Helium isotopic and concentration variations in a clinopyroxenite vein: Implications for mantle evolution

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In an effort to constrain the behavior of noble gases during melting and melt migration in the mantle, we have measured helium concentrations and isotopic compositions in a 10 centimeter transect through a clinopyroxenite vein in the Josephine Ophiolite (Oregon, USA). The 4 cm thick clinopyroxenite is hosted by harzburgite and was sampled with 1-2 millimeter resolution. The vein has ^{4}He concentrations up to 10 times higher than the host harzburgite (5.0 to 9.0 x 10^{-7}, as compared to 3.4 x 10^{-8} to 1.7 x 10^{-7} cc STP/gram). Because the veins are thought to form through mantle melt percolation, the enrichment confirms that helium behaves as an extremely incompatible element. There is a sharp helium concentration contrast at the vein/host interface, suggesting that the concentration variations were produced during vein emplacement, and that clinopyroxene has higher helium storage capacity. Total ^{3}He/^{4}He in the host harzburgite ranges from 6.5 to 7.1 times atmosphere (Ra), in agreement with previous measurements of the area, suggesting that mantle helium isotopic compositions are dominant (Recanati *et al.*, 2012). The bulk ^{3}He/^{4}He in the vein varies between 4.5 and 5.3Ra, significantly lower than the harzburgite, reflecting radiogenic production since vein emplacement or slab related fluxes. These data demonstrate that isotopic and concentration variations have been preserved since emplacment at ~ 157 Ma, and that mantle helium isotopic compositions are retained. The isotopic variations suggest that it may be possible to determine Th-U-He vein emplacement ages. The short length scale variations place time limits for diffusion and post-emplacement cooling below the closure temperature. This study may not be representative of the mantle, as the Josephine veins are thought to derive from a sub-arc or back-arc basin setting, and are preserved only by rapid cooling. However, these preliminary data do suggest that preferential melting of this vein type will yield lower ^{3}He/^{4}He than the host mantle, and that vein melting models therefore may not explain elevated values (unradiogenic helium) found in some oceanic basalts.

The Mo-isotopic composition of late Archean Iron Formations

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The timing of the first appearance of free oxygen in Earth's atmosphere remains highly debated in the literature. The general view places the Great Oxidation Event (GOE) between 2.4 and 2.32 billion years ago (Ga), when oxygen concentrations rose for the first time from 10^{-5} to 10^{-2} of the present atmospheric level. However, some redox-sensitve elements seem to indicate a pre-GOE increase in atmospheric oxygen concentrations at extremely low levels. Mo isotopes and concentrations in late Archean sediments (carbonates and black shales), for example, show δ^{98}Mo values higher than the continental crust average some 100 million years before the GOE. These positive δ^{98}Mo values are attributed to oxidation-reduction processes that per se require oxygenated oceans, in which light Mo is preferentially adsorbed onto Mn- and Fe-(oxyhydr)oxides. The subsequent increase in seawater δ^{98}Mo is thought to be preserved in black shales and carbonates. The occurrence of heavy Mo-isotope signatures in late Archean shales and carbonates infers the presence of a light Mo-reservoir in the sedimentary record. Fe-(oxyhydr)oxides are a possible candidate for such a light Mo reservoir. During early diagenesis they would form Fe-carbonates, -oxides, or -silicates and eventually iron formations (IF's). Consequently, IF's may represent the missing late Archean reservoir for isotopically light Mo.

Here, we tested this hypothesis by measuring Mo isotopes in 2.63 to 2.45 Ga old black shales and IF's of the Pilbara Craton, Australia. Both, black shales and IF's show a similar increase in δ^{98}Mo as time-equivalent shales and carbonates from the Kapvaal craton, South Africa. The youngest IF shows a highly positive δ^{98}Mo value of 1.5‰. Thus, the proposal that IF's represent the reservoir for light Mo is not confirmed by our measurements. The similarity in magnitude and trend of δ^{98}Mo through time suggests a similar removal mechanism of molybdenum from seawater by carbonates, shales and IF's. Furthermore, this observation requires the build-up of a sizeable seawater Mo-reservoir that was linked to more oxidizing conditions before the GOE.

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