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UV induced mass-independent sulfur isotope fractionation in stratospheric volcanic sulfate

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[1] Sulfuric acid aerosols produced in the stratosphere following massive volcanic eruptions possess a mass-independent sulfur isotopic signature, acquired when volcanic SO₂ experiences UV photooxidation. The volcanic data are consistent with laboratory SO₂ photooxidation experiments using UV light at 248 nm (maximum absorption of ozone), whereas sulfur isotopic anomalies previously observed in Archean samples are consistent with photodissociation at 190–220 nm. A mechanism of SO₂ photooxidation, occurring in the early stage of a stratospheric volcanic plume, in the range of 220–320 nm (weak band absorption of SO₂), is also proposed. Since mass-independent sulfur isotope anomalies in stratospheric volcanic sulfate appear to depend on the exposure of SO₂ to UV radiation, their measurements might therefore offer the possibility to determine the degree of UV penetration in the ozone-absorption window for the present and past atmospheres. They can also be used to determine the stratospheric or tropospheric nature of volcanic eruptions preserved in glaciological records, offering the possibility to reassess the climatic impact of past volcanic eruptions. **INDEX TERMS:** 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0370 Atmospheric Composition and Structure: Volcanic effects (8409); 1040 Geochemistry: Isotopic composition/chemistry; 1827 Hydrology: Glaciology (1863). **Citation:** Savarino, J., A. Romero, J. Cole-Dai, S. Bekki, and M. H. Thiemens, UV induced mass-independent sulfur isotope fractionation in stratospheric volcanic sulfate, *Geophys. Res. Lett.*, 30(21), 2131, doi:10.1029/2003GL018134, 2003.

1. Introduction

[2] The discovery of mass-independently fractionated sulfur isotopic compositions (sulfur MIF: $\Delta^{33}\text{S} = \delta^{33}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{0.515} - 1] \neq 0$ per mil (‰) and $\Delta^{36}\text{S} = \delta^{36}\text{S} - 1000 \times [(1 + \delta^{34}\text{S}/1000)^{1.90} - 1] \neq 0$ ‰) in Archean crustal and sedimentary rocks has significantly advanced our understanding of the Earth's sulfur cycle [Farquhar *et al.*, 2000; 2002]. The simultaneous oxygenation of the Archean atmosphere and the disappearance of anomalous sulfur isotopic compositions lead to the hypoth-

esis that atmospheric photochemistry involving sulfur dioxide in a primitive atmosphere with reduced oxygen and ozone levels was the cause of the observed sulfur isotopic anomaly [Farquhar *et al.*, 2000]. Isotopic results of laboratory experiments where SO₂ was subjected to UV radiation below 220 nm support this postulate [Farquhar *et al.*, 2001]. As a result, mass-independent sulfur isotopic composition is a tracer of the UV transparency of the Earth's atmosphere. In today's atmosphere, only SO₂ present in the stratosphere at altitudes above 20 km experiences UV photolysis in the 190–210 nm spectral region [Finlayson-Pitts and Pitts, 2000]. Below 20 km, SO₂ photolysis does not occur due to the lack of high energy ($\lambda < 300$ nm) UV radiation, and consequently, SO₂ oxidation proceeds via other thermochemical mechanisms that are mass dependent for sulfur isotopes.

[3] Sulfate deposition on the Antarctic continent is predominantly regulated by the tropospheric oxidation of biogenic marine emissions of reduced sulfur species (dimethylsulfide or DMS) and sea-salt sulfate input, the latter representing generally less than 10% of the total sulfate [Minikin *et al.*, 1998; Wagenbach *et al.*, 1998]. Sporadic, large volcanic eruptions in the mid and low latitudes emit copious amounts of SO₂. This sulfur dioxide is oxidized in, and transported through the stratosphere to the polar regions where it may dominate the atmospheric sulfur budget for short time periods with significant climatic consequences [Cole-Dai *et al.*, 2000; Robock, 2000]. Volcanic sulfate is deposited onto the polar ice sheet and can be preserved in snow and ice layers. Large eruptions are generally marked by unusually high sulfuric acid levels in ice [Hammer *et al.*, 1981]. Long and detailed records of past volcanism can be reconstructed from polar ice core sulfate measurements [Cole-Dai *et al.*, 2000; Zielinski *et al.*, 1994].

[4] Here we report nonzero $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values for volcanic sulfates preserved in South Pole glaciological records. Implications of our results are discussed with respect to the characteristics of paleovolcanism recorded in ice cores, the sulfur cycle and the potential use of mass-independent sulfur isotopic compositions to trace the extent and mechanism of modification of UV transmission (i.e., ozone shielding) in the atmosphere.

2. Sampling and Method

[5] We extracted sulfate from Antarctic snow blocks, ice cores and aerosol filters. Chemical analysis of soluble species revealed that the snow blocks and two ice cores contain the 1991 Pinatubo, the 1991 Cerro Hudson volcanic eruptions and the well-dated 1259 A.D. eruption of an unknown volcano (1259 UE), respectively. Background tropospheric sulfates surrounding these volcanic events

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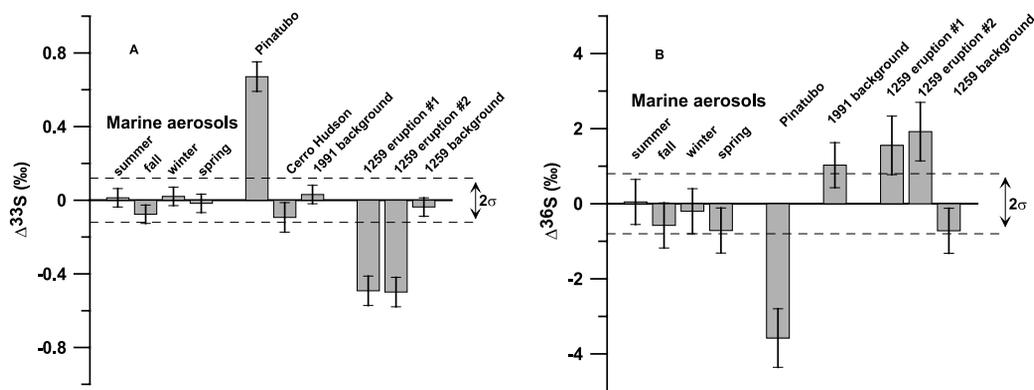


Figure 1. Plot of $\Delta^{33}\text{S}$ (A) and $\Delta^{36}\text{S}$ (B) sulfur isotope anomalies of different sulfate sources. The dashed lines represent the 2σ level of the detection limit. Uncertainty bars include analytical and propagation of error. Volcanic eruptions have been corrected for the background sulfate.

were also isolated from snow and ice layers immediately above and below the volcanic events, and were used to remove the background contribution of the volcanic events. Daily aerosol filters, covering the full 1999 year, were combined by season in order to provide sufficient material for isotopic analysis. After extraction of the sulfate from the solution, sulfur isotopic ratios were measured following well-established procedure using SF_6 as the working gas (see supplemental materials for details¹). Based on replica standard and sample measurements, $\delta^{33}\text{S}$, $\delta^{34}\text{S}$, $\delta^{36}\text{S}$, $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ uncertainties are estimated to be $\pm 0.05\text{‰}$, $\pm 0.03\text{‰}$, $\pm 0.1\text{‰}$, $\pm 0.05\text{‰}$, and $\pm 0.5\text{‰}$ (1σ), respectively.

3. Results and Discussion

[6] $\delta^{34}\text{S}$, $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values of aerosol and background (i.e., non-volcanic) sulfate are all within small isotopic ranges (Auxiliary Table 1), $+13.6$ to $+18.01\text{‰}$, $+7.01$ to $+9.22\text{‰}$, and $+26.77$ to $+33.78\text{‰}$, respectively, indicating similar isotopic sources. This is consistent with a single source-tropospheric oxidation of marine biogenic sulfur (mainly DMS), which is the predominant source of sulfur over the high Southern latitudes [Arimoto *et al.*, 2001; Minikin *et al.*, 1998]. Sulfur dioxide is believed to be the key intermediate in the tropospheric degradation of DMS [Barnes *et al.*, 1996] and SO_2 oxidation to sulfate follows a fast gas-particle conversion process. No UV photolysis is involved, as no high energy UV light is available in the troposphere. Therefore, aerosol and background sulfate are formed through mass dependent processes and no significant sulfur isotope anomalies are expected. This is borne out by the data: all $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ are within the 2σ uncertainty range of zero for these samples (Auxiliary Table 1 and Figure 1).

[7] Sulfur isotopes demonstrate a significant range of variations for volcanic sulfate. Sulfates from the three events, Cerro Hudson, Pinatubo and 1259 UE, possess different isotopic values (Auxiliary Table 1). The near-zero $\Delta^{33}\text{S}$ (-0.09‰) of Cerro Hudson sulfate indicates that the sulfate was formed primarily through a mass dependent

process. Observations during the atmospheric distribution and transport of the 1991 Cerro Hudson SO_2 clouds indicated that the eruption was a predominantly upper tropospheric/lower stratospheric (11–16 km) event [Cacciani *et al.*, 1993; Schoeberl *et al.*, 1993]; the amount of sulfur emitted (1.5 Tg SO_2) was relatively small [Doiron *et al.*, 1991], with a substantial fraction of volcanic debris reaching Antarctica via the middle/upper troposphere (8–12 km) [Deshler *et al.*, 1992; Legrand and Wagenbach, 1999]. Volcanic SO_2 in the upper troposphere and lower polar stratosphere is not subjected to photodissociation since little high energy UV light (<220 nm) is available at this altitude, making it similar to the case of tropospheric aerosol and background sulfates. This is consistent with the observed near-zero $\Delta^{33}\text{S}$ value for Cerro Hudson sulfate. The lack of any substantial fractionation in $\delta^{34}\text{S}$ value of Cerro Hudson sulfate reinforces the premise of fast gas-particle conversion and transport within the troposphere [Krueger *et al.*, 1995]. In contrast, the Pinatubo and 1259 UE sulfates are characterized by significant sulfur isotope anomalies and fractionations: $\delta^{34}\text{S}$ of $+10.89\text{‰}$, $\Delta^{33}\text{S}$ of $+0.67\text{‰}$ and $\Delta^{36}\text{S}$ of -3.58‰ for Pinatubo and -5.71‰ (average $n = 2$), -0.50‰ (average $n = 2$) and $+1.7\text{‰}$ (average $n = 2$), respectively for 1259 UE (Auxiliary Table 1, Figure 1). These anomalies provide unquestionable, evidence of mass-independent processes for this specific volcanic sulfur debris.

[8] Close comparison of SO_2 photolysis experiments and the Archean samples leads to the conclusion that photolysis in the 190 to 220 nm spectral range is responsible for the mass-independent sulfur composition in the Archean atmosphere [Farquhar *et al.*, 2001], with mass-independent compositions of reduced sulfur species (elemental sulfur, pyrite) in opposite direction of the oxidized sulfur species (sulfate) [Farquhar *et al.*, 2000, 2001]. A recent photochemical model [Pavlov and Kasting, 2002] demonstrates that sulfur MIF initiated by the photolysis of SO_2 below 220 nm in an anoxic atmosphere can be distributed among oxidized and reduced sulfur species, fulfilling the isotopic mass balance requirement. This is not possible today as reduced sulfur species are oxidized before they arrive at the Earth's surface, and could explain the apparent rarity of sulfur MIF in modern geological deposits. Figure 2 illustrates the linear relationships between $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$

¹ Auxiliary material is available at <ftp://ftp.agu.org/apend/g/1/2003GL018134>.

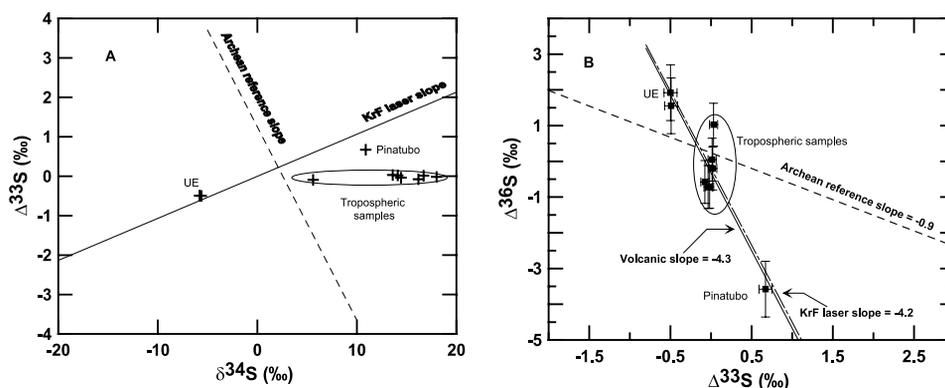


Figure 2. (A) Plot of $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$. The plot shows that $\Delta^{33}\text{S}$ of stratospheric volcanic sulfate is a function of the $\delta^{34}\text{S}$ fractionation and coincide with the photolysis experiment at 248 nm rather than the Archean reference line. Plot of (B) $\Delta^{36}\text{S}$ versus $\Delta^{33}\text{S}$. The dashed line represents the reference Archean slope obtained by [Farquhar et al., 2000]. The semi continuous line is the mass independently fractionated line obtained from photolysis experiment of SO_2 performed at 248 nm (KrF excimer laser) taken from [Farquhar et al., 2001].

(Figure 2a) and between $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (Figure 2b) for the Archean samples and for laboratory photolysis experiments using a KrF laser at 248 nm. Our volcanic sulfur isotope data appear to fit the slope of the laser photolysis experiment in both figures, indicating that sulfur anomalies of volcanic sulfate in the present-day oxygen-rich stratosphere is controlled mainly through UV photochemistry in the 248 nm wavelength region, and not below 220 nm as it is observed for the Archean samples. Photolysis of SO_2 below 220 nm forms $\text{SO} + \text{O}$ but because of the high content of molecular oxygen in today atmosphere, SO is almost instantaneously converted back to SO_2 . The net effect of SO_2 photodissociation for the sulfur is null and therefore this process cannot introduce any sulfur anomalies in an oxygen-rich atmosphere. Our data are in accordance with this observation. The absorption at 248 nm produces only SO_2^* (excited triplet and singlet states) [Okabe, 1978]. Usually SO_2^* species are neglected in chemical stratospheric models as they are efficiently quenched by air molecules [Sidebottom et al., 1972]. However, in environments with high SO_2 concentration (e.g., in a photocell of pure SO_2 as in Farquhar [2001]), SO_2^* may self react to an appreciable rate with SO_2 to form SO_3 and SO [Turco et al., 1982]. In today's atmosphere, SO_3 will be quickly converted to H_2SO_4 , whereas SO will give back SO_2 . Using a 1-D photochemical model (see supplemental materials), we find that this photo-oxidation pathway could represent a significant fraction of the sulfate produced during the first few days following the Pinatubo eruption and even dominate the SO_2 oxidation for the first month following the 1259 UE eruption. Depending on the kinetic fractionation, which is unknown, this process may be sufficient to produce the observed sulfur isotopic anomalies. This photooxidation process opens a way to generate sulfur anomalies in a high O_2 atmosphere when SO_2 is abundant (for instance at an early stage of a volcanic plume), and high levels of 220–340 nm radiation are available (e.g., in the stratosphere), two constraints not filled out by the background and Cerro Hudson events. H_2SO_4 aerosols and gaseous SO_2 formed in this way may carry opposing sign anomalies and be temporally and geographically separated by transport [Castleman et al., 1974]. Recently, sulfur MIF has been

observed in tropospheric aerosols from locations with multiple sulfate sources [Romero and Thiemens, 2003]. The authors attribute their sulfur MIF to stratospheric input of sulfate into the troposphere, further supported by ^{35}S specific activity measurements [Romero and Thiemens, 2003]. These observations are therefore not in contradiction with our explanation.

[9] The $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values are of opposite sign for a given stratospheric volcanic event. This characteristic is also observed in laboratory experiments [Farquhar et al., 2001] and Archean samples [Farquhar et al., 2000]. Pinatubo and 1259 UE possess opposing $\Delta^{33}\text{S}$ (positive for Pinatubo and negative for 1259 UE) and $\Delta^{36}\text{S}$ values (negative for Pinatubo and positive for 1259 UE). The observation of opposite sign in sulfur anomalies between Pinatubo and 1259 UE is likely the result of their specific dynamics. The Pinatubo eruption was a large, stratospheric event, with an estimated 17 ± 3 Tg of SO_2 directly injected into the stratosphere [Krueger et al., 1995] to altitudes between 20 and 27 km [McCormick and Veiga, 1992]. Since the 1259 eruption is estimated to have emitted approximately 20 times more SO_2 (320 ± 80 Tg) than Pinatubo, and is clearly a massive global event [Cole-Dai et al., 2000; Langway et al., 1995], it is very likely that the 1259 UE volcanic plume attained much higher altitudes, exposing volcanic SO_2 to higher UV levels. Different dynamics and UV exposure of the SO_2 plumes will result in different photochemistry which could explain the opposing mass-independent signatures of these two eruptions. The fact that these two volcanic events possess distinct oxygen isotopic compositions [Savarino et al., 2003] and that the conversion rate of SO_2 to H_2SO_4 is highly dependent on plume altitude [Krueger et al., 1995] further reinforces this interpretation.

[10] The 248 nm wavelength corresponds to the maximum O_3 absorption in the Hartley band (230–300 nm). Therefore, the presence of O_3 in the stratosphere can influence the sulfur anomalies of H_2SO_4 by determining the penetration of UV radiation needed for SO_2 photolysis. The control of UV transmission by O_3 in today's atmosphere represents a major difference with the Archean atmosphere in which the O_2 column is believed to be the regulator of the sulfur anomaly. Our result suggests that, in

the post-Archean oxygen-rich atmosphere, the mass-independent isotopic compositions of atmosphere-oxidized sulfur may reflect the degree of UV penetration and hence the level of screening ozone, a hypothesis that must be tested in the future with the improvement of the analytical procedure. Nonetheless, the present results indicate that mass independent sulfur isotope fractionation processes do occur in today's atmosphere via UV photochemistry in and above the ozone screening window, thus providing a unique method of using sulfur isotopes to track this photochemistry.

[11] Polar ice cores are used to study the climatic impact of explosive volcanism. Explosive eruptions produce sulfate spikes in ice cores [Hammer *et al.*, 1981], and Greenland and Antarctica ice cores provide volcanic records of thousands of years [Zielinski *et al.*, 1994]. However, sulfate records usually can not distinguish stratospheric from tropospheric eruptions. The former, in which volcanic gases are directly injected into the stratosphere, is more important climatically since stratospheric aerosols have relatively long residence times and are spread globally. The many volcanic signals from frequent tropospheric eruptions in nearby Icelandic and Aleutian arcs makes it difficult to evaluate the climatic impact with Greenland ice core records. A bi-polar comparison technique may be used to identify large, low latitude stratospheric eruptions, for they produce contemporaneous signals in both polar ice sheets [Langway *et al.*, 1995]. One drawback of the technique is that occasional sub-Antarctic tropospheric eruptions can coincide with some in the Northern Hemisphere [Cole-Dai *et al.*, 1997, 2000]. Our results suggest that sulfur isotopic analysis of ice core volcanic sulfate can be an independent method to identify climatically significant eruptions in the investigation of the climate-volcanism connection.

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