Supporting Online Material for

Mass-Independent Sulfur Isotopic Compositions in Stratospheric Volcanic Eruptions

Mélanie Baroni,* Mark H. Thiemens, Robert J. Delmas, Joël Savarino*

*To whom correspondence should be addressed. E-mail: baroni@lgge.obs.ujf-grenoble.fr (M.B.); jsavarino@lgge.obs.ujf-grenoble.fr (J.S.)

Published 5 January 2007, Science 315, 84 (2007)

DOI: 10.1126/science.1131754

This PDF file includes:

Materials and Methods
SOM Text
Fig. S1
Tables S1 and S2
References
Supporting online material:

Materials and Methods

We have studied two major events of the last 50 years at a high time resolution. The Agung (8°S, 115°E, March 1963) and the Pinatubo (15°N, 120°E, June 1991) eruptions injected 12 and 17 Tg of SO₂ directly into the stratosphere (1, 2) to an altitude up to 22-23km and 20-27km (3, 4), respectively. They exhibit similar characteristics as both were located close to the equator and erupted approximately at the same time of year.

The Agung sulfate deposition over the Antarctic Plateau initiated by the end of 1963 (5) and lasted 1.3 year while the Pinatubo sulfate was deposited from mid-1992 to mid-1994 (6). These two events were recovered from a 6m deep snow pit dug in the clean area of Dome C (75°06’S, 123°17’E, East Antarctica) in January 2004. Background samples containing no volcanic sulfate were taken just before the two eruptions.

The Agung sulfate deposition over the Antarctic Plateau initiated by the end of 1963 (5) and lasted 1.3 year while the Pinatubo sulfate was deposited from mid-1992 to mid-1994 (6). These two events were recovered from a 6m deep snow pit dug in the clean area of Dome C (75°06’S, 123°17’E, East Antarctica) in January 2004. Background samples containing no volcanic sulfate were taken just before the two eruptions.

The layers in contact with the excavation tools used for the snow pit were carefully decontaminated by removing the snow on the first twenty centimeters before the sampling step. The operators worked with gloves, and recovered their clothes and their boots with dust-free clothes. The snow pit covers a period of 60 years from 1943 to 2003, approximately, based on a snow accumulation of 10cm.year⁻¹. One sample of 3 to 4.5 kg was taken every 4 to 5 cm, representing approximately two to three samples per year. The snow was then stored in polyethylene bags. The large snow quantities taken, allow the collection of enough sulfate to proceed to the isotopes measurements. In parallel to this collection, another sampling with a higher time-resolution (10 g of snow taken every 2 to 3 cm) was made thanks to clean polyethylene tubes directly pushed into the snow pit wall. The ion-chromatography analysis of these samples allows establishing a detailed sulfate profile of the snow pit and as a consequence a precisely identification of the volcanic sulfate peaks. Then the bags containing the large quantities of snow associated to the Agung and Pinatubo signals could be easily identified. In a clean room (class 10,000), each snow sample is melted in glass beakers and filtered on a Whatman 41 filter, both rinsed several times with deionized water (resistivity = 18 MΩ). An aliquot of 10mL is taken to proceed to the ion concentrations analysis by ion chromatography. Then, the water is placed in a 4 L polyethylene Dionex® bottle (usually used for eluents in ion-chromatography) which is pressurized with helium to avoid any contamination with trace of sulfur dioxide present in the air. The bottle is connected to the ion-chromatography and the sample is loaded on a first column Ionpac AS 11-HC (Dionex®), with a flow rate of 0.9mL.min⁻¹, in order to pre-concentrate it. When the totality of the sample is pre-concentrated, the anions are injected in a second column Ionpac AS 11 (Dionex®), and the sulfate is collected in polyethylene tube in a volume lower than 10 mL. The sulfate is then converted to silver sulfate by adding silver oxide. The silver sulfate is combusted according to the procedure described by Savarino et al. [2001] (7) and decomposed in Ag, O₂ and SO₂. O₂ is analyzed on a Finnigan MAT 251. The produced SO₂ is oxidized to sulfuric acid by reaction with hydrogen peroxide (30%) (7). H₂SO₄ is converted to BaSO₄ by reaction with BaCl₂ 1.3N. The solution is dried, and a solution composed of HCl, HI and H₃PO₄ is added (8-10). The mixture is heated at 100°C for 3 hours and the H₂S vapors are carried by a high purity nitrogen flow into a cadmium acetate (0.2 M) solution to form cadmium sulfide. Cadmium sulfide is converted to silver sulfide by reaction with silver nitrate (0.2 M). The procedure to convert silver sulfide to sulfur hexafluoride (SF₆), is described
Commentary

We decide to not interpret the $\Delta^{36}\text{S}$ values in this paper. Because of the sample sizes, we found $\Delta^{36}\text{S}$ highly variable and therefore unreliable even if generally the sign and range of this isotopic anomaly are in good agreement with previous measurements. The $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$ figure represents only mass-independent fractionation. The $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$ representation fits quite well the SO$_2$ photolysis experiments (12) and reinforce the $\Delta^{33}\text{S}$ vs. $\delta^{34}\text{S}$ interpretation. For the Agung, the $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$ slope is equal to -3.3 and is close to the KrF laser experiments conducted at 248nm. For Pinatubo, the points at 130, 126 and 122cm depth align themselves on a slope of -0.98 close to the archean slope. The points at the end of the sulfate deposition (110 and 117.5cm), displaying negative $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$, fit a slope of 0.49 quite similar to the slope obtained from SO$_2$ photolysis with a mercury lamp at 184.9nm. However, even if such observations are in line with past ones, more data are needed to statistically increase the significance of the present $^{36}\text{S}$ measurements. In the future, this representation will be useful to discriminate different sulfur mass-independent formation pathways for different kind of samples, as a consequence it is important to document and measure the 4 sulfur isotopes. Up to present, three kinds of samples were listed in the representation $\Delta^{36}\text{S}$ vs. $\Delta^{33}\text{S}$: the Archean samples which align themselves on a -0.9 slope (13, 14), the Phanerozoic samples which are fitted on a -6.85 slope (15) and samples from the end of the Paleoproterozoic aligning themselves on a -6.28 slope (16). (The two last kinds of samples are created through a mass-dependent process but their interpretation is beyond the scope of this manuscript).
Figure S1: Plot of $\Delta^{36}S$ vs. $\Delta^{33}S$ for both the Agung and the Pinatubo volcanic sulfate. Comparison with archean rocks and SO$_2$ photolysis experiments at 184.9 and 248nm wavelengths (12). Error bars (2σ) are indicated on the graph. The numbers associated to the points are the depths. The point at a 135cm depth can be neglected because of the bias created by the Cerro Hudson eruption.

Table S1: isotope measurements of a commercial standard

<table>
<thead>
<tr>
<th>$n_{SO_4}$ (µmol)</th>
<th>$\delta^{33}S$ (%)</th>
<th>$\delta^{34}S$ (%)</th>
<th>$\delta^{36}S$ (%)</th>
<th>$\Delta^{33}S$ (%)</th>
<th>$\Delta^{36}S$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.2</td>
<td>0.71</td>
<td>1.35</td>
<td>0.84</td>
<td>0.02</td>
<td>-0.39</td>
</tr>
<tr>
<td>3.5</td>
<td>0.67</td>
<td>1.21</td>
<td>0.60</td>
<td>0.04</td>
<td>-0.50</td>
</tr>
<tr>
<td>std. dev. $\sigma$ (%)</td>
<td>0.034</td>
<td>0.095</td>
<td>0.264</td>
<td>0.06</td>
<td>0.32</td>
</tr>
<tr>
<td>2σ (%)</td>
<td>0.07</td>
<td>0.19</td>
<td>0.53</td>
<td>0.12</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The commercial standard has not been calibrated against an international reference material, as a result, the $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ values are unknown but as expected it does not possess any sulfur isotopic anomaly. These measurements allow getting $\delta^{33}S$, $\delta^{34}S$ or $\delta^{36}S$ standard deviations used in an error propagation formula to calculate the $\Delta^{33}S$ and $\Delta^{36}S$ standard deviations. The commercial standard (Ag$_2$S) underwent all the chemical reactions to get SF$_6$ such as the volcanic samples and was measured with a SF$_6$ working standard calibrated versus CDT (Canyon Diablo Troilite). The CDT measurements are described by Rai et al. [2005] (11).
Also are represented the interval depth of sampled snow and mean depths, $f_v$ and $f_{bg}$ which are the mass fraction of volcanic and non volcanic sulfate, respectively for each sample.

\[
f_{bg} + f_v = 1 \quad \text{(1)}
\]

\[
f_{bg} = \frac{[SO_4^{2-}]_{bg}}{[SO_4^{2-}]_{tot}} \quad \text{(2)}
\]

\[
f_v = 1 - \frac{[SO_4^{2-}]_{bg}}{[SO_4^{2-}]_{tot}} \quad \text{(3)}
\]

where $[SO_4^{2-}]_{bg}$ and $[SO_4^{2-}]_{tot}$ stand for the sulfate concentrations of the background and volcanic samples, respectively. The backgrounds or non volcanic sulfares are composed of sea-salt and marine biogenic sulfate and are represented by the samples noted 430cm and 146cm, respectively for Agung and Pinatubo.

The isotopic composition of each volcanic sample can be described by the following relationship:

\[
\delta_{\text{meas}} = f_{bg} \delta_{bg} + f_v \delta_v \quad \text{(4)}
\]

with $\delta_{\text{meas}}$ representing $\delta^{33}S$, $\delta^{34}S$ or $\delta^{36}S$ of the total sulfate measured; $\delta_{bg}$ and $\delta_v$ stand for the isotopic composition of non-volcanic and volcanic sulfates, respectively. The corrected values are obtained by subtracting the background component using the isotopic mass balance (4): $\delta_v = (\delta_{\text{meas}} - f_{bg} \delta_{bg})/ f_v$

The $\delta^{33}S$, $\delta^{34}S$ and $\Delta^{33}S$ standard deviations are determined in table S1. Because of the low $^{36}S$ abundance and the small sample sizes, the standard deviation are high and when the mass-spectrometer gave a higher standard deviation than the one calculated from the commercial standard, we chose to take the higher one.

* Due to the natural variability of background sulfate, the sulfate concentration of this Agung sample is lower than the background sample. Consequently it was impossible to use the isotopic mass balance to correct this sample with this background value. Instead, we used the background concentration measured after the Agung eruption (50ng.g$^{-1}$, 372cm) but we were unable to measure its isotopic composition due to the sample size and thus assigned the isotopic composition of the previous background.
Supporting references