

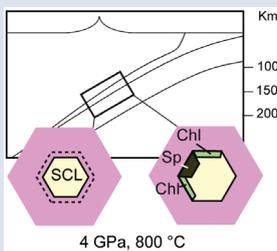
## Primary spinel + chlorite inclusions in mantle garnet formed at ultrahigh-pressure

M. Campione<sup>1\*</sup>, S. Tumiatì<sup>2</sup>, N. Malaspina<sup>1</sup>



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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 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-precipitation mechanism, triggered by a dilute, non-equilibrated slab fluid.

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### 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; Stöckhert *et al.*, 2001; Carswell and van Roermund, 2005; Ferrando *et al.*, 2005; Korsakov and Hermann, 2006; Malaspina *et al.*, 2006). 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 pressures above 3 GPa. Here, we demonstrate that even a mineral association characterised by phases usually considered stable at relatively low pressure in mantle systems (*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 from the

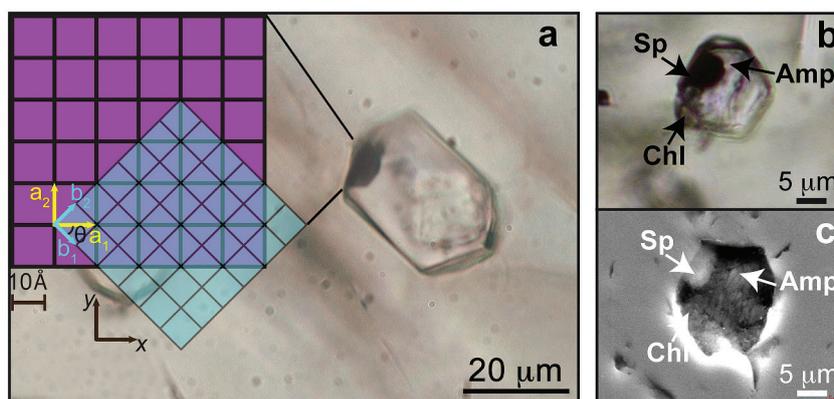
interaction of previous harzburgites and slab-derived silica-rich liquids ( $P = 4 \text{ GPa}$ ,  $T = 800 \text{ °C}$ ) at the slab-mantle interface (Malaspina *et al.*, 2006; Chen *et al.*, 2017). These multiphase inclusions have negative crystal shapes and constant volume proportions of the mineral infillings consisting of spinel  $\pm$  orthopyroxene, and hydrous phases gedrite/pargasite, chlorite, phlogopite,  $\pm$  talc,  $\pm$  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  $\pm$  talc  $\pm$  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 chlorite rim + 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, spinel should be stable at UHP conditions neither in hydrous peridotites (Niida and Green, 1999), nor in a chemical system characterised by pyrope +  $\text{H}_2\text{O}$ , at any P-T range (Fig. 2). Surprisingly, in nature we can count a number of examples where spinel occurs in peridotites in garnet-hosted primary diamond-bearing (hence UHP) multiphase inclusions from Bardane, Ugelvik and Svartberget in the Western Gneiss Region (van Roermund and Drury, 1998; Van Roermund *et al.*, 2002; Carswell and van Roermund, 2005; Vrijmoed *et al.*, 2006, 2008; van Roermund, 2009; Malaspina *et al.*, 2010; Scambelluri *et al.*, 2010). We will show that the growth of spinel, driven by a garnet dissolution-precipitation mechanism triggered by precise constraints on the composition of the supercritical liquid phase released by the slab, is possible also at UHP conditions.

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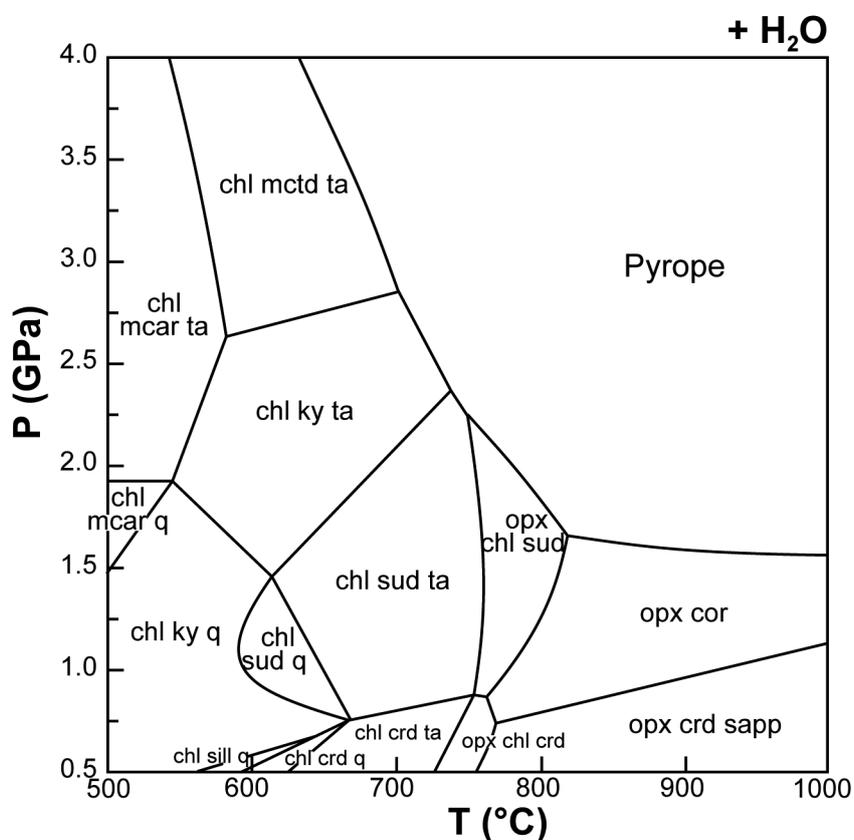
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**Figure 1** (a) Photomicrograph of a multiphase solid inclusion in metasomatic garnet from Maowu Ultramafic Complex (Dabie Shan, China). Inset represents the relative orientation of the spinel {100} surface lattice (light blue) with respect to the garnet {100} surface lattice (violet) for the coincidence at  $\theta = -45^\circ$  (from Malaspina *et al.*, 2015). (b) and (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).

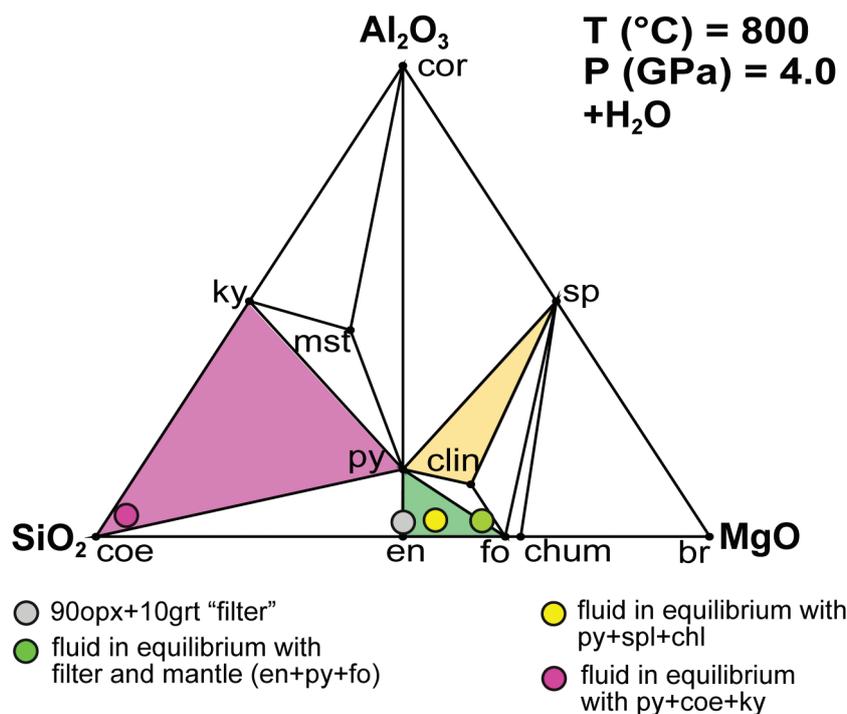


**Figure 2** Isochemical P-T section in the MASH system showing the predicted mineral assemblages calculated with Perple\_X software package (Connolly, 1990), for a bulk composition corresponding to pyrope [MgO (3 mol) – SiO<sub>2</sub> (3 mol) – Al<sub>2</sub>O<sub>3</sub> (1 mol)] + excess H<sub>2</sub>O. 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.

## 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 derive 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 as nucleation initiator for the solid phases occupying the cavity. Here, we obtain deeper insights into the crystallisation mechanism by the analysis of solution-solid equilibrium in a model MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (MASH) system and the application of principles of mass conservation.



**Figure 3** Chemography of the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system at 4 GPa and 800 °C, projected from water, showing the stable assemblages coe-ky-py (purple field), py-en-fo (green), and py-sp-clin (yellow). 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-clin assemblage is indicated by a yellow dot. The bulk composition of the orthopyroxene containing multiphase inclusions in garnet is indicated by a grey dot. Mineral abbreviations same as in Figure 2 and coe = coesite, clin = clinocllore, sp = spinel, fo = forsterite, chum = clinohumite, br = brucite.

If aqueous fluids released by the slab equilibrate with solid phases, their molal composition would be close to 0.11, 0.18, and 3.7, in terms of dissolved MgO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> 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 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 slab-derived fluids are undersaturated with respect to peridotite minerals, the latter might undergo dissolution. Dissolution might be negligible if the fluid flow 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 an orthopyroxene-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 orthopyroxene-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<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> molalities (Dvir *et al.*, 2011, Fig. 3).

As far as process i) is concerned, one should evaluate whether a subsequent event of dissolution-precipitation 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 examine a hypothesis for 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 clinocllore can be reasonably considered the products of this precipitation, since the stable assemblage

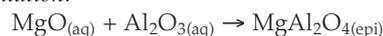
pyrope-spinel-clinocllore occurs only at P ≥ 4 GPa, and forsterite, corundum, Mg-stauroilite, and coesite are never present within the cavity (Fig. S-1). Hence, the cavity should contain, at equilibrium, spinel and clinocllore as phases nucleated on pyrope after its dissolution, leaving a fluid with a composition in equilibrium with the pyrope-spinel-clinocllore assemblage.

Pertinent chemical equations read:

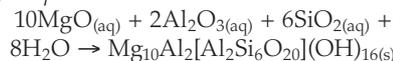
*Pyrope congruent dissolution:*



*Spinel precipitation:*



*Clinocllore precipitation:*



If one refers to 1 kg H<sub>2</sub>O, 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<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> of the fluid entrapped in the cavity, H are the moles of free water, p<sub>y</sub>, s<sub>p</sub>, and c<sub>l</sub> are the moles of congruently dissolved pyrope, precipitated spinel, and precipitated clinocllore, 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 constraint 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-clinoclchlore assemblage is known. Such a fluid was calculated to have a composition of  $M = 0.15$ ,  $A = 0.0096$ , and  $S = 0.12$  (Supplementary Information, Fig. 3). 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-clinoclchlore assemblage to have concentrations within the intervals  $M = 0.15 \div 0.39$ ,  $A = 0.0096 \div 0.13$ , and

$$S = 0.12 \div 0.39, \text{ which give } p_y = (0.01 \div 0.13) - \frac{a}{2} - \frac{2s}{3} + \frac{m}{2},$$

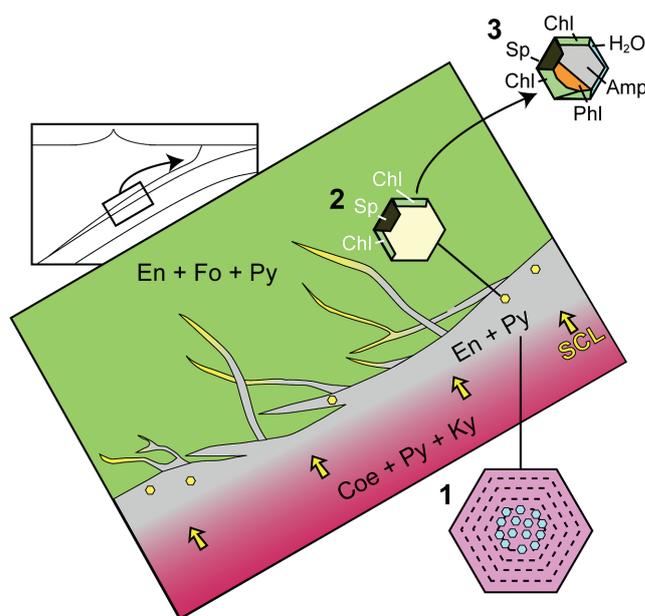
$$s_p = (0.0 \div 0.030) + a - \frac{s}{3}, \quad c_l = (-0.015 \div 0) - \frac{a}{4} - \frac{s}{6} + \frac{m}{4}.$$

A trivial upper limit of initial molalities is  $m = M$ ,  $a = A$ , and  $s = S$ , which set to 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 constraint 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 an example, consider a fluid with composition  $m = 0.20$ ,  $a = 0$ , and  $s = 0$ . Under this hypothesis the roots are  $p_y = 0.11 \div 0.23$ ,  $s_p = 0 \div 0.030$ , and  $c_l = 0.035 \div 0.050$  ( $H$  undergoes a decrement of  $0.5 \div 0.7$  %, which gives rise to a negligible correction of the previous molalities). By scaling these results on the volume of a typical cavity ( $10^4 \mu\text{m}^3$ ), considering that the molar volume of water is  $14 \text{ cm}^3 \text{ mol}^{-1}$  at 4 GPa and  $800 \text{ }^\circ\text{C}$  (Zhang and Duan, 2005), the moles of pyrope dissolved in the cavity and the moles of precipitated spinel and clinoclchlore are  $(1.4 \div 2.9) \times 10^{-12}$ ,  $(0 \div 3.8) \times 10^{-13}$ , and  $(4.5 \div 6.4) \times 10^{-13}$ , respectively. Assuming a molar volume of 110, 40 and  $1100 \text{ cm}^3 \text{ mol}^{-1}$  for pyrope, spinel, and clinoclchlore, respectively, the dissolved volume of pyrope is  $150 \div 300 \mu\text{m}^3$ , whereas the volume of precipitated spinel is  $0 \div 15 \mu\text{m}^3$  and that of clinoclchlore is  $500 \div 700 \mu\text{m}^3$ . All these volume predictions are consistent with what is 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. These fluids are non-equilibrated fluids released by the slab minerals having the ability to dissolve garnet (Fig. 4). If slab-derived fluids are  $\text{SiO}_2$ -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-clin assemblage (Fig. S-1) 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). In light of the drawn conclusions, spinel-chlorite bearing multiphase inclusions can be considered as witnesses of crystallisation processes at UHP. The fingerprint of such processes is sometimes revealed by a "surprising" composition which, if analysed solely by equilibrium arguments, would lead to incorrect inferences about their formation history.



**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 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 the retrograde P-T path (3) leaves an eventual residue of water solution (light blue rim). Modified after Malaspina *et al.* (2017).

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## Additional Information

Supplementary Information accompanies this letter at [www.geochemicalperspectivesletters.org/article1730](http://www.geochemicalperspectivesletters.org/article1730)



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

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### Supplementary Information

The Supplementary Information includes:

- Thermodynamic Modelling
- Table S-1
- Figure S-1
- Supplementary Information References

### 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 ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ) at  $\text{H}_2\text{O}$ -saturated conditions. We used the thermodynamic database and equation of state for  $\text{H}_2\text{O}$  of Holland and Powell (1998).

The compatibility diagrams of Figure 3 and Figure S-1 were calculated with the software Perple\_X in the MASH system ( $\text{MgO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$ ), projected from water.

$\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  dissolved in water in equilibrium with py + coe + ky (purple in Fig. 3), en + fo + py (green in Fig. 3), and py + cl + sp (yellow in Fig. 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 Table S-1 for comparison with experimental (EXP) solubilities (molalities) found in literature.

**Table S-1**  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  molalities of aqueous solutions in equilibrium with different assemblages, calculated using the aqueous speciation-solubility code EQ3 adapted to include equilibrium constants calculated with the Deep Earth Water (DEW) model.

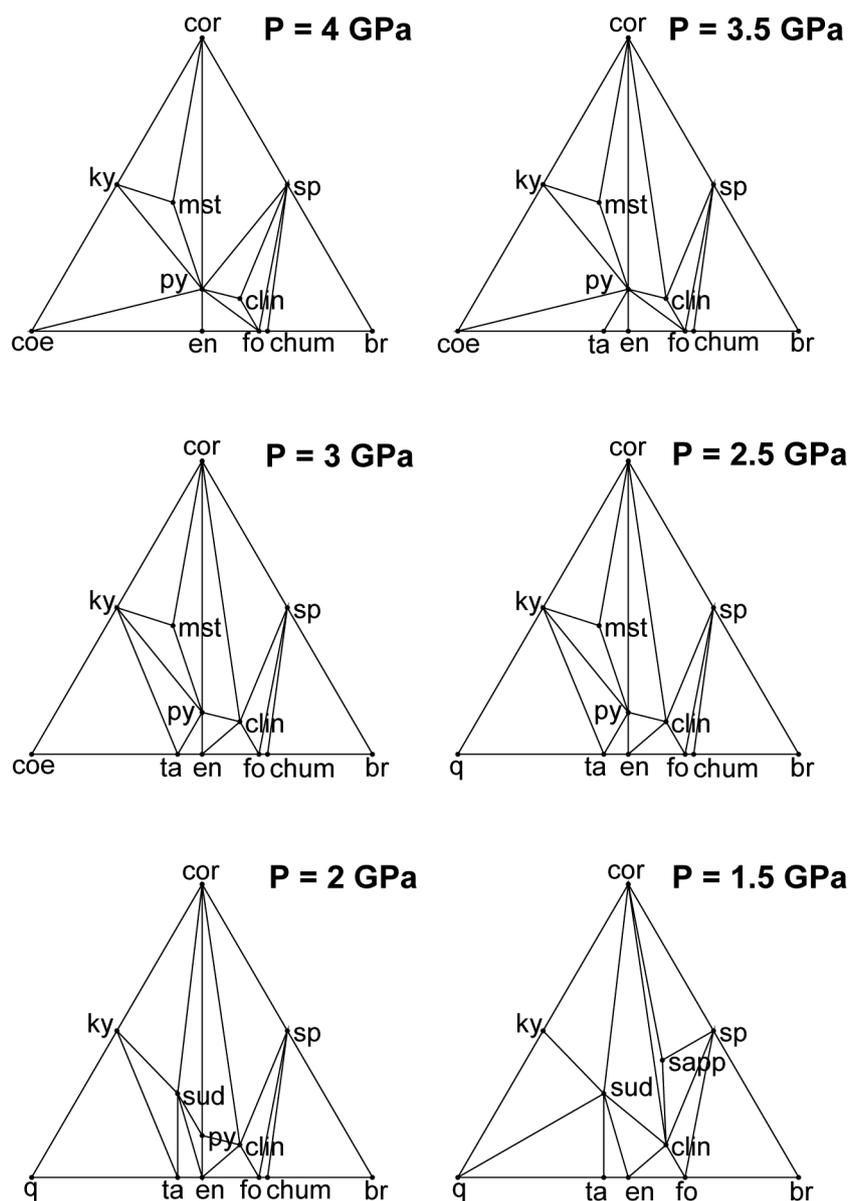
Equilibrium slab-fluid	
DEW-EQ3 (py-coe-ky assemblage) $m = 0.017$ $a = 0.0037$ $s = 1.77$	EXP (Kessel <i>et al.</i> , 2005) purple dot in Figure 3 $m = 0.11$ $a = 0.18$ $s = 3.7$
Equilibrium mantle-fluid	
DEW-EQ3 (en-fo-py assemblage) $m = 0.25$ $a = 0.0026$ $s = 0.20$	EXP (Dvir <i>et al.</i> , 2011) green dot in Figure 3 $m = 5.29$ $a = 0.31$ $s = 3.0$
Fluid in equilibrium with py-sp-clin assemblage	
DEW-EQ3 $m = 0.15$ $a = 0.0096$ $s = 0.12$	EXP (Fockenberg <i>et al.</i> , 2008) yellow dot in Figure 3 $m = 0.39$ $a = 0.13$ $s = 0.39$

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**Figure S-1** Compatibility diagrams of the water-saturated MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system at 800 °C and 1.5–4 GPa, projected from water, showing that the stable assemblage pyrope-spinel-clinoclone occurs only at UHP conditions. Mineral abbreviations same as Figures 2 and 3 of the manuscript.

### Supplementary Information References

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