

The effects of garnet, amphibole and fluid on uptaking of trace elements in zircon during quartz veining within eclogite in the Dabie orogen

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Simultaneous *in situ* analyses of trace elements, U-Th-Pb and Lu-Hf isotopes were carried out for zircons from quartz vein and its host retrograded UHP eclogite in the Dabie orogen, China. The results are used to trace uptaking of trace elements in metamorphic zircon during continental subduction. Metamorphically grown zircons from both the vein and eclogite are characterized by no or weak zoning in CL images, Th/U ratios of 0.004 to 0.09, concordant U-Pb ages of 226 ± 3 Ma and 227 ± 2 Ma, no negative Eu anomaly in REE patterns, low $^{176}\text{Lu}/^{177}\text{Hf}$ but high $^{176}\text{Hf}/^{177}\text{Hf}$ ratios, and low contents of REE and other trace elements with respect to the inherited magmatic zircons. U-Pb dating of solid-state recrystallized zircons give consistent protolith ages of ca. 770 Ma for the vein and eclogite, indicating their origin from the same ages of magmatic rocks. However, the vein has low $\varepsilon_{\text{Hf}}(t)$ values and old Hf model ages of ca. 1.8 Ga, whereas the eclogite has high $\varepsilon_{\text{Hf}}(t)$ values and young Hf model ages of ca. 1.3 Ga. This indicates that the vein-forming fluid was not derived from *in situ* dehydration of the host eclogite itself, but a transported one that may come from the country rock of the eclogite – regional granitic gneiss that has Hf model ages of ca. 1.8 Ga.

The metamorphic growths from the vein exhibit shallow MREE-HREE patterns, suggesting insignificant effect of garnet coprecipitation in the presence of aqueous fluid. This is consistent with the low solubility of both MREE and HREE in the aqueous fluid. In contrast, most of the metamorphic growths from the eclogite show flat HREE patterns typical of the garnet effect; a few grains display reduced MREE contents and thus shallow MREE-HREE patterns, suggesting the effect of MREE-rich amphibole instead of HREE-rich garnet. This is supported by the presence of amphibole in the eclogite. Therefore, the metamorphic growths from both the vein and eclogite have respectively inherited their source characteristics of elements and isotopes. Although the vein-forming fluid traveled a long distance from the country rock of granitic gneiss to the eclogite, elemental and isotopic equilibria were not achieved between the vein-forming fluid and the host eclogite.

Surface complexation of Cu on Birnessite ($\delta\text{-MnO}_2$): Controls on abundance and isotopic composition in the deep ocean

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Hexagonal birnessite ($\delta\text{-MnO}_2$) is a close analogue to the dominant phase in hydrogenetic marine ferromanganese crusts and nodules. These deposits contain ~0.25 wt. % Cu which is believed to be scavenged from the overlying water column where Cu concentrations are near 0.1 $\mu\text{g/l}$. We measured the sorption and isotopic fractionation of Cu on $\delta\text{-MnO}_2$ as a function of pH and surface loading. We characterized the nature of the Cu sorption complex at pH 4 and 8 using EXAFS spectroscopy and first-principles structural optimizations based on density functional theory. Hexagonal birnessite is a phyllosulfate structure with ordered vacancies (e.g., Drits *et al.*, 1997). We find that Cu sorbs to birnessite by inner-sphere complexation over vacancy sites to give a four-fold coordinated (tetrahedral, not square planer) complex at pH 4. At pH 8, however, we find that Cu becomes structurally incorporated into the MnO_2 layer by occupying the vacancy sites. We will show that this is a consequence of the pH dependent protonation of oxygens surrounding the vacancy sites and that the transformation between structural incorporation and surface complexation is reversible. By fitting the Cu sorption edge data, we developed a thermodynamic model for the sorption of Cu onto birnessite. We find that equilibrium concentrations of uncomplexed Cu in the deep oceans should be much lower than the observed values of total dissolved Cu. This is consistent with the hypothesis that, even in the deep ocean, Cu is complexed by microbially produced ligands. Based on our emerging molecular picture of Cu speciation, we are determining the isotopic fractionation factors based on ab initio calculated vibrational frequencies of Cu surface complexes.