Fluid-deposition of graphite with apatite in an Eoarchean banded iron formation from the Nuvvuagittuq Supracrustal Belt, Québec, Canada

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Banded iron formations (BIFs) are among the oldest sedimentary rock-types on Earth and it has been hypothesized that they may have formed under the influence of microbial oxidation of Fe^{2+}. Biological remains of early microorganisms may thus be preserved in BIFs as mineral associations between graphite and apatite, which can form from the diagenetic oxidation of organic carbon. However in highly metamorphosed BIFs, fluid-deposition of graphite may be an alternative mechanism of graphitization with apatite, although this remains to be documented. In a thin section of an Eoarchean BIF from the Nuvvuagittuq Supracrustal Belt (NSB) in northern Québec, which is at least 3.75 Ga and was metamorphosed at the upper amphibolite facies, we have so far documented 43 apatite grains in their petrogrpahic context and found at least six to be associated with graphitic carbon. In one of these mineral associations, Raman micro-spectroscopic imaging revealed a relatively strong D* band at 2700 cm^{-1}, which may be indicative of curled graphite structures. The Raman spectrum of this graphite is also characterized by sharp and intense D- and G-bands, which suggest a partly disordered graphite structure or partly hydrogenated graphene sheets. High-resolution TEM imaging of a FIB-extracted foil of this graphite revealed that it occurs as a ~300nm thick layer in contact with a grain of chalcopyrite + sphalerite about 300nm in size and enveloped in a thin amphibole layer coating the apatite grain. This mineral assemblage was most likely fluid-deposited under high-temperature hydrothermal conditions. A first survey of carbon isotope compositions of whole-rock powders from a dozen BIF samples revealed a large range of $\delta^{13}C_{org}$ values with an average of -34.9 ± 8.9‰ (1σ), which can be used to assess possible sources of carbon in graphite from NSB BIFs. These new datasets suggest that fluid-deposited graphite associated with apatite can form at high temperatures that can obscure the identification of carbon sources. Combined micro-analytical approaches have provided crucial details to establish the mechanisms of graphitization, which is vital to the search for biological signatures in metasedimentary rocks.

Variations in the osmium isotopes record during the *Azolla* phase (IODP Expedition 302)

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We report on a preliminary reconstruction of the seawater $^{187}Os/^{188}Os$ ratios in organic-rich and anoxic sediments of the Lomonosov Ridge (IODP Expedition 302) from the *Azolla* event (49.3-48.1Ma) [1] and compare it with a newly reconstructed $^{187}Os/^{188}Os$ record from an open ocean site (ODP Site 1263). The *Azolla* phase is a stratigraphic marker in the Arctic and surroundings seas and indicates strong salinity-stratification and limited exchange with the open ocean. If we assume that the Os isotopic composition of the Arctic Ocean is homogenous and represents a mixture of unradiogenic dissolved Os from hydrothermal and extraterrestrial ($^{187}Os/^{188}Os$ ~ 0.13) and radiogenic from continental sources ($^{187}Os/^{188}Os$ ~ 1.4), the Re-Os isotope system can be used as a proxy to estimate the ventilation of the Arctic Ocean. We have measured Os and Re using both bulk fusion-leachates and Carius Tubes digestion methods to calculate the initial $^{187}Os/^{188}Os$ and compare methods. Significant authigenic enrichment of Re-Os suggests that these organic-rich sediments have the potential to record the Os isotopic composition of the Middle Eocene Arctic Sea. Measured $^{187}Os/^{188}Os$ ratios range from 1.2 to 1.6. This is indicative of significant *in situ* decay of ^{187}Re to ^{187}Os. During the *Azolla* time interval where multiple analyses yield initial $^{187}Os/^{188}Os$ close to 0.8, with two post-*Azolla* samples yielding values as high as 1.2. These ratios are significantly larger than contemporaneous values of seawater $^{187}Os/^{188}Os$ ratios measured in Site 1263 (0.45-0.5). Thus we interpret these data as supportive of a highly restricted Arctic Ocean at this time.

[1] Brinkhuis, H., *et al.* (2006), *Nature*, **441**, 606– 609. [2] Stein, R., B. *et al.* (2006), *Geophys. Res. Lett.*, **33**, L18606, doi:10.1029/2006GL026776.[3] Backman, J., *et al.* (2008), *Paleoceanography*, **23**, PA1S03, doi:10.1029/2007PA001476.