

# Combined bromine and chlorine release from large explosive volcanic eruptions: A threat to stratospheric ozone?

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## ABSTRACT

Large explosive volcanic eruptions inject gases, aerosols, and fine ashes into the stratosphere, potentially influencing climate. Emissions of chlorine (Cl) and bromine (Br) from such large eruptions play an important role for catalytic destruction of ozone in the stratosphere, but hitherto the global effects of simultaneous catastrophic release of volcanic Br and Cl into the stratosphere have not been investigated. The Br release from 14 large explosive eruptions throughout Nicaragua covering an entire subduction zone segment in the past 70 ka was determined with petrologic methods. Melt inclusions in volcanic phenocrysts were analyzed using a new optimized synchrotron-X-ray fluorescence microprobe set-up. Single eruptions produced Br outputs of 4–600 kt, giving an average Br emission of 27 kt per eruption. Using the assumption that 10% of the emitted halogens reach the stratosphere, the average Br and Cl loading to the stratosphere would be 3 ppt and 1500 ppt, respectively, which together would account for 185% of the preindustrial equivalent effective stratospheric Cl loading. We thus conclude that many large tropical volcanic eruptions had and have the potential to substantially deplete ozone on a global scale, eventually forming future ozone holes.

## INTRODUCTION

Approximately 50–60 volcanoes erupt worldwide each year. Only Plinian eruptions, with large mass eruption rates and high eruption columns, inject ash particles, aerosols, and gases into stratosphere, where they influence atmospheric chemistry and in particular ozone concentrations (Textor et al., 2003a; von Glasow et al., 2009), as well as the radiation budget, causing climate changes (McCormick et al., 1995; Robock, 2000). Br and Cl are known to have a major effect on catalytic destruction of stratospheric ozone (McCormick et al., 1995; von Glasow et al., 2009). Although Br is typically more than two orders of magnitude less abundant than Cl in volcanic gases (Bureau et al., 2000), its efficiency in ozone destruction is ~60 times higher than for Cl (Sinnhuber et al., 2009). While the Cl release from large eruptions is comparatively well studied (Gerlach et al., 1996; Wallace, 2005), the release of Br is largely unknown. Only limited data exist for quiescent plumes and fumaroles (Pyle and Mather, 2009) and for small- to medium-sized eruptions (Bobrowski et al., 2003). Model calculations on the effects of Br in the stratosphere strongly indicate that volcanic aerosols combined with elevated Br and Cl are particularly efficient for ozone destruction in the mid-latitude lower stratosphere, where a large fraction of the Br-induced ozone loss is dominated by the  $\text{BrO}_x/\text{HO}_x$  catalytic cycle;  $\text{BrO}/\text{ClO}$  ratios are also relevant regarding ozone loss in polar latitudes (Sinnhuber et al., 2009). Thus Br and Cl from large explosive volcanic eruptions can be an important factor for the stratospheric halogen and ozone contents (von Glasow et al.,

2009). This scenario has not been considered in the current World Meteorological Organization (Montzka et al., 2011) ozone assessment, since observations on relative small or larger wet eruptions (e.g., Mount Pinatubo, Philippines) only showed small amounts of reactive Cl in the stratosphere (Mankin and Coffey, 1984; McCormick et al., 1995). There is an increasing body of evidence, derived by ground-based, aircraft, and satellite measurements from small volcanic eruptions at low and high latitudes, indicating that reactive Br enters tropospheric

and stratospheric levels (Bobrowski et al., 2003; Millard et al., 2006; Rose et al., 2006; Theys et al., 2009).

## DATA

To better characterize the output produced by explosive eruptions we investigated 14 basaltic to rhyodacitic tephra deposits (Tables DR1 and DR3 in the GSA Data Repository<sup>1</sup>) emplaced during large Plinian eruptions at 5 volcanic centers along the Nicaraguan subduction zone segment during the past 70 ka (Kutterolf et al., 2007; Fig. 1). In contrast to the pilot study from the Laacher See Tephra (Germany) (Textor et al., 2003a), our study provides a complete time series for Br release from paleo-Plinian eruptions on an entire arc segment and delivers the first data as input for further modeling. Using an optimized synchrotron-X-ray fluorescence microprobe and an electron microprobe, we obtained a new comprehensive data set of Br and Cl contents from 70 selected melt inclusions in minerals (2–9 per sample; Figs. 1 and 2) and the corresponding degassed matrix glasses (for errors and further methods, see the Data Repository). In order to estimate the spatial variations of Br contents in the crystals, we also produced microchemical Br maps of phenocrysts with inclusions (Fig. 1).

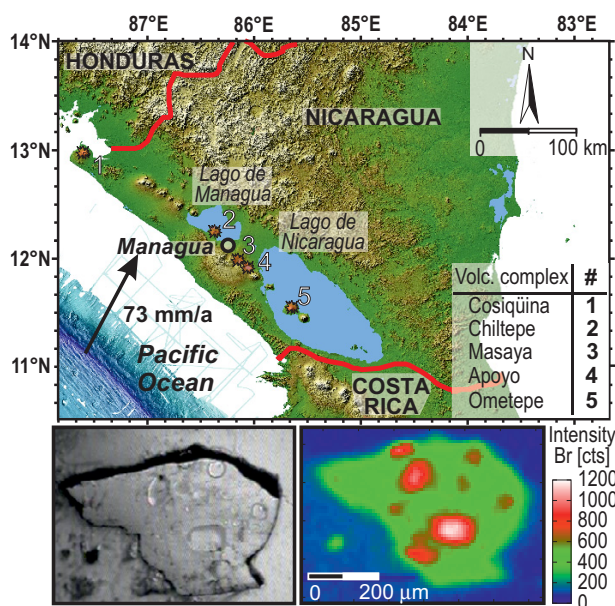
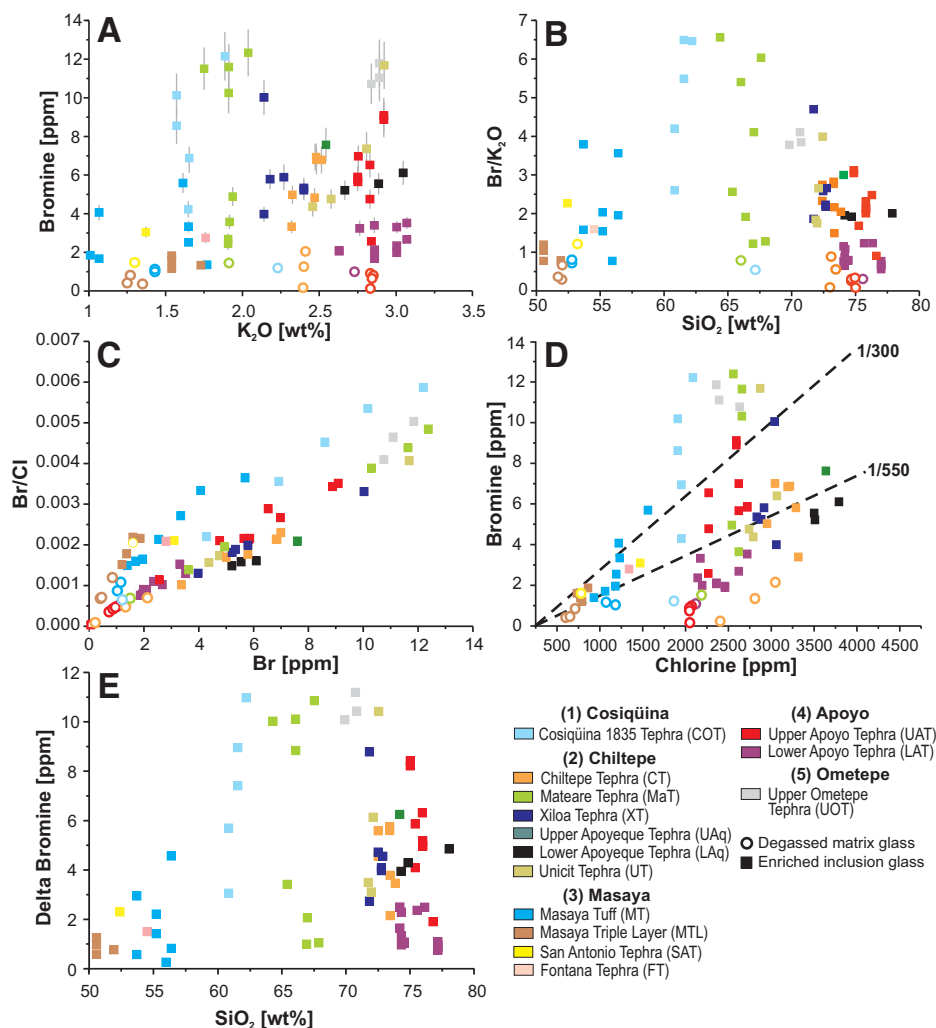


Figure 1. Modified shaded and colored Shuttle Radar Topography Mission elevation model of Nicaragua (after Kutterolf et al., 2008). Volcanoes parallel to the subduction trench are indicated by numbers and orange symbols. Lower left panel: reflected-light microphotograph of plagioclase phenocryst with several ellipsoid melt inclusions. Lower right panel: Br intensity distributions (green-blue = low intensity; red-white = high intensity) obtained by synchrotron-X-ray fluorescence microprobe mapping with 10  $\mu\text{m}$  photon beam.

<sup>1</sup>GSA Data Repository item 2013192, analytics, atmospheric assumptions, and individual measurements, is available online at [www.geosociety.org/pubs/ft2013.htm](http://www.geosociety.org/pubs/ft2013.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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**Figure 2.** A: Br concentrations of melt inclusions and matrix glasses versus  $K_2O$  content of the respective glasses. Gray—error bars for Br (see text). B:  $Br/K_2O$  ratio versus silica contents. C: Br versus Br/Cl of melt inclusions and matrix glasses. D: Br versus Cl. A Cl/Br value of 300 represents typical magmatic ratio (Bureau et al., 2000), while higher Cl/Br values suggest partial degassing supported by low  $Br/K_2O$  in B. Cl/Br ratios >550 for degassed matrix glasses equal data in literature (Pyle and Mather, 2009). E: Delta Br versus silica content.

## RESULTS

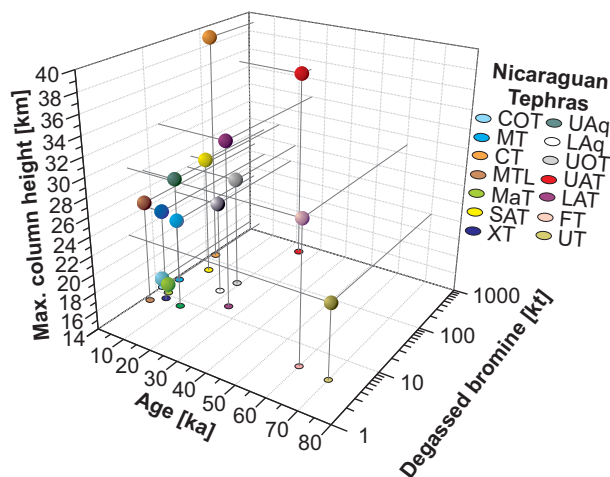
All matrix glasses of the Nicaraguan tephra have low Br contents (<1 to 2 ppm), independent of bulk composition, and represent the residual gas contents in the melts after syneruptive degassing and quenching (Fig. 2A). These values are comparable to the bulk rock powder samples from the 1902 Santa Maria, Guatemala, eruption determined by pyrohydrolysis and ion chromatography (Balcone-Boissard et al., 2010) as well as the Laacher See eruption (Textor et al., 2003a). Because degassing during eruption is highly effective, the concentrations of residual Br in the glasses are similar for all eruptions investigated. The mostly undegassed melt in inclusions has Br concentrations between 2 and 13 ppm (Table DR2; Figs. 2A and 2C); i.e., it is strongly Br enriched compared to the corresponding matrix glasses. Intrasample variations are 5%–35% relative, which we interpret

to reflect relative variations in entrapment times of the melt inclusions from a melt that evolved by fractional crystallization. Because all investigated samples contain magmatic fluid inclusions indicating fluid supersaturation at magma chamber depths, some of the observed variations are due to pre-eruptive degassing during late-stage magma chamber processes. During closed-system fractional crystallization of the melts considered here, Br, Cl, and  $K_2O$  were similarly incompatible elements and should covary such that the  $Br/K_2O$  ratios remain approximately constant. At similar  $K_2O$  concentrations, Br contents and  $Br/K_2O$  ratios vary widely in some samples (Figs. 2A and 2B), reflecting partial volatile exsolution from the melt at magma chamber depths into a coexisting aqueous fluid, according to their differing fluid/melt partition coefficients of  $D_{Br} = 2$ –375 (pressure dependent; Bureau et al., 2010) and  $D_{Cl} = 0.9$ –6 (at 200 MPa

and basaltic to andesitic composition; Webster et al., 1999). Petrologic experiments show that  $D_{Br}$  is typically much larger than  $D_{Cl}$  (Bureau et al., 2000), and the ratio Br/Cl in a melt should steeply decrease during partial degassing, which can be observed in particular in the Cosiquina 1835, Masaya Tuff, and Masaya Triple Layer melt inclusions (Fig. 2C). The intrasample variations in Br contents are best explained by pre-eruptive partial degassing. This is corroborated by the observation that the matrix glasses define end points of the suggested degassing trends at the end of a curved decrease in a Cl versus Br diagram, with Br showing a stronger decrease in concentration (Fig. 2D). We estimate that pre-eruptive, rather than syneruptive, partitioning into a coexisting fluid phase led to a 9%–75% reduction of the original Br contents in the magmas (Table DR1). We consider the highest Br concentration value determined from each sample as our best estimate for the initial Br contents in the melts at magma chamber depth before onset of degassing. Consequently, we estimate the Br fraction released during magmatic degassing, including the amount in the fluid phase, as the difference between the maximum Br abundance in the least degassed inclusions and the average concentration in matrix glass (Fig. 2E). We also note that some of that fluid phase may have escaped from the magma reservoirs prior to eruption.

The degassed Br fractions were converted to erupted Br masses for each eruption using the respective erupted magma masses of Kutterolf et al. (2007, 2008) (Table DR1). Erupted Br masses of the 14 stratospheric (>17 km column height) eruptions range from ~4 to ~600 kt (Fig. 3; Table DR1). Of those, the 2 largest magnitude eruptions, Chiltepe and Upper Apoyo, discharged 125 kt Br and 602 kt Br, respectively. For comparison, the annual anthropogenic Br emission into the troposphere amounts to ~37 kt/yr (in 2008; Montzka et al., 2011). In contrast, Br emissions by quiescent volcanic degassing and from smaller eruptive events (assuming short- and long-lived volcanogenic BrX species and maximal upper tropospheric column heights of 12 km) have been estimated by ground-based and satellite monitoring to be between 3 and 350 kt/yr (Bobrowski et al., 2003; Oppenheimer et al., 2006; Pyle and Mather, 2009; Theys et al., 2009).

Numerical models used to simulate the microphysical and chemical processes in an ascending eruption column show that halogens are partly scavenged by hydrometeors such that only a fraction of the halogen mass emitted at the vent actually reaches the stratosphere. First quantification of this phenomenon assumes the loss of almost all halogen load before reaching the stratosphere through scavenging by condensed water (Tabazadeh and Turco, 1993). More recent, complex model studies (Textor



**Figure 3.** Three-dimensional diagram showing age (ka), maximum eruption column height (km) (Kutterolf et al., 2007, 2008), and degassed Br mass (kt) for each eruption investigated. All eruption columns penetrated the tropopause (15 km high in Nicaragua). Gray bars indicate intersection of each data point with individual diagram planes. See Figure 2 for abbreviations.

et al., 2003a, 2003b) revised this assumption to 10% to >25% of emitted halogens that may reach the stratosphere; the higher percentage of scavenging efficiency strongly depends on the composition of the gas phase, the salinity of the fluid, the formation of ice crystals, and the dry versus wet nature of the atmosphere (Textor et al., 2003b) and the properties of the ash particles therein controlling the ability to capture halogen-rich precipitates and aerosols from the gas phase (Gislason et al., 2011). The 1982 El Chichón (Mexico) event in Central America is an excellent example of a Plinian eruption in the tropics leading to increased halogen concentrations in the stratosphere. The total hydrogen chloride column in lat 20°–40°N was 40% higher than before even 3–6 months after the eruption (Woods et al., 1985). Furthermore, measurements in the lower stratospheric Hekla (Iceland) 2000 eruption cloud at high latitudes (dry atmosphere) revealed only limited halogen scavenging, and the eruption generated local ozone depletion (Millard et al., 2006; Rose et al., 2006). However, the wet and, compared to eruptions at the Central America Volcanic Arc, halogen-poor (e.g., Gerlach et al., 1996) Mount Pinatubo eruption over the Philippine peninsula island of Luzon on 15 June 1991 caused no measurable accumulation of stratospheric halogens because it occurred simultaneously with the typhoon Yunya, probably leading to efficient wash-out of volcanic halogens over a large region (McCormick et al., 1995; von Glasow et al., 2009). Unfortunately, the paleoparameters controlling the microphysical and chemical reactions as well as the weather conditions of the 14 investigated tropical eruptions are largely unknown. However, scavenging due to humid conditions in tropical regions can be partly compensated for by large Plinian eruptions, due to the high ascent rate leading to halogen-bearing ice crystals and even solid salt particles (NaCl containing Br) preserving the halogens for stratospheric release (e.g., Textor et al., 2003a; Woods et al., 1985); like observed for the tropical

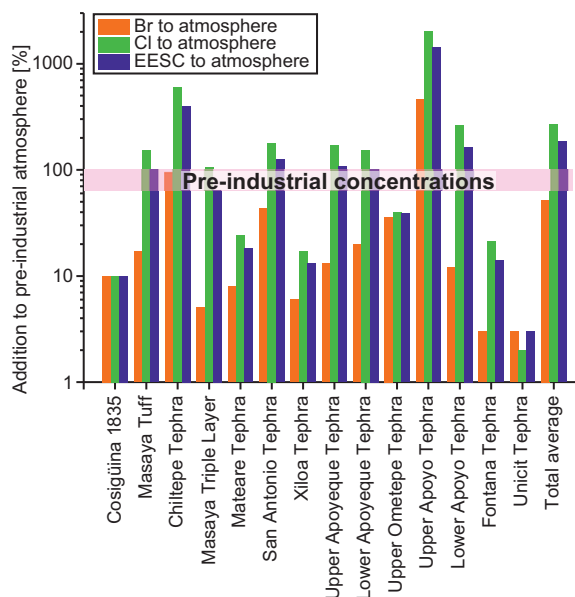
El Chichón 1982 eruption (Woods et al., 1985). We assume that at least 10% of the emitted halogens from the halogen-rich subduction zone volcanoes, together with other volatiles, reached the preindustrial stratosphere, which is a conservative minimum estimate in the light of currently available observations and modeling results (Woods et al., 1985; Rose et al., 2006; Textor et al., 2003b). The resulting stratospheric injections per eruption are 0.4–60 kt Br and 12–10,600 kt Cl, leading to atmospheric concentrations similar to those of the 1980s (Table DR1). In contrast to rapid scavenging from the wet troposphere, these inorganic halogen compounds can remain in the dry extratropical stratosphere for as long as 3–6 yr, the stratosphere turnover time (Waugh and Hall, 2002).

## DISCUSSION

To assess the ozone-destroying potential of these volcanic halogen emissions from large explosive eruptions in the past, we first compare them with anthropogenic surface emissions

of long-lived species, which are responsible for much of the present-day ozone depletion, and with the stratosphere's content of ozone-destroying substances. All the Nicaraguan eruptions (Table DR1) yielded instantaneous Br and Cl releases of magnitudes comparable to or larger than the current annual anthropogenic emissions. Moreover, these eruptions generated widespread aerosol clouds, leading to larger reactive surface areas, facilitating enhanced heterogeneous ozone-consuming reactions (Sinnhuber et al., 2009).

The current Br loading in the stratosphere is ~20 ppt and was ~6 ppt before 1980 (Montzka et al., 2011), the beginning of halogen measurements in the stratosphere and therefore the nearest value that can serve as a proxy of preindustrial conditions. The minimum Br emissions (10% of total) by the Nicaraguan eruptions would have added ~0.2–27.5 ppt Br to the stratosphere (Table DR1). Taking a conservative average addition of 1 ppt Br (Table DR1), which ignores the large Upper Apoyo eruption, this implies an average 21% increase of Br per eruption in the preindustrial stratosphere. The corresponding average preindustrial Cl addition of 731 ppt would be ~133% (Fig. 4; Table DR1). The equivalent effective stratospheric chlorine (EESC = Cl + 60 × Br; Danilin et al., 1996) is a measure of the ozone destruction potential (Montzka et al., 2011; Sinnhuber et al., 2009) that weights the ozone-destroying potential of Br relative to Cl. The EESC prior to the massive anthropogenic input, approximated by the 1980 benchmark, is ~1200–2200 ppt for the mid-latitude to polar stratosphere (Montzka et al., 2011), to which the Nicaraguan volcanic eruptions may have added EESC of 23–12,770 ppt (Table DR1). With respect to an assumed pre-1980 mean stratospheric background of 900 ppt EESC (Montzka et al., 2011), this implies,



**Figure 4.** Addition of Br, Cl, and equivalent effective stratospheric chlorine (EESC) per eruption to preindustrial stratospheric concentration (in %) in relation to total atmospheric volume for 14 Nicaraguan Plinian eruptions in the past 70 ka assuming 10% halogen loading to the stratosphere. Preindustrial concentrations are approximated on the basis of the WMO ozone assessment (cf. Montzka et al., 2011) as Br = 6 ppt, Cl = 550 ppt, EESC = 900 ppt for 1980 values. Of 14 eruptions, 9 emitted within one event the same or more EESC compared to the global averaged preindustrial value.



conservatively, an average of 185% EESC addition per Nicaraguan Plinian eruption (Fig. 4).

## CONCLUSIONS

We conclude that most, if not all, of the Plinian eruptions that occurred at the Nicaraguan subduction zone segment during the past 70 ka were probably able to generate temporary substantial ozone depletion in the paleostratosphere. This likely enhanced the ultraviolet stress at the surface, affecting humans and different ecosystems like has been proposed on different time scales but similar degassed masses for the Siberian Trap volcanism (Beerling et al., 2007). For example, if only 10% of the emitted halogens from the Upper Apoyo eruption at 24.5 ka reached the stratosphere (4× and 20× the preindustrial Br and Cl, respectively), this would have resulted in a strong depletion of the paleo-ozone layer.

Globally, an eruption of similar magnitude (M 4–6) and intensity occurs every 5–10 yr and is predominantly associated with subduction zones (Deligne et al., 2010). The Br release during Plinian eruptions may vary between different arcs or arc segments, like other volatiles (e.g., Oppenheimer et al., 2011), but no other arc has yet been studied in similar detail with respect to Br. If we assume the Nicaraguan arc segment to be representative of global subduction zones, and combine this with the fact that 75% of the global subduction zones are located in the tropics, every stratospheric turnover cycle would be affected by considerable volcanically induced ozone depletion. Our results stress the importance of considering volcanic Br emissions along with Cl and sulfate aerosol in order to assess the naturally induced ozone depletion in the stratosphere and their harmful ultraviolet radiation affecting the Earth surface, and therefore Earth's living organisms.

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