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Primary spinel+chlorite inclusions in mantle garnet formed at UHP: implications for the crust-to-mantle redox budget

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Multiphase inclusions represent microenvironments where the interaction between fluid and host mineral is preserved during the rock geological path. Under its peculiar chemical-physical constraints, the entrapped solute-rich fluid might follow a crystallisation mechanism which is not predictable through simple equilibrium arguments. By the modelling of solid-solution equilibrium and the application of principles of mass conservation, we demonstrate that cavities in mantle garnet filled with slab-derived fluids can re-equilibrate to a pyrope + spinel + chlorite assemblage at the same high P-T of their formation. The basis of this occurrence is a dissolution-reprecipitation mechanism, triggered by a dilute, non-equilibrated slab fluid.

A case study of supra-subduction mantle affected by metasomatism from crust-derived fluid phases is the Maowu Ultramafic Complex (China) deriving from harzburgite precursors metasomatised at $\sim$ 4 GPa, 750-800°C by a silica- and incompatible trace element-rich fluid phase [1,2]. This metasomatism produced poikilitic orthopyroxene and inclusion-rich garnet porphyroblasts. Solid multiphase primary micro-inclusions in garnet display negative crystal shapes and infilling minerals (spinel, $\pm$orthopyroxene, amphiboles, chlorite, $\pm$ talc, $\pm$ mica) occur with constant modal proportions, indicating that they derive from trapped solute-rich aqueous fluids. A single-crystal X-ray diffraction experiment performed by synchrotron radiation at Diamond Light Source [3] demonstrated the epitaxial relationship between spinel and garnet and between some hydrous minerals. Moreover, FT-IR hyper spectral imaging analyses and micro-Raman spectroscopy, together with X-ray microtomography performed on single inclusions, indicate that liquid water is still preserved at least in some inclusions. The Fe3+ concentration of the micron-sized precipitates of the multiphase inclusions has been measured for the first time using EELS on a TEM to investigate the redox budget of these fluid phase. Results indicate that spinel contains up to 12% of Fe3+, amphibole about 30%, while in chlorite and phlogopite may reach 70%. The Fe3+ fraction of the host garnet is equal to that measured in spinel as also confirmed by Flank Method EPMA measurements.

Oxygen mass balance, performed both on the Maowu hybrid orthopyroxenite and on metasomatised supra-subduction garnet peridotites, indicate that the excess of oxygen (nO_2) is the same (10 mol m-3). An oxygen mass balance of the crust- derived fluids also indicates that the fluid precipitates are more oxidised than the host rock, reaching up to 400 mol m-3 of nO_2. This suggests that even after their interaction with the metasomatic orthopyroxenites, the residual fluid phases could be potentially carrier of oxidised components when escaping the slab-mantle interface.

References:
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