A $\delta^{30}Si_{diatom}$ reconstruction of Holocene productivity of the Southern Ocean, east Antarctica

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Coastal and continental shelf zones are among the most productive ecological provinces of the Southern Ocean and account for c.76% and 3.5% of the total primary productivity of the marginal ice zone and southern ocean respectively [1]. Diatoms account for a large proportion of primary productivity in these regions. Piston core MD03-2601 was recovered in 2003 off the coast of Adélie Land, east Antarctica (66°03.07′S, 138°33.43′E, 746 m water depth) and $\delta^{30}Si_{diatom}$ as analysed by MC-ICP-MS were conducted on a total of 29 samples at regular intervals across a total 2700 cm (c.1000-8000 years BP) of the core to reconstruct productivity changes. $\delta^{30}Si_{diatom}$ is reported as delta values relative to the NBS28 standard. $\delta^{30}Si_{diatom}$ values fluctuate between -0.01 and +0.82‰, with analytical standard errors less than ±0.08, over the duration of the record, with higher values indicating increased utilisation. Increasing $\delta^{30}Si_{diatom}$ values are concomitant with increases in *Chaetoceros* resting spores, reflecting periods of higher diatom productivity associated with longer periods of surface water stratification. These correspond with millennial periodicities of increased productivity [1]. Main trends in the percentage abundance of summer diatom species (predominantly *Fragilariopsis kerguelensis*) show a decline after c.3500 years BP and a change to the dominance of spring diatom assemblages (e.g. *Fragilariopsis curta*), reflecting prolonged sea ice cover [2]. Overall results show that after the Hypsithermal period (c.3500 years BP), during the late Holocene Neoglacial, productivity is reduced.

[1] Denis *et al*. (2009) *Paleoceanography* **24**, PA3207. [2] Crosta *et al*. (2008) *Marine Micropaleontology* **66**, 222–232.

Isotopically heavy sulfur in banded iron formations from the Eoarchean Nuvvuagittuq Supracrustal Belt

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All known Eoarchean (*c*. 3.85–3.60 Ga) volcano-sedimentary successions (i.e. supracrustal rocks) are restricted to high-grade gneissic terranes where biological signatures are challenging to recognize. Although they can be complicated by metamorphic overprinting, sulfur isotopes from Archean supracrustal rocks have the potential to preserve signatures of atmospheric redox chemistry and metabolic fractionation from the original depositional environment. Such sulfur isotope signatures have pushed the record of microbial sulfur metabolism back to 3.49 Ga (Shen *et al*. 2001; Philippot *et al*. 2007) and that of the anoxic atmosphere to 3.8 Ga (e.g. Papineau and Mojzsis, 2006). In order to further extend the Eoarchean sulfur isotope record, we undertook a study of multiple sulfur isotopes from various types of banded iron formations (BIFs) and associated rocks in the 3.77 to 4.28 Ga Nuvvuagittuq Supracrustal Belt (NSB). NanoSIMS was used to analyze sulfides with spot sizes of 15x15 μm for ^{32}S, ^{33}S, and ^{34}S. Analytical conditions yield a 2σ reproducibility for $\delta^{34}S$ and $\delta^{33}S$ better than 0.6 and 0.4‰, respectively, for a combined $\Delta^{33}S$ reproducibility better than 0.3‰. In sulfides from NSB BIFs, we measured the largest range of $\delta^{34}S$ values between -5.7 and +14.6‰ so far reported in Eoarchean rocks, along with a range of $\Delta^{33}S$ values between -0.9 to +3.3‰, that point to an anoxic sulfur cycle. The heaviest $\delta^{34}S$ values were of chalcopyrite grains, up to 2 mm in size, randomly distributed in jaspilitic BIFs in the southwestern part of the NSB. Associated metavolcanic rocks had a comparatively small range of $\delta^{34}S$ values between -2.8 to +1.1‰ along with a range of MIF $\Delta^{33}S$ values between -2.6 to +1.7‰, that suggest that some sedimentary sulfur was remobilized in volcanic rocks. The heavy $\delta^{34}S$ values in NSB BIFs may be an indication of biological metabolic fractionation, but alteration of isotope compositions by post-depositional isotope diffusion cannot be excluded. To independently verify the ranges measured by NanoSIMS, we are currently performing continuous flow isotope ratio mass spectrometric analyses of multiple sulfur isotopes in microdrilled sulfides from polished slabs from these rocks.