Detailed “supervolcanic” ash record in dry Lake Tecopa, California: $\delta^{34}S$, $\delta^{18}O$ and $\Delta^{17}O$ of soluble volcanic sulfate

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When emitted into the atmosphere, volcanic SO_2 is oxidized into sulfate (SO_4^{2-}) aerosols that are capable of changing the chemical and physical properties of the troposphere and stratosphere. Large quantities of SO_2 are released during super-eruptions and have an unquantified impact on the Earth’s climate. The significant ^{17}O excess in volcanogenic sulfate requires that volcanic SO_2 was oxidized by ozone-derived compounds such as OH radicals [1-3] and this signature is preserved in the geologic record despite potential dilution by sediment-derived sulfate without $\Delta^{17}O$-anomaly.

We present new analyses of oxygen ($\delta^{18}O$, $\delta^{17}O$) and sulfur ($\delta^{34}S$) isotopes in soluble sulfate leached from meters-tick three volcanic ash layers deposited in dry Lake Tecopa in California. We sampled and analyzed 45 volcanic samples from the 0.64Ma Lava Creek Tuff and 2.04Ma Huckleberry Ridge Tuff eruptions of Yellowstone (1000km^3 and 2500km^3), the 0.76Ma Bishop Tuff eruption from Long Valley caldera (750km^3), and 23 enclosing sediments.

The whole data set shows a significant range in $\delta^{34}S$ (12-20‰), $\delta^{18}O$ (0-12‰) and $\Delta^{17}O$ (0-2.26‰) but the maximum $\Delta^{17}O$ of up to 2.3‰ are found only in the sulfates from the three volcanic ash layers. Sediment leached sulfate does not possess $\Delta^{17}O$ >0.5 ‰ and the existence of $\Delta^{17}O$ >0.5 ‰ in sulfate can be interpreted as coming from the ash. Based on the isotopic ratios we provide proportion of sediment-derived sulfate in ash, and ash-derived sulfate in sediment. Our previous analyses of ^{33}S and ^{36}S in five sulfate leachates from Lake Tecopa ash beds did not yield mass independent S behavior [3].

The ash layers sampled here are not interpreted as only resulting from stratospheric deposits. Instead, we infer that sulfuric acid rains that follows large eruption events are able to transfer the ozone-derived $\Delta^{17}O$ signature into the ash layer blankets covering the surface soon after the eruption, via percolation and then precipitation of gypsum having a ^{17}O excess.We speculate on the potential impact of large amounts of SO_2 on the depletion of the ozone layer.

[1] Thiemens (2006) *EPSL* **34**, 217. [2] Bao *et al.* (2003) *GRL* **30,** 1843. [3] Bindeman *et al.* (2007) *GCA* **71,** 2326.

Sanukitoids: Transition from felsic melt- to fluid-dominated mantle metasomatism in subduction zones

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Sanukitoid and Closepet type granites occur in most Archaean terrains where they mostly emplace near the Archaean Proterozoic boundary. They display geochemical characteristics intermediate between Archaean TTG (low Yb and high (La/Yb) and modern calc-alkaline magmas (high K/Na). Their petrographic and geochemical characteristics suggest that they derived from melting of a mantle peridotite, previously metasomatised by felsic melts of TTG composition.

Experimental studies of the melting of peridotite—TTG mixtures reveals that, over a very large range of P-T conditions and TTG:peridotite ratios, the melts formed cluster around an intermediate, magnesian composition similar to the sanukitoid primitive magmas, (nearly) insensitive to the nature of the residual phases or the degree of melting. The differences between sanukitoids and Closepet-type plutons can be ascribed to different degrees of melting of the source.

A subduction environment seems the most realistic setting to allow melting of the hydrous basaltic source of TTG under a peridotite slice such that TTG—mantle interactions would be possible. We propose that the limited temporal occurrence of sanukitoids can be explained as follows:

In the Archaean, important heat production allowed the relatively shallow melting of the subducted slabs. As the Earth cooled down, melting became possible only at greater depth, and in lower proportions, resulting in increasing TTG-mantle interactions. At the end of the Archaean, the TTG generation had so much declined that the TTG melts were completely consumed during interactions with the mantle, whose subsequent melting yielded sanukitoids (and Closepet-type) magmas. Eventually, after the end of the Archaean slab melting became impossible or very rare, and the dominant process was slab dehydration ultimately leading to the formation of BADR series.