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The Permeability Evolution of Tuffisites and Implications for Outgassing Through Dense Rhyolitic Magma

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Key Points:
- Permeability of variably sintered tuffisites from Chaitén and Cordón Caulle is between 10^{-16} and 10^{-15} m^2
- Surface tension and compaction-driven sintering timescales are between 2 min and 13.6 h and between 3.5 s and 5 min, respectively
- Inferred timescales of sintering-driven tuffisite compaction coincide with observed vent pulsations during hybrid rhyolitic activity

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Abstract There is growing evidence that outgassing through transient fracture networks exerts an important control on conduit processes and explosive-effusive activity during silicic eruptions. Indeed, the first modern observations of rhyolitic eruptions have revealed that degassed lava effusion may depend upon outgassing during simultaneous pyroclastic venting. The outgassing is thought to occur as gas and pyroclastic debris are discharged through shallow fracture networks within otherwise low-permeability, conduit-plugging lava domes. However, this discharge is only transient, as these fractures become clogged and eventually blocked by the accumulation and sintering of hot, melt-rich pyroclastic debris, drastically reducing their permeability and creating particle-filled tuffisites. In this study we present the first published permeability measurements for rhyolitic tuffisites, using samples from the recent rhyolitic eruptions at Chaitén (2008–2009) and Cordón Caulle (2011–2012) in Chile. To place constraints on tuffisite permeability evolution, we combine (1) laboratory measurements of the porosity and permeability of tuffisites that preserve different degrees of sintering, (2) theoretical estimates on grainsize- and temperature-dependent sintering timescales, and (3) H_2O diffusion constraints on pressure-time paths. The inferred timescales of sintering-driven tuffisite compaction and permeability loss, spanning seconds (in the case of compaction-driven sintering) to hours (surface tension-driven sintering), coincide with timescales of diffusive degassing into tuffisites, observed vent pulsations during hybrid rhyolitic activity (extrusive behavior coincident with intermittent explosions), and more broadly, timescales of pressurization accompanying silicic lava dome extrusion. We discuss herein the complex feedbacks between fracture opening, closing, and sintering and their role in outgassing rhyolite lavas and mediating hybrid explosive-effusive activity.

1. Introduction

Unprecedented observations of recent subaerial rhyolite eruptions in Chile have demonstrated that effusive extrusion of rhyolitic lava can be coincident with intermittent explosions of ash, lapilli, and bombs (Castro et al., 2014; Lara, 2009; Schipper et al., 2013). Such hybrid activity demands reappraisal of existing paradigms of eruptive style transitions (Eichelberger et al., 1986) and highlights that outgassing mechanisms are of critical importance (e.g., Chevalier et al., 2017; Collinson & Neuberg, 2012; Farquharson et al., 2017; Gonnermann & Manga, 2003; Kushnir et al., 2017; Ryan et al., 2019). Chaitén volcano (Chile) exhibited prolonged hybrid activity in 2008 (Castro et al., 2014), whereas longer-lived hybrid (nine months) activity occurred at Cordón Caulle (also in Chile) during 2011–2012 (Schipper et al., 2013). In both cases pulsatory pyroclastic discharge occurred from fractures in vent-filling lava (Figure 1), a process now believed to have accompanied ancient silicic lava dome eruptions in other localities (e.g., Black et al., 2016). For example, the photograph taken during the 10 January 2012 activity at Cordón Caulle ($t = +4$ s) shows that localized outgassing occurred via pathways with fracture (i.e., plane) geometries (Figure 1a), rather than outgassing through permeable foam (e.g., Eichelberger et al., 1986). Indeed, recent experimental work by Ryan et al. (2019) has shown that it is difficult to create permeability in initially impermeable, high-porosity foams, describing them as "persistently impermeable." Dense obsidian bombs emitted during hybrid activity characteristically hosted tuffisites, which are centimetric fractures infilled with pyroclastic material (Castro et al., 2012; Heiken et al., 1988; Saubin et al., 2016; Stasiuk et al., 1996; Tuffen et al., 2003; Figure 2a). Tuffisites

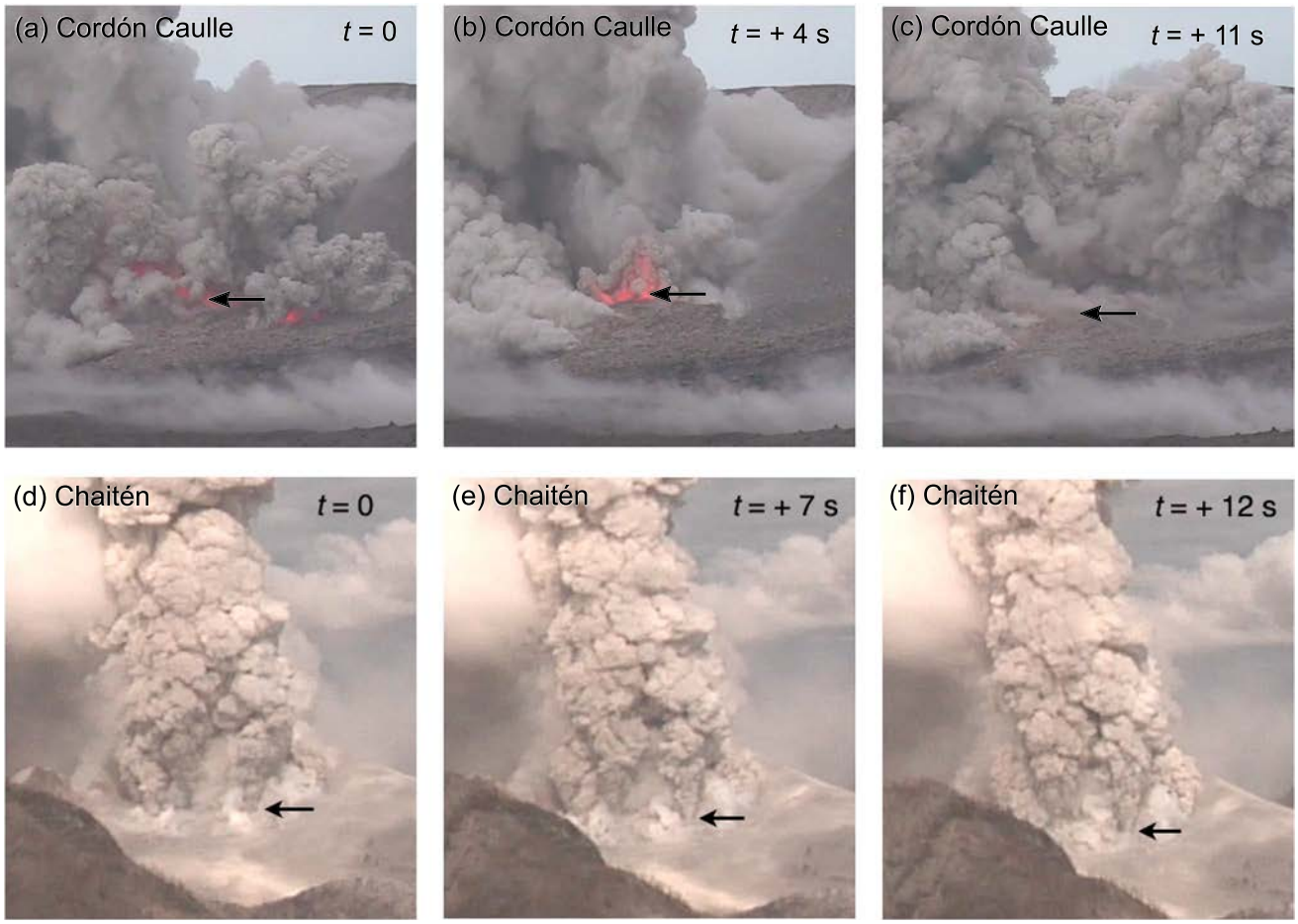

Figure 1. Explosive ash venting at (a) Cordón Caulle (10 January 2012) and (b) Chaitén (10 May 2008): (a) $t = 0$ ash venting from a newly opened fracture (indicated by the arrow); $t = 4$ ash venting reaches a climax; and $t = 11$ ash venting from the fracture has stopped, highlighting the transient, pulsatory nature of the process. See also Schipper et al. (2013). (b) The time-stamped Chaitén frames illustrate the formation of a funnel shaped ash jet indicated by the arrow (scale 100 m). This jet is one of many pyroclastic vents that emanate from a lava plug that will days later form a voluminous obsidian dome.

have been interpreted to record the transient opening and occlusion of the permeable pathways that provide fleeting escape routes for pressurized gas prior to eventual blockage and violent ejection (Saubin et al., 2016). H_2O concentration gradients at the tuffisite-host rock interface (Berlo et al., 2013; Castro et al., 2012) and within fracture-filling clasts (Saubin et al., 2016) provide constraints on tuffisite depths (hundreds of meters), timescales of fracture opening (tens of minutes to several hours), and gas pressure changes associated with fracture opening (reductions of up to several MPa).

Modeling approaches (e.g., Collinson & Neuberg, 2012; Diller et al., 2006) and field measurements (e.g., Stix et al., 1993) have shown a low-permeability magmatic plug in the upper conduit can render outgassing ineffective, promoting gas accumulation and pressurization (a "closed system"). More recent modeling by Chevalier et al. (2017) has shown that although the dome can increase the pressure on the system and reduce gas loss at the conduit walls, the permeability of the conduit walls is of greater importance that the permeability of the dome in controlling gas loss and pressurization. In the case of a "closed system," the initially highly permeable fracture networks, thought to be ultimately recorded as tuffisites, must play a key role in mediating gas release and pressurization cycles. Recent modeling by Farquharson et al. (2017), focused on the time-dependent permeability evolution of compacting fractured volcanic systems, defined three regimes: (1) an "outgassing" regime, where pore pressure does not increase during compaction; (2) a "diffusive relaxation" regime, where the ongoing reduction in porosity is compensated by the molecular diffusion of water; and

Figure 2. (a) Photograph of a large bomb in the crater of the 2008 Chaitén eruption containing a tuffisite (the parent of the BTB block). The BTB tuffisite is 30 mm wide with remarkably planar walls. It is connected to a network of sub-millimeter subsidiary tuffisites in the dense obsidian host material (Saubin et al., 2016). (b) Photograph of the decametric breadcrust bomb from the June 2011 hybrid activity at Cordón Caulle. (c) Photograph of a 20-mm-diameter cylindrical sample of tuffisite CH5F (Chaitén). (d) Photograph of a 20-mm-diameter cylindrical sample of tuffisite BTB (Chaitén). (e) Photograph of a 10-mm-diameter cylindrical sample of tuffisite CH5G (Chaitén). (f) Photograph of a 20-mm-diameter cylindrical sample of tuffisite B1 (Cordón Caulle).

(3) a "pore pressure increase" regime, where Darcian or diffusive processes cannot compensate for the porosity reduction and pore pressure builds. As improved modeling of conduit dynamics requires better constraints on the temporal evolution of tuffisite permeability, recent work has addressed the porosity and permeability of variably sintered pyroclastic material (Gardner et al., 2018; Heap et al., 2014, 2015; Kendrick et al., 2016; Kolzenburg & Russell, 2014; Okumura & Sasaki, 2014; Ryan, Friedlander, et al., 2018; Ryan, Russell, et al., 2018; Vasseur et al., 2013) and provided models of compaction and viscous sintering (i.e., the agglutination of glassy particles held at or above their corresponding glass transition temperature; Farquharson et al., 2017; Russell & Quane, 2005; Wadsworth et al., 2014; Wadsworth, Vasseur, Scheu, et al., 2016; Wadsworth, Vasseur, Llewellin, et al., 2016; Wadsworth, Vasseur, Llewellin, & Dingwell, 2017). These recent data and modeling provide a blueprint for placing firmer constraints on permeability evolution within volcanic conduits.

We present herein porosity and permeability measurements for tuffisites hosted within dense obsidian bombs ejected from recent rhyolitic eruptions at Chaitén (2008–2009) and Cordón Caulle (2011–2012). These data, which represent the first permeability measurements of rhyolite-hosted tuffisites, are combined with models for viscous sintering and pressure timescale constraints from H_2O diffusion gradients to provide a detailed description of tuffisite permeability evolution and thus explore the role of fracture-assisted outgassing within shallow silicic conduits.

2. Anatomy of a Tuffisite

Three rhyolitic tuffisites (CH5F, BTB, and CH5G) hosted within decametric dense obsidian bombs that were ejected during hybrid activity in May 2008 at Chaitén volcano (an example is provided as Figure 2a) and found within the pyroclastic density current deposits about 800 m from the 2008–2009 vent were selected for this study. Several field campaigns at Chaitén volcano have highlighted that bombs on the crater rim and flanks commonly host tuffisites. The width of these tuffisites typically ranged from a couple of millimeters up to a few tens of millimeters. The tuffisites within these bombs comprise poorly sorted and variably sintered angular fragments of dense obsidian, pumice, and lithics within a fine ash grade matrix (Figure 2a). The three samples chosen for this study were selected because of visible differences in density/porosity (photographs of core samples prepared from these three tuffisites are provided as Figures 2c–2e), suggesting underlying differences in their degree of sintering. As a result, we consider that these samples provide snapshots in time of the viscous sintering process. We complement these samples with a tuffisitic bomb fragment from Cordón Caulle, part of a decametric breadcrust bomb found 1.5 km NW of the vent (Figure 2b). The bomb was ejected between 7 and 15 June 2011, as the vent constricted prior to and during the onset of lava effusion and thus hybrid activity. It comprises glassy, tuffisitic material that has partly vesiculated after fragmentation, with inflation of the largest, most volatile-rich clasts (Figures 2b and 2f).

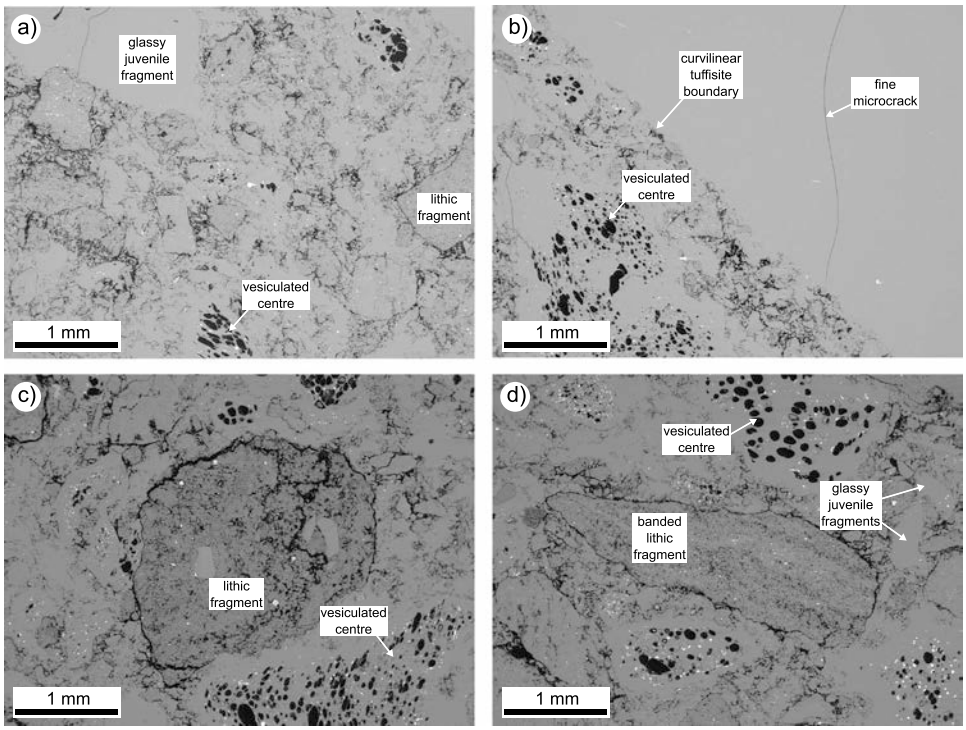

Figure 3. Backscattered scanning electron microscope images of the BTB tuffisite. The images show that the BTB tuffisite contains mixture of ash- and lapilli-sized juvenile and lithic fragments. Some of the juvenile fragments have vesiculated centers (a–d). Lithic clasts (rhyolite fragments) can be rounded (c) or banded/angular (d). Panel (b) shows that the tuffisite-host rock boundary is curvilinear on the microscale.

Backscattered scanning electron microscope images of the four tuffisites were collected using a Tescan Vega 2 XMU system, and representative tuffisite textures are shown in Figures 3 and 4. The tuffisites comprise a similar population of ash- and lapilli-sized juvenile and lithic fragments (Figures 3 and 4). The juvenile fragments within the tuffisites are glassy and often angular, but their edges can be rounded or diffuse, depending on the degree of viscous sintering. For example, the sintering of juvenile clasts in sample CH5F is sufficiently advanced that it is difficult to distinguish individual fragments (Figures 4a and 4b), with remaining porosity preferentially located at the margins of lithic clasts (Figure 4b). Viscous sintering is least well developed in sample CH5G, with individual glassy juvenile fragments often easily identifiable (Figure 4c and 4d). Indeed, the matrix porosity is noticeably higher in the CH5G sample than the other three samples and is not restricted to lithic clast margins (Figure 4c and 4d). Individual glassy particles in sample B1 appear rounded and are only distinguishable because of the interstitial pore space, which has been compacted and deformed (Figure 4f).

Some juvenile clasts in the BTB (Figure 3), CH5G (Figure 4d), and B1 (Figures 4e and 4f) samples have vesiculated centers leading to a frothed appearance. Quantification of vesicle size distributions and H_2O concentrations in sample BTB (Saubin et al., 2016) has facilitated a detailed reconstruction of the relative timing of clast vesiculation and fracture opening, together with the evolution of gas pressure in the system. Results show that, for sample BTB, the strongly vesiculated clasts had vesiculated prior to their incorporation into the fracture by pressurized gas from deeper in the conduit. However, it is likely that the common vesiculated juvenile clasts in sample B1 (Figure 4e) have predominantly vesiculated after bomb ejection. Vesiculated juvenile clasts are rare in sample CH5F (Figures 4a and 4b).

Lithic fragments in these tuffisites can be angular, but they are often subrounded (Figures 3 and 4). Most lithics are rhyolite fragments that are banded and microporous with cristobalite and minor plagioclase phases protruding into pore spaces (Figures 3 and 4). Finally, we highlight that the boundary

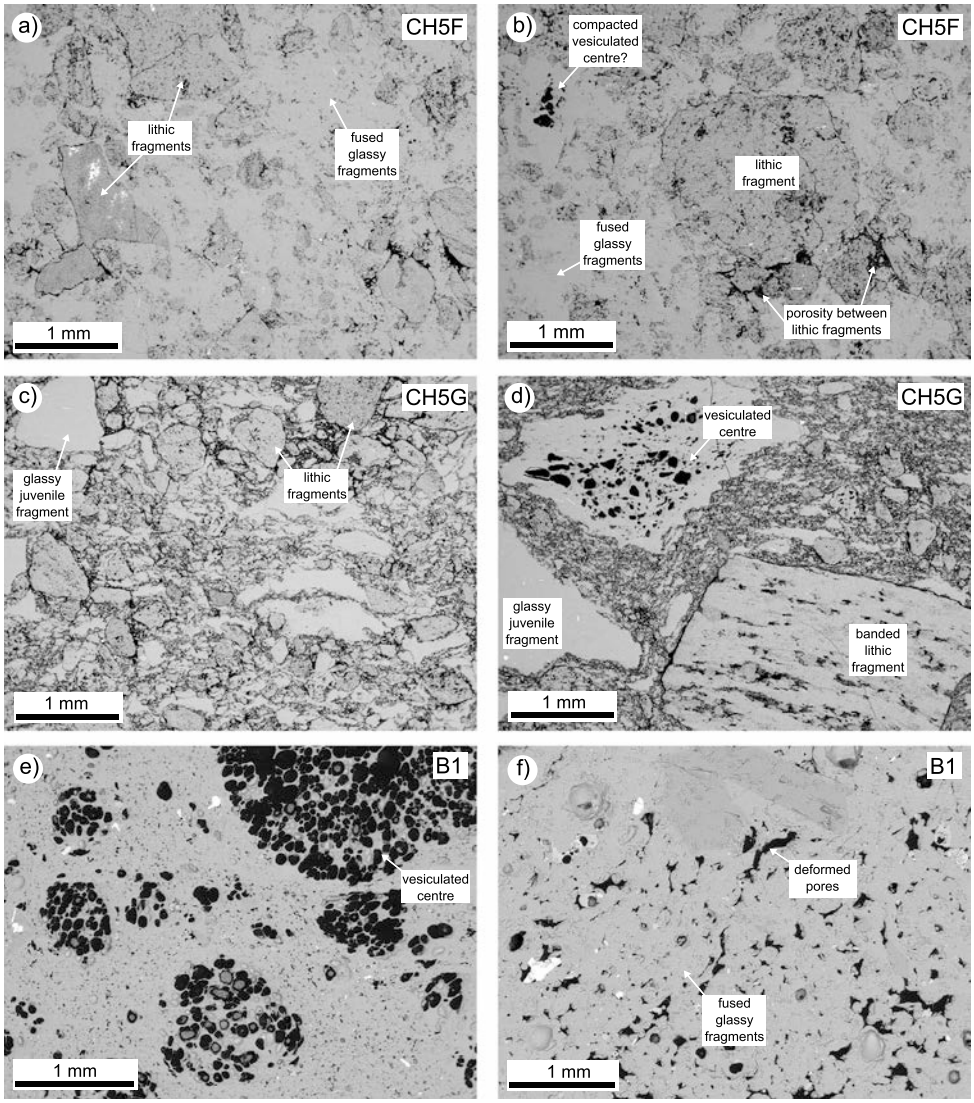

Figure 4. Backscattered scanning electron microscope images of the CH5F (a, b), the CH5G (c, d), and the B1 (e, f) tuffisites. The images show that the tuffisites contain mixture of ash- and lapilli-sized juvenile and lithic fragments. Lithic clasts (rhyolite fragments) can be rounded (b and c) or banded/angular (a and d). Juvenile fragments with vesiculated centers can be seen in samples CH5G (d) and B1 (e), but are rare in sample CH5F (b). Glassy fragments are angular in sample CH5G (c, d), have diffuse boundaries in sample CH5F (a, b), and appear rounded in sample B1 (f).

between the tuffisite and the obsidian host rock is curvilinear on the microscale (Figure 3b). Further details on the clast population within the BTB tuffisite, including grainsize distribution and componentry, and the relationship between the timing of fracture opening and clast vesiculation, can be found in Saubin et al. (2016).

3. Experimental Methods

Cylindrical samples (either 20 or 10-mm diameter) of the tuffisitic material were cored from each bomb. Samples were cored such that their axis is parallel to the fracture plane, so as to maximize the number of samples extracted from each of the blocks collected (see inset on Figure 2a). Samples from the Cordón Caulle bomb were prepared to avoid large vesiculated fragments and the approximately decameter-spaced cooling contraction fractures associated with breadcrusting (see Figure 2b). We also prepared a 20-mm-diameter sample of the dense obsidian host rock from the BTB bomb. These samples were precision

ground to lengths of 30–40 mm (for the 20-mm-diameter samples) or 20–40 mm (for the 10-mm-diameter samples) and dried for a minimum of 48 hr inside a vacuum oven at 40 °C. All samples were prepared such that their length-diameter ratio is greater than one. Recent experiments by Heap (2019) highlighted that reliable laboratory measurements of permeability are possible on small cores (e.g., 10-mm-diameter cores) as long as the pore/grain size is small with respect to the core dimensions.

The connected porosity and permeability was then measured for each cylindrical sample. The connected porosity of each sample was calculated using the bulk volume of the sample (calculated using the sample dimensions) and the skeletal (i.e., connected) volume given by a Micromeritics AccuPyc II 1340 helium pycnometer. The total porosity of each sample was determined using the solid density of each block (measured using a hand-powdered aliquot of each sample and the helium pycnometer) and the bulk sample density of each cylindrical sample (calculated using the mass and dimensions of each sample). The isolated porosity of each sample could then be determined by subtracting the connected porosity from the total porosity. Permeability was measured using a gas (argon or nitrogen) permeameter following the operating procedure given in Farquharson et al. (2016) and Heap and Kennedy (2016). Permeability was measured under a confining pressure of 1 MPa (a confining pressure is needed to ensure that the gas travels through the sample, rather than between the jacket and the sample edge) using the steady state method. The permeability of a sample of BTB was also measured under confining pressures up to 10 MPa to cover the range of pressures inferred during tuffisite formation (equivalent to 400- to 500-m lithostatic; Castro et al., 2014; Saubin et al., 2016) and using the same procedure described above.

To measure permeability, the volumetric flow rate, Q_v (in m^3/s) was measured using a gas flowmeter for several different pressure differentials, ΔP (we define ΔP as the upstream pore fluid pressure, P_u [in Pa], minus the downstream pore fluid pressure, P_d [in Pa]). In our permeameter setup, P_d is the atmospheric pressure (assumed to be 101,325 Pa). The Darcian permeability, k_D (in m^2), was then determined for each of the pressure differentials using the following relationship for compressible gas:

$$k_D = \frac{Q_v}{P_m \Delta P} \frac{\mu L P_d}{A}, \tag{1}$$

where μ is the pore fluid viscosity (viscosity of argon and nitrogen at 20 °C was taken as 2.22×10^{-5} and 1.76×10^{-5} Pa s, respectively; values taken from the National Institute of Standards and Technology, https://www.nist.gov/), A (in m^2) and L (in m) are the sample cross sectional area and the sample length, respectively, and P_m is the mean pore fluid pressure (i.e., $(P_u+P_d)/2$). We calculate k_D for a range of different pressure differentials (typically six) to assess whether fluid flow departs from Darican flow (i.e., equation (1)). We assume a constant pore fluid density and viscosity for our measurements, a valid assumption for the very low pressure differentials used in this study (the pressure differential never exceeded 0.5 MPa). Fluid flow can be complicated by gas slippage (the Klinkenberg effect; Klinkenberg, 1941) and/or by turbulence (the Forchheimer effect; Forchheimer, 1901). We first check whether a Forchheimer correction is needed. To do so, we plot $1/k_D$ for each pressure differential, ΔP, as a function of Q_v. If these data can be well described by a positive linear slope, the Forchheimer-corrected permeability k_{forch} is the inverse of the y intercept of the best fit linear regression of this relationship. If the Forchheimer correction is needed, it is then necessary to check whether the Klinkenberg correction is needed. To check whether the Klinkenberg correction is needed, we calculate k_{forch} for each pressure differential, ΔP, using the following relation:

$$\frac{1}{k_D} = \xi Q_v + \frac{1}{k_{\text{forch}}}, \tag{2}$$

where the slope of the plot of $1/k_D$ as a function of Q_v is given by ξ. The Klinkenberg correction is needed if the data on a plot of k_{forch} as a function of $1/P_m$ can be well described by a positive linear slope. If this is true, the permeability is the y intercept of the best fit linear regression of these data. If the data cannot be well described by a positive linear relationship, the permeability is the inverse of the y intercept of the best fit linear regression on the plot of $1/k_D$ as a function of Q_v (i.e., k_{forch}). If the Forchheimer correction is not needed, we assess the need for the Klinkenberg correction by plotting k_D as a function of $1/P_m$. If the data can well described by a positive linear slope, a Klinkenberg correction is required and the permeability is the y intercept of the best fit linear regression on the graph of k_D as a function of $1/P_m$. If no corrections are needed, the permeability is

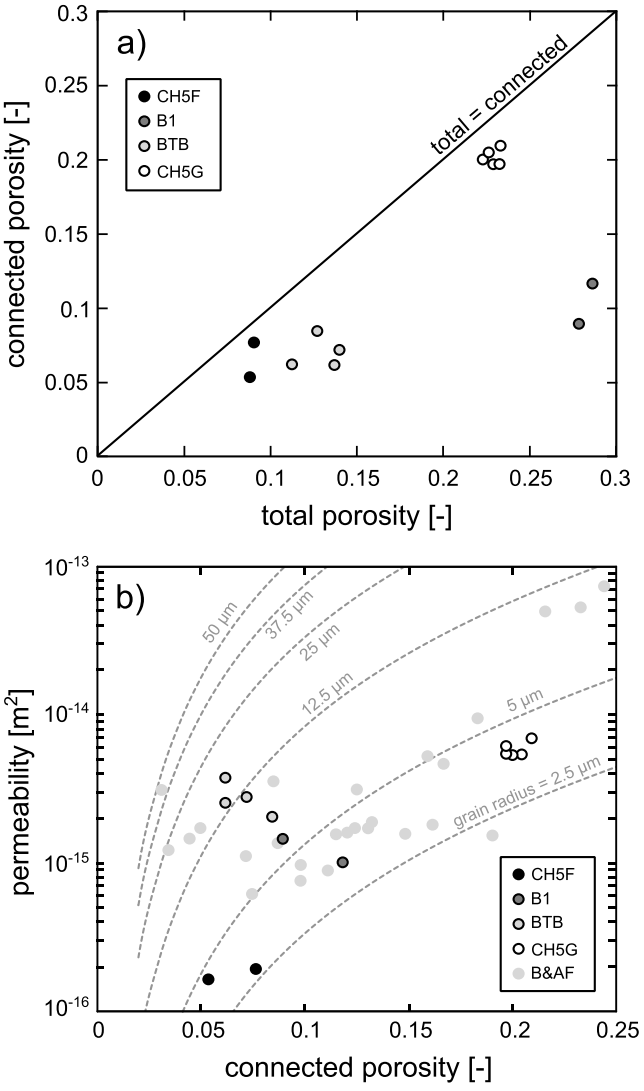

Figure 5. (a) Connected porosity as a function of total porosity for the four tuffisite samples (BTB, CH5F, CH5G, and B1). Measurement errors are smaller than the symbol size. (b) Permeability as a function of porosity for the four tuffisite samples (BTB, CH5F, CH5G, and B1). Measurement errors are smaller than the symbol size. Model curves (equation (5)) for a given initial particle radii are also provided as grey dashed lines (Wadsworth, Vasseur, Scheu, et al., 2016; see discussion for details). Data for variably sintered, granular volcanic material (welded block-and-ash flow; B&AF) from Heap et al. (2015) are plotted to provide a comparison (light grey circles).

taken as the positive slope of the plot of Q_v as a function the mean pore fluid pressure P_m multiplied by ΔP. These ancillary corrections were implemented on a case-by-case basis (we refer the reader to Heap, Reuschlé, Farquharson, et al., 2018, for examples). The values of the coefficient of determination (R^2) for the best fit regressions, when applied, were between 0.98 and 0.99, where a value of unity represents perfect agreement. A more detailed description of our permeability data analysis technique can be found in Heap et al. (2017).

To assess the size of the smallest pore apertures of a tuffisite, we performed mercury injection porosimetry on a piece (4.7 g) of the BTB sample using a Micromeritics Autopore IV 9500. The mercury equilibration time and filling pressure were 10 s and ~3,585 Pa, respectively. The evacuation time and evacuation pressure were 5 min and 50 µmHg, respectively. The pressure range was ~690 Pa up to ~414 MPa. Data from a mercury injection test were used to calculate the pore throat size distribution of the sample (ASTM D4404-10, 2010). We corrected the mercury injection data for the "low pressure correction," as recommended by the American Society for Testing and Materials (ASTM D4404-10, 2010).

The dissolved H_2O concentration was measured along a profile from the boundary of the tuffisite in the CH5G sample (position of the profile is shown on an inset in Figure 6c) using synchrotron source Fourier transform infrared spectroscopy at the Diamond Light Source (UK) MIRIAM beamline. A Hyperion 3000 microscope with a broadband MCT detector was coupled to a Bruker Vertex 80 V Fourier transform infrared spectroscopy interferometer with KBr beamsplitter. A 10-µm square aperture was used and 128 spectra were collected in transmission mode at 8 cm^{-1} spectral resolution between 4,000 and 1,000 cm^{-1}. Wafer thickness (average thickness of 90 µm) was measured using either a digital micrometer (precision ±3 µm) or by the reflection fringe method (von Aulock et al., 2014). Peak heights at 3,550 cm^{-1} (H_2O_t) and 1,630 cm^{-1} (H_2O_m) were determined using 18-point linear baseline corrections. Using the Beer-Lambert law, a glass density of 2,281 kg/m^3 (Saubin et al., 2016), and absorption coefficients of 80 l mol^{-1}/cm (3,550 cm^{-1}; Ihinger et al., 1994) and 55 l mol^{-1} cm (1,630 cm^{-1}; Newman et al., 1986; Okumura et al., 2003), we converted these data to species concentrations. The combined uncertainty of this method, which depends on the wafer thickness and density and the choice of molar absorption coefficient, is typically <10% (von Aulock et al., 2014). We compare these data with those already collected for the BTB sample (presented in Saubin et al., 2016) using the same technique.

4. Results

Connected porosity as a function of total porosity is shown in Figure 5a (data available in Table 1). The connected porosity of these tuffisites varies from ~0.05 to ~0.2 (Figure 5a and Table 1). All of the measured tuffisites contain isolated porosity. The three samples from Chaitén contain isolated porosities between ~0.01 and ~0.075, whereas the B1 sample from Cordón Caulle contains a very high isolated porosity of ~0.17–0.19 (Figure 5a and Table 1).

Permeability as a function of connected porosity is shown in Figure 5b (data available in Table 1). CH5G contains the largest connected porosity (~0.2) and has the largest permeability (~6×10^{-15} m^2). Although BTB and CH5F contain similar connected porosities (~0.07), BTB is approximately an order of magnitude more permeable (~3×10^{-15} m^2 compared to ~6×10^{-16} m^2; Figure 5b and Table 1). The connected porosity of B1 is larger (up to ~0.12) than both CH5G and BTB but has a permeability close to that of BTB (Figure 5b and

Table 1
Summary of the Porosity/Permeability Measurements Performed for This Study

Sample	Total porosity	Connected porosity	Isolated porosity	Confining pressure (MPa)	Pore fluid	Permeability (m^2)	Correction	Klinkenberg slip factor (MPa)	Average pore radius (μm)
BTB-01	0.127	0.085	0.042	1	Argon	2.04×10^{-15}	Klinkenberg	0.0365	0.75
BTB-01	0.127	0.085	0.042	2	Argon	1.93×10^{-15}	Klinkenberg	0.0375	0.73
BTB-01	0.127	0.085	0.042	4	Argon	1.84×10^{-15}	Klinkenberg	0.0385	0.71
BTB-01	0.127	0.085	0.042	6	Argon	1.80×10^{-15}	Klinkenberg	0.0385	0.71
BTB-01	0.127	0.085	0.042	8	Argon	1.77×10^{-15}	Klinkenberg	0.0390	0.70
BTB-01	0.127	0.085	0.042	10	Argon	1.73×10^{-15}	Klinkenberg	0.0390	0.70
BTB-02	0.140	0.072	0.068	1	Nitrogen	2.77×10^{-15}	Forchheimer	—	—
BTB-03	0.113	0.062	0.051	1	Nitrogen	2.54×10^{-15}	Forchheimer	—	—
BTB-04	0.137	0.062	0.075	1	Nitrogen	3.73×10^{-15}	Forchheimer	—	—
BTB-07	0	0	0	1	Nitrogen	0	—	—	—
CH5_F-01	0.090	0.077	0.014	1	Nitrogen	1.91×10^{-16}	None	—	—
CH5_F-02	0.088	0.054	0.034	1	Nitrogen	1.63×10^{-16}	None	—	—
CH5_G-01	0.232	0.197	0.035	1	Nitrogen	6.12×10^{-15}	Forchheimer	—	—
CH5_G-02	0.223	0.200	0.023	1	Nitrogen	5.33×10^{-15}	Forchheimer	—	—
CH5_G-03	0.226	0.205	0.022	1	Nitrogen	5.37×10^{-15}	Forchheimer	—	—
CH5_G-04	0.233	0.209	0.023	1	Nitrogen	6.87×10^{-15}	Forchheimer	—	—
CH5_G-05	0.229	0.197	0.031	1	Nitrogen	5.40×10^{-15}	Forchheimer	—	—
B1	0.286	0.118	0.170	1	Nitrogen	1.03×10^{-15}	Forchheimer	—	—
B1	0.278	0.090	0.189	1	Nitrogen	1.48×10^{-15}	Forchheimer	—	—

Note. Porosities quoted were measured at ambient laboratory pressure; the quoted confining pressure refers to the pressure used for the permeability measurements. Average pore radii were estimated using the Klinkenberg slip factor (see equation (4) and text for details).

Table 1). The porosity and permeability of the obsidian host were found to be within error of zero (Table 1). Data at elevated confining pressure show that tuffisite permeability does not change significantly up to 10 MPa (Figure 6a). The permeability of the BTB sample was reduced from 2.04×10^{-15} m^2 at a confining pressure of 1 MPa to 1.73×10^{-15} m^2 at a confining pressure of 10 MPa (Figure 6a and Table 1).

The data from the mercury injection experiment (Figure 6b) indicate that about 8% of the connected void volume is connected by pore throats that are >5 μm in radius, 72% of the connected void volume is connected by pore throats between 0.05 and 5 μm in radius, and 20% of the connected void volume is connected by pore throats <0.05 μm in radius.

In sample CH5F, the H_2O concentration is 0.46 wt.% at the tuffisite boundary and reaches a constant value of 1.04 wt.% at ~400 μm from the boundary (black symbols on Figure 6c). The H_2O concentration in the BTB sample (data from Saubin et al., 2016) is ~0.65 wt.% at the boundary of a vesicular clast and increases to ~0.9 wt.% at a distance of ~100 μm (grey symbols on Figure 6c).

5. Discussion

5.1. Isolated Porosity Within the Tuffisites

Our data show that the all of the measured tuffisites contain isolated porosity (Figure 5a and Table 1). The high isolated porosity of these samples is due to the presence of vesiculated juvenile clasts, which typically contain glassy rim with a porosity and therefore permeability of zero (Figures 3 and 4). Sample B1, from Cordón Caulle, contains abundant vesiculated juvenile clasts (Figures 4e and 4f) and, as a result, contains the largest isolated porosity of ~0.17–0.19 (Figure 5a and Table 1). Since the porosity in these clasts is isolated (encapsulated within a zero porosity glassy rim; Figures 3 and 4), it does not therefore contribute to the permeability of the samples.

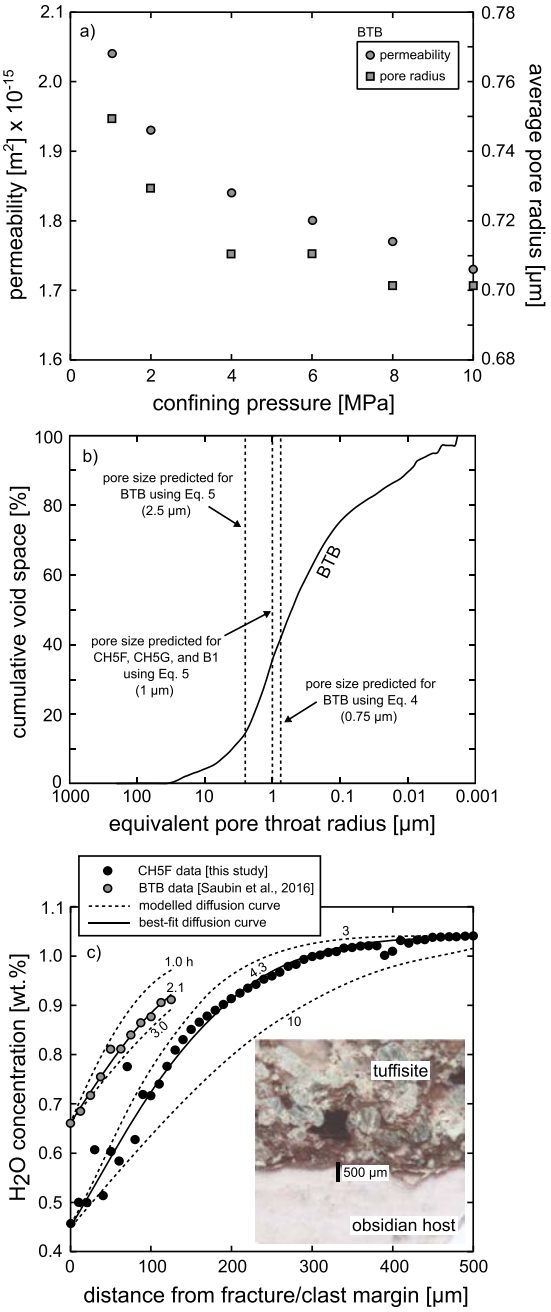

Figure 6. (a) Permeability as a function of confining pressure (up to 10 MPa) for a sample of BTB. Also shown is the average pore radius used by the gas molecules, as calculated using the Klinkenberg slip factor (equation (4); see discussion for details). (b) Pore throat size distribution (plot of cumulative void space as a function of pore throat diameter) determined using mercury porosimetry. The pore throat diameters determined using the Klinkenberg analysis (equation (4)) and the permeability modeling (equation (5)) are also indicated on the plot. (c) Measured spatial variation in H_2O from a clast margin for BTB (data from Saubin et al., 2016) and from the host rock obsidian for CH5F. Best-fit modeled 1-D diffusion curves (solid lines) are given for each dataset (number in hours; see discussion for details). We also provide neighboring modeled 1-D diffusion curves (dashed lines; number in hours; see discussion for details). Inset on panel (c) shows a photograph showing the location of the profile in sample CH5F. Images of the transect for the BTB sample can be found in Saubin et al. (2016).

5.2. Permeability Modeling: Pore and Grainsize Analyses

The collected porosity and permeability data can be interrogated to better understand (1) the average pore radius used by the gas molecules to travel through the tuffisite and (2) the particle size that likely controls the efficiency of viscous sintering.

First, we estimate of the average radius of the pores used by the gas molecules using the Klinkenberg slip factor, b (a calculation only possible for the data that required a Klinkenberg correction, see Table 1). Since the mean free path is inversely proportional to the mean pore fluid pressure, Poiseuille's law for gas flow in a cylindrical tube and Darcy's law for flow in a porous medium provide the following relation:

$$k_{\text{klink}} = k_D\left(1+\frac{b}{P_m}\right), \tag{3}$$

where k_{klink} is gas permeability corrected by the Klinkenberg correction (see section 3 for details). Assuming a cylindrical pore shape, the average pore radius a used by the gas molecules can then be estimated using the following relationship (Civan, 2010; Firouzi et al., 2014):

$$a = \frac{4}{b}\mu\sqrt{\frac{\pi R_g T}{2M_w}}, \tag{4}$$

where T is the temperature (293 K for room temperature laboratory conditions), M_w is the molar mass of the argon pore fluid (0.03995 kg/mol), and R_g is the ideal gas constant (8.31 J mol^{-1} K^{-1}). This method has been used to estimate the average pore radius of the flow path in shales (e.g., Firouzi et al., 2014; Heller et al., 2014; Letham & Bustin, 2016), volcanic rocks (Heap, Reuschlé, Farquharson, et al., 2018), and limestones (Heap, Reuschlé, Baud, & et al., 2018). We find an average pore radius of 0.75 μm for the BTB sample at a confining pressure of 1 MPa (Figure 6a). The average pore radius estimated using equation (4) is reduced only slightly (to 0.70 μm) when the confining pressure is increased to 10 MPa (Figure 6a). The average pore radius estimated using the Klinkenberg slip factor highlights the complexity of the flow path within the BTB tuffisite. For example, although 40% of the void space within the tuffisite is connected by pore throats with a radius greater than 1 μm (Figure 6b), the gas travels through narrow microstructural elements (with a radius <1 μm). Because the permeability and the average pore radius used by the gas do not vary considerably with pressure (Figure 6a), it is likely that these narrow microstructural elements are the tortuous intergranular pores characteristic of sintering systems (microcracks are easily closed as confining pressure is increased; e.g., Nara et al., 2011). These data therefore highlight that our measurements at 1 MPa are relevant for in situ tuffisites and that their compressibility is low even under relevant upper conduit pressures.

Wadsworth, Vasseur, Scheu, et al. (2016) provide a model for predicting first the characteristic lengthscale of the pore network, $1/s$, and second the permeability, k_D, of sintered granular materials for which the intergrain spaces are the pore network. The modeled permeability is given by (Wadsworth, Vasseur, Scheu, et al., 2016)

$$k_D = \frac{2[1-(\phi-\phi_c)]}{s^2}(\phi-\phi_c)^{\bar{e}}, \tag{5}$$

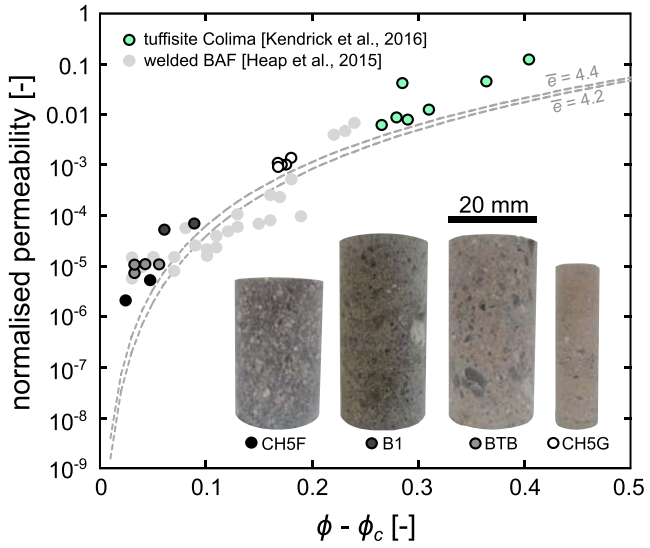

Figure 7. Normalized permeability (see text for details) as a function of $\phi - \phi_c$ (porosity minus the porosity of the percolation threshold at which the permeability can be considered zero, taken here as $\phi_c = 0.03$). The circles represent the experimental data (data unique to this study and data from Heap et al., 2015, and Kendrick et al., 2016) and collapse to a single permeability description consistent with $4.2<\bar{e}<4.4$ (the two grey dashed curves; see text for details).

where s is the specific surface area, that is, the ratio of pore surface area within the sample to the sample volume (in m^{-1}), ϕ_c is the porosity of the percolation threshold at which the permeability can be considered zero, and $\bar{e}$ is a percolation exponent. As noted by Wadsworth, Vasseur, Scheu, et al. (2016), this model has the appealing features that the permeability falls to zero as $\phi \rightarrow \phi_c$, and for all ϕ above ϕ_c, it has a power law dependence on ϕ, for which the exponent is $\bar{e}$, similar to theoretical constraints (Feng et al., 1987). Feng et al. (1987) constrained $\bar{e} = 4.4$ based on theoretical scaling, while empirical fits to a large range of data collected for variably welded granular rocks yield $\bar{e} = 4.2 \pm 0.3$ (Wadsworth, Vasseur, Scheu, et al., 2016). ϕ_c is typically around 0.03 for initially granular systems (Rintoul, 2000; Wadsworth, Vasseur, Llewellin, et al., 2016). The specific surface area is then related to the pore radius via $s = 3(1 - \phi)\ln(1 - \phi)/a$ assuming that the pore network can be approximated as a pack of overlapping spherical pores (see Torquato, 2013). Finally, the pore radius a is predicted at the initial packing porosity ($\phi_i = 0.5$) from the grainsize distribution, using the mean of the distribution R and the porosity after Torquato and Avellaneda (1991), with the full solution provided in Wadsworth, Vasseur, Scheu, et al. (2016). We then compare the modeled permeability curves (using equation (5)), solved for a range of mean grainsize R, with our porosity and permeability measurements for the tuffisite samples (Figure 5b). The measured porosity and permeability data are consistent with initial grain radii of $2.5 < R < 15$ μm (Figure 5). Although these inferred radii are small compared to the fragments readily identifiable in our microstructural work (Figures 3 and 4), they are consistent with previous measurements of the fine fraction that dominates the matrix in the BTB sample (Saubin et al., 2016). This range of predicted grainsizes is therefore likely to represent the grainsize that controls the efficiency of viscous sintering—a result of the inverse grainsize dependence of the sintering rate (Wadsworth et al., 2014). The grainsizes predicted using this approach are similar to those predicted for similar variably sintered, granular volcanic material (welded block-and-ash flow deposits, BAF, from Mt. Meager in Canada; data taken from Heap et al., 2015), shown as light grey circles in Figure 5b.

Next we use an empirical fitting procedure to predict the pore radii for each tuffisite. We assume that equation (5) is a valid description of the permeability as a function of the porosity and that $\bar{e} = 4.2$ and $\phi_c = 0.03$. We use the Excel Solver tool to minimize for a single controlling value of s for each sample and to assess the uncertainties that result using the method outlined in Kemmer and Keller (2010). This yields a fitted s that can be converted to a mean pore radius characteristic of flow through the sample using the above $s(a, \phi)$ result. The output is $a = 2.5 \pm 0.9$ μm for the BTB sample and $a = 1.0 \pm 0.4$ μm for the CH5F, CH5G, and B1 samples. This provides a natural method to normalize the permeability by $ks^2/(2[1 - (\phi - \phi_c)])$. In Figure 7 we demonstrate that this method results in a collapse of the data to a single permeability description that is consistent with both $4.2<\bar{e}<4.4$, as predicted by theory (Feng et al., 1987; Wadsworth, Vasseur, Llewellin, & Dingwell, 2017; Wadsworth, Vasseur, Scheu, et al., 2016). We also plot the welded block-and-ash flow data from Heap et al. (2015) and the data for tuffisites found on the dome of Volcán de Colima, an andesitic stratovolcano in Mexico (permeability measured using the TinyPerm II field permeameter; Kendrick et al., 2016). These data also collapse on our permeability description (Figure 7). Additionally, the pore radii resulting from this method (1–2.5 μm) are within a factor of 2 of those calculated from the Klinkenberg factor (0.7–0.75 μm) and within the range measured by mercury injection porosimetry (Figure 6b).

The above approach provides several methods for predicting the controlling lengthscales for fluid flow through samples of this type, including direct measurements. We have shown that use of equation (5) results in good collapse of the data (and data for other welded volcanic materials and tuffisites from Mt. Meager and Volcán de Colima, respectively; Figure 7) to a single dimensionless description, which lends confidence to the

generality of this model. We propose that this may be a useful tool for predicting the permeability decay of evolving tuffisites as they sinter and heal in silicic volcanoes.

5.3. H_2O Diffusion Modeling

Modeling the depletion in H_2O adjacent from the tuffisite-host rock boundary, or from the boundary of a vesicular clast within the tuffisite, provides an estimate of the time between fracture filling and final quenching (e.g., Castro et al., 2012). Our modeling of the H_2O diffusion profiles employed an error function solution to Fick's general diffusion equation cast in 1-D Cartesian coordinates for a constant diffusivity (after Crank, 1979):

$$\frac{c_x - c_b}{c_0 - c_b} = 1 - \mathrm{erf}\left[\frac{x}{2\sqrt{Dt}}\right], \tag{6}$$

where c_x denotes the concentration of H_2O (in wt.%) at a distance of x from the fracture/clast boundary (m), c_b is the H_2O concentration of the far field in the host obsidian (in wt.%), c_0 is the (lower) H_2O concentration within the tuffisite defining the limit at the tuffisite wall (in wt.%), t is time (s), and the H_2O diffusivity (m^2/s) is given by D. H_2O molecules were assumed to be the only species diffusing (e.g., Behrens & Nowak, 1997) and the magmatic temperature was assumed to be constant at 825 °C (a value constrained by the petrological experiments of Castro & Dingwell, 2009). Boundary conditions were fixed at the far-field H_2O concentration c_0, as defined from diffusion profiles, and the lowest H_2O concentration c_b as measured at the fracture/clast boundary. The H_2O diffusivity was calculated using the concentration- and temperature-dependent model for rhyolitic melt of Zhang (1999):

$$D_{H_2O_t} = \left(\frac{c}{c_r}\right) \exp\left[-16.83 - \frac{10992}{T}\right], \tag{7}$$

where c is the local H_2O concentration (in wt.%), c_r is a reference H_2O concentration of 1 wt.% (see Figure 6c and Zhang, 1999), and T is the temperature (K). As the error function diffusion solution assumes a constant diffusivity, which we take to be the diffusivity calculated using equation (7) for a value of $c = 0.75$ wt.%, which is the arithmetic mean of the measured c_0 and c_b (yielding $D_{H_2O_t} = 1.6 \times 10^{-12}$ m^2/s). Because the difference between diffusivities at c_0 and c_b is modest (1×10^{-12} m^2/s at 0.46 wt.% H_2O, and 2.3×10^{-12} m^2/s at 1.04 wt.% H_2O), using this mean value provides a reasonable approximation of the diffusivity over the whole profile. We note that taking the mean of the two end-member diffusivities additionally assumes that the nonlinearity of $D_{H_2O_t}(H_2O_t)$ is negligible. Using this method and fitting the diffusion model to the measured H_2O depletion adjacent to the fracture/clast boundary of the CH5F and BTB tuffisites with the time as an adjustable parameter (and fitting using a least squares minimization method described above) yields times of ~4 and ~2 hr, respectively, for the time between fracture opening and final quenching (Figure 6c). It is important to highlight these timescales are *minima*, and they depend heavily on the model assumptions, such as the temperature. For example, Castro et al. (2012) showed that reducing the temperature by 200 °C increased this timescale from minutes to several tens of hours. Nevertheless, these predicted timescales compare well with other estimates of the lifetimes of tuffisites from Chaitén volcano (Castro et al., 2012).

5.4. The Lifespan of a Tuffisite

In the general conceptual scheme explored here, we envisage conduit-filling rhyolite lava that is periodically fractured by high-pressure gas and ash from below (e.g., Schipper et al., 2013). These processes involve the opening of the fracture, the transport of gas and ash, the clogging of the fracture, and a slower, time-dependent sintering of the fracture infill. In concert then, the outgassing time available for removing pressurized gas through the fractures is therefore the sum of the time from opening to clogging with pyroclastic debris, λ_1, and the time for sintering once the tuffisite is formed and welds shut, λ. The time λ_1 from video footage of fractures opening and closing appears to be on the order of tens of seconds (Figure 1). The mass of gas and ash removed during this time, which could be used to compute the pressure decrease, is difficult to assess. But it is clear from the video footage (Figure 1; Schipper et al., 2013) that the outgassing continues, albeit more slowly, during the postclogging sintering of the fracture infill, with the emission of vapor only (i.e., without the ash phase).

Once the fracture has become clogged with pyroclastic debris, the process of sintering will act to reduce porosity and permeability toward zero. It is the timescale of sintering that is the key quantity in determining the efficacy of tuffisites as outgassing pathways after the open fracture is clogged with particles. In the absence of applied force on the sides of the fracture, the characteristic timescale associated with this process is the sintering timescale $\lambda = R\mu/\Gamma$, where μ is the viscosity of the melt and Γ is the melt vapor surface tension. R, the mean grainsize, has been shown to capture sintering dynamics even in highly polydisperse distributions (Wadsworth, Vasseur, Llewellin, & Dingwell, 2017). In other words, although estimates of R are small compared to the larger fragments readily identifiable in our microstructural work (Figures 3 and 4), it is the finer particle fraction that dictates the efficiency of viscous sintering—a result of the grainsize dependence of the sintering time (Gardner et al., 2018; Wadsworth et al., 2014; Wadsworth, Vasseur, Llewellin, et al., 2016). When a force is applied to the fracture walls (such as a lithostatic pressure or the stress imparted by a recently opened adjacent fracture), however, λ will not be the controlling timescale, and the system is more likely to close over a compaction timescale $\lambda_2 \approx \mu/(\sigma\alpha)$, where σ is the applied stress (in Pa) on the fracture walls and α is an empirical factor (Farquharson et al., 2017; Quane et al., 2009) that was calibrated for sintering polydisperse particles similar to the tuffisites studied here (the block-and-ash flow deposits from Mt. Meager; Figure 5) to be $\alpha \approx 2$ (Heap et al., 2014). This is broadly similar to other compaction timescale approximations (Kennedy et al., 2016; McKenzie, 2011). If surface tension stress $2\Gamma/R$ dominates over the stress applied to the fracture walls σ, then λ should be used. If instead the opposite is true, and the fracture wall stress dominates the surface tension stress, then λ_2 should be used. In each respective case, the total outgassing time is $\lambda_1+\lambda$ or $\lambda_1+\lambda_2$.

To illustrate how λ and λ_2 vary, we take $\Gamma = 0.3$ N/m for moderately dry rhyolites (Gardner & Ketcham, 2011). We note that Γ is significantly lower in rhyolites with up to ~4 wt.% dissolved water, but there are no measurements in the intermediate range of water contents, and these rhyolites are erupted close to the dry limit (Castro et al., 2014; Saubin et al., 2016). The melt viscosity of tuffisites from Chaitén (samples BTB and CH5F) and Cordón Caulle (sample B1) can be estimated using a multicomponent viscosity model (Giordano et al., 2008), using major element composition (using the compositions provided in Castro & Dingwell, 2009, for Chaitén and in Alloway et al., 2015, for Cordón Caulle), an inferred eruptive temperature of 825 °C for Chaitén (Castro & Dingwell, 2009) and 890 °C for Cordón Caulle (Alloway et al., 2015; Castro et al., 2013), and measured H_2O concentrations. H_2O concentrations of 0.74 and 0.34 wt.% were taken for, respectively, the host obsidian and tuffisite in the BTB sample (Saubin et al., 2016, and 1.04 and 0.46 wt.% were taken for the host obsidian and tuffisite in the CH5F sample, see Figure 6c). For the B1 sample, measurements on eruptive products from the 2012–2013 Cordón Caulle eruption provided a range of H_2O concentration between 0.1 and 0.5 wt.% (Militzer, 2013). The resulting viscosity range estimations were calculated to be $10^{8.05} < \mu < 10^{9.07}$ Pa s for the BTB sample, $10^{7.64} < \mu < 10^{8.65}$ Pa s for the CH5F sample, and $10^{7.15} < \mu < 10^{8.23}$ Pa s for the B1 sample.

We assume, given the relationship between sintering timescale and grainsize (Wadsworth et al., 2014), that the viscosity of the fine-grained matrix controls viscous sintering. For the variability in R predicted here ($2.5 < R < 15$ μm; Figure 5b), sintering times in the absence of applied forces λ are between 6 min and 5 hr, between 16 min and 13.6 hr, and between 2 min and 2.4 hr for CH5F, BTB, and B1 respectively (Figure 8). To compute λ_2, as a first-order estimate, we take $\sigma = 2$ MPa, which is computed by matching the solubility of water (assuming 100% of the pressure is water vapor pressure) based on Liu et al. (2005), to the value measured at the tuffisite wall c_0. This yields values of λ_2 (for the variability in R predicted here) between 11 s and 2 min, between 28 s and 5 min, and between 3.5 s and 42 s for CH5F, BTB, and B1 respectively (Figure 8). We again highlight that these timescales depend on the model input parameters: differences in viscosity (resulting from changes to the eruptive temperature and/or the water content, for example) can significantly modify these predictions. We also plot on Figure 8 an estimated range for the time from fracture opening to clogging with pyroclastic debris, λ_1 (10–20 s, estimated using available video footage form Cordón Caulle; Figure 1; Schipper et al., 2013) and the interfracture timescale ($\lambda_1+\lambda$ or $\lambda_1+\lambda_2$; 20–120 s; Schipper et al., 2013). These observed timescales are faster than the timescales solely predicted from surface tension and are much more consistent with the estimated range of compaction timescales (Figure 8), suggesting that compaction driven by the overburden (lithostatic) stress plays a key role in governing the lifetimes of these tuffisites. Although

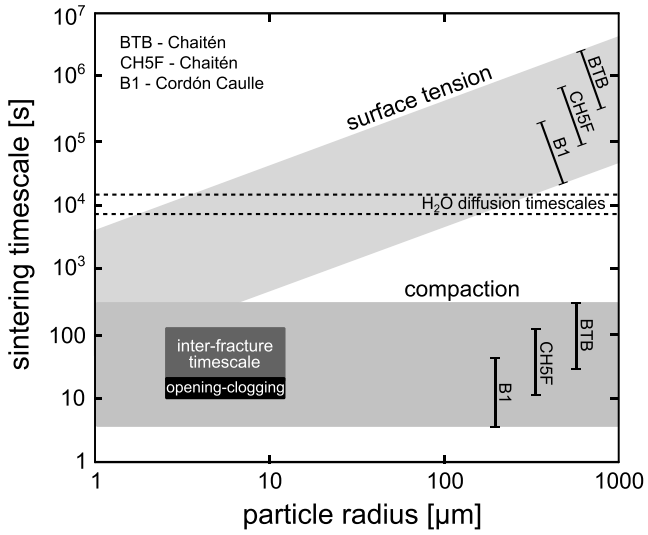

Figure 8. Sintering timescale as a function of particle radius for the two sintering regimes: surface tension and compaction (grey zones). Timescales are provided for tuffisites from Chaitén (samples BTB and CH5F) and Cordón Caulle (sample B1) using the range of viscosities determined using a multicomponent viscosity model (Giordano et al., 2008; see text for details). For the range of particle radii thought to control sintering in the tuffisites of this study ($2.5 < R < 15$ μm; estimated using a permeability model for granular materials; Wadsworth, Vasseur, Scheu, et al., 2016; see Figure 5), the sintering times for the surface tension regime are between 6 min and 5 hr, between 16 min and 13.6 hr, and between 2 min and 2.4 hr for CH5F, BTB, and B1, respectively. Sintering times in the compaction regime are predicted to be between 11 s and 2 min, between 28 s and 5 min, and between 3.5 s and 42 s for CH5F, BTB, and B1, respectively. We also plot the estimated range for the time from fracture opening to clogging with pyroclastic debris, λ_1 (10–20 s, estimated using video footage; Figure 1; Schipper et al., 2013) and the inter-fracture timescale ($\lambda_1+\lambda$ or $\lambda_1+\lambda_2$; 20−120 s; Schipper et al., 2013). The calculated diffusion timescales for BTB and CH5F (~2 and ~4 hr, respectively) are indicated by the dashed lines. As these relate to diffusive H_2O depletion in an approximately millimetric clast (BTB) and the tuffisite wall (CH5F), they are independent of the grainsize of the far finer-grained matrix (abscissa) and thus appear as horizontal lines.

depth estimations for tuffisites at Cordón Caulle are shallower (depth of about 50 m; Schipper et al., 2013) than those estimated for Chaitén, we note that a reduction in σ from 2 to 1 MPa only doubles the λ_2 timescale and, even in this scenario, our estimated compaction timescales are still in line with the observed timescales. We further note that our estimated compaction timescales consider lithostatic pressures only and do not take stresses imparted by recently opened adjacent fractures into account.

H_2O diffusion offers an independent tuffisite chronometer to these estimated viscous sintering timescales. The best fit diffusion model (Figure 6c) to the measured H_2O depletion adjacent to the fracture/clast boundary of the CH5F and BTB tuffisites yields timescales λ_d (time between fracture opening and final quenching) of ~4 and ~2 hr, respectively (as shown in the previous section). These predicted timescales compare well with other estimates of the lifetimes of tuffisites from Chaitén volcano and elsewhere (Berlo et al., 2013; Cabrera et al., 2011; Castro et al., 2012; Saubin et al., 2016). Further, we highlight that viscous sintering timescales were also found to coincide with H_2O re-equilibration timescales in obsidian pyroclasts from Mono Craters (United States) that were assembled from juvenile particles during magma ascent (Gardner et al., 2017), suggesting that viscous sintering plays an important role in cyclic fragmentation behavior and apparent open system degassing (Gardner et al., 2017; Rust et al., 2004; Tuffen et al., 2003; Watkins et al., 2017). Our predicted H_2O diffusion timescales are, however, longer than the observed interfracture timescales and the timescales predicted for compaction-driven sintering (Figure 8). Because H_2O diffusion can continue even after compaction renders permeable gas flow ineffective, we consider that λ_d is the sum of the fracture opening timescale (λ_1), the sintering or compaction timescale (λ or λ_2), and a quenching timescale. According to our analysis, the quenching timescale is therefore likely to be on the order of a couple of hours, consistent with conductive cooling of bombs tens of centimeters in diameter (e.g., Saubin et al., 2016). We also highlight the numerous model assumptions that may influence our predicted H_2O diffusion

timescales, such as, for example, using a steady eruptive temperature and a single step in H_2O activity at the fracture walls. Furthermore, observations at Cordón Caulle highlight that ash jetting can occur from the same fracture and, since H_2O diffusion would necessarily continue, the repeated use of the same fracture could also help explain the discrepancy between the H_2O diffusion timescales and the timescales required for compaction, pressurization, and fragmentation.

5.5. Pressurization and Outgassing at Silicic Lava Flows and Domes

Before discussing the potential role of tuffisites in influencing conduit processes and outgassing during silicic eruptions, it is important to address the question: how common are tuffisites? Providing a robust answer to this question for active volcanoes such as Chaitén or Cordón Caulle is problematic, in part because fully mature, densely welded tuffisite is likely indistinguishable from dense obsidian (see Castro et al., 2014). Calculations presented in Castro et al. (2012) suggest that a dense spacing of tuffisites (approximately a tuffisite every 0.01–0.001 m) would be required to fully degas a silicic magma in the approximate times available. Such high tuffisite number densities are considered consistent with evidence that obsidian lavas have been thoroughly fractured and then rehealed (or annealed) to dense glass (Castro et al., 2012, 2014). Further, several field campaigns at Chaitén volcano have highlighted that bombs on the crater rim and flanks commonly host tuffisites, the width of which typically ranged from a couple of millimeters up to a few tens of millimeters. Evidence of high tuffisite number densities from dissected rhyolitic conduits in Iceland (McGowan, 2016) provides support to the high densities predicted for Chaitén volcano by Castro et al. (2012). For example, a 5-m line transect in a dissected rhyolitic conduit in Iceland contained 282 tuffisites (McGowan, 2016). Although the tuffisite number density from this dissected conduit may contains different generations of tuffisites (i.e., all 282 tuffisites may not have been active at the same time), this number speaks to the ubiquity, and therefore potential importance, of these features in rhyolitic conduits. We also note that even if tuffisites are relatively uncommon, their influence on the permeability of an otherwise impermeable magmatic plug can be very large. For example, a single permeable pathway within an large low-permeability rock mass can increase the equivalent permeability of the system by many orders of magnitude, as discussed in, for example, Heap and Kennedy (2016), Farquharson et al. (2017), and Farquharson and Wadsworth (2018). Finally, although the outgassing flux could be computed using either Darcy law (low Reynolds number) or the Forchheimer equation using the constraints of permeability provided herein, we note that while our determination of the porosity-permeability relationship is valid locally, the depth-dependent stress and the coupling between the evolving gas pressure and the sintering rates demands a full numerical solution (e.g., Michaut et al., 2013). We propose that fertile future research could use our model, validated using empirical data on tuffisites, to provide a tuffisite outgassing model for rhyolitic volcanoes.

In upper conduits characterized by dense, impermeable magmatic plugs and host rock (i.e., a "closed system"; see the modeling of Diller et al., 2006; Collinson & Neuberg, 2012), we propose here that the recurrence timescale of explosive venting must, in a broad sense, equal the sum of the timescales of tuffisite sintering, pressurization, and fragmentation. Our study provides estimates spanning seconds (in the case of compaction-driven sintering) to hours (in the case of surface tension-driven sintering) for the thorough sintering of tuffisites, and we can assume that the timescale for fragmentation is necessarily small compared to the other timescales. The timescale for pressurization, which will depend on, among other factors, the ascent rate and volatile budget of the magma, is the missing constraint. Therefore, the sintering times estimated herein must be less than or equal and cannot be longer than the explosive venting timescale. Indeed, the observed range of cyclic pressurization and ash venting timescales at erupting silicic lava domes at, for example, Santiaguito volcano (Guatemala) and Soufriere Hills volcano (Montserrat; Holland et al., 2011; Johnson et al., 2008; Voight et al., 1999), is consistent with our timescale estimates for the thorough sintering of tuffisites. This may imply that pressurization timescales can be short or, and perhaps more likely, that pressurization begins before the tuffisites are completely sintered shut. Indeed, the presence of an H_2O-rich clast population within the BTB sample demonstrated that deeper, pressurized gas entered the shallower, lower-pressure fracture system, consistent with the pressurization of fractures/tuffisites prior to the destruction of their permeability.

The low permeabilities attained by the CH5F (~10^{-16} m^2; Figure 5b and Table 1) and the BTB tuffisites (~10^{-15} m^2; Figure 5b and Table 1) coincide with that of healed gas escape routes modeled by Collinson

and Neuberg (2012). We consider that the effective healing of tuffisites likely therefore contributed to the upper conduit pressure accumulation that ultimately led to their explosive ejection. Although clast vesiculation contributed to porosity loss within the BTB tuffisite (alongside other mechanisms), the BTB tuffisite failed to attain the low permeability of CH5F, interpreted here as the result of a shorter pre-ejection healing time within the conduit. Nonetheless, the permeability attained by BTB (~10^{-15} m^2) must have been sufficiently low to render gas loss inefficient over its lifespan (pressure equilibrium time at this permeability >11 days; see also the modeling of Collinson & Neuberg, 2012; Chevalier et al., 2017). We note that it is also possible that a healed tuffisite is not immediately ejected and undergoes additional viscous compaction prior to ejection in a later fragmentation event—a plausible scenario given the repetitive nature of tuffisite formation and healing (Tuffen et al., 2003). In this scenario, we would expect the diffusion timescale to greatly exceed the sintering timescale.

The modeled source depths of upper conduit pressurization are additionally consistent with ejected bomb depths at Chaitén volcano, as inferred from bomb volatile concentrations (see above and Saubin et al., 2016). It is therefore plausible that upper conduit pressurization cycles are modulated by sintering-driven blockage of initially permeable tuffisite networks, especially in crystal-poor rhyolitic systems where melt-rich magma readily sinters. Equivalent observational data from the 2008 eruption of Chaitén volcano is unfortunately lacking, but the filming of pulsatory ash venting during the eruption of Cordón Caulle in 2011–2012 revealed significantly shorter interexplosion intervals (<40 s, Schipper et al., 2013; Figure 1), perhaps controlled by the sintering of finer material. The rhyolite at Cordón Caulle is also of lower silica content than Chaitén volcano and was erupted at comparatively higher temperatures (~890 °C; Castro et al., 2013), factors that reduce melt viscosity and therefore sintering timescales (e.g., Gardner et al., 2018; Figure 8). Nonetheless, limited video footage prior to the onset of the hybrid phase at Chaitén volcano in 2008 (Figure 1b) records a key phase of eruption development, in which the initially broad pyroclastic vent had constricted to several distinct vents tens of meters across above the yet-to-emerge lava dome (also observed at Cordón Caulle). Such focusing of pyroclastic discharge requires sintering of initially loose pyroclastic vent-filling material to gain strength and reduce permeability (e.g., Heap et al., 2015; Kolzenburg et al., 2012; Kolzenburg & Russell, 2014). This indicates that sintering processes can act to reconfigure conduit architecture during eruptions, and the transition from initially Plinian to hybrid activity at Chaitén volcano can be conceptualized as a decrease in the width of venting tuffisites from the entire conduit, through an intermediate phase characterized by multiple vents tens of meters in breadth, to, finally, pathways only centimeters wide such as observed in the BTB tuffisite (Figure 2a). Occlusion of outgassing pathways by sintering encourages greater pressurization of the upper conduit, and this is proposed to be responsible for the forceful intrusion of a shallow laccolith at Cordón Caulle, whose emplacement coincided with a marked narrowing of the vent prior to the onset of hybrid activity (Castro et al., 2016).

The variable initial particle radius of a tuffisite relates to the efficiency of fragmentation (Kueppers et al., 2006), together with sorting phenomena associated with clastic transport and deposition (Tuffen et al., 2003). Fowler and Scheu (2016) demonstrate that for a given porosity, a larger overpressure release at fragmentation results in a smaller average grainsize. Owing to the fact that viscous sintering timescales are shorter at small grainsizes (Gardner et al., 2018; Wadsworth et al., 2014; Wadsworth, Vasseur, Llewellin, et al., 2016), we conclude that violent decompression events associated with fracture opening will create tuffisites capable of more rapid healing (for a given melt viscosity). As healing can provoke repressurization and explosive failure, the most energetic venting likely involves the shortest duration cycles of pyroclast and gas ejection from fracture systems.

The accuracy of the calculations presented herein invariably rests on the accuracy of the numerous model input parameters (such as the inferred temperatures used in our H_2O diffusion modeling and viscosity calculations) and, therefore, although we consider our assumptions as well reasoned, the model predictions should still be treated with some caution. Further outstanding complications include the time evolution of particle viscosity during sintering as diffusive mass transport of water occurs in tuffisites (Castro et al., 2014), grain size sorting during transport and accumulation of clastic particles (Tuffen & Dingwell, 2005), frictional heating and its potential role as a sintering accelerant, the entrainment of cooler lithics into tuffisites (although we highlight that lithics represent a very small fraction of the total fracture fill; e.g., Saubin et al., 2016, found that the lithic content of the BTB sample was <0.5 vol.%), and the effect of high particle-particle pressures in pore networks exceeding the capillary pressures of sintering (Wadsworth, Vasseur, Llewellin, et al., 2016).

We further note that the tuffisites documented here are also end-members in that they are hosted in dense obsidian; tuffisites in other systems characterized by a more permeable host rock may behave and be preserved, differently (e.g., tuffisites in a pumiceous rhyolite host rock: Castro et al., 2012; the fractures documented at Volcán de Colima: Farquharson et al., 2016; Kendrick et al., 2016; Kolzenburg et al., 2012; or the fractures seen within pyroclasts from Katla, Iceland: Owen et al., 2019). Nevertheless, even in this scenario it is likely that the initially granular fracture fill will be of a higher permeability than the host rock. Therefore, although outgassing can occur through the host rock, we suggest that sintering timescales will be similar to those reported herein for rhyolitic systems and that tuffisites that form within a more permeable host rock will still play an important role in the cyclic bleeding and accumulation of pore pressure thought to drive episodic explosive events at active volcanoes. Indeed, connectivity between pumice-hosted tuffisites and exsolved gas in their vesicular walls can greatly facilitate outgassing and may be a key process assisting the formation of dense, compacted magma in shallow silicic conduits.

6. Concluding Remarks

We conclude that if fractures in silicic lavas, domes, and vents are primary outgassing pathways for local and deep-seated magma (Castro et al., 2014), then the longevity of open-system outgassing from those fractures will scale with the timescale of viscous sintering. Our analyses suggest that it is the timescale for sintering driven by compaction that provides the most realistic timescale estimates and is likely therefore an important process dictating the lifespan of these tuffisites. Importantly, the permeability of those fractures will decay toward zero over that same timescale, rendering outgassing ineffective and permitting the pore pressure to build, eventually driving subsequent explosions and rapid concomitant lava extrusion rates (e.g., Pallister et al., 2013). The grainsize dependence of viscous sintering (Gardner et al., 2018; Wadsworth et al., 2014; Wadsworth, Vasseur, Llewellin, et al., 2016) suggests that the most energetic venting (i.e., the most efficient fragmentation; Kueppers et al., 2006) likely involves shorter duration cycles of pyroclast and gas ejection from fracture systems. The first-order constraint on lava and lava dome permeability evolution presented herein could be used to compare with cycles of proximal geophysical and geochemical signals such as conduit inflation, low-frequency seismicity, and surface emissions of gas and ash.

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