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Supporting Information for

**Preferential Formation of Chlorite over Talc during Si-metasomatism of Ultramafic Rocks in Subduction Zones**

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**Methods**

Thermodynamic reaction path models were set up to assess changes in mineralogy and fluid composition during Si-metasomatism of distinct ultramafic rocks at subduction zone conditions.

First, to simulate Si-enrichment of aqueous fluids, the fluids were equilibrated with metamorphosed mid-ocean ridge basalt (MORB, metabasalt) or a metapelite. The choice of starting mineral assemblages was guided by the predicted closed–system phase equilibria of precursor metabasalt and metapelite compositions at water-saturation constrained by pseudosection models (Hacker et al., 2003; Wei and Powell, 2004). The assumption of water-saturation is substantiated by geologic evidence for the former presence of free aqueous fluid within exhumed subduction interface rocks (Bebout and Penniston-Dorland, 2016; Condit and French, 2022). The composition of the metapelite is characterized by having excess molar Al2O3 relative to the sum of alkalis (molar Na2O + K2O + CaO). In contrast, the metabasalt has higher CaO content than metapelite and displays a metaluminous composition, i.e. having a deficit in its molar Al2O3 relative to the sum of alkalis.

In the second modeling step, we evaluate the effects of ultramafic protolith compositions on talc formation during Si-metasomatism at subduction zone conditions using monomineralic antigorite [Mg48Si34O85(OH)62], lherzolite (depleted MORB mantle, DMM), harzburgite (HR1), and a more refractory harzburgite (HR2). The range in peridotite compositions reflects various extents of melt depletion expected for subduction zone environments and is presented in the Supplementary Table (Le Roux et al., 2007; Workman and Hart, 2005). Models were calculated using the EQ3/6 software package version 6 (Wolery, 1992) with the DEW database containing equilibrium constants of reactions involving minerals and aqueous species (Huang and Sverjensky, 2019; Sverjensky et al., 2014). We used the equation of state for water of Zhang and Duan (2005), and the dielectric constants from Sverjensky et al. (2014). Thermodynamic calculations were performed over a range of *P-T* conditions relevant to the global range of slab-top geotherms (1–2.5 GPa, 300–600 °C), and a range of fluid-to-rock (f/r) mass ratios, defined as the mass of fluid present divided by the mass of rock reacted. Activity coefficients for aqueous species were calculated using the B-dot equation (Helgeson, 1969).

The oxygen fugacity of the fluid (*f*O2) was set to values close to the quartz-fayalite-magnetite buffer (QFM, within the redox stability of magnetite). This assumption is supported by the common occurrence of magnetite in high-pressure serpentinite (Deschamps et al., 2013). However, the lack of solid solutions of key Mg-Fe minerals in the current thermodynamic database including serpentine, brucite, and talc, prevents us from capturing the complexity of Fe-distribution and H2 formation in natural serpentinization systems.

We modeled the isobaric and isothermal metasomatism of ultramafic rocks by allowing them to react with a fluid that was previously in equilibrium with metabasalt or metapelite over a range of fluid-to-rock ratios. The concentrations of dissolved Ca and Fe in equilibrium with metapelite are initially set to 10 mmol/kg to prevent the saturation of Ca-rich (e.g., Cpx, lawsonite) and Fe-rich oxide phases before reacting with ultramafic rock. We found that 10 mmol/kg of dissolved Ca or Fe (in the absence of buffering Ca or Fe-rich phase) can closely reproduce the reported equilibrium mineral assemblage of a metapelite or a metabasalt (Hacker et al., 2003; Wei and Powell, 2004). This assumption is also supported by experimental data on fluid/rock partitioning conducted at temperatures higher than our modeled conditions. For instance, an aqueous fluid in equilibrium with Cpx and garnet (Ca and Fe-rich eclogitic assemblage) contains approximately 10-1 molal Ca and 10-1.5 molal Fe (Kessel et al., 2005). This implies that the dissolved Ca and Fe concentrations in equilibrium with metapelite at lower temperatures (300–600 °C) modeled in this study are expected to be lower than those reported for an aqueous fluid in equilibrium with an eclogitic assemblage at 700 °C. To simulate Si-metasomatism, the ultramafic rock was titrated in small mass increments into the fluid. The reaction-path portrays a system that is initially fluid-dominated, such as in a fracture or vein, but that becomes increasingly rock-dominated as more ultramafic rock is added, such as in the rock matrix adjacent to a fracture or vein. We explored a range of f/r ratios (i.e. f/r >> 1) to simulate conditions likely relevant to high permeability zones, such as along lithologic contacts and shear zones. We limit our model predictions to f/r >> 1 as key minerals (e.g., serpentine, brucite, clinopyroxene, amphibole, garnet, spinel) and their solid solutions anticipated to form at lower f/r (< 1) are presently not included in the DEW database.

To provide a frame of reference, we also calculated a series of reaction-path models for the same *P-T* conditions to investigate the fluid-mediated metasomatism of ultramafic rocks by fluids buffered by quartz only (i.e. the compositions of other dissolved elements are set to trace concentrations). This highlights the importance of the concentrations of other dissolved elements in the reactant fluid in determining the alteration mineralogy during the metasomatism of ultramafic rocks by slab-derived fluids. All the model results that support the findings of this study are freely available at <https://doi.org/10.5281/zenodo.6760195>. Companion spreadsheets (see Supplementary Tables S4–S15) that were used to tabulate and plot the model results are also included in the Supplementary Information.

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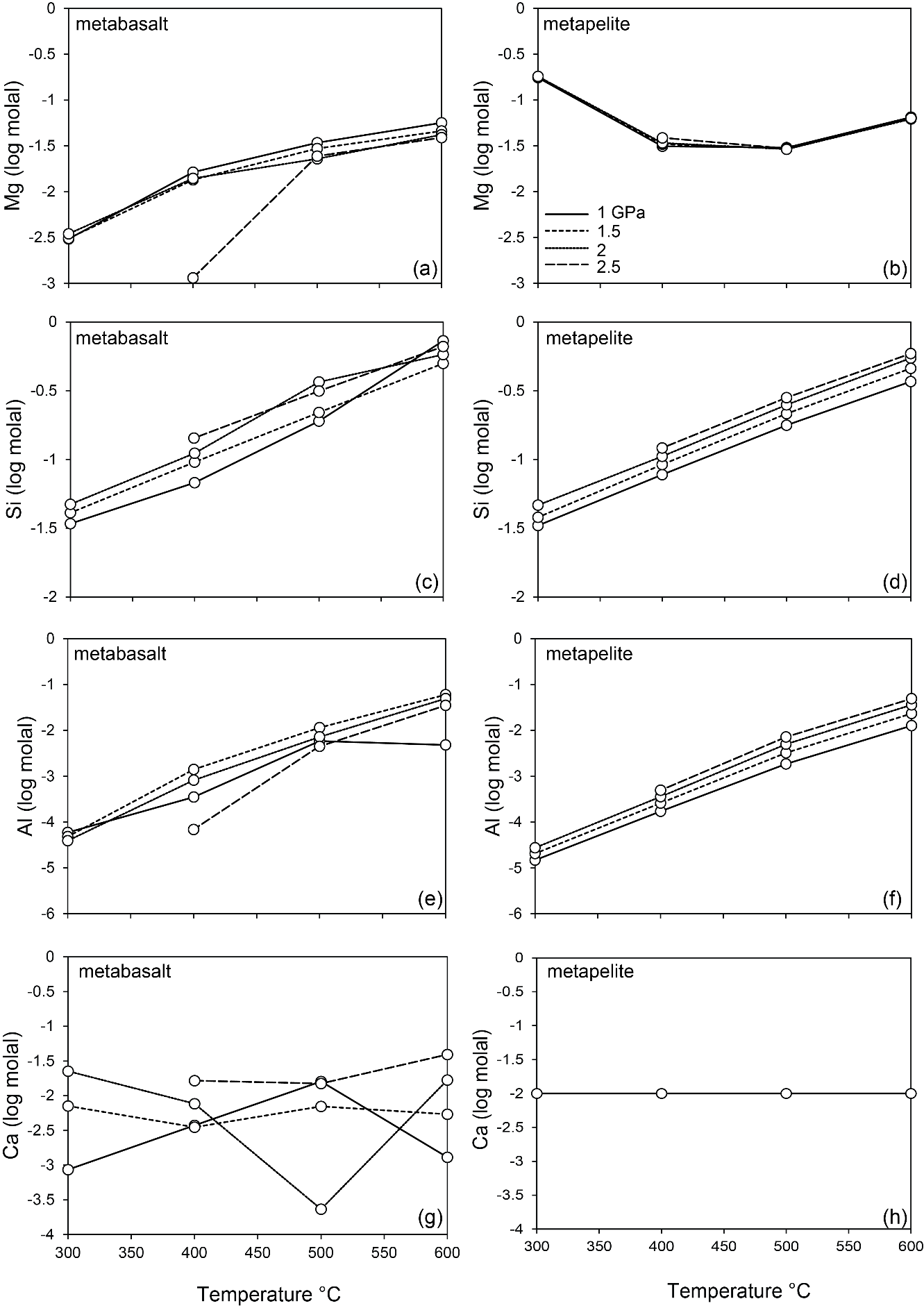
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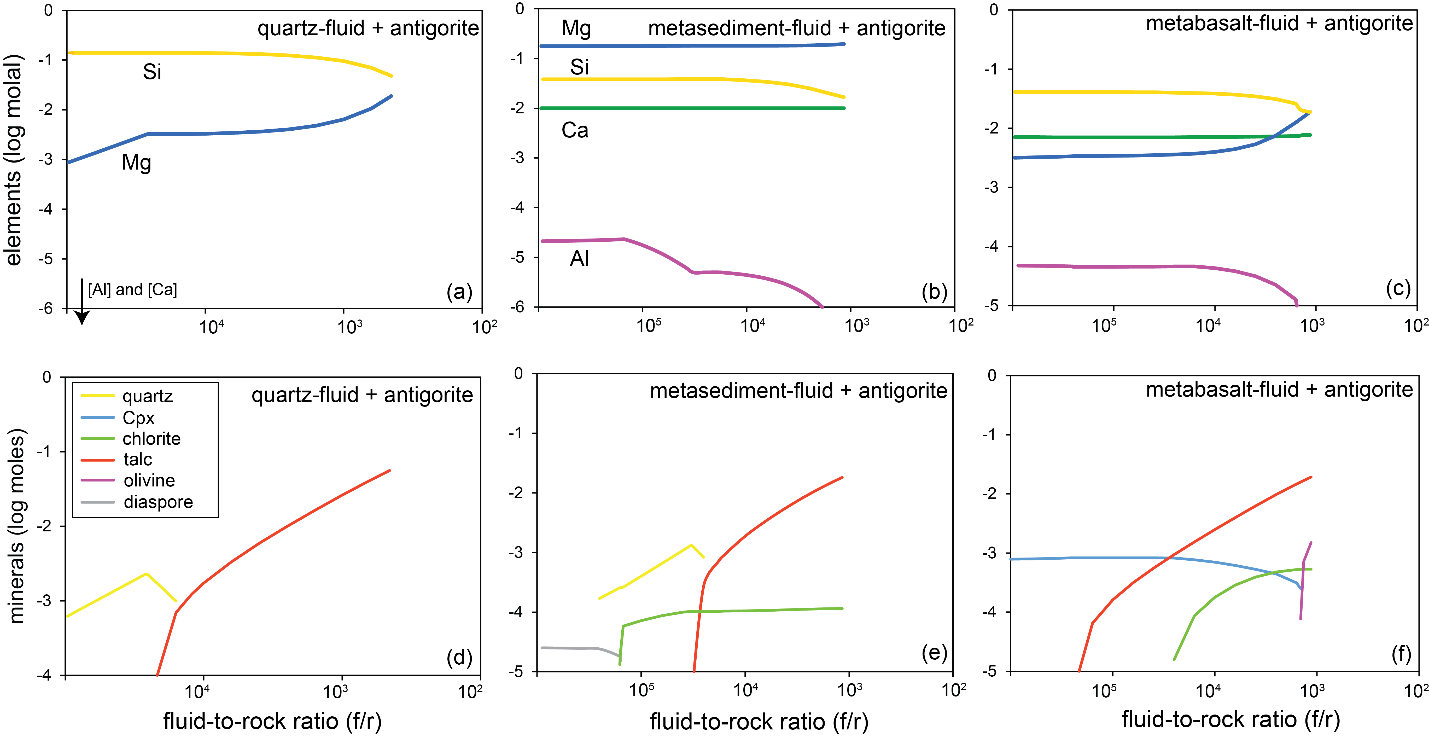
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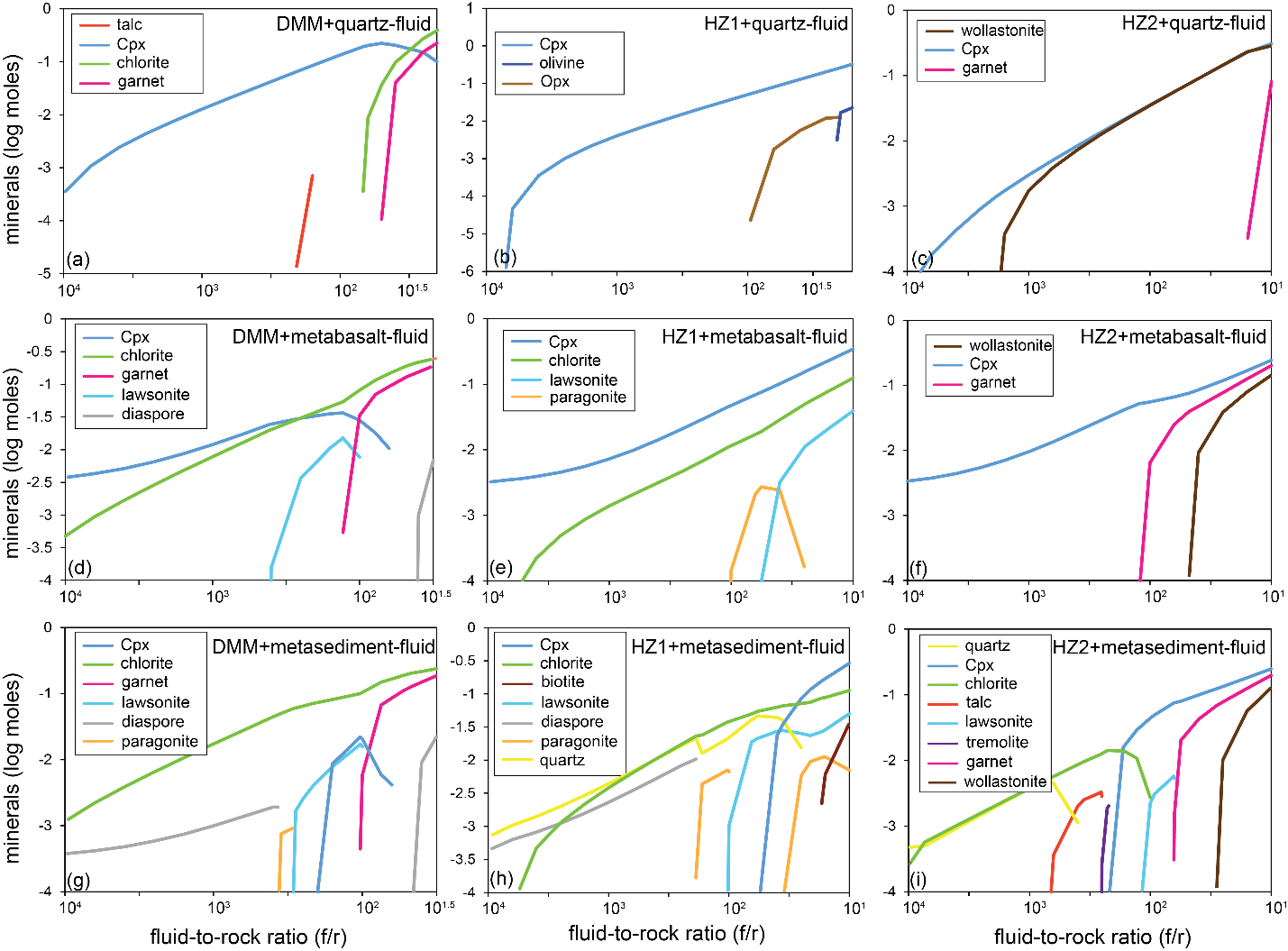
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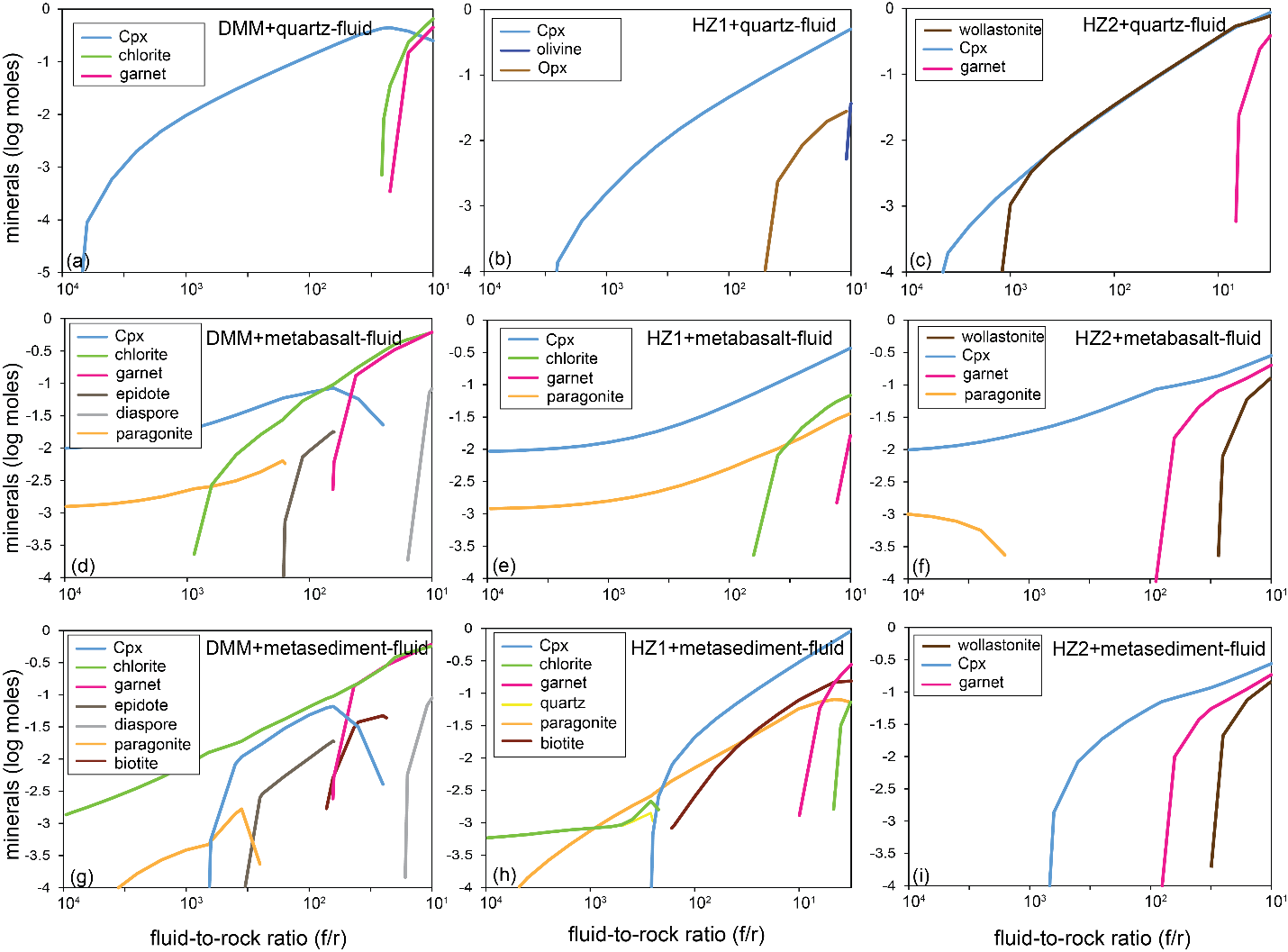
**Fig. S1.** The predicted composition of fluids in equilibrium with a metabasalt (a,c,e) and a metapelite (b,d,f) from 300–600 °C, 1–2.5 GPa.



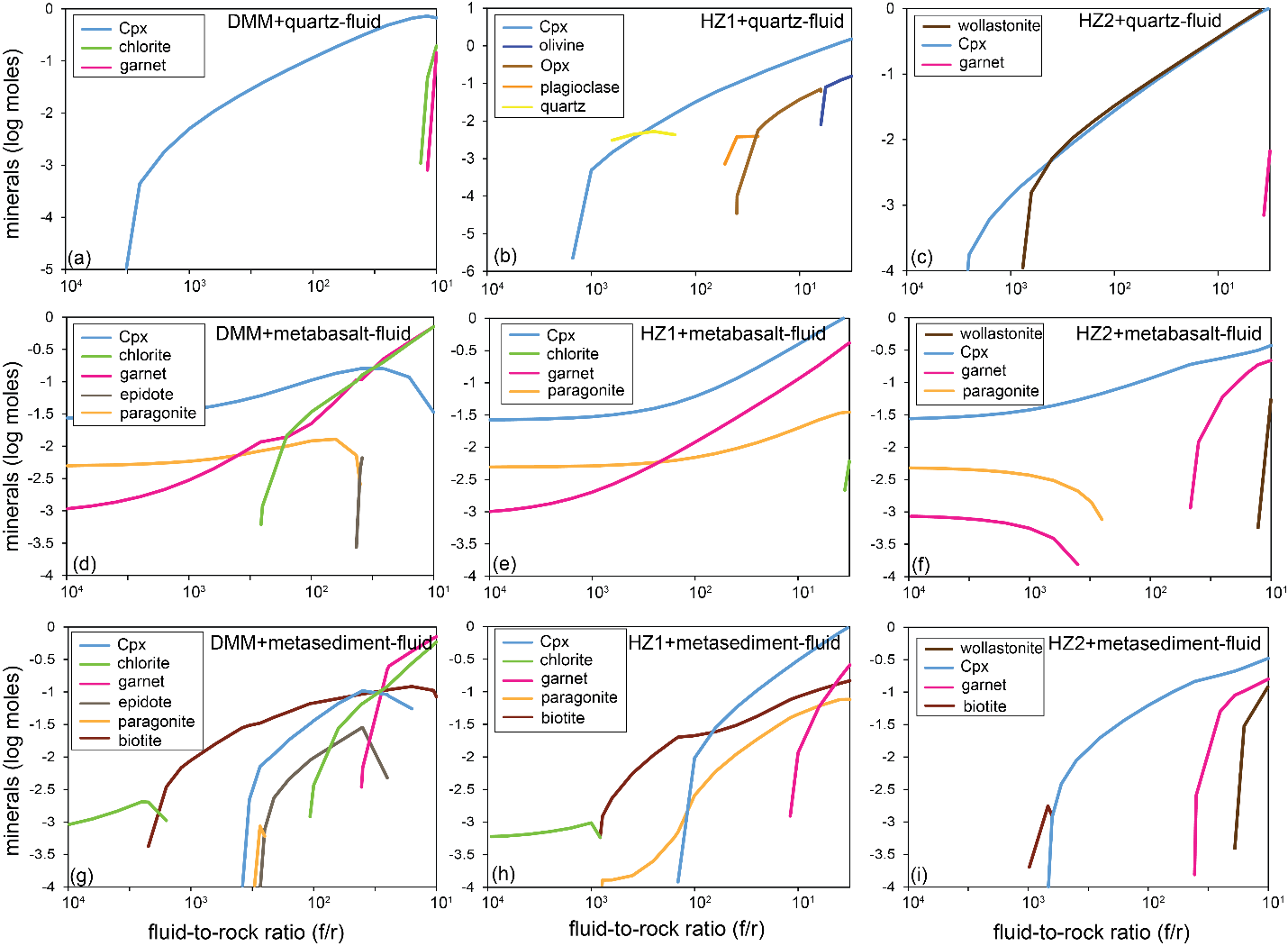
**Fig. S2.** Predicted mineral assemblages and pore fluid compositions of reaction-path models that simulated metasomatism of antigorite at 300°C and 1.5 GPa as a function of fluid-to-rock ratio. A fluid equilibrated with quartz (a,d), metasediment (b,e), or metabasalt (c,f) is subsequently allowed to react with ultramafic compositions (DMM, HZ1, and HZ2). The f/r decreases as ultramafic rock is titrated into the fluid. Mineral abbreviations are from Whitney and Evans (2010).

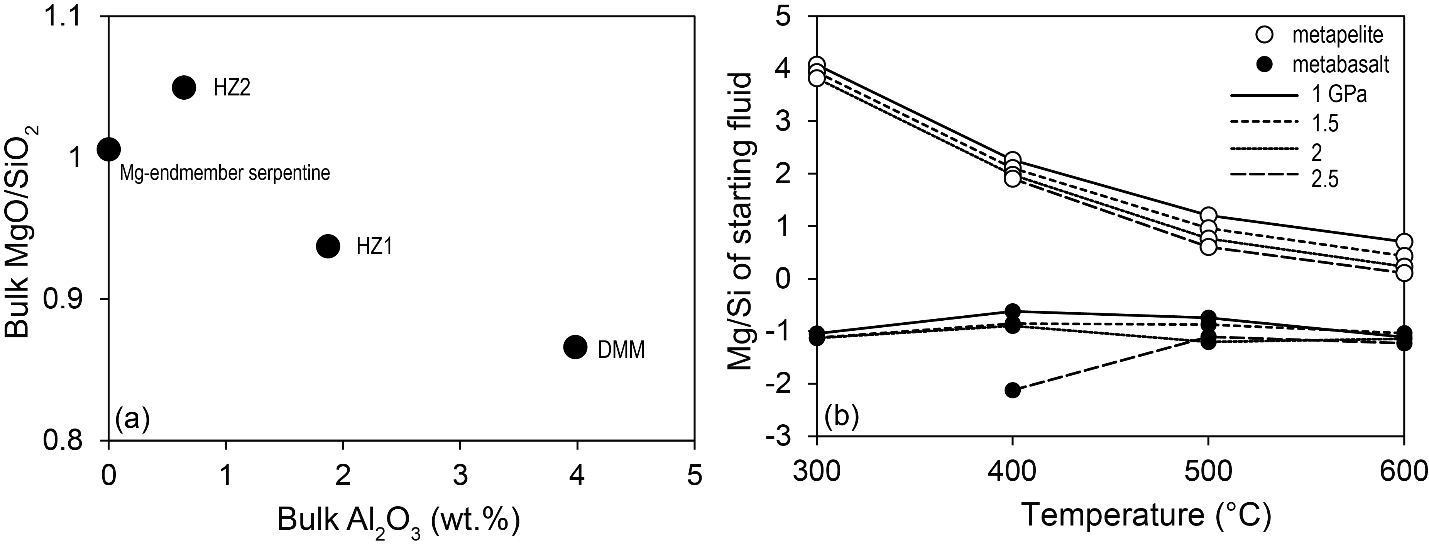


**Fig. S3.** Predicted mineral assemblages of reaction-path models that simulated metasomatism at 400°C and 1.5 GPa as a function of fluid-to-rock ratio. A fluid equilibrated with quartz (a-c), metabasalt (d-f), or metasediments (g-i) is subsequently allowed to react with ultramafic compositions (DMM, HZ1, and HZ2). The f/r decreases as ultramafic rock is titrated into the fluid. Please see the Supporting Information for additional model predictions including fluid compositions over a wider range of pressures and temperatures. Mineral abbreviations are from Whitney and Evans (2010).

**Fig. S4.** Predicted mineral assemblages of reaction-path models that simulated metasomatism at 500°C and 1.5 GPa) as a function of fluid-to-rock ratio. A fluid equilibrated with quartz (a-c), metabasalt (d-f), or metasediments (g-i) is subsequently allowed to react with ultramafic compositions (DMM, HZ1, and HZ2). The f/r decreases as ultramafic rock is titrated into the fluid. Please see the Supporting Information for additional model predictions including fluid compositions over a wider range of pressures and temperatures. Mineral abbreviations are from Whitney and Evans (2010).

**Fig. S5.** Predicted mineral assemblages of reaction-path models that simulated metasomatism at 600°C and 1.5 GPa as a function of fluid-to-rock ratio. A fluid equilibrated with quartz (a-c), metabasalt (d-f), or metasediments (g-i) is subsequently allowed to react with ultramafic compositions (DMM, HZ1, and HZ2). The f/r decreases as ultramafic rock is titrated into the fluid. Please see the Supporting Information for additional model predictions including fluid compositions over a wider range of pressures and temperatures. Mineral abbreviations are from Whitney and Evans (2010).



**Fig. S6.** (a) MgO/SiO2 vs. Al2O3 plot of the starting ultramafic compositions. (b) Predicted Mg/Si of fluids in equilibrium with a metabasalt and a metapelite from 300–600 °C, 1–2.5 GPa.