Earth and Planetary Science Letters 429 (2015) 234–246

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Bromine and chlorine emissions from Plinian eruptions along the Central American Volcanic Arc: From source to atmosphere

Steffen Kutterolf [a,*], Thor H. Hansteen [a], Armin Freundt [a], Heidi Wehrmann [a], Karen Appel [b,1], Kirstin Krüger [c], Wendy Pérez [a]

[a] GEOMAR Helmholtz Centre for Ocean Research Kiel SFB574, Wischhofstrasse 1-3, 24148 Kiel, Germany
[b] HASYLAB at DESY, Notkestrasse 85, 22607 Hamburg, Germany
[c] Meteorology and Oceanography Department of Geosciences, University of Oslo, Norway

ARTICLE INFO

Article history:
Received 28 February 2015
Received in revised form 29 July 2015
Accepted 30 July 2015
Available online 20 August 2015
Editor: T.A. Mather

Keywords:
explosive volcanism
CAVA
bromine
chlorine
stratospheric load

ABSTRACT

Large explosive volcanic eruptions inject gases, aerosols, and fine ashes into the stratosphere, potentially influencing climate and atmosphere composition on a global scale. Although the potential climate effect of chlorine (Cl) and bromine (Br) injections into the stratosphere is known, the global mass fluxes are poorly constrained. In this study we focus on the magmatic degassing systematics and budgets of Br and Cl, and on constraining the major sources of Br in a subduction setting. We therefore present a regional time series of Br and Cl emissions from 29 highly explosive eruptions throughout the Central American Volcanic Arc (CAVA), covering the last 200 ka, and a range of magmatic compositions and eruption magnitudes. We have measured Br and Cl in matrix glasses and melt inclusions using synchrotron radiation micro X-ray fluorescence spectrometry (SR micro-XRF) and electron microprobe, respectively. Melt inclusions of the CAVA tephras generally have higher Br (0.9 to 17.9 ppm) and Cl (770 to 3800 ppm) contents than the matrix glasses (0.39 to 1.5 ppm Br, 600 to 2800 ppm Cl). Moreover, the difference between maximum and minimum concentrations observed in melt inclusions of a given sample ranges between 9 and 90% of the maximum observed concentration for Br, and between 2 and 40% for Cl. Such intra-sample variations arise from variable pre-eruptive degassing of these halogens into a magmatic fluid phase. The relative loss of Br from the melt is 4 to 68 times higher than that of Cl.

The masses of Br (2–1100 kt) and Cl (0.1 to 800 Mt) emitted by the eruptions generate instantaneous additions to the stratosphere potentially amounting to ~6–5600% of the present-day stratospheric annual global loading of Equivalent Effective Stratospheric Chlorine. As the size of the stratospheric impact is primarily a function of eruption magnitude, we use magnitude-frequency relationships to estimate that eruptions adding ~10% to resident EESC loading would occur every <40 years while every ~200 years an eruption would double the EESC loading.

Comparing the variations in Br and Cl concentrations and particularly minimum Cl/Br ratios in melt inclusions with geochemical trace-element proxies (e.g. U/La, Ba/Th) and lead-isotope compositions, which change along the arc in response to changing subduction conditions, we suggest that subducted calcareous sediment is a major source of magmatic Br but also infer an important role of fluids expelled from serpentinized subducted mantle. Extrapolation of CAVA volcanic Br emissions to the global subduction system thus needs to consider variations in the nature of subducted lithologies.

1. Introduction

Mass balances and element cycling in subduction zones, particularly regarding the flux of volatile species from source to atmosphere has been investigated for decades, and several attempts have been made to extrapolate the data available from single subduction zones to the global scale (e.g. Devine et al., 1984; Freundt et al., 2014; Jarrard, 2003; Pyle and Mather, 2009; Shinohara, 2013). However, an important constraint missing in these approximations has been the combined Cl and Br budgets for magmas erupted through large explosive eruptions, and their relevance for climate and atmospheric chemistry.

The modern Central American Volcanic Arc (CAVA) is an area with one of the largest densities of active volcanoes in the world, and has produced numerous felsic tephras from highly explosive eruptions during the late Pleistocene through the Holocene. Recent

* Corresponding author.
E-mail address: skutterolf@geomar.de (S. Kutterolf).
[1] Now at European XFEL, Albert-Einstein-Ring 19, 22761 Hamburg, Germany.

http://dx.doi.org/10.1016/j.epsl.2015.07.064
0012-821X/

volcanological studies at the CAVA have addressed the along-arc tephrostratigraphy (Kutterolf et al., 2008a, 2007), evolution of single eruptive centers (e.g. Kutterolf et al., 2011; Newhall et al., 1987; Pérez et al., 2009; Peterson and Rose, 1985; Wundermann and Rose, 1984), geochemical along-arc variations with a special focus on the magma genesis (Carr et al., 1990; Hoernle et al., 2008; Patino et al., 2000) and crustal contamination (Vogel et al., 2006; Walker et al., 2007). Volatiles (H_2O, CO_2, Cl and S) in melt inclusions of mostly primitive magma compositions have been analyzed to reveal their influence on eruptive style (e.g., Roggensack et al., 1997) as well as the various contributions of their sources to magma genesis as subduction conditions change along the arc (Roggensack et al., 1997; Sadofsky et al., 2008). Additionally, Freundt et al. (2014) budgeted the cycling of H_2O, CO_2, Cl and S through the subduction system and into the atmosphere.

Recent studies on halogen cycling processes and compositions of source rocks in subduction zones has led to a refined understanding of how subduction zones work (e.g. Kendrick et al., 2014, 2013). However, the heterogeneity of subducted rocks requires the use of geochemical proxies for source identification prior to determination of regional mass budgets (e.g. Bolge et al., 2009; Deschamps et al., 2013; Freundt et al., 2014). Igneous processes in subduction zones are relatively well investigated, but still exsolution and degassing processes and thus halogen release from subduction zone volcanoes are only partly understood (cf. reviews of Aiuppa et al., 2009; Pyle and Mather, 2009). The atmosphere and climate effect of large eruptions has been controversially discussed (e.g. Devine et al., 1984; Montzka et al., 2011; Robock, 2000; and references therein). Several model studies mainly consider emissions of sulphur-containing species (SO_2 and H_2S) into the stratosphere (Robock, 2000; Timmreck, 2012), although both Cl and Br have the potential to destroy the stratospheric ozone layer by chemical reactions that are particularly efficient when halogens interact with sulphur aerosols and salt precipitates on ash particles (e.g. Martin et al., 2012). Recent studies thus show that halogens may have a significant effect on atmospheric chemistry and climate (Montzka et al., 2011; Balcone-Boissard et al., 2010; Bobrowski et al., 2003).

Bromine budgets for past eruptions based on melt inclusion measurements are rare, and this is the first study that provides a complete 200 ka time series for an entire subduction zone, the CAVA. The usefulness of such a long-term regional data set in modeling global atmospheric effects of volcanic sulfur and halogen releases has been demonstrated in recent studies (Krüger et al., 2015; Metzner et al., 2014).

Our pilot study of Br and Cl melt-inclusion concentrations in Nicaraguan tephras (Kutterolf et al., 2013) indicated that volcanic Br emissions, in addition to the Cl emissions, could have a significant impact on the stratosphere. This triggered the present study in which we extend the analytical data base from 14 Nicaraguan eruptions of <70 ka (Kutterolf et al., 2013) to cover the 1200 km length of the entire CAVA over a 200 ka period, comprising 29 large eruptions in total. This also implies a significant extension of the range of eruption magnitudes by including all the very large (VEI > 6) eruptions from the Northern CAVA. Moreover, the subduction setting now ranges from oceanic arc crust (Nicaragua) through transitional arc crust (Costa Rica, El Salvador) to continental crust (Guatemala).

We use this extended data set of bromine and chlorine concentrations and masses discharged during large explosive eruptions to address the following questions: 1) Where does the magmatic bromine originate from? 2) How do bromine and chlorine partition between melt and fluid/vapor phases during magma storage? 3) Does the arc-wide data set confirm the more locally restricted findings from Nicaragua in Kutterolf et al. (2013) that Br and Cl emissions of past eruptions had the power to impact past ozone layers? 4) If so, what would be the implications for the present-day atmosphere?

2. Geological setting

The CAVA is located 150–200 km away from the Middle America trench (Fig. 1) where the Cocos plate subducts beneath the Caribbean plate at convergence rates of 70–90 mm/year (e.g. Barckhausen et al., 2001). The CAVA extends ~1200 km from Guatemala in the northwest to Costa Rica in the southeast. The volcanic arc itself is tectonically divided into ten segments by offsets in strike such that the trench-arc distance decreases northward on each segment (Agostini et al., 2006; Bolge et al., 2009). Systematically changing tectonic parameters such as convergence rate and subduction angle, the tectonic, volcanic, and sedimentary structures of the subducting Cocos Plate, the age, thickness and composition of the overlying Caribbean plate, and variable degrees of magmatic differentiation lead to magmatic compositional diversity along the CAVA (e.g. Carr et al., 1990; Heydolph et al., 2012; Hoernle et al., 2008; Lücke, 2014; Patino et al., 2000; Syracuse and Abers, 2006).

Upper Pleistocene (since ~500 ka) to Holocene arc volcanism has formed a number of large caldera volcanoes at the Northern CAVA (Guatemala and El Salvador), which have produced at least 92 large-magnitude eruptions of highly evolved, silicic magmas resulting in widespread felsic and rare mafic tephras (Kutterolf et al., 2008b, 2008a; Metzner et al., 2014). In the South (Nicaragua and Costa Rica) stratovolcanoes dominate the volcanic arc, and mafic compositions of the erupted widespread tephras occur equally often as silicic ones (Fig. 1).

For this study 29 widespread, mostly felsic, Quaternary tephras are investigated. Complementary to the 14 tephras from Nicaraguan volcanoes (Masaya and Apoyo calderas, Chiltepe, Cosigüina and Ometepe volcanic complexes; see Fig. 1) that were studied by Kutterolf et al. (2013) 15 tephras from Guatemalan (Ayarza, Amatitlán and Atitlán calderas, Santa María volcano), El Salvadorian (Berlin–Chinameca complex, the Ilopango, and Coatepeque calderas) and Costa Rican (Rincón de la Vieja and Poás volcanoes) volcanic centres were investigated (see Fig. 1).

Compositions of these tephras range from typically moderately evolved dacites in the south (Nicaragua) with plagioclase + pyroxene ± amphibole phenocryst assemblages, to predominantly highly-evolved rhyolites in the north (El Salvador and Guatemala) that have amphibole, biotite and even quartz and zircon phenocrysts. Exceptions are some plagioclase, pyroxene and olivine bearing basalts and basaltic andesites from Masaya Caldera in Nicaragua.

Volumes of these tephras range between 1 km^3 to ~100 km^3 (Kutterolf et al., 2008b; Metzner et al., 2014; Table 2). However, an exception is the ~84 ka old Los Chocoyos tephra from Atitlán Caldera in Guatemala, which has about 800 km^3 tephra volume and represents the largest known eruption in Central America. Next to Los Chocoyos, the most prominent, and presumably climate-relevant additional eruptions included in this study are those of the L-Tephra (~191 ka), W-Tephra (~159 ka) and E-Tephra (~60 ka) in Guatemala (e.g. Kutterolf et al., 2008b; Rose et al., 1999), the Arce (~72 ka), Congo (~53 ka) and Tierra Blanca Joven tephras (~1.5 ka) in El Salvador (e.g. Hart, 1983; Kutterolf et al., 2008b). These complement the most climate relevant examples of the Nicaraguan case study; the Upper Apoyo (~25 ka) and Chiltepe tephras (~2 ka) in Nicaragua (Kutterolf et al., 2011, 2007; Metzner et al., 2014).