The oxidation state of metasomatised mantle wedge: insights from C-H-bearing garnet peridotite

Nadia Malaspina (1), Stefano Poli (1), Patrizia Fumagalli (1)

(1) Dipartimento di Scienze della Terra, Università degli Studi di Milano, Italy

In subduction environments the fluid phases released by the subducting plates are vehicles for the slab-to-mantle element transfer, leading to the metasomatism, re-fertilisation and partial melting of the mantle. Occurrences of hydrous minerals coexisting with carbonates and C polypmorphs (e.g. phlogopite + magnesite + graphite/diamond) in mantle wedge peridotites evidence that such fluids are represented by C-O-H solutions, derived by dehydration reactions and decarbonation of the slab. The equilibria involving the volatile elements play an important role in controlling the iron oxidation state of mantle silicates and oxides by redox reactions. Alternatively, Fe^{3+}/Fe^{2+} equilibria between mantle minerals may buffer the fluid speciation, and therefore oxygen fugacities (fO_2). Despite a number of studies have been devoted to determine the redox state of the upper mantle, the fO_2 of supra-subduction mantle wedge, used as monitor of its oxidation state, is still poorly investigated.

An essential input for fO_2 estimates is therefore represented by an accurate determination of the ferric-ferrous iron content of key mantle minerals such as garnet. As case study, we selected samples of a mantle wedge garnet peridotite from the UHP Sulu belt (Eastern China), where magnesite + phlogopite occur in equilibrium with olivine + orthopyroxene + garnet ± clinopyroxene (Malaspina et al., in press). For the olivine + orthopyroxene + Fe^{3+}-garnet assemblage, fO_2 can be calculated from the reaction (1): $2\ Fe_3^{2+}Fe_2^{3+}Si_3O_{12}$ (skiagite) = $4\ Fe_2^{2+}SiO_4$ (fayalite) + $2\ Fe_2^{2+}Si_2O_6$ (ferrosilite) + O_2 (Gudmundsson and Wood, 1995). Fe^{2+}/Fe^{3+} ratio in garnet has been measured by the "flank method" electron microprobe analyses (Höfer et al., 1994). These measurements reveal that the Sulu peridotite garnet contains considerable amounts of Fe^{3+}, showing a zonation in Fe^{3+}/Fe_{tot} ratios, which vary from 0.06 up to 0.21. The "flank

method" has been calibrated on almandine, andradite and skiagite end-members with fixed Fe^{3+}/Fe_{tot} (0, 1 and 0.4 respectively). We have synthesised the end-member skiagite and garnet along the almandine-skiagite join, where Al and Fe^{3+} substitute on the octahedral sites. The experiments were performed with a glass and slag with a fixed ratio of Fe^{3+}/Fe_{tot} in a multianvil apparatus using tungsten carbide cubes with a 14-mm truncated edge and Au capsule, at P=10 GPa. The correct Fe^{3+}/Fe_{tot} ratio of the starting material was achieved by controlling the fO_2 of the furnace atmosphere using CO-CO_2 gas mixes.

Up to date, the lack of thermodynamic data for the Fe^{3+}-garnet component (skiagite), and of an appropriate solid solution model for this phase, limited the applicability of equilibrium (1). We therefore modelled non-ideal mixing of Al and Fe^{3+} on the octahedral site by a symmetric regular solution model, combining previous experimental and thermochemical data on skiagite and almandine (Woodland and O'Neill, 1993; Ottonello et al., 1996). This enabled us to calculate garnet-peridotite fO_2, given the presence of Fe^{3+} in the garnet from equilibrium (1).

The determination of fO_2, and therefore of the oxidation state, of this garnet-peridotite would be a powerful tool to compare the buffering capacity of Fe^{2+}/Fe^{3+} in the mantle wedge, relative to the C-O-H fluid speciation. This will permit to unravel the devolatilisation processes in subduction zones and the transfer of C-O-H components from the slab to the mantle wedge.

Gudmundsson and Wood (1995) CMP, 119, 56-67; Höfer et al. (1994) EJM, 6, 407-418; Malaspina et al. (in press) Lithos; Ottonello et al. (1996) AM, 81, 429-447; Woodland and O'Neill (1993) AM, 78, 1002-1015.