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Fe and S redox states during serpentinite dehydration in subduction settings

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Serpentinite rocks formed by hydrothermal alteration of oceanic peridotites compose ~70% of the oceanic crust (Hacker et al., 2003), which later sinks into subduction zone and experiences metamorphic reactions. Serpentinites carry ~12 wt.% H_2O and thereby introduces large amount of water in the upper mantle during dehydration in subduction (Ulmer and Trommsdorff, 1995). In addition, serpentinites are known to contain such minerals as magnetite Fe3O4 and pyrite FeS2 in the amounts of ~5 wt.% (Debret et al., 2014) and 1.5 wt.% (Alt et al., 2013), respectively. During metamorphic reactions speciations of Fe and S are tended to change and affect oxygen fugacity. In turn, oxygen fugacity influences the mobility of fluid mobile elements and metals (Pokrovski and Dubrovinsky 2011).

We characterized Fe and S speciation and amount of released water during serpentinite dehydration at different temperature and pressure intervals along a subduction zone. We performed three sets of experiments using piston-cylinder apparatus. Three different starting materials composed of powdered mineral mixtures were used: Fe(III)-antigorite (atg), atg + magnetite, atg + pyrite. Experimental runs were performed at 2 GPa, between 400 and 900°C. Experimental products were first characterized by X-ray diffraction and electron microprobe. Speciation of Fe and S were characterized by X-ray absorption spectroscopy (XANES) at iron and sulfur K-edges. In addition, thermodynamic modeling was applied in this work with constrained thermodynamical data for Fe-bearing antigorite.

The results demonstrate the continuous dehydration of serpentinites with the main water releasing domain between 670 and 700°C, which is happening due to breakdown of antigorite. Fe K-edge XANES measurements show that the amount of ferric iron dramatically decreases between 550-650°C, leading to a release of free oxygen in the system. As a result, we show that the first fluids released from the slab dehydration most likely present highly oxidizing properties. At higher P-T conditions, higher amounts of water are released with minor oxygen release. In addition, sulfur is shown to be progressively reduced at temperature 450-500°C due to pyrite to pyrrhotite transition. The reaction of pyrite reduction was observed to happen with sequestration of Fe from silicates and a release of oxygen. Effectively, the presence of sulphides in serpentinites contribute additional oxygen to the fluid, whereas the release of S may be negligible.

The detailed study of the evolution of redox conditions during serpentinite dehydration in subduction zones will help constraining, 1) the behavior and mobility, from slab to the upper mantle, of elements of economical interest, as well as 2) the global geochemical cycling of elements.

References:

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