

Surge in sulphur and halogen degassing from Ambrym volcano, Vanuatu

Philipson Bani · Clive Oppenheimer · Vitchko I. Tsanev · Simon A. Carn ·
Shane J. Cronin · Rachel Crimp · Julie A. Calkins · Douglas Charley · Michel Lardy ·
Tjarda R. Roberts

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Abstract Volcanoes provide important contributions to atmospheric budgets of SO₂ and reactive halogens, which play significant roles in atmospheric oxidative capacity and radiation. However, the global source strengths of volcanic emissions remain poorly constrained. These uncertainties are highlighted here by the first measurements of gas emission rates from Ambrym volcano, Vanuatu. Our initial airborne ultraviolet spectroscopic measurements made in January 2005 indicate fluxes of 18–270 kg s⁻¹ of SO₂, and 62–110 gs⁻¹ of BrO, into the atmosphere, placing Ambrym amongst the largest known contemporary point sources of

both these species on Earth. We also estimate high Cl and F fluxes of ~8–14 and ~27–50 kg s⁻¹, respectively, for this period. Further observations using both airborne and spaceborne remote sensing reveal a fluctuating SO₂ output between 2004 and 2008, with a surge in the first half of 2005, and underline the substantial contribution that a single passively degassing volcano can make to the atmospheric budget of sulfur and halogens.

Keywords Ambrym volcano · SO₂ and BrO fluxes · DOAS · OMI

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P. Bani (✉) · M. Lardy
Institut de Recherche pour le Développement,
BP A5 98848 Nouméa Cedex, New Caledonia
e-mail: Philipson.Bani@noumea.ird.nc

P. Bani
Pôle Pluridisciplinaire de la Matière et de l'Environnement,
University of New Caledonia,
BP R4 Noumea, New Caledonia

C. Oppenheimer
Department of Geography, University of Cambridge,
Downing Place,
Cambridge CB2 3EN, UK
e-mail: co200@cam.ac.uk

V. I. Tsanev
School of Chemistry, University of Cambridge,
Lensfield Road,
Cambridge CB2 1EW, UK
e-mail: vip20@cam.ac.uk

S. A. Carn
Department of Geological and Mining Engineering & Sciences,
Michigan Technological University,
1400 Townsend Drive,
Houghton, MI 49931-1295, USA
e-mail: scarn@mtu.edu

S. J. Cronin · R. Crimp
Institute of Natural Resources, Massey University,
Private Bag 11 222,
Palmerston North, New Zealand

J. A. Calkins
Environment Department, University of York,
Heslington,
York YO10 5DD, UK
e-mail: jac517@york.ac.uk

D. Charley
Department of Geology, Mines and Water Resources,
PMB 01 Port-Vila, Vanuatu

T. R. Roberts
School of Chemistry,
Lensfield Road,
Cambridge CB2 1EW, UK

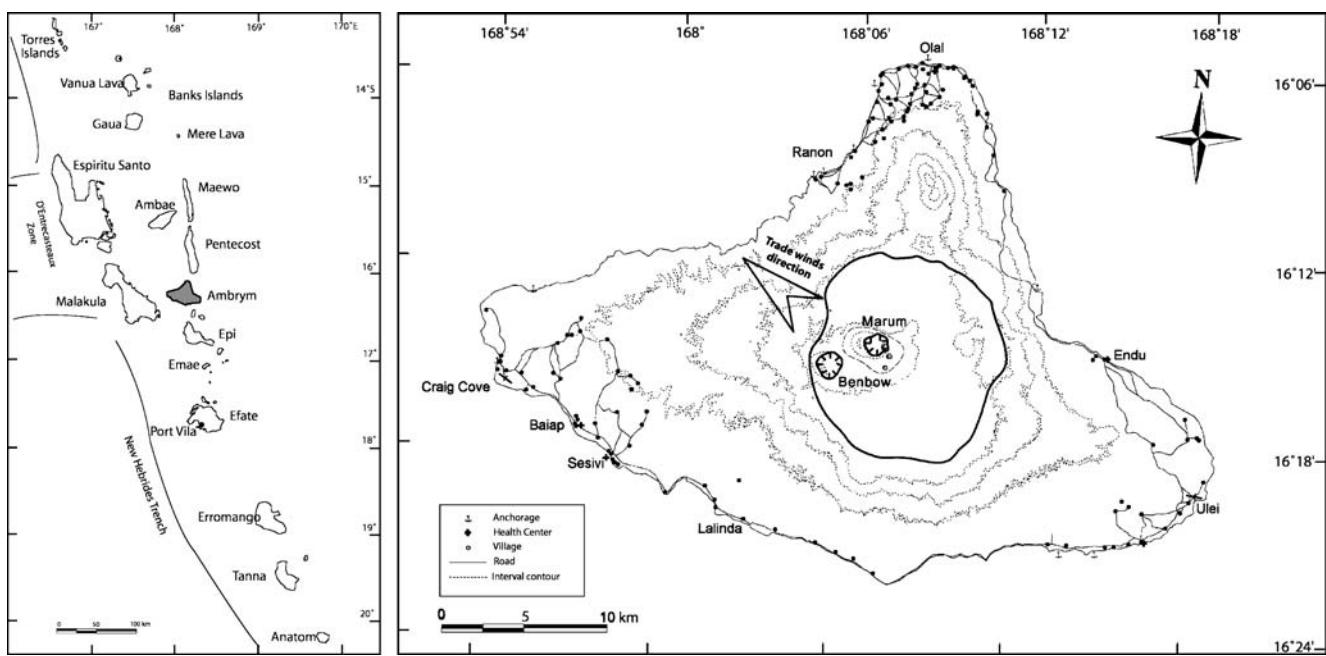


Fig. 1 Maps showing (a) regional setting of Ambrym volcano within the Vanuatu archipelago, and (b) of Ambrym island. Note the lack of settlements in the northwest sector of the island which is regularly fumigated by the summit plume by the prevailing trade winds

Introduction

Few volcanoes are known to have sustained SO_2 emission rates above 150 kg s^{-1} through “passive degassing” (i.e., outside of periods of vigorous eruption). Mt. Etna, renowned as one of the most prodigiously degassing volcanoes on Earth emits SO_2 at a much lower rate: $\sim 50 \text{ kg s}^{-1}$ based on long-term measurements (Allard et al.

1991) and $<30 \text{ kg s}^{-1}$ according to more recent data (Burton et al. 2005). Reports of higher rates tend to be associated with ephemeral eruptions lasting a matter of hours, such as Nyamuragira (Democratic Republic of Congo) whose February 2001 and October 1998 eruptions released an estimated 8500 and 2500 kg s^{-1} of SO_2 , respectively (Carn and Bluth 2003). Because there remain many volcanoes for which limited, if any, information is available concerning

Fig. 2 Map of the summit caldera of Ambrym showing the principal degassing sites

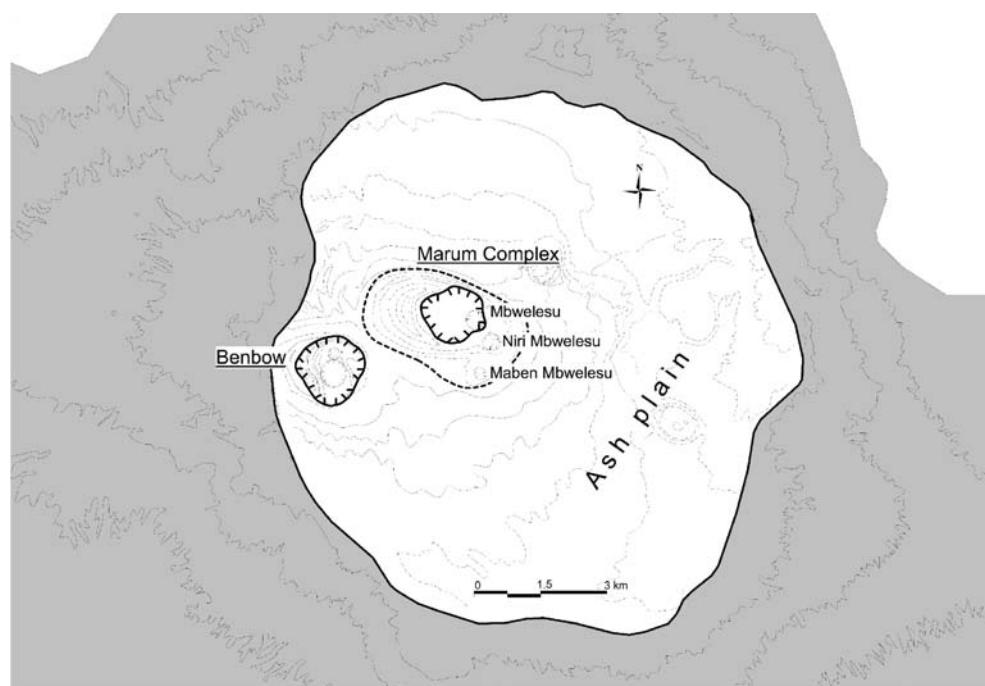
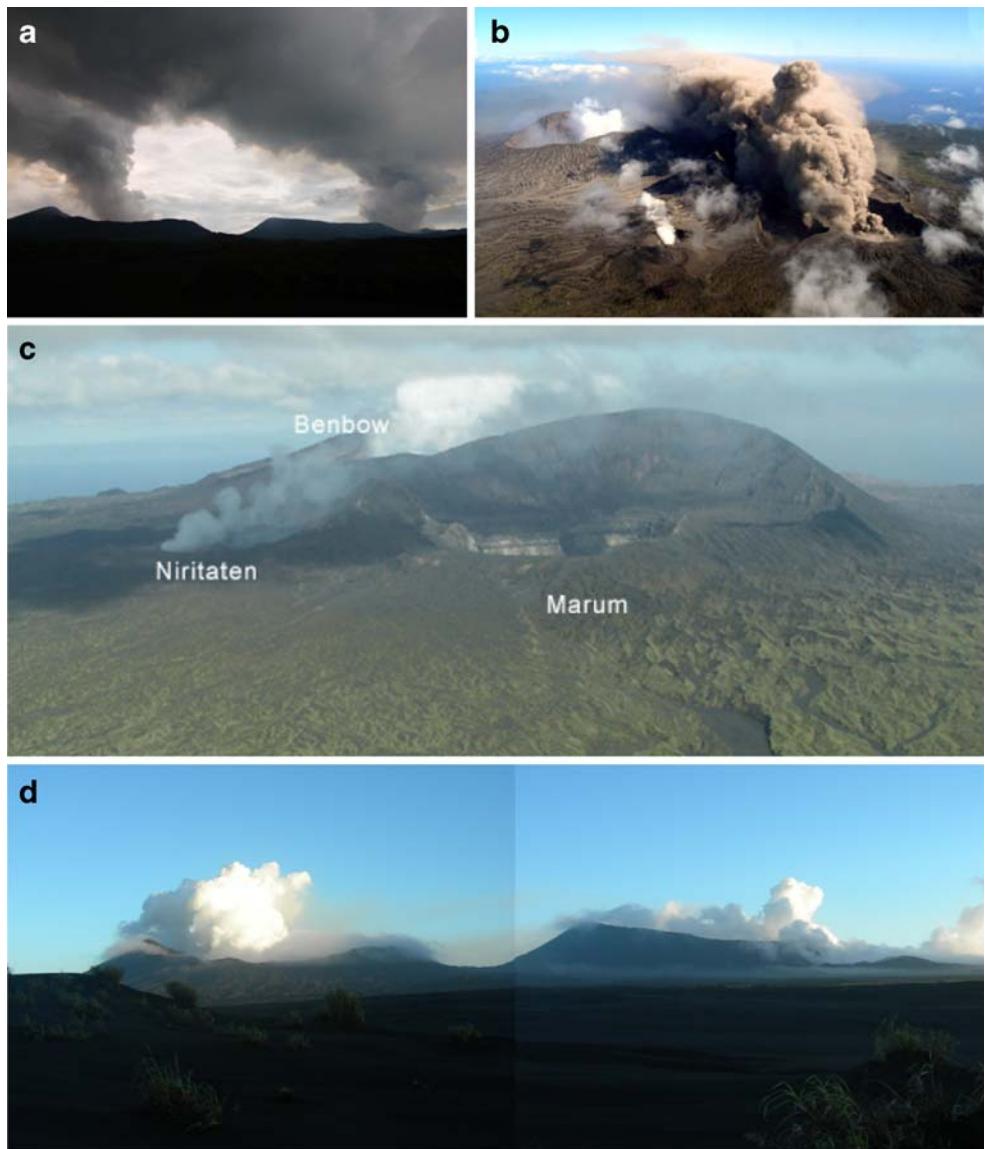


Fig. 3 Photographs of Ambrym taken on (a) 12 January 2005, (b) 2 August 2005, (c) 28 August 2007 and (d) 12 August 2007



gas emissions, the global source strength of volcanic sulphur emissions remains only partly characterised (Andres and Kasgnoc 1998; Halmer et al. 2002). One volcano, which has been persistently active but hitherto

unobserved in respect of degassing rates, is Ambrym, a 35×50 km volcanic island rising 1334 m above sea-level, in the central part of Vanuatu (Fig. 1). Much of Ambrym's historic activity has been focused at two cones – Benbow

Fig. 4 Plot showing the spectral dependence of the SO₂ cross section. Cyan line shows the high resolution data of Rufus et al. (2003), and red line shows the result of its convolution with a Gaussian instrumental function of FWHM=0.5 nm. Red arrow shows the selected short wavelength boundary (310.8 nm) for the fitting window

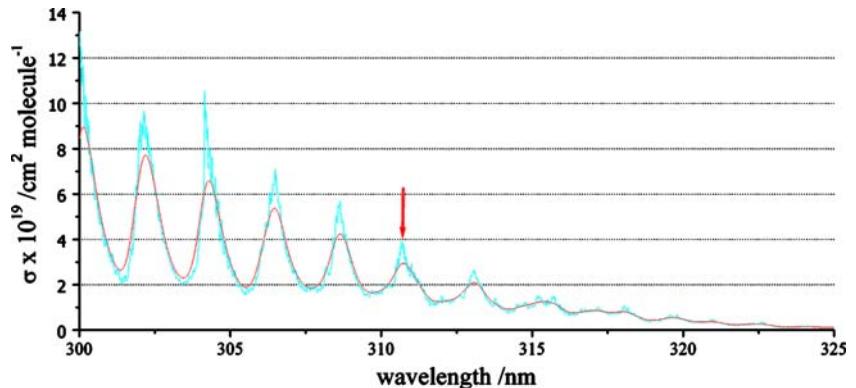
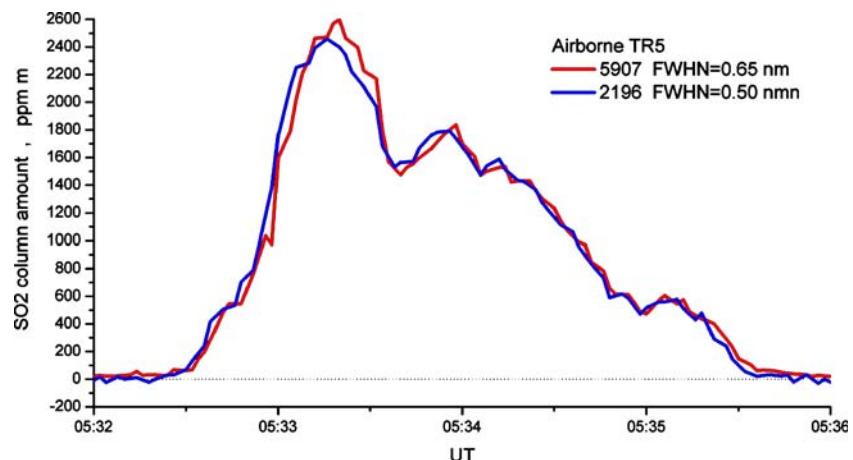


Fig. 5 As a check on the retrieval accuracy, the measurements in January 2005 were made with two Ocean Optics spectrometers, operating side-by-side, with FWHM spectral responses of 0.5 nm and 0.65 nm. The results obtained coincide within experimental error



and Marum (Fig. 2) – within its 12 km diameter caldera, both of which have frequently hosted lava lakes. Lava flows that erupted from these centres, and from another vent located inside the eastern wall of the caldera, have ponded on the caldera floor and, at times, breached lower

parts of the caldera rim (e.g., Purey-Cust 1896). Frequent strombolian eruptions from Benbow and Marum mantle the caldera and western flank of the volcano with scoria fall deposits, but arguably the most remarkable feature of Ambrym is its prodigious degassing, of which historical

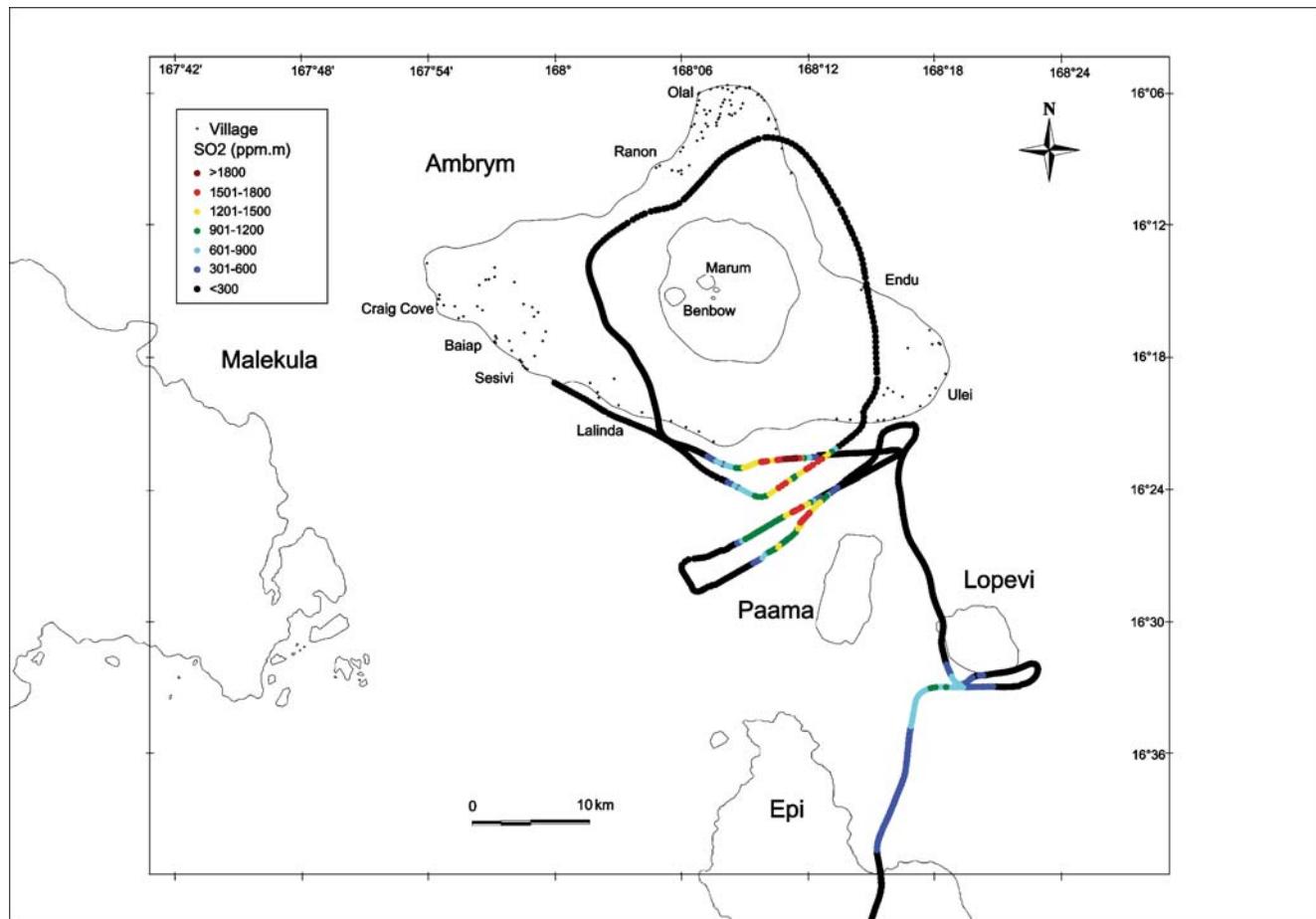
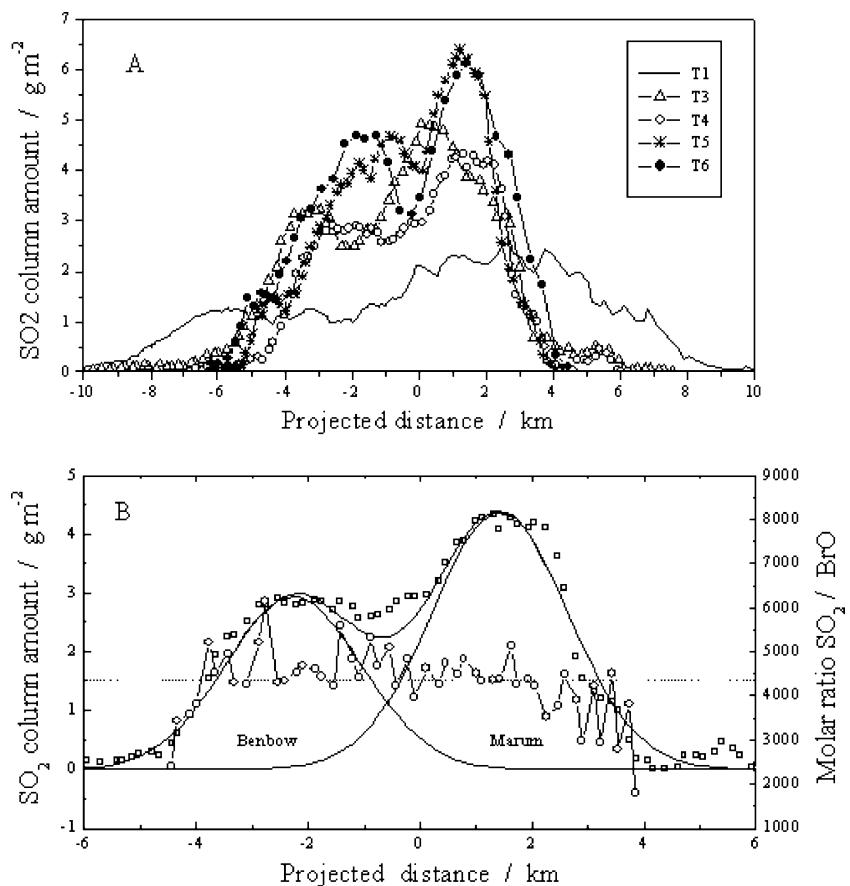


Fig. 6 Map view of the SO₂ column amounts recorded on the 5 traverses made by aircraft beneath the plume on 12 January 2005

Fig. 7 Representative ultraviolet DOAS measurements plots of Ambrym plume on 12 January 2005. (a) SO₂ column amounts for 5 traverses beneath the plume (see Table 1). (b) SO₂ and BrO column amounts from Traverse 5. (b) Traverse 4 column amounts of SO₂ (squares) and corresponding SO₂/BrO ratios (circles). Solid curves (no symbols) indicate two Gaussian functions fit to the SO₂ column amount data, to represent the individual emissions from Benbow and Marum craters, and the sum of the two Gaussians. The distance scales run from east to west (left to right) and give the projected distance on to the horizontal perpendicular to the plume transport direction. The origin corresponds to the plume centre in each traverse



evidence points to a long history. Passing Ambrym in July 1774 on his second voyage, Captain James Cook noted:

"on the part nearest to us, which is of a considerable height, we observed two very large columns of smoak, which I judge ascended from Volcanos" (Beaglehole 1961).

This description fits remarkably to the present-day appearance of the volcano. Long-lived degassing is also indicated by the sparse habitation on the northwest sector of the island, which lies downwind of the summit in respect of prevailing Trade Wind flows (note the dearth of place names in that sector, see Fig. 1). The intense emissions appear linked to adverse health impacts, with reports of grounding of the acid gas and aerosol plume, acid rain damage to food crops, and contamination of water resources (Smithsonian Institution 2005), that may be associated with malnutrition, respiratory disease and fluorosis documented in the local population (Crimp et al. 2006).

As a basis for evaluating and understanding the impacts of the plume on terrestrial ecology, human health, and the atmospheric environment, we initiated the first direct measurements of gas emission rates from the volcano, starting on 12 January 2005. We simultaneously measured

SO₂ and BrO column amounts with an Ocean Optics USB2000 UV spectrometer, using zenith scattered Sun light as the UV source (e.g., Galle et al. 2002), and traversing beneath the plume.

Methods

The first measurements were made on 12 January 2005. The spectrometer was carried on board a Brittan-Norman Islander, flying at 60 ms⁻¹ at altitudes of 500–1000 m above sea level, and to the south of the island (15–40 km from the active craters, equivalent to plume ages of ~33–86 min). The plume dispersion was to the south at that time, contrary to prevailing winds because of the proximity of Cyclone Kerry, then around 1800 km southwest of Vanuatu. Both Benbow and Marum were sites of vigorous degassing (Fig. 3). Further airborne UV spectroscopic measurements were made in March and July 2005, and August 2007.

The principal UV spectrometer used (Ocean Optics USB2000, serial # 2196) spanned 280–400 nm with a spectral resolution of 0.5 nm (full-width-at-half-maximum), and was coupled by a fibre optic bundle to a simple telescope pointed to zenith. Exposure time for individual spectra was 200 ms, and we co-added four spectra to enhance the signal-to-noise

ratio. The position of each UV spectrum was determined from the log of a continuously recording GPS unit.

BrO and SO₂ columns were retrieved following standard differential optical absorption spectroscopy (DOAS) procedures (Platt 1994; Kraus 2006; Platt and Stutz 2008). The best fitting window (310.8–373.6 nm), used to fit both gases simultaneously but primarily for the SO₂ retrieval, was found by obtaining a near random fit residual structure with minimal standard deviation. We also used a narrower window (330.0–373.6 nm) for the BrO retrieval and obtained very similar results (for BrO using the two windows). The necessary reference spectra were obtained by convolving high-resolution spectra for BrO (Wahner et al. 1988) and SO₂ (Bogumil et al. 2003), with our instrument line shape, and then removing the low frequency component. The SO₂ spectrum was deconvolved to the resolution of the BrO spectrum using WinDOAS software (Van Roozendael and Fayt 2001). Figure 4 shows the spectral dependence of the SO₂ cross section both at high resolution and convolved to the spectral response of our instrument. We used the prominent maximum at 310.8 nm as the short wavelength boundary of the fitting window. Simple calculations reveal that the absorption spectrum at this wavelength remains unsaturated up to 2500 ppm m (20°C and 1013 mbar) hence there were no concerns for non-linearity in our retrievals.

The overall errors (2σ) of the retrieved column amounts remain within experimental error and correspond to ± 52 mg m⁻² for SO₂ and ± 0.39 mg m⁻² for BrO. For a full discussion of error budgets on the spectroscopy see Mather et al. (2006). As a check on the retrieval we used a second spectrometer with a different resolution, and obtained near identical results (Fig. 5).

The observed SO₂ and BrO column amounts were projected on to the plane perpendicular to the plume transport direction. The SO₂ and BrO emission rate for each traverse was then obtained from the product of the integrated column amounts across this plane. Plume speeds were measured at plume altitude using the aircraft navigation system.

Results

Figure 6 shows the SO₂ retrievals for 12 January 2005 in map view, and Fig. 7 shows the corresponding plots for SO₂ and BrO retrievals, and an example of the SO₂/BrO ratios. The results of flux calculations are reported in Table 1. These indicate one of the highest recorded SO₂ emission rates for a passively degassing volcano, with a range of 180–270 kg s⁻¹ (equivalent to 15–23 Gg d⁻¹) in January 2005. The profiles of the column amounts recorded on the five traverses obtained in January 2005 are all bimodal (Fig. 7) (though this is less evident in the first traverse T1, which was made 40 km from the crater), and suggest dispersion and overlap of the

Table 1 SO₂ and BrO fluxes from Ambrym volcano measured by UV-DOAS in January, March and July 2005 and August 2007

Date	Traverse #	Start time in UT (local time + 11h)	Distance from source (km)	Full plume width ^a (km)	Average column amount (mg m ⁻²)	SO ₂ flux from Benbow (kg s ⁻¹)	SO ₂ flux from Marum (kg s ⁻¹)	Total SO ₂ flux (kg s ⁻¹)	SO ₂ /BrO Ratio (mol mol ⁻¹)	Total BrO flux (gs ⁻¹)	Flux error % ^b
12/01/05–21.1	T1	05:00	40	21	1151	49	135	184	2457	112	+20.0
	T3	05:20	21	18	2532	73	152	225	3050	111	+18.7–19.8
T4	05:26	20	13	2317	72	108	179	4356	62	+17.1–18.2	
T5	05:32	15	11	2640	114	120	234	3157	111	+18.2–19.3	
T6	05:54	17	11	2817	135	133	268	3540	113	+16.2–16.1	
21/03/05	T1	03:34	11	34	1600	108	274	382	71845	8	+2.8–3.8
11/07/05	T1	04:36	4	4	1210	10	15	25	18583	2	-8.2–9.0
12/08/07	T1	03:42	13	7	1320	-	-	59	2208	40	+13.5–16.0
T2	03:48	13	5	1210	-	-	42	1852	34	+13.2–15.7	
T3	03:53	14	5	1060	-	-	39	1425	41	+10.8–13.3	

^a Determined in the direction perpendicular to the plume transport direction.

^b Determined according to Mather et al. (2006), from estimated relative errors in SO₂ column amounts (± 0.2 – 0.4%), plume transport speed ($\pm 15\%$) and direction (± 0.5 – 5.4%), and distance measurements (± 0.3 – 0.5%).

Local time = UT + 11 h

individual plumes emitted from Marum and Benbow craters (which are ~ 3 km apart; Fig. 1). On this basis, we can estimate the SO_2 fluxes for each crater by superposing Gaussian functions. In the majority of cases Marum is the stronger source.

We collected rain that fell through the summit plume 2 km south from vents within the caldera in January 2005 the day after the spectroscopic measurements. Given the wind direction to the south at that time it is likely that the rain samples were collected under Marum plume. Analyses of four samples by ion chromatography indicated a consistent ionic composition with mean F/Br and Cl/Br mass ratios of ~ 150 and ~ 520 , respectively. If we assume that F, Cl and Br were scavenged quantitatively from the plume by rainfall due to their high solubility (Edmonds et al. 2003; Aiuppa et al. 2006), and that the mass ratios are representative of the whole plume, then, based on the observed BrO flux, the Cl and F fluxes from the volcano in January 2005 were $\sim 27\text{--}50$ and $\sim 8\text{--}14 \text{ kg s}^{-1}$, respectively. This calculation is crude given uncertainty in the uptake of the halogens by rain drops and also considering that the BrO flux we measure may substantially under-represent the total emission of inorganic bromine in the plume (e.g., Oppenheimer et al.

2006) but it nevertheless suggests a high output of the lighter halogens.

We have repeated the airborne surveys at Ambrym three more times (Table 1), finding an even higher SO_2 emission rate of 380 kg s^{-1} (33 Gg d^{-1}) in March of 2005 but a much lower emission of 25 kg s^{-1} (2.2 Gg d^{-1}) in July 2005. Our latest set of airborne measurements carried out in August 2007 indicated a SO_2 flux of $\sim 47 \text{ kg s}^{-1}$ (4.0 Gg d^{-1}).

To gain a longer temporal perspective on this variability we have made a preliminary investigation of satellite-based UV observations capable of detecting SO_2 . In fact, the first instrumental observations of SO_2 emissions from Ambrym were provided by the spaceborne Total Ozone Mapping Spectrometer (TOMS), which sporadically detected SO_2 emissions from Ambrym between 1978 and 2005 (Carn 2005a). Subsequently, the Ozone Monitoring Instrument (OMI; Carn 2005b) has detected Ambrym's emissions near-continuously since operational data were first acquired in September 2004. The increased frequency of detection by OMI does not necessarily imply a recent escalation in SO_2 flux from Ambrym, since OMI is more than five times more sensitive to SO_2 than TOMS, and hence can detect weaker emissions and plumes at lower altitude (Krotkov et al. 2006).

Fig. 8 The main chart shows the SO_2 burden measured by OMI in a $\sim 10^\circ \times 10^\circ$ box over Vanuatu (includes contributions from Ambrym, Aoba, Lopevi and Yasur) for the period September 2004 to July 2008 and indicates a period of strong degassing from Aoba volcano on Ambae to the north of Ambrym (see Fig. 1). This assumes a plume altitude of ~ 3 km. The inset focuses on the period of elevated Ambrym degassing from late 2004 through August 2005. Also indicated is the average scene reflectivity at 360 nm (grey curve; data have been smoothed using a 14-day centred moving average); this provides a proxy for cloud cover, which can obscure the SO_2 plume. Note the significant OMI data gaps from 1–5 Sep, 16–23 Sep, and 19 Nov–1 Dec 2004 inclusive. The uppermost plot shows the SO_2 burden over a region in the central South Pacific (presumed to be free of SO_2 sources) for the same time period, to give an impression of the “noise” in the SO_2 charts (the scale is 0–1 kt). The average background noise in this region is ~ 0.2 kt. The origin of the apparent seasonal cycle is uncertain

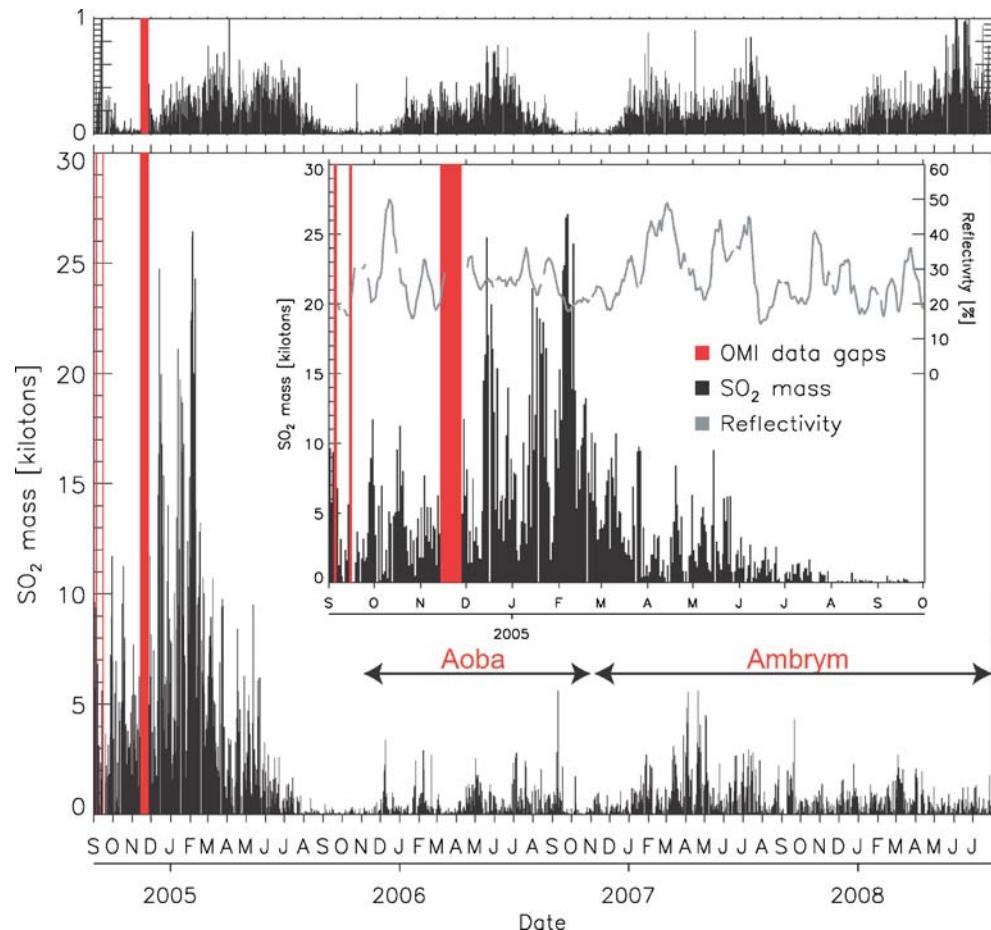
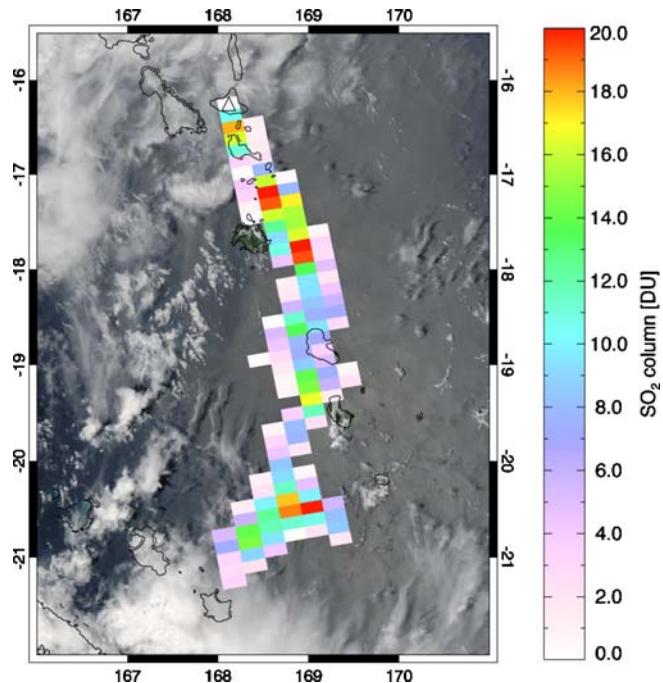


Fig. 9 SO₂ column amounts (in Dobson Units [DU]; 1 DU=28.5 mg m⁻²) retrieved from OMI measurements at 02:30 UT on 12 January (colour-coded pixels), superimposed on a true-colour Moderate Resolution Imaging Spectroradiometer (MODIS) image acquired at 02:10–02:15 UT showing coincident cloud cover. OMI data were processed with the operational SO₂ algorithm assuming a plume in the planetary boundary layer with a centre of mass at 0.9 km altitude



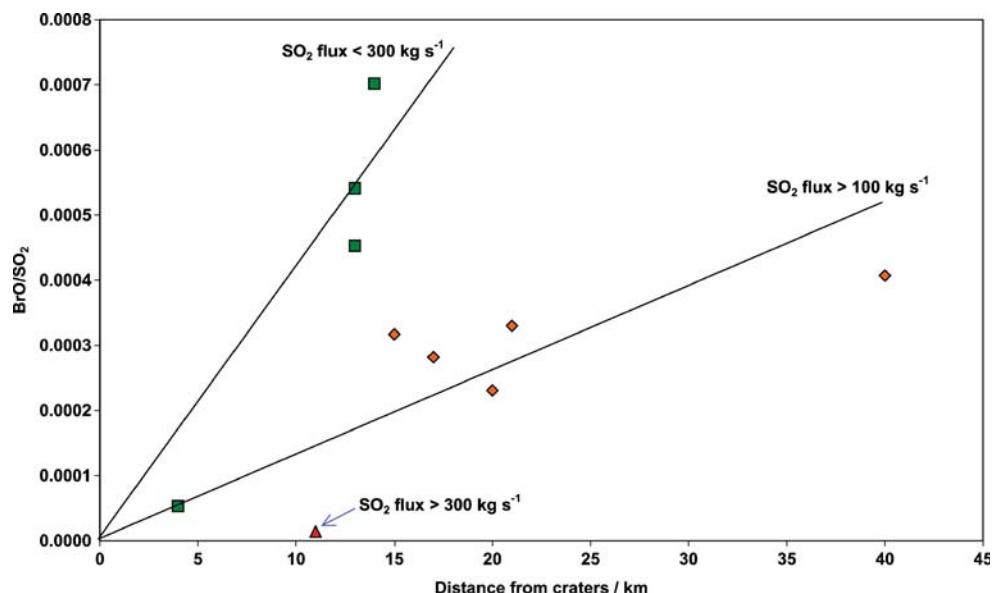
OMI-based SO₂ measurements between September 2004 and July 2008 corroborate the extreme rates of degassing we recorded in January and March 2005 (Fig. 8). This period of elevated degassing continued at least through June 2005. One of the OMI datasets we have studied was acquired on 12 January 2005, just a few hours prior to our airborne measurements (Fig. 9). Near-source meteorological cloud at the time of the OMI overpass and the time difference preclude direct comparison with airborne DOAS results though the retrieved column amounts are broadly

comparable. Although TOMS and OMI have yet to provide robust quantitative estimates of emission rates from Ambrym to date, it is certain that the volcano is one of the world's major sources of volcanic gases.

Discussion and conclusions

Few volcanoes are known to emit SO₂ at rates comparable to those we have measured at Ambrym during passive

Fig. 10 BrO/SO₂ molar ratio as a function of distance from the craters, subdivided by SO₂ flux : squares for measurements <100 kg s⁻¹, diamonds for measurements between 100 and 300 kg s⁻¹, and the triangle for the one observation above 300 kg s⁻¹. The high variability in BrO/SO₂ strongly reflects the nonlinear tropospheric chemistry of BrO



degassing. Of comparable magnitude are the emissions from Nyiragongo (Democratic Republic of Congo), for which satellite observations provided an estimated mean SO₂ emission rate of 185 kg s⁻¹ associated with lava lake degassing (Carn 2004); Popocatépetl (Mexico) where passive SO₂ emission rates of 110–150 kg s⁻¹ were reported following an explosive eruption in 1996 (Delgadillo-Granados et al. 2001); and Miyakejima (Japan), a basaltic island volcano with a remarkable degassing history since its eruption in 2000 (Nakada et al. 2004). Miyakejima began degassing at a high rate in 2000, emitting at a time-averaged rate of ~140 kg s⁻¹ of SO₂ up to June 2005. From late 2000 through mid 2001, SO₂ fluxes exceeded 450 kg s⁻¹ then declined between June 2004 and June 2005 to around 30–60 kg s⁻¹ (Kazahaya et al. 2004; Kazahaya 2005). Such emission rates emphasize that even during passive degassing, a single volcano is capable of emitting SO₂ into the atmosphere at rates equivalent to a widely quoted minimum estimate for the total, time-averaged volcanic SO₂ flux from all volcanoes (e.g., 13 Tg yr⁻¹ “conservative minimum” flux of SO₂ reported by Andres and Kasgnoc 1998).

The BrO emission from Ambrym is also high: the flux we measured in January 2005 (62–110 gs⁻¹) is 5–8 times greater than the 13.4 gs⁻¹ or 3.1 gs⁻¹ observed at Soufrière Hills Volcano, Montserrat (Bobrowski et al. 2003) and Etna respectively (Oppenheimer et al. 2006). However, inspection of Table 1 shows that we have observed highly variable molar proportions of SO₂ and BrO between our four field campaigns. For instance, on 21 March 2005, when the SO₂ flux is the highest in our dataset, the BrO emission rate is as low as 8 gs⁻¹ – while this is still comparable to that measured at Etna, it is an order of magnitude lower than measured three months earlier. This reflects a very high SO₂/BrO ratio of ~7×10⁴ mol mol⁻¹. The ratio was also high (2×10⁴ mol mol⁻¹) in July 2005 but was only a tenth of this in August 2007 (~2×10³ mol mol⁻¹, amongst the lowest SO₂/BrO ratios yet reported for a volcanic plume; Bobrowski and Platt 2007). BrO is formed by atmospheric oxidation of magmatic HBr (Oppenheimer et al. 2006; Bobrowski et al. 2007; Roberts et al. 2009) and the proportions of SO₂ and BrO observed in the plume will depend only partly on the proportions of SO₂ and HBr in the magmatic gas phase. The striking variability of the BrO/SO₂ ratio observed is consistent with recent modelling studies reported by Roberts (2009) and Roberts et al. (2009). These show that the BrO/SO₂ ratio varies with distance from source, plume strength, windspeed, plume dispersion rate, and aerosol loading, due to nonlinearities in the BrO tropospheric chemistry. Two effects – both simulated in the models – are apparent in our dataset: an increase in BrO/SO₂ downwind and lower BrO/SO₂ for the strongest plume (Fig. 10). Nevertheless, the reactive Br source (and probably Cl, Bobrowski et al. 2007) has the

potential for impacting on ozone abundance in this region of the Pacific free troposphere, especially during convective atmospheric conditions that may transport the plume well above the meteorological boundary layer. Where the observations allow comparison, the SO₂/BrO proportions in the plumes from each crater (Marum and Benbow) are indistinguishable (~3.3×10⁻⁴ mol mol⁻¹ in January 2005; Table 1).

Since these are the first measurements of Ambrym’s emission rate, the absence of the volcano as a sustained source in previous compilations of volcanic SO₂ data may point to a significant underestimation of the total volcanic SO₂ source strength (Andres and Kasgnoc 1998).

Deposition of halogen acids, combined with SO₂ and sulphuric acid aerosol, has caused significant defoliation of vegetation on the island, and the high fluorine flux, which represents 5–38 % of the 0.6–8.1 Tg of global estimates of volcanic F release into the atmosphere (Halmer et al. 2002), may result in long-term human exposure to excessive fluoride levels, which appears to be reflected in the incidence of dental fluorosis, some severe (Smithsonian Institution 2005; Cronin and Sharp 2002; Crimp et al. 2006). The origin for both halogens and sulphur can be assumed to be magma degassing through the lava lakes, which appear to be connected to subjacent magma sources located at a depth of <3 km below sea level (Legrand et al. 2005). The D’Entrecasteaux Zone collision with the Vanuatu arc (Fig. 1) and the influx of enriched mantle material associated with the detached slab located at depth between Gaua and Efate islands (e.g., Monzier et al. 1997) may be linked to the exceptional degassing of Ambrym. The remarkable emission rates of both sulphur and halogens warrant further inquiry into the impacts of the plume on the atmospheric environment, human health and terrestrial ecology.

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