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Slab-to-mantle "oxidation" transfer: insights from subduction peridotites metasomatised by C-bearing fluids

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Subduction zones are key geodynamic settings in the global geochemical cycle of many light elements, such as C, O and H, where the volatile transfer from slab to mantle is accomplished by fluid phases released by dehydration, partial melting and/or decarbonation reactions in the slab lithologies. Evidence of recycling in the mantle of slab-derived fluids enriched in C-O-H components is given by the occurrence of hydrous minerals coexisting with C-bearing phases in orogenic suprasubduction mantle peridotites, sampled by the lithosphere during subduction and/or exhumation. Hydrates coexisting with carbonates and C polymorphs (e.g. phlogopite + magnesite + graphite/diamond) have also been found as precipitates in polyphase inclusions hosted by garnet of mantle peridotites. The mechanism of slab-to-mantle volatile transfer is strongly related to the fluid speciation, which in turn is a function of oxygen chemical potential (expressed as oxygen fugacity, fO_2) in a system buffered by equilibria between redox-sensitive elements (e.g. Fe, S, V) in mineral assemblages. Although much is known about the oxidation state of the upper mantle, the redox state of the metasomatised mantle at subduction zones is poorly investigated and the oxidising power of fluids is still unknown.

fO_2 in ultrahigh pressure (UHP) peridotites is traditionally determined from the Fe2+ and Fe3+ contents of garnet in equilibrium with olivine and orthopyroxene. However, in most metasomatised garnet peridotites several phases, besides garnet, incorporate both ferric and ferrous iron (e.g. clinopyroxene). We have evaluated the oxidation degree of subduction garnet peridotites from the Dabie-Sulu Belt (Eastern China), by measuring the Fe3+ distribution of the major phases combining Flank Method electron probe microanalyses and Electron Energy Loss Spectroscopy (EELS). These samples record a multistage metasomatism by an alkali-rich silicate melt at high temperature, and a subsequent influx of a slab-derived incompatible element and silicate-rich fluid during the Triassic UHP metamorphism. The results indicate that pyrope-rich metasomatic garnets present a chemical zoning, with the complementary decrease in $Al2O_3$ ($\sim$26 to $\sim$21 wt%), relative to the increase of $Fe2O_3$ ($\sim$0.8 to $\sim$2.5 wt%). Diopsidic clinopyroxenes contain relatively high Fe3+/ΣFe ratios (0.48-0.51) and Na contents (0.13-0.17 a.p.f.u.). Interestingly, also orthopyroxene may contain Fe3+/ΣFe up to 0.10. The enrichment in Fe3+ of Ca-clinopyroxene requires the incorporation of a NaFe3+Si2O6 component, particularly in garnet peridotites where the Al content of clinopyroxene is buffered by its coexistence with garnet. The coupled Na-Fe3+ enrichment of clinopyroxene likely suggests a corresponding enrichment in the whole rock. Such a substitution into clinopyroxene could be therefore favoured by the influx of alkali-rich metasomatic fluid phases.

In order to investigate the role of deep fluids in the redox processes of the suprasubduction mantle we measured for the first time the Fe3+ concentration of the microprecipitates in polyphase inclusions by EELS with TEM high resolution investigations. These inclusions are hosted by garnets of metasomatic orthopyroxenites from Dabie-Sulu, formed at the slab-mantle interface after the reaction between a metasomatic silicate-rich hydrous melt and the overlying mantle. Preliminary data indicate that the solute content of UHP slab fluids may contain high Fe3+ concentrations. If net bulk rock oxidation can be demonstrated, silicate- and/or alkali-rich C-bearing fluids could be regarded as potential carriers of Fe3+, alkali (and S), able to “oxidise” the supra subduction mantle. Such mechanisms open new possibilities to unravel the redox processes occurring in the portion of mantle wedge interfacing the subducting slab, which is a key location where the mantle redox reactions likely occur.