

**BrO/SO₂ in relation
with volcanological
observations**

N. Bobrowski and
G. Giuffrida

This discussion paper is/has been under review for the journal Solid Earth (SE).
Please refer to the corresponding final paper in SE if available.

Bromine monoxide/sulphur dioxide ratios in relation to volcanological observations at Mt. Etna 2006–2009

N. Bobrowski¹ and G. Giuffrida²

¹Institute for Environmental Physics, Heidelberg, Germany

²Istituto Nazionale Geofisica e Vulcanologia, Palermo, Italy

Received: 6 March 2012 – Accepted: 9 March 2012 – Published: 16 March 2012

Correspondence to: N. Bobrowski (nicole.bobrowski@iup.uni-heidelberg.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

Over a three year period, from 2006 to 2009, frequent scattered sun light DOAS measurements were conducted at Mt. Etna in a distance of around six kilometres downwind from the summit craters. During the same period and in addition to these measurements, volcanic observations were made by regularly visiting various parts of Mt. Etna.

Results from these measurements and observations are presented and their relation is discussed. The focus of the investigation is the bromine monoxide/sulphur dioxide (BrO/SO₂) ratio, and its variability in relation to volcanic processes.

That the halogen/sulphur ratio can serve as a precursor or indicator for the onset of eruptive activity was already proposed by earlier works (e.g. Noguchi and Kamiya, 1963; Menyailov, 1975; Pennisi and Cloarec, 1998; Aiuppa, 2002). However, there is still a limited understanding today because of the complexity with which halogens are released, depending on magma composition and degassing conditions. Our understanding of these processes is far from complete, for example of the rate and mechanism of bubble nucleation, growth and ascent in silicate melts (Carroll and Holloway, 1994), the halogen vapour-melt partitioning and the volatile diffusivity in the melt (Aiuppa et al., 2009).

With this study we aim to add one more piece to the puzzle of what halogen/sulphur ratios might tell about volcanic activities. Our data set shows an increase of the BrO/SO₂ ratio several weeks prior to an eruption, followed by a decline before and during the initial phase of eruptive activities. Towards the end of activity or short afterwards, the ratio increases to baseline values again and remains more or less constant during quiet phases. To explain the observed evolution of the BrO/SO₂ ratio, a first empirical model is proposed. This model suggests that bromine, unlike chlorine and fluorine, is less soluble in the magmatic melt than sulphur.

By using the DOAS method to determine SO₂, we actually observe most of the emitted sulphur of Mt. Etna. Regarding bromine however, we are aware that by determining only the bromine monoxide (BrO) radical we might just observe a small or even

SED

4, 475–505, 2012

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

a variable fraction of the total emitted bromine. Therefore we present first studies to justify the assumption that despite the disadvantage just mentioned, the BrO/SO₂ ratio can nevertheless serve as a new parameter to indicate the state of a volcano, when measurements are conducted under certain, but rather convenient conditions.

1 Introduction

Etna is a significantly and continuously degassing volcano with frequently occurring eruptive activity. It is situated on the eastern side of Sicily and has four active summit craters. Being a rather developed tourist destination in Europe, there are less logistical challenges than at most other volcanic sites. Therefore Mt. Etna is a perfect place to study variations in the composition during volcanic phenomena.

Halogen/sulphur ratios, in particular chlorine/sulphur ratios, in volcanic plumes are considered to be geochemical tools for monitoring volcanic activity (e.g. Tazieff, 1983). Most of the studies have been carried out for chlorine, less for fluorine and nearly none for bromine and iodine. The probably main reason for this is the limited sensitivity for the detection of the much less abundant heavier halogens. Most investigations showed decreasing chlorine/sulphur (Cl/S) ratios prior or during volcanic activity (e.g. Noguchi and Kamiya, 1963; Stoiber and Rose, 1970; Menyailov, 1975; Pennisi and Chloarec, 1998; Aiuppa et al., 2002). Nevertheless careful interpretations and differentiated discussions on the data in context of the volcanic environment are necessary like e.g. discussed in Edmonds et al. (2001). The authors showed that the HCl flux could be used as a proxy for the extrusion rate, whilst the variations in the SO₂ emissions were closely related to changes in the soil permeability. Edmonds et al. (2001) showed that in the case of Soufriere Hills volcano, Montserrat, this information can be used to find conclusions about the state of the eruption. The eruptive events were finishing there when SO₂ emissions remain consistently low, HCl emission rates are less than 100 t d⁻¹ and the HCl/SO₂ ratio is less than 0.1.

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**BrO/SO₂ in relation
with volcanological
observations**N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In early studies, Cl/S ratios were collected only by dangerous sampling directly from the emission source. More recently, remote sensing techniques, in particular Fourier transform infrared spectroscopy (FTIR), are applied as well (e.g. Edmonds et al., 2001, Horrocks et al., 2003; Burton et al., 2007; Oppenheimer et al., 2008; Burton et al., 2010). This new possibility due to the improvements of measurement technology allows studies with a higher time resolution (e.g. Caltabiano et al., 2004; Burton et al., 2003) and therefore provides a better understanding, especially of rapid processes like explosions (e.g. Burton et al., 2007; Edmonds et al., 2009). Unfortunately this method is often applied in a safe distance only during clear sky conditions, because usually direct sunlight is used as light source. Other light sources can be e.g. hot lava bodies in the background or artificial lights, commonly used only for the case of crater rim measurements or active eruptive sites, but in those cases the measurements are carried out in a close distance (hundreds of meters) to the active volcanic source.

Furthermore recent laboratory and model studies of vapour-melt partition coefficients and diffusion properties of sulphur and chlorine (e.g. Villemant and Boudon, 1999; Bureau et al., 2000; Moretti et al., 2003; Aiuppa et al., 2004; Spilleart et al., 2006; Aletti et al., 2007) contributed to an improved understanding of volcanic processes as well (e.g. Aiuppa et al., 2004; Spilleart et al., 2006; Burton et al., 2007). However, it has to be mentioned that many questions remain still open (e.g. Aiuppa, 2009; Shinohara, 2009) and disagreements between some of the studies prove the incomplete understanding of the process (see Aiuppa et al., 2004, Figs. 5 and 6 in comparison to Spilleart et al., 2006, Fig. 4).

Beside chlorine, as mentioned above, fluorine, bromine and iodine are also emitted from volcanoes (e.g. Aiuppa et al., 2005), but much less research was undertaken on these halogens until now. Most halogens are predicted (thermodynamically) to escape from magmas as halogen halides (HCl, HBr etc, e.g. Gerlach, 2004) and in small parts as halogen molecules or even in the form of atoms. However more recent studies of von Glasow, 2010 propose that HBr at the crater rim would only have a proportion of 60% of the total emitted bromine and decrease rapidly in an ageing plume down to

below 20 % after roughly 10 min, instead BrO would have a fraction of about 10 % in any case and does not even change dramatically in the ageing plume after the first few minutes (e.g. Bobrowski et al., 2009; Vogel et al., 2010).

In this study we explore the possibility of using BrO/SO₂ measurements as a further parameter to enhance our knowledge of gas emission changes as indicators of magma movements. BrO and SO₂ are both easily measurable with DOAS instruments under conditions less limited to weather than measurements of HCl and HF with the FTIR technique at safe distances from the emission source. Therefore BrO/SO₂ ratios could provide a convenient and continuous additional measurement parameter.

BrO is not thought to exist as a significant bromine species in the magmatic gas, and it is predicted to be formed once the plume comes into contact with the surrounding atmospheric. In fact, BrO mixing ratios are predicted to increase rapidly (by photolysis) in the presence of sunlight (e.g. Oppenheimer et al., 2006; Bobrowski et al., 2007; von Glasow, 2010), due to the autocatalytic bromine explosion mechanism (Wennberg, 1997). In the light of this disadvantage first sensitivity studies are presented of the behaviour of BrO under various meteorological conditions and plume ages.

The presented three year time series during which two eruptions have taken place will demonstrate that BrO/SO₂ ratios might become a proper tracer of volcanic activity in the future.

2 Measurements

Beside the MAX-DOAS measurements between 2006–2009, also 2004 and 2005 BrO/SO₂ measurements were carried out using a mini-Max-DOAS instrument approximately six km from the summit of Mt. Etna (Rifugio Citelli, see Fig. 1). Since 2006, attempts have been made to perform more regular and frequent measurements at the same distance of six km, depending on the wind direction at Rifugio Citelli (eastern flank), Rifugio Sapienza (southern flank), Mt. Maletto (western flank) or Mt. Conca (northern flank) (see Map, Fig. 1). Apart from small periods in which no data were

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



taken due to instrumental failure, very bad weather condition or absence of the authors and helpers data were collected once or several times a week for at least an hour until 2009.

The measurements for determining the BrO/SO₂ ratios were carried out with a scanning DOAS instrument (mini-MAX-DOAS, see e.g. Bobrowski et al., 2003) in the late morning, midday or early afternoon. In the beginning of the longer eruptive periods July 2006 and May–July 2008, BrO/SO₂ ratios were measured with a higher frequency, about every two days.

The miniaturized MAX-DOAS-system consists of an entrance optic (quartz lens, $f = 40$ mm, $d = 20$ mm, field of view approximately 10 mrad) coupled to a quartz fiber bundle (4×200 μm , which transmits the light into a commercial miniature spectrometer (OceanOptics Inc., USB2000). This unit is placed inside a metal box. An attached stepper motor is mounted on a tripod and can therefore rotate the whole unit to point the telescope to different elevation angles between 0 and 130 degrees. Automatic data acquisition was performed with the software package DOASIS (Kraus et al., 2001) running on a notebook computer, or with the software PocketDOAS (Lowe, 2004) running on a small Pocket PC.

For the evaluation of the data the software WinDoas V2.10 from IASB (Belgium Institute for Space Aeronomy, (Fayt and Van Roozendael, 2001)) was used to derive the slant column densities (SCD) in molecules cm^{-2} of BrO and SO₂ from the recorded spectra. For details of the BrO and SO₂ evaluation see Bobrowski et al. (2004). The only slight difference in the SO₂ evaluation was a shift in the wavelength range from 307.5–315 nm to 315–325 nm, for a better signal to noise ratio and to better account for non-linearity effects in case of high SO₂ concentrations (see also Kern et al., 2010; Bobrowski et al., 2010). Also the data of 2004 and 2005 were re-evaluated in this way for a better comparison. The whole data set is shown in Fig. 2. Every data point in Fig. 2 presents a single measurement day and was obtained from a BrO-SO₂ correlation plot.

BrO/SO₂ in relation with volcanological observationsN. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3 Sensitivity studies

To demonstrate the potential value of BrO in relation with SO₂ as a tracer of changes in volcanic activity, investigations of possible environmental effects which could influence the concentration of BrO and therefore the BrO/SO₂ ratio must be carried out. For BrO this is particularly important as BrO is a highly reactive molecule.

As already mentioned above BrO is supposed to be not directly emitted by volcanoes, at least not the major part of it (e.g. Gerlach et al. 2004; Martin et al., 2006). BrO is mainly formed by interaction of the volcanic plume with the atmosphere (e.g. Oppenheimer et al. 2006; Bobrowski et al., 2007; Roberts et al., 2009; von Glasow et al., 2009).

At first sight this might lead to the conclusion that BrO is not a suitable parameter for volcanic activity studies, but we will show in this paper that the situation is much better than one might expect.

3.1 Timing of bromine monoxide formation

First experimental and model studies on the formation of BrO in volcanic plumes were done by Oppenheimer et al. (2006) and Bobrowski et al. (2007). Some further model studies were carried out by Martin et al. (2009), Roberts et al. (2009), von Glasow (2010) and experimental studies by Kern et al. (2009) and Vogel et al. (2010). Model and experimental data generally seems to fit, leading to the conclusion that the main reaction cycles are understood. Nevertheless, some more detailed questions remain open (e.g. Vogel et al., 2012).

To get a more general idea about the BrO formation rate, we summarized in Fig. 3 already published and additionally unpublished experimental data sets available to us. The BrO/SO₂ ratio is presented as a function of distances, which can be used as an indirect indicator for the plume age. The plume age is controlled by distance as well as by wind velocity. We did not convert our data to plume ages because of the lack of the wind velocities, which are not available for each of the data sets. Even though

SED

4, 475–505, 2012

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



we do not have an exact timing for the formation process of BrO for this reason, Fig. 3 shows that most of the BrO is formed in the first kilometres after release (corresponding to the first minutes after the gas is released). No significant additional increase of the BrO/SO₂ ratio can be identified at a distance larger than five kilometres from the emission source and we neither see a significant decrease for the next ten km. This might stand in contrast to earlier published data by the first author of this article. The interpretation indeed has to be changed from the earlier publications where an increase of the BrO/SO₂ was thought to continue for more than 20 km as a result of model calculations. But this former interpretation was mainly caused by a lack of data or rather insufficient amounts of data. Our Fig. 3 is just an update of Fig. 4 in Bobrowski et al., 2007 including the former data set (cyan triangle Etna 2004 and blue quadrangular Etna 2005) and additional data from Nyiragongo 2004, Popocateptl 2008 and Etna 2008. Having now acquired a larger amount of BrO/SO₂ ratios over several distances at various volcanoes it seems that the maximum BrO/SO₂ ratio might be reached in a much shorter time/closer distance from the vent than previously assumed (e.g. Bobrowski et al., 2007; Roberts et al., 2009). Afterwards the BrO/SO₂ ratio seems to stay constant for a while at least up to a distance of 15 km from the emission source, which would account for a 25 min old plume, assuming a wind velocity of 10 m s⁻¹.

Together with the sensitivity studies on meteorological parameters (see Subsect. 3.2.), we propose the assumption that if we measure in a distance of more than five km and less than fifteen km the BrO/SO₂ ratio will not vary significantly under otherwise stable conditions (no volcanic activity changes).

3.2 Meteorological influences on BrO/SO₂

Meteorological parameters often influence measured gas concentrations or gas ratios but if the dependencies are known, corrections are often possible. Therefore the seasonal dependency and two important meteorological factors, wind velocity and humidity were investigated.

3.2.1 Seasonal influences on BrO/SO₂ ratio

Three years of data are available for the BrO/SO₂ ratio at Mt. Etna. To discuss an eventual seasonal dependency of the data the three years already displayed as one entire data set in Fig. 2 are shown in Fig. 4 (a–c) separated for each single year, one below each other for a better comparison. During the first year, 2006, the major BrO/SO₂ peak was determined in April, followed by a decrease and remaining on a lower level nearly until the end of the year. In 2007 peaks can be identified during the summer months, June and September, and the graph is characterised by generally larger variations in the BrO/SO₂ ratio compared to 2006. In contrast to 2007, in 2008 the summer values are of relatively low values and higher values are identified in spring 2008, like 2006 but also in autumn 2008, where BrO/SO₂ were relatively low in autumn 2006.

No clear pattern for a variation with seasons can be identified.

3.2.2 Wind velocity

Wind velocity (v_w) determines the age of the plume (t) at every known distance (d) of the measurement to the emission source. Our measurements are carried out at a distance of around six km from the emission source (see map in Fig. 1). We attempted to scan the plume perpendicular to the wind direction. The distance from the emission source to the point of measurement is not the only parameter for determining the plume age. As already mentioned the plume age is influenced by the wind velocity as well

$$t = d/v_w \quad (1)$$

As described above, only first studies have been done regarding the question on which time scales BrO is formed and how fast it is decomposed again, some more studies are in progress (e.g. Vogel et al., 2012). All BrO/SO₂ ratios for our data set at Mt. Etna during 2006–2009, for which wind speeds from balloon sounding were available¹, were

¹(<http://weather.uwyo.edu/upperair/sounding.html>)

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



plotted as a function of wind velocity to try to identify possible correlations. The result can be seen in Fig. 5a. No correlation could be identified. Therefore we keep the assumption that BrO for a certain time frame remains in a kind of steady state.

3.2.3 Relative humidity

The influence of relative humidity was investigated as well. First of all because relative humidity will influence condensation and therefore influence the amount of available surfaces for heterogeneous reactions, which are essential for the bromine explosion mechanism (Wennberg, 1999) and also influences the solubility of HBr in aerosols. Figure 5b shows the BrO/SO₂ ratio as a function of humidity, and equal to the wind velocity study no correlation can be identified.

Although unexpected, neither seasonal variations nor wind velocity nor relative humidity show a correlation to the BrO/SO₂ in this preliminary investigation. It is planned to do a more sophisticated study during the upcoming years, including solar irradiance, condensation conditions and wind velocity measured as close as possible to the plume.

4 Observations of volcanic activity between 2006 and 2009

The beginning of 2006 was characterized by several slight ash emissions. A bigger explosion occurred in the middle of January inside the Central Crater. In general mainly quiescent degassing activity could be observed at the summit craters. On 10 April 2006 some intense black ash emission was observed by the authors. In mid July 2006, during the night of the 14 July, a new eruptive phase of Mt. Etna began. A lava flow could be seen just before midnight and strombolian explosions started in the morning afterwards. This explosive and effusive activity continued for a week, with a peak of activity in the late evening of 20 July, when lava fountaining was observed on the South East crater (SE crater). On 23 of July 2006 all eruptive activity ended. The first signs of renewal of activity were seen in the end of August 2006. On 4 of

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**BrO/SO₂ in relation
with volcanological
observations**N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



September new lava effusion took place directly coming from the top of the SE crater. During the following weeks, the activity of Etna was characterised by discontinuous lava effusions and strombolian activity at or close to the SE crater. On 12 October, a

5 On 26 October 2006, an additional, discontinuous lava flow started on the flank of the Bocca Nuova crater. In mid November 2006 the volcanic activity changed its character to a more explosive one, including small pyroclastic density flows close to the SE crater (e.g. 16 November 2006), destruction and rebuilding of the main hornito at the vent of
10 the continuous lava flow, and strong ash emissions. These ash emissions led to a closing of the airport of Catania at the end of November 2006. At the beginning of December 2006 the lava effusion stopped to be continuous. The lava effusion ended probably on 13 December 2006.

On 31 of March 2007, after a bit more than three months of relatively quiet degassing, a new eruptive event happened at the SE crater (strombolian explosions and lava flow)
15 but lasted just for some hours. Similar events could be observed also on the 11 of April, 29 of April and 7 of May, 2007. In the middle of August 2007 strombolian explosions started on the flank of the SE crater and culminated in spectacular lava fountains and lava effusion in the night from 4 to 5 of September 2007. On 23 November 2007 a similar event took place on the same site as on the 4 of September 2007.

20 During the first month of 2008 small ash emissions (e.g. 14/15 February, 20 February, and 25 February) were frequently observed at the summit area and enhanced seismic activity was reported by the INGV Catania (www.ct.ingv.it). On the 10 of May 2008 a violent explosive phase accompanied by lava fountains and a large lava flow started in the afternoon and lasted until the evening of the same day.

25 Three days later on 13 May, 2008 again a violent paroxistic phase together with strong seismic activity took place, but was only poorly observed due to the bad meteorological conditions. However, this was the start of a new eruption which should last more than one year – until mid of July 2009.

The months between mid July and beginning of November 2009 were characterized by the absence of eruptive activities. This changed on the 6 November 2009 when a small new vent was opening on the flank of the SE crater. A red glowing light could be seen for the rest of the year from all villages on the south- and eastern flanks of Mt. Etna.

5 Discussion and interpretation of measurement data in context with volcanological observations

After excluding several ambient factors to be responsible for the observed BrO/SO₂ changes, we propose that the observed variations of BrO/SO₂ ratios are primarily caused by volcanic activity changes. We hypothesise that BrO/SO₂ ratios can give us indications of the movements of magma due to the different solubility of bromine and sulphur in the melt, like other gases do as well (e.g. Spilleart et al., 2006). Due to the absence of model studies and experimental measurements regarding the excess of bromine from melt we can only draw interpretations using an empirical approach.

After a short description of the principal BrO/SO₂ variations in context of volcanic activity (see also Figs. 6 and 7 and Table 1 for a summarizing overview) we present an interpretation of our three years data set of the BrO/SO₂ ratios, comparing their variations with our visual observations and already by other authors published geophysical data.

As partly described above, May 2005 (after the end of the 2004/2005 eruption in March 2005) and the beginning of 2006 as well as 2007 are assumed to be periods of relatively quiescent degassing (Fig. 7a). That is not completely true for the beginning of 2006 where at least one bigger explosion took place in Mt. Etna's summit region in the middle of January 2006. However, in the context of the limited time series of our measurements and visual observations these were periods of relatively calm volcanic activity of Mt. Etna. During non eruptive periods we measured a mean BrO/SO₂ ratio of about 2×10^{-4} (Fig. 7a). In comparison to this value we observed relatively high

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



BrO/SO₂ in relation with volcanological observationsN. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



BrO/SO₂ ratios three months before the eruption in 2006 and 2008. Mean values for the third month before the eruption are shown as violet columns in Fig. 6b. In April 2006 the BrO/SO₂ ratio reached 3.1×10^{-4} (see Fig. 2). In the middle of February and May 2008 again a high BrO/SO₂ ratio $>3 \times 10^{-4}$ was determined, 3.6×10^{-4} and 3.9×10^{-4} , respectively as shown in Fig. 2. Also before the events of lava fountaining in 2007 we measured before the two most violent cases an increase of the BrO/SO₂ ratio to over 3×10^{-4} . First, in June 2007 BrO/SO₂ values reached 3.2×10^{-4} followed by lava fountaining and a lava flow three months later on 4 September 2007. In the middle of September 2007 a second increase of BrO/SO₂ to 3.5×10^{-4} was again preceding lava fountaining combined with lava effusion two month later – on 23 November 2007.

During the investigated period in this work, 2006 to 2009, the described maxima of the BrO/SO₂ ratios were usually followed by a decreasing trend until the start of the eruptive activities. Figure 6b mirrors this decrease by showing the mean BrO/SO₂ ratios one month before the eruption (columns in magenta) – June 2006, August 2007, October 2007, and April 2008. A certain exception is the 2008 eruption, when BrO/SO₂ remained relatively high until short before the start of the eruption. With the start of eruptive activities the BrO/SO₂ ratio mainly continued to decrease at least for the activities in 2006 (and 2007). For the 2008/2009 eruption we observed a more variable BrO/SO₂ ratio. However, also during the 2008/2009 eruption the mean BrO/SO₂ ratio was with 1.4×10^{-4} significantly lower than during the non-eruptive period before with a mean value of 2.1×10^{-4} . The mean BrO/SO₂ ratio has been even lower – 1.1×10^{-4} during the eruption of 2006. Figure 6a shows the mean values during the eruptions as red columns and the mean ratios of non-eruptive periods are displayed as blue columns. For a summary of the described BrO/SO₂ ratio in relation to Etna's activity see also Table 1 which describes the mean values for the various time frames.

In the following for an interpretation of our data we assume that bromine, in contrast to the more frequently studied halogens – chlorine and fluorine; would be less soluble in the melt than sulphur. With this hypothesis we can interpret our time series as illustrated in Fig. 7 by including our visual observations and geophysical data published

by e.g. Bonforte et al., 2008; Aloisi et al., 2009; Aiuppa et al., 2010; Bonaccorso et al., 2011.

Assuming that bromine is less soluble in magmatic melt than sulphur, bromine should be emitted earlier compared to sulphur when fresh magma is rising up. Therefore an increase of the BrO/SO₂ ratios would be expected in the first phase of magma rising (Fig. 7b).

In the investigated period increasing BrO/SO₂ ratios were determined slightly after ash emissions and enhanced seismic activities had been reported from the INGV Catania (www.ingv.ct.it) in February/March 2006 and in January/February 2008, respectively. These activities could have been caused due to magma movements or changes in the conduit systems. After the eruption of 2004/2005 an inflation of the volcano before the 2006 eruption has been observed (Bonforte et al., 2008; Bonaccorso et al., 2011) which was interpreted as a period of new magma up-rise. For our data set that could mean that magma reached in April 2006 the level where a significant amount of bromine starts to be exsolved. Aloisi et al., 2009 and also Aiuppa et al., 2010 document a further recharging phase of Mt. Etna starting in the beginning of 2007 which led to the eruption in 2008. In Bonforte et al., 2008 and Aiuppa et al., 2010 the authors present among others displacement data. Comparing the displacement data shown in Fig. 2c of Aiuppa et al., 2010 with the BrO/SO₂ ratios in Fig. 2 of this article the two maxima in 2007 before the lava fountain events (September and November 2007) as well as the general increasing trend from the beginning 2007 to May 2008 can be observed for both data sets, – displacement data and BrO/SO₂ ratios.

Further the decrease of BrO/SO₂ ratios, which started already some month before the eruptive events took place in 2006 and in 2007, can be explained in our model if we assume that magma continues to rise without further new magma replacements from below (see Fig. 7c). Sulphur therefore started to be emitted in larger amounts as well and might have overtaken bromine. Therefore the BrO/SO₂ ratio decreased. Even if the bromine emissions were still high, at higher SO₂ fluxes a decreasing BrO/SO₂ ratio would be expected. For the 2006 eruption we indeed measured an increase of

SED

4, 475–505, 2012

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

SO₂ fluxes already before the eruption started, during the period of already decreasing BrO/SO₂ ratios (Giuffrida et al., 2007), and determining still high “BrO fluxes”² – if we calculate a “BrO flux” by multiplying the BrO/SO₂ ratio with a parallel measured SO₂ flux.

5 With the start of eruptions the BrO/SO₂ ratio continues to decrease in our data at least for the activities in 2006 (and 2007), which we explain with the fact that no new magma up-rise continued (Fig. 7d). An explication could be a melt already depleted in bromine that is still relatively rich in sulphur and therefore the BrO/SO₂ values were continuing to diminish.

10 After the onset of the 2008/2009 eruption we observed a more variable BrO/SO₂ ratio, which could be explained assuming magma movements from a deeper source to more shallow reservoirs also after the beginning of the eruption. A further indication for this interpretation is that our higher BrO/SO₂ values in October 2008 during the ongoing eruption are observed simultaneously with an increased seismic activity in the beginning of September and October 2008 reported by INGV Catania.

15 We just showed that assuming an earlier bromine excess from the magmatic melt than sulphur we can describe our data set in accordance with several other observations and already published data. An exception would be, but only in some details, the work of Aiuppa et al., 2006. There the authors published a two year data set of CO₂/SO₂ ratios of the Voragine crater, one of the four summit craters at Mt. Etna. Aiuppa and co-workers conclude from their data that magma started not to rise before
20 May 2006 and a stagnant and non convective magma body inside the entnean edifice is still considered in spring 2006. Looking up the CO₂/SO₂ ratio, at first glance, this seems to be an obvious conclusion and we do not want to rule it out. But it is in contrast to our interpretation of our own data-set, where magma movements took place
25 already before May 2006. Some facts should be pointed out. First, a stagnant and

² BrO is not a primarily emitted volcanic gas, but rather formed in an ageing plume. Talking about a BrO flux is therefore not correct in a literal sense.

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



non convective magma body does not necessarily fit with enhanced seismic activity and ash emission in spring 2006 (www.ingv.ct.it and observation of ash emission by N. Bobrowski in April 2006 and Bonaccorso et al., 2011). Second the authors have just one data point for the whole month of April 2006, which could have led to a misleading interpretation. Third, in contrast to our measurements of a mixed plume from all craters, the authors were observing gas emissions of the Voragine crater which made up a minor part to the total budget in the investigated time period and it is quite uncertain if the Voragine crater was involved in the eruptive activity in 2006. However little the contrast in interpretations is, it makes clear that future studies and collaborations are necessary to improve our understanding of the real processes inside Mt. Etna. In general CO₂/SO₂ ratios and BrO/SO₂ ratios seem to behave similar, for instance by comparing CO₂/SO₂ values for the period (2007–2009) investigated by Aiuppa et al., 2010 with the data presented in this work. Both show maxima some month before the lava fountain events in 2007 and also a tendency to increase during the first month of 2008 prior the start of the eruption. However the tendency of a slow increase from the beginning of 2007 to May 2008 is shown by the BrO/SO₂ ratios and the displacement study, but not in the CO₂/SO₂ ratios. All the mentioned points are in agreement with our hypothesis of a lower solubility of bromine in comparison to sulphur.

Nevertheless, if we try to interpret our data set assuming that bromine behaves similar to chlorine and fluorine, therefore would have a higher solubility in melt than sulphur, we run into some contradictions with visual and geophysical observations rather quickly. Thus, after a period of quiescent degassing and a relatively constant BrO/SO₂ ratio of 2×10^{-4} , an increase in the BrO/SO₂ ratio could be interpreted as a decline of SO₂ degassing due to a magma rather depleted in its gas content. This is neither the case for 2006 nor for the 2007 eruptive events, as the SO₂ fluxes (see Giuffrida et al., 2007; Salerno et al., 2009 and weekly reports www.ct.ingv.it) as well as the inflation of the volcanic system is in disagreement with such an interpretation. If we ignore this fact for a moment, the following decrease before the eruption could be caused by an increasing SO₂ emission due to the arrival of new magma. For the 2006 and the 2007

events this may be reasonable. For the start of the 2008 eruption this would mean that the new magma arrives instantaneously with the start of the eruption or that the gas emissions were blocked due to a sealing of the summit craters. The first assumption is highly improbable and also in contrast to e.g. Aiuppa et al., 2010 and Aloisi et al., 2009. The second one is also in disagreement with reported SO₂ flux data of INGV Catania (www.ct.ingv.it). Already at this point we see that there are difficulties with the hypothesis that bromine is better soluble in the magmatic melt than sulphur, and we fail if we attempt to interpret our data in a logical way. With our current knowledge we conclude that the hypothesis of a higher solubility of bromine in a basaltic melt in comparison to sulphur is less probable than our earlier hypothesis.

6 Conclusions

A “long” time series of relatively frequent MAX-DOAS measurements was obtained to investigate variations of BrO/SO₂ ratios as a function of volcanic activity changes. First sensitivity studies to check with non volcanic parameters were carried out, with none of them yielding any kind of dependency. We still cannot answer how much of the total emitted bromine in whatever form emitted gets converted into BrO and how long these transformation processes exactly need under the various ambient conditions. We still need detailed studies, in which other molecules containing bromine are measured simultaneously and the bromine content of aerosol is determined with increasing distance from the source. However even without knowing the percentage of BrO of the total emitted bromine – we show measurements that lead to the assumption that the ratio of BrO to total emitted bromine does not change in a certain range of plume ages, which is quite commonly used for measurements. If we want to use BrO as a tracer of emission changes, it is of minor importance if only 5% or even 70% are converted to BrO as long as this relation is constant.

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**BrO/SO₂ in relation
with volcanological
observations**N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc


Printer-friendly Version

Interactive Discussion



Above we proposed a provocative hypothesis, by assuming that bromine releases earlier from a magmatic melt than sulphur. This is in contrast to the already in more detail studied halogens chlorine and fluorine. However, it explains our data set well. Our empirical model based on this hypothesis explains the evolution of the ratio well in relation to our observations and other data already published. Maxima BrO/SO₂ ratios were observed some months prior to eruptive events when magma was rising up the conduit, and particular low values are seen during eruptive events when the new magma body gets exhausted in its bromine content.

Unfortunately hardly any laboratory measurements are done for bromine and its behaviour in the magmatic melt. Therefore it is difficult to prove our interpretation at this moment. But the great advantage with the BrO/SO₂ ratio is the easiness and safeness of the measurements and these first results look promising that BrO/SO₂ ratios can be an additional parameter to gain insights into a volcanic system. It will be worth to spend time and energy on laboratory investigations and further field studies to investigate the above mentioned issues. Only more precise sensitivity studies and longer time series will show if the here presented empirical model remains valid or has to be changed in the future.

Acknowledgements. We like to thank all persons who were assisting us in the field, especially Nuccio Faro, who helped a lot with the acquisition of the Mini-MAX-DOAS data. We further thank Christoph Hörmann, Johannes Zielcke and Peter Lübcke for critical questions on the interpretation and improvements of English wording in this manuscript. 

References

- Aiuppa, A.: Degassing of halogens from basaltic volcanism: insights from volcanic gas observations, *Chem. Geol.*, 263, 99–109, 2009.
- Aiuppa, A., Federico, C., Paonita, A., Pecoraino, G., and Valenza, M.: S, Cl and F degassing as an indicator of volcanic dynamics: The 2001 eruption of Mt. Etna, *GRL*, 29, 11, 1559–1562, doi:10.1029/2002GL015032, 2002.

**BrO/SO₂ in relation
with volcanological
observations**N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Aiuppa, A., Federico, C., Giudice, G., Gurrieri, S., Paonita, A., and Valenza, M.: Plume chemistry provides insights into mechanisms of sulfur and halogen degassing in basaltic volcanoes, *EPSL*, 222, 469–483, 2004.

Aiuppa, A., Federico, C., Franco, A., Giudice, G., Gurrieri, S., Inguaggiato, S., Liuzzo, M., McGonigle, A. J. S., and Valenza, M.: Emission of bromine and iodine from Mount Etna volcano, *Geochem. Geophys. Geosyst.* 6, Q08008, doi:10.1029/2005GC000965, 2005.

Aiuppa, A., Moretti, R., Federico, C., Gaetano, G., Gurrieri, S., Liuzzo, M., Papale, P., Shinohara, H., and Valenza, M.: Forecasting Etna eruptions by real-time observation of volcanic gas composition, *Geology*, 35, 1115–1118, 2007.

Aiuppa, A., Baker, D. R., and Webster, J. D.: Halogens in volcanic systems, *Chem. Geol.*, 263, 1–18, doi:10.1016/j.chemgeo.2008.10.005, 2009.

Aiuppa, A., Cannata, A., Cannavò, F., Di Grazia, G., Ferrari, F., Giudice, G., Gurrieri, S., Liuzzo, M., Mattia, M., Montalto, P., Patanè, D., and Puglisi, G.: Patterns in the recent 2007–2008 activity of Mount Etna volcano investigated by integrated geophysical and geochemical observations, *Geochem. Geophys. Geosyst.*, 11, Q09008, doi:10.1029/2010GC003168, 2010.

Alletti, M., Baker, D., and Freda, C.: Halogen diffusion in basaltic melts, *GCA*, 71, 3570–3580, 2007.

Aloisi, A., Bonaccorso, A., Cannavò, F., Gambino, S., Mattia, M., Puglisi, G., and Boschi, E.: A new dyke intrusion style for the Mount Etna May 2008 eruption modelled through continuous tilt and GPS data, *Terra Nova*, 21, 4, 316–321, doi.org/10.1111/j.1365-3121.2009.00889, 2009.

Bobrowski, N., Hönninger, G., Galle, B., and Platt, U.: Detection of Bromine Monoxide in a Volcanic Plume, *Nature*, 423, 273–276, 2003.

Bobrowski, N., Louban, I., von Glasow, R., Whaba, O. I., Platt, U., Aiuppa, A., and Inguaggiato, S.: Bromine chemistry in volcanic plumes, *J. Geophys. Res.*, 112, 136, doi:10.1029/2006JD007206, 2007.

Bobrowski, N., Vogel, L., Kern, C., Giuffrida, G. B., Delgado-Granados, H., and Platt, U.: Bromine oxidation in volcanic plumes Volcanic plumes, *EGU*, Vienna, 2009.

Bobrowski, N., Kern, C., Platt, U., Hörmann, C., and Wagner, T.: Novel SO₂ spectral evaluation scheme using the 360–390 nm wavelength range, *Atmos. Meas. Tech.*, 3, 879–891, doi:10.5194/amt-3-879-2010, 2010.

Bonaccorso, A., Bonforte, A., Calvari, S., Del Negro, C., Di Grazia, G., Ganci, G., Neri, M., Vicari, A., and Boschi, E.: The initial phases of the 2008–2009 Mount Etna erup-

tion: A multidisciplinary approach for hazard assessment, *J. Geophys. Res.*, 116, B03203, doi:10.1029/2010JB007906, 2011.

Bonforte, A., Bonaccorso, A., Guglielmino, F., Palano, M., and Puglisi, G.: Feeding system and magma storage beneath Mt. Etna as revealed by recent inflation/deflation cycles, *J. Geophys. Res.*, 113, B05406, doi:10.1029/2007JB005334, 2008.

Bureau, H., Kepler, H., and Metrich, N.: Volcanic degassing of bromine and iodine: experimental fluid/melt partitioning data and applications to stratospheric chemistry, *EPSL*, 183, 51–60, 2000.

Burton, M., Allard, P., Murè, F., and Oppenheimer, C.: FTIR remote sensing of fractional magma degassing at Mount Etna, Sicily, in: *Volcanic Degassing*, edited by: Oppenheimer, C., Pyle, D. M., and Barclay, J., Special Publications, 213, 281–293, Geological Society, London, 2003.

Burton, M. R., Allard, P., Murè, F., and La Spina, A.: Magmatic Gas Composition Reveals the Source Depth of Slug-Driven Strombolian Explosive Activity, *Science*, 317, 227, doi:10.1126/science.1141900, 2007.

Burton, M. R., Allard, P., La Spina, A., and Murè, F.: One decade of OP-FTIR monitoring of Mount Etna gas plume emissions: lessons and implications, *EGU, Vienna*, 2010.

Caltabiano, T., Burton, M., Giammanco, S., Allard, P., Bruno, N., Mure, F., and Romano R.: Volcanic Gas Emission from the Summit Craters and Flanks of Mt. Etna, 1987-2000, in: *Mt. Etna: Volcano Laboratory*, edited by: Bonaccorso, A., Calvari, S., Coltelli, M., Del Negro, C., and Falsaperla, S., American Geophysical Union Geophysical Monograph, 143, 111–128, 2004.

Carroll, M. R. and Holloway, J. R.: *Volatiles in Magmas*, Washington: Mineralogical Society of America, 1994.

Edmonds, M., Pyle, D. M., and Oppenheimer, C.: A model for degassing at Soufrière Hills Volcano, Montserrat, West Indies, based on geochemical data, *Earth Planet Sc. Lett.*, 186, 159–173, 2001.

Edmonds, M., Gerlach, T. M., and Herd, R. A.: Halogen degassing during ascent and eruption of water-poor basaltic magma, *Chemical Geology*, 263(1–4), Halogens in Volcanic Systems and Their Environmental Impacts, 122–130, ISSN0009-2541, doi:10.1016/j.chemgeo.2008.09.022, 2009.

Fayt, C. and van Roozendaal, M.: *WinDOAS 2.1—Software User Manual*. Belgisch Instituut voor Ruimte-Aeronomie Institut d'Aeronomie Spatiale de Belgique, Brussels, Belgium,

SED

4, 475–505, 2012

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



2001.

Gerlach, T. M.: Volcanic sources of tropospheric ozone-depleting trace gases, *Geochem. Geophys. Geosyst.*, 5, 9, Q09007, doi:10.1029/2004GC000747, 2004.

Giuffrida, G. B., Bobrowski, N., Vita, F., Sollami, A., and Inguaggiato, S.: BrO/SO₂ studies at Mt. Etna during 2006 and 2007, AGU, San Francisco, USA, 2007.

Horrocks, L. A., Oppenheimer, C., Burton, M. R., and Duffell, H. J.: Compositional variation in tropospheric volcanic gas plumes: evidence from ground-based remote sensing, in: *Volcanic degassing*, edited by: Oppenheimer, C., Pyle, D. M. and Barclay, J., Geological Society, London, Special Publication, 213, 349–369, 2003.

Jambon, A., Weber, A. H., and Braun, O.: Solubility of He, Ne, Ar, Kr and Xe in a basalt melt in the range 1250–1600°C. Geochemical implications, *Geochimica et Cosmochimica Acta*, 50, 401–408, ISSN0016-7037, doi:10.1016/0016-7037(86)90193-6, 1986.

Kern, C., Sihler, H., Vogel, L., Rivera, C., Herrera, M., and Platt, U.: Halogen oxide measurements at Masaya volcano, Nicaragua using active long path differential optical absorption spectroscopy, *B Volcanol*, 71, 6, 659–670, doi:10.1007/s00445-008-0252-8, 2008.

Kern, C., Deutschmann, T., Vogel, L., Wöhrbach, M., Wagner, T., and Platt, U.: Radiative transfer corrections for accurate spectroscopic measurements of volcanic gas emissions, *Bull. Volcanol.*, 72, 233–247, doi:10.1007/s00445-009-0313-7, 2010.

Kraus, S.: DOASIS, DOAS Windows Software, Presentation at the 1st international DOAS Workshop, 13–14 September 2001, Heidelberg, Germany, 2001.

Lowe, G.: PocketDOAS Manuel, University of Heidelberg, 2004.

Martin, R. S., Mather, T. A., and Pyle, D. M.: High-temperature mixtures of magmatic and atmospheric gases, *Geochem. Geophys. Geosy.*, 7, Q04006, doi:10.1029/2005GC001186, 2006.

Martin, R. S., Roberts, T. J., Mather, T. A., and Pyle, D. M.: The implications of H₂S and H₂ stability in high-T mixtures of magmatic and atmospheric gases for the production of oxidized trace species (e.g., BrO and NO_x), *Chem. Geol.*, 263, 143–150, 2009.

Menyailov, I. A.: Prediction of eruptions using changes in composition of volcanic gases, *Bull. Volcanol.*, 39, 112–125, 1975.

Moretti, R., Papale, P., and Ottonello, G.: A model for the saturation of C-O-H-S fluids in silicate melts, in: *Volcanic degassing*, edited by: Oppenheimer, C., Pyle, D. M., and Barclay, J., *Geol. Soc. London S. P.*, 213, 81–101, 2003.

Noguchi, K. and Kamiya, H.: Prediction of volcanic eruption by measuring the chemical com-

SED

4, 475–505, 2012

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



BrO/SO₂ in relation with volcanological observationsN. Bobrowski and
G. Giuffrida[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

position and amounts of gases, *Bull. Volcanol.*, 26, 367–378, 1963.

Oppenheimer, C., Tsanev, V. I., Braban, C. F., Cox, R. A., Adams, J. W., Aiuppa, A., Bobrowski, N., Delmelle, P., Barclay, J., and McGonigle, A. J. S.: BrO formation in volcanic plumes, *Geochim. Cosmochim. Ac.*, 70, 2935–2941, 2006.

5 Oppenheimer, C. and Kyle, P. R.: Probing the magma plumbing of Erebus volcano, Antarctica, by open-path FTIR spectroscopy of gas emissions, *Journal of Volcanology and Geothermal Research*, *Volcanology of Erebus volcano, Antarctica*, 177, 743–754, ISSN 0377-0273, doi:10.1016/j.jvolgeores.2007.08.022, 2008.

Pennisi, M. and Le Cloarec M.: Variations of Cl, F, and S in Mount Etna's plume, Italy, between 1992 and 1995, *JGR*, 103, 5061–5066, 1998.

10 Roberts, T. J., Braban, C. F., Martin, R. S., Oppenheimer, C., Adams, J. W., Cox, T., Jones, R. L., and Griffiths, P. T.: Modeling reactive halogen formation and ozone depletion in volcanic plumes, *Chem. Geol.*, 263, 151–163, 2009.

15 Salerno, G. G., Burton, M. R., Oppenheimer, C., Caltabiano, T., Randazzo, D., Bruno, N., and Longo, V.: Three-years of SO₂ flux measurements of Mt. Etna using an automated UV scanner array: Comparison with conventional traverses and uncertainties in flux retrieval, *J. Volcanol. Geoth. Res.*, 183, 76, 2009.

Shinohara, H.: A missing link between volcanic degassing and chloride partitioning experiments, *Chem. Geology*, 263, 51–59, 2009.


20 Spilliaert, N., Metrich, N., and Allard, P.: S–Cl–F degassing pattern of water rich alkali basalt: modelling and relationship with eruption styles of Mount Etna volcano, *Earth Planet. Sci. Lett.*, 248, 772–786, 2006.

Stoiber, R. E. and Rose, W. I.: The geochemistry of Central American volcanic gas condensates, *Geol. Soc. Am. Bull.*, 81, 2891–2911, 1970.

25 Tazieff, H. and Sabroux, J. C.: *Forecasting Volcanic Events (Developments in Volcanology)*, Elsevier Science, Ltd, London, Amsterdam, New York, 1983.

Villemant, B. and Boudon, G.: H₂O and halogen (F, Br, Cl) behaviour during shallow magma degassing process, *EPSL*, 168, 271–286, 1999.

Vogel, L., Kern, C., Bobrowski, N., Hörmann C., v. Glasow, R., and Platt, U.: Observation of halogen oxides in volcanic plumes at Different Plume Ages, EGU, Vienna, 2010.

30  Vogel, L., Bobrowski, N., Fickel, M., Hörmann, C., Kern, C., v. Glasow, R., and Platt, U.: Volcanic plumes: BrO formation during the first 100 minutes after emission, EGU, Vienna, 2012.
von Glasow, R., Bobrowski, N., and Kern, C.: The effects of volcanic eruptions on atmospheric

chemistry, Chem. Geol., 263, 131–142, doi:10.1016/j.chemgeo.2008.08.020, 2009.
von Glasow, R.: Atmospheric chemistry in volcanic plumes, Proc. Natl. Acad. Sci., 107, 6594–6599, 2010.
Wennberg, P.: Bromine explosion, Nature, 397, 299–300, 1999.

SED

4, 475–505, 2012

**BrO/SO₂ in relation
with volcanological
observations**

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. Summary of mean BrO/SO₂ values during the various time periods as described in the text. The table also displays the number of data points available for the various time frames.

Time period	BrO/SO ₂ mean	Number of data points included	Volcanic activity
September–October 2004	1.4×10^{-4}	8	eruptive period
Between May 2005–July 2006	1.8×10^{-4}	40	non eruptive period
July–December 2006 ^a	1.1×10^{-4}	35	eruptive period
January 2007–May 2008	2.1×10^{-4}	71	non eruptive period
May 2008–June 2009	1.4×10^{-4}	85	eruptive period
April 2006	2.3×10^{-4}	8	3 month before eruption
June 2006	1.6×10^{-4}	4	1 month before eruption
June 2007	2.4×10^{-4}	10	3 month before eruption
August 2007	1.8×10^{-4}	7	1 month before eruption
September 2007	2.1×10^{-4}	6	2 month before eruption
October 2007	1.6×10^{-4}	2	1 month before eruption
February 2008	2.2×10^{-4}	5	3 month before eruption
April 2008	2.1×10^{-4}	5	1 month before eruption

^aAugust 2006 is not included as eruptive period.



Fig. 1. Map of Mt. Etna. The small houses (Rifugio Sapienza, Rifugio Citelli, Mt. Maletto and Mt. Conca) indicate the measurements sites of the Mini-MAX-DOAS measurements in a distance of about 6 km from the source, the main routes for the SO₂ traverses during 2006 are indicated by blue lines, in red are the rarely used routes.

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and G. Giuffrida

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

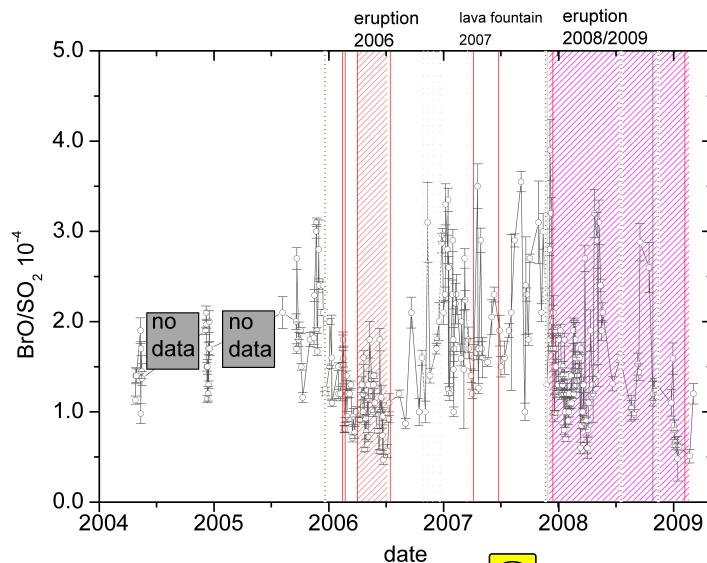


Fig. 2. For each day, a linear fit of the BrO-SO₂ correlation was obtained. The slope of this linear fit with its standard deviation in form of an error bar is plotted as function of time. Note that the slope and its standard deviation were obtained by including the one sigma-fit error of the BrO evaluation in the fitting process of the linear slope. The SO₂ fit error was neglected as it was small (two orders of magnitude smaller) compared to the SO₂ measurement values. Besides the data 2006–2009, data of 2004 and 2005 were added. Before both eruptions (2006 and 2008) an increase in the BrO/SO₂ ratio can be noted; followed by a general decrease in bromine monoxide in comparison to sulphur dioxide during periods of explosive and effusive volcanic activity. In 2006, the BrO/SO₂ ratio decreased until the end of the year and basically until the end of the enhanced activity of Etna. Also with the end of the 2008/2009 eruption the BrO/SO₂ ratio stopped its decreasing trend. The eruption periods are indicated by an underlying rectangle of magenta and higher activity events are shown by red lines. The year on the x-axis indicates the middle of the same year. For more detailed information see text.


[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)

[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

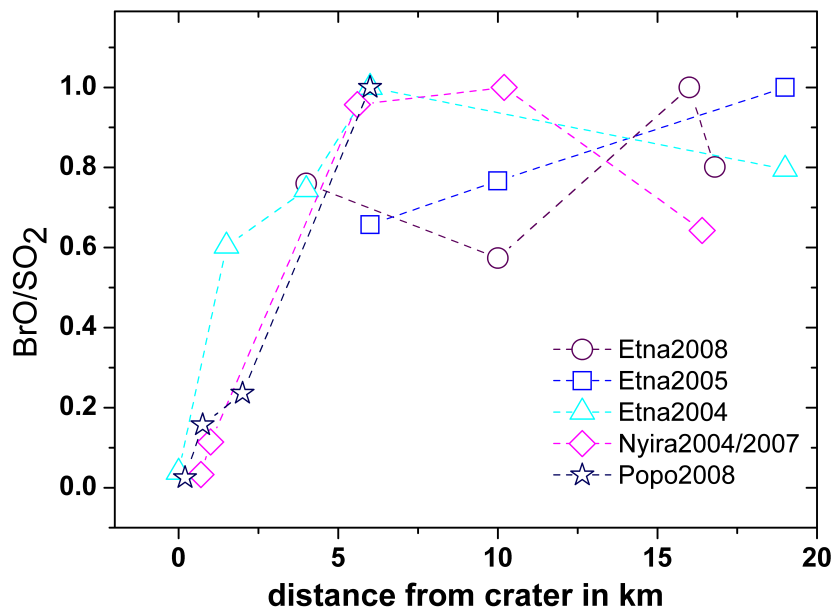

BrO/SO₂ in relation with volcanological observationsN. Bobrowski and
G. Giuffrida

Fig. 3. BrO is formed by volcanic atmospheric-gas-interaction, but strong increase is (only) seen up to about 5 km (young plume of some minutes), BrO/SO₂ ratios seem to move into a plateau afterwards. The BrO/SO₂ ratios were normalised for a better comparison of the various sites. For more information see text.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

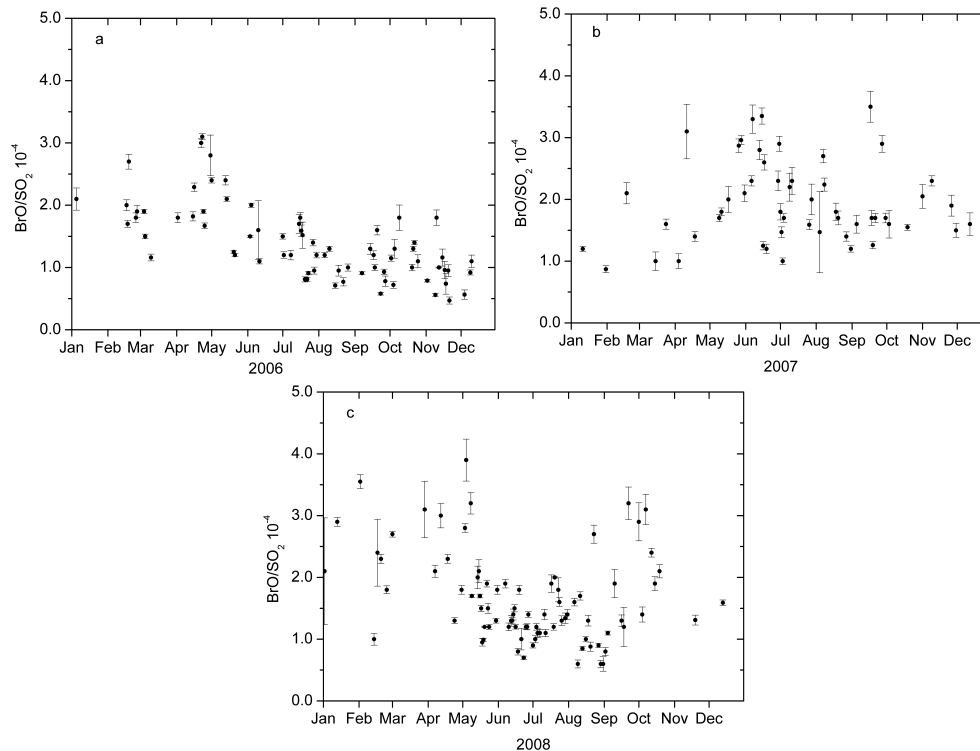
BrO/SO₂ in relation with volcanological observationsN. Bobrowski and
G. Giuffrida

Fig. 4. BrO/SO₂ ratios are shown as a function of time split into three years of observations **(a)** 2006–2007 highest BrO/SO₂ values in spring, **(b)** 2007–2008 highest BrO/SO₂ peaks during the summer, generally higher variability than under **(a)**, **(c)** 2008–2009 highest BrO/SO₂ values in spring and autumn. No periodicity of seasons can be identified. Data points and error bars calculated as in Fig. 2.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

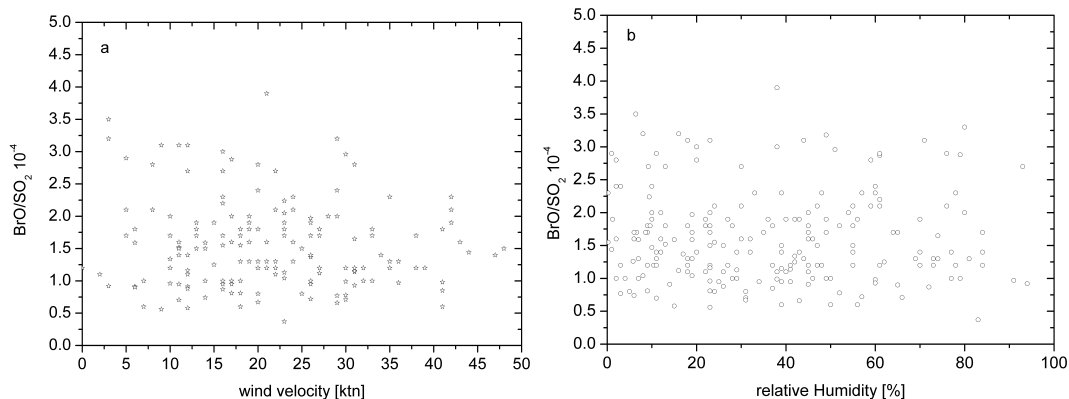
BrO/SO₂ in relation with volcanological observationsN. Bobrowski and
G. Giuffrida

Fig. 5. (a) BrO/SO₂ ratio taken in a distance of about 6 km from the summit of Etna shown as a function of wind velocity, data taken from (<http://weather.uwyo.edu/upperair/sounding.html>) for the day of measurements and altitude of about 3000 m, no dependency visible. (b) BrO/SO₂ ratio taken in a distance of about 6 km from the summit of Etna shown as a function of relative humidity, data taken from (<http://weather.uwyo.edu/upperair/sounding.html>) for the day of measurements and altitude of about 3000 m, no dependency visible.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

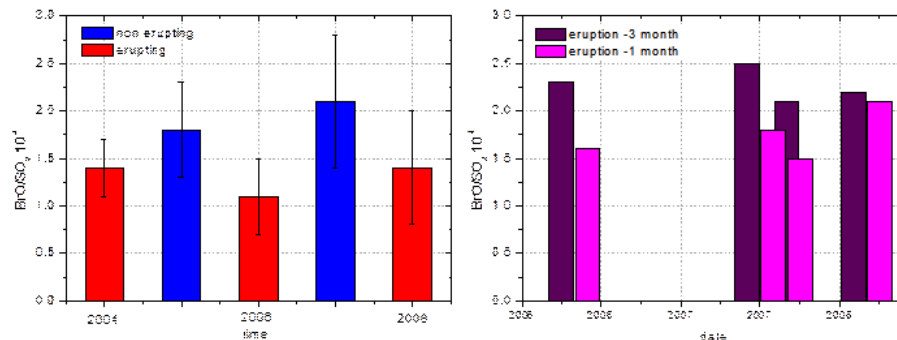


Fig. 6. (a) Measurement data were averaged for eruptive and non-eruptive periods. The BrO/SO₂ mean is plotted as function of time. Eruptive data are presented as red columns and non-eruptive data as blue columns. Although this is only a small statistical approach, it demonstrates that during eruptions lower BrO/SO₂ ratios have been measured. (b) Additionally to (a) mean BrO/SO₂ values of the third month before the eruption (violet columns) and mean BrO/SO₂ values of the month just before the eruption (magenta columns) have been compared for the four eruptive events described in the text. Clear enhanced mean BrO/SO₂ values are determined for the third month before the eruption and smaller mean BrO/SO₂ values the month before the eruption see also Table 1.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

BrO/SO₂ in relation with volcanological observations

N. Bobrowski and
G. Giuffrida

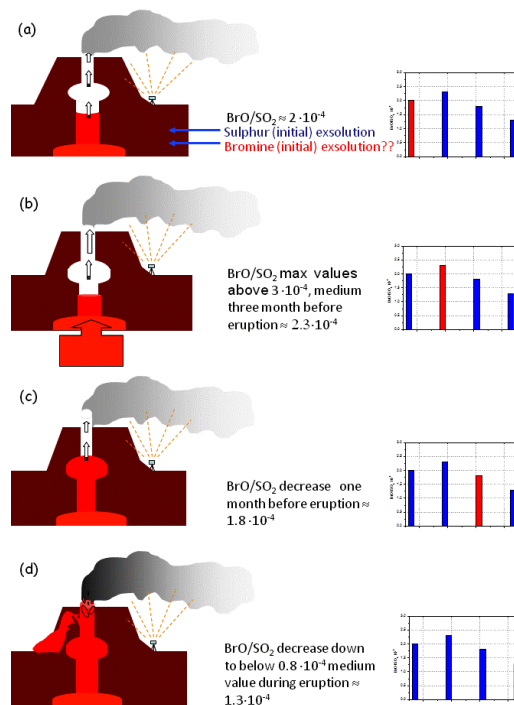


Fig. 7. Sketch of the empirical model, for detailed information see text. **(a)** In contrast to chlorine and fluorine, we assume that bromine is less soluble in the magmatic melt than sulphur. The mean value of non-eruptive periods during 2006–2009 is around 2×10^{-4} . **(b)** Assuming bromine is less soluble in magmatic melt than sulphur, bromine starts to be released earlier in comparison to sulphur when fresh magma is rising up –> maxima BrO/SO_2 ratios rise over 3×10^{-4} . The mean value is around 2.3×10^{-4} in month three before the 2006 and 2008 eruptions as well as in month three and two before the two violent lava fountaining events in 2007. **(c)** When magma is rising further, sulphur starts to be released and might overtake bromine; BrO/SO_2 ratios decrease (SO_2 fluxes should increase). The mean BrO/SO_2 value of the last month before the observed eruption is 1.8×10^{-4} . **(d)** Further decrease – no further magma rise from below, melt already depleted in bromine, sulphur out-gasing is determining the ratio. The lowest BrO/SO_2 value during eruptions observed was 0.47×10^{-4} . The mean BrO/SO_2 ratio was calculated to 1.3×10^{-4} .

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)