Atmospheric Environment 45 (2011) 3856–3866

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

On bromine, nitrogen oxides and ozone depletion in the tropospheric plume of Erebus volcano (Antarctica)

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ARTICLE INFO

Article history:
Received 12 October 2010
Received in revised form
8 March 2011
Accepted 9 March 2011

Keywords:
Volcanic plume
Antarctic troposphere
Reactive bromine chemistry
Reactive nitrogen chemistry
Ozone depletion
Phonolitic magma

ABSTRACT

Since the discovery of bromine oxide (BrO) in volcanic emissions, there has been speculation concerning its role in chemical evolution and notably ozone depletion in volcanic plumes. We report the first measurements using Differential Optical Absorption Spectroscopy (DOAS) of BrO in the tropospheric plume of the persistently degassing Erebus volcano (Antarctica). These are the first observations pertaining to emissions from an alkaline phonolitic magma. The observed BrO/SO_2 ratio of 2.5×10^{-4} is similar to that measured at andesitic arc volcanoes. The high abundance of BrO is consistent with high abundances of F and Cl relative to sulfur in the Erebus plume.

Our estimations of HBr flux and BrO production rate suggest that reactive bromine chemistry can explain a 35% loss of tropospheric O_3 observed in the Erebus plume at approximately 30 km from source (Oppenheimer et al., 2010).

Erebus also has a permanent lava lake, which could result in generation of NO_x by thermal fixation of atmospheric N_2 at the hot lava surface. Any NO_x emission could play a potent role in reactive bromine chemistry. However, the presence of NO_2 could not be detected in the plume, about 400 m above the lake, in our DOAS observations of 2005. Nor could we reproduce spectroscopic retrievals that reportedly identified NO_2 in DOAS observations from 2003 made of the Erebus plume (Oppenheimer et al., 2005). Based on the NO_2 detection limit of our analysis, we can state an upper limit of the NO_2/SO_2 ratio of $\leq$0.012, an order of magnitude lower than previously reported. Our new result supports a rapid oxidation of NO_x in the young plume and is more consistent with measurements of NO_y species measured using an instrumented aircraft flying in the plume. Model simulations, tuned for Erebus, were performed to reproduce the BrO/SO_2 observed in the young plume and to investigate the impact of NO_x emissions at source on the subsequent formation of BrO in the plume. They support our hypothesis of rapid conversion of NO_x to NO_y in the vicinity of the lava lake. This study thus places new constraints on the interaction between reactive nitrogen and bromine species in volcanic plumes, and its effects on ozone.

1. Introduction

Both the sustained 'quiescent' degassing of volcanoes (Halmer et al., 2002) and sporadic explosive eruptions contribute significant quantities of reactive gases and aerosols to the atmosphere (Robock and Oppenheimer, 2003; Oppenheimer et al., 2003; Mather, 2008; von Glasow et al., 2009). Much attention has been paid to major gases including CO_2, an important greenhouse gas, SO_2 a precursor for sulfate aerosols which impact radiative forcing, and HCl and HF responsible for acid deposition with potentially significant environmental and agronomic impacts. The reactive trace halogen species, BrO, was first reported in volcanic plumes by Bobrowski et al. (2003) (see Table 1 for a review of all available observations to date). Also, reactive trace nitrogen species have been identified (Hobbs et al., 1982, 1991; Huebert et al., 1999; Mather et al., 2004b; Oppenheimer et al., 2005). Reactive nitrogen oxides (NO_x) are thought to be generated initially via thermal fixation of atmospheric N_2 near the surface of a hot lava

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doi:10.1016/j.atmosenv.2011.03.027

Table 1
Table of reported worldwide volcanogenic BrO observations (sorted according to decreasing BrO/SO_2 molar ratio).

Date	Volcano	BrO/SO_2 (molec) $\times 10^{-4}$	Max (or avg) BrO CA ($\times 10^{14}$ molec/cm^2)	SO_2 flux (kg/s)	Distance from source where plume is crossed (km)	Reference
May 02	Soufrière Hills	10	8.4		4	Bob03
May 04	Sakurajima	10	10	—	A few km	Lee05
Aug 07	Ambrym	4.5–7.0	6.6–8.3×l0^3 (avg)	39–59	13–14	Ban09
Jan 07		2.3–4.1	1.7×l0^4 (avg)	179–268	15–40	Ban09
Mar 07		0.1	1.0 $\times 10^4$ (avg)	382	11	Ban09
Jul 07		0.5	7.5 $\times 10^3$ (avg)	25	4	Ban09
Sep 03	Etna	4.8	1.**1**	—	7	Bob07
Aug 04/ May 05		0–4.5	5	—	0–19	Bob07
Aug 04		2.1	4.8	—	2.5	Bob07
Aug 04		1.9	3	11	2–3	0pp06
Dec 05	**Erebus**	2.5	5.1	0.7±0.3	~ 0.4	Boi11a
Sep 04	Stromboli	2.1	6.9	—	2	Bob07
Nov 04	Villarica	1.3	1,3	—	4	Bob07
Mar 03	Masaya	0.8	1.9	—	0.6	Bob07
Apr 07		0.3	2.7		Above crater	Ker09
Nov 08	Popocatépetl	0.3	3	16–31	~ 0.4	Boi11b

Ban09: Bani et al. (2009), Bob03; Bobrowski et al. (2003), Bob07: Bobrowski and Platt (2007), Boi11a: *[This study]*, Boi11b: (Boichu in preparation), Ker09; Kern et al. (2009), Lee05: Lee et al. (2005), 0pp06: Oppenheimer et al (2006).

body and/or in a high-temperature mixture of magmatic and atmospheric gases, followed by in-plume oxidation (Huebert et al., 1999; Mather et al., 2004b; Oppenheimer et al., 2005; Martin et al., 2006). Reactive halogens are not emitted directly from magma, but are formed from hydrogen halides (e.g., HCl and HBr) (Gerlach, 2004) as a result of heterogeneous chemical reactions during plume transport and mixing with background air (Oppenheimer et al., 2006; Bobrowski et al., 2007). The autocatalytic formation of BrO (also called the 'BrO explosion') is the result of a complex sequence of reactions taking place in the plume. It first involves gas phase reactions generating HOBr and $BrONO_2$ and/or $BrNO_2$ which then heterogeneously interact with acid aerosols to form Br_2 or BrCl species. Further photolysis and reaction with O_3 sourced by entrainment of ambient air, generates BrO. Readers are referred to the review of von Glasow and Crutzen (2003) and papers of Oppenheimer et al. (2006), Bobrowski et al. (2007), Roberts et al. (2009) and von Glasow (2010) for a more complete and detailed description of these sequences of chemical reactions. Despite their low abundances, reactive halogens can play a key role in a volcanic plume as they have the potential to consume ambient O_3 (Bobrowski et al., 2003; Roberts et al., 2009), which is fundamental in the troposphere, as the primary source of hydroxyl radicals and as a strong oxidizing agent. NO_x species also deserve attention since they can strongly perturb reactive halogen chemistry. Whereas observations of ozone depletion have been made in volcanic plumes from Mt. St. Helens (Hobbs et al., 1982), Hekla (Rose et al., 2006) and Eyjafjallajökull (Schumann et al., 2010), the simultaneous presence of reactive halogens in a tropospheric plume has not been reported previously.

Erebus volcano provides an exceptional opportunity to understand the chemical evolution of volcanic plumes and their impact on the troposphere. Because of its southerly location on Ross Island in Antarctica (77° 32′ S, 167° 10′ E), this volcano affects the near pristine polar atmosphere (Graf et al., 2010). It also presents a sustained activity, as it degasses persistently from a permanent lava lake, first observed in the 1970s (Giggenbach et al., 1973; Kyle et al., 1982), but possibly already present in 1841 (Ross, 1847). The summit crater of the volcano reaches up to 3794 m in altitude typically entraining the plume at a height of close to 4000 m above sea level. This promotes a long atmospheric lifetime of gas and aerosol species and a consequently wide dispersion (Graf et al., 2010). The influence of Erebus' degassing has been identified more than 1000 km away above the polar plateau thanks to numerous observations: particle, trace metals and chlorine deposits (Chuan et al., 1986; Chuan, 1994; Zoller et al., 1974; Meeker et al., 1991; Zreda-Gostynska et al., 1997), as well as airborne sulfate aerosols, SO_2 and gas phase NO_y species (Slusher et al., 2010). Ice cores from East Antarctica contain also evidence of volcanic (Erebus) input (Vallelonga et al., 2002). Determining the exact influence of Erebus' emissions, including reactive trace species, is thus important for understanding the state of the Antartic troposphere and even for interpretation of glaciochemical records extracted from the polar ice.

The data already gathered at this volcano are extensive. They include near-source rim observations of gas flux and composition (Zreda-Gostynska et al., 1993, 1997; Kyle et al., 1994; Wardell et al., 2004; Sweeney et al., 2008; Oppenheimer and Kyle, 2008; Boichu et al., 2010), and of particle emissions (Meeker et al., 1991; Zreda-Gostynska et al., 1997; Wardell et al., 2008; Ilyinskaya et al., 2010), but also airborne in-situ measurements of aerosols (Radke, 1982; Chuan et al., 1986; Chuan, 1994; Oppenheimer et al., 2010) and various gas species in the aged plume (Rose et al., 1985; Oppenheimer et al., 2010). Oppenheimer et al. (2010) recently showed evidence for ozone depletion in the plume, ~30 km downwind from source. This result importantly demonstrates ozone depletion in plumes within the free troposphere, in contrast to boundary-layer ozone depletion events (ODE's) that occur during springtime in Antarctica as solar radiation becomes available (see Simpson et al., 2007, for a review). As a consequence, the impact of in-plume reactive bromine chemistry on this destruction of O_3 begs investigation.

Here we report the first differential optical absorption spectroscopy (DOAS) observations of BrO in the Erebus plume in December 2005. These are the first observations pertaining to phonolitic magma (see Table 1). Together with calculations of HBr source emissions, this enables evaluation of the dynamics of the 'BrO explosion' at this volcano.

Oppenheimer et al. (2005) reported the presence of NO_2 in the Erebus plume based on evaluation of ultraviolet spectra collected in December 2003. However, NO_2 was not detected in DOAS measurements and observations from instrumented aircraft flying in the plume (Oppenheimer et al., 2010) collected in December 2005. To investigate this puzzling observation, we also carry out here a reassessment of the DOAS observations reported by