New metal complexes in upper mantle fluids

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Upper mantle fluids such as those released by subducting slabs may carry carbon into the mantle wedge, causing partial melting, and possibly oxididation of this part of the mantle[1]. However, the nature of these fluids is poorly constrained. A myriad of aqueous species dissolved in fluids can influence fluid-rock interactions in the mantle and the identity as well as the concentrations of these species are important for understanding the deep carbon cycle.

Experimental measurements of the solubility of eclogite and peridotite at upper mantle conditions[2] provide valuable constraints on the possible aqueous complexes of major elements, including Mg, Fe, Al, Ca, Na, and Si. These constraints, together with thermodynamic data derived by analysis of experimental studies at lower temperatures and pressures (e.g. Manning and co-workers), enable further calibration and extension of the Deep Earth Water (DEW) model[3], which can then be used to predict the behavior of fluids in the upper mantle.

We used the DEW model to predict equilibrium constants that were in turn used in an aqueous speciation solubility model for comparison with experimental studies of the solubilities of K-free coesite-bearing eclogite (KFCE) and K-free peridotite (KFP)[2]. The predicted Si solubility in fluids with KFCE agrees well with experiments up to 800°C and 5 GPa. However, the predicted Si in fluids with KFP is strongly underestimated, as the experimental data at 800°C increases dramatically from about 3 to 6.6 molal from 4.0 to 6.0 GPa. This result, together with corresponding results for Mg and Al, strongly suggests the existence of some important aqueous metal complexes of OH and/or silicate. Based on previous studies[4], we suggest that metal-silicate complexes of Fe, Mg, Ca and Al may account for a significant part of the speciation in the experimental systems. Our results emphasize how different these fluids might be from the traditional upper mantle CHO fluid model and could be of major importance for the deep carbon cycle.

[1] Frost and McCammon (2008), *Annu. Rev. Earth Planet. Sci.* **36**:389–420; [2] Kessel *et al.* (2005), *EPSL* **237**(**3**); 873-892; Dvir *et al.* (2011), *Contrib. Mineral Petrol.* **161**(**6**): 829-844; [3] Sverjensky *et al.* (2014), *GCA*, **129**, 125-145; [4] Pokrovski *et al.* (1998) *Mineralogical Magazine A* **62**: 1194-1195.