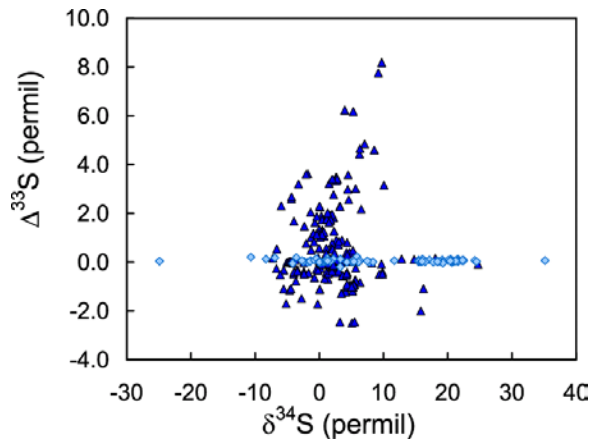


**Implications of sulfur isotopes for the evolution of atmospheric oxygen:** J. Farquhar<sup>1</sup> and D.T. Johnston<sup>1</sup>, Christina Calvin<sup>2</sup>, and Kent Condie<sup>3</sup> <sup>1</sup>Department of Geology and ESSIC, University of Maryland, College Park, MD, 20742, <sup>2</sup>Geological Sciences, Brown University, Providence RI, 02912, <sup>3</sup>Dept of Earth & Environmental Science New Mexico Tech, Socorro, NM 87801.

**Introduction:** The observation of large nonzero  $\Delta^{33}\text{S}$  ( $= \delta^{33}\text{S} - 1000 * ((1 + \delta^{34}\text{S}/1000) - 1)$ ) in samples older than 2.45 Ga and not in younger samples (Fig 1) has been interpreted to reflect the rise of atmospheric oxygen [1-5].

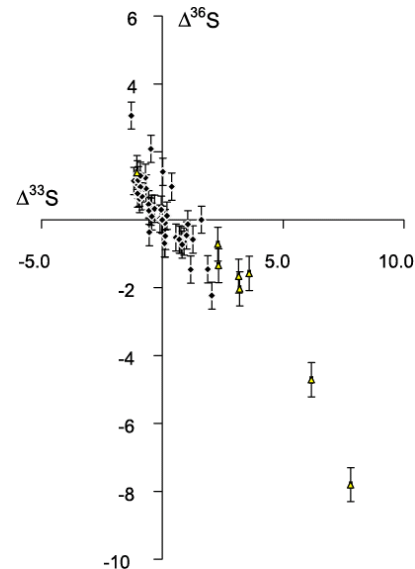


**Fig. 1.** Plot of  $\Delta^{33}\text{S}$  vs  $\delta^{34}\text{S}$  for Samples older than 2.45 Ga (triangles) and samples younger than 2.0 Ga (diamonds). Data from [1,3,6-8] and also includes data from UMCP.

This interpretation hinges on three related hypotheses: (1) that the nonzero  $\Delta^{33}\text{S}$  is produced by an atmospheric reaction that occurs as a result of penetration of solar deep UV radiation throughout the atmosphere (this requires a limited ozone shield and implies low oxygen levels) [3], (2) that preservation of the nonzero  $\Delta^{33}\text{S}$  in the surface sulfur cycle reflects limited interconversion between sulfide and sulfate as a result of a subdued role of oxidative weathering in the surface sulfur cycle [1], and (3) that the transfer of sulfur species with nonzero  $\Delta^{33}\text{S}$  from the atmosphere to the surface is efficient, and that these transfer processes themselves depend on atmospheric oxidation state – principally on the rates assigned to the oxidation pathways for the reduced sulfur species S and  $\text{S}_2$  that recycle sulfur back to  $\text{H}_2\text{SO}_4$  aerosol form [4].

The present theory for the origin of mass independent fractionations (large nonzero  $\Delta^x\text{M}$ , where x is the mass of a rare isotope and M is the atomic symbol for the element) attributes them to processes associated with synthesis (nucleosynthesis, cosmic ray-induced nuclear reactions, radiogenic sources or sinks), nuclear spin selective chemical reactions, self-shielding reac-

tions, or reactions that involve chemical selection rules other than those that directly relate to isotopic mass. The observed relationship between  $\Delta^{36}\text{S}$  and  $\Delta^{33}\text{S}$  (Fig 2.) has been interpreted to indicate that the first two possibilities (isotope synthesis and spin selective reactions) do not explain the observations, and that the effect originates as a result of either shielding reaction (atmospheric), or gas-phase (atmospheric) chemistry involving chemical selection rules other than those that directly relate to mass. Ultimately, candidate reactions responsible for producing the  $\Delta^{33}\text{S}$  signature in the pre 2.45 Ga record must also reproduce the  $\Delta^{36}\text{S}$  vs.  $\Delta^{33}\text{S}$  relationship.



**Fig 2.** Plot of  $\Delta^{36}\text{S}$  vs.  $\Delta^{33}\text{S}$  for samples older than 2.45 Ga. Diamonds are data from [1] and triangles are data collected at UMCP for samples from South Africa.

There are presently only a few candidates for the reactions that produced the sulfur isotope systematics observed in the pre 2.45 Ga samples and these include the reactions associated with the interactions between deep UV radiation and  $\text{SO}_2$ . Laboratory experiments undertaken with  $\text{SO}_2$  and UV radiation at 193 nm and  $>220$  nm have produced products that exhibit similar relationships between  $\Delta^{36}\text{S}$  and  $\Delta^{33}\text{S}$ . These experiments have not been as successful in reproducing the observed relationships between  $\Delta^{33}\text{S}$  and  $\delta^{34}\text{S}$  (Fig 3.). Notwithstanding this, chemistry driven by deep ultra-

violet UV radiation and atmospheric SO<sub>2</sub> is presently the best candidate to account for the observations. Further experiments and theoretical treatments are clearly needed however, to identify the reactions responsible for the observations.

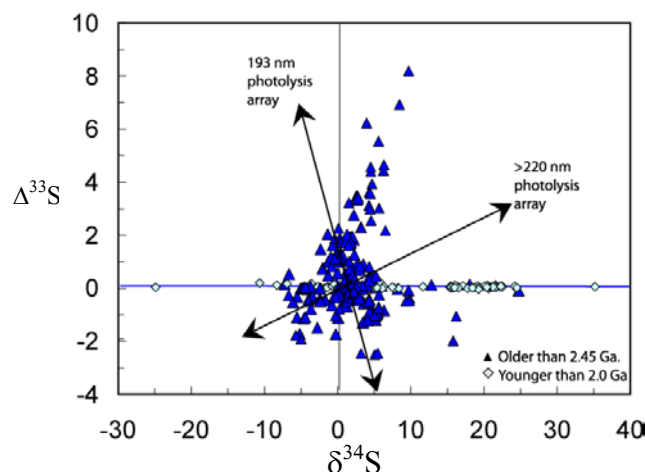


Fig. 3. Plot of  $\Delta^{33}\text{S}$  vs.  $\delta^{34}\text{S}$  for Samples older than 2.45 Ga (triangles) and samples younger than 2.0 Ga (diamonds). Vectors represent sense of arrays generated by products of photochemical experiments with SO<sub>2</sub>. Data from [1,3,6-8].

**Summary:** An atmospheric origin for the origin of non-zero  $\Delta^{33}\text{S}$  is preferred, and the disappearance of large nonzero  $\Delta^{33}\text{S}$  at  $\sim 2.45$  Ga is interpreted to reflect the initial rise of atmospheric oxygen. It is not known whether oxygen rose to near present levels, or intermediate levels immediately after 2.45 Ga, or whether oscillations in atmospheric oxygen levels occurred. The responsible mechanism for these mass-independent fractionations must similarly produce a  $\Delta^{36}\text{S}$  anomaly that is correlated with  $\Delta^{33}\text{S}$ .

**References:** [1] Farquhar et al., (2003) *Science*, 289, 756, [2] Kasting, (2001), *Science*, 293, 819, [3] Farquhar et al., (2001) *Jour. Geophys. Res.*, 106, 32829, [4] Pavlov and Kasting, (2002) *Astrobiology*, 2,27, [5] Bekker et al., (2004) *Nature*, 427,117, [6] Mojzsis et al. (2003), *Geochim. Cosmochim. Acta.*, 67,1635, [7] Ono et al., et al. (2003), *Earth and Planet Sci Lett.*, 213 15, [8] Hu et al. et al. (2003), *Geochim. Cosmochim. Acta.*, 67,17.