Observations on the distribution of high $^3He/^4He$ in OIB

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Picritic lavas from the ancestral Iceland plume have the highest $^3He/^4He$ yet recorded. About 30 lavas from Baffin Island and West Greenland have $^3He/^4He$ (35 - 50 R_a [1, 2]) significantly higher than the highest OIB. Contrary to established mantle models, these picrites are dominantly MORB-like but span a significant range of ε_{Nd}. While the lowest ε_{Nd} are consistent with small degrees of crustal contamination, a significant range of ε_{Nd}^{60} (+10 to +6.8) is best attributed to mantle heterogeneity. Thus, in the North Atlantic Palaeogene province, any putative high $^3He/^4He$ component shows Nd isotope heterogeneity that is comparable to that which in many OIBs would be attributed to multiple discrete sources.

A similar picture emerges from the global OIB database. Even excluding extreme $^{143}Nd/^{144}Nd$ samples from Hawaii and Samoa, the higher $^3He/^4He$ (20-32 R_a) OIB are dominantly depleted, but still span about 4 ε_{Nd} units [3]. Thus, any depleted high $^3He/^4He$ component is not an 'end-member' in the sense that it can be defined within the anaytical uncertainty of the data used to define it. Rather, there is a general tendency of the highest $^3He/^4He$ OIB to be associated with a relatively depleted ε_{Nd} composition. However, there are some notable exceptions because some of the lowest ε_{Nd} OIB have high $^3He/^4He$ while OIB with MORB-like $^3He/^4He$ also show a wide range of ε_{Nd}.

A single high $^3He/^4He$ mantle reservoir with a discrete Sr, Nd, Pb etc. isotopic composition does not seem consistent with the data. We suggest that the apparent association between high $^3He/^4He$ and elevated ε_{Nd} is simply a volumetric consequence of mantle heterogeneity; most of the mantle sampled by OIB is depleted, so most high $^3He/^4He$ mantle is depleted. Whatever the cause of high $^3He/^4He$ in OIB, it does not exert a strong influence on the lithophile isotopes and readily overprints the He isotope composition of all OIB sources encountered. A component whose high [He] exerts such influence on mixtures with other mantle sources is inconsistent with the generation of high $^3He/^4He$ by melt extraction irrespective of the relative partition coefficients of U, Th and He.

[1] Starkey *et al.* (2009) *Earth Planet. Sci. Lett.* **277**, 91–100. [2] Stuart *et al.* (2003) *Nature* **424**, 57–59. [3] Class & Goldstein (2005) *Nature* **436**, 1107–1112.

Diagenesis of jarosite and hematite: A low temperature path to nanophase iron oxides and 'specular' c-axis aligned hematite on Mars

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The association of c-axis aligned 'specular' hematite with low temperature mineral assemblages, including clays, sulphates, and evaporites on Mars does not fit previous models of specular hematite formation which require hydrothermal alteration of iron hydroxide precursors or dry oxidation of mafic glass. Laboratory experiments examining the rate of jarosite dissolution over temperatures from 277- 323K and a range of aqueous compositions (pH 2-6, varying ionic strength) demonstrate that jarosite converts dominantly to hematite at rates of 10^{-7}- 10^{-9} mol m^{-2} s^{-1}, resulting in abundant nanophase hematite platelets. Based on transmission electron microscopy observations, these hematite platelets replace jarosite within the original particles, nucleate on the surface of jarosite particles, and may also nucleate from the bulk solution at pH≥3. At pH 2, no secondary hematite was observed in short term experiments.

In separate experiments, c-axis aligned 'specular' hematite was synthesized through freeze-thaw treatment of synthetic hematite nanoparticles, similar to those produced by jarosite dissolution. Freezing followed by desiccation also produced specular hematite with thermal emission spectra indicative of c-axis aligned particles nearly identical to thermal emission spectra of Meridiani Planum. Scanning and transmission electron microscopy (SEM and TEM) images suggest that aqueous suspensions of hematite nanoparticles crystallographically align parallel to the basal surfaces during confined freezing to form larger domains. Stacking of the aligned domains leads to mm-scale particles with specular reflectance. These results suggest that aqueous alteration of jarosite to hematite followed by freezing of porewaters may produce c-axis oriented hematite similar to that observed on Mars. While this process alone does not generate spherules, freezing may align particles prior to spherule formation or alter spherules of disordered nanophase iron oxides to form c-axis aligned hematite.