



## **Thermodynamic investigations of redox state in subduction zone fluids (invited)**

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The redox state and speciation of subduction zone fluids determines the capacity of these fluids to oxidise the sub-arc mantle, and extent to which the deep Earth could be oxidized by the addition of dehydrated subducted material. Oxidised sub-arc mantle is critical to many genetic models for the formation of arc-related ore deposits, and the redox evolution of the deep Earth is fundamental to our understanding of temporal change in geological processes. In spite of this importance, there is no consensus on the redox state of these fluids. Subducted ultramafic rocks, in particular, have the capacity to produce oxidized fluids via changes to the stability of magnetite and sulfide minerals. Magnetite produced by serpentinisation carries redox budget in the form of ferric iron, and it has been proposed that this redox budget is transferred to oxidized sulfur species dissolved in subduction zone fluids, and onwards to the sub-arc mantle.

THERMOCALC simulations of high pressure-low temperature metamorphism of ultramafic rocks replicate observed mineral assemblages but, rather than predicting release of oxidized species, predict release of methane and hydrogen sulfide. Loss of these reduced species results in a small increase in the redox budget of the subducting slab, and infiltration of such fluids into the sub-arc mantle would not produce oxidation. However, there are limitations to these models that require careful consideration, and these will be presented and discussed.

An alternative approach, that circumvents some of the limitations inherent in the THERMOCALC calculations, but imposes others, is to compare the predictions of activity-activity diagrams in the system Ni-Fe-O-H-S to oxide-sulfide-alloy assemblages in subducted ultramafic rocks. Application of this approach to serpentinised ultramafic rocks from supra-subduction zone mantle in New Caledonia, from high pressure-low temperature rocks from the Zermatt-Saas ophiolite, and to rocks from different tectonic settings in Alpine Corsica, reveal that fluids sufficiently reducing to stabilize awaruite, and sufficiently oxidizing to stabilize pyrite are found in different settings.

It is concluded that subduction of ultramafic rocks can produce either reducing or oxidizing fluids, depending on factors that include, but are not limited to, geodynamic setting of the protolith, the extent of open system fluid interactions, and the proximity of contrasting lithologies.