Multiple Sulfur isotope constraint of environmental VOSCs and related Sulfur compounds: Implication for organosulfur production and cycling in natural systems

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We report results from a study to examine volatile organic sulfur compounds. We have developed methods to convert volatile organic sulfur compounds (VOSCs) into a form that can be analyzed for the four sulfur isotopic compositions. Compounds studied include dimethylsulfide (DMS), methanethiol (MT), carbonylsulfide (OCS), dimethyl disulfide (DMDS), and carbon disulfide (CS_2).

Results will also be reported for analysis of multiple sulfur isotopes of VOSCs and their precursor (DMSP) from three different field sites – the York River Estuary in Virginia, Fayetteville Green Lake in New York, and the Delaware Great Marsh near Lewes Delaware.

DMSP extracted from the York River Estuary was identified by electrospray mass spectrometry and analyzed for its sulfur isotope composition, using cell extracts isolated by standard methods. This DMSP had $\delta^{34}S$ values of +18.5 ‰ to +19.2 ‰, and $\Delta^{33}S$ and $\Delta^{36}S$ similar to seawater sulfate. The DMSP is slightly ^{34}S-depleted relative to seawater sulfate. This observation is consistent with the origin of sulfur in DMSP being related to assimilatory pathways of sulfate.

Analyses of VOSC extracts from Fayetteville Green Lake, a stratified sulfidic freshwater system and the Delaware Great Marsh yield strikingly different $\delta^{34}S$, $\Delta^{33}S$, and $\Delta^{36}S$ values of total VOSCs (inferred to be mostly MT and DMS) that are similar to but slightly ^{34}S-enriched relative to the compositions of coexisting sulfide (negative $\delta^{34}S$ and $\Delta^{36}S$, and positive $\Delta^{33}S$). These differences are interpreted to reflect different pathways for VOSC production.

The analytical methods and the implications of the isotopic results for interpreting the pathways for formation of VOSCs in these three systems will be discussed.

Biological diversity in the Archean: New results from NanoSIMS

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NanoSIMS carbon (C^-), nitrogen (CN^-), sulphur (S^-), silicon (Si^-) and oxygen (O^-) compositions of fossil spheroids and spindles in the ~3 Ga Farrel Quartzite (FQ) of Australia have been assessed to gain insight to their biogenicity and syngeneity.

Results show that the spheroids and spindles have parallel C^-, CN^-, and S^- distributions as well as a 1:1 correspondence of C^- and CN^- to microstructures imaged by optical microscopy. These features suggest biogenicity [1]. NanoSIMS maps further demonstrate an internal, organic network in the spindles that is difficult to reconcile with possibilities that the spindles might be aggregates of organic particles on crystal surfaces. The FQ microstructures have Si^- and O^- distributions that mimic the C^- and CN^- distributions, suggesting an intimate association between organic matter and silica that likely reflects syngeneity [2].

Thus, the FQ assemblage joins a host of other examples of probable Archean microfossils and organic biosignatures. Moreover, the spindles demonstrate an architecture that is remarkable for ~3 Ga organisms. Our results align with those of Waldbauer *et al*. [3] which suggest that the Archean was a time of evolutionary innovation and diversification.

[1] Oehler *et al*. (2006) *Astrobiology* **6**, 838–850. [2] Oehler *et al*. (2009) *Prec. Res*. **173**, 70–78. [3] Waldbauer *et al*. (2009) *Prec. Res*. **169**, 28–47.