S$_8$ aerosols in the Archean atmosphere

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Mass-independent fractionation (MIF) of sulfur isotopes has been reported in sediments of Archean and Early Proterozoic Age (> 2.3 Ga) but not in younger rocks. Furthermore, Farquhar et al. (2001) showed that sulfur MIF can be generated in atmospheric photochemical reactions (SO$_2$ and SO photolysis). In our previous work (Pavlov and Kasting, 2002), we demonstrated that in atmospheres with O$_2$ concentrations $\geq 10^{-5}$ PAL, all sulfur-bearing species would have passed through the sulfate reservoir before being incorporated into sediments, so any signature of MIF would have been lost. Therefore, the Archean atmosphere should have been essentially anoxic.

Recently, Ono et al. (2003) reported large positive mass-independent anomalies (Δ^{33}S up to +6.9 ‰) in the core samples from two carbonaceous shale units (2.5 - 2.7 Ga). Here we show that the anoxic Archean atmosphere is a necessary but not sufficient condition to explain this new geologic data.

Even if the Archean atmosphere were anoxic, the exchange between the reduced (H$_2$S, HS etc.) and oxidized (SO$_2$, H$_2$SO$_4$) sulfur species would have been fast. In our simulation, we have used a one-dimensional photochemical isotopic model (Pavlov and Kasting, 2002) to simulate this exchange. We show that the initially large Δ^{33}S signature, acquired during SO$_2$ and/or SO photolysis (at ~ 9-10 km) would have been significantly decreased (to less than +2 ‰) in the gaseous sulfur species, as they would reach the ground level. Hence, it is highly unlikely that gaseous sulfur bearing species could deliver large positive MIF into Archean rocks.

We propose that the large Δ^{33}S signature can be explained consistently if the reduced sulfur aerosols (S$_8$) were present in the anoxic Archean environment. Our model predicts S$_8$ formation at about 5 - 6 km. Once formed, the S$_8$ aerosols would not exchange isotopes with the rest of the atmosphere and could deliver large Δ^{33}S to the ground essentially intact.

We find that the magnitude of Δ^{33}S in S$_8$ aerosols should have been a strong function of S$_8$ atmospheric abundance, what in turns allows us to constrain the redox state of the Archean atmosphere and the SO$_2$ outgassing rate. Important climatic and biological aspects of the S$_8$ aerosols will be discussed.

References

Farquhar J. et al., (2001), *JGR* **106**, 32829-32839.
Pavlov A. A. and Kasting J. F. (2002), *Astrobiology* **2**, 27-41.
Ono et al., (2003), *EPSL* – accepted.

Quantifying element transfer from slab to mantle at subduction zones

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In principle, the addition of subduction-mobile elements to the mantle wedge above subducting oceanic lithosphere can be quantified from analyses of arc volcanic rocks by comparing the observed concentrations of these elements with the concentrations of subduction-immobile elements of similar petrogenetic properties. Essentially, the concentrations of the subduction-immobile elements form a baseline from which the concentrations of the subduction-mobile elements prior to subduction-addition can be calculated. If the value of a given subduction-mobile element in an arc volcanic rock is termed 'observed' or 'o' and the value estimated from the immobile elements is termed 'expected' or 'e', then (e-o)/z gives the absolute addition to the arc mantle source, where z is the product of mantle enrichment/depletion, partial melting, and assimilation-fractional crystallization operators. The ratio (e-o)/e gives the relative proportion of the element in the mantle source which can be attributed to subduction. Linear programming provides a basis for simultaneously computing additions of the full suite of incompatible, subduction-mobile elements.

This approach clearly depends on good estimates of e and z (for absolute additions) or e only (for proportional additions). In the case of e, the key question is whether the immobile elements (particularly Nb, Ta, Hf, Zr, HREE, Ti) are truly immobile. The Hf isotope ratio (the most accessible, immobile element isotope ratio) potentially provides a test of the immobility of Hf and this, in turn, allows the immobility of other elements to be tested. Key evidence in favour of immobility includes a horizontal trend on plots of Hf isotope ratios against known mobile element isotope ratios. Results indicate that Hf is mobile under conditions of high slab temperatures such as those found at the initiation of subduction, ridge-subduction and continent-arc collision but, more controversially, that Hf is effectively immobile during most steady-state subduction processes. In the case of z, the lowest error estimates may be obtained by studying lavas which crystallized only in the olivine phase field, although such lavas are rare in arcs. For most arcs, therefore, the high errors in estimates of z mean that relative additions of subduction-mobile elements to the mantle wedge can be calculated much more reliably than absolute additions.

Examples from a variety of arcs (particularly the South Sandwich, Vanuatu, Izu-Bonin-Mariana, Tonga and Lesser Antilles) highlight the problems in quantifying subduction fluxes from arc lava geochemistry, but also highlight some successes in identifying and explaining flux variations along- and between-arcs.