

## Effect of precipitation on anomalous oxygen in soil nitrate and sulfate

S.A. EWING<sup>1</sup>, G. MICHALSKI<sup>2</sup>, M. THIEMENS<sup>2</sup>  
AND R. AMUNDSON<sup>1</sup>

<sup>1</sup>University of California at Berkeley, 151 Hilgard Hall #3110, Berkeley CA 94720-3110 (saewing@nature.berkeley.edu, earthy@nature.berkeley.edu)

<sup>2</sup>University of California at San Diego, 5108 Urey Hall, 9500 Gilman Dr., La Jolla CA 92093-0356 (gmichalski@ucsd.edu, mthiemens@ucsd.edu)

In the Atacama desert of northern Chile, hyperarid conditions have preserved atmospheric sulfate and nitrate salts in soils for several million years. We consider the utility of the oxygen isotope anomaly ( $\Delta^{17}\text{O} \approx \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$ ) in soil nitrate and sulfate as a tracer of paleo-atmospheric conditions by examining a series of soils along a hyperarid climate gradient ( $\sim 0$ – $\sim 20$  mm rain  $\text{y}^{-1}$ ).

Nitrate  $\Delta^{17}\text{O}$  varies from 19‰ at the driest site to 6‰ at the most humid site (atmospheric dust = 23‰). This strong correlation with mean annual precipitation (MAP) is a result of the relationship between MAP and soil biological activity rather than atmospheric processing. Moreover, despite other evidence of climate change from wetter to drier conditions over time, nitrate  $\Delta^{17}\text{O}$  varies by <3‰ with depth at any site, suggesting that most soil nitrate represents relatively recent climate conditions.

Sulfate  $\Delta^{17}\text{O}$  in the top meter of soil profiles increases from 0.5‰ to 0.7‰ as MAP increases from  $\sim 0$  to  $\sim 20$  mm. A similar increase with depth (2 m) at the driest site corresponds to other evidence of a previously wetter climate, and both results suggest that the proportion of sulfate from aqueous phase oxidation increases with MAP. Strong positive correlation of  $\delta^{18}\text{O}$  with  $\delta^{34}\text{S}$  but not  $\Delta^{17}\text{O}$  in the top meter of the driest soil indicates significant mass dependent fractionation with in-soil transport, whereas variation in the sulfate entering the soil from the atmosphere is suggested by weak negative correlation of  $\delta^{18}\text{O}$  with both  $\delta^{34}\text{S}$  and  $\Delta^{17}\text{O}$  under more humid conditions.

Our results support careful use of these tracers in soils and sedimentary deposits formed under hyperarid conditions. Atmospheric sulfate oxidation pathways may be more sensitive to small changes in rainfall than those of nitrate, and the variation in the resulting oxygen isotopic anomaly is better preserved in soils due to lower solubility and reduced biological influence.

## Multiple sulfur isotope evidence for dual sulfur sources in the 3.24 Ga Sulphur Springs VHMS deposit

S.D. GOLDING AND E. YOUNG

Earth Sciences, The University of Queensland, QLD 4072, Australia (s.golding@earth.uq.edu.au)

The 3.24 Ga Panorama district in the East Pilbara granite-greenstone terrain (Australia) hosts well-preserved volcanic-hosted massive sulfide (VHMS) deposits within variably silicified, clastic sediments at the base of the Gorge Creek Group. The underlying Kangaroo Creek Formation comprises basic to felsic volcanics and is intruded by the synvolcanic Strelley Granite. Systematically zoned alteration zones underlying Sulphur Springs and other VHMS deposits in the district record seawater-rock interaction at depth and the return of this hydrothermal fluid to the seafloor [1, 2]. A zone of sulfur depletion at the base of the volcanic pile characterised by  $\delta^{34}\text{S}$  whole rock values up to 10 per mil is interpreted to result from inorganic seawater sulfate reduction coupled with dissolution of volcanic sulfides [2]. On the other hand sulfides from the Sulphur Springs deposit (this study) and the Kangaroo Caves deposit [2] exhibit a narrow range of  $\delta^{34}\text{S}$  values around 0 per mil that suggest volcanic and/or primary magmatic sulfur predominate in the deposits.

The identification of mass-independent sulfur isotope fractionation (MIF) in the Archaean rock record provides a new way of tracing the movement of sulfur through various reservoirs in the Archaean crust and mantle [3]. We have determined the  $^{34}\text{S}/^{33}\text{S}/^{32}\text{S}$  isotope composition of sulfides from the Sulphur Springs deposit to establish the relative contributions of magmatic and atmospheric sulfur sources. Massive sulfide mineralisation shows no MIF consistent with a volcanic and/or primary magmatic sulfur source, whereas minor pyrite and base metal sulfides in hangingwall strata show positive  $\Delta^{33}\text{S}$  up to 2 per mil. The lack of variation in sulfide  $\delta^{34}\text{S}$  and positive  $\Delta^{33}\text{S}$  values in the latter are attributed to mixing between sulfur from microbial reduction of atmospheric sulfur aerosols and volcanic sulfur leached from the volcanic pile. The absence of sulfides with negative  $\Delta^{33}\text{S}$  is in contrast to late Archaean VHMS mineralisation and inconsistent with a significant role for microbial sulfate reduction.

### References

- [1] Brauhart, C.W., Huston, D.L., Groves, D.I., Mikucki, E.J. and Gardoll, S.J., 2001. *Econ. Geol.*, 96: 1263-1278.
- [2] Huston, D.L., Brauhart, C.W., Driberg, S.L., Davidson, S.L. and Groves, D.I., 2001. *Geology*, 29:687-690.
- [3] Farquhar, J., Bao, H. and Thiemens, M., 2000. *Science*, 289:756-758.