The effect of oxygen fugacity on the stability and ferric iron content of antigorite

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Serpentinisation leads to oxidation of the lithosphere through the formation of ferric iron in serpentine minerals and magnetite. The $Fe^{3+}/\Sigma Fe$ ratio of alpine serpentinites, for example, can vary from 0.1 to 0.8 but no thermodynamic data exist for the ferric iron serpentine end member and the effect of the ferric iron component on the stability of serpentinites has not been examined. More importantly, however, changes in the partitioning of ferric iron during the subduction and dehydration of serpentinites could influence the oxygen fugacity during subduction and have implications for the speciation of fluids and the stability of carbonates, reduced carbon and sulphides.

We have studied the stability of antigorite-bearing serpentine and a carbonated serpentinite (ophicarbonate) as a function of P, T and fO_2. Multi-anvil experiments were performed over the antigorite stability field using either metal oxide buffers such as Re and ReO_2 or redox sensors of Fe-Ir alloy to determine the fO_2. Starting materials were natural serpentinites mainly composed of antigorite but different samples were employed with initially high and low $Fe^{3+}/\sum Fe$ ratios. Varying proportions of calcium carbonate were then added to some assemblages to create an ophicarbonate. Experiments were performed for approximately 3 days. Run products were examined using the electron microprobe and the $Fe^{3+}/\sum Fe$ ratios were determined using Mössbauer spectroscopy.

Varying the Fe^{3+} content of antigorite was found to have a relatively minor effect on the dehydration temperature. The experimental results, however, allow the $Fe^{3+}/\sum Fe$ ratio of antigorite to be determined as a function of oxygen fugacity. The antigorite $Fe^{3+}/\sum Fe$ ratio was found to decrease rapidly during dehydration at a buffered oxygen fugacity. In a subducting assemblage with a constant bulk $Fe^{3+}/\sum Fe$ ratio the oxygen fugacity must, therefore, increase as antigorite dehydration occurs. This may lead to the oxidation and mobilisation of reduced carbon and sulphides in the subducting slab.