

## Eoarchean TTG formation by melting of thickened mafic arc crust

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The processes leading to the formation of the earliest preserved continental crust are strongly debated. Here we present trace element and radiogenic isotope data combined with petrological and geochemical modelling that provides evidence for the formation of massive Eoarchean TTGs from southern West Greenland from mafic precursors emplaced in an arc related setting. New trace element and Hf-Nd isotope data of well preserved tholeiites from the Isua Supracrustal Belt (ISB) confirm an island-arc origin and yield decoupled Hf-Nd isotope values with near chondritic initial  $\epsilon_{\text{Hf}}$  (-0.7 to +2.5) and depleted  $\epsilon_{\text{Nd}}$  (ca. -0.1 – +4.4) [1]. The TTGs from the Itsaq Gneiss Complex (IGC;  $\epsilon_{\text{Hf}}$  = -1.1 – +1.3;  $\epsilon_{\text{Nd}}$  = -2.2– +4.1) overlap the ISB tholeiites in their Hf-Nd isotope composition and also share positive  $^{142}\text{Nd}$  anomalies [e.g., 2] both arguing for a genetic relationship. Thermodynamic calculation of mineral assemblages in a partially molten typical ISB tholeiite using the Theriak/Domino software predicts 10-20 % of tonalite melt between 800-950 °C at pressures of 10-14 kbars. Calculated co-existing residues are garnet-amphibolite and amphibole/rutile-bearing eclogite. Trace element modelling of melt compositions in equilibrium with the calculated assemblages yields compositions that are very similar to those of representative juvenile Eoarchean TTGs from the IGC [3]. In contrast, melting of N-MORB at equal pressures does not produce similar trace element patterns in the TTGs, because the stability field of plagioclase is enlarged if compared to IAT residues.

New high-precision HFSE data for the best preserved Eoarchean juvenile TTGs from Greenland, in particular Nb/Ta compositions, confirm the source compositions indicated by the modeling approach, suggesting residual amphibole, ilmenite and rutile to control the HFSE budget.

Altogether, our results suggest formation of the earliest TTG components of the IGC by partial melting of thickened mafic crust with island arc affinity rather than through direct melting of the subducting slab.

[1] Hoffmann *et al.* (in review) *GCA*. [2] Bennett *et al.* (2007) *Science* **318**,1907–1910. [3] Hoffmann *et al.* (2011) *GCA*. doi:10.1016/j.gca.2011.04.027

## Hydrogen sulfide reaction with natural organic matter: Implications for arsenic binding

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Natural organic matter (NOM) represents a major source and sink of sulfur (S). As part of the S-cycle, the incorporation of S into NOM has been shown to proceed via different pathways involving hydrogen sulfide ( $\text{HS}^-$ ) ions [1]. Nucleophilic introduction of S into NOM can generate highly reactive S species such as thiol groups, which in turn strongly interact with soft metal cations or metalloids. In our study we tested the reactivity of NOM towards arsenite (As(III)) and arsenate (As(V)) after its equilibration with  $\text{HS}^-$  at pH 7 under anoxic conditions ( $p\text{O}_2 < 1\text{ppm}$ ). We hypothesized that this reaction increases the content of reduced S species in NOM and thus its ability to retain arsenic.

Natural organic matter (40-250  $\mu\text{m}$ ) was extracted from an oxic ombrotrophic peat bog and reacted with  $\text{HS}^-$  solutions (1-29 mmol S/mol C) at pH 7. Afterwards the sorption of arsenic to pure and  $\text{HS}^-$ -reacted NOM was studied in batch experiments. The speciation of S in untreated and  $\text{HS}^-$ -treated NOM was characterized by S K-edge X-ray absorption near edge structure (XANES) spectroscopy. The coordination of arsenic reacted with NOM was investigated by both As K-edge XANES and extended X-ray absorption fine structure (EXAFS) spectroscopy.

Reaction of NOM with  $\text{HS}^-$  solutions increased its S content from 1210 up to 28000 mg/kg. Sulfur K-edge XANES spectra of pure NOM revealed that S in reduced (-I to I) and intermediate (II to IV) oxidation states prevailed. Sulfur incorporation did not result in a preferential formation of reduced S species, suggesting the partial oxidation of thiol groups.

Arsenate was not retained by pure and  $\text{HS}^-$ -reacted NOM. While As(III) did not sorb to pure NOM, its sorption increased linearly with S content of  $\text{HS}^-$ -reacted NOM. Arsenic K-edge EXAFS spectra showed that the first coordination shell of As(III) was progressively dominated by S atoms with increasing S content of NOM.

Our results document that NOM can rapidly incorporate S under sulfate-reducing conditions. The organic S species formed are highly reactive towards potentially toxic metals and metalloids such as As(III). Our findings provide a possible explanation for recently observed As accumulations in peatlands [2].

[1] Aizenshtat, Z., *et al.* (1995), *Geochemical Transformation of Sedimentary Sulfur*, *ACS Symp. Series*, **612**, 16-37. [2] González A, Z.I., *et al.* (2006), *Environmental Science & Technology*, **40**, 6568-6574.