The modification of hydrothermal Fe–isotopic signature during plume-processes

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The Fe isotope composition of the hydrothermal plume, and plume-derived sediments at the Rainbow hydrothermal field on the Mid-Atlantic Ridge (MAR) at 36ºN have been investigated. Serpentinization of the underlying ultramafic basement rocks produces high-temperature fluids with a chemistry that is high in Fe (26 mM), and has a Fe/H_2S ratio of ~24.

Iron from high temperature vents constitutes a significant contribution to the dissolved Fe pool in the deep ocean. Changes in the relative flux, or isotopic composition of hydrothermal Fe will control the Fe isotopic composition of the world's oceans through time. Metalliferous sediments near the ridge-axis preserve a historical record of the metal- and thus heat-flux at mid-ocean ridges. Significantly, the δ^{56}Fe values measured in plume particulates from the Rainbow plume and underlying sediments exhibit a much wider range in Fe-isotopic composition (-0.32 to +1.20‰) compared to the narrow range previously reported for hydrothermal end-member fluids (-0.2 to -0.5‰). The heaviest δ^{56}Fe values (+1.2 ‰) are observed in the buoyant part of the plume, whereas particles in the neutrally buoyant plume are relatively constant at -0.18±0.05 ‰. The deviation in δ^{56}Fe from the high-temperature fluid source, namely the heavy δ^{56}Fe values in the early stage of the plume, are consistent with fractionation during redox-transformation of Fe(II) to Fe(III) as the reducing fluids mix with oxidising seawater. Experimental studies have shown that the equilibrium fractionation factor between dissolved Fe(II) and Fe(III) is 3.0‰, where the lighter isotopes are enriched in the reduced Fe pool. Fe-isotopic fractionation of similar magnitude and direction could also be produced during kinetic processes or bacterial Fe oxidation. Due to the rapid oxidation kinetics of Fe^{2+} in oxygenated seawater, it is, however, unlikely for biological processes to make a significant contribution to the redox-transformation of hydrothermal Fe in the plume. Irrespective of the exact mechanism, it follows that the isotopic composition of hydrothermal fluids will undergo considerable modification within the plume.

Trace element, REE and ^{13}C melt-restite partitioning in graphite-bearing metapelitic migmatites

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Pan-African graphitic stromatic migmatites of the Kerala Khondalite Belt, Southern India, were examined to determine elemental partitioning and isotope fractionation during partial melting. The granitic leucosome of the metapelites are enriched in alkalis (total alkalis ≈ 7-11 wt %), have positive Eu anomalies, slightly enriched LREE, and are depleted in HREE {e.g. (La/Yb)N up to 858 for the melt vs. 232 for restite}. The maximum amount of observed leucosome (~20 %), the distribution of the trace elements and the model composition of the leucosome (K-feldspar > quartz > sodic-plagioclase >> inclusion-free garnet and cordierite) suggest that the melting occurred by fluid-absent dehydration melting of biotite via the reaction: biotite + plagioclase + quartz + K-feldspar + aluminosilicate = melt + garnet + cordierite. Maximum P-T estimates of c. 850-900°C and c. 6-7 kbar during migmatisation correlate well with experimental studies of melting of biotite + sillimanite + plagioclase. It is suggested that partial melts maintained chemical equilibrium with the restite (quartz-inclusion-rich garnet-sillimanite-biotite-cordierite-K-feldspar-graphite) during crystallization. The observed trace element and REE patterns in melt-restite pairs suggests an insitu partitioning of compatible elements, strongly controlled by the mineralogy of the restite.

Aggregates of coarse -grained graphite occur at the contact between leucosome and restite, whereas the restitic portions retain fine grained desseminated graphite. Carbon isotope studies of graphite in melt-restite pairs suggests that the restite preserves carbon isotope signature of sedimentary biogenic compostions ($\delta^{13}C_{PDB}$ ~-25‰), whereas graphite leucosome is highly enriched in ^{13}C ($\delta^{13}C_{PDB}$ = -10 ~ -15‰). Biotite dehydration melting in metapelites is associated with reduction of Fe^{3+} that increases the oxygen fugacity of the system, thereby oxidizing graphite to form CO_2. Within grain microscale isotope zonation relates to the fractionation of ^{13}C between graphite and fluids exsolved from the crystallizing leucosome in a closed system. Partitioning of carbon isotope during reductive deposition from a COH fluid exsolving from the crystallising leucosomes can explain the observed observed carbon isotopic variation in graphite from the metapelitic migmatites. Therefore, the carbon isotope composition of the continental crust can be significanly modified during anatexis.