption), we outline our results from four methods below.

6.4.1 Fe-Ti oxide geothermometry

To determine magmatic temperatures and oxygen fugacities, we analyzed compositions of touching (and neighboring) magnetite-ilmenite pairs via the QUILF algorithm of Andersen et al. (1993) and the model of Ghiorso and Evans (2008). We provide results from both algorithms, as neither is perfectly suited to the conditions of the Augustine samples; QUILF overestimates temperatures at high f_{O_2} (Geschwind and Rutherford, 1992; Larsen et al., 2010), and the model of Ghiorso and Evans (2008) is intended for temperatures between 800 and 1300°C. Because touching grains are rare, we expanded our dataset to include grain pairs within 250 μm of each other in thin sections, as has been done previously at Augustine (Roman, 2001). Pairs were subject to the Mg-Mn equilibrium test (Bacon and Hirschmann, 1988) prior to further analysis. The flow-banded lithology yielded five suitable oxide pairs, the white eight, and the yellow five.

Using the QUILF algorithm, oxide pairs from the white and yellow pumices give temperatures that cluster tightly around 830°C ($\pm 5^\circ\text{C}$) and f_{O_2} of NNO+2.38. The oxides from the flow-banded pumice display more scatter, with an average temperature of $860 \pm 22^\circ\text{C}$ and a range from ~ 830 -890°C. Oxygen fugacity estimated from flow-banded pumice oxides is slightly more reducing, at NNO+2.16. Because the QUILF algorithm is known to overestimate temperatures at f_{O_2} near NNO+2 (Geschwind and Rutherford, 1992; Larsen et al., 2010), we correct our QUILF temperatures down by 30° to 800°C for the white and yellow pumice lithologies and to 830°C for the flow-banded as in Larsen et al. (2010).

Temperatures yielded by the Ghiorso and Evans (2008) algorithm are lower than those determined by QUILF for the white and yellow pumices, at $759 \pm 6^\circ\text{C}$ and $762 \pm 3^\circ\text{C}$, respectively. The flow-banded temperature was closer to the corrected QUILF temperature at $827 \pm 48^\circ\text{C}$. The spread of temperatures for the oxides from the flow-banded pumice spans a

greater range, from 778 to 887°C. Calculated f_{O_2} for each of the three samples were lower than those given by QUILF: NNO+1.56 for the white pumice, NNO+1.55 for the yellow lithology, and, again, a slightly more reduced NNO+1.47 for the flow-banded pumice.

Temperatures and f_{O_2} calculated using both algorithms are presented in Table 5 and Figure 12. For the remainder of this text, we consider those from the Ghiorso and Evans (2008) model to be the best estimate of temperatures and f_{O_2} , as calculated temperatures lie only slightly below the calibrated limit for the model, whereas f_{O_2} is considerably higher than the appropriate range for the QUILF model. Further, the lower Ghiorso and Evans (2008) temperatures agree with constraints on the temperature given the presence and stability of cummingtonite in the samples; the phase is not stable above ~790°C (Geschwind and Rutherford, 1992).

6.4.2 Amphibole geothermobarometry

We investigated calcic amphibole compositions for calculation of crystallization temperatures, pressures, and f_{O_2} , as well as the H₂O content of the coexisting melt at the time of crystallization using formulae of Ridolfi et al. (2010) and Ridolfi and Renzulli (2012). Nearly all of our amphiboles fit within the compositional ranges of the models; a handful at the lower-Al end of the range were slightly high in SiO₂ and MnO, and slightly low in TiO₂, CaO, Na₂O, and K₂O. It is also of note that the Ridolfi and Renzulli (2012) formulae were only stated to be applicable above 800°C; based on Fe-Ti oxide thermometry, our samples fall slightly below the model's range, perhaps adding some inaccuracy to the results. P-T pairs for flow-banded amphiboles follow a continuous trend and range from ~820°C at ~140 MPa to ~1000°C at ~700 MPa. Conditions calculated for the white pumice range from ~830°C at ~145 MPa to ~940°C at ~400 MPa, though most are below ~885°C at 275 MPa. Corresponding log f_{O_2} values for the flow-banded pumice are NNO+0.54 to NNO+2.02 and values for the white are

487 NNO+1.02 to NNO+1.89, with more reducing conditions corresponding to higher temperatures
488 and pressures. Water contents of coexisting melt were calculated to range from 6-10 wt% for the
489 calcic amphiboles of the flow-banded lithology and 6-8 wt% for those of the white pumice.

490 As the aforementioned algorithms have been shown to often be unreliable with respect to
491 all four parameters above (Pamukcu and Gualda, 2013; Erdmann et al., 2014), especially given
492 that our temperatures were slightly out of the model range, we also employ the second Holland
493 and Blundy (1994) plagioclase-amphibole geothermometer in combination with the
494 geobarometer of Anderson and Smith (1995) as suggested by Pamukcu and Gualda (2013). We
495 note that our assemblage is not ideal for this barometer either, as it is based on an equilibrium
496 assemblage including alkali feldspar and titanite. However, Anderson and Smith (1995) note that
497 the absence of these phases does not appear to affect pressure estimates significantly. The model
498 also is formulated for plagioclase compositions significantly lower in calcium than ours,
499 potentially causing pressures calculated here to be overestimates. We identified both touching
500 pairs and plagioclase inclusions in amphibole; for pairs, analyses were made close to the
501 touching edges, while for inclusions, the host was measured adjacent to the inclusion along the
502 same growth zone. Because of the relatively low crystallinity of the white pumice, we were able
503 to find only one suitable plagioclase-amphibole pair, which gave a crystallization temperature of
504 845°C and pressure of 137 MPa. With more crystals, the flow-banded pumice yielded 23 useable
505 plagioclase-amphibole pairs, which gave calculated average temperatures and pressures of 874°C
506 and 119 MPa. However, some calculations indicated negative pressures and are clearly
507 erroneous. As the negative pressures generally correlate with higher temperatures, our calculated
508 averages are skewed to higher temperature and lower pressure. Removing the mineral pairs that
509 give negative pressures, we arrive at temperature and pressure averages of 858°C and 192 MPa

for the flow-banded pumice. As these algorithms are appropriate only for calcic amphiboles, we have no results for the calcic amphibole-free yellow pumice.

Despite lacking calcic amphiboles, the yellow pumice does contain cummingtonite. The aforementioned amphibole algorithms cannot be applied to cummingtonite, but experimental data on cummingtonite does limit magma chamber conditions. Geschwind and Rutherford (1992) conducted experiments on dacitic tephra (unit Yn) from Mount St. Helens and arrived at conclusions similar to those of Wood and Carmichael (1973): that cummingtonite is stable in the phenocryst assemblage of silicic magmas at temperatures below 800°C and pressures below ~400 MPa. Further, coexisting melt compositions restrict pressure of crystallization to ~250-300 MPa. SiO₂ contents of the matrix glass of our three Augustine lithologies are comparable, and when evaluated in tandem with Fe-Ti oxide-derived temperatures of ~765°C, indicate comparable pressures to the St. Helens tephra. Gardner et al. (1995) further interpret the St. Helens experimental data and suggest somewhat higher pressures of equilibration (270-330 MPa) given a mixed H₂O-CO₂ fluid phase ($X_{\text{H}_2\text{O}}^{\text{fluid}} = 0.7\text{-}0.9$ at a $P_{\text{H}_2\text{O}}$ of 250 MPa), which may be applicable to Augustine samples as well. Given that the barometers for calcic amphiboles are not entirely suited to the assemblage and temperatures of these rhyolites, the presence of cummingtonite may be the best amphibole-based constraint on chamber conditions.

6.4.3 Melt inclusion geobarometry

To evaluate magmatic pressures based on melt inclusion compositions combined with volatile solubilities, we used SIMS-derived data for H₂O and CO₂ in the melt inclusions (Table 6) alongside isobars derived by VolatileCalc 2.0 (Newman and Lowenstern, 2002) to estimate the pressures of melt inclusion entrapment. We did not obtain useable volatile data from inclusions in the white pumice, but were successful using melt inclusions from both the yellow

and flow-banded samples. As seen in Figure 12, H₂O and CO₂ contents of melt inclusions hosted in phenocrysts from the yellow pumice delineate an isobaric crystallization curve. Additional yellow pumice-hosted inclusions plot with lower CO₂ concentrations, along with low-CO₂ inclusions from the phenocrysts of the flow-banded pumice. Using the magmatic temperature of 765°C based on Fe-Ti oxide geothermometry of Ghiorso and Evans (2008), we find that phenocrysts in the magma of the yellow pumice unit yield the highest entrapment pressures, at roughly 260 MPa. Over the course of crystallization, the system evolved from an $X_{\text{H}_2\text{O}}^{\text{fluid}}$ of roughly 0.4 (~3.75 wt% H₂O and ~1400 ppm CO₂ in the coexisting melt) to an $X_{\text{H}_2\text{O}}^{\text{fluid}}$ much closer to 1 (~6 wt % H₂O and <200 ppm CO₂ in the melt), at which point our measured melt inclusions of the flow-banded pumice were entrapped.

Use of this method to estimate pressures of melt inclusion entrapment is predicated on fluid saturation of the host magma at the time of inclusion entrapment; if the melt was not saturated, the pressures yielded will be erroneously low. In this instance, potential evidence for fluid saturation in the Augustine magmatic system is the high H₂O and Cl contents of the basaltic melt inclusion relative to the rhyolitic inclusions. While the basalt may or may not be the source of the rhyolite itself, the rhyolite was erupted roughly coevally with basalt (Johnston, 1979; Waitt and Begét, 2009; Coombs and Vazquez, 2014). The high volatile contents of basaltic melt inclusions both here and in other studies (Zimmer, 2009) attest to the volatile-rich state of the Augustine magmatic system at the time. If we assume a parental melt with similarly elevated volatile contents that evolved into the rhyolitic melt via fractional crystallization, fluid-absent crystallization would have resulted in significantly higher Cl contents in the silicic melt inclusions relative to that in the basaltic inclusions. Sequestration of Cl from residual melt by amphibole crystallization is minor given the low Cl concentrations in Augustine amphiboles.

Figure 14 displays the likelihood of Cl loss to a fluid phase, thus indicating fluid saturation by the onset of rhyolitic melt inclusion entrapment. Additionally, these pressure results are also broadly consistent with those from amphibole stability and MELTS-Excel (below). This consistency supports our hypothesis that the rhyolitic magma was fluid saturated because, otherwise, as noted, we would expect to see systematically lower pressures from melt inclusion barometry.

6.4.4 Quartz-feldspar-melt geobarometry

Because our samples from Augustine contain quartz and feldspar, we estimated magmatic pressure via the haplogranite system ternary, as explored initially by Tuttle and Bowen (1958). In a system with both quartz and feldspar(s), the quartz-feldspar cotectic is predominantly pressure-sensitive, with the equilibrium melt composition shifting to more silicic compositions with decreasing pressure. Blundy and Cashman (2001) applied this principle in using melt composition as a geobarometer for Mount St. Helen's eruptive products, developing equations to project through anorthite to the haplogranite ternary. Gualda and Ghiorso (2014) have developed a Visual Basic program for Microsoft Excel (MELTS-Excel), based on rhyolite-MELTS (Gualda et al., 2012), that calculates the equilibrium crystallization pressure of the crystallized assemblage based on matrix or melt inclusion glass composition. Unlike melt inclusion geobarometry, fluid saturation is not necessary for this method; the calculations require only that quartz is present with the feldspar. Accordingly, quartz-hosted melt inclusions are most reliable. In this case, as we have few suitable quartz-hosted inclusions, we attempted to use matrix glass analyses ($n = 15$) and melt inclusions with reasonable totals that did not show Na-loss ($n = 30$), regardless of host mineral phase. All but one matrix composition and four melt inclusion compositions gave results that converged to produce a pressure estimate. Equilibrium quartz-

feldspar crystallization pressures yielded by matrix glass compositions range from 171-290 MPa, with matrix from each lithology covering approximately the full range of pressures. Amphibole-hosted inclusions gave pressures from 349-422 MPa, pyroxene-hosted from 276-370 MPa, and plagioclase from 175-303 MPa. Quartz-hosted inclusions, the only liquid definitively present with quartz, yielded a range of pressures from 240-328 MPa, though such inclusions were only in the flow-banded pumice. As such, we can roughly infer an order of crystallization during ascent for all lithologies of calcic amphibole, followed by pyroxene, then feldspar and quartz. Small sample sizes prohibit inferences of different dominant pressures for the different lithologies. We summarize the results of the various thermometers and barometers in Table 7.

7 DISCUSSION

This is the first systematic petrologic and geochemical study of Augustine rhyolite. Though rhyolite at Augustine had been identified prior to this study (Johnston, 1979; Begét and Kienle, 1992; Waitt and Begét, 2009), little in-depth investigation of this more silicic material had been done until Coombs and Vazquez (2014) dated zircons from a rhyolite block in the fall deposit. Zircon ages revealed crystallization at ~26,000 ka, and while they did not perform a detailed study of the mineralogy of the deposit, they were able to link the rhyolite, via zircon age and trace elements, to dioritic inclusions erupted in 2006 andesites. They postulate that the rhyolite was filter-pressed from a crystal-rich dacite, leaving the diorite residuum in the chamber to be entrained in 2006. While further fieldwork and geochemical data would be needed to confirm that the lithologies studies here are the same as those evaluated by Coombs and Vazquez (2014), we keep their work and the dacite-mush origins of rhyolite in mind as we examine the

results of our work. Below we synthesize our collected data and evaluate each of the three lithologies to elucidate the conditions under which these rhyolites were generated.

7.1 Constraints on origins of the yellow pumice

The lowest in section of the three lithologies studied, and thus inferred to be oldest, the yellow pumices have the simplest phenocryst assemblage relative to the white or flow-banded pumices; main silicate phases include plagioclase, quartz, orthopyroxene, and cummingtonite.

Mineral zonation is mild, if present at all, so we assume the phenocryst assemblage is largely in equilibrium. As such, the presence of cummingtonite places constraints on magma chamber conditions. Experiments indicate that cummingtonite is generally stable to a maximum temperature of approximately $\sim 790^{\circ}\text{C}$ (Geschwind and Rutherford, 1992). Further, cummingtonite is a low-pressure phase, with a maximum pressure of ~ 400 MPa, and also requires high f_{O_2} , above NNO+1 (Geschwind and Rutherford, 1992). The bounds for temperature and f_{O_2} set by the presence of cummingtonite are consistent with our results from Fe-Ti oxide equilibria, which give an average temperature of 765°C (ranging from 760 to 778°C) and a $\log f_{\text{O}_2}$ of NNO+1.55. Phase equilibria for orthopyroxene, cummingtonite, and quartz yield slightly higher temperatures ($\sim 775^{\circ}\text{C}$) and lower $\log f_{\text{O}_2}$ ($\sim \text{NNO}+0.5$) for 200 MPa (Evans and Ghiorso, 1995). The discrepancy is not unlike similar magmatic condition mismatches at Mount St. Helens and Mount Pinatubo, which Evans and Ghiorso (1995) ascribe to phenocryst disequilibrium resulting from either magma mixing or a late-stage increase in f_{O_2} that is recorded by the oxides but not the silicate assemblage.

Dissolved volatiles in melt inclusions also yield information regarding magma chamber conditions, including fluid composition and pressure at crystallization (Figure 12).

Concentrations of CO_2 and H_2O within some melt inclusions plot along an isobaric crystallization curve such that the phenocryst assemblage was crystallizing and entrapping melt at a constant pressure of ~ 260 MPa while the system was undergoing continuous loss of primarily CO_2 (with lesser H_2O) and the coexisting fluid becoming more H_2O -rich. Other melt inclusions plot at progressively lower pressures, perhaps indicating ascent and coincident degassing and exsolution of further CO_2 (and lesser H_2O). The indicated pressure of ~ 260 MPa is consistent with the low pressures required to crystallize cummingtonite and would place the magma body that fed the yellow pumice eruption at a depth of ~ 9 km. InSAR data are consistent with the presence of a persisting modern-day magma chamber at such a depth; Lee et al. (2010) modeled deformation at Augustine from 1992 to 2005 using a dual-source Mogi model. In addition to a shallow, contracting chamber at 2-4 km depth that fed recent eruptions, they place an inflating longer-term magma storage zone at 7-12 km depth, equivalent to ~ 210 -360 MPa.

Volatiles also play a role in the stability of cummingtonite within a vapor-saturated magma such that it requires that $P_{\text{H}_2\text{O}}$ is a large proportion of P_{total} , with $P_{\text{H}_2\text{O}} \approx P_{\text{total}}$. Wood and Carmichael (1973) place the lower limit of $P_{\text{H}_2\text{O}}$ at 75-80% of P_{total} and Gardner et al. (1995) calculate the $X_{\text{H}_2\text{O}}^{\text{fluid}}$ of the cummingtonite-bearing Yn pumice of Mount St. Helens to be $X_{\text{H}_2\text{O}}^{\text{fluid}} = 0.7$ -0.9 for a $P_{\text{H}_2\text{O}}$ of 250 MPa. Vapor composition isopleths (calculated using Newman and Lowenstern, 2002) indicate that some melt inclusions in yellow pumice phenocrysts were trapped under conditions when the activity of water in the system was not sufficient to stabilize cummingtonite. However, melt inclusions were not identified in any cummingtonite phenocrysts, so it is possible that cummingtonite is a later phase that only began crystallizing once $X_{\text{H}_2\text{O}}^{\text{fluid}}$ was sufficiently high, at pressures lower than ~ 260 MPa.

7.2 Constraints on origins of the white and flow-banded pumices

Above the yellow pumice in the stratigraphic column, the massive white pumice unit contains ~10% dispersed fragments of the denser flow-banded pumice. Because these two lithologies, like the yellow pumice, contain cummingtonite, the same conditions should exist for these magmas in terms of temperature, pressure, and f_{O_2} . From Fe-Ti oxide equilibria, we find that the conditions for the white pumice are indeed quite similar to those for the yellow pumice, with a calculated temperature of ~760°C and an f_{O_2} of ~NNO+1.55. However, despite also containing cummingtonite, the flow-banded pumice yields not only higher temperatures, but also a larger range of temperatures, from 778 to 886°C. Similarly, f_{O_2} ranges from similar to the other pumices, at NNO+1.57 but extends down to NNO+1.36.

Unlike the yellow pumice, both the white and flow-banded pumices also contain calcic amphiboles, which have been used to attempt to place further constraints on magmatic conditions. Temperatures derived from calcic amphibole compositions are higher than those from Fe-Ti oxides for both lithologies, but particularly for the white pumice (~830-940°C versus ~760°C). Pressures for both lithologies generally extend as low as ~140 MPa, but range up to over 400 MPa for the white pumice and up to 700 MPa for the flow-banded. Higher pressures for the flow-banded pumice result from higher concentrations of aluminum and iron than in the white pumice (Table 3; Figure 8; Ridolfi et al., 2010). However, these apparently higher pressures and temperatures for the flow-banded lithology may just represent a shift in magma composition resulting from additional mixing of more mafic, amphibole-bearing magma (Erdmann et al., 2014)

Though no temporal gap between the yellow and other pumices has been constrained, the change of assemblage represents a shift in composition or magmatic conditions (which could

simply be location in a large chamber), or both, between the eruption of the yellow unit and these two lithologies, perhaps during a single eruption.

7.2.1 Relationship between the white and flow-banded lithologies

In addition to differences in pressure, temperature, f_{O_2} , and calcic amphibole composition, stark textural changes exist between the white and flow-banded lithologies. Considering all of the differences, aside from the flow-banded pumice being distributed throughout the white pumice deposit, the relationship between the two lithologies in the mixed large unit is not immediately clear. Banding often represents mingling of two magmas, in this case perhaps between the main white pumice magma and a more mafic magma that may have triggered eruptions. However, measurements indicate that banding is textural in the flow-banded sample, with more vesicular (white) bands and a more dense, ‘crumbly’ gray set of bands (Figure 4c). Neither major nor trace (Ba, Sr, Zr) elements show any evidence of significant variation between the matrix glass of the two types of bands. Given uniform glass chemistry from band to band, we can infer that the banded pumice derives from a single uniform magma and that the banding resulted from some mechanism of eruption. Phenocryst alignment also indicates shear at some point in the magmatic history. Shearing may occur along conduit margins during eruption, which can lead to variable vesicularity between sheared and non-sheared bands. Such variations have been seen in rhyolitic obsidian samples (Connor et al., 2001; Rust et al., 2003) and similarly sheared textures in lava flows and domes exist in chemically homogenous lavas (K. Cashman, pers. comm.). In addition to the textural difference, there is also a distinct difference in the chemistry of the amphiboles from the white to flow-banded lithologies. As such, it seems unlikely that the two lithologies are derived from identical magmas that merely encountered different eruptive mechanisms.

7.3 Potential magmatic interactions and eruptive processes

Mixing and mingling processes have proved to be fairly common in Holocene Augustine products (Daley, 1986; Roman et al., 2006; Tappen et al., 2009; Larsen et al., 2010). While such processes are likely not the cause of the banding present in the texturally banded pumice, we still find textural and chemical evidence of multiple magmas influencing the final rhyolite products studied. Most importantly, mafic xenocrysts with basaltic to basaltic-andesite melt inclusions are clear indications that a second, non-rhyolitic melt was present at Augustine either before or contemporaneous with the rhyolitic melt(s). This corroborates field observations of Pleistocene basalt found locally interbedded with the rhyolitic deposits on Augustine Island (Waitt and Begét, 2009). Second, a number of plagioclase phenocrysts in all three lithologies exhibit oscillatory zoning, hinting at variable conditions and chemistry within the magma chamber. There is also a bimodal (or perhaps trimodal) distribution of plagioclase compositions in all three lithologies, which may indicate multiple batches of magma mixing, each with a distinct plagioclase populations. Further evidence of a hotter, mafic magma present at the time of the rhyolitic chamber may lie in the textures of melt inclusions and phenocrysts. The lack of daughter phases in nearly all of the melt inclusions may be indicative of reheating of felsic magma and its phenocrysts, post-entrapment, as could happen if the chamber was underplated by a new basaltic intrusion. Likewise, some possible resorption textures in amphiboles and quartz may also be a result of reheating of the rhyolite-forming melt(s).

If we extend interpretation of amphibole textures further, the absence of reaction rims indicates that each lithology ascended relatively quickly from P-T conditions of the amphibole stability field to those at the surface. In decompression experiments on the Mount St. Helens 1980-86 dacites, reaction rims remained absent if the melt and phenocryst assemblage were

brought from 8 km depth to the surface in less than 5 days (Rutherford and Hill, 1993), with actual ascent rates determined to be much faster on the basis of seismic data (~4 hrs; Endo et al., 1990). This is comparable to the findings of Castro and Dingwell (2009) for the rhyolitic eruption of Chaitén volcano, Chile, in 2008. Using experimental phase equilibria and decompression rates, they were able to determine that magma ascended from >5 km in ~4 hrs, for an approximate ascent rate of 0.5 m/s. We can approximate a minimum eruptive ascent rate for the Augustine rhyolite on the basis of our geobarometry and a maximum ascent time for amphiboles of 5 days. Using the low end of MELTS-Excel calculations for pressures based on matrix glass and feldspar-hosted melt inclusions (~180 MPa, or ~6.5 km depth), we determine a minimum ascent rate of 0.015 m/s. This ascent rate would be higher had we used higher pressures derived from other geobarometric methods and may well be even higher, given potentially shorter ascent times on the order of those at Mount St. Helens and Chaitén. A rapid ascent rate is consistent of the relatively low viscosity this rhyolite would have had given the relatively high water contents (Dingwell et al., 1996).

Coombs and Vazquez (2014) suggest that rhyolite at Augustine originated as residual liquid extracted from a crystal-rich dacite, the residuum of which erupted as dioritic inclusions in 2006 andesites. Commonalities between the samples they studied and ours tend to suggest that the rhyolites may represent the same unit(s). If we assume that the rhyolites of this study also originated as liquid filter-pressed from a crystal mush, we still must evaluate the processes that led to three distinct lithologies at the surface.

Interpretation of the yellow pumice appears to be most straightforward based on our data. The melt underwent crystallization at roughly 260 MPa in the presence of a mixed H₂O-CO₂-dominated fluid phase that became progressively H₂O-dominated with time. Cummingtonite

crystallized as part of this assemblage once $X_{\text{H}_2\text{O}}^{\text{fluid}}$ was sufficiently high. Because we do not have a constraint on the temporal gap between the eruptions of the yellow and white/flow-banded pumices, we cannot determine if calcic amphiboles, which are absent in the yellow pumice, began crystallizing in the remaining melt following the eruption of the yellow pumice or were simply not present in the shallow portion of the chamber that was tapped for the eruption of the yellow pumice. Orthopyroxene would also likely have been crystallizing prior to the eruption of the yellow pumice given that the pyroxene compositions are consistent, with almost no scatter, throughout the three lithologies.

The mechanism of eruption for the white and flow-banded pumices is likely more complicated. Calcic amphiboles are present in both, though with different compositional ranges. It is possible that the amphibole was an equilibrium phase crystallizing throughout the chamber following the eruption of the yellow pumice, or simply in only the deeper sectors of the chamber while the shallow yellow pumice source magma was erupted. However, if we assume the melt extraction model of (Coombs and Vazquez, 2014) to be correct for the rhyolite of this study, we can explore the amphibole-bearing residuum (seen in 2006 deposits as dioritic inclusions) as a potential source of calcic amphiboles in the white and flow-banded pumices. Perhaps the residual crystal mush remained at the base of the rhyolite chamber, and upon evacuation during the eruption of the white and flow-banded pumices, became entrained and mixed throughout the melt, with varying proportions of different compositions of amphibole leading to the two separate lithologies. If stable amphiboles were only added to the main rhyolitic magma via entrainment at the time of eruption, that would be consistent with the lack of reaction rims and required fast ascent. We did also find a clot of over 20 amphibole crystals in the white pumice (Figure 7c). Amphiboles from the dioritic inclusions, however, contain $<10 \text{ wt\% } \text{Al}_2\text{O}_3$ (De

Angelis et al., 2013). This is consistent with amphibole compositions from the white pumice, but only for part of the compositional range of amphiboles from the flow-banded pumice, which contains tschermakites with Al_2O_3 contents up to 15 wt% (Figure 8). Such compositions are similar to amphiboles of a more mafic origin (Daley, 1986; De Angelis et al., 2013), invoking a more complicated scenario involving both entrainment of crystal mush and mixing of a separate mafic melt, though this is perhaps consistent with our potentially trimodal plagioclase compositional distributions. Also problematic is that mixing and entrainment would have had to have been very efficient and quick to lead to the uniform glass compositions and textures that we see in the white and flow-banded lithologies. We find no evidence of incomplete mixing or mingling, which may not be realistic for such a large volume of rhyolite in the short time period required to erupt pristine amphiboles. This scenario also does not address why the flow-banded lithology would have developed a distinct texture in addition to having more Al-rich amphiboles. Finally, the dioritic inclusions interpreted to be the rhyolite's cumulate residuum included clinopyroxene (Coombs et al., 2010), which we have not found in either the white or flow-banded lithologies; the only clinopyroxene found at all was a very rounded xenocryst in the yellow pumice.

If the calcic amphibole was an equilibrium phase in the chamber rather than entrained, other scenarios must be considered to explain the surface deposits. The flow-banded lithology is scattered throughout the larger white pumice deposit, requiring it to be located either at a similar depth as or more shallow than the white pumice source magma in order for it to be entrained during the eruption of the white pumice. Accordingly, the flow-banded source magma must have ascended from depth (indicated by its apparently higher-pressure amphiboles) to either a) a more shallow location still within the stability field of amphibole, b) to a more shallow location

782 outside the stability field of amphibole but with the caveat that its residence time there must have
783 been quite short, or c) to the surface, where unreacted amphiboles would be preserved by fast
784 cooling. None of the three possibilities is without problems. A surface eruption as a dome or
785 flow would generate textural banding, but would have had to already sufficiently degassed so as
786 to not result in an explosive eruption instead of the extrusive eruption. Further, the flow-banded
787 pumice makes up 10% of the voluminous white pumice deposit, or an equivalent thickness of
788 3 m; it seems unlikely that such a quantity of banded material already on the surface could be
789 entrained by the eruption of the white pumice. Finally, the unsheared vesicular bands in the
790 banded pumice would have needed to retain enough volatiles and heat to still degas and deform
791 melt following the bulk of the flow and shear, which may not be likely. In the case of the deeper,
792 flow-banded source magma ascending to a shallower level still within the amphibole stability
793 field, the magma would still need to be quite deep (below 6.5 km in the case of Mount St.
794 Helens; Rutherford and Hill, 1993), which may not be shallow enough to generate or sustain
795 sheared textures having to do with degassing, especially the ‘crumbly’ nature of some voids.
796 Also, any significant time spent in a shallower portion of the amphibole stability field would
797 likely generate noticeable zonation of the amphibole phenocrysts, which is generally not
798 observed. The flow-banded source magma ascending to a level intermediate to the surface and
799 the amphibole stability field seems ideal in terms of partial degassing, shearing in narrower
800 portions of the conduit, and potential volume of the lithology, but, given the lack of reaction rims
801 on the amphiboles, would require a very short residence at such shallow levels and eruption soon
802 after. Regardless of possible stalling at intermediate levels, it is clear that all of the magmas must
803 have ascended from depth quickly; assuming that required ascent rates for no reaction rims on
804 amphiboles at Mount St. Helens would be comparable for the slightly more evolved and cooler

Augustine rhyolite, ascent time should also be on the order of less than ~5 days. There is also the matter of why or how the flow-banded source magma ascends high enough to be entrained in the eruption of the white pumice. While the mechanism is not clear, it may be related to heating from below. Temperatures indicated by Fe-Ti oxide equilibria are indeed higher than those of the other two lithologies, but again would require a short residence time at shallow (and cooler) levels so that the oxides retained their hotter signature. Further work to elucidate the heating, mixing, and mingling histories of the source magmas may shed light on these unclear issues.

7.4 Future Augustine hazards?

Each of the three most recent eruptions (1976, 1986, 2006) consisted largely of vent-clearing explosive activity and ash emission followed by extrusion of viscous lava with VEIs (volcanic explosivity index; Newhall and Self, 1982; Houghton et al., 2013) of 2-4 (McNutt et al., 2010; Global Volcanism Program, 2014). Wallace et al. (2010) assert that fall deposits from the 2006 eruption of Augustine (<2 m thickness, including reworking) are unlikely to be well-preserved in the geologic record, even on Augustine Island itself, owing to their small volume and potential further reworking. It follows that deposits likely need to be larger than those associated with VEIs 2-4 in order to be preserved. In contrast to the recent deposits, the fall deposit described in this paper has the potential to be the most voluminous on the island. Given that the rhyolite may have previously been eroded by glaciation or other means, the fact that they retained a thickness of ~30 m for upwards of 20,000 years indicates that a VEI as low as those of recent eruptions is incongruous with the large modern thickness observed in the field. Additionally, the largest observed pumice fall blocks observed in situ in the rhyolitic deposits were on the order of 2 m, whereas the smaller 2006 eruption's ejecta reached a maximum size in the coarse lapilli range. The massive Pleistocene rhyolite eruption was therefore more likely to

828 be of a VEI 5 or higher, though additional fieldwork is necessary to constrain erupted volumes,
829 including material off Augustine Island.

830 VEIs of 5 or 6 would put this rhyolitic eruption on par with other well-known eruptions
831 including Vesuvius 79 (VEI 5), Santa Maria 1902 (VEI 6), Novarupta 1912 (VEI 6), Mount St.
832 Helens 1980 (VEI 5), and Mount Pinatubo 1991 (VEI 6) (Global Volcanism Program, 2014). An
833 eruption of this scale in modern times would have significant consequences locally, and perhaps
834 globally. Even the VEI 4 eruption of Augustine in 1976 was strong enough to induce a ‘blizzard’
835 of ash in the city of Homer, prohibiting cars from driving because of reduced visibility. Ash and
836 mud fell over the bulk of the Kenai Peninsula, and 1.5 mm of ash coated the Anchorage area
837 (Shackelford, 1978). The similarly-sized 1986 eruption also resulted in ashfall in Anchorage
838 (Swanson and Kienle, 1988). The 2006 Augustine eruption was smaller (VEI 3), but ash plumes
839 still resulted in numerous flight diversions and cancellations (Neal et al., 2010). Closer to
840 Anchorage, the main population center in the area, Redoubt Volcano has erupted recently, also
841 causing problems; the 1989-1990 eruption of Redoubt (VEI 3) is famous for the near-crash of a
842 Boeing 747 passenger jet after inadvertently flying into an ash cloud and temporarily losing
843 power to all 4 engines (Casadevall, 1994). Additional effects were debris flows down the Drift
844 River, at least one of which reached Cook Inlet and caused flooding in and temporary closure of
845 an oil terminal (Miller and Chouet, 1994). While not near significant population centers, the
846 largest recent Alaskan eruptions (Okmok and Kasatochi in 2008; VEI 4) erupted significant
847 plumes of ash and SO₂ that led to numerous aircraft encounters over the United States, Canada,
848 and Europe (Rose et al., 2008).

849 The presence of such a voluminous rhyolite eruption in preglacial times does not
850 necessarily indicate that Augustine is currently capable of a similarly-sized eruption, with all

associated hazards. It may be that the magmatic system has evolved to a point that it cannot support the volumes of magma required to replicate the rhyolitic eruption. However, InSAR does seem to indicate that there is still an active magma chamber beneath the more commonly referenced shallow plumbing system (Lee et al., 2010). If this is the case, and if the deeper chamber was the original source of the rhyolitic magma, the potential exists for a similar eruption in the future. To best understand potential hazards of such an eruption, further study of the magmas feeding the ancient rhyolitic eruptions is warranted.

8 CONCLUSIONS

While recent eruptive products from Augustine Volcano are in the intermediate range of chemical compositions, older large pumice fall deposits exposed by erosive lahars in 2006 exhibit a distinct mineral assemblage and a rhyolitic bulk composition. Mineralogy varies further between the three distinct lithologies found, with the lowest stratigraphic unit, the yellow pumice, containing cummingtonite, but no calcic amphiboles. The white pumice, comprising the vast majority of the exposure's material contains cummingtonite, but also low-aluminum calcic amphiboles. Banded pumices dispersed throughout the main white pumice unit display textural banding and contain calcic amphiboles with higher aluminum and lower magnesium contents than those in the white pumices. Quartz is also present in each of the three lithologies, unlike most younger deposits, and both minor anhydrite and sulfide minerals were identified as mineral inclusions in phenocrysts. Two mafic xenocrysts were also found within the rhyolite: a forsteritic olivine in the white pumice and a diopsidic clinopyroxene in the yellow.

The apparent volatile contents of magmas supplying these ancient rhyolitic eruptions were different from modern magmas. Melt inclusions in a variety of minerals (orthopyroxene, plagioclase, calcic amphibole, and quartz) indicate that melt compositions are depleted in Cl relative to those representing more recent eruptions; apatite compositions display distinctly lower Cl and F contents than recent apatites as well. CO₂ and H₂O concentrations of melt inclusions from the yellow and flow-banded pumices indicate low concentrations of CO₂ in the flow-banded pumice's melt inclusions. Higher CO₂ concentrations in an earlier stage of magmatic evolution are indicated by the yellow pumice, lowest in section, and show mostly isobaric crystallization of the yellow pumice at a pressure of ~260 MPa. Quartz-feldspar-melt geobarometry on matrix glasses gives a similar pressure window of ~170 to ~290 MPa, while melt inclusions often indicate higher pressures at melt entrapment. Geothermometry based on Fe-Ti oxide equilibria indicates temperatures of ~760°C for the white and yellow pumices and somewhat higher temperatures for the flow-banded lithology.

Based on knowledge amassed in this study, we are able to conclude that the source magma for the yellow pumice evolved in a relatively deep magma chamber whose melt became progressively more H₂O-dominated with time and melt evolution. Following an eruption of the yellow pumice, either a) the source magma for the white and flow-banded pumices either entrained calcic amphibole-bearing crystal mush ($\pm$ mafic melt and high Al-amphiboles) to varying degrees to become two distinct lithologies, or b) the flow-banded pumice source magma was a distinct melt that ascended from depth to shallower in the magma chamber or conduit, or to the surface, followed by the white pumice eruption that entrained fragments of the flow-banded pumice with it. In all cases, these various eruptions were likely influenced by the

893 presence of a mafic magma that mixed or mingled with the more silicic melt, while also
894 providing additional heat.

895 These conclusions are preliminary, but the serious hazards presented by further eruptions
896 of this sort warrant additional study at Augustine to better understand the magmatic system.
897 Further constraints on mixing processes, chamber depth, and volatile evolution would yield
898 valuable insight into the processes at work during the ancient eruptions and also help discern
899 whether similar events are likely to occur in the future. This paper lays the groundwork for future
900 studies of Augustine's voluminous and potentially hazardous silicic eruptions and, most
901 importantly, extends the range of knowledge with respect to erupted products.

902 **9 ACKNOWLEDGEMENTS**

903 We thank the Augustine field expedition crew of summer 2006 for facilitating field work
904 and sample collection. Juliane Gross was generous in helping with EMP analyses and Denton
905 Ebel, Ellen Crapster-Pregont, and Shawn Wallace helped with stitching EMP element maps. We
906 also thank Michelle Coombs for valuable discussions of Augustine's rhyolites. Guilherme
907 Gualda is thanked for his generosity in sharing his MELTS-Excel program as well as his
908 patience and help in troubleshooting. Filippo Ridolfi is thanked for providing assistance in
909 utilizing his amphibole programs. Funding for PAN was generously provided by the Kathryn W.
910 Davis Fellowship program at the American Museum of Natural History. Financial support for
911 JDW came in part from NSF grant EAR-0836741. This manuscript was significantly improved
912 by the thoughtful reviews of Michelle Coombs, Jorge Vazquez, and two anonymous reviewers.

10 TABLE CAPTIONS

Table 1: Whole-rock (fused glass) and matrix glass compositions in weight % with standard deviations. Total iron (FeO_t) as FeO. n is number of points averaged to representative composition.

Table 2: Modal mineralogy and vesicularity of the 3 lithologies, based on Fisher linear discriminant analysis classification analysis of EMP element maps of a polished thin section for each lithology.

Table 3: Representative major-element analyses for all phenocryst types and sub-types. Numbers reported represent average compositions of all measured phenocrysts with standard deviations (S.D.), unless otherwise specified; compositions reported for low- and high-component sub-types are 5-point averages of the most extreme compositions.

Table 4: a) Representative silicic melt inclusion compositions b) Representative mafic melt inclusion compositions

Table 5: Comparison of derived 2-oxide temperatures and log oxygen fugacities relative to that of NNO buffer. n is number of pairs averaged to reach representative results.

Table 6: H_2O and CO_2 contents of melt inclusions.

Table 7: Summary of magma chamber parameters derived from geochemistry of the three rhyolitic lithologies. References for methods column include: Ghiorso and Evans

935 (2008) for Fe-Ti oxides; Ridolfi et al. (2010) and Ridolfi and Renzulli (2012) for calcic
936 amphiboles, with the exception of those marked with *, which were determined via Anderson
937 and Smith (1995); Geschwind and Rutherford (1992) and Gardner et al. (1995) for
938 cummingtonite; Holland and Blundy (1994) for calcic amphibole/plagioclase pairs; Newman and
939 Lowenstern (2002) for melt inclusions; and Gualda and Ghiorso (2014) for glasses via MELTS-
940 Excel.

941

11 FIGURE CAPTIONS

Figure 1: Map of area surrounding Augustine Volcano

Figure 2: Sample image of EMP-based mineralogical map of flow-banded pumice. Area chosen to show mineralogical diversity but proportions of minerals are not representative of lithology.

Figure 3: Total alkali versus SiO₂ diagram, with data for whole rocks, matrix glasses, and melt inclusions for the three pumiceous lithologies of this study. Rhyolitic melt inclusion data falling below ~5.25 wt% Na₂O+K₂O likely suffered Na-loss during EMP analysis. Pleistocene data from Larsen et al. (2010). Basaltic melt inclusion data from Zimmer (2009). Holocene whole-rock data from the Alaska Volcano Observatory geochemical database (Cameron et al., 2014).

Figure 4: Examples of textures from the three lithologies, either in plane polarized light or BSE. A) White pumice B) Yellow pumice C) Flow-banded pumice showing both vesicular and dense textures D) Elongate vesicles radiating away from phenocryst in vesicular band of flow-banded lithology E) Large jagged, ‘torn’ or ‘crumbly’ voids at ends of aligned phenocryst in dense band of flow-banded pumice. Blue in D and E is colored epoxy.

Figure 5: Sample plagioclase (Pl) textures from flow-banded lithology. A) Highly sieve-textured, subhedral, broken crystal B) Euhedral crystal. Blue is colored epoxy. Opx = orthopyroxene

Figure 6: Histograms of plagioclase anorthite content for point analyses of the three lithologies.

Figure 7: Sample amphibole textures. A) Euhedral calcic amphibole (tschermakitic pargasite; Ts-Prg) in flow-banded pumice showing typical cross-section B) Resorption texture of calcic amphibole in flow-banded pumice C) Glomerophyric clot of calcic amphiboles (magnesian hornblende; Mhb), plagioclase (Pl), and magnetite (Mt) in white pumice D) Typical cross-section of euhedral cummingtonite (Cum) from yellow pumice. Blue is colored epoxy.

Figure 8: Al_2O_3 vs. MgO plot comparing amphibole compositions of individual grains from the current study to compositions of more recently erupted amphiboles. Data for 2006 from Larsen et al. (2010), De Angelis et al. (2013), and Webster et al. (2010). Prehistoric data from Tappen et al. (2009).

Figure 9: Example of euhedral quartz (Qz) in thin section, from white pumice. Blue is tinted epoxy.

Figure 10: Sample Fe-Ti oxide textures A) Large, sub- to anhedral magnetite (Mt) in glass (unlabeled light gray material) of white pumice B) Sub- to euhedral magnetite in glass of yellow pumice C) Small, euhedral ilmenite (Ilm) in glass of flow-banded pumice D) Subhedral ilmenite in glass of yellow pumice. Pl = plagioclase, Ap = apatite, Opx = orthopyroxene

Figure 11: Ternary diagram of apatite compositions for modern (Webster, unpublished) and ancient (flow-banded, white, and yellow pumice) eruptive units of Augustine volcano (calculated on an atomic basis).

Figure 12: Log f_{O_2} versus temperature for Fe-Ti oxide pairs for three lithologies of this study and other published data for comparison. Data from 2006 are from Larsen et al. (2010) and Coombs and Vazquez (2014), data from ~2000 BP are from Tappen et al. (2009), data from 1986 are from Roman (2001), and data for diorite inclusions and other rhyolite are from Coombs

and Vazquez (2014). Because Roman et al. (2006), Tappen et al. (2009), and Larsen et al. (2010) originally calculated equilibrium conditions using QUILF (Andersen et al., 1993) instead of our preferred algorithm, we have recalculated those results from their raw data using the Ghiorso and Evans (2008) model for comparison here.

Figure 13: CO_2 and H_2O contents of melt inclusions from the three lithologies of this study, as measured via SIMS. Solid curves are modeled vapor-saturation isobars for rhyolitic melts at 765°C and dashed curves show coexisting vapor compositions as determined using VolatileCalc 2.0 (Newman and Lowenstern, 2002). Light gray curve shows 260 MPa isobar presumed to indicate isobaric crystallization for magma represented by four of the melt inclusions.

Figure 14: Cl versus Larsen Index of magma differentiation ($[(\text{SiO}_2/3 + \text{K}_2\text{O}) - (\text{CaO} + \text{FeO} + \text{Mg})]$, in weight percent) for studied melt inclusions compiled from all three lithologies of the current study. Mafic melt inclusions are assumed to represent potential starting melt composition and Cl content, and contain roughly the same amount of Cl as the more evolved inclusions from all mineral hosts. The difference in expected Cl contents of evolved felsic melts and actual Cl concentrations is interpreted to indicate sequestration of Cl by fluid phases. Included are dashed arrows indicating the expected chlorine contents of crystallizing melts absent a fluid phase, as well as chlorine loss.

12 REFERENCES

- Andersen, D.J., Lindsley, D.H. and Davidson, P.M., 1993. QUILF: A pascal program to assess equilibria among Fe-Mg-Mn-Ti oxides, pyroxenes, olivine, and quartz. *Comput Geosci*, 19(9): 1333-1350.
- Anderson, J.L. and Smith, D.R., 1995. The effects of temperature and fO_2 on the Al-in-hornblende barometer. *Am Mineral*, 80: 549-559.
- Bacon, C.R. and Hirschmann, M.M., 1988. Mg/Mn partitioning as a test for equilibrium between coexisting Fe-Ti oxides. *Am Mineral*, 73(1-2): 57-61.
- Begét, J.E. and Kienle, J., 1992. Cyclic formation of debris avalanches at Mount St Augustine volcano. *Nature*, 356(6371): 701-704.
- Blundy, J. and Cashman, K., 2001. Ascent-driven crystallisation of dacite magmas at Mount St Helens, 1980–1986. *Contrib Mineral Petrol*, 140(6): 631-650.
- Cameron, C.E., Snedigar, S.F. and Nye, C.J., 2014, Alaska Volcano Observatory Geochemical Database: Alaska Division of Geological & Geophysical Surveys Digital Data Series 8, <https://www.avo.alaska.edu/geochem/index.php>, doi:10.14509/29120
- Casadevall, T.J., 1994. The 1989–1990 eruption of Redoubt Volcano, Alaska: impacts on aircraft operations. *J. Volcanol. Geotherm. Res.*, 62(1–4): 301-316.
- Castro, J.M. and Dingwell, D.B., 2009. Rapid ascent of rhyolitic magma at Chaiten volcano, Chile. *Nature*, 461(7265): 780-783.
- Chaigneau, M., Massare, D. and Clocchiatti, R., 1980. Contribution à l'étude des inclusions vitreuses et des éléments volatils contenus dans les phénocristaux de quartz de roches volcaniques acides. *Bull Volcanol*, 43(1): 233-240.
- Connor, C.B., Hill, B.E., Winfrey, B., Franklin, N.M. and La Femina, P.C., 2001. Estimation of Volcanic Hazards from Tephra Fallout. *Natural Hazards Review*, 2(1): 33-42.
- Coombs, M.L., Bull, K.F., Vallance, J.W., Schneider, D.J., Thoms, E.E., Wessels, R.L. and McGimsey, R.G., 2010. Timing, Distribution, and Volume of Proximal Products of the 2006 Eruption of Augustine Volcano. In: J.A. Power, M.L. Coombs and J.T. Freymueller (Editors), *The 2006 eruption of Augustine Volcano, Alaska*. U.S. Geological Survey.
- Coombs, M.L. and Vazquez, J.A., 2014. Cogenetic late Pleistocene rhyolite and cumulate diorites from Augustine Volcano revealed by SIMS ^{238}U - ^{230}Th dating of zircon, and implications for silicic magma generation by extraction from mush. *Geochemistry, Geophysics, Geosystems*: in press.
- Daley, E.E., 1986. *Petrology, Geochemistry, and the Evolution of Magmas from Mt. St. Augustine Volcano, Alaska*, M.S. Thesis, University of Alaska, Fairbanks, 106 pp.

1040 De Angelis, S.H., Larsen, J. and Coombs, M., 2013. Pre-eruptive Magmatic Conditions at Augustine
1041 Volcano, Alaska, 2006: Evidence from Amphibole Geochemistry and Textures. *Journal of*
1042 *Petrology*, 54(9): 1939-1961.

1043 Dingwell, D.B., Romano, C. and Hess, K.U., 1996. The effect of water on the viscosity of a
1044 haplogranitic melt under P-T-X conditions relevant to silicic volcanism. *Contrib Mineral*
1045 *Petrol*, 124(1): 19-28.

1046 Eastman, J.R., 2012. IDRISI Selva. Clark University, Worcester, MA.

1047 Endo, E.T., Dzurisin, D. and Swanson, D.A., 1990. Geophysical and observational constraints for
1048 ascent rates of dacitic magma at Mount St. Helens. *Magma transport and storage*: 318-334.

1049 Erdmann, S., Martel, C., Pichavant, M. and Kushnir, A., 2014. Amphibole as an archivist of
1050 magmatic crystallization conditions: problems, potential, and implications for inferring
1051 magma storage prior to the paroxysmal 2010 eruption of Mount Merapi, Indonesia. *Contrib*
1052 *Mineral Petrol*, 167(6): 1-23.

1053 Evans, B.W. and Ghiorso, M.S., 1995. Thermodynamics and petrology of cummingtonite. *Am*
1054 *Mineral*, 80: 649-663.

1055 Gamble, J.A., Price, R.C., Smith, I.E.M., McIntosh, W.C. and Dunbar, N.W., 2003. $^{40}\text{Ar}/^{39}\text{Ar}$
1056 geochronology of magmatic activity, magma flux and hazards at Ruapehu volcano, Taupo
1057 Volcanic Zone, New Zealand. *J. Volcanol. Geotherm. Res.*, 120(3-4): 271-287.

1058 Gardner, J.E., Carey, S. and Sigurdsson, H., 1998. Plinian eruptions at Glacier Peak and Newberry
1059 volcanoes, United States: Implications for volcanic hazards in the Cascade Range. *Geological*
1060 *Society of America Bulletin*, 110(2): 173-187.

1061 Gardner, J.E., Rutherford, M., Carey, S. and Sigurdsson, H., 1995. Experimental constraints on pre-
1062 eruptive water contents and changing magma storage prior to explosive eruptions of Mount
1063 St Helens volcano. *Bull. Volcanol.*, 57(1): 1-17.

1064 Geschwind, C.-H. and Rutherford, M.J., 1992. Cummingtonite and the evolution of the Mount St.
1065 Helens (Washington) magma system: An experimental study. *Geology*, 20(11): 1011-1014.

1066 Ghiorso, M.S. and Evans, B.W., 2008. Thermodynamics of Rhombohedral Oxide Solid Solutions
1067 and a Revision of the FE-TI Two-Oxide Geothermometer and Oxygen-Barometer.
1068 *American Journal of Science*, 308(9): 957-1039.

1069 Global Volcanism Program, 2014, Volcanoes of the World Database. Smithsonian Institution,
1070 http://www.volcano.si.edu/search_volcano.cfm, accessed August 28, 2014.

1071 Gualda, G.A.R., Ghiorso, M.S., Lemons, R.V. and Carley, T.L., 2012. Rhyolite-MELTS: a Modified
1072 Calibration of MELTS Optimized for Silica-rich, Fluid-bearing Magmatic Systems. *Journal*
1073 *of Petrology*, 53(5): 875-890.

1074 Gualda, G.R. and Ghiorso, M., 2014. Phase-equilibrium geobarometers for silicic rocks based on
1075 rhyolite-MELTS. Part 1: Principles, procedures, and evaluation of the method. *Contrib*
1076 *Mineral Petrol*, 168(1): 1-17.

1077 Holaske, R. and Rose, W., 1991. Anatomy of 1986 Augustine volcano eruptions as recorded by
1078 multispectral image processing of digital AVHRR weather satellite data. *Bull. Volcanol.*,
1079 53(6): 420-435.

1080 Holland, T. and Blundy, J., 1994. Non-ideal interactions in calcic amphiboles and their bearing on
1081 amphibole-plagioclase thermometry. *Contrib Mineral Petrol*, 116(4): 433-447.

1082 Houghton, B.F., Swanson, D.A., Rausch, J., Carey, R.J., Fagents, S.A. and Orr, T.R., 2013. Pushing
1083 the Volcanic Explosivity Index to its limit and beyond: Constraints from exceptionally weak
1084 explosive eruptions at Kīlauea in 2008. *Geology*, 41(6): 627-630.

1085 Johnson, K.E., Harmon, R.S., Richardson, J.M., Moorbath, S. and Strong, D.F., 1996. Isotope and
1086 Trace Element Geochemistry of Augustine Volcano, Alaska: Implications for Magmatic
1087 Evolution. *Journal of Petrology*, 37(1): 95-115.

1088 Johnston, D.A., 1979. Onset of volcanism at Augustine Volcano, lower Cook Inlet. In: K.M.
1089 Johnson and J.R. Williams (Editors), *The United States Geological Survey in Alaska:
1090 accomplishments during 1978*, U.S. Geological Survey Circular C 0804-B, pp. B78-B80.

1091 Larsen, J.F., Nye, C.J., Coombs, M.L., Tilman, M., Izbekov, P. and Cameron, C., 2010. Petrology
1092 and geochemistry of the 2006 eruption of Augustine Volcano. In: J.A. Power, M.L. Coombs
1093 and J.T. Freymueller (Editors), *The 2006 eruption of Augustine Volcano, Alaska*. U.S.
1094 Geological Survey.

1095 Leake, B.E., Woolley, A.R., Arps, C.E.S., Birch, W.D., Gilbert, M.C., Grice, J.D., Hawthorne, F.C.,
1096 Kato, A., Kisch, H.J., Krivovichev, V.G., Linthout, K., Laird, J., Mandarino, J.A., Maresch,
1097 W.V., Nickel, E.H., Rock, N.M.S., Schumacher, J.C., Smith, D.C., Stephenson, N.C.N.,
1098 Ungaretti, L., Whittaker, E.J.W. and Youzhi, G., 1997. Nomenclature of amphiboles: report
1099 of the subcommittee on amphiboles of the International Mineralogical Association,
1100 Commission on New Minerals and Mineral Names. *The Canadian Mineralogist*, 35: 219-246.

1101 Lee, C.-W., Lu, Z., Jung, H.-S., Won, J.-S. and Dzurisin, D., 2010. Surface Deformation of
1102 Augustine Volcano, 1992–2005, from Multiple-Interferogram Processing Using a Refined
1103 Small Baseline Subset (SBAS) Interferometric Synthetic Aperture Radar (InSAR) Approach.
1104 In: J.A. Power, M.L. Coombs and J.T. Freymueller (Editors), *The 2006 eruption of
1105 Augustine Volcano, Alaska*. U.S. Geological Survey.

1106 McNutt, S.R., Tytgat, G., Estes, S.A. and Stihler, S.D., 2010. A Parametric Study of the January 2006
1107 Explosive Eruptions of Augustine Volcano, Using Seismic, Infrasonic, and Lightning Data.
1108 In: J.A. Power, M.L. Coombs and J.T. Freymueller (Editors), *The 2006 Eruption of
1109 Augustine Volcano, Alaska*. U.S. Geological Survey

1110 Miller, T.P. and Chouet, B.A., 1994. The 1989–1990 eruptions of Redoubt Volcano: an introduction.
1111 *J. Volcanol. Geotherm. Res.*, 62(1–4): 1-10.

1112 Neal, C.A., Murray, T.L., Power, J.A., Adleman, J.N., Whitmore, P.M. and Osienky, J.M., 2010.
1113 Hazard Information Management, Interagency Coordination, and Impacts of the 2005–2006
1114 Eruption of Augustine Volcano. In: J.A. Power, M.L. Coombs and J.T. Freymueller
1115 (Editors), *The 2006 Eruption of Augustine Volcano, Alaska*. U.S. Geological Survey.

1116 Newhall, C.G. and Self, S., 1982. The volcanic explosivity index (VEI) an estimate of explosive
1117 magnitude for historical volcanism. *Journal of Geophysical Research: Oceans*, 87(C2): 1231-
1118 1238.

1119 Newman, S. and Lowenstern, J.B., 2002. VolatileCalc: a silicate melt–H₂O–CO₂ solution model
1120 written in Visual Basic for excel. *Comput Geosci*, 28(5): 597-604.

1121 Newnham, R.M., Lowe, D.J. and Alloway, B.V., 1999. Volcanic hazards in Auckland, New Zealand:
 1122 a preliminary assessment of the threat posed by central North Island silicic volcanism based
 1123 on the Quaternary tephrostratigraphical record. Geological Society, London, Special
 1124 Publications, 161(1): 27-45.

1125 Nielsen, C.H. and Sigurdsson, H., 1981. Quantitative methods for electron microprobe analysis of
 1126 sodium in natural and synthetic glasses. *Am Mineral*, 66: 547-552.

1127 Pamukcu, A.S. and Gualda, G.A.R., 2013, How deep, how hot: comparing pressure and temperature
 1128 estimates from amphibole and rhyolite-MELTS thermobarometry, Abstract V53A-2761
 1129 presented at AGU Fall Meeting, San Francisco, CA, 9-13 Dec.

1130 Power, J.A., Coombs, M.L. and Freymueller, J.T., eds., 2010. The 2006 eruption of Augustine
 1131 Volcano, Alaska. U.S. Geological Survey Professional Paper 1769, 667 pp.

1132 Ridolfi, F. and Renzulli, A., 2012. Calcic amphiboles in calc-alkaline and alkaline magmas:
 1133 thermobarometric and chemometric empirical equations valid up to 1,130°C and 2.2 GPa.
 1134 *Contrib Mineral Petrol*, 163(5): 877-895.

1135 Ridolfi, F., Renzulli, A. and Puerini, M., 2010. Stability and chemical equilibrium of amphibole in
 1136 calc-alkaline magmas: an overview, new thermobarometric formulations and application to
 1137 subduction-related volcanoes. *Contrib Mineral Petrol*, 160(1): 45-66.

1138 Roman, D., Cashman, K., Gardner, C., Wallace, P. and Donovan, J., 2006. Storage and interaction
 1139 of compositionally heterogeneous magmas from the 1986 eruption of Augustine Volcano,
 1140 Alaska. *Bull. Volcanol.*, 68(3): 240-254.

1141 Roman, D.C., 2001. The 1986 eruption of Augustine Volcano, Alaska: magma storage and ascent,
 1142 M.S. Dissertation, University of Oregon, 129 pp.

1143 Rose, W.I. and Chesner, C.A., 1987. Dispersal of ash in the great Toba eruption, 75 ka. *Geology*,
 1144 15(10): 913-917.

1145 Rose, W.I., Nadeau, P.A., Carn, S. and Schneider, D.J., 2008. Aged volcanic clouds – Are they an
 1146 aviation hazard and why? *Eos Trans. AGU*, 89(53), Fall Meet. Suppl., Abstract A52A-04.

1147 Rust, A.C., Manga, M. and Cashman, K.V., 2003. Determining flow type, shear rate and shear stress
 1148 in magmas from bubble shapes and orientations. *J. Volcanol. Geotherm. Res.*, 122(1-2): 111-
 1149 132.

1150 Rutherford, M.J. and Hill, P.M., 1993. Magma ascent rates from amphibole breakdown: An
 1151 experimental study applied to the 1980–1986 Mount St. Helens eruptions. *Journal of*
 1152 *Geophysical Research: Solid Earth*, 98(B11): 19667-19685.

1153 Samaniego, P., Le Pennec, J.-L., Robin, C. and Hidalgo, S., 2011. Petrological analysis of the pre-
 1154 eruptive magmatic process prior to the 2006 explosive eruptions at Tungurahua volcano
 1155 (Ecuador). *J. Volcanol. Geotherm. Res.*, 199(1–2): 69-84.

1156 Shackelford, D.C., 1978. Augustine: in Annual report of the world volcanic eruptions in 1976 with
 1157 supplements to the previous issues. *Bulletin of Volcanic Eruptions*, 16: 53-55.

1158 Swanson, S.E. and Kienle, J., 1988. The 1986 Eruption of Mount St. Augustine: Field Test of a
 1159 Hazard Evaluation. *Journal of Geophysical Research: Solid Earth*, 93(B5): 4500-4520.

1160 Symonds, R., Rose, W., Gerlach, T., Briggs, P. and Harmon, R., 1990. Evaluation of gases,
1161 condensates, and SO₂ emissions from Augustine volcano, Alaska: the degassing of a Cl-rich
1162 volcanic system. *Bull. Volcanol.*, 52(5): 355-374.

1163 Tappen, C.M., Webster, J.D., Mandeville, C.W. and Roderick, D., 2009. Petrology and geochemistry
1164 of ca. 2100–1000 a.B.P. magmas of Augustine volcano, Alaska, based on analysis of
1165 prehistoric pumiceous tephra. *J. Volcanol. Geotherm. Res.*, 183(1–2): 42-62.

1166 Turner, M.B., Cronin, S.J., Stewart, R.B., Bebbington, M. and Smith, I.E.M., 2008. Using
1167 titanomagnetite textures to elucidate volcanic eruption histories. *Geology*, 36(1): 31-34.

1168 Tuttle, O.F. and Bowen, N.L., 1958. Origin of Granite in the Light of Experimental Studies in the
1169 System NaAlSi₃O₈–KAlSi₃O₈–SiO₂–H₂O. *Geological Society of America Memoirs*, 74: 1-
1170 146.

1171 Waitt, R.B. and Begét, J.E., 2009. Volcanic processes and geology of Augustine Volcano, Alaska.
1172 USGS Professional Paper 1762, 78 pp.

1173 Wallace, K. and Coombs, M.L., 2013, Constructing a reference tephrochronology for Augustine
1174 Volcano, Alaska, Abstract V23C-2839 presented at AGU Fall Meeting, San Francisco, Calif.,
1175 9-13 Dec.

1176 Wallace, K.L., Neal, C.A. and McGimsey, R.G., 2010. Timing, Distribution, and Character of
1177 Tephra Fall from the 2005–2006 Eruption of Augustine Volcano. In: J.A. Power, M.L.
1178 Coombs and J. Freymueller (Editors), *The 2006 Eruption of Augustine Volcano, Alaska*.
1179 U.S. Geological Survey

1180 Webster, J.D., Mandeville, C.W., Goldoff, B., Coombs, M.L. and Tappen, C.M., 2010. Augustine
1181 Volcano - The Influence of Volatile Components in Magmas Erupted A.D. 2006 to 2,100
1182 Years Before Present. In: J.A. Power, M.L. Coombs and J.T. Freymueller (Editors), *The*
1183 *2006 eruption of Augustine Volcano, Alaska*. United States Geological Survey.

1184 Wood, B.J. and Carmichael, I.S.E., 1973. P_{total} , $P_{\text{H}_2\text{O}}$ and the occurrence of cummingtonite in
1185 volcanic rocks. *Contrib Mineral Petrol*, 40(2): 149-158.

1186 Zimmer, M.M., 2009. Water in Aleutian magmas: Its origin in the subduction zone and its effects on
1187 magma evolution, Ph.D. thesis, Boston University, Boston, MA, 448 pp.

1188 Zimmer, M.M., Plank, T., Hauri, E.H., Yogodzinski, G.M., Stelling, P., Larsen, J., Singer, B., Jicha,
1189 B., Mandeville, C. and Nye, C.J., 2010. The Role of Water in Generating the Calc-alkaline
1190 Trend: New Volatile Data for Aleutian Magmas and a New Tholeiitic Index. *Journal of*
1191 *Petrology*, 51(12): 2411-2444.

1192

1193

1 **Table 1:** Whole-rock (fused glass) and matrix glass compositions in weight % with standard deviations. Total iron (FeO_t) as FeO. *n* is number of
2 points averaged to representative composition.

Sample Type	Yellow Bulk	S.D.	Flow Banded Bulk	S.D.	White Bulk	S.D.	Yellow Matrix	S.D.	Flow Banded Matrix	S.D.	White Matrix	S.D.
SiO ₂	67.05	0.27	66.22	0.35	67.77	1.18	74.75	0.24	76.30	2.01	75.07	1.11
TiO ₂	0.20	0.04	0.29	0.05	0.20	0.02	0.14	0.05	0.16	0.01	0.16	0.03
Al ₂ O ₃	14.86	0.25	14.82	0.19	14.44	0.33	12.90	0.11	13.17	0.10	13.11	0.47
FeO	1.94	0.10	2.48	0.20	1.66	0.05	1.26	0.13	1.41	0.17	1.31	0.14
MnO	0.11	0.01	0.12	0.02	0.10	0.02	0.09	0.04	0.13	0.02	0.11	0.02
MgO	0.59	0.02	0.88	0.02	0.65	0.02	0.39	0.00	0.45	0.07	0.40	0.04
CaO	2.78	0.08	3.53	0.08	3.10	0.13	1.82	0.05	1.94	0.16	1.86	0.10
Na ₂ O	3.89	0.09	4.08	0.11	4.01	0.17	4.28	0.27	4.30	0.17	4.22	0.25
K ₂ O	1.20	0.07	1.08	0.05	1.13	0.09	1.41	0.04	1.60	0.16	1.45	0.04
P ₂ O ₅	0.13	0.05	0.11	0.06	0.11	0.04	0.06	0.03	0.08	0.02	0.06	0.02
SO ₂	0.01	0.01	0.00	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.01
Cl	0.15	0.01	0.12	0.01	0.14	0.01	0.23	0.00	0.23	0.03	0.22	0.05
F	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.20	0.04	0.03	0.02	0.04
Total	92.90	0.49	93.73	0.48	93.34	0.89	97.48	0.71	99.80	2.25	98.00	1.82
<i>n</i>	5		5		5		3		5		7	

Table 2: Modal mineralogy and vesicularity of the 3 lithologies, based on Fisher linear discriminant analysis classification analysis of EMP element maps of a polished thin section for each lithology.

<i>(In percent⁺)</i>	Yellow Pumice	Flow Banded Pumice	White Pumice
Vesicularity	49	35	62
Glassy Matrix*	88	88	89
Phenocrysts	12	12	11
Quartz	0.43	0.43	0.73
Plagioclase	10.3	9.3	8.7
Orthopyroxene	0.30	0.38	0.24
Cummingtonite	0.38	0.33	0.27
Ca-amphibole	n.p.	1.1	0.35
Ilmenite	0.05	0.02	0.05
Magnetite	0.15	0.29	0.29
Apatite	0.07	0.09	0.07

⁺Vesicularity is reported as a percent of the bulk rock. All other percentages are based on only the solid fraction of the bulk rock.

*Matrix glass proportion includes ~1-4% microlites. Pixel sizes of thin section mapping were too small to capture individual microlites.

n.p. = not present

1 **Table 3: Representative major-element analyses for all phenocryst types and sub-types. Numbers reported represent average compositions of all**
2 **measured phenocrysts with standard deviations (S.D.), unless otherwise specified; compositions reported for low- and high-component**
3 **sub-types are 5-point averages of the most extreme compositions.**

Mineral Lithology	Quartz		OPX		Cummingtonite		Cummingtonite Low-Mg		Cummingtonite High-Mg	
	All	S.D.	All	S.D.	All	S.D.	All	S.D.	All	S.D.
SiO ₂	99.73	0.70	52.70	0.09	52.87	0.66	52.46	1.58	54.05	0.39
TiO ₂	0.03	0.03	0.09	0.04	0.39	0.08	0.53	0.13	0.30	0.06
Al ₂ O ₃	0.09	0.16	1.47	0.36	3.37	0.50	4.27	0.86	2.63	0.18
FeO	0.03	0.03	20.60	0.37	17.47	0.36	17.16	0.43	17.74	0.19
MnO	0.01	0.01	1.54	0.09	1.39	0.07	1.31	0.04	1.41	0.04
MgO	0.01	0.01	23.37	0.44	20.04	0.52	18.64	0.09	21.17	0.17
CaO	0.01	0.02	0.43	0.04	1.89	0.45	3.14	0.98	1.42	0.10
Na ₂ O	0.02	0.04	0.02	0.03	0.46	0.10	0.58	0.15	0.35	0.06
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01
P ₂ O ₅	—	—	0.01	0.01	0.01	0.01	—	—	—	—
Cr ₂ O ₃	0.01	0.01	0.02	0.02	0.02	0.03	0.05	0.06	0.02	0.02
BaO	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
SrO	0.00	0.00	0.03	0.04	0.03	0.04	0.03	0.04	0.00	0.00
SO ₂	—	—	0.01	0.01	0.01	0.00	—	—	—	—
Cl	0.01	0.02	0.01	0.01	0.03	0.01	0.03	0.00	0.03	0.00
F	0.07	0.13	0.05	0.09	0.11	0.14	0.08	0.06	0.14	0.13
NiO	—	—	—	—	—	—	—	—	—	—
CuO	—	—	—	—	—	—	—	—	—	—
V ₂ O ₃	—	—	—	—	—	—	—	—	—	—
Total	100.05		100.34		98.09		98.32		99.28	

4 — = not measured
5 FB = flow-banded

Mineral Lithology	Ca-Amphibole		Ca-Amphibole		Ca-Amphibole		Ca-Amphibole		Ca-Amphibole		Ca-Amphibole	
	FB	S.D.	FB High-Al	S.D.	FB Low-Al	S.D.	White	S.D.	White High-Al	S.D.	White Low-Al	S.D.
SiO ₂	44.85	1.86	42.44	2.97	47.54	1.00	46.22	0.98	44.72	1.24	47.91	0.43
TiO ₂	1.26	0.15	1.28	0.25	1.19	0.16	1.23	0.13	1.30	0.12	1.06	0.09
Al ₂ O ₃	10.97	1.51	14.84	0.19	8.17	0.34	9.34	0.94	10.98	0.95	7.96	0.41
FeO	13.78	0.75	13.75	1.27	13.29	0.34	13.53	0.30	13.49	0.75	13.43	0.19
MnO	0.44	0.13	0.25	0.07	0.53	0.13	0.50	0.06	0.45	0.05	0.53	0.05
MgO	14.13	0.90	12.06	1.31	15.03	0.30	14.58	0.45	13.94	0.55	15.19	0.42
CaO	10.51	0.53	11.05	0.63	10.48	0.20	10.19	0.36	10.77	0.37	9.78	0.27
Na ₂ O	1.80	0.26	2.19	0.43	1.38	0.14	1.52	0.17	1.77	0.14	1.30	0.10
K ₂ O	0.14	0.04	0.18	0.05	0.09	0.02	0.13	0.02	0.12	0.03	0.11	0.02
P ₂ O ₅	0.02	0.02	—	—	—	—	0.01	0.02	—	—	—	—
Cr ₂ O ₃	0.02	0.03	0.00	0.00	0.01	0.01	0.01	0.02	0.00	0.01	0.01	0.01
BaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SrO	0.01	0.02	0.02	0.03	0.01	0.02	0.01	0.02	0.02	0.04	0.02	0.02
SO ₂	0.01	0.01	—	—	—	—	0.01	0.00	—	—	—	—
Cl	0.05	0.02	0.05	0.03	0.05	0.01	0.06	0.01	0.05	0.01	0.06	0.00
F	0.10	0.11	0.05	0.12	0.15	0.17	0.13	0.14	0.22	0.18	0.17	0.17
NiO	—	—	—	—	—	—	—	—	—	—	—	—
CuO	—	—	—	—	—	—	—	—	—	—	—	—
V ₂ O ₃	—	—	—	—	—	—	—	—	—	—	—	—
Total	98.06		98.13		97.90		97.46		97.81		97.50	

7 — = not measured
8 FB = flow-banded

9

10

Mineral Lithology	Plagioclase All	S.D.	Plagioclase FB	S.D.	Plagioclase White	S.D.	Plagioclase Yellow	S.D.	Plagioclase FB High-Ca	S.D.	Plagioclase FB Low-Ca	S.D.	Plagioclase White High-Ca	S.D.	Plagioclase White Low-Ca	S.D.
SiO ₂	52.88	3.50	52.40	3.63	53.26	3.51	53.76	3.01	46.18	0.68	57.65	0.55	48.13	1.05	57.45	0.82
TiO ₂	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.02	0.00	0.00	0.03	0.02	0.00	0.00	0.01	0.01
Al ₂ O ₃	30.13	2.32	30.68	2.39	29.41	2.02	29.33	2.01	34.87	0.36	27.26	0.54	32.17	0.75	27.20	0.76
FeO	0.38	0.16	0.42	0.17	0.35	0.13	0.29	0.10	0.59	0.10	0.22	0.05	0.39	0.16	0.25	0.10
MnO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.03	0.02	0.02	0.02	0.02
MgO	0.02	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.00	0.02	0.01
CaO	12.25	2.64	12.65	2.74	11.80	2.60	11.61	2.31	17.26	0.42	8.60	0.47	15.81	0.94	8.87	0.60
Na ₂ O	4.55	1.56	4.39	1.63	4.71	1.58	4.84	1.37	1.59	0.14	6.66	0.23	2.38	0.48	6.44	0.33
K ₂ O	0.06	0.04	0.06	0.04	0.07	0.04	0.07	0.03	0.02	0.01	0.12	0.01	0.03	0.02	0.11	0.01
P ₂ O ₅	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01	—	—	—	—	0.01	0.01	—	—
Cr ₂ O ₃	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	—	—
BaO	0.01	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.02	0.03	0.02	0.02	—	—
SrO	0.10	0.06	0.09	0.05	0.09	0.09	0.11	0.05	0.07	0.04	0.10	0.05	0.07	0.05	—	—
SO ₂	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Cl	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.01
F	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.10
NiO	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CuO	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
V ₂ O ₃	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Total	100.51		100.87		99.89		100.15		100.68		100.76		99.07		100.47	

11 — = not measured
12 FB = flow-banded

Mineral Lithology	Plagioclase		Plagioclase		Apatite		Apatite		Apatite		Ilmenite		Magnetite		CPX	Olivine
	Yellow	S.D.	Yellow	S.D.	All	S.D.	All	S.D.	All	S.D.	All	S.D.	All	S.D.	Yellow	White
	High-Ca		Low-Ca				Low-OH		High-OH							
SiO ₂	49.44	0.32	56.78	0.84	0.17	0.10	0.12	0.01	0.25	0.05	0.05	0.09	0.12	0.22	52.38	39.76
TiO ₂	0.01	0.02	0.03	0.03	0.01	0.02	0.02	0.02	0.01	0.01	29.69	0.64	4.97	0.34	0.26	0.01
Al ₂ O ₃	32.24	0.93	27.15	0.84	0.18	0.09	0.18	0.10	0.23	0.02	0.41	0.03	2.55	0.24	2.63	0.03
FeO	0.36	0.08	0.29	0.06	0.52	0.12	0.48	0.02	0.53	0.18	64.08	0.80	84.80	1.04	4.88	13.59
MnO	0.03	0.02	0.01	0.02	0.37	0.05	0.39	0.02	0.28	0.08	0.41	0.04	0.72	0.05	0.10	0.21
MgO	0.02	0.02	0.02	0.01	0.05	0.09	0.05	0.10	0.00	0.00	1.07	0.17	1.18	0.12	16.30	46.07
CaO	15.01	0.15	9.00	0.56	53.85	0.68	54.05	0.48	54.09	0.41	—	—	—	—	21.90	0.16
Na ₂ O	2.99	0.22	6.20	0.37	0.15	0.13	0.13	0.02	0.40	0.49	—	—	—	—	0.25	0.01
K ₂ O	0.03	0.01	0.11	0.01	0.01	0.01	0.00	0.00	0.01	0.01	—	—	—	—	0.00	0.01
P ₂ O ₅	0.01	0.01	0.01	0.01	41.08	0.61	41.40	0.33	40.92	0.25	—	—	—	—	0.03	0.01
Cr ₂ O ₃	0.01	0.01	—	—	—	—	—	—	—	—	0.01	0.01	0.02	0.03	—	—
BaO	0.00	0.00	—	—	0.01	0.02	0.03	0.04	0.00	0.01	—	—	—	—	—	—
SrO	0.10	0.02	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SO ₂	0.00	0.00	0.01	0.01	0.24	0.12	0.22	0.04	0.37	0.13	0.01	0.01	0.01	0.01	0.00	0.00
Cl	0.01	0.00	0.01	0.01	1.90	0.19	2.00	0.11	1.32	0.17	—	—	—	—	0.00	0.00
F	0.00	0.00	0.03	0.07	0.97	0.16	1.30	0.10	0.67	0.12	—	—	—	—	0.03	0.07
NiO	—	—	—	—	—	—	—	—	—	—	0.01	0.01	0.01	0.01	—	—
CuO	—	—	—	—	—	—	—	—	—	—	0.00	0.01	0.00	0.01	—	—
V ₂ O ₃	—	—	—	—	—	—	—	—	—	—	0.39	0.43	0.23	0.10	—	—
Total	100.26		99.65		99.52		100.38		99.09		96.14		94.61		98.77	99.92

14

15

— = not measured

FB = flow-banded

1 **Table 4: a) Representative silicic melt inclusion compositions b) Representative mafic melt inclusion compositions**

a) Host Mineral Lithology Sample	Quartz Yellow Y3-MI1	Quartz FB 13-30_8	Quartz White W3- MI7	OPX Yellow 13-49_6b	OPX FB 13-27_13b	OPX White 13-17_2	Plag Yellow 13-11_5	Plag FB FB3-MI3	Plag White W2-MI3	Ca-Amph FB 12-03-I	Ca-Amph White 12-13_1b
SiO ₂	72.66	72.55	72.49	71.14	71.94	71.71	73.28	73.49	74.25	71.04	71.93
TiO ₂	0.12	0.13	0.13	0.16	0.14	0.14	0.16	0.17	0.19	0.14	0.15
Al ₂ O ₃	12.35	12.28	12.82	13.36	13.02	13.46	12.36	12.08	12.31	14.86	15.16
FeO	1.03	1.17	1.18	1.57	1.16	0.82	1.60	1.56	1.38	1.36	1.36
MnO	0.12	0.13	0.12	0.13	0.11	0.11	0.12	0.16	0.13	0.05	0.07
MgO	0.38	0.33	0.37	0.26	0.15	0.11	0.57	0.53	0.59	0.15	0.15
CaO	1.67	1.63	1.64	2.08	1.99	2.05	1.65	1.28	1.46	3.67	2.57
Na ₂ O	3.79	4.34	4.18	4.26	4.13	4.51	4.41	4.22	4.74	5.03	5.75
K ₂ O	1.52	1.49	1.58	1.23	1.35	1.25	1.49	1.52	1.57	1.09	1.26
P ₂ O ₅	0.08	0.05	0.07	0.05	0.06	0.09	0.08	0.05	0.09	0.16	0.08
SO ₂	0.02	0.02	0.03	0.02	0.04	0.04	0.02	0.02	0.02	0.01	0.01
Cl	0.20	0.20	0.22	0.21	0.17	0.14	0.23	0.28	0.29	0.25	0.22
F	0.00	0.00	0.00	0.17	0.03	0.00	0.00	0.00	0.25	0.00	0.05
Total	93.94	94.32	94.83	94.64	94.30	94.42	95.97	95.37	97.27	97.82	98.77

*FB = flow-banded

b)

Host Mineral	CPX	Olivine
Lithology	Yellow	White
Sample	13-32_1c	13-22_2
SiO ₂	51.84	45.83
TiO ₂	0.79	0.99
Al ₂ O ₃	17.22	18.11
FeO	10.09	6.32
MnO	0.17	0.14
MgO	4.14	4.13
CaO	8.44	11.78
Na ₂ O	2.90	2.49
K ₂ O	0.54	0.38
P ₂ O ₅	0.22	0.14
SO ₂	0.24	0.75
Cl	0.32	0.26
F	0.00	0.00
Total	96.90	91.32

1 **Table 5: Comparison of derived 2-oxide temperatures and log oxygen fugacities relative to that of NNO**
2 **buffer. n is number of pairs averaged to reach representative results.**

	Yellow Pumice	Flow Banded Pumice	White Pumice
Temperature (°C)			
QUILF*	803	830	799
<i>min.</i>	794	802	794
<i>max.</i>	816	856	803
<i>s.d</i>	8	22	3
G&E, 2008	765	827	759
<i>min.</i>	760	778	748
<i>max.</i>	778	886	765
<i>s.d</i>	7	48	6
f_{O_2} (ΔNNO)			
QUILF	2.36	2.16	2.40
<i>min.</i>	2.29	1.99	2.38
<i>max.</i>	2.39	2.30	2.46
<i>s.d</i>	0.04	0.15	0.03
G&E, 2008	1.54	1.47	1.56
<i>min.</i>	1.52	1.36	1.54
<i>max.</i>	1.55	1.57	1.59
<i>s.d</i>	0.01	0.10	0.02
<i>n</i>	5	5	8

3 *QUILF is known to overestimate temperature at high oxygen fugacities; temperatures reported here for
4 QUILF have been adjusted down by 30°C following Larsen et al. (2010)

1 **Table 6: H₂O and CO₂ contents of melt inclusions.**

Melt inclusion ID	Host mineral	Lithology	H₂O (wt%)	CO₂ (ppm)
13-28-12	Ca-amph	FB	4.87	88
13-31-2	Ca-amph	FB	2.62	116
13-06-1	Ca-amph	FB	3.39	48
13-19-11	plag	FB	3.93	16
13-31-3	opx	FB	4.33	97
13-31-13b	qtz	FB	4.25	24
13-31-13c	qtz	FB	2.00	224
13-11-5	plag	Y	5.69	84
12-06-4	plag	Y	4.52	59
13-11-4	plag	Y	5.56	706
13-21-8	plag	Y	5.18	768
13-33-3	opx	Y	3.69	1385
13-46-2	opx	Y	5.81	144
13-49-6a	opx	Y	5.94	501

2
3 ***FB = flow-banded, Y = yellow**
4

Table 7: Summary of magma chamber parameters derived from geochemistry of the three rhyolitic lithologies. References for methods column include: Ghiorso and Evans (2008) for Fe-Ti oxides; Ridolfi et al. (2010) and Ridolfi and Renzulli (2012) for calcic amphiboles, with the exception of those marked with *, which were determined via Anderson and Smith (1995); Geschwind and Rutherford (1992) and Gardner et al. (1995) for cummingtonite; Holland and Blundy (1994) for calcic amphibole/plagioclase pairs; Newman and Lowenstern (2002) for melt inclusions; and Gualda and Ghiorso (2014) for glasses via MELTS-Excel.

Parameter	Method	Yellow	White	Flow-banded
f_{O_2} (ΔNNO)	Fe-Ti oxides	1.52-1.55	1.54-1.59	1.36-1.57
	Calcic amphibole	—	1.02-1.89	0.54-2.02
T	Fe-Ti oxides	760-777°C	748-765°C	778-886°C
	Cummingtonite	<790-800°C	<790-800°C	<790-800°C
	Calcic amphibole	—	~830-940°C	820-990°C
	Calcic amphibole/plagioclase	—	845°C	810-900°C
P	Cummingtonite	~250-330 MPa	~250-330 MPa	~250-330 MPa
	Calcic amphibole	—	145-408 MPa	140-700 MPa
	Calcic amphibole*	—	137 MPa	64-315 MPa
	Melt inclusions	~130-260 MPa	—	~70-150 MPa
$P_{Ca-amph}$	MELTS-Excel	—	—	349-422 MPa
P_{opx}	MELTS-Excel	340-370 MPa	340-348 MPa	276-351 MPa
P_{fsp}	MELTS-Excel	213-303 MPa	175-278 MPa	180-266 MPa
P_{qtz}	MELTS-Excel	—	—	240-328 MPa
P_{matrix}	MELTS-Excel	189-266 MPa	171-276 MPa	192-280 MPa
$X_{H_2O}^{fluid}$	Cummingtonite	>0.7	>0.7	>0.7
	Melt inclusions	0.4-1	—	~1
H ₂ O	Calcic amphibole	—	~6-8.3 wt%	~6-10 wt%
	Melt inclusions	4.5-6 wt%	—	2-5 wt%
CO ₂	Melt inclusions	~100-1400 ppm	—	~25-200 ppm

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8 (PRINT)

Figure 8 (ONLINE)

Figure 9

Figure 10

Figure 11 (PRINT)

Figure 11 (ONLINE)

Figure 12 (PRINT)

Figure 12 (ONLINE)

Figure 13

Figure 14