

Cause of the maximum S-MIF scatter in the late Archean: atmospheric organic sulfur and episodic volcanism

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Sulfur Mass-Independent Fractionation (S-MIF) has been useful to monitor chemistry of the Earth's early atmosphere. In the latest Archean, from 2.7 to 2.5 Ga, $\Delta^{33}\text{S}$ values of sedimentary sulfides exhibit exceptionally large variation compared to older period. The maximum scatter of S-MIF may indicate anomalous chemistry of atmosphere or climatic system of the late Archean Earth, though the primary cause of the large MIF is still poorly understand. We have developed a sulfur isotopic model by improving atmospheric reaction model [1,2]. The improvements to our model includes the addition of hydrocarbon chemistry, chemical formation and deposition of organic sulfur haze, together with newly determined high-accuracy ultraviolet absorption cross sections of SO_2 isotopologues. Our model results suggest that after a volcanic injection of SO_2 into the Archean atmosphere, a significant fraction of the sulfur is converted into organic sulfur and could be accumulated in an atmosphere over a timescale of 10 years, if background atmosphere is reducing enough to yield hydrocarbon haze and volcanic sulfur input is large and episodic. Such model could explain the large $\Delta^{33}\text{S}$ preserved in sedimentary rocks. Moreover, isotopically fractionated two reservoirs (i.e. atmosphere and ocean) can be mixed episodically and thus possible to explain the observed small scale heterogeneity of S-MIF even within a hand specimen level. Preservation process of the S-MIF could have been more dynamical than previously thought.

[1] Danielache *et al.* (2008) *J Geophys Res* **113**, D17314. [2] Ueno *et al.* (2009) *PNAS* **106**, 14784-14789.

The relation between metasomatism and redox state of the upper mantle below the Massif Central, France

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Several studies have demonstrated the existence of two geochemically and texturally distinct mantle domains lying north and south of $45^\circ 30'$, respectively [1,2]. These two domains are also reflected by differences in their redox state [3] and record different metasomatic overprints. The aim of this study is to combine redox and trace element data to more closely investigate these metasomatic processes at various length scales.

Preliminary trace element data indicate multiple types of enrichment in LREE, MREE and HSE. These different signatures occur regionally as well as locally, which implies variations in metasomatic style with depth. Most northern domain samples have high La/Nd (>10), but low Sm/Yb (<0.8) and $\log f\text{O}_2$ values $> \text{FMQ}+0.9$. The southern domain appears to have been affected by several different types of metasomatic overprints with variable intensity (e.g. high $(\text{Ce}/\text{Yb})_N$). Oxidation states are also a function of rock type, with harzburgites having $\log f\text{O}_2 \sim \text{FMQ}+1.0$ and lherzolites lying by $\sim \text{FMQ}+0.5$. The harzburgites appear to be more sensitive to changes in oxidation state, presumably due to their generally low spinel contents. The presence of small amounts of amphibole does not correlate with degree of enrichment or the highest $f\text{O}_2$ values. Investigation of how geochemical and redox heterogeneities are influenced by rock type and texture are currently underway.

[1] Downes H. *et al.* (2003) *Chem. Geol.*, 200, 71-87. [2] Lenoir, X. *et al.* (2000) *Earth Planet. Sci. Lett.* 181, 359-375. [3] Uenver-Thiele L. *et al.* (2013) EGU abstract 11398.