Reduced fluids released at sub-arc depth from subducting ultramafic rocks

PICCOLI F. [1], KEMPF E. [1], VIERA DUARTE J.F. [1], HERMANN J. [1], PETTKE T. [1], CONNOLLY J.A.D. [2]

[1] University of Bern, Institute of Geological Sciences, Balzerstrasse 1+3, 3012 Bern, Switzerland (correspondence: francesca.piccoli@geo.unibe.ch)
[2] Department of Earth Science, Swiss Federal Institute of Technology, Zurich, Switzerland

Much effort has been devoted to understanding the oxidizing/reducing capacity of slab-derived fluids, with important consequences on fluid-mediated processes distinctive of subduction settings including modification of the redox budget of the mantle wedge. Here we combine observations on natural samples with thermodynamic modelling to track the evolution of redox state in subducting, dehydrating ultramafic rocks.

The modelling indicates that serpentinites evolve from reduced conditions (-4 log units below the Fayalite-Magnetite-Quartz, FMQ, redox buffer) to relatively oxidized conditions (+1 *Δlog FMQ*) during the metamorphic transformation from brucite + antigorite + magnetite, to antigorite + olivine + orthopyroxene + magnetite . At UHP conditions (~2.8 GPa / ~800°C) corresponding to sub-arc conditions, Al-spinel and garnet become stable together with chromite and olivine, indicating that the rock is buffered at 3 to 4 log units below the FMQ. This evolution in fO_2 has consequences on the stability of redox sensitive phases including sulfides, and fluid composition.

Petrographic observations were made on samples from different localities representative of the three main dehydration reactions. At the brucite-out reaction (Zermatt-Saas; Switzerland) and the antigorite-out reaction (Cerro del Almirez, Spain) magnetite + pentlandite + pyrrhotite coexist with silicates, whereas at the chlorite-out reaction (Cima di Gagnone; Switzerland) Cr-spinel with a minor magnetite component is stable together with Cu-sulfide and Fe-Ni aresenides. These observations document the stability of magnetite together with low S-fugacity sulfides (pentlandite and pyrrhotite) until UHP conditions are reached. Both petrographic observations and thermodynamic modelling indicate that at the chlorite-out conditions, high temperature and low fO_2 allow for a more significant mobilization of S into the fluid. Importantly, S speciation into the fluid is predicted to be reduced, in the form of H_2S. Such a fluid would act as a reducing agent during interaction with overlying altered oceanic crust, sediments or the mantle wedge.