

Is a biotic sulfur cycle isotopically necessary prior to ~2.45 Ga?

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The geological sulfur isotope record exhibits a bimodal character. Mass-independent isotopic fractionation distinguishes the record prior to ~2.45 Ga, and mass-dependent isotopic fractionation dominates the record afterwards [1]. Laboratory experiments [2] as well as theoretical calculations [e.g. 3] identify an atmospheric source for the mass-independent S isotope fractionation, while most of the isotopic variability in the record's mass-dependent domain has long been taken to reflect biological processing [4]. This conceptual decoupling has carried over to interpretations of the full isotopic record in earliest Paleoproterozoic and Archean rocks, with isotopic anomalies exiting the atmosphere and much of the mass-dependent isotopic fractionation being associated with microbially-driven redox reactions [1, 5]. Exceptions to this framework are made only when there is a clear covariation of $\Delta^{33}\text{S}$ values ($\approx \delta^{33}\text{S} - 0.5 \delta^{34}\text{S}$) with associated $\delta^{34}\text{S}$ measurements [5]. Atmospheric processes, however, are well known to impart significant isotopic fractionation [e.g. 6], which may explain a substantial component of the full geological S isotope record prior to ~2.45 Ga. Despite early attention drawn to this possibility [1], the net consequences of mass-dependent atmospheric isotopic fractionation have not been explored.

This contribution examines the conditions under which the geologic S isotope record reflects contributions solely from atmospheric processes. I use a minimal model of isotopic fractionation during transfer through an atmospheric reaction network, constrained by laboratory experiments on S isotope fractionation, published S isotope fractionation factors, as well as fractionation factors estimated from basic theoretical considerations. Surprisingly, this exercise indicates that the full isotopic character of the earliest Paleoproterozoic-Archean S cycle could have apparently been set in the atmosphere. As a result, it is unclear whether the evolutionary history of microbial S metabolisms can be isotopically distinguished prior to ~2.45 Ga.

[1] Farquhar *et al.* (2000) *Science* **289**, 756–758. [2] Farquhar *et al.* (2001) *JGR* **106**, 32829–32839. [3] Ueno *et al.* (2009) *PNAS* **106**, 14784–14789. [4] Thode & Monster (1965) *AAPG Mem.* **4**, 366–377. [5] Ono *et al.* (2003) *EPSL* **213**, 15–30. [6] Eriksen (1972) *Acta Chem. Scand.* **26**, 573–580.

Partial and biased preservation of the mantle signal in Icelandic phenocryst compositions

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The progression of mixing of heterogeneous mantle melts can account for the large range of incompatible trace element ratios observed in olivine-hosted melt inclusions in primitive Icelandic basalts and the decrease in this variability with degree of crystal fractionation. We show that melts sourced from different parts of the melting region follow different crystallisation paths in the Icelandic crust, controlling the ability of clinopyroxene to record the full range of melt compositions present in the magmatic system. Ion microprobe and LA-ICPMS trace element analyses were performed on high Mg# (85-92) clinopyroxene and high An content (80-90) plagioclase from the primitive Borgarfraun flow, N. Iceland. Major and trace element compositions were used to search for cpx-melt pairs close to equilibrium and thus suitable for thermobarometry. Thermobarometry results indicate that clinopyroxene crystallized at ~9 (± 2) kbar, close to the Moho. The forsterite content of olivine in Mg-Fe equilibrium with the clinopyroxene and the trace element content of the equilibrium melt were estimated using crystal-crystal and crystal-melt partition coefficients. This conversion allows the compositions of clinopyroxene point analyses to be compared with those of melt inclusions and their host crystals. Both converted clinopyroxene compositions and olivine-hosted melt inclusion data show a wide range in incompatible trace element ratios close to Mg#~90, requiring mixing of mantle melts during crystal fractionation. However, the trace element enriched part of the range observed in the olivine-hosted melt inclusions is absent from clinopyroxene compositions. While the range in La/Yb of 92 olivine-hosted melt inclusions is 0.09-3.23, that for 167 converted clinopyroxene compositions is 0.11-1.29. Phase relations can explain this observation: deep-sourced, enriched melts have a long olivine-only crystallization path and cannot form high Mg# clinopyroxene prior to mixing with more depleted melts. The results have implications for the provenance of crystals hosted in basalts. Non-equilibrium textures, major and trace element compositions, or isotopic ratios differing from whole-rock values may not always be used to infer a simple xenocrystic origin. Instead, these features may be vestiges of the chemically and isotopically diverse mantle melts from which phases crystallized before melt mixing and eruption.