

## Explaining the structure of the Archean mass-independent sulfur isotope record

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The Archean record of mass-independent fractionation of sulfur isotopes (S-MIF) is widely accepted as recording low levels of atmospheric oxygen [1, 2]. With a growing body of data, there appears to be structure beyond the binary distinction between the presence and absence of S-MIF; early Archean anomalies of a few permil [e.g. 3], followed by a mid-Archean minima in preserved S-MIF [e.g. 4], with a sharp increase to more than 10‰ in the latest Archean [e.g. 5]. Variability in the record has been attributed to changes in atmospheric composition and in S-MIF production pathways [4, 6–8], which lead to a change in either the fluxes to the surface or the isotopic composition of anomalously fractionated compounds, notably  $\text{H}_2\text{SO}_4$  and  $\text{S}_8$ . Little attention has been paid to the role of the marine sulfur cycle, however, despite its inevitable role in delivery of atmospheric sulfur to the sediments and modification of the isotopic signal through a variety of processes, including biological activity.

A model of the Archean ocean-atmosphere, which considers the effect of abiological and biological processes on the preservation of atmospherically-derived S-MIF, yields critical insight into the operation of the Archean sulfur cycle. In addition to the atmospheric oxidation state, we find that the magnitude of preserved S-MIF is sensitive to three properties of the system: *i*) the atmospheric partial pressure of  $\text{CO}_2$ , *ii*) the ratio of  $\text{SO}_2$  to  $\text{H}_2\text{S}$  in volcanic gases and *iii*) biological cycling between pools of sulfur with different oxidation states. Based on tectonic, geochemical and isotopic evidence, we assign time-dependent values to these properties, which in turn allows alternative explanations of the structure in the Archean S-MIF record. In addition, given reasonable ranges of the partial pressure of  $\text{CO}_2$  and the ratio of volcanic  $\text{SO}_2$  to  $\text{H}_2\text{S}$ , constraints can be placed on the levels of sulfur-metabolic activity that would still allow preservation of S-MIF of the observed magnitude.

[1] Farquhar *et al.* (2000) *Science* **289**, 756–758. [2] Farquhar & Wing (2003) *EPSL* **213**, 1–13. [3] Mojzsis *et al.* (2003) *GCA* **67**, 1635–1658. [4] Farquhar *et al.* (2007) *Nature* **441**, 706–709. [5] Kaufman *et al.* (2007) *Science* **317**, 1900–1903. [6] Ohmoto *et al.* (2006), *Nature* **442**, 908–911. [7] Zahnle *et al.* (2006) *Geobiology* **4**, 271–283. [8] Domagal-Goldman *et al.* (2008) *EPSL* **269**, 29–40.

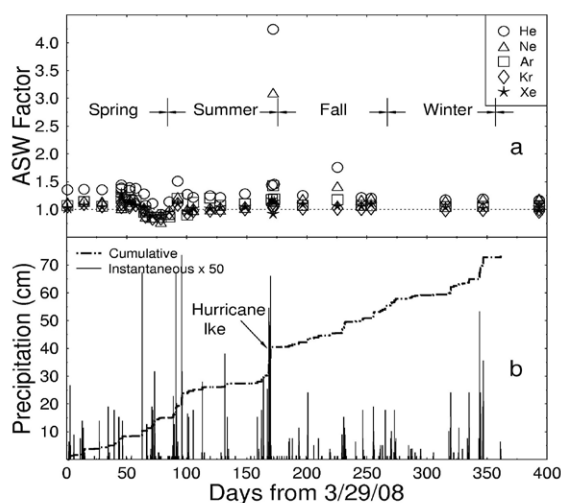
## A year-long field record of groundwater noble gases

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In order to further test the noble gas temperature models put forth by Hall *et al.* [1] and Sun *et al.* [2], a sonde equipped with sensors for T, pH, salinity, ORP, water depth and dissolved  $\text{O}_2$  was installed into the monitoring well in a shallow unconfined aquifer described by Sun *et al.* [2]. Sensor readings were taken every 15 min. and indicate that physical and chemical responses occur within hours of major precipitation.



**Figure 1.** a) normalized noble gas concentrations and b) AAMA weather station precipitation values

Figure 1 shows concentration data normalized to ASW at 9.6°C and 300m altitude, correlated with precipitation. In late spring, concentrations drop but then recover to values above 1. Except for a sample taken immediately following Hurricane Ike there is little evidence for excess air. Generally, variations in concentrations exhibit time constants much longer than groundwater chemical variations, suggesting a relatively stable gas environment in the unsaturated zone.

[1] Hall *et al.* (2005) *Geophys. Res. Lett.* **32**, L18404, doi:10.1029/2005GL023582. [2] Sun *et al.* (2008) *Geophys. Res. Lett.* **35**, L19401, doi:10.1029/2008GL035018.