



Apatite as a monitor for sulfur redox reactions during fluid-rock interaction in the subduction channel

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The oxidation state of sulfur in slab fluids is controversial, with both dominantly oxidized and reduced species proposed. Here we use *in situ* X-ray absorption spectroscopy analysis of sulfur-in-apatite to monitor changes in the oxidation state of sulfur during high-P metasomatism by slab fluids in the subduction channel. Our samples include a 73 cm continuous transect of reaction zones between a metagabbroic eclogite block and serpentinite matrix from a mélange zone on the island of Syros, Greece. The block core consists of garnet, omphacite, phengite, paragonite, epidote-clinozoisite, and rutile. In this region, apatite is only observed as elongate inclusions in omphacite cores. From the core outwards micas are increasingly replaced by epidote-clinozoisite, garnets are smaller and more frequent, pyrite + bornite is observed as inclusions in recrystallized omphacite, and apatite is increasingly abundant in the matrix and inclusions in garnet. A major transition at 48 cm separates an assemblage of Ca-Na amphibole, omphacite, chlorite, pyrite, and apatite from the inner garnet-bearing eclogite assemblages. Omphacite disappears from the assemblage at ~56 cm and amphibole compositions sharply transition to tremolite at 59 cm. Finally, the assemblage tremolite + talc + pyrite is observed after ~70 cm.

Apatites in the eclogite assemblages exclusively display S^{6+} peaks in their absorption spectra. This includes apatite inclusions in omphacite in the least altered lithology, as well as matrix apatite and isolated apatite inclusions in garnet in the outermost metasomatized eclogite zone. In the intermediate pyrite-rich (~1–5 vol %) amphibole + omphacite + chlorite zone, apatite displays a strong S^{1-} absorption peak in most grains, with rare analyses showing mixed S^{1-} and S^{6+} . Finally, apatite in the outermost tremolite-bearing assemblages only displays a S^{6+} peak. The pyrite-rich zone at 48 cm occurs at the initial interface between the serpentinite matrix and eclogite block, characterized by a dramatic decrease in Na content and Mg#. Our data suggest that reduction of S^{6+} in infiltrating fluids to S^{1-} in pyrite became focused as Fe diffused across the steep Mg# gradient, resulting in pyrite precipitation. In contrast, S reduction in the Mg-rich tremolite-dominant portions of the transect was limited by a lack of Fe, resulting in low modes of pyrite and fluid buffered S^{6+} in apatite. Finally, S^{6+} -bearing apatite is also observed in reaction zone lithologies from elsewhere on Syros, suggesting our observations are not isolated.

Two important conclusions are drawn from these data and observations: (1) In the case of Syros, slab fluids at eclogite-facies conditions carried oxidized S^{6+} , and (2) The interaction of these fluids with eclogites composed of ferrous-Fe silicates resulted in extensive sulfide precipitation.