Oxygen-17 excesses in products of stratospheric volcanic eruptions and depletion of the ozone layer

I. BINDEMAN[1,2], J. EILER[2] AND A.M. SARNA-WOJCICKI[3]

[1]Geological Sci, Univ. Oregon, Eugene, OR, USA, ilya@uoregon.edu;
[2]GPS, Caltech, Pasadena, CA, USA
[3]Tephrochronology Lab, USGS, Menlo Park, CA, USA

Volcanic eruptions inject tens to many hundreds of megatons of SO_2 into the troposphere and stratosphere. The intensity and duration of climate cooling are dependent on the residence time of sulfate aerosols, which in turn are controlled by oxidative pathways of SO_2 by ozone, H_2O_2, or OH radicals. These reactions lead to mass independent fractionations (MIF) of sulfur and oxygen isotopes in sulfate aerosols (Bao et al. 2003 and Savarino et al. 2003a,b), measured in ash leachates and Antarctic ice. Previous studies have not revealed a clear relationship between the sizes of volcanic eruption and magnitude of MIF's in the sulfate deposited by those eruptions. We present results of a survey of stable isotope compositions, including $\Delta^{17}O$, of sulfate associated with 9 explosive eruptions between 2 Ma and the present that cover much of the diversity of sizes and the character of volcanic eruptions. We studied the 0.64Ma, Lava Creek Tuff of Yellowstone in particular detail. We also measured pedogenic sulfate cements in loess, till, soil, and salts that underlie and overly ash layers; we found that they either do not contain sulfate, or contain sulfate with $\Delta^{17}O$ <0.2‰. Thus, the observed anomaly in the ash is a property of the volcanogenic sulfate and not of other sulfate.

Sulfate in any single ash unit can span a significant range in $\delta^{34}S$, $\delta^{18}O$, and $\Delta^{17}O$ (up to 20‰, 30‰, and 3.5‰, respectively). We suggest this range is a result of 1) variable amount of reaction with high-$\delta^{18}O$, high-$\Delta^{17}O$ radicals and ozone; 2) rain-out effects related to transport.

$\delta^{18}O$ and $\Delta^{17}O$ values are positively correlated, while $\delta^{34}S$ and oxygen isotope compositions are uncorrelated. Small eruptions exhibit narrower ranges in $\delta^{34}S$, $\delta^{18}O$ (~12‰) and $\Delta^{17}O$ (0-0.3), than do large caldera-forming eruptions. We suggest this is because sulfur-gases emitted by small eruptions are predominantly oxidized in the troposphere, whereas a large fraction of the sulfur gases emitted by large eruptions is oxidized in the stratosphere. Variable but large $\Delta^{17}O$ anomaly (0.4-3.5‰), which we observe in products of 1000km^3 Lava Creek tuff eruption of Yellowstone may record significant episode of ozone depletion.

Fractionation of isotopes in Maryland precipitation nitrate

K.S. COONEY[1], J. FARQUHAR[1], AND M.L. FOGEL[2]

[1]ESSIC and Department of Geology, University of Maryland, College Park, MD 20742, USA (kscooney@geol.umd.edu) (jfarquha@essic.umd.edu)
[2]Geophysical Laboratory, Carnegie Institution of Washington, Washington DC 20015, USA (m.fogel@gl.ciw.edu)

Increasing evidence supports the hypothesis that the fractionation of the three oxygen isotopes in atmospheric nitrate exhibits a deviation from conventional mass dependent behavior ($\Delta^{17}O = \delta^{17}O - 1000 \times ((1 + \delta^{18}O/1000)^{0.52} - 1)$ as a result of reactions between NO_x and ozone. This study examines variations in the $\Delta^{17}O$ of precipitation nitrate in the framework of potentially relevant parameters.

Silver nitrate was prepared from precipitation collected during storm events in Maryland between February 2003 and May 2004 using techniques modified from Chang et al. (1999). The $\Delta^{17}O$ of nitrate was determined by dual inlet IRMS analysis of O_2 using thermal decomposition methods modified from Michalski et al. (2002). The $\delta^{15}N$ and $\delta^{18}O$ of nitrate were measured using a TCEA and CF-IRMS. Overall reproducibility of nitrate standards (1σ) was 0.1‰ for $\Delta^{17}O$ and 0.5‰ for $\delta^{15}N$ and $\delta^{18}O$. Major ion concentrations were measured by ion chromatography and colorimetric methods. Storm track data was collected using the HYSPLIT model.

Results for $\Delta^{17}O$, $\delta^{18}O$, and $\delta^{15}N$ of precipitation nitrate were highest in the winter and lowest in the summer. Values of $\Delta^{17}O$ exhibited a broader range (+15.1 to +30.1‰) and varied on shorter time scales than previously reported. Similarly, there was a wide range of $\delta^{18}O$ (+42.5 to +80.3‰ vs. VSMOW), and data fluctuated considerably within seasons. The range of $\delta^{15}N$ (-5.1 to +5.9‰ vs. AIR) agreed with earlier reports, and values varied seasonally.

Interpretations of the isotopic data are not simple. We are currently investigating the possibility of a contaminant such as that identified by Heaton et al. (2004) and consider our results preliminary. Remarkable seasonal variation in $\delta^{15}N$, despite complex storm track data, suggests that the observed trend could reflect fractionations associated with NO_x chemistry and not solely processes that introduce NO_x to the troposphere (e.g. lightning, fossil fuel combustion). We will also present an assessment of analytical techniques and the relevance of concentration and meteorological data.

References

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