Primary spinel+chlorite inclusions in mantle garnet formed at ultrahigh-pressure

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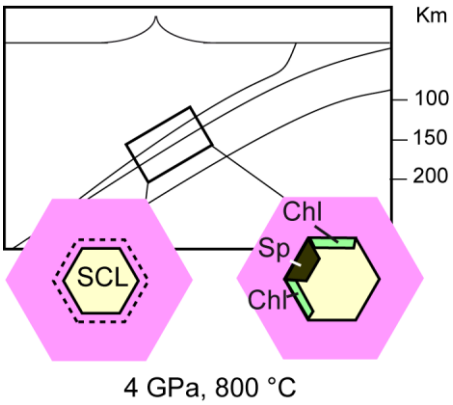
ABSTRACT



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. In this letter, by 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 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.

Introduction

Primary inclusions (fluid or solid multiphase) in mantle minerals represent the remnant of the fluid phase produced by dehydration reactions in the subducted slab and subsequently equilibrated with the overlying supra-subduction mantle peridotites. Natural and experimental studies demonstrated that saline aqueous inclusions with variable solute load prevail in high pressure (HP) rocks (Scambelluri and Philippot, 2001; Touret, 2001), whereas multiphase solid inclusions in some ultrahigh pressure (UHP) rocks have been attributed to silicate-rich fluids or hydrous melts at supercritical conditions, namely supercritical liquids (Bureau and Keppler, 1999; Carswell and van Roermund, 2005; Ferrando *et al.*, 2005; Korsakov and Hermann, 2006; Malaspina *et al.*, 2006; Stöckhert *et al.*, 2001). These inclusions are frequently hosted by minerals stable at mantle depths, such as garnet, and show the same textural features as fluid inclusions (Frezzotti and Ferrando, 2015; Fig. 1). The mineral infillings of the solid multiphase inclusions are generally assumed to have crystallised by a simultaneous precipitation from the solute load of dense supercritical liquids equilibrating with the host rock. Moreover, the occurrence of phases stable at UHP, such as coesite or microdiamond, has long been considered evidence of precipitation from such liquids at pressure above 3 GPa. Here, we demonstrate that even a mineral association characterised by phases usually considered stable at relatively low pressure in mantle system (*e.g.* spinel + chlorite), would potentially crystallise at UHP by chemical fluid/host interaction.

We will consider as a case study a well-known example of multiphase solid inclusions occurring in the cores of garnets forming orthopyroxenites from the Maowu Ultramafic Complex (Eastern China), interpreted as hybrid rocks resulting by the interaction of previous harzburgites and slab-derived silica-rich liquids (P = 4 GPa, T = 800 °C) at the slab-mantle interface (Chen *et al.*, 2017; Malaspina *et al.*, 2006). These multiphase inclusions have negative crystal shapes and constant volume proportions of the mineral infillings consisting of spinel ± orthopyroxene, and hydrous phases gedrite/pargasite, chlorite, phlogopite, ±talc, ±apatite (Malaspina *et al.*, 2006, 2015; Fig. 1).

Some inclusions still preserve liquid water at the interface between mineral infillings and the cavity wall (Malaspina *et al.*, 2017). Recently, Malaspina *et al.* (2015) demonstrated the epitaxial relationship between spinel and garnet (Fig. 1A) which suggested nucleation of spinel under near-to-equilibrium conditions. On the contrary, hydrous phases (amphiboles, chlorite and ±talc ±phlogopite) nucleate in a non-registered manner and likely under far-from-equilibrium conditions. The epitaxial growth of spinel with respect to garnet and the ring-shaped chlorite + water assemblage filling the space between the host garnet and the other inclusion minerals (Malaspina *et al.*, 2017), suggest that spinel and chlorite formed at UHP together with the garnet cores. However, from a thermodynamic point of view, spinel should never be stable in a chemical system characterised by pyrope + H_2O, at any P-T range (Fig. 2). Surprisingly, in nature we can count a number of examples where spinel occurs in garnet-hosted primary diamond-bearing (hence UHP) multiphase inclusions from Bardane, Ugelvik and Svartberget in the Western Gneiss Region (Carswell and van Roermund, 2005; Malaspina *et al.*, 2010; Scambelluri *et al.*, 2010; van Roermund, 2009; van Roermund and Drury, 1998; Van Roermund *et al.*, 2002; Vrijmoed *et al.*, 2008, 2006). We will show how this occurrence is driven by a dissolution-reprecipitation mechanism triggered by precise constraints on the composition of the supercritical liquid phase released by the slab.

Results

Multiphase solid inclusions in garnet represent the heritage of a series of processes comprising: i) formation of the cavity, and ii) crystallisation of the solute within the cavity. The determined morphological and compositional features of the solid phases can be exploited in order to gain insights into the dynamics of these processes. Among the identified solid phases within microcavities in garnet, spinel occupies a distinctive position (Fig. 1). The reasons for that derives from the following characteristics, which were already evidenced by (Malaspina *et al.*, 2015): i)

spinel is not present in all the cavities, ii) spinel is the only (anhydrous) oxide phase when present, iii) spinel is the only epitaxial phase with garnet when present. On the basis of these characteristics, spinel was attributed a role of nucleation initiator for the solid phases occupying the cavity. Here, we obtain deeper insights into the crystallization mechanism by the analysis of solution-solid equilibrium in a model MgO-Al_2O_3-SiO_2-H_2O (MASH) system and the application of principles of mass conservation.

If aqueous fluids released by the slab are under the condition to equilibrate with solid phases, their molal composition would be close to 0.11, 0.18, and 3.7, in terms of dissolved MgO, Al_2O_3, and SiO_2 components, in accordance with the experimental composition of the fluid phase in equilibrium with a K-free eclogite at 4 GPa and 800 °C (Kessel *et al.*, 2005, Fig. 3). This means that the water released by the dehydration of slab minerals might enrich by significant amounts of the sole silica component, as far as its path is sufficiently long before the slab-mantle interface is reached. The effects of such fluids on the peridotite layer at the slab-mantle interface might be distinguished as follows: i) if in contact with a pure water fluid, the minerals of the peridotite layer might undergo dissolution. Dissolution might be negligible if the transition of fluids is fast and alternated by periods of dry conditions. On the contrary, dissolution might persist if the fluid is entrapped in cavities. ii) If in contact with a silica-rich fluid, the forsteritic component of the peridotite layer might react with the fluid, giving rise to a pyroxene-rich layer, according to the reaction $Mg_2SiO_4 + SiO_{2\,(aq)} = Mg_2Si_2O_6$, acting as a "filter".

At a late stage of process ii), the fluid escaping the pyroxene-rich filter might be at a composition in equilibrium with the mantle peridotite, namely 5.3, 0.31, and 3.0 in terms of MgO, Al_2O_3, and SiO_2 molalities (Dvir *et al.*, 2011, Fig. 3).

As far as process i) is concerned, one should evaluate if a subsequent event of dissolution-reprecipitation within pyrope cavities might bring about an equilibration of the fluid-solid system at the same P-T conditions of its formation. In order to demonstrate this evolution of the cavity, we must perform a hypothesis on the precipitating phases. On the basis of the assessed composition of

our multiphase inclusions in pyrope-rich garnet (Malaspina *et al.*, 2015), it is clear that spinel and clinochlore can be reasonably considered the products of this precipitation, since stable assemblage pyrope-spinel-clinochlore occurs only at P ≥ 4 GPa, and forsterite, corundum, Mg-staurolite, and coesite are never present within the cavity (Fig. S1). Hence, the cavity should contain, at equilibrium, spinel and clinochlore as phases nucleated on pyrope after its dissolution, leaving a fluid with a composition in equilibrium with the pyrope-spinel-clinochlore assemblage.

Pertinent chemical equations read:

Pyrope congruent dissolution: $Py_{(s)} \rightarrow 3MgO_{(aq)} + Al_2O_{3(aq)} + 3SiO_{2(aq)}$

Spinel precipitation: $MgO_{(aq)} + Al_2O_{3(aq)} \rightarrow MgAl_2O_{4(epi)}$

Clinochlore precipitation: $10MgO_{(aq)} + 2Al_2O_{3(aq)} + 6SiO_{2(aq)} + 8H_2O \rightarrow Mg_{10}Al_2[Al_2Si_6O_{20}](OH)_{16(s)}$

If one refers to 1 kg H_2O, the mass balance of the whole process reads:

$$M = m + 3p_y - s_p - 10c_l$$

$$A = a + p_y - s_p - 2c_l$$

$$S = s + 3p_y - 6c_l$$

$$H = 56 - 8c_l$$

Where M, A, and S (m, a, and s) are the final (initial) molalities of MgO, Al_2O_3, and SiO_2 of the fluid entrapped in the cavity, H are the moles of free water, p_y, s_p, and c_l are the moles of congruently dissolved pyrope, precipitated spinel, and precipitated clinochlore, respectively. The solution of this system of equations gives:

$$p_y = \frac{A-a}{2} + \frac{2(S-s)}{3} - \frac{M-m}{2}$$

$$s_p = \frac{S-s}{3} - (A-a)$$

$$c_l = \frac{A-a}{4} + \frac{S-s}{6} - \frac{M-m}{4}$$

The constrain of positive values for p_y, s_p, and c_l allows us to define the space of the m, a, and s parameters, which determine the composition of the slab-derived fluid when the composition of the fluid in equilibrium with the pyrope-spinel-clinochlore assemblage is known. Such fluid was calculated to have a composition of M = 0.15, A = 0.0096, and S = 0.12 (Supplementary Information, Fig. 3B). These concentrations appear reliable if compared with the 0.13 molal experimental congruent solubility of garnet grossular (Fockenberg *et al.*, 2008). For our purposes, we consider the fluid in equilibrium with the pyrope-spinel-clinochlore assemblage to have concentrations within the intervals M = 0.15÷0.39, A = 0.0096÷0.13, and S = 0.12÷0.39, which give

$$p_y = (0.01 \div 0.13) - \frac{a}{2} - \frac{2s}{3} + \frac{m}{2}, \quad s_p = (0.0 \div 0.030) + a - \frac{s}{3}, \quad c_l = (-0.015 \div 0) - \frac{a}{4} - \frac{s}{6} + \frac{m}{4}.$$

A trivial upper limit of initial molalities is $m = M$, $a = A$, and $s = S$, which zero the first member of the equations, whereas the lowest limit of pure water ($m = a = s = 0$) is admitted. Since the m term is positive in each equation, the mass balance gives no constrain on the upper limit of m and, while c_l increases with m, s_p is independent of m. On the contrary, a silica-rich fluid as that in equilibrium with the slab (m = 0.11, a = 0.18, s = 3.7) would give rise to negative p_y, s_p, and c_l.

By way of example, consider a fluid with composition m = 0.20, a = 0, and s = 0. Under such hypothesis the roots are p_y = 0.11÷0.23, s_p = 0÷0.030, and c_l = 0.035÷0.050 (H undergoes a decrement of 0.5÷0.7%, which gives rise to a negligible correction of the previous molalities). By scaling these results on the volume of a typical cavity (10^4 μm^3), considering that the molar volume of water is 14 cm^3 mol^{-1} at 4 GPa and 800 °C (Zhang and Duan, 2005), the moles of pyrope dissolved in the cavity and the moles of precipitated spinel and clinochlore are (1.4÷2.9)×10^{-12}, (0÷3.8)×10^{-13}, and (4.5÷6.4)×10^{-13}, respectively. Assuming a molar volume of 110, 40 and 1100 cm^3 mol^{-1} for pyrope, spinel, and clinochlore, respectively, the dissolved volume of pyrope results

150÷300 μm^3, whereas the volume of precipitated spinel is 0÷15 μm^3 and that of clinochlore is 500÷700 μm^3. All these volume predictions are consistent to what observed in nature (Fig. 1).

Conclusions

The systematic presence of spinel+chlorite inclusions in many subduction zone mantle peridotites reflects a slab-mantle interface characterised by the transit of dilute aqueous fluids which may consist of pure H_2O. These fluids are non-equilibrated fluids released by the slab minerals having the attitude to dissolve garnet (Fig. 4). If slab-derived fluids are SiO_2-enriched (Fig. 3), they will react with the overlying mantle peridotites forming orthopyroxenite layers (grey zone in Fig. 4). Once entrapped in the metasomatic-forming garnet (stage 1 in Fig. 4), they can dissolve it and bring the system to an equilibrium state of py-sp-cl assemblage (Fig. S1) through a dissolution-reprecipitation mechanism (stage 2 in Fig. 4). The subsequent retrograde path undergone by the inclusion-bearing rock triggers the crystallisation of the other hydrous phases (gedrite, phlogopite, pargasite, talc), leaving an eventual residue of water solution (stage 3 in Fig. 4). On the light of the drown conclusions, spinel-chlorite bearing multiphase inclusions can be considered as witnesses of crystallization processes at UHP. The fingerprint of such processes is sometimes revealed by a "surprising" composition which, if analysed by sole equilibrium arguments, would lead to wrong inferences about their formation history.

Acknowledgements

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Figure 1

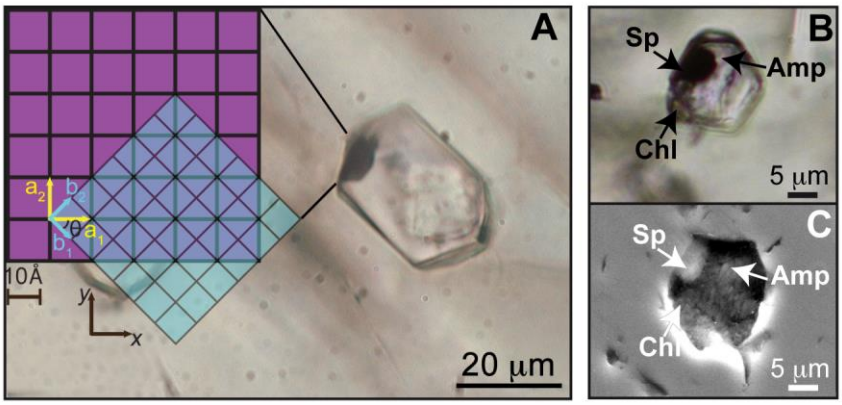

Figure 1 A) Photomicrograph of a multiphase solid inclusion in metasomatic garnet from Maowu Ultramafic Complex (Dabie Shan, China). Inset represents the relative orientation of the spinel {100} surface lattice (light blue) with respect to the garnet {100} surface lattice (violet) for the coincidence at $\theta = -45°$ (from Malaspina *et al.*, 2015); B, C) Negative-crystal shaped multiphase solid inclusion (plane polarised transmitted light and Secondary Electron image) with evident microstructural relations between spinel, chlorite and amphibole (gedrite).

Figure 2

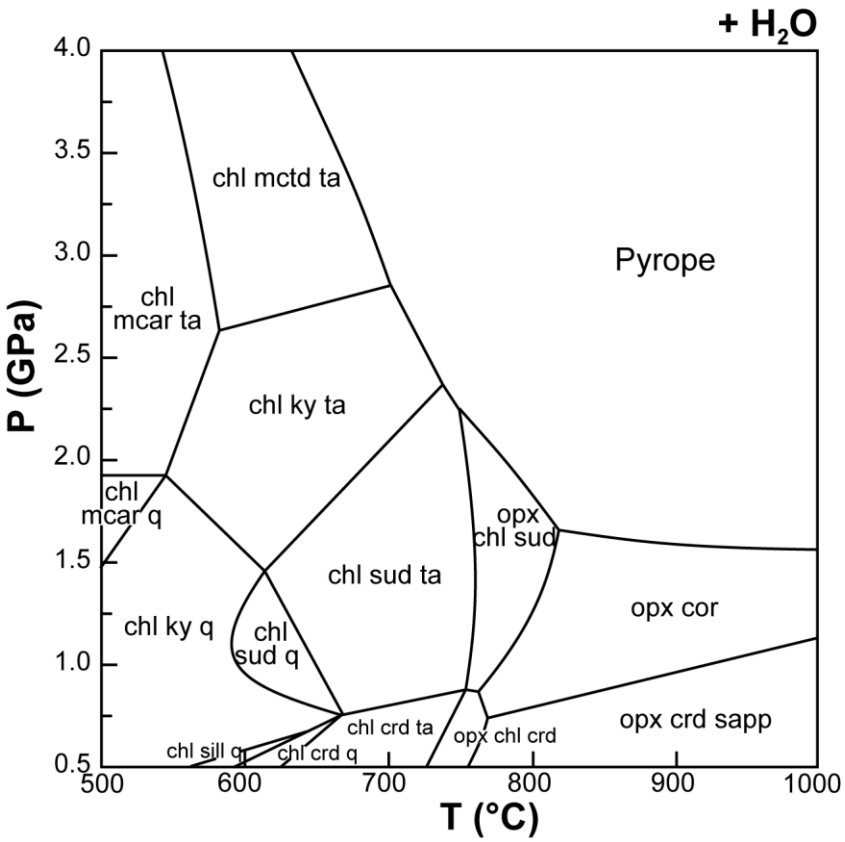

Figure 2 Predicted P-T stability fields for mineral assemblages in the simplified system MgO (3 mol) - SiO_2 (3 mol) - Al_2O_3 (1 mol) + H_2O calculated with Perple_X software package (Connolly, 1990). Mineral abbreviations: chl=chlorite, mctd=Mg-clorithoid, ta=talc, mcar=Mg-carpholite, ky=kyanite, q=quartz, opx=orthopyroxene, sud=sudoite, cor=corundum, sill=sillimanite, crd=cordierite, sapp=sapphirine.

Figure 3

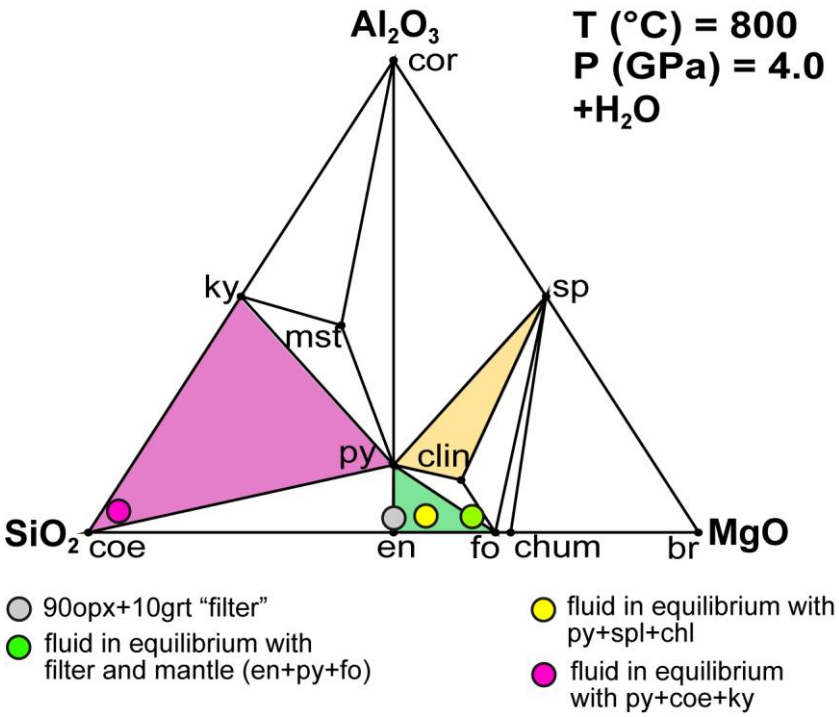

Figure 3 Chemographic projection of a water-saturated MgO-Al_2O_3-SiO_2 system at 4 GPa and 800 °C, showing stable assemblages of coe-ky-py, py-en-fo, and py-sp-clin. Experimental equilibrium slab fluid compositions and mantle fluid compositions are indicated by purple and green dots, respectively. Calculated compositions of a fluid in equilibrium with py-sp-chl assemblage is indicated by yellow dot. The composition of the orthopyrexenite containing multiphase inclusions in garnet is indicated by a grey dot. Mineral abbreviations same as in Figure 2 and coe=coesite, mst=Mg-staurolite, py=pyrope, en=enstatite, clin=clinochlore, sp=spinel, fo=forsterite, chum=clinohumite, br=brucite.

Figure 4

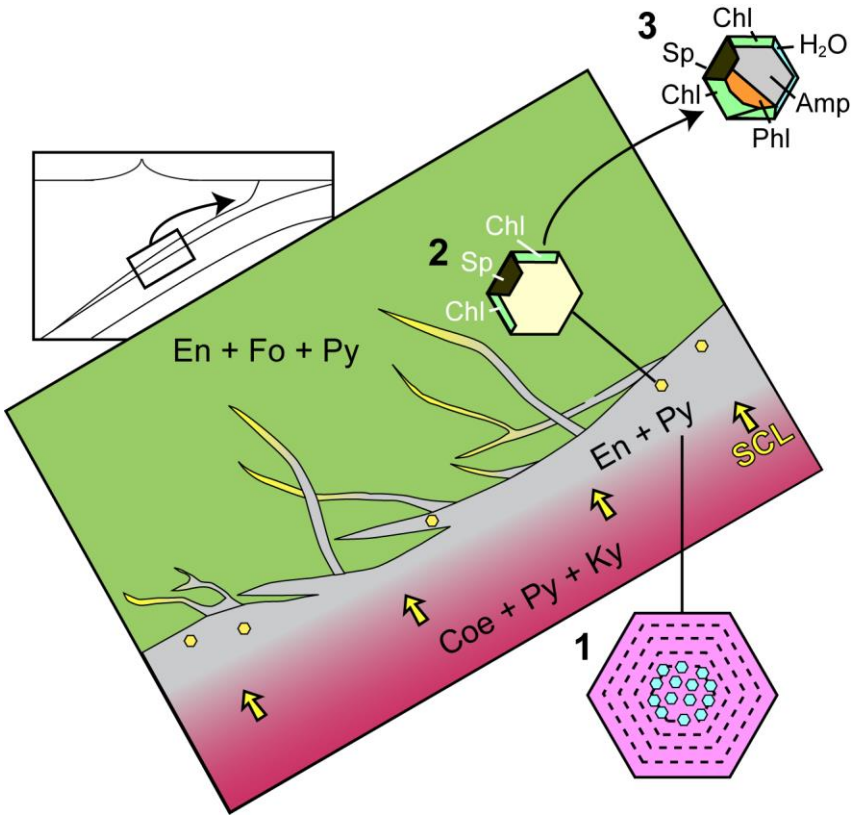

Figure 4 Schematic cartoon showing aqueous fluid entrapped by growing metasomatic garnet (1) after the interaction of slab-derived supercritical liquid (SCL) and the supra-subduction mantle peridotite forming garnet orthopyroxenite (grey layer and veins). Light blue hexagons represent primary aqueous inclusions in pyrope. Garnet/fluid interaction yields to a dissolution and precipitation process that triggers epitaxial nucleation of spinel and chlorite during garnet growing at UHP (2). Subsequent post-entrapment crystallisation of the other hydrous phases such as gedrite, phlogopite, pargasite and talc during retrograde P-T path (3) leaves an eventual residue of water solution (light blue rim). Modified after Malaspina *et al*. (2017).

Primary spinel+chlorite inclusions in mantle garnet formed at ultrahigh-pressure

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Supplementary Information

Thermodynamic modelling. The P–T isochemical section of Figure 2 was calculated by Gibbs free energy gridded minimisation with the software Perple_X (Connolly, 2005), considering a fixed bulk composition corresponding to pure pyrope ($Mg_3Al_2Si_3O_{12}$) at H_2O-saturated conditions. We used the thermodynamic database and equation of state for H_2O of Holland and Powell (1998).

The compatibility diagrams of Figure 3 and Figure S1 were calculated with the software Perple_X in the MASH system (MgO-Al_2O_3-SiO_2-H_2O), projected from H_2O.

MgO, Al_2O_3 and SiO_2 dissolved in water in equilibrium with py+coe+ky (pink in Figure 3), en+fo+py (green in Figure 3), and py+cl+sp (yellow in Figure 3) were calculated using the aqueous speciation-solubility code EQ3 (Wolery, 1992) adapted to include equilibrium constants calculated with the Deep Earth Water (DEW) model (Facq *et al.*, 2014; Sverjensky *et al.*, 2014). The results

of such calculations are reported in the following tables for comparison with experimental solubilities found in literature:

Equilibrium slab-fluid	
DEW-EQ3 (py-coe-ky assemblage)	EXP (Kessel et al. 2005) pink dot in Fig. 3
0.017	0.11
0.0037	0.18
1.77	3.7

Equilibrium mantle-fluid	
DEW-EQ3 (en-fo-py assemblage)	EXP (Dvir et al. 2011) green dot in Fig. 3
0.25	5.29
0.0026	0.31
0.20	3.0

Fluid in equilibrium with py-sp-cl assemblage	
DEW-EQ3	EXP (Fockenberg et al. 2008) yellow dot in Fig. 3
0.15	0.39
0.0096	0.13
0.12	0.39

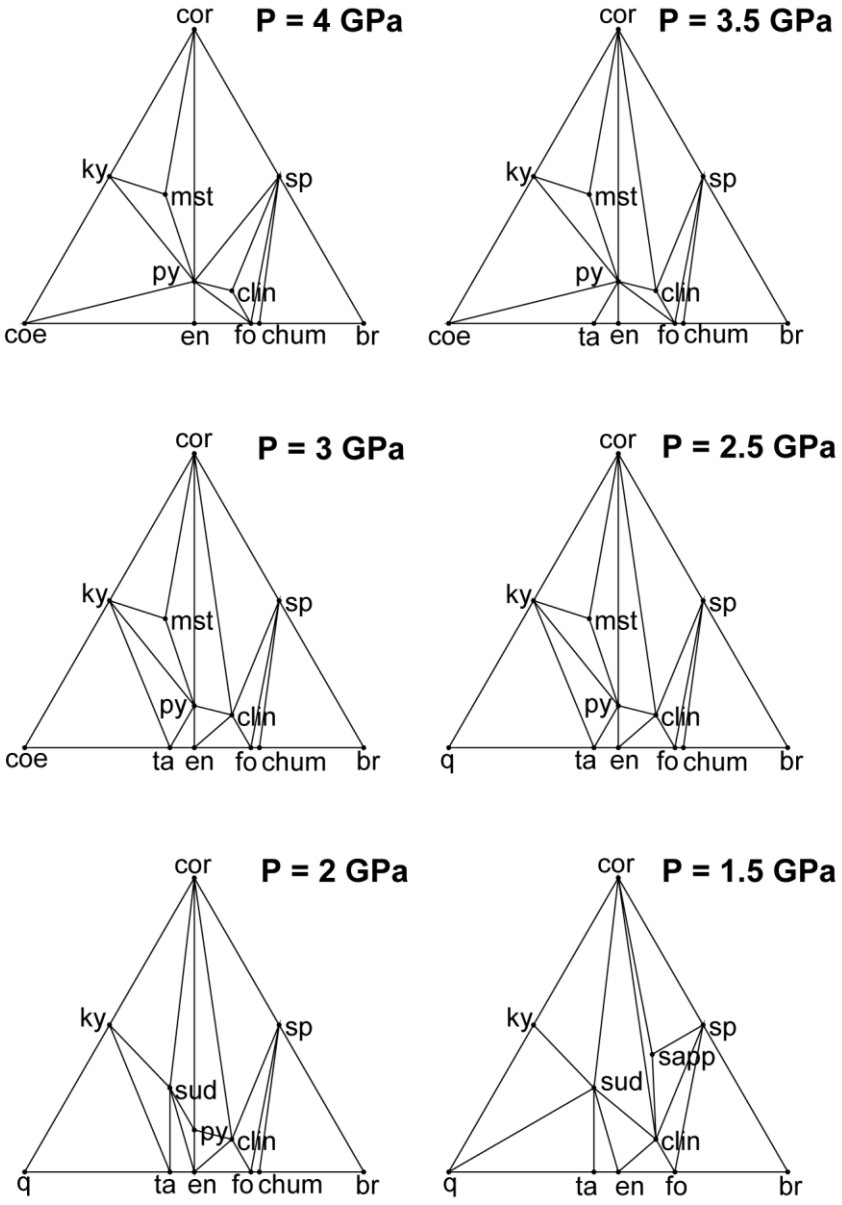

Figure S1 Compatibility diagrams of water-saturated MgO-Al_2O_3-SiO_2-H_2O system at 800 °C and 1.5–4 GPa, projected from H_2O, showing that the stable assemblage pyrope-spinel-clinochlore occurs only at UHP conditions. Mineral abbreviations same as Figures 2 and 3 of the manuscript.

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