

Infrared satellite observations of hydrogen sulfide in the volcanic plume of the August 2008 Kasatochi eruption

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[1] Hydrogen sulphide (H_2S) is one of the main trace gases released from volcanoes with yearly global emissions estimated between 1 and 37 Tg. With sulfur dioxide (SO_2 , 15–21 Tg/year), it dominates the volcanic sulfur budget, and the emission ratio $\text{H}_2\text{S}:\text{SO}_2$ is an important geochemical probe for studying source conditions, sulfur chemistry and magma-water interactions. Contrary to SO_2 , measurements of H_2S are sparse and difficult. Here we report the first measurements of a large H_2S plume from space. Observations were made with the infrared sounder IASI of the volcanic plume released after the 7–8 August 2008 eruption of Kasatochi volcano. The eruption was characterized by 5 consecutive explosive events. The first events were phreatomagmatic producing a plume rich in water vapor and poor in ash and SO_2 . We show that the observed H_2S plume, calculated at 29 ± 10 kT with integrated columns exceeding 140 ± 25 Dobson Units (DU), is likely associated with these first explosions. $\text{H}_2\text{S}:\text{SO}_2$ ratios with maximum values of 12 ± 2 are found, representative of redox conditions in the hydrothermal envelop. With a detection threshold of 25 DU, future space observations of H_2S plumes are certain. These will be important for improving the atmospheric sulfur budget and characterizing the $\text{H}_2\text{S}:\text{SO}_2$ fingerprint of different eruptions. **Citation:** Clarisse, L., P.-F. Coheur, S. Chefderville, J.-L. Lacour, D. Hurtmans, and C. Clerbaux (2011), Infrared satellite observations of hydrogen sulfide in the volcanic plume of the August 2008 Kasatochi eruption, *Geophys. Res. Lett.*, 38, L10804, doi:10.1029/2011GL047402.

1. Introduction

[2] Volcanoes emit large quantities of sulfur, mainly as SO_2 (15–21 Tg/year) and H_2S (1–37 Tg/year) [Halmer *et al.*, 2002]. Atmospheric SO_2 is straightforwardly and routinely measured from ground and via satellite, owing to the presence of strong absorption bands in the ultraviolet and the infrared [Rix *et al.*, 2009; Thomas and Watson, 2010]. Optical measurements are much harder for H_2S because of the rather unfortunate position of the absorption bands. There is a large vibrational band in the infrared (ν_2 centered at 1182 cm^{-1}), but most of the lines are overlapped with strong water vapor lines [Oppenheimer *et al.*, 1998]. The ultraviolet absorption band is located at very short

wavelengths (maximum is located near 200 nm) where the solar spectrum is weak in intensity and molecular scattering becomes important [O'Dwyer *et al.*, 2003].

[3] In-situ measurements of H_2S or the emission ratio $\text{SO}_2:\text{H}_2\text{S}$ are possible using either direct sampling techniques [Aiuppa *et al.*, 2005] or UV sounding with an artificial light source [O'Dwyer *et al.*, 2003]. They give important insights in sulfur chemistry and magma-water interactions as H_2S is typically favoured over SO_2 in hydrothermal fluids with (1) increasing magmatic pressure, (2) increasing water concentration, (3) decreasing temperature, and (4) decreasing oxygen concentration [Giggenbach, 1987]. For measurements at degassing fumaroles the emission ratio $\text{H}_2\text{S}:\text{SO}_2$ is extremely variable, in the range of 0.01–100 [O'Dwyer *et al.*, 2003; Aiuppa *et al.*, 2005, 2007; Badalamenti *et al.*, 2001; Liotta *et al.*, 2010].

[4] In the atmosphere H_2S oxidizes to SO_2 in a few days and increases in SO_2 mass observations in satellite time-series are sometimes attributed to this [Rose *et al.*, 2000]. The effect is usually modest but exceptions exist. For example in the 1980 eruption of Mount St. Helens 20% of sulfur may have been released as H_2S [Hobbs *et al.*, 1981], while for the El Chichón eruption in March 1982 it has been estimated that as much as 80% of the 3.5 Tg of sulfur was released as H_2S [Textor *et al.*, 2003; Kotra *et al.*, 1983]. Unfortunately there has not been a single direct observation of a large H_2S plume and much of the sulfur chemistry and in-plume kinetics remain only partially understood [Aiuppa *et al.*, 2005, 2007; Martin *et al.*, 2009].

[5] Here we present the first satellite measurements of H_2S . These were made with the Infrared Atmospheric Sounding Interferometer (IASI) on-board MetOp-A [Clerbaux *et al.*, 2009]. IASI is an infrared nadir sounder which provides global coverage twice a day (polar orbiting with mean overpass times at 0930 and 2130 local time) with a pixel size of 12 km diameter at nadir. It has state of the art instrumental characteristics featuring a wide spectral range $645\text{--}2760\text{ cm}^{-1}$, low radiometric noise at 0.2 K NEDT and a high spectral resolution of 0.5 cm^{-1} (sampled at 0.25 cm^{-1}).

[6] The observations were made on 8 August 2008 (at 0730 and 0900 UTC) over central Aleutian Islands, where just 11 hours earlier Kasatochi volcano had violently erupted. A detailed description and analysis of the eruption is given by Waythomas *et al.* [2010]. In all, there were 5 explosive eruptions and these are summarized here. The first two explosions (at 2201 UTC on 7 August and 0150 UTC on 8 August) were phreatomagmatic, driven by interactions of magma and the crater lake. They produced ash-poor and water-rich eruption plumes. The first event was also poor in SO_2 , producing only about 0.003 Tg of SO_2 . The third event (0435 UTC on 8 August) was a more energetic magmatic

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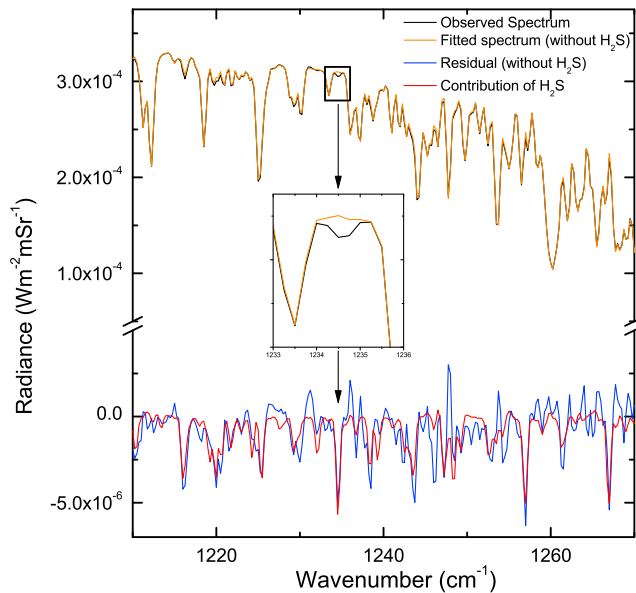


Figure 1. Example IASI spectrum of the Kasatochi plume of 8 August (black line). The orange line is a fit of this spectrum without H₂S taken into account. The blue line is the difference between these two and the red is the isolated H₂S contribution, calculated at the top of the atmosphere. The inset shows the strongest H₂S feature at 1234.5 cm⁻¹, visible in both the spectrum and the residual.

eruption and produced an ash rich plume. After the third explosive event there was a period of 10 hours of continuous ash emissions, which included the fourth (0712 UTC on 8 August) and fifth (1142 UTC on 8 August) explosive events. For the whole eruption an estimated 2 Tg of SO₂ was emitted [Karagulian *et al.*, 2010; Krotkov *et al.*, 2010; Prata *et al.*, 2010].

[7] In the next section we analyze a single IASI spectrum and using an optimal estimation technique we demonstrate unambiguously the presence of H₂S. We then present a simple and stable retrieval approach and derive lower bounds for observable quantities. In section 3 we apply the methodology on the whole Kasatochi plume of 8 August, and discuss and interpret the results in connection with concurrent ash and SO₂ retrievals.

2. First Observation

[8] Figure 1 shows in black an IASI observed spectrum of the plume on August 8 at 49.80 N, 171.36 W. A standard way of retrieving atmospheric parameters from a nadir satellite observation is the optimal estimation method, which, starting from the best available a priori knowledge makes an optimal estimate (in the Bayesian sense) of the true state of these parameters. This is done by iteratively adjusting atmospheric parameters, aiming for a best fit of the simulated spectrum to the observed spectrum [Rodgers, 2000]. The spectrum in orange shows such a synthetic fit achieved by adjusting atmospheric water vapor loading. H₂S was excluded from this calculation. The difference between observed and fitted spectrum is shown in blue and apart from instrumental noise shows a number of absorption lines (most notably at 1234.5, 1257 and 1267 cm⁻¹) which can be

attributed to H₂S. This is shown in red as the top the atmosphere contribution of H₂S, with maximum values larger than $5 \cdot 10^{-6} \text{ W m}^{-2} \text{ m sr}^{-1}$, or more than an order of magnitude larger than the spectral noise of $4 \cdot 10^{-7} \text{ W m}^{-2} \text{ m sr}^{-1}$ in this region [Clerbaux *et al.*, 2009]. It is by virtue of IASI's high resolution and low instrumental noise that such an unambiguous identification is possible. The selected fitting range 1210–1270 cm⁻¹ covers only a small part of the ν_2 band of H₂S which has strong lines from 1000 to 1500 cm⁻¹ [Ulenikov *et al.*, 1996]. Towards the longer wavelengths ash and SO₂ can severely hamper the retrieval [Clarisse *et al.*, 2010], whereas towards the shorter wavelengths water vapor and a strong SO₂ signal easily saturate and can conceal the H₂S signature.

[9] For weak signals, optimal estimation retrievals can be unstable and fits can diverge. To determine the H₂S columns, we have applied a robust retrieval approach [Clarisse *et al.*, 2009] able to cope with very weak signatures, based on brightness temperature differences in the narrow range 1234–1235 cm⁻¹. There are 4 strong H₂S absorption lines between 1234.4 and 1234.6 cm⁻¹ and the resulting absorption in the channels 1234.5 and 1234.75 cm⁻¹ is shown in an inset in Figure 1. A large difference $\Delta\text{H}_2\text{S}$ between the brightness temperature of these two channels and the background channels 1234.25 and 1235 cm⁻¹ indicates the presence of H₂S. The position of this absorption feature around 1234.5 cm⁻¹ is extremely fortunate, as its fall right in between two very strong water lines and as these channels are almost not affected by SO₂ (ν_1 band ends at 1230 cm⁻¹, while the ν_3 band starts at 1340 cm⁻¹). Forward simulations of IASI spectra with varying amounts of H₂S reveal that there is a very good linear correlation between $\Delta\text{H}_2\text{S}$ and the input total column of H₂S. For $\Delta\text{H}_2\text{S} < 1 \text{ K}$ (the maximum values we found were below 0.5 K), the deviation from linearity is an order of magnitude lower than IASI's instrumental noise. Using representative temperature and humidity profiles and assuming a plume altitude of 15 km, we found $\Delta\text{H}_2\text{S} = 1 \text{ K}$ to correspond to 632 DU (1 Dobson Unit is $2.69 \cdot 10^{16} \text{ molecules/cm}^2$) of H₂S at nadir and all H₂S retrievals were carried out using this conversion factor. We estimate the lower detection limit and error bar of this retrieval approach to be about 25 DU for ash-free pixels, corresponding to the IASI noise of 0.04 K in this region.

3. The Kasatochi Plume

[10] Retrieval results of SO₂, of an ash indicator and of H₂S are gathered in Figures 2a–2c. Data includes measurements from the partially overlapping orbits (at 0730 and 0900 UTC) on 8 August. The largest retrieved H₂S column is $140 \pm 25 \text{ DU}$. The total H₂S plume adds up to $29 \pm 10 \text{ kT}$ and spans a projected surface area of 28000 km² for columns exceeding 25 DU. SO₂ loadings were retrieved using the ν_3 band and the algorithm presented by Haywood *et al.* [2010]. SO₂ retrievals are accurate for low and moderately high columns (below 150 DU) with a detection limit around 0.5 DU and accuracy within 10%. Uncertainties are larger for larger columns and loadings will be underestimated for ash contaminated observations [Karagulian *et al.*, 2010]. As an ash indicator, we have employed the baseline difference between 280 K (mean surface temperature for the area) and the channel at 966 cm⁻¹. This was found to be a suitable

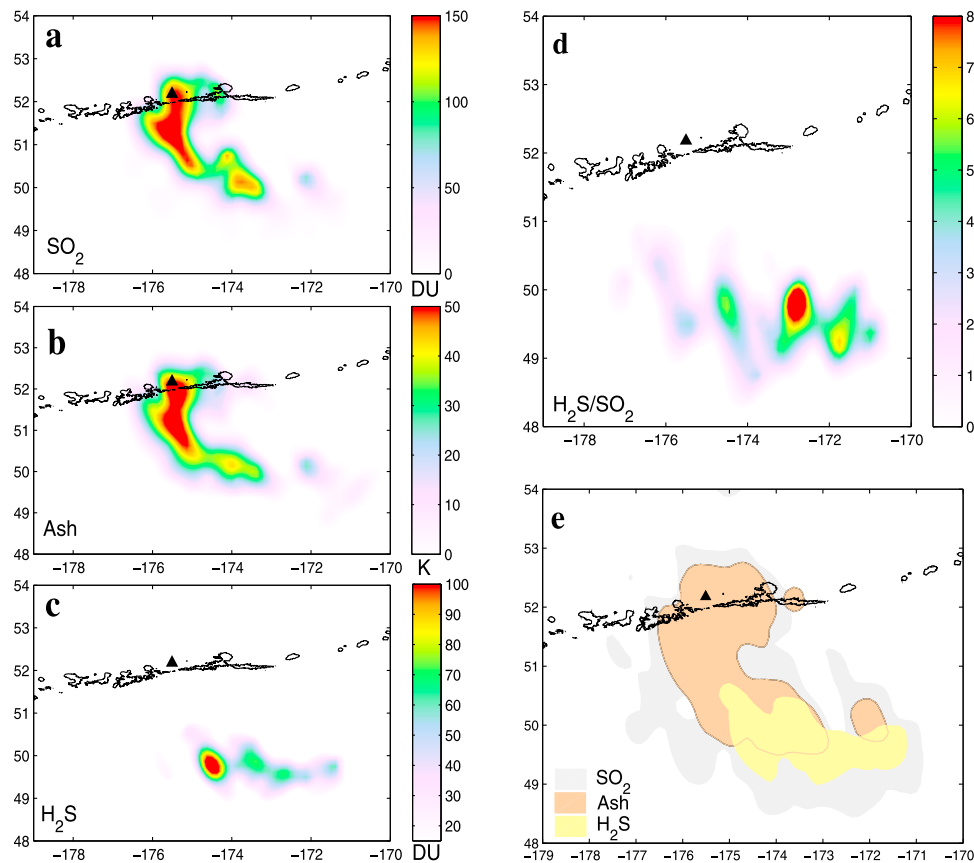


Figure 2. Spatial distribution of the Kasatochi plume on 8 August between 0730 and 0900 UTC, with isolated contribution of (a) SO₂ in DU, (b) ash in K, (c) H₂S in DU. (d) H₂S:SO₂ ratio and (e) contour of SO₂ at 1 DU, ash at 10 K and H₂S at 25 DU.

indicator here, as the region was relatively cloud free and a large part of the ash plume was opaque, which traditional split window techniques cannot visualize [Clarisse *et al.*, 2010].

[11] There is a good correlation between the ash and SO₂ plume, while there seems to be little or no correspondence with the H₂S plume. To visualize the different components in the plume, three contours from the left panel have been retained and plotted in the lower right panel, that is, H₂S at 25 DU, SO₂ at 1 DU and ash at 10 K. The SO₂ plume spans the largest area, which is characteristic of its remote traceability and usefulness as a probe of volcanic activity. Ash loadings are highest in the northern part of the plume, close to the volcano, whereas the H₂S plume is only visible in the southern part of the plume. Given the fact that the first two explosive events on 7 and 8 August were known to be ash-poor, it is likely that these events produced the southern part of the plume, and thus most of the visible H₂S plume. HYSPLIT forward trajectories have been performed for the first two explosions considering an injection height of 12 km [Karagulian *et al.*, 2010; Kristiansen *et al.*, 2010]. They confirm that the two events respectively ended up around 50°N latitude and 174°W and 172°W longitude at the IASI overpass time. The third and possibly fourth eruptive events produced the large SO₂ and ash plume observed closest to the volcano. The different parts of the plume, simultaneously captured by IASI, are best visible in the SO₂ plume, top left panel.

[12] It comes as no surprise to see H₂S in the phreatomagmatic plumes of the first two events as magma-water interactions are known to produce prodigious amounts of H₂S as first observed by Kotra *et al.* [1983]. They presented aircraft measurements of a plume arising from El Chichón volcano in November 1982 and found H₂S to be the dominant sulfur species which they attributed to the interaction of magma with lake or ground water.

[13] The H₂S:SO₂ ratio is shown in Figure 2d. The first explosion produced very little SO₂ [Waythomas *et al.*, 2010], and this is consistent with our image of the plume, with the highest ratios (up to 12 ± 2) in the furthest tip downwind of the volcano. This is even higher than the ratio of 4 reported from aircraft measurements of the El Chichón plume, which was exceptionally rich in H₂S [Kotra *et al.*, 1983]. Limiting ourselves to the part of the plume exceeding 25 DU of H₂S, the average ratio still equals 1.2, giving convincing evidence that most of the sulfur was emitted as H₂S in the first two explosions. This conclusion is strengthened by the fact that this part of the plume is between 6 and 11 hours old and some H₂S already underwent oxidation to SO₂.

[14] The third and subsequent eruptions produced no detectable quantities of H₂S, while emitting approximately 2 Tg of SO₂. It is possible that the strong ash load in the centre of the plume obscures part of the H₂S. It should be noted however, that H₂S is readily observed for ash loadings up to 30K (see Figure 2), and if it was present in large quantities in the upper part of the plume, it would be

observable in the broad plume edges, where concentrations up to 500 DU of SO₂ were observed. When we look at IASI's next overpass twelve hours later, only traces of H₂S can be seen. No conclusions can be made regarding its lifetime, as by then the plume is approximately 3.5 times larger, and even neglecting chemical reaction this puts the maximum concentrations at 40 DU, only slightly exceeding the detection threshold.

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