The redox state of subduction zones and the implications for the speciation of volatiles

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The speciation of volatile components in subuduction zones will depend to some extent on the surrounding redox state and its evolution with pressure and temperature. Serpentinites, for example, account for a significant proportion of H_2O subducted into the mantle but the serpentinisation process itself also leads to oxidation of the lithosphere. The $Fe^{3+}/\Sigma Fe$ ratio of serpentinites can vary from 0.1 to 0.8. While a significant portion of this ferric iron is in magnetite, serpentine minerals themselves also contain some ferric iron, although how this proportion changes with fO_2 is unknown. Serpentinites also transport other volatile elements such as sulphur and carbon into the mantle. The changes in the partitioning of ferric iron during the subduction and dehydration of serpentinites will influence the fO_2, which should have implications for the speciation of fluids and the stability of carbonates, reduced carbon and sulphides.

We have used the results of multianvil experiments to derive a thermodynamic model to describe the relationship between fO_2 and the ferric iron content of lizardite and antigorite during subduction. The results show that in the fore-arc region even significant proportions of ferric iron in serpentine minerals results in relatively low oxygen fugacities such that carbonate rocks would start to be reduced to graphite. As the sub arc region is approached the fO_2 will increase but depending on the initial ferric iron content it is still possible that conditions remain relatively reduced. We use existing constraints on the redox states of other mineral phases to determine how the speciation of volatile elements may further change with depth. We also examine how the redox state of subducting slabs may be related to deep diamond formation.