

# Efficient release of bromine by super-eruptions

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## ABSTRACT

**Bromine is a key halogen element in the quantification of volcanic volatiles, but analytical difficulties in measuring its very low abundances have prevented progress in understanding its behavior and its role in volcanic emissions. We present a new data set of bromine, chlorine, and fluorine concentrations in melt inclusions and matrix glasses for two rhyolitic super-eruptions from the Toledo and Valles calderas, New Mexico, USA. We show that before eruption, Br and Cl were efficiently partitioned from the gas-saturated magma into a separate fluid phase, and we calculate the mass of halogens in the fluid phase. We further demonstrate that syn-eruptive magma degassing was negligible during the super-eruptions, so that the main source of halogen emissions must have been the fluid phase. If the fluid phase were erupted, the large mass of Br and Cl could have severely impacted the atmospheric chemistry upon eruption.**

## INTRODUCTION

Halogens are an essential component of magmatic volatile systems and play a crucial role in magma degassing (Aiuppa et al., 2009), atmospheric ozone destruction (Aiuppa et al., 2009; von Glasow et al., 2009), and metal transport (Williams-Jones and Heinrich, 2005). Bromine concentrations in magmas are typically two orders of magnitude lower than those of chlorine, yet its higher volatility (Bureau and Métrich, 2003) and potential for ozone destruction (Daniel et al., 2007) make bromine a particularly useful element to study when evaluating the potential impact of an explosive eruption. We analyzed the enrichment of halogens in a super-volcanic system and quantified the masses of Br and Cl that were fractionated from the melt and potentially released into the atmosphere.

## STUDY AREA AND METHODOLOGY

We studied the Bandelier Tuff eruptions, which were vented from the Toledo and Valles calderas in northwestern New Mexico, United States. The first super-eruption from Toledo caldera took place at 1.61 Ma (Spell et al., 1990), erupted an estimated 400–500 km<sup>3</sup> dense-rock equivalent (DRE) of magma (Cook et al., 2016), and deposited the high-silica rhyolitic lower

Bandelier Tuff (LBT). The second super-eruption, similar in both composition and volume, deposited the upper Bandelier Tuff (UBT) at 1.26 Ma (Phillips et al., 2007). Both eruptions experienced an initial Plinian phase followed by ignimbrites. Between the two super-eruptions, the top of the magma chamber was periodically tapped by small rhyolitic eruptions that formed the tephros, flows, and domes of the Valle Toledo Member, which span ~350 k.y. (Spell et al., 1996; Gardner et al., 2010). The initial phase of the Valle Toledo eruptions is geochemically related to the LBT and interpreted as the last pulse from the emptying magma chamber, after which new silicic magma entered the chamber and started to differentiate (Stix and Gorton, 1993). Similarly, the Deer Canyon Member of the Valles Rhyolite (Deer Canyon Rhyolite herein) erupted immediately after the UBT as resurgence was taking place in Valles caldera (Phillips et al., 2007). This unit is geochemically related to the UBT and represents the final pulse from the UBT magma chamber before fresh magma replenished the system anew (Spell et al., 1993; Wilcock et al., 2013).

We collected pumice samples from (1) the base and the top of the LBT and UBT Plinian phases, (2) the two key units of the Valle Toledo

representing the initial phase related to the LBT and the first phase immediately after magma recharge, and (3) the Deer Canyon Rhyolite. Phenocrysts in the pumices dominantly consist of melt inclusion-rich quartz and sanidine. Bromine (Br), chlorine (Cl), and fluorine (F) were measured by ion microprobe in melt inclusions, with ~10 melt inclusions analyzed per unit as well as one to two matrix glasses per unit. Analytical details are provided in the Supplemental Material<sup>1</sup>.

## RESULTS

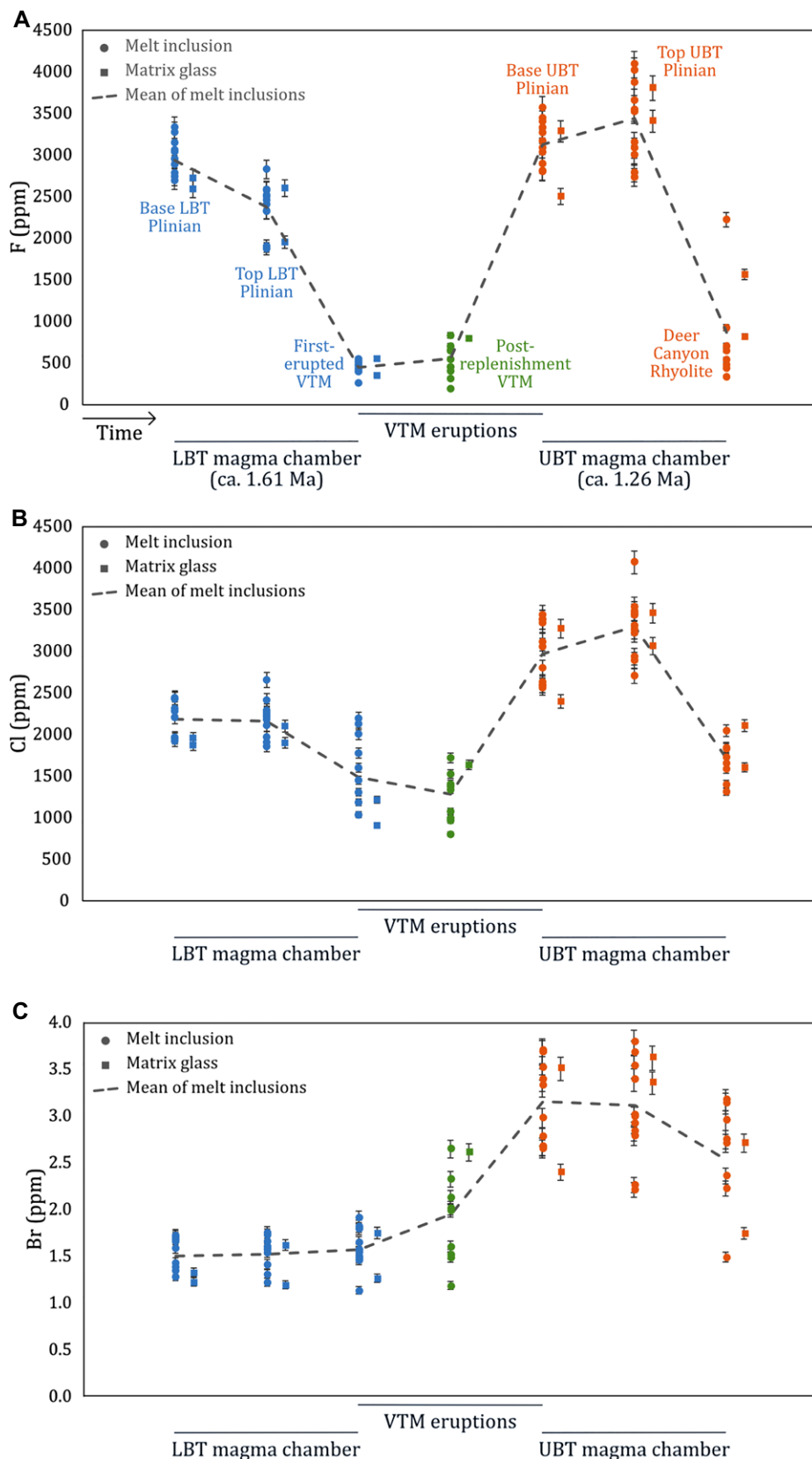
### Lower Bandelier Tuff

In the LBT sequence, F measured in melt inclusions shows a steady decrease upsection, hence deeper into the magma chamber (Fig. 1). Fluorine decreases from 2700 to 3340 ppm in the base of the Plinian, then to 1880–2830 ppm in the top, and finally to 260–550 ppm in the first-erupted Valle Toledo unit. Chlorine follows a similar, although less pronounced, trend, decreasing from 1920 to 2440 to 1860–2660 ppm through the Plinian, and further to 1030–2190 ppm in the first-erupted Valle Toledo. By contrast, Br exhibits no variation in the LBT sequence; Br values of 1.3–1.7 ppm are found at the base of the Plinian, 1.2–1.8 ppm at the top of the Plinian, and 1.1–1.9 ppm at the end of the LBT. For the entire LBT sequence, F exhibits a 6.6× decline from base of the LBT to the earliest Valle Toledo, while the decrease for Cl is 1.5×, and Br remains constant.

### Upper Bandelier Tuff

Trends in the UBT are similar to those in the LBT, with several key differences: (1) the ranges in concentrations are substantially larger in the UBT; (2) the halogen concentrations themselves are higher; (3) there is a slight increase in Cl and F from the base to top of

<sup>1</sup>Supplemental Material. Expanded methodology, information on calibration standards, data table, and comments on calculations. Please visit <https://doi.org/10.1130/GEOL.S.15023007> to access the supplemental material, and contact [editing@geosociety.org](mailto:editing@geosociety.org) with any questions.



**Figure 1.** Fluorine, chlorine, and bromine concentrations throughout the Toledo-Valles caldera sequence (New Mexico, USA). (A) Fluorine concentrations display a 6.6 $\times$  decline through the lower Bandelier Tuff (LBT) sequence, followed by a 5.6 $\times$  increase in the Valle Toledo Member (VTM) and a 3.6 $\times$  decrease in the upper Bandelier Tuff (UBT). (B) For Cl, the general trend is similar to that of F but less pronounced, with a 1.5 $\times$  decrease in LBT, a 2.3 $\times$  increase in VTM, and a 1.7 $\times$  decrease in UBT. (C) For Br, constant concentrations in LBT are followed by a 1.6 $\times$  increase in VTM and a 1.2 $\times$  decrease in UBT. Error bars based on 1 $\sigma$  reproducibility of in-run standard glass.

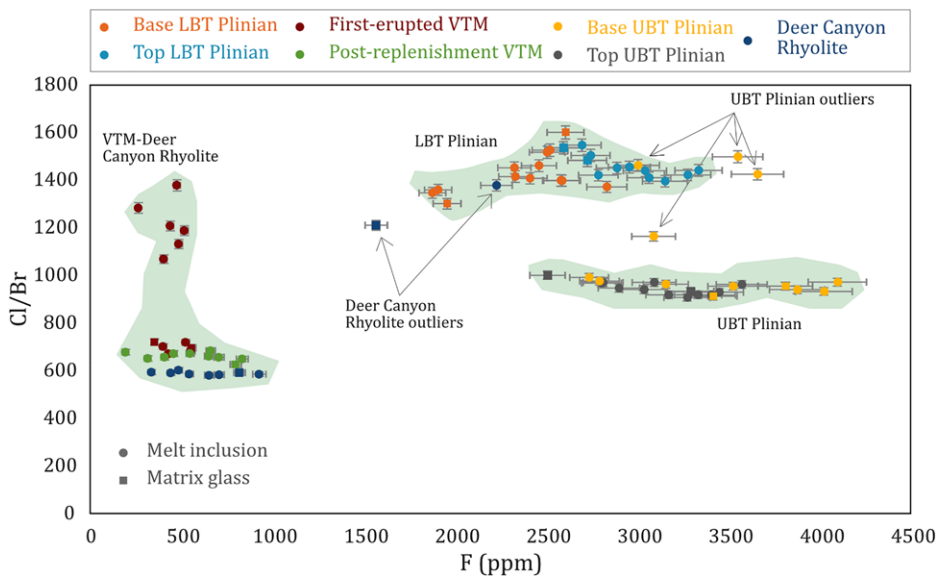
the Plinian, rather than a decrease; and (4) Br also decreases, rather than remaining constant. Fluorine evolves from 2800 to 3570 ppm to 2740–4100 ppm through the Plinian, then plummets to 340–930 ppm in the Deer Canyon Rhyolite, which is the deepest erupted magma, with one high outlier at 2230 ppm. Chlorine starts at 2560–3440 ppm in the base of the Plinian, increases to 2710–4080 ppm, then strongly declines to 1310–2050 ppm in the Deer Canyon. In the same sequence, Br varies from 2.7 to 3.7 to 2.2–3.8 ppm, and finally to 1.5–3.2 ppm. The decrease over the entire UBT sequence is 3.6 $\times$  for F (4.4 $\times$  if the high Deer Canyon outlier is not considered), 1.7 $\times$  for Cl, and 1.2 $\times$  for Br.

### Valle Toledo Member Rhyolites

The Valle Toledo samples that we analyzed comprise three units: the first-erupted material, which marks the end of the LBT sequence (ca. 1.61 Ma; Spell et al., 1996); the first post-replenishment eruption (1.54 Ma; Spell et al., 1996); and the base of the UBT Plinian (1.26 Ma; Phillips et al., 2007), which represents the end of Valle Toledo differentiation. The three halogens show variable enrichment during this 0.35 m.y. interval. Fluorine starts at 260–550 ppm in the earliest Valle Toledo, then goes to 190–830 ppm after replenishment, culminating in strong enrichment of 2800–3570 ppm at the base of the UBT. Chlorine concentrations follow a similar trend, from 1030 to 2190 ppm to 800–1720 ppm after replenishment, then enrichment to 2560–3440 ppm. The Br trend is similar yet less pronounced than for F and Cl, ranging from 1.1 to 1.9 ppm to 1.2–2.7 ppm and ending at 2.7–3.7 ppm at the base of the UBT. Enrichment factors for F, Cl, and Br from immediately after replenishment to the UBT eruption are 5.6, 2.3, and 1.6, respectively.

### DISCUSSION

The systematic difference in enrichment factors for the three halogens indicates the presence of a fluid-saturated magma, whereby Br and Cl partitioned principally into the fluid while F accumulated almost entirely in the magma. Fluorine has been shown in previous studies to be nearly perfectly incompatible in these rocks, similarly to Cs (Stix and Layne, 1996), indicating that mineral phases such as apatite play a negligible role in sequestering halogens. Bromine has higher fluid-melt partition coefficients than Cl (Bureau et al., 2000; Bureau and Métrich, 2003; Cadoux et al., 2018), which results in a lesser enrichment in the melt as proportionally more Br fractionates to the fluid phase. If the magma were not fluid saturated, Br and Cl would exhibit the same enrichment as F (Balcone-Boissard et al., 2010). Hence, the difference indicates the amounts of Br and Cl that were lost to the fluid phase. The observed



**Figure 2.** Cl/Br plotted versus F for measured melt inclusions and matrix glasses. Cl/Br increases with degassing to fluid phase, while F increases with the degree of magmatic differentiation. Higher Cl/Br ratios of Plinian phases indicate that they experienced a greater degree of fractionation of Br to a separate fluid phase. Error bars are based on  $1\sigma$  reproducibility of in-run standard glass. VTM—Valle Toledo Member; LBT—lower Bandelier Tuff; UBT—upper Bandelier Tuff.

enrichment of F, Cl, and Br throughout the Valle Toledo eruptions reflects re-establishment of concentration gradients, with F accumulating in the melt while Cl and Br were partially lost to a fluid phase. Taken together, our results demonstrate that the Bandelier magmatic system was always fluid saturated during its evolution.

#### Matrix Glasses and Syn-Eruptive Degassing

For each sample we analyzed, we also measured F, Cl, and Br concentrations in one to two matrix glasses (Fig. 1). For all samples and all three halogens, the matrix glass analyses plot in the same range as the melt inclusions. Only at the base of the LBT do both matrix glasses plot at the lower end of the range for melt-inclusion concentrations. Given there is no systematic difference between the matrix glasses and the melt inclusions, syn-eruptive degassing cannot have played any significant role in the Bandelier eruptions, which is explained by the slow diffusion of halogens in rhyolitic magma compared to other volatiles such as  $H_2O$  (Baker and Balcone-Boissard, 2009). The similar Br and Cl contents also indicate that the magma erupted shortly after crystallization of the host crystals, given that little further loss of Br and Cl to the fluid phase took place between melt inclusion capture and eruption.

#### Cl/Br Ratios

Continental crust is estimated to have a Cl/Br ratio of 273, while Cl/Br ratios measured in magmatic rocks cluster at  $\sim 300$  (Bureau et al., 2000). Given the higher fluid-melt partition coefficient of Br versus Cl, Cl/Br ratios in the melt phase would progressively

increase in the presence of a fluid phase. The melt inclusions we analyzed have Cl/Br ratios from 600 to 1600 (Fig. 2), indicating that pre-eruptive halogen fractionation to a fluid phase played a dominant role in the magma chamber. Despite some spread for a few samples, plotting the Cl/Br ratios reveals three distinct groups: (1) the LBT Plinian has the highest Cl/Br ratios, with most melt inclusions between 1300 and 1600, and therefore experienced the most Br and Cl loss to a fluid phase; (2) the UBT Plinian exhibits less spread in values, with all melt inclusions having Cl/Br ratios  $\sim 900$ –1000, indicating that the higher Br and Cl values in the UBT can be explained by less-efficient partitioning to a fluid phase than in the LBT; and (3) the two Valle Toledo samples and the Deer Canyon samples exhibit the lowest Cl/Br values, which are tightly clustered between 600 and 700 (except for a few outliers with high Cl/Br), reflecting the lesser degree of fractionation to a fluid phase in the more primitive rhyolitic magma.

Previous studies of Br in melt inclusions have focused on arc magmas (Kutterolf et al., 2013, 2015; Cadoux et al., 2015, 2017, 2018; Balcone-Boissard et al., 2018). In all these studies, Br contents are substantially higher (5–15 ppm) than those we measured for the Bandelier system, with high Br levels linked to input from subducted sediments and serpentinized subducted mantle (Straub and Layne, 2003; Kutterolf et al., 2015). We ascribe the lower Br values observed in the Bandelier melt inclusions to a combination of the non-arc setting of Toledo and Valles calderas and the major role of pre-eruptive halogen loss.

#### Masses of Bromine and Chlorine Fractionated

The lack of syn-eruptive degassing during the Bandelier eruptions, indicated by the similar halogen concentrations in melt inclusions and matrix glasses, means that the fluid phase is the only major source of Cl and Br released to the atmosphere. To calculate the mass of Cl and Br lost to the fluid phase, we assume they would have exhibited the same concentration gradient as F if no fluid phase had been present. We integrate this theoretical concentration gradient for Cl and Br over the depth of the LBT magma chamber and assume a quasi-cylindrical chamber with the same cross-sectional area as the caldera and a magma volume of  $550 \text{ km}^3$  (maximum estimate; Cook et al., 2016) to calculate the mass of Cl and Br in the magma if no fluid phase were present. Doing the same exercise for the observed concentration gradient and then calculating the difference yields the mass of Cl and Br released from the melt into the fluid phase. For the LBT, this results in 4800 Tg Cl and 5.7 Tg Br, while the same calculation for the UBT, assuming a magma volume of  $400 \text{ km}^3$  (best estimate; Goff, 2010), yields 2100 Tg Cl and 3.6 Tg Br.

Although part of the fractionated fluid phase may be lost through passive degassing or via fractures into a hydrothermal system, and the eruption efficiency depends upon the physical state of the fluid phase, the release of buoyant gases directly from a vapor-rich fluid phase located at the top of the magma chamber (Stix and Layne, 1996; Wallace et al., 2003) can propel them efficiently into the stratosphere, as was observed for the 1982 El Chichón (Mexico) and 2000 Hekla (Iceland) eruptions (Schneider et al., 1999; Rose et al., 2006). The calculated masses in the fluid phase are thus maximum amounts of Br and Cl released from the system upon eruption. For comparison, maximum estimates for the Minoan eruption of Santorini (Greece), with an erupted volume an order of magnitude less than that of the Bandelier eruptions, are 675 Tg Cl and 1.5 Tg Br emitted (Cadoux et al., 2015); a study of Plinian eruptions along the Central American volcanic arc yielded maxima of 800 Tg Cl and 1.1 Tg Br (Kutterolf et al., 2015); and an estimated 227 Tg Cl and 1.3 Tg Br were emitted by the 1257 Samalas (Indonesia) eruption, which erupted  $40 \text{ km}^3$  DRE (Vidal et al., 2016).

#### Fluid-Melt Partition Coefficients

The calculation of Cl and Br masses exsolved into the fluid phase allows us to establish the Cl/Br ratio in the fluid. We calculate ratios of 843 for the LBT and 580 for the UBT. Our analysis of halogen partitioning to a fluid phase also permits an independent estimate of partition coefficients for Cl and Br in the Bandelier system.  $H_2O$  concentrations in the LBT

and UBT indicate respective fluid phases of 6.7 and 4.2 wt% of the total magma mass (details in the Supplemental Material). This fluid-mass estimate allows us to calculate an average Br and Cl concentration in the fluid (68 ppm Br and  $57 \times 10^3$  ppm Cl for the LBT, 93 ppm Br and  $54 \times 10^3$  ppm Cl for the UBT), which we then divide by average Br and Cl concentrations in the melt to yield associated fluid-melt partition coefficients ( $D^{f-m}$ ).  $D_{Br}^{f-m}$  is 41 for the LBT and 33 for the UBT, while  $D_{Cl}^{f-m}$  is 30 for the LBT and 23 for the UBT. These coefficients are higher than experimentally determined for rhyodacites ( $D_{Br}^{f-m} = 20.2$ ; Cadoux et al., 2018;  $D_{Cl}^{f-m} = 16$ ; Webster et al., 2009; both at 900 °C and 200 MPa), probably because the Bandelier magmas were both more silicic and colder.

### Atmospheric Impact

Halogens emitted from volcanoes can impact atmospheric chemistry and lead to ozone depletion (Textor et al., 2003; von Glasow et al., 2009). Although typically present in lower concentrations than Cl, Br is  $\sim 60\times$  more efficient than Cl at destroying ozone molecules, hence is of major significance in evaluating ozone destruction potential from volcanoes (Daniel et al., 2007). An influx of 5.7 Tg Br to the atmosphere results in an increase of the bromine mixing ratio (moles of Br per moles of air in the whole atmosphere) of 397 pptv (parts per trillion per volume of air), while 3.6 Tg Br during the UBT yields an additional increase of the bromine mixing ratio of 248 pptv. As a comparison, the anthropogenic, chlorofluorocarbon (CFC)-fueled input from pre-industrial times to 1995 has been only  $\sim 15$  pptv (Daniel et al., 2007). A similar calculation for Cl results in an increase of the atmospheric chlorine mixing ratio of 753 ppbv for the LBT and 327 ppbv for the UBT eruption. The scale of this Cl input dwarfs anthropogenic, CFC-generated increases of  $\sim 3$  ppbv for Cl (Daniel et al., 2007). The exact impact of the eruptions depends on how efficiently the fluid phase was erupted and on scavenging of halogens in the eruption column. Nevertheless, the large masses of Br and Cl fractionated from the Bandelier magma could have severely impacted the paleo-atmosphere.

### CONCLUSIONS

We present a new data set of halogen concentrations in eruptive products and calculate the maximum amount of halogens released during eruption. We interpret similar halogen concentrations in melt inclusions and matrix glasses as indicative of a negligible role for syn-eruptive halogen diffusion and degassing, while large masses of Cl and Br were stored in a fluid phase. The halogen-rich fluid phases of the Bandelier magma chamber could have been released upon eruption to cause severe ozone depletion in the troposphere and strato-

sphere. Measured Br concentrations for the Bandelier system are lower than in arc magmas (5–15 ppm), which suggests similar-sized eruptions in arc settings such as the 26.5 ka Oruanui eruption in Taupo (New Zealand) could have emitted even larger masses of Br. Our study confirms that large explosive volcanic eruptions can play an important role in atmospheric chemistry and that the contribution of volatiles from erupted fluid phases should not be underestimated.

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