AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER
10.1002/2013GL058416

Key Points:
- First observation of a volcanic plume of OClO from space
- Observations of BrO and HCl support the volcanic origin of the OClO detected
- Heterogeneous chemistry on volcanic aerosols is the cause of halogen activation

Supporting Information:
- Readme
- Table S1
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Citation:
Theys, N., I. De Smedt, M. Van Roozendael, L. Froidevaux, L. Clarisse, and F. Hendrick (2014), First satellite detection of volcanic OClO after the eruption of Puyehue-Cordón Caulle, *Geophys. Res. Lett.*, *41*, 667–672, doi:10.1002/2013GL058416.

Received 22 OCT 2013
Accepted 20 DEC 2013
Accepted article online 27 DEC 2013
Published online 23 JAN 2014

First satellite detection of volcanic OClO after the eruption of Puyehue-Cordón Caulle

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Abstract Volcanoes release large amounts of halogen species such as HCl and HBr, which can be converted into reactive halogens by heterogeneous photochemical reactions that are currently not fully characterized. Here we report on the first satellite detection of volcanic chlorine dioxide (OClO). Measurements were performed using the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography instrument for the ash-laden plume emitted after the 2011 eruption of Puyehue-Cordón Caulle in Chile. We also identified volcanic BrO using the Ozone Monitoring Instrument, as well as enhanced HCl in data of the Microwave Limb Sounder instrument. These observations suggest that OClO was formed in the plume by the ClO + BrO reaction in presence of a large excess of ClO. The present satellite data set could help better understand reactive halogen chemistry in volcanic plumes and its impact on atmospheric composition.

1. Introduction

Volcanic degassing produces large amounts of H_2O, CO_2, SO_2, H_2S, and halogens (HCl, HBr, HF). The study of these volatiles provides key information on magmatic processes and eruptive styles [*Symonds et al.*, 1994]. Halogen species are believed to play an important role in magmatic systems [*Aiuppa et al.*, 2009] and once emitted, they are known to affect the atmospheric chemistry [*von Glasow et al.*, 2009]. A key chemical process is arguably the conversion of HBr and HCl into reactive species via a series of fast heterogeneous catalytic reactions on the surface of volcanic aerosols [*Oppenheimer et al.*, 2006; *Bobrowski et al.*, 2007]. While this mechanism can strongly affect ozone budgets locally, its relevance on the global scale is not known because total volcanic halogen source strengths are only poorly constrained [*Halmer et al.*, 2002; *Aiuppa et al.*, 2009; *Pyle and Mather*, 2009].

Atmospheric measurements of reactive halogen species in volcanic plumes (see references, e.g., in *Saiz-Lopez and von Glasow* [2012]) have focused a lot on the detection of BrO, from ground-based [*Bobrowski et al.*, 2003, 2007; *Oppenheimer et al.*, 2006], aircraft [*Heue et al.*, 2011], and satellite platforms [*Theys et al.*, 2009; *Hörmann et al.*, 2013]. Conversely, there has been only a handful of papers dealing with measurements of volcanic chlorine oxides as ClO and OClO (a species formed by the reaction of BrO and ClO) or molecular chlorine and these were all obtained using ground-based instruments [*Lee et al.*, 2005; *Bobrowski et al.*, 2007; *Zelenski and Taran*, 2012]. From space, HCl has been identified in volcanic plumes from several explosive eruptions [*Prata et al.*, 2007; *Read et al.*, 2009] but there has not been a single detection of reactive chlorine of volcanic origin that could help better understand plume composition and chemistry.

Ultraviolet satellite nadir observations of OClO have been used extensively to study stratospheric chlorine activation in polar winters [e.g., *Kühl et al.*, 2004; *Oetjen et al.*, 2011]. Here we report the first satellite detection of OClO in a volcanic plume, complemented by simultaneous measurements of BrO and HCl. The observations were performed after the explosive eruption of the Puyehue-Cordón Caulle (PCC) volcano in Chile (40.59°S, 72.12°W; 2236 m above sea level) which started on 4 June 2011 around 19:15 UTC. The volcano emitted about 200 kT of SO_2 [*Theys et al.*, 2013] and copious amount of ash [*Clarisse et al.*, 2013] in the atmosphere. The plume was injected at tropopause levels (12-14 km) and then transported by strong westerly winds. It circled around the globe for several days close to the terminator, providing favorable conditions to measure OClO (the formation of OClO is mitigated at high sun due to rapid photolysis).

2. Data

This work is based on satellite observations from the polar sun-synchronous EOS Aura/Microwave Limb Sounder (MLS), Envisat/Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), and EOS Aura/Ozone Monitoring Instrument (OMI).

We used version 3.3 Level 2 MLS HCl retrievals [*Froidevaux et al*., 2008] at 146.7 mb (~14 km) and for latitudes southward of 20°S. The HCl data were extracted using a fixed threshold of 1.35 ppbv, which corresponds to values above the background plus noise at the 3σ level. The estimated accuracy of HCl mixing ratios from MLS is about 0.3 ppbv.

OClO and BrO slant columns were retrieved using differential optical absorption spectroscopy (DOAS) [*Platt and Stutz*, 2008] from SCIAMACHY and OMI nadir spectra, respectively. The retrieval of OClO was performed in the wavelength interval from 365 to 389 nm, using similar settings as described by *Oetjen et al*. [2011]. In addition to the cross-section of OClO, the DOAS fit includes spectral signatures for NO_2, SO_2, O_4, the Ring effect and corrections for the undersampling and polarization sensitivity of the instrument. As the PCC volcano is located in the region of the South Atlantic Anomaly (SAA), we have also applied a procedure to remove spikes in the spectra [*Richter et al*., 2011]. The analysis of BrO was made in the fitting window 328.5–359 nm [*De Smedt et al*., 2012; *Theys et al*., 2011] and includes spectra for BrO, H_2CO, O_3, NO_2, OClO; the Ring effect; and a spike correction as well. The OMI BrO retrieval also includes reference radiance spectrum selection and accurate wavelength calibration separately for each of the 60 detector rows of OMI.

To convert the retrieved slant columns of OClO and BrO into vertical columns, we have used geometrical air mass factors adequate for a stratospheric absorber. To isolate the signal from nonvolcanic background, we applied two different kinds of offset corrections to the measurements. For OClO, the slant columns are normalized to the daily values as a function of solar zenith angle (SZA). The offset correction for BrO removes the total atmospheric (troposphere and stratosphere) BrO background. It applies to the vertical columns and depends on latitude and cross-track position (to reduce stripes in the retrievals). The OMI data affected by the so-called row anomaly issue and exhibiting high fitting residuals are filtered out.

From the data scatter, we evaluate the lower detection limit for the retrieved vertical columns of OClO and BrO to be about 2×10^{13} molecules/cm^2 for individual pixels. We estimate the typical accuracy of the OClO and BrO columns to be around 35% and 25%, respectively.

To help identify and characterize the volcanic plume, we have also used SO_2 column and aerosol/ash index products from satellite nadir instruments, available at http://sacs.aeronomie.be [*Brenot et al*., 2013].

3. Results and Discussion

Figure 1 (top) shows MLS HCl mixing ratios at 146.7 mb for June 2011. Several data points are located at high latitudes and are probably due to the presence of the Antarctic polar vortex, but elevated HCl values (up to 2.5 ppbv) are also detected at midlatitudes and are distributed as a ring-like structure collocated with the volcanic ash cloud from PCC detected by Infrared Atmospheric Sounding Interferometer (IASI) [*Clarisse et al*., 2013]. This suggests a volcanic origin. Our hypothesis is further strengthened by the statistics of HCl values above the background (as defined above) at mid-latitudes in austral winter for 2010–2012 (Figure 1, bottom), which show a sharp increase in the number of HCl detections only in June 2011. Note that the first sounding of the volcanic plume by MLS was on 7 June 2011, i.e., about 60 h after the emission peak of the PCC eruption [*Theys et al*., 2013]. Hence, the MLS HCl values are not representative of the young plume of PCC. Investigation of MLS data also reveals SO_2 (not shown) from the PCC eruption up to 77 ppbv (with a detection limit of ~15 ppbv). By considering the data for which both HCl and SO_2 mixing ratios are above their respective limits of detection, we estimate a range of values for the ratio HCl:SO_2 of 0.03 to 0.11 which is similar to that found for the eruptions of Soufrière Hills [*Prata et al*., 2007] and Hekla [*Rose et al*., 2006]. It should be stressed that the MLS HCl mixing ratios underestimate the volcanic cloud concentrations, because the plume vertical extent is smaller by about a factor of 3 than the vertical resolution of the MLS HCl product [*Froidevaux et al*., 2008]. Taking this feature into account, we can estimate the concentration of HCl in the young portion of the volcanic plume (not sampled by MLS) by applying a factor for the atmospheric dispersion that is the ratio of the

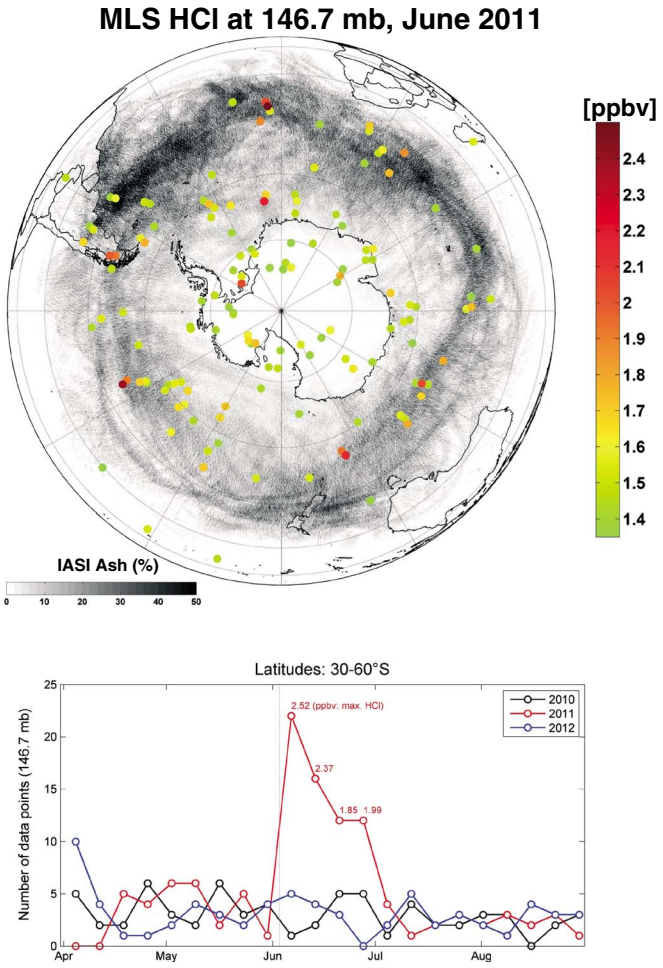

Figure 1. (top) Southern Hemisphere MLS measurements of HCl (ppbv) at 146.7 mb overlay on volcanic ash detection by IASI in percentages per grid cell, for June 2011. (bottom) Weekly number of MLS HCl values above the background (see text) at 146.7 mb for the austral winters of 2010, 2011, and 2012 (latitudes: 30–60°S). The dashed line indicates the start of the PCC eruption on 4 June 2011. The numbers (in red) are the maximum HCl values (ppbv) measured in June 2011.

maximum SO_2 columns measured by IASI on 5 June (the closest overpass after the start of the eruption) to the columns measured on 7 June 2011. The range of deduced values for HCl in the young plume is about 30–50 ppbv, which is similar to in-situ measurements of HCl by *Rose et al*. [2006] for the 2000 Hekla plume (comparable in terms of total SO_2 released to PCC).

Retrieval results of OClO and BrO are presented in Figure 2 for the period 5–9 June, corresponding to near-twilight conditions (60–85° SZA range). For five consecutive days, a plume of elevated OClO and BrO was detected after the eruption of PCC with column values well above or close to the detection limits. An excellent correlation was found between the spatial extent of the plume and the corresponding ash plume (white lines) measured by SCIAMACHY and Atmospheric Infrared Sounder (AIRS)—which is used here because the sensor has a better sensitivity to ash and similar overpass time than OMI. Note that the enhanced OClO columns outside the volcanic plume contours are artifacts due to the SAA.

To demonstrate the unambiguous detection of volcanic OClO, an exemplary fitting result for an averaged spectrum of the five SCIAMACHY measurements with the highest OClO slant columns is given in Figure 3, showing clear OClO absorption signatures for the PCC eruption plume. In order to consolidate the observations presented here, we have conducted a series of tests to retrieve OClO from spectra acquired by OMI and GOME-2 (onboard MetOp-A) and we also inspected the SCIAMACHY and GOME-2 BrO column data [*Theys et al*., 2011]. In general, the data quality was found to be lower than in Figure 2; notably, the

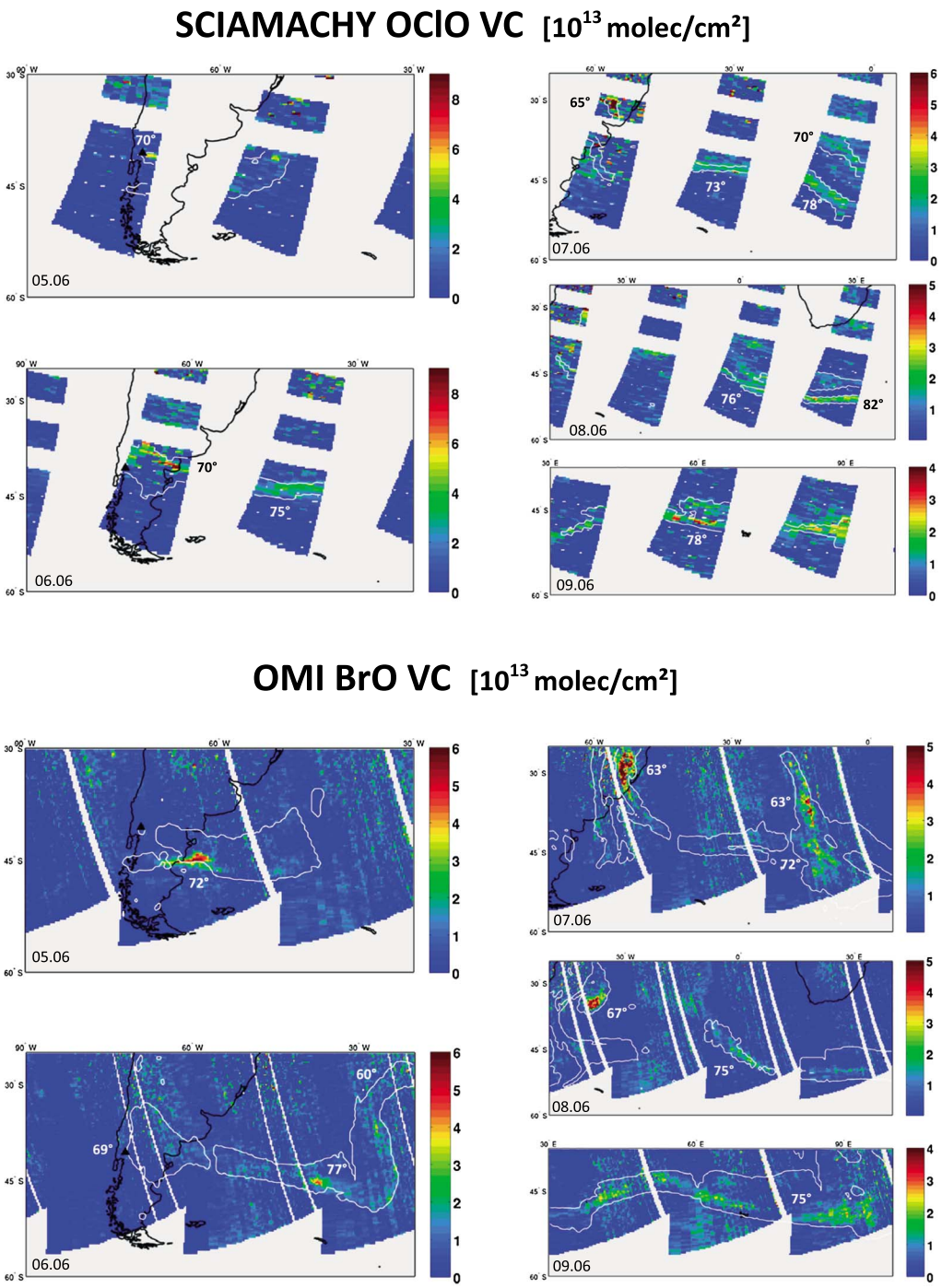

Figure 2. Vertical column measurements of (top) OClO by SCIAMACHY and (bottom) BrO by OMI after the eruption of the PCC volcano (marked by a black triangle) during the period of 5–9 June 2011. Note that the color scales have been chosen in a way that the OClO and BrO plumes can be best visualized. The volcanic plume is identified with the white line contour based on the aerosol index products from SCIAMACHY and AIRS (onboard EOS Aura), respectively. The numbers inset are indicative of the solar zenith angle in degree for a selection of satellite hotspots.

scatter of data is larger. It is believed to reflect differences in instrumental performances (e.g., in terms of signal-to-noise ratio and spectral resolution), fitting windows used, and overpass times-SZA. Nevertheless, signals of volcanic OClO and BrO from PCC could be identified in all these data sets (see Figures S1 and S2 in the supporting information).

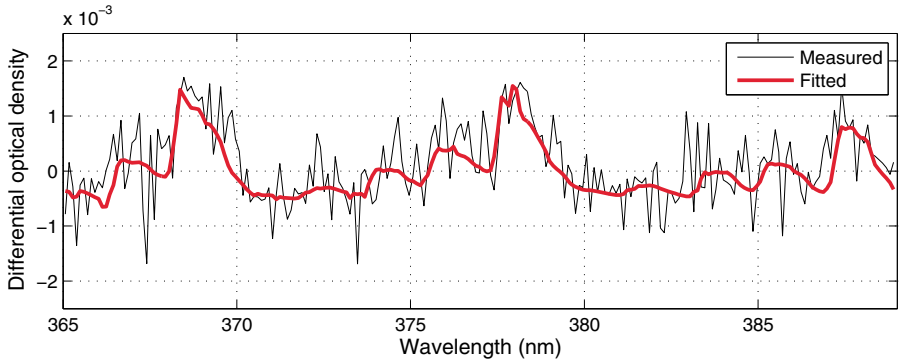

Figure 3. Example of a fit of OClO for a spectrum obtained by averaging five SCIAMACHY measurements of the PCC plume with the highest OClO slant columns (6 June 2011).

Generally speaking, BrO was only measured for scenes with modest SZA (60–75°) while OClO could be detected for SZA up to 82° (Figure 2). This behavior is consistent with the expected photochemical tie between BrO and OClO:

$$BrO + ClO \rightarrow OClO + Br \quad (R1)$$

$$OClO + h\nu \rightarrow ClO + O \quad (R2)$$

Interestingly, the OClO and BrO vertical columns in Figure 2 vary in similar ranges with maximum values of 10 and 7×10^{13} molecules/cm^2, respectively, which correspond to mixing ratios of ~ 170 and 120 parts per trillion by volume for a 1 km thick plume. Our understanding of this feature is that the OClO and BrO abundances reflect a photostationary state ($[OClO] = k_1[BrO][ClO]/J_{OClO}$) and that the ClO mixing ratio in the PCC plume should have been typically in excess, i.e., about 1 ppbv or larger ($\approx J_{OClO}/k_1$).

From Figure 2, one can also see differences in the measured patterns of OClO and BrO. They are due—to some extent—to differences between SCIAMACHY and OMI instruments in terms of spatial coverage and overpass time. However, the heterogeneous photochemical processes releasing halogen oxides, and leading to the steady state between BrO and OClO, rely on many parameters that are very variable and depend on the age of the volcanic plume and its composition [*Bobrowski et al.*, 2007]. Therefore, it is likely that differences between OClO and BrO in Figure 2 (see also the supporting information) reflect local changes in the concentration of halogens in the aerosol and gas phases, the particle surface areas available for the recycling of halogen oxides, and the solar radiation extinction by volcanic aerosols (e.g., affecting J_{OClO}).

A striking feature in Figure 2 is the low abundances of BrO and OClO in the early plume of the PCC eruption, which conversely was the most rich in SO_2 [e.g., *Theys et al.*, 2013]. This is most apparent on 5 June 2011 on the eastern part of the volcanic plume. One explanation is that the scavenging of halogen halides (HCl and HBr) by water, ice, or ash [*Textor et al.*, 2003] was very efficient in the early stage of the eruption so that the production of BrO and OClO was limited. Another possibility that cannot be ruled out is a time shift in the initial volcanic emissions of halogens compared to SO_2, resulting, e.g., from differences in magmatic solubility [see, e.g., *Aiuppa et al.*, 2009].

4. Conclusions

We have reported the first space-based measurement of a large volcanic OClO plume, with vertical columns up to 1×10^{14} molecules/cm^2, that could be tracked for 5 days after the 2011 eruption of Puyehue-Cordón Caulle. This was complemented by simultaneous observations of BrO and HCl enhancements in the plume. As the main production channel of OClO is the reaction of ClO with BrO, the latter measurements support the positive detection of volcanic OClO. These observations suggest that ozone has likely been depleted in the volcanic cloud through the ClO/BrO catalytic cycle [*McElroy et al.*, 1986].

The evidence for volcanic halogens activation for many days points to a very efficient recycling mechanism of halogen oxides on the surface of volcanic aerosols. The satellite observations presented here, combined with

measurements of volcanic aerosol parameters (composition, size distribution, and concentration), offer the opportunity to further study and model reactive halogen chemistry in volcanic plumes and help to better characterize the potential of such volcanic emissions to deplete ozone, especially for large explosive volcanic eruptions [*Kutterolf et al*., 2013].

The potential for observing volcanic OClO in the future is important as forthcoming space nadir ultraviolet instruments will have improved spectral performances and improved spatial and temporal resolution.

Acknowledgments

This research has been financially supported through the Belgium Prodex A3C and TRACE-S5P projects, the EUMETSAT O3M-SAF CDOP-2 project, and the ESA SACS-2 and S5P projects. Work at the Jet Propulsion Laboratory was performed under contract with the National Aeronautics and Space Administration; contributions from Bill Read are also acknowledged.

The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

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