



## Ultra-oxidized redox conditions in subduction mélanges? Decoupling between oxygen fugacity and oxygen availability in a metasomatic environment

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The manganese ore of Praborna (Italian Western Alps) is embedded within a metasedimentary sequence belonging to a subduction mélange equilibrated at high-pressure conditions ( $\sim 2$  GPa) during the Alpine orogenesis and record environmental conditions typical for a subducting slab setting. The pervasive veining of the ore and the growth of “pegmatoid” HP minerals suggest an open system with large fluid/rock ratio and a strong interaction with slab-derived fluids. This natural case provides an excellent natural laboratory for the study of the oxygen mobility in subducting oceanic slab mélanges at high-P, fluid-present conditions. The Mn-rich rocks in contact with the underlying sulphide- and magnetite-bearing metabasites, in textural and chemical equilibrium with the veins, contain braunite ( $\text{Mn}_2+\text{Mn}_3+6\text{SiO}_{12}$ ) + quartz + pyroxmangite ( $\text{Mn}_2+\text{SiO}_3$ ), and minor hematite, omphacite, the epidote piemontite and spessartine-rich garnet. Similarly to Fe-bearing systems, Mn oxides and silicates can be regarded as natural redox-sensors, capable to monitor a process of fluid infiltration that could fix externally the intensive variable  $f\text{O}_2$  (or  $\mu\text{O}_2$ ). Sulphides are absent in these Mn-rich rocks, sulphates (barite, celestine) occurring instead together with As- and Sb oxides and silicates. On the basis of the observed assemblages, new thermodynamic calculations show that these mélange rocks are characterized by unrealistic ultra-oxidized states ( $\Delta\text{FMQ}$  up to +12) if the chemical potential of oxygen (or the oxygen fugacity) is accounted for. However, if the molar quantity of oxygen in excess with reference to with reference to a system where all iron and manganese are considered to be ferrous, the ore appears only moderately oxidized, and comparable to typical subduction-slab mafic eclogites. Therefore, oxygen can be hardly considered a perfectly mobile component, even in the most favourable conditions. In the Earth’s interior redox reactions take place mainly among solid oxides and silicates, as oxygen is a negligible species in the fluid phase, if any. Therefore, the description of the redox state of petrological systems requires the introduction of the conjugate oxygen molar quantity, becoming the oxygen chemical potential a dependent variable. As a consequence,  $\mu\text{O}_2$ , and therefore  $f\text{O}_2$ , should not be regarded as long-range properties, indicative of the redox state of the entire rock column of a subduction zone, from the dehydrating oceanic crust to the overlying mantle wedge. On a more general basis, the comparison of  $f\text{O}_2$ s retrieved from different bulk compositions and different phase assemblages may lead to apparent redox heterogeneities. On the contrary, the distribution of oxygen is expected to be much more continuous moving from a maximum in the subducted mafic eclogites, formed from the altered oceanic basalts and gabbros, down (upward) to a minimum in the peridotites of the mantle hanging-wall.