Further constraints on Helium partitioning in mantle minerals

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The He isotopic composition of the Earth's mantle varies by at least factor ≈5, with mid-ocean ridges characterized by more radiogenic He than ocean islands. There has clearly been significant, ancient He - U fractionation in the mantle but does less radiogenic He represent less or more processed mantle processed?

Heber *et al* [1] measured $D_{He}^{mantle\text{-}melt}$ by growing olivine and pyroxene from a He-saturated melt whereas Parman *et al* [2] 'doped' existing olivine grains with a He atmosphere (without melting the olivine). The presence of inclusions in artificially grown minerals could bias the grown olivine results of [1] (which nevertheless provide a maximum estimate of $D_{He} = 1.7 \times 10^{-4}$) whereas the Parman approach - using gem-quality olivine as a starting material - should not be affected by inclusions therefore *should* result in $D_{He} \leq$ that of grown olivines. Surprisingly, equilibration with a He atmosphere resulted in $D_{He} = 2.5 – 6 \times 10^{-3}$ or > 15 times higher that of the grown olivines.

We equilibrated 100µm thick forsterite wafers with 100% ^{4}He at 1600C; the wafers were then irradiated with 220 MeV protons following [3]. Proton irradiation produces ^{3}He homogeneously in the olivine matrix [3].

Helium was extracted from doped-irradiated olivines by stepped-heating and measured by mass spectrometry at CIT. ^{4}He/^{3}He is highly variable (10 - 1000) in these samples, in contrast to a constant ^{4}He/^{3}He which would be the only solution consistent with homogeneous ^{4}He dissolution in the olivine matrix. While difficult to interpret, these data imply that a) He is not simply in a single solubility site in the olivine matrix; b) the concentration of He in doped olivines probably overestimate He solubility, and therefore D_{He}; c) Heber *et al*'s estimate (3×10^{-4}) remains the best $D_{He}^{ol/melt}$ upper limit.

References

[1] Heber *et al* (2006) *Geochim. Cosmochim. Acta* **71**, 1041-1061;
[2] Parman *et al* (2005) *Nature* **437**, 1140-1143
[3] Schuster *et al* (2006) *EPSL* **249**, 148-161

Schwertmannite reduction and iron(II)-monosulfide formation in acidified coastal lowlands: Iron-sulfur geochemistry and implications for water quality

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Drainage of formerly waterlogged-sulfidic soils in coastal lowlands has resulted in widespread pyrite oxidation in many areas. This oxidation process liberates acidity, Fe and S; which, in turn, leads to the accumulation of schwertmannite ($Fe_8O_8(OH)_6SO_4$). Here we present the results of in-situ studies and laboratory-based experiments examining Fe-S geochemistry and the effects on water quality when schwertmannite accumulations are subjected to reducing conditions. This occurs (1) during diagenesis in the benthic sediments of acidified estuarine waterways; and (2) during prolonged waterlogging of acid sulfate soils as a result of wetland re-establishment.

In acidic (pH 3 – 4) and organic-rich (10% – 25% organic C) soils/sediments, bacterial reduction of schwertmannite-derived Fe(III) occurs readily under anoxic conditions. This produces abundant Fe^{2+}, SO_4 and HCO_3, which thereby drives pH increases to pH 6 – 7 and sequesters some Fe^{2+} via precipitation of siderite ($FeCO_3$). As the pH increases above pH 5, adsorption of Fe^{2+} to schwertmannite catalyses the very rapid transformation of schwertmannite to goethite. The combination of near-neutral pH and the effective replacement of schwertmannite by goethite is accompanied by the formation of elemental S and acid-volatile sulfide. Examination by X-ray diffraction, electron microscopy and electron diffraction show that the acid-volatile sulfide mainly comprises nanoparticulate mackinawite (tetragonal FeS). The formation of elemental S and mackinawite reflect significant levels of SO_4-reduction, even though the soils/sediments contain very large amounts of oxalate-extractable Fe(III). This is curious, as traditional theory (based on overall free energy yields) indicates that SO_4-reduction should not occur significantly until near-complete reduction of Fe(III). The apparently anomalous co-occurence of Fe(III)- and SO_4-reduction (as observed in both the field and laboratory) can be explained by an alternative partial equilibrium model of the thermodynamic favourability of Fe(III)- versus SO_4-reduction. Central to this alternative model is the Fe^{2+}-catalysed transformation of schwertmannite to goethite – a process that facilitates co-occurence of Fe(III)- and SO_4-reduction, and that promotes the accumulation of nanoparticulate mackinawite. The formation and fate of mackinawite has important water quality implications with regard to acidity fluxes and trace element behaviour.