The oxygen fugacity of serpentinites: implications for subduction zone redox evolution

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At subduction zones H_2O and CO_2 are returned to the Earth' s mantle, bound within hydrous and carbonate minerals. Serpentinites are considered to be major carriers of H_2O into the mantle but natural exposures indicate that some sections of serpentinized mantle also contain significant amounts of carbonate minerals. Determining the fate of so called ophicarbonate rocks presents an important challenge because it involves the interaction between both H_2O- and CO_2- bearing fluids. A further aspect however is that serpentine minerals also contain ferric in addition to ferrous iron. Natural serpentinites record in fact a very wide range of Fe^{3+}/Fe^{tot} ratio but the effect of this ratio on the high pressure stability of serpentine and the relationship with the speciation of coexisting C-O-H fluid phases is unknown.

We have examined the stability of the serpentinite mineral antigorite within ophicabonate assemblages at subarc conditions as a function of P, T and fO_2. Multi-anvil experiments were performed both inside the stability field of antigorite, but also at conditions where antigorite starts to dehydrate. Natural serpentinites are used as starting materials with initially high and low Fe^{3+}/Fe^{tot} ratios. Calcium carbonate was then added to these assemblages to simulate ophicarbonate composition. Iridium metal was added to some nominally unbuffered experiments to allow the oxygen fugacity to be determined, whereas in other experiments the oxygen fugacity was fixed using powders of Ru + RuO_2 and Re + ReO_2 distributed throughout the sample. Ferrous Fe is located in the octahedral site of antigorite whereas ferric Fe may additionally occupy the tetrahedral site of the trioctahedral 1:1 sheet silicates, providing charge balance. We have determined the location and speciation of the Fe atoms in serpentinites as a function of fO_2, P and T by using Mössbauer spectroscopy to examine the run products of the multi-anvil experiments.

The experiments were run for approximately 3 days during which it was possible to change the Fe^{3+}/Fe^{tot} ratios of the starting materials to both higher and lower ratios depending on the redox buffers employed. We found that the relationship between the Fe^{3+}/Fe^{tot} ratio of antigorite and the oxygen fugacity is very temperature dependent with antigorite Fe^{3+}/Fe^{tot} ratios decreasing sharply at the same oxygen fugacity as dehydration commences. This behaviour should cause the oxygen fugacity within subducting lithosphere to increase as dehydration takes place, which will have important implications for fluid speciation. On the other hand the stabilisation of ferric iron in antigorite at high oxygen fugacities appears to have a minimal effect on the temperature of dehydration.

Keywords: Serpentine, subduction zone, f(O2), Multi-anvil, Mössbauer spectroscopy