Diopside, enstatite and forsterite solubilities in H$_2$O and H$_2$O-NaCl solutions at lower crustal and upper mantle conditions

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ABSTRACT

The interaction of fluids with rock-forming minerals plays an important role in the chemical evolution of mafic and ultramafic rocks in the lower crust and upper mantle. Recent work highlights the importance of salt-rich fluids in element transport in settings such as the mantle wedge above subduction zones and high-grade granulite facies metamorphism. Forsterite (Mg$_2$SiO$_4$), enstatite (MgSiO$_3$) and diopside (CaMgSi$_2$O$_6$) are key rock-forming minerals in these settings in the system CaO-MgO-SiO$_2$. We determined experimentally the solubilities of diopside, enstatite and forsterite in H$_2$O-NaCl fluids at a range of pressures and temperatures. Forsterite solubility was determined at 1 GPa, 800 and 900 °C, in pure H$_2$O and in H$_2$O-NaCl solutions. Forsterite dissolved congruently at nearly all conditions. Its solubility in pure H$_2$O is low, but increases greatly with rising NaCl concentration in the fluid. Enstatite solubility was investigated in H$_2$O-NaCl solutions at 1 GPa, 800 and 900 °C. Enstatite dissolved incongruently to yield forsterite at all conditions. Addition of excess silica led to suppression of forsterite and showed that fluids in equilibrium with enstatite with or without forsterite are strongly enriched in Si relative to Mg, though Mg solubility is significant at high salinity. Diopside solubility was determined in pure H$_2$O at 650 to 900 °C and 0.7 to 1.5 GPa, and in H$_2$O-NaCl solutions at 800 °C and 1 GPa, with NaCl concentrations approaching halite saturation. Diopside dissolves incongruently yielding residual forsterite at all conditions investigated. The solubility of diopside in pure H$_2$O increases with increasing pressure, temperature, and salinity. Diopside dissolution in H$_2$O-NaCl solutions displays a dependence on fluid salinity similar to that of forsterite and wollastonite. The results of forsterite solubility experiments in H$_2$O-NaCl solutions were used to calculate the compositions of fluid coexisting with enstatite or diopside where forsterite was present. The concentration of solutes coexisting with enstatite decreases with rising NaCl, similar to quartz. In contrast, bulk...
solute coexisting with diopside increase with NaCl, similar to wollastonite and forsterite. These patterns imply complexing among rock-forming components and fluid components, that Ca-chloride species are substantially more stable than Mg-chloride species, and that hydrous Na-silicate complexes are important components of deep H$_2$O-NaCl fluids. The results show that salt-bearing brines have substantial metasomatic power and may exert significant control on the chemical evolution of lower crustal and upper mantle mafic and ultramafic rocks.

1 INTRODUCTION

The release of aqueous fluids by devolatilization of hydrous minerals and magmas drives mass transfer in a wide range of high-pressure geologic settings. These deep fluids differ fundamentally from shallow and surficial fluids. Shallow fluids range from water rich to saline brines whose maximum salinity is limited by relatively low concentrations at salt-mineral saturation, and the total concentrations of other dissolved solutes are comparatively low (Yardley and Graham, 2002; Yardley and Bodnar, 2014). In contrast, deep fluids are chiefly comprised of H$_2$O, CO$_2$, halogen salts (mainly metal chlorides), and dissolved rock components, and may be present as a single phase or an immiscible mixture of CO$_2$-rich vapor and salt-rich brine (e.g. Manning, 2018). The presence of CO$_2$ tends to reduce silicate mineral solubility in aqueous fluids and thus lower the capacity for metasomatic mass transfer (e.g., Newton and Manning, 2000a; 2009; 2010). However, halogen salts can dramatically increase solubility and are increasingly recognized as important components of fluids in the lower crust and upper mantle (Newton et al., 1998; Newton and Manning, 2010; Manning and Aranovich, 2014).

The most abundant halogen in terrestrial fluids is chlorine. Chloride-rich solutions play an important role in metasomatic mass transfer in subduction-zones (Scambelluri and Philippot, 2001;
Keppler, 2017; Barnes et al., 2018). Evidence includes fluid inclusions in slab lithologies (e.g., Philippot and Selverstone, 1991) and in the mantle wedge (e.g., Kawamoto et al., 2013), melt inclusions in arc volcanics (e.g., Wallace, 2005), and the Cl contents of arc magmas (Métrich and Wallace, 2008). Other high-pressure processes in which mass transfer is influenced by chloride-rich fluids include mantle metasomatism, as recorded in fluid inclusions in mantle xenoliths (e.g., Anderson et al., 1984) and diamonds (e.g., Weiss et al., 2014, 2015), and granulite-facies metamorphism (e.g., Newton et al., 1998; Newton and Manning, 2010; Manning and Aranovich, 2014). Chloride-rich fluids are also associated with the formation of metasomatic features and ore deposition in mafic intrusions at a range of pressures (e.g., Clochiatti et al., 1981; Schiffries, 1982; Boudreau et al., 1986; Shmelev, 2011). Critical to assessing the extent and nature of metasomatism by chloride fluids in these high-pressure settings is knowledge of the solubility of mantle silicate minerals, including olivine, orthopyroxene and clinopyroxene, in aqueous saline solutions.

Here we report new experimental results on the solubilities of forsterite (Mg$_2$SiO$_4$), enstatite (MgSiO$_3$) and diopside (CaMgSi$_2$O$_6$) in H$_2$O-NaCl fluids. Forsterite and enstatite were studied at 1 GPa, 800 and 900 °C, to NaCl concentrations approaching halite saturation. Diopside solubility was determined in pure water at conditions ranging from 650 to 900 °C and 0.7 to 1.5 GPa, and in H$_2$O-NaCl solutions at 800 °C and 1 GPa at NaCl concentrations approaching halite saturation. The range of $P$-$T$ conditions investigated is directly relevant to the lower crust and upper parts of the mantle wedge in convergent margin settings, at depths between about 25 and 40 km (pink shaded region in Fig. 1a). Phase relations for a model KLB-1 ultramafic composition in equilibrium with H$_2$O with reduced activity of 0.67, which is relevant for saline fluids, show that assemblages involving olivine, clinopyroxene, and orthopyroxene are stable at the conditions of our experiments (Fig. 1b), consistent with thermodynamic calculations in the system CaO-MgO-
SiO$_2$-H$_2$O-NaCl (Newton and Manning, 2000b). In addition to the specific conditions investigated, the trends in solubility established by our experiments can aid in interpreting metasomatic processes at higher pressures and/or temperatures, such as the slab-mantle interface in subduction zones (Fig. 1a).

The new data fill key gaps in knowledge of mineral solubility at high pressure conditions. While there is an increasingly comprehensive data set on the solubilities in saline fluids of minerals associated with felsic or calc-silicate lithologies (Newton and Manning, 2000a, 2002b, 2006, 2007; Shmulovich et al., 2001, 2006; Wykes et al., 2008; Makhluf et al., 2016), studies of the mafic silicates are more limited (Newton and Manning, 2002a). Diopside solubility in pure H$_2$O has been investigated at relatively high $P$-$T$ of 1100 and 1200 °C at 2 GPa and 1180 °C at 3 GPa (Eggler and Rosenhauer, 1978; Schneider and Eggler, 1986), as well as in pure H$_2$O and H$_2$O-NaCl solutions at intermediate to relatively low $P$-$T$: 650 °C and 0.2 – 0.75 GPa (Budanov and Shmulovich, 2000; Shmulovich et al., 2001). The $P$-$T$ range of previous studies on diopside solubility are also shown on a cross-section of a model ‘warm’ subduction zone (Fig. 1a) for comparison. Our experimental conditions extend results in saline fluids from lower $P$ and $T$ and are over a wider $P$-$T$ range than any previous single study in pure H$_2$O (Fig. 1b). Similarly, solubilities of enstatite + forsterite at mantle $P$-$T$ have been investigated only in pure H$_2$O (Ryabchikov et al., 1982; Zhang and Frantz, 2000; Stalder et al., 2001; Mibe et al., 2002; Newton and Manning, 2002a), though mineral solubilities in the system MgO-SiO$_2$-H$_2$O-HCl have been investigated at low $P$-$T$ and low total Cl (Frantz and Popp, 1979; Luce et al., 1985). Thus, the present work, in combination with previous solubility studies of wollastonite and quartz, provides new data with which to directly compare mobilities of Mg, Ca, and Si in mafic and ultramafic systems, giving insight into the transport of these components in subduction zone/mantle wedge.
and lower crustal settings.

2 METHODS

Starting materials were single crystals of high-purity natural diopside and synthetic forsterite, enstatite and quartz, as well as reagent-grade NaCl, and ultrapure H$_2$O. The starting material used in diopside experiments were chips broken off of a single, gem-quality natural diopside crystal obtained from the mineral collection of the Department of Earth, Planetary, and Space Sciences at the University of California, Los Angeles. The diopside starting material was analyzed by electron probe microanalyzer (EPMA) and determined to be almost pure CaMgSi$_2$O$_6$, containing <1 wt% other constituents (Table S1). Pieces from a large forsterite crystal grown by H. Takei by a flux-melt method (Takei and Hosoya, 1985) were used in our experiments. The pieces were ground and polished to a roughly cylindrical shape using Al$_2$O$_3$, SiC, and diamond abrasive paper, then cleaned with distilled H$_2$O in an ultrasonic bath. Single orthoenstatite crystals grown by a flux-melt method (Ito, 1975) were used. Rare crystals with visible flux inclusions were discarded. Small broken chips of Brazilian quartz (Manning, 1994; Newton and Manning, 2000a) were used as supplementary SiO$_2$ source in enstatite solubility experiments (see below).

In all experiments, forsterite, enstatite or diopside grains (~0.2–4.5 mg) were placed in an inner Pt capsule (1.6 mm outer diameter), which was then crimped shut on both ends and punctured in two to four places to allow fluid penetration. The crimped and punctured capsules were placed in an outer capsule of 3.5 mm OD Pt tubing along with ultrapure H$_2$O ± NaCl ± quartz. The outer capsules were then sealed by carbon-arc welding. Weighing of capsules before and after welding revealed negligible (0.1 mg) average mass loss which is attributable entirely to sputtered Pt. Successful sealing of outer capsules was confirmed if no mass loss was observed after 1 hour in a...
110 °C oven. Masses of inner capsules, crystals and any added SiO$_2$ (as quartz) were determined using a Mettler UMX2 ultramicrobalance (0.2 µg reproducibility). Outer capsule, H$_2$O and NaCl and all other masses were determined using a Mettler MX3 microbalance (2 µg reproducibility).

Experiments were conducted in 19.05 mm or 25.4 mm end-loaded piston-cylinder apparatus. Capsules were loaded in a transverse (low temperature-gradient) orientation into furnace assemblies consisting of a cylindrical graphite heater, NaCl filler parts, and a concentric MgO and two-bore mullite thermocouple insulator (e.g., Manning and Boettcher, 1994). Temperature was monitored and controlled with Type-S thermocouples. Thermocouple EMF was not corrected for pressure effects. Pressure was monitored by a 12-inch Heise Bourdon-tube pressure gauge. Experiments were conducted by the piston-out method of pressing and heating, wherein assemblies were pressed cold to a pressure 0.3 GPa below the final desired pressure, then heated to the final temperature. For example, in 1.0 GPa experiments, assemblies were initially pressurized to 0.7 GPa, followed by heating to run conditions (650-900°C) at 50°C/min. Thermal expansion of the NaCl pressure medium resulted in 1.0 GPa sample pressure at ~600°C during the temperature ramp (i.e. piston-out). Oil pressure was subsequently bled to maintain pressure within 40 MPa (typically 15 MPa) of 1.0 GPa for the duration of the experiment. Calibration tests conducted in our laboratory show that this approach requires no friction correction and yield an accuracy of ±0.03 GPa.

Experiments were terminated by switching off the electrical heating power. Temperature dropped to 200 °C in <30 seconds in 25.4 mm assemblies, and about four times faster in 19.05 mm assemblies. Adhering NaCl from the furnace assembly was dissolved from the quenched capsule exterior. The capsule was then dried at 110 °C and weighed to check that no fluid was lost during the run. Capsules were punctured with a needle and dried at 115 °C for at least 1/2 hour and
reweighed as an additional check on H$_2$O content. In general, the apparent weight of H$_2$O after an
experiment was slightly greater than the weight in; this is because there was inevitable minor loss
of dissolved and finely particulate matter in the puncturing process. The starting H$_2$O weight was
used in all solubility calculations.

After drying and weighing, the outer capsule was cut open with a razor blade to retrieve
the inner capsule, which was then soaked in distilled water at 80 °C with a magnetic stirrer for
periods of 5-10 minutes, dried at 110 °C and reweighed. The process was repeated until attainment
of constant mass, indicating removal of soluble NaCl. The weight change of the cleaned and dried
inner capsule provided one measure of solubility. The contents of the inner capsule were then
removed, examined optically under a binocular microscope, and weighed, giving a second
solubility constraint. Selected run products were mounted and examined with a scanning electron
microscope for composition and textural characteristics of residual crystals and quench material.

The composition of H$_2$O-NaCl fluids is presented as NaCl mole fraction ($X_{NaCl} = \frac{n_{NaCl}}{n_{NaCl} + n_{H2O}}$, where $n$ is moles). Mineral solubility as determined from weight changes is
presented in molality ($m$, mol/kg H$_2$O). Forsterite dissolution was generally congruent, and crystals
could readily be extracted and weighed. Accordingly, $m_{Fo}$ was simply determined from the mass
loss of the crystal. In one experiment with pure H$_2$O, forsterite was found to dissolve incongruently
to brucite + fluid. In this case, a brucite-absent fluid composition was calculated using the midpoint
between crystal and inner-capsule mass loss, determining congruent solubility at a range of excess
SiO$_2$ concentrations, and projecting to zero excess silica (see below).

Determination of enstatite solubility utilized a different method because of its incongruent
dissolution producing forsterite. Forsterite generally formed a tough coating on enstatite grains,
and the resulting crystal aggregate withstood post-run manipulation. It was therefore possible to
obtain robust, separate weights of both the inner capsule and the crystal aggregate. We use the midpoint between these values for solubility calculations. We also conducted additional experiments, in which excess silica was introduced in the form of quartz. The quartz dissolved quickly and completely in the fluid to yield a starting solution closer to final equilibrium with the run products. Where sufficient SiO$_2$ was added to prevent forsterite growth, a clean, uncoated enstatite crystal resulted. Although the final crystal weights in such runs had higher accuracy, we nevertheless report solubility as the midpoint between inner capsule and crystal weights to maintain consistency with the forsterite-saturated runs. At a given $P$, $T$ and NaCl content, the fluid composition at the forsterite saturation point solubility was constrained by adding progressively greater SiO$_2$ concentrations (as quartz) and bracketing the fluid composition at which forsterite disappears from enstatite surfaces.

Diopside also dissolves incongruently at the conditions studied. As with enstatite and forsterite, the weight losses of inner capsules yield lower limits for diopside solubility, and upper limits are constrained by the weight loss of forsterite coated diopside crystals. Solubility results are reported as the midpoint between the two values, unless one of the weights was compromised. Runs with excess quartz were not conducted in the diopside solubility study.

Incongruent dissolution complicates the determination of solubility by our methods. The mass of total dissolved solutes is readily obtained from the measured weight change, $\Delta w$.

However, it is more desirable to know the absolute concentrations of the constituents derived from the dissolving solids, $w_i$, which are related to $\Delta w$ by mass balance:

$$\Delta w = \sum_i w_i$$  \hspace{1cm} (1)

where $i$ is the number of solute constituents. Congruent dissolution constrains the solute stoichiometry to that of the dissolved mineral, so $i = 1$ and $w_i = \Delta w$, which leads to what can be
termed a “true” solubility once any added solutes (e.g., SiO\(_2\) in the present work) are taken into account. Incongruent dissolution involving a residual phase of different stoichiometry yields \(i > 1\), and values of \(w_i\) cannot be determined from \(\Delta w\) alone. In molar form, for enstatite and diopside dissolution:

\[
x\text{MgSiO}_3 \rightarrow y\text{Mg}_2\text{SiO}_4 + (x - 2y)\text{MgO}_{(aq)} + (x - y)\text{SiO}_2_{(aq)}
\]

(2)

enstatite forsterite dissolved solutes

and

\[
x\text{CaMgSi}_2\text{O}_6 \rightarrow y\text{Mg}_2\text{SiO}_4 + x\text{CaO}_{(aq)} + (x - 2y)\text{MgO}_{(aq)} + (2x - y)\text{SiO}_2_{(aq)}
\]

(3)

diopside forsterite dissolved solutes

Equations (2) and (3) state that \(x\) moles of starting mineral are converted to \(y\) moles of forsterite and stoichiometrically determined amounts of dissolved oxide components (subscripted “\((aq)\)”; these are solely stoichiometric entities for the purposes of mass balance and do not imply discrete solute species). Thus, incongruent dissolution prevents direct determination of solubility because, for each experiment, \(x\) and \(y\) are both unknown but only \(x - y\) (i.e., \(\Delta w\) in mass units) is measured.

We addressed this problem in two ways. First, we calculated an “apparent” solubility assuming that the concentration of \(\text{MgO}_{(aq)}\) is zero (i.e., forsterite is insoluble), motivated by the very low Mg concentrations in equilibrium with forsterite in pure H\(_2\)O (Newton and Manning, 2002a; this study). In this case, \(x = 2y\), and the bulk solute stoichiometry is SiO\(_2\) for enstatite and CaSi\(_{1.5}\)O\(_4\) for diopside.

More accurate solubility results can be obtained at conditions where high-precision determinations of the solubility of forsterite have been made; in the present study, this was at 800 and 900 °C, 1 GPa. At these conditions, forsterite dissolves congruently or very nearly so (see below). If we assume that solute Mg/Si in equilibrium with forsterite alone equals that with
forsterite + enstatite, and that there is no complexing between the Mg and the other solutes (Si for enstatite; Si and/or Ca for diopside), then the dissolved $\text{Mg}_2\text{SiO}_4$ concentration in fluids with forsterite + enstatite or diopside is constrained. Thus, dissolution of $x$ moles of starting mineral produces $z$ moles of dissolved $\text{Mg}_2\text{SiO}_4$, $\frac{x}{2} - z$ moles of forsterite and $2z$ moles of $\text{MgO}_{(aq)}$, along with either $\frac{x}{2} + z$ moles of $\text{SiO}_2_{(aq)}$ for enstatite (Eq. 2), or $x$ moles of $\text{CaO}_{(aq)}$ and $\frac{3x}{2} + z$ moles of $\text{SiO}_2_{(aq)}$ for $x$ diopside (Eq. 3). This approach yields fluid compositions adjusted for known forsterite solubility. We therefore refer to concentrations calculated this way as “adjusted” solubilities.

Given the assumptions, the concentrations of dissolved oxide components in Eqs. (2) and (3) may be calculated from the weight change $\Delta w$ by rewriting Eq. 1 as:

$$\Delta w = w_{\text{Mg}_2\text{SiO}_4_{(aq)}} + w^*_{(aq)}$$

(4)

where $w^*_{(aq)}$ is $\text{SiO}_2$ for enstatite and $\text{CaSi}_{1.5}\text{O}_4$ for diopside. For apparent solubilities, $w_{\text{Mg}_2\text{SiO}_4_{(aq)}} = 0$; for adjusted solubility, $w_{\text{Mg}_2\text{SiO}_4_{(aq)}}$ corresponds to independently determined forsterite solubility. In each case, Eq. 4 was solved for $w^*_{(aq)}$, which then allowed determination of the concentrations of individual oxide or element components for an experiment after accounting for any $\text{SiO}_2$ where quartz was added.

### 3 EXPERIMENTAL RESULTS

#### 3.1 Forsterite experiments

##### 3.1.1 Textures

Results of forsterite solubility experiments are presented in Table 1 and Fig. 2. Run products from run Fo-09 in pure H$_2$O at 800 °C yielded a residual forsterite grain plus small (10-30 µm) flakes of newly grown crystals on the forsterite surface (Fig. 2a, b). Index of refraction and
energy dispersive X-ray analyses indicate brucite (Fig. 2a, b). We interpret the brucite to result from slightly incongruent dissolution of forsterite in pure H$_2$O at these conditions. Additional experiments at the same conditions with added SiO$_2$ (Table 1) yielded no brucite, consistent with this interpretation. All other run conditions were free of brucite and yielded the starting forsterite crystal (Fig. 2c) ± halite cubes (depending on presence or absence of NaCl). The absence of brucite crystals on residual forsterite at 900 °C, and at 800 °C with NaCl, indicates congruent dissolution of forsterite. During H$_2$O-NaCl experiments, the starting crystals developed smooth surfaces and incipient facets (Fig. 2c), consistent with the high solubility calculated from mass loss relative to pure H$_2$O experiments.

3.1.2 Forsterite solubility

At 800 °C, run durations of ~1 day yielded consistently low solubilities (runs Fo-01 through Fo-05). Runs of ≥48 h yielded higher solubilities that were independent of duration within error. These runs are taken to reflect equilibrium and are reported in Table 1. Experiments conducted at 900 °C, $X_{NaCl} = 0.3$, and varying times showed that runs of 11-32 h yielded similar values. A shorter run (Fo-23, 6 h) likely had insufficient time to equilibrate, whereas a longer experiment (Fo-20, 70 hr) resulted in higher solubility (Fig. S1a) due to growth of new forsterite crystals in the outer capsule. These “vapor transport crystals” (Newton and Manning, 2006; Tropper and Manning, 2007; Antignano and Manning, 2008b) may nucleate and grow in longer runs as a consequence of convective mass transfer generated by the small temperature gradient. Such crystals cause apparent solubility to be higher than the equilibrium value. We limited run times at 900 °C to <70 h and carefully checked for the absence of these crystals.

Formation of brucite prevented direct determination of forsterite solubility in pure H$_2$O at
800 °C, 1 GPa. Instead it was found by linear extrapolation of the results of experiments with added SiO$_2$ (runs Fo-6, 7, 8, Table 1) to zero excess silica. Using the midpoint between solubility determined from the weight change of the forsterite crystal and the inner capsule yields $m_{\text{Fo}} = 0.0012 \pm 0.0003$. Forsterite solubility in pure H$_2$O at 900 °C is 0.0046(1) molal. In H$_2$O-NaCl solutions, forsterite solubility increased with $X_{\text{NaCl}}$ over the range of fluid compositions investigated, with a solubility of $m_{\text{Fo}} = 0.0424(10)$ molal at $X_{\text{NaCl}} = 0.471$ and 800 °C, a ~35-fold increase in solubility (Fig. 3). At 900 °C, forsterite solubility increases to $m_{\text{Fo}} = 0.0900(1)$ molal at $X_{\text{NaCl}} = 0.450$, an increase of ~20 times relative to the pure H$_2$O solubility. The solubility data at 800 and 900 °C and 1.0 GPa can be described by

$$m_{\text{Fo}} = 0.0013 + 0.0311X_{\text{NaCl}} + 0.0377X_{\text{NaCl}}^{1/2}$$

at 800 °C, and

$$m_{\text{Fo}} = 0.0047 + 0.1212X_{\text{NaCl}} + 0.0446X_{\text{NaCl}}^{1/2}$$

at 900 °C, with R of 0.998 and 0.999, respectively. These fit curves are plotted with the data in Figure 3.

3.2 Enstatite Experiments

3.2.1 Textures

Enstatite solubility experiments yielded run products with textures similar to those reported by Newton and Manning (2002a). Enstatite dissolved incongruently to forsterite + SiO$_2$-rich solute over the entire salinity range investigated (Fig. 2d). In each run product, euhehedral, equant, granular forsterite crystals coat part or all of the enstatite crystal, depending on degree of dissolution; the external shape of the pseudomorphically replaced enstatite crystal retains that of the original
crystal. Addition of SiO$_2$ yielded progressively smaller quantities of forsterite until only a
subhedral enstatite crystal was found in the run products.

### 3.2.1 Enstatite solubility

Results of enstatite solubility experiments are given in Table 2 and Figure 4. As described
above, apparent solubility in forsterite-saturated runs was estimated by assuming zero MgO in
solution. The apparent enstatite solubility (as SiO$_2$) is shown in Fig. 4a in the upward pointing
triangles. True solubilities are obtained in the presence of fluid with excess SiO$_2$ and no forsterite
(downward pointing triangles, Fig. 4a). In the absence of other constraints, the fluid composition
at a given $X_{NaCl}$, at which forsterite disappears from the surface, constrains the composition of a
forsterite+enstatite-saturated fluid and lies between the two types of experimental result. Linear
least-squares fits to the midpoints between forsterite-present and forsterite-absent runs give

$$m_{Si} = 0.297 - 0.0567X_{NaCl}$$  \hspace{1cm} (7)

and

$$m_{Si} = 0.499 + 0.0140X_{NaCl}$$  \hspace{1cm} (8)

at 800 and 900 °C respectively. The NaCl content of the fluid at 1.0 GPa and 800-900 °C has only
a minor effect on apparent solubility relative to values in pure H$_2$O from Newton and Manning
(2002a).

Using our results on forsterite solubility in H$_2$O-NaCl, the adjusted solubility was
calculated by combining Eqs. 4-6 to determine the fluid composition where forsterite was present
(Table 2). Calculated concentrations confirm that dissolved Si is greater than dissolved Mg at all
\(X_{\text{NaCl}}\) (Fig. 4b). With rising salt content, Mg increases significantly while Si declines slightly, regardless of temperature. The calculated dissolved Mg/Si (Fig. 4c) increases from relatively small values in pure H\(_2\)O to \(\sim 0.3\) at \(X_{\text{NaCl}} = 0.3\) and is independent of temperature at 800-900 °C.

### 3.3 Diopside Experiments

#### 3.3.1 Textures

Run products from all diopside experiments consisted of the original diopside crystal with smaller forsterite crystals growing on the surface (Fig. 5). The forsterite occurs as \(\sim 25\text{-}100 \mu\text{m}\) sub- to euhedral residual crystals on diopside grain surfaces (Fig. 5a-c). In some runs, loose crystals are also present in inner capsules (Fig. 5d) and/or adhered to the inner capsule walls. This textural evidence indicates that diopside dissolves incongruently producing residual forsterite at all conditions investigated. In addition, blades and acicular sprays of wollastonite (in pure H\(_2\)O runs) and wollastonite plus enstatite (in H\(_2\)O-NaCl runs; Fig. 5c) occurred on grain surfaces, along with minor silica material, which forms as both small spheres (“fish roe”; Fig. 5d) and an amorphous coating on some crystal surfaces. These materials form a randomly distributed coating on the surface of residual diopside and forsterite crystals and walls of the inner and outer capsules. The morphology, random distribution, and abundance of the silica, wollastonite, and enstatite, lead us to interpret these fine crystals and amorphous materials as quench phases, which were dissolved in solution at high \(P\text{-}T\) conditions. These types of quench products are typical of high \(P\text{-}T\) solubility studies of silicate minerals (e.g., Newton and Manning, 2006, 2007). The formation of enstatite quench crystals in run products from H\(_2\)O-NaCl experiments, but not in pure H\(_2\)O runs in this study, indicates a substantial increase in Mg\(^{2+}\) mobility in brines relative to pure H\(_2\)O, consistent with the results of our enstatite solubility experiments (Table 2). The overall mass of quench
materials is small and can be neglected.

3.3.2 Diopside solubility

Results from diopside experiments are given in Table 3. Experiments in pure H$_2$O at 700 °C and varying times showed that solubilities achieved by 10 h were identical within error to solubilities at 40 h (Fig. S1b); it is therefore assumed that run times $\geq$10 h were sufficient to attain equilibrium. SEM analyses revealed that in several experiments small diopside crystals nucleated and grew in the outer capsule or on the walls of the inner capsule. These are interpreted as vapor-transport crystals as in forsterite experiments; any runs showing evidence for these crystals were discarded.

Experiments in pure H$_2$O were conducted from 0.7 to 1.5 GPa and 650 to 900 °C. The apparent solubility of diopside ($m_{Di\,app}$) increases with increasing pressure and temperature. At 1 GPa, the apparent solubility increases from 0.0060(5) molal at 650 °C to 0.0141(8) molal at 900 °C (Fig. 6a). At 800 °C and 0.7 to 1.5 GPa, apparent solubility increases from 0.0028(6) to 0.0208(6) molal (Fig. 6b). A least-squares fit to these data yields the equation:

$$\log m_{Di\,app} = -1.269 - \frac{1758}{T} + 0.910P$$

(9)

where $T$ is in K and $P$ is in GPa. Average absolute deviation between data and fit is 9% relative for all experiments, excepting gdi15 at 800 °C, 0.7 GPa (Table 3), which was not included in the fitting because the midpoint solubility could not be obtained (Table 3). The fit yields higher solubility than measured at 1.5 GPa, 800 °C. A functional form that is linear in $P$ would improve the fit, but Eq. 9 reproduces previous work at higher $P$ and $T$ reasonably well (see §4.2 below).
We therefore chose to retain the form of the fit equation. We investigated the influence of NaCl on diopside solubility at 800 °C and 1 GPa (Fig. 7a). Figure 7a shows that apparent diopside solubility is significantly enhanced with increasing NaCl concentration, rising from 0.0107(6) molal in pure H₂O and then leveling off to a maximum of 0.1761(37) molal (X_{NaCl} = 0.5), near halite saturation (X_{NaCl} = 0.62, Aranovich and Newton, 1996). A least-squares fit to the variation of diopside apparent solubility (m_{Di,app}) with X_{NaCl} at 800 °C, 1 GPa, yields the equation:

\[
m_{Di,app} = 0.0049 + 0.0716X_{NaCl} + 0.1994X_{NaCl}^{1/2}
\]  

(R = 0.995) (Fig. 7a).

At 800 °C, 1 GPa, the solute composition in H₂O-NaCl fluid coexisting with diopside + forsterite can be estimated using Equations 4 and 5. The procedure outlined in §2 was followed to obtain Si, Ca and Mg concentrations as a function of X_{NaCl} (Fig. 7b). The solutions are enriched in Si relative to Ca over the full compositional range. Mg concentrations are lower than Si and Ca, as required by the residual forsterite coating. Calculated molar Si/Ca, Mg/Si and Ca/Mg are nearly constant at ~1.8, 0.33 and 1.7, respectively, in all NaCl-bearing solutions.

4 DISCUSSION

4.1 Accuracy of calculated solute concentrations

Apparent solubilities of enstatite and diopside were calculated assuming that forsterite is insoluble (m_{MgO(aq)} = 0), whereas adjusted solubilities account for forsterite’s solute contribution. In pure H₂O, where forsterite solubility was found to be very low (Fig. 3), the...
difference between apparent and adjusted solubilities is small. In the case of enstatite, apparent
solubilities at 800 and 900 °C, 1 GPa, are respectively 0.296±0.001 m and 0.497±0.001 m,
compared to adjusted solubilities of 0.294±0.002 m and 0.495±0.002 m. For diopside, apparent Ca
solubility at 800 °C and 1 GPa is 0.0107±0.006 m vs. adjusted solubility of 0.0095±0.0012 m. (Si
solubility is 1.5 times these values; errors are 1σ). It is evident that the adjustment leads to smaller
values, but the differences are so small that, for pure H₂O, apparent solubilities are adequate for
quantifying changes with P and T, and comparing results among different studies. However,
differences between apparent and adjusted solubilities increase with increasing concentration and
increasing forsterite solubility, so where NaCl is present in solution, adjusted solubilities are
essential for quantifying the fluid composition.

We can also evaluate the assumptions underlying the calculation of adjusted solubility. The
assumption that the dissolved Mg concentration is fixed and corresponds to that at forsterite
saturation is required to compute adjusted fluid compositions in enstatite + forsterite and diopside
+ forsterite experiments. Two factors could invalidate the assumption. First, it is possible that the
dissolved Mg concentration in equilibrium with forsterite alone is non-negligibly different from
that with forsterite and enstatite or diopside. Because the latter equilibrium point dictates higher
SiO₂ activity and lower MgO activity than equilibrium with forsterite alone, the MgO
concentration could be lower, and SiO₂ higher, where two minerals are present. The second factor
is that interaction between dissolved SiO₂, Mg, and Ca are possible via metal-silicate complexing
(e.g., Sverjensky et al., 1997; Huang and Sverjensky, 2019).

The assumptions can be evaluated in the case of enstatite by comparing calculated Mg
concentrations with those in comparatively silica-rich solutions that resulted in enstatite without a
forsterite coating, which allows direct determination of the Mg concentration. Figure 8 compares
Mg concentrations in equilibrium with only forsterite and only enstatite. At any given $X_{NaCl}$, Mg concentration in equilibrium with forsterite + enstatite lies on the forsterite curves. The lack of systematic deviation of the enstatite-only data either above or below the curves indicates that the Mg concentrations in fluids coexisting with forsterite alone, enstatite alone, or forsterite + enstatite are similar within our detection limits. This supports the accuracy of the calculated fluid compositions in enstatite + forsterite experiments. In addition, thermodynamic data on Mg-silicate complexing, as represented by the aqueous species $\text{Mg(HSiO}_3\text{)}^+$, imply negligible concentrations at 1 GPa, 800 and 900 °C, and $X_{NaCl}$ up to ~0.15 (Sverjensky et al., 2014; Huang and Sverjensky, 2019). We take this as sufficient to assume accuracy of the derived fluid compositions in diopside + forsterite experiments, though a similar test was not performed.

4.1 Comparison to previous results

4.1.1 Forsterite and enstatite

Limited data are available for direct comparisons at the $P$ and $T$ of this study. The solubility behavior of CaO-MgO-SiO$_2$-H$_2$O minerals was investigated in previous studies, with and without HCl, at lower $P$ and $T$ (e.g., Hemley et al., 1977a,b; Frantz and Popp, 1979; Luce et al., 1985), but we are not aware of previous studies of forsterite or enstatite solubility in NaCl-bearing H$_2$O. Forsterite and enstatite solubilities in pure H$_2$O have been more extensively investigated, but typically at higher $P$ and $T$ near the wet solidus in the system forsterite-quartz-H$_2$O. An exception is the study by Newton and Manning (2002a), who found that forsterite solubility in pure H$_2$O was below their detection limit at the conditions investigated here. Our new results with improved detection limits and precision quantify forsterite solubility in pure H$_2$O for the first time.

Experiments by Newton and Manning (2002a) showed that enstatite dissolved
incongruently to forsterite + fluid in pure H$_2$O at 800 and 900 °C, 1 GPa. Similar behavior was observed by Ryabchikov et al. (1982) at 3 GPa, 900 °C. Incongruent dissolution appears to persist to higher $T$ at these pressures (e.g., Nakamura and Kushiro, 1974; Zhang and Frantz, 2000); however, the data of Stalder et al. (2001) and Mibe et al. (2002) imply congruent enstatite dissolution at $\geq$6 GPa. A transition from incongruent to congruent dissolution at 3-6 GPa implies increasing Mg/Si in enstatite+forsterite saturated fluid with pressure (e.g., Stalder et al., 2001; Kawamoto et al., 2004). Combining our results with previous work confirms this trend: at 1 GPa, 800 and 900 °C, we find Mg/Si of 0.009 and 0.020, respectively. At 3 GPa, 900 °C, Mg/Si = 0.33 (Ryabchikov et al., 1982), while at 6 GPa it is ~1 (Stalder et al., 2001). The results and trends in pure H$_2$O differ from a recent determination of enstatite+forsterite solubility in H$_2$O at 800 °C, 1 GPa. Using a diamond-trap technique, Tiraboschi et al. (2018) found $m_{\text{Si}} = 0.22$, $m_{\text{Mg}} = 0.28$, and Mg/Si = 1.3. While $m_{\text{Si}}$ agrees reasonably well with Newton and Manning (2002a), Mg and Mg/Si differ substantially from our adjusted solubilities ($m_{\text{Mg}} = 0.0026$ $m$ and Mg/Si = 0.0088). The datum of Tiraboschi et al. is also inconsistent with the trend of rising Mg/Si with pressure in that it is greater than values at 3-6 GPa determined by Ryabchikov et al. (1982) and Stalder et al. (2001). We do not know the source of this discrepancy.

Increasing NaCl concentration has the same effect as pressure in pure H$_2$O (Fig. 4c). For example, the trends in Fig. 4c imply that Mg/Si of 900 °C, 3 GPa (0.33) is attained at $X_{\text{NaCl}} = 0.38$ at 1 GPa.

Our results can also be compared to solubilities calculated using high $P$-$T$ thermodynamic data for aqueous species in the Deep Earth Water (DEW) model (Sverjensky et al., 2014) and the EQ36 package (Wolery, 1992; Wolery and Daveler, 1992). At 800 °C, forsterite is predicted to dissolve incongruently to brucite at $X_{\text{NaCl}} = 0$ to 0.014, but congruently at higher $X_{\text{NaCl}}$; and
predicted solubility in pure H\textsubscript{2}O (0.0012 molal) agrees well with that measured (0.0012 molal). However, a substantially smaller dependence on NaCl is predicted. For example, at \(X_{\text{NaCl}} \sim 0.05\) (3 molal) measured forsterite solubility is 0.011 molal, but the predicted value is about 10 times lower (0.0012), and the disparity grows with increasing NaCl. Enstatite is predicted to dissolve incongruently at 800 °C in pure H\textsubscript{2}O and H\textsubscript{2}O-NaCl solutions and there is good agreement with the measured values in pure H\textsubscript{2}O, but solubility is again significantly under predicted as NaCl is added. These results imply that thermodynamic data for Mg-chloride and Na-silicate species may need revision.

4.1.2 Diopside

Early experiments investigated diopside solubility at very high \(P-T\) in H\textsubscript{2}O. Eggler and Rosenhauer (1978) determined the solubility of diopside in H\textsubscript{2}O by phase equilibria, and reported that diopside dissolved stoichiometrically (i.e., congruently) at 1200 °C, 2.0 GPa and 1180 °C, 3.0 GPa; resulting in solubilities of 0.48±0.07 and 0.5 ±0.07 molal, respectively. Schneider and Eggler (1986) found that, in H\textsubscript{2}O vapor at 1100 °C, 2.0 GPa, diopside dissolved incongruently to forsterite and fluid. They obtained an apparent solubility of 0.14 molal by weight loss methods (no error was reported). The discrepancies between these studies may be due to differences in experiment durations – Eggler and Rosenhauer (1978) run durations were 1.17 and 2.25 h, while Schneider and Eggler (1986) run durations were 24 h – and/or from differences in methods used to determine solubility. Comparisons of the 2 GPa experiments from both studies with the results of this work (Fig. 9a) show excellent agreement between our Eq. 9 and the Schneider and Eggler (1986) datum, but not that of Eggler and Rosenhauer (1978), suggesting that shorter experiment durations and the phase equilibrium approach yielded results of low accuracy. The good agreement between our
Eq. 9 and the data of Schneider and Eggler (1986) lends confidence to the accuracy of extrapolation of our results to higher pressures and temperatures than those investigated directly, and support our choice of run durations.

Two more recent studies focused on diopside solubility at $P$ and $T$ relevant to crustal metamorphism. One reported experiments at 650°C, 0.2-0.75 GPa, including investigation of diopside solubility in pure H$_2$O and in H$_2$O-NaCl solutions (Budanov and Shmulovich, 2000). Another investigated diopside solubility at 650 °C and 0.5 GPa in pure water and in a 53.22 mol% NaCl solution (Shmulovich et al., 2001). Both studies found that diopside dissolved incongruently at all investigated conditions. The apparent diopside solubilities in pure H$_2$O from Budanov and Shmulovich (2000) and Shmulovich et al. (2001) are compared with our results at 0.5 GPa in Fig. 9b, and at 650 °C in Fig. 9c. Figure 9b shows that our Eq. 9 predicts that apparent solubility lies between the results of the two studies. Comparisons at 650 °C and a range of pressures (Fig. 9c) reveal that while our data agree well with the Budanov and Shmulovich (2000) datum at 0.5 GPa, the 0.7 GPa experiment from their study yielded a higher $m_{Di \text{ app}}$ than predicted by Eq. 9. This could be due to undetected vapor transport crystals in the 0.7 GPa experiment of Budanov and Shmulovich (2000), which would result in an erroneously high weight loss and solubility.

Direct comparisons of the apparent solubility of diopside in H$_2$O-NaCl solutions from this study with those of Budanov and Shmulovich (2000) are hampered by the different $P$-$T$ conditions investigated. However, Fig. 9d shows that $m_{Di \text{ app}}$ increases with increasing $X_{\text{NaCl}}$ at all conditions from both studies. Moreover, comparison of our results with the 0.2 and 0.5 GPa data of Budanov and Shmulovich (2000) reveals that the form of the dependence of apparent solubility on $X_{\text{NaCl}}$ is similar. In contrast, the results of Budanov and Shmulovich (2000) at 0.75 imply a smaller relative increase with $X_{\text{NaCl}}$. However, this is likely a consequence of their very high apparent diopside...
solubility in pure H₂O at this P and T. If the value predicted from our Eq. 9 is substituted, the trend
at 0.75 GPa is similar to that at other conditions (dashed red line in Fig. 9d). This further supports
the suggestion that the 650 °C, 0.75 GPa experiment of Budanov and Shmulovich (2000) may
have had undetected vapor transport crystals.

At 800 °C, 1 GPa, the DEW model predicts that diopside dissolves incongruently to
merwinite and forsterite in pure H₂O, and to forsterite in H₂O-NaCl solutions. Predicted Si, Ca,
and Mg concentrations in equilibrium with diopside + forsterite in pure H₂O and H₂O-NaCl are all
lower than measured.

4.3 Dependence of solubility on solvent composition

The results at 800 °C, 1 GPa, allow comparison of the relative roles of H₂O and NaCl on
the solubilities of key CaO-MgO-SiO₂ minerals, based on data from this study and that of Newton
and Manning (2000a, 2006) on quartz (SiO₂) and wollastonite (CaSiO₃). Wollastonite and quartz
dissolve congruently at these conditions. Similar behavior of forsterite means that dissolved molar
Mg/Si is fixed at 2 in solutions formed by dissolving this mineral alone. Using the molality scale
(Fig. 10a), forsterite solubility rises with NaCl, but is significantly lower than that of the other
minerals shown. In the case of diopside, Si, Ca and Mg molalities all rise with NaCl (Fig. 7b), and
– with the exception of pure H₂O – molar element ratios are nearly constant (Table 3). Comparing
diopside to other minerals using Si, the most abundant solute, reveals a trend of increasing molality
lying between the trends for forsterite and wollastonite. For enstatite, the behavior of Si and Mg
differ: whereas Mg increases with NaCl content, Si declines (Fig. 4b). Mg/Si in the fluid rises
steadily with NaCl, but \(m_{\text{Mg}}\) is significantly lower than \(m_{\text{Si}}\) (Fig. 4c). Therefore, Si molality can
again be used to compare to congruently dissolving minerals. Figure 10a shows that, like quartz,
Si molality in equilibrium with enstatite declines with $X_{NaCl}$, though to a much smaller degree. The enstatite trend lies between the forsterite and quartz trends.

The molality scale is based on the H$_2$O component of the solvent, so it helps differentiate between the role of the water and the role of NaCl in controlling solubility behavior. Declines with $X_{NaCl}$, as seen for quartz and enstatite, suggests that solute hydration controls dissolution. In contrast, an increase with $X_{NaCl}$, as for forsterite, diopside and wollastonite, implies that formation and stability of Cl- and Na- complexes primarily dictate solubility.

In detail, both solute hydration and Na- and Cl- complexing control dissolution behavior to varying degrees. Insight into their relative contributions can be obtained using mass-based or mole-fraction based solute concentrations in the H$_2$O-NaCl solution (Figs. 10b and c). Concentrations in parts per million (ppm) for diopside and enstatite were computed using the sums of calculated solute masses. On this concentration scale (Fig. 10b), quartz and enstatite solubility decline in log-linear fashion. Forsterite, diopside and wollastonite increase sharply at low $X_{NaCl}$, then define weak maxima near $X_{NaCl}$ ~ 0.3.

Concentrations on the mole-fraction scale (Fig. 10c) take explicit account of the dissociation of NaCl in the solution via

$$X_i = \frac{m_i}{m_i + 55.51(1 + (1 + \alpha)X_{NaCl})} \frac{X_{NaCl}}{X_{H_2O}}$$

(11)

(Newton and Manning, 2006), where $\alpha$ is the NaCl dissociation parameter calculated following Aranovich and Newton (1996), $X_{NaCl}$ and $X_{H_2O}$ are calculated from bulk water and salt added to an experiment, and 55.51 is the number of moles in 1 kg H$_2$O. For congruently dissolving minerals, $X_i$ is determined from the molality of $i$ in solution. For diopside and enstatite, which dissolve
incongruently, we calculate $X_i$ using the sum of solute molalities. To highlight trends of solubility enhancement or suppression, mole fractions relative to those in pure H$_2$O are depicted. Figure 10c clearly differentiates minerals for which NaCl suppresses solubility relative to pure H$_2$O (enstatite and quartz) from those for which it enhances solubility (forsterite, diopside, wollastonite). Of note is the much stronger relative enrichment of forsterite compared to diopside and wollastonite, which display analogous enhancement behavior.

The trends in Figure 10c give insight into solute-solvent interactions that control solubility. The log-linear salting out of quartz in NaCl solutions is less pronounced than in CO$_2$ solutions at equal activities of H$_2$O (Newton and Manning, 2000a, 2009). This is likely a consequence of Na-Si complexing and/or NaCl-SiO$_2$ complexing (Newton and Manning, 2006, 2010, 2016). The smaller decline in enstatite solubility with $X_{\text{NaCl}}$, relative to quartz signals an important role for Mg-Cl complexing (as MgCl$^+$ or MgCl$_2$).

In contrast to quartz and enstatite, the solubilities in NaCl solutions of forsterite, diopside and wollastonite show enhancement (salting in) relative to solubilities in pure H$_2$O (Fig. 10c). For forsterite at 800 °C, the solubility at 30 mol% NaCl is about 15 times that in pure H$_2$O (at 900 °C, it is 30 times higher). Values of log$X/X_\circ$ rise to a maximum between $X_{\text{NaCl}}$ of 0.2 to 0.3, then show a slight decline. The relative increase in diopside solubility is very similar to that observed for wollastonite. It was previously shown that wollastonite solubility displayed a maximum enhancement of ~8x at $X_{\text{NaCl}}$ of ~0.33 before declining to higher $X_{\text{NaCl}}$ (Newton and Manning, 2006). We observe similar behavior for diopside, which shows a maximum enhancement of 7x observed at $X_{\text{NaCl}} = 0.31$.

Insight into the nature of the solvent interactions that cause salting in Mg silicates can be gained in a manner similar to that for wollastonite, for which Newton and Manning (2006)
suggested that the weak maximum is due to the formation of Ca chloride and a Na-Si hydroxide complexes. This results in the overall decline in relative solubility enhancement at high $X_{NaCl}$ owing to a decrease in $H_2O$ activity. Controls on the relative solubility pattern of forsterite can be constrained by expressing the dissolution reaction as

$$Mg_2SiO_4 + yNaCl + zH_2O = n \text{ solute species}$$ \hspace{1cm} (12)

forsterite

Assuming ideal solution of solute species (Newton and Manning, 2006, 2010), the equilibrium constant $K_{eq}$ for Equation 12 at a given $P$ and $T$ is

$$K_{eq} = \frac{x_{f_0}^n}{a_{NaCl}^y a_{H_2O}^z}$$ \hspace{1cm} (13)

where the $a$ is the activity of the subscripted solvent component in their mixtures and $x_{f_0}$ is the mole fraction of $Mg_2SiO_4$ based on all molecules and ions of the solution. Assuming ideal mixing, the activities of NaCl and $H_2O$ are, respectively,

$$a_{NaCl} = (1 + \alpha)^{(1+\alpha)} \left( \frac{x_{NaCl}}{1 + \alpha x_{NaCl}} \right)^{(1+\alpha)}$$ \hspace{1cm} (14)

and

$$a_{H_2O} = \frac{x_{H_2O}}{1 + \alpha x_{H_2O}}$$ \hspace{1cm} (15)
(Aranovich and Newton 1996), where $\alpha$ is again the measure of NaCl dissociation. This model yields $\alpha = 1.0$ at 800 °C, 1 GPa.

Assuming that $y$ and $z$ are integers and that $X_{Fo}$ is too small to affect the activities in Equations 13 and 14, the forsterite solubility data may be fitted by least squares to determine $y$, $z$, $n$ and $K_{eq}$. As an additional constraint, the relative solubility of a congruently dissolving mineral $X_i$ is at a maximum with respect to $X_{NaCl}$ when the latter quantity is equal to $y/(y+z)$ (Newton and Manning, 2010). This criterion limits the ratio $y/z$ to between 0.3 and 0.5, based on the solubility measurements. Using the above equations, the optimal values of $y$, $z$ and $n$ were found to be 1, 3 and 3, respectively, at 800 °C, $K_{eq} = 8.9 \times 10^{-10}$, with a solubility maximum at $X_{NaCl} = 0.25$. These results are shown with the purple line in Figure 10c. At 900 °C a best fit is obtained with $y$, $z$ and $n$ of 1, 2 and 3, with a maximum at 0.33 and $K_{eq} = 4.3 \times 10^{-9}$ (not shown).

The number of discrete solute species per NaCl reacted is quite robust at $n = 3$. This suggests that Mg and Si dissolve independently, without Mg-silicate complexing, consistent with the conclusions drawn above. The Mg solute is likely to be a chloride, whereas the Si likely complexes with Na to produce a very soluble Na-silicate species. A number of combinations of species, charged and uncharged, may be imagined that satisfy reaction stoichiometry and charge balance. Suitable but non-unique reactions written as neutral solute species are:

\begin{align*}
Mg_2SiO_4(xl) + 3H_2O + NaCl &= MgClOH + Mg(OH)_2 + NaSiO(OH)_3 \\
Mg_2SiO_4(xl) + 2H_2O + NaCl &= MgClOH + Mg(OH)_2 + NaSiO_2OH
\end{align*}
at 900 °C. The higher hydration state of solutes at 800 °C than at 900 °C (H₂O/NaCl = 3:1 vs. 2:1) seems plausible in light of the expected effects of temperature.

The approach outlined above is strictly applicable only to congruently dissolving minerals. But it provides insights into solute species associated with the incongruent dissolution of diopside. Diopside solubility and solubility enhancement are very similar to wollastonite, which dissolves in H₂O-NaCl chiefly as very soluble Ca-chloride and hydrous Na-silicate complexes (Newton and Manning, 2006). In contrast, while the relative enhancement of forsterite solubility by NaCl is even greater than that of wollastonite and diopside (Fig. 10c), it is much lower on an absolute basis (Figs. 10a and b). The generally refractory nature of Mg relative to Ca at these conditions, which is expressed as solubilities and solubility enhancements that are lower for the Mg-bearing phases at all X_{NaCl}, suggests that Ca-chloride complexes are substantially more stable than Mg-chloride complexes at the experimental conditions.

4.4 Comparison to other minerals

Figure 11 presents a compilation of solubility data at 800 °C and 1 GPa for many different mineral classes, including silicates, phosphates, sulfates, carbonates, oxides, and halides. These data are presented in order of increasing solubility (in ppm) in pure H₂O (blue diamonds). Where available, solubilities at X_{NaCl} ≈ 0.1 and X_{NaCl} ≈ 0.3 are shown as red and green diamonds, respectively. While this comparison is restricted to experimentally studied minerals, several observations can still be made from the limited data set. First, solubilities of oxides of high field-strength elements in pure H₂O are lower than Ca salts and silicates, consistent with the general expectation from ambient conditions that cations with high charge-to-radius ratio are relatively
insoluble. In general, silicates have high solubility and Si-rich tectosilicates (quartz, albite) are more soluble in H₂O than neso- and inosilicates, consistent with the strong solubility of silica and the SiO₂-rich nature of deep crustal fluids (Manning, 2018). With respect to changes due to NaCl addition, the enhancement in solubility of Ca-salts (phosphate, fluoride, sulfate, carbonate) continues to the highest NaCl concentrations, to X_{NaCl} at least 0.3, compared to that of corundum and silicates, for which there is either a plateau in enhancement or a decrease with salt addition. In addition, while all Ca-bearing minerals show solubility increases with NaCl, among the other oxides and silicates, only corundum and forsterite exhibit similar behavior, whereas quartz, enstatite and albite decrease in solubility with increasing X_{NaCl}.

While changes in solubility relative to that in pure H₂O are measures of the relative stabilities and hydration state of solute species (e.g., Newton and Manning, 2010), Fig. 11 suggests that roles for mineral constitution and structure can also be discerned. Figure 12 compares solubilities in pure H₂O at 800 °C, 1 GPa, plotted versus cation radius, ionic potential and average force constant, a measure of bond strength (see spreadsheets ‘Supplement Calculations 1’ and ‘Supplement Calculations 2’ for values used in Fig. 12). Cation radii in Fig. 12a (Shannon, 1976) are shown as filled symbols when referring to the inter-radical cation in the mineral, and open symbols of the same color when referring to the intra-radical cation(s) in the mineral structure. In the case of a mineral having more than one intra-radical cation, a weighted average of both cations are plotted according to mineral stoichiometry. For example, in grossular (Ca₃Al₂Si₃O₁₂) the inter-radical cation is Si⁴⁺, with an effective ionic radius of 0.26 Å; and there are two intra-radical cations Ca²⁺ and Al³⁺, with effective ionic radii of 1.12 and 0.535 Å, respectively. A value of 0.886 Å is plotted to represent the intra-radical cations, calculated using a weighted average based on mineral stoichiometry: \((1.12 \times 3 + 0.535 \times 2)/5 = 0.886\). In general, larger cations have weaker
bonds, and we might expect that minerals with weaker bonds would be more soluble. However, comparing cation radii with mineral solubilities reveals no obvious solubility trends among minerals.

A plot of average ionic potential for each mineral (Fig. 12b), calculated according the equation $z/r$, where $z$ is the charge of a cation, and $r$ is its radius (again using effective ionic radii of Shannon, 1976), shows minerals clustering according to mineral class and the appearance of trends correlating mineral solubility and the ionic potentials of the mineral structures. Solubilities of fluorides, oxides, and phosphates show a roughly linear negative correlation (on a log scale) with average ionic potential, while silicates have a steeply positive correlation. The carbonate and sulfate minerals do not appear to lie on either trend. Ionic potentials are calculated for each cation in a mineral structure, then the average ionic potential is calculated using a weighted average of all cations according to mineral stoichiometry. Again using grossular as an example, the ionic potentials of Ca$^{2+}$, Al$^{3+}$, and Si$^{4+}$ are 1.786, 5.607, and 15.38 Å$^{-1}$, respectively. The average ionic potential for the mineral is calculated as the weighted average according to mineral stoichiometry:

$$\frac{(1.79 \times 3) + (5.61 \times 2) + (15.38 \times 3)}{8} = 7.84.$$  

Another potential indicator of susceptibility to dissolution for a mineral is the strength of the bonds in the mineral’s structure. The force constant ($K_{ij}$) for a bond between cation $i$ and anion $j$, is a measure of bond strength or stiffness, and is calculated according to the equation,

$$K_{ij} = \frac{z_i z_j \varepsilon^2 (1-n)}{4 \pi \varepsilon_0 r_{ij}^3}$$  \hspace{1cm} (18)  

where $z_i$ and $z_j$ are the cation and anion valences, $\varepsilon_0$ is the dielectric constant (vacuum permittivity for simplicity), $e$ is the charge of an electron, $n$ is the exponent in the Born-Mayer formulation for
ion repulsion (Born and Mayer, 1932), and $r_{ij}$ is the equilibrium interionic distance between cation $i$ and anion $j$ (see Macris et al. (2015) and Young et al. (2009) for detailed discussions of this parameter and its applications). To calculate the average force constant for a mineral, we used the crystal structures program, CrystalMaker®, to determine the average bond lengths between each cation-anion bond pair in a mineral’s structure, which were used as the equilibrium interionic distances, $r_{ij}$, in Eq. 18.

When plotting average force constant vs. mineral solubility (Fig. 12c), two clear trends emerge: (1) a negative (approximately) linear trend consisting of fluoride, oxide, and phosphate minerals, which crosses (2) a positive, roughly linear trend consisting of silicate, carbonate, and sulfate minerals. Trend (1) is consistent with the idea that, in comparatively simple structures, weaker bonds (lower average $K_f$) lead to higher solubilities in H2O. Given the minerals that comprise trend (2), it may be that despite stronger average bonds in silicate, carbonate, and sulfate minerals, the balance of solubility among constituents may supersede bond strength. For the silicate minerals, average force constant generally increases with SiO$_2$ content. The positively correlated rise in solubility may be related to the stability of silica in pure water. Similarly, the carbonate and sulfate anion groups in calcite and anhydrite likely have greater relative stability as aqueous solutes than fluoride and phosphate. However, these minerals are alone in their class (i.e., calcite is the only carbonate, and anhydrite is the only sulfate plotted), so more data is necessary to fully interpret their behavior in this context.

4.5 Geological applications

These experimental results allow evaluation of fluid composition along specific high $P$-$T$ fluid flow paths in the lower crust and upper mantle, for model ultramafic rocks containing olivine,
orthopyroxene (opx), and clinopyroxene (cpx). Regardless of setting, our results suggest that
where fluids are relatively H$_2$O rich and NaCl poor, orthopyroxene solubility is substantially
higher than olivine or clinopyroxene, so fluids will be rich in silica relative to Ca and Mg. The
presence of cpx yields Ca > Mg. Hence, where all three phases are present, even in minor
abundance, concentrations of major cations in associated fluids will scale as Si > Ca > Mg. In
NaCl-rich fluids (brines), cpx becomes the most soluble mineral, but the order of solute
concentrations remains the same. Hence, Si > Ca > Mg across the entire range of H$_2$O-NaCl
concentrations at conditions investigated thus far.

In subduction zones, fluid moving towards the Earth’s surface from the slab to the mantle
wedge heats up as it decompresses. Temperature increase and pressure decrease have competing
effects on mineral solubility in this system (e.g., Fig. 6 and Newton and Manning, 2002a). The
spatial scales are such that, in the mantle wedge, temperature may increase greatly over a narrow
depth range (e.g., Fig 1a and Syracuse et al., 2010). Thus, we can predict that as a fluid moves
from slab to wedge and therefore decompresses and heats up, forsterite, enstatite and diopside
solubilities will all increase despite decreasing pressure. Fluids equilibrated with model ultramafic
rocks containing olivine, opx and cpx along this path will increase in total dissolved solids at a
given $X_{NaCl}$, with Si > Ca > Mg. This is consistent with theoretical predictions on the composition
of fluids in equilibrium with eclogites (Manning, 1998), experimental investigations on fluid
compositions in equilibrium with high-pressure mantle rocks (e.g., Schneider and Eggler, 1986;
Ayers et al., 1997), and also manifested in vein minerals in blueschists and eclogites which are
Na-Ca-Al-Si rich (Gao and Klemd, 2001; Becker et al., 1999) and poor in Mg. In lower-crustal
settings, fluid flow paths can be expected to mainly involve cooling and decompression, resulting
in declining solubilities while the solubility order is maintained. This can yield metasomatic
addition of Si, Ca and Mg downstream through precipitation of CMSH minerals in flow conduits.

Our results have particular significance for Ca mobility in fluids interacting with ultramafic and mafic rocks. At all $X_{\text{NaCl}}$ investigated, the solubility of wollastonite is greater than diopside, which in turn is greater than forsterite. As $X_{\text{NaCl}}$ increases, these solubility differences are amplified. Brines in contact with ultramafic and mafic rocks at high pressures and temperatures will preferentially strip Ca relative to Mg, resulting in a Ca/Mg ratio of >1 in solution. These results provide a foundation for quantifying the nature of interaction between ultramafic rocks and complex brines in the deep crust and upper mantle.

In general, the high solubility of Ca minerals (silicates, carbonates, sulfates, phosphates; Fig. 11) in alkali halide-bearing solutions may have an important effect on processes affecting the upper mantle source regions for basaltic magmas. For example, O’Reilly and Griffin (2013) found evidence in mantle xenoliths for refertilization of depleted harzburgite by metasomatic introduction of Ca, Al and trace elements. They suggested that both carbonatitic and ultrasaline fluids could have accomplished the alteration. Newton and Manning (2002b) showed that calcite is so soluble in concentrated NaCl solutions at high temperatures and pressures that supercritical mixing occurs over a large portion of the system CaCO$_3$-H$_2$O-NaCl. In this regard, there may be a continuum of compositions between carbonate-rich and chloride-rich fluids capable of restoring fertility to depleted harzburgite. Evidence supporting the existence of such fluids include carbonatite samples retrieved from deep drill holes well below the circulation of groundwater, which contain abundant halite intergrown with silicate minerals and carbonates (Kamenetsky et al., 2015), and the spectrum of fluid compositions found in diamonds grown in the presence of a fluid phase (Weiss et al., 2014, 2015).
Our results also provide insights into metasomatic processes at shallower crustal levels, as the element solubility order and role of NaCl are likely to be little affected by pressure. An example is the dunite and pyroxenite bodies found in the ultramafic sequences of some large layered intrusions, where monomineralic lenses, often discordant to the igneous layering, have received much discussion because some host deposits of the Pt-Group elements Pt, Ir, Os and Pd in associated chromitite lenses (e.g., in the Bushveld and Stillwater Complexes). Ophiolitic podiform chromitites are typically located within dunite lenses (Arai, 1997). There are diverse interpretations of the origins of dunite and pyroxenite veins in ultramafic bodies by magmatic processes (Scoon and Mitchell, 2004; Batanova and Sobolev, 2000; Tait and Jaupart, 1992; Kelemen et al., 1992; Büchl et al., 2002; Abbou-Kebir et al., 2011). An alternative is alteration by late-igneous or post-consolidation Cl-rich hydrothermal fluids (Schiffries, 1982; Schiffries and Rye, 1990). Ballhaus and Stümpfl (1986) found halite-saturated brine inclusions in quartz from the highly mineralized Merensky Reef zone of the Bushveld, and Boudreau et al. (1986) found Cl enrichment of minerals in zones of the Stillwater complex. Our results, combined with those of Newton and Manning (2002a), lend support to this model in two ways. The first is the great pressure and temperature dependence of enstatite and diopside solubility. In the crustal pressure range up to 1.0 GPa the solubility of enstatite in pure H\textsubscript{2}O increases by a factor of fifty between 0.2 GPa at 700 °C and 1.0 GPa at 900 °C (Newton and Manning 2002a). Diopside solubility behaves similarly, though changes with \(P\) and \(T\) are smaller. Pyroxenite veins are thus explainable by rising and cooling hydrothermal solutions. Second, our finding of great solubility increase of forsterite and diopside in NaCl-rich solutions could account for metasomatism at deep levels of a cooling gabbro/ultramafic intrusion, with deposition of dunite or clinopyroxenite veins, while the
The high solubility of enstatite in such fluids could cause desilication of harzburgite to dunite. Cl
metasomatism and metal transport would be natural associates of brine percolation.

Finally, peridot gems of the Zabargad Island (Red Sea) peridotite contain inclusions of
halite and fluid that indicate great crystal growth of forsterite in extremely concentrated brines
(Clochiatti et al., 1981). The possible source of NaCl in this case is infiltration of sea water into a
hot diapiric peridotite. This occurrence shows that concentrated NaCl solutions retain great fluxing
power for ferromagnesian silicates even at near-surface pressures.

5 CONCLUSIONS

1. Forsterite dissolution in H$_2$O-NaCl solutions was measured at 1 GPa, 800°C and 900 °C.
   In pure H$_2$O at 800 °C, dissolution is very slightly incongruent, with minute brucite flakes
   on the surface. Addition of excess silica allowed projection to obtain apparent solubility.
   At all other conditions forsterite dissolved congruently. Solubility isotherms show initial
   enhancement by addition of NaCl at both temperatures. The curves reach weak maxima at
   $X_{\text{NaCl}} \sim 0.25-0.33$. Mg-chloride and hydrous Na-silicate are likely the most abundant
   species in these solutions.

2. Enstatite dissolution in H$_2$O-NaCl solutions was measured at 1 GPa, 800°C and 900 °C.
   Dissolution is incongruent, to forsterite + solutes, at all conditions studied. Additional
   experiments with excess SiO$_2$ reveal that only minor additional silica is required to
   suppress forsterite growth. Combination of the forsterite results permitted derivation of the
   compositions of fluids coexisting with enstatite + forsterite to constrain Si and Mg. Si and
   bulk solute concentrations decline slightly with rising NaCl; Mg content increases, similar
   to forsterite. Enstatite salts out with increasing NaCl. The behavior is similar to that of
quartz, though the magnitude is less pronounced. This is likely because formation of Mg-chloride complexes promotes greater relative amounts of enstatite dissolution, leading to higher relative Si concentrations than in Mg-free, quartz-saturated solutions.

3. Diopside dissolution was investigated in pure H$_2$O at 0.7-1.5 GPa at 800 °C and at 650-900 °C at 1 GPa. Diopside solubility was also measured in H$_2$O-NaCl at 1 GPa and 800 °C. Diopside dissolves incongruently to forsterite + solutes at all conditions. In pure H$_2$O, apparent solubility rises with increasing temperature and pressure. Apparent solubility also rises with NaCl. Our new results are generally consistent with previous work. The compositions of H$_2$O-NaCl fluids could be derived at 800 °C, 1 GPa, where forsterite solubility was also determined. Results show that $m_{Si} > m_{Ca} > m_{Mg}$. The pattern of bulk diopside solubility enhancement is similar to that of wollastonite, and points to greater stability of Ca-chloride complexes relative to Mg-chloride complexes.

4. As a fluid moves from slab to wedge and therefore decompresses and heats up, forsterite, enstatite and diopside solubilities will all increase despite decreasing pressure. Fluids equilibrated with ultramafic rocks containing olivine, opx and cpx along this path will increase in total dissolved solids at a given $X_{NaCl}$, with Si > Ca > Mg. These fluids may then interact with lower mantle/upper crustal minerals assemblages and melts as they migrate, providing a mechanism for refertilization of depleted harzburgite.

5. In lower-crustal settings, fluid flow paths can be expected to mainly involve cooling and decompression, resulting in declining solubilities of forsterite, diopside and enstatite, while the solubility order is maintained. This can yield metasomatic addition of Si, Ca and Mg downstream through precipitation of CMSH minerals in flow conduits. Pyroxenite veins are thus explainable by rising and cooling hydrothermal solutions.
6. The significant solubility increase of forsterite and diopside in NaCl-rich solutions could account for metasomatism at deep levels of a cooling gabbro/ultramafic intrusion, with deposition of dunite or clinopyroxenite veins, while the high solubility of enstatite in such fluids could cause desilication of harzburgite to dunite.

6 ACKNOWLEDGEMENTS

Supported by NSF grants EAR-1347987 and 1732256.
Figure Captions

Fig. 1. The range of P-T conditions investigated in this study (pink shaded region) compared to previous work on diopside solubility, including the relatively low P-T data of Schmulovich et al. (2001) at 650 °C and 0.5 GPa and Budanov and Shmulovich (2000) at 650 °C and 0.2 – 0.75 GPa (yellow shaded region), and the much hotter and deeper conditions of the early experiments by Eggler and Rosenhauer (1978) (1200 °C and 2 GPa and 1180 °C and 3 GPa) and Schneider and Eggler (1986) (1100 °C and 2 GPa) (orange shaded regions). Also shown in (b) (in green) is the P-T range of previous experimental investigation of the solubility of MgO-SiO$_2$-H$_2$O minerals in chloride fluids (Frantz and Popp, 1979; Luce et al., 1985). (a) Cross section of a model ‘warm’ subduction zone showing isotherms and H$_2$O released from hydrous minerals in the slab (light blue arrows) and wedge (dark blue arrows). Figure modified from Till et al. (2008); their Fig. 8. Regions where experimental studies are relevant, shown as colored boxes (colors as described above). (b) Pressure-temperature phase diagram showing model ultramafic phase relations and locations of experimental studies (colors as described above). Abbreviations: clinopyroxene (Cpx), clinoamphibole (Camp), garnet (Grt), olivine (Ol), plagioclase (Pl), talc (Ta), antigorite (atg), chlorite (Chl), orthopyroxene (Opx). Phase relations calculated for simplified KLB-1 (Davis et al., 2009): Na$_2$O (0.24 mol%), CaO (2.82 mol%), FeO$_{tot}$ (5.88 wt%), MgO (50.53), Al$_2$O$_3$ (1.77 mol%), SiO$_2$ (38.47 mol%), O (0.096 mol%) H$_2$O (saturated, a$_{H2O}$ = 0.67), with 0.3 wt% Fe$_2$O$_3$ (Jennings et al 2015). Constructed using PERPLE_X (v. 6.8.8, Connolly and Kerrick, 1987; Connolly, 2005), thermodynamic datafile DS6.22 (Holland and Powell, 2011), and activity-composition relations as follows: Cpx, Grt, Pl and Ol (Jennings and Holland, 2015), Camp (Green et al., 2016), Opx (Holland et al., 2013), Chl (White et al., 2014), Tlc (Holland and Powell, 1998), Atg (Padrón-Navarta et al., 2013). Melt composed of forsterite (foL), fayalite (faL), wollastonite
Fig. 2. Backscattered electron (BSE) images of run products from forsterite and enstatite solubility experiments. (a) Image of forsterite crystal from run Fo-09 in pure H$_2$O (800 °C, 1 GPa, Table 1) showing small brucite grains growing in pits on the surface as a result of incongruent dissolution. (b) Higher magnification image of Fo-09 showing detail of brucite crystals on the surface of the residual forsterite grain. (c) Forsterite crystal from run Fo-20 (900 °C, 1 GPa, $X_{\text{NaCl}}=0.300$, Table 1) showing absence of brucite crystals; i.e., congruent dissolution. (d) BSE image of synthetic enstatite crystal partially converted to forsterite in run En-03 (Table 2). Note the hole in the forsterite crust, with smooth surface of original enstatite visible within. Larger forsterite grain size suggests the opening was present during the run. Higher BSE intensity spherules are Si-rich quench. Fo, forsterite; Br, brucite; En, enstatite.

Fig. 3. Solubility of forsterite in molality ($m_{\text{Fo}}$) versus $X_{\text{NaCl}}$ at 1 GPa and 800 °C (purple squares) and 900 °C (crimson squares). $2\sigma$ errors shown where larger than symbol size. Curves correspond to Eq. 5 (purple) and Eq. 6 (red) in the text, with the form $y = m_0 + m_1 X_{\text{NaCl}} + m_2 X_{\text{NaCl}}^{1/2}$. $1\sigma$ errors in the $m_0$-$m_2$ fit parameters are respectively 0.0011, 0.01, and 0.007 at 800 °C, and 0.0016, 0.016, and 0.011 at 900 °C. (For interpretation of the references to color in the figure legend, the reader is referred to the web version of this article.)

Fig. 4. (a) Apparent solubility of enstatite at 800 and 900 °C, 1 GPa, versus NaCl mole fraction.
Upward pointing triangles represent apparent solubility in the presence of forsterite, which is assumed to be insoluble (see text). Downward pointing triangles are true solubility in the absence of forsterite, in experiments to which excess Si was added. The two types of experiments respectively constrain lower and upper bounds on the solubility of enstatite alone at Si concentration just sufficient to suppress forsterite. Lines are linear best fits to the midpoints between these bounds. Values at $X_{NaCl} = 0$ from Newton and Manning (2002a). (b) Calculated molalities of Si and Mg versus $X_{NaCl}$ in enstatite + forsterite saturated fluids. Solute concentrations derived using results of forsterite solubility experiments (Eqs. 5 and 6; see text). Lines are linear best fits to the results. (c) Molar Si/Mg versus $X_{NaCl}$. The blue curve is a best fit to the combined data: $Mg/Si = 0.00825 + 0.6956 X_{NaCl} + 0.1685 X_{NaCl}^2$. In all panels, $2\sigma$ errors are shown where larger than symbol size. (For interpretation of the references to color in the figure legend, the reader is referred to the web version of this article.)

Fig. 5. Backscattered electron (BSE) images of run products from diopside solubility experiments showing textures of residual diopside and forsterite crystals, as well as quench phases (wollastonite and enstatite). (a) Image of diopside crystal from run gdi5 (650 °C, 1 GPa, pure H$_2$O) showing subhedral forsterite grains growing in pits on the surface. (b) Image of diopside crystal from run gdi3 (700 °C, 1 GPa, pure H$_2$O) showing details of forsterite grains growing in pits on the surface. (c) Diopside crystal from run db4 (800 °C, 1 GPa, $X_{NaCl}=0.317$) with forsterite crystals partially covered by acicular sprays of quench wollastonite and enstatite. (d) Materials retrieved from the inner capsule of run db6 (800 °C, 1 GPa, $X_{NaCl}=0.496$): quench wollastonite blades, amorphous silica spheres and residual forsterite (diopside crystal not shown). Fo: forsterite; Di: diopside; Wo: wollastonite; En: enstatite.
Fig. 6. Apparent solubility of diopside in pure H$_2$O as function of temperature at 1 GPa (a) and of pressure at 800 °C (b). Curves calculated from Eq. 9. 2σ errors are shown where larger than symbol size.

Fig. 7. (a) Apparent solubility of diopside with increasing X$_{NaCl}$ at 1 GPa and 800 °C. Curve calculated from Eq. 10. 2σ errors are shown where larger than symbol size.

Fig. 8. Comparison of Mg concentration in H$_2$O-NaCl solutions coexisting with forsterite and enstatite at 1 GPa, 800 and 900 °C. Forsterite data are shown in purple (800 °C) and red (900 °C) squares. Purple and red curves calculated from Eqs. 5 and 6. Downward pointing dark blue and light blue triangles correspond to the Mg content at 800 and 900 °C in experiments in which only enstatite was present as a run product (Table 2). 2σ errors shown where larger than symbol size. The similarity of the Mg concentrations in fluids coexisting with enstatite and forsterite supports assumptions used to derive the adjusted compositions of fluids coexisting with forsterite+enstatite. (For interpretation of the references to color in the figure legend, the reader is referred to the web version of this article.)

Fig. 9. Comparisons of diopside apparent solubility determined in this study (Eqs. 9 and 10, green curves) with results of previous work. (a) 2.0 GPa, pure H$_2$O (Schneider and Eggler, 1986 (S86); Eggler and Rosenhauer, 1978 (E78), blue circle). There is good agreement between our predicted values and the datum of Schneider and Eggler (1986). Discrepancy with the results of Eggler and Rosenhauer (1978) is likely due to their short run times, phase equilibrium methods, and possibly...
nonobservation of incongruent dissolution (see text). (b) 0.5 GPa, pure H$_2$O (Budanov and Shmulovich, 2000 (B00), red circle; Shmulovich et al., 2001 (S01), purple circle). Our predicted solubility at 650 °C lies between the previous results. (c) 650 °C, pure H$_2$O (Budanov and Shmulovich, 2000 (B00), red circles; Shmulovich et al., 2001 (S01), purple circle). The results are in reasonable agreement with the exception of the 0.75 GPa datum of Budanov and Shmulovich (2000). (d) 650 °C, H$_2$O-NaCl solutions (Budanov and Shmulovich, 2000 (B00) at 0.2 GPa (orange circles), 0.5 GPa (purple circles), and 0.75 Gpa (red circles). The Budanov and Shmulovich (2000) data at 0.2 and 0.5 GPa display a dependence on $X_{NaCl}$ that is similar to that in our study, but apparent solubilities are lower, consistent with the lower $P$ and $T$. In contrast, the data at 0.75 GPa display a different $X_{NaCl}$ dependence, likely due to inaccurately high measured solubility in pure H$_2$O. A similar functional form of the $X_{NaCl}$ dependence is obtained if the data are refit using the pure H$_2$O value predicted from Eq. 9 (dashed red line; see text). Errors in previous work are $2\sigma$ where given, and shown only where larger than symbols. (For interpretation of the references to color in the figure legend, the reader is referred to the web version of this article.)

**Fig. 10.** Plots comparing the solubility behavior of selected minerals with increasing $X_{NaCl}$ at 800 °C and 1 GPa, using different concentration scales. Minerals depicted are: quartz (black triangles), enstatite (dark blue triangles), forsterite (purple squares), wollastonite (light blue circles) and diopside apparent (dark green diamonds). (a) Mineral solubility on the molal concentration scale. Enstatite and diopside shown as Si molality, the most abundant solute. (b) Mineral solubility on parts per million concentration scale. Enstatite shown where coexisting with forsterite. (c) Mineral solubilities on mole fraction concentration scale ($X$), relative to the mole fraction in pure H$_2$O ($X^\circ$). Enstatite and diopside solubilities depicted using total moles of solute, as calculated where
coexisting with forsterite. The contrasting trends of solubility change with NaCl reflect omission
(a) vs. inclusion (b and c) of NaCl in the solvent. 2σ errors shown where larger than symbol size;
the comparatively large errors in forsterite in (c) arise from the projection method used to obtain
solubility in pure H₂O (X°, see text). (For interpretation of the references to color in the figure
legend, the reader is referred to the web version of this article.)

Fig. 11. Comparison of forsterite, enstatite and diopside solubilities from this study with other
mineral solubility data from previous studies as a function of fluid NaCl content (X_{NaCl}) at 800°C,
1.0 GPa. Solubilities here are presented in parts per million (ppm) on a log scale for more direct
inter-mineral comparison. Minerals (x-axis) are ordered in terms of increasing solubility in pure
H₂O. Forsterite solubility is low relative to other silicates such as quartz, wollastonite, grossular,
and diopside. Note the significant solubility enhancement experienced by Ca-salts (phosphate,
fluoride, sulfate) in concentrated NaCl solutions, compared to that of silicates. Enstatite and quartz
show the opposite behavior, with decreasing solubility in brines. Solubility data are from Newton
and Manning (2000a, 2002a,b, 2005, 2006, 2007), Tropper and Manning (2007), Antignano and
Manning (2008a,b), Tropper et al. (2011) and this study.

Fig. 12. Solubilities in ppm (log scale) of phosphate, oxide, silicate, halide, carbonate, and sulfate
minerals in pure H₂O at 800 °C and 1 GPa, plotted against (a) cation radius, (b) average ionic
potential, and (c) average force constant. The legend on the right applies generally to all plots,
except in (a) filled symbols refer to the inter-radical cation in the mineral and open symbols of the
same color refer to the intra-radical cation(s) in the mineral structure. In the case of a mineral
having more than one intra-radical cation, a weighted average of both cations are plotted according
to mineral stoichiometry. Average ionic potential in (b) is defined as cation charge \( z \) divided by radius \( r \) (cation radii used here are the effective ionic radii of Shannon (1976)). Average force constant \( K_f \) in (c) is a measure of bond strength calculated using Eq. 5 in Macris et al. (2015). See supplementary material for a complete discussion of the force constant calculations. Solubility data as in Fig. 11.

**Fig. S1.** Solubility versus experiment duration at fixed \( P, T \), and fluid composition. (A) Forsterite solubility at 900 °C, 1 GPa, \( X_{NaCl} = 0.3 \). Runs of 11-32 hours yield a constant solubility of 0.0636 molal; however, a spuriously high solubility was observed in a longer experiment due to formation of vapor-transport crystals (see text). (B) Apparent diopside solubility at 700 °C, 1 GPa, in pure \( H_2O \). Vapor transport crystals grew in the 18 h experiment, yielding a spuriously high solubility compared to the mean of the other runs of varying duration (0.0061 molal).
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**Fig. 3**

Backscattered electron (BSE) images of run products from forsterite solubility experiments.

(a) Image of forsterite crystal from run Fo-09 in pure H$_2$O showing small brucite grains growing in pits on the surface as a result of incongruent dissolution.

(b) Higher magnification image of Fo-09 showing detail of brucite crystals on the surface of the residual forsterite grain.

(c) Forsterite crystal from run Fo-20 in NaCl+H$_2$O showing absence of brucite crystals, i.e., congruent dissolution.

(d) Materials retrieved from the inner capsule of run Fo-20: quench enstatite sprays and amorphous silica spheres.

Fo: forsterite; Br: brucite; En: enstatite.

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Pure H$_2$O
$800 ^\circ C$, 1 GPa

$X_{NaCl} = 0.30$
$900 ^\circ C$, 1 GPa

250 µm

100 µm

500 µm

200 µm
$y = m_1 + m_2 \cdot M_0 + m_3 \cdot M_0^{0.5}$

Error Value

$m_1 = 0.0103 \pm 0.0072651$
$m_2 = 0.031103 \pm 0.037725$
$m_3 = 4.0292e^{-6}$

$\text{Chisq} = 0.99818$

$R = 0.99818$

$H_2O-NaCl$

$1 \text{ GPa}$

Forsterite solubility (mol/kg $H_2O$) vs. $X_{NaCl}$
Pure H$_2$O
650 °C, 1 GPa

Pure H$_2$O
700 °C, 1 GPa

$X_{\text{NaCl}} = 0.053$
800 °C, 1 GPa

$X_{\text{NaCl}} = 0.37$
800 °C, 1 GPa

Fig 3
Diagram a: Diopside at 1 GPa and Pure H$_2$O

Diagram b: Diopside at 800 °C and Pure H$_2$O

Apparent molality vs. Temperature (°C) for 1 GPa and Pure H$_2$O

Apparent molality vs. Pressure (GPa) for 800 °C and Pure H$_2$O
Diopside
800 °C, 1 GPa
H₂O-NaCl

Apparent molality

\[ y = m_1 + m_2 \cdot M_0 + m_3 \cdot M_0^{0.5} \]

Error

Value

0.0064976
0.0049304

m_1

0.057322
0.071644

m_2

0.042383
0.19941

m_3

NA
0.00021208

Chisq

NA
0.99541

R

0.00
0.05
0.10
0.15
0.20
0.25
0.30

0.0
0.1
0.2
0.3
0.4
0.5
0.6

X

NaCl

Element molality

Si
Ca
Mg

b
**Figure a**: Apparent molality of pure water at 2 GPa. The graph shows the relationship between temperature (°C) and apparent molality. The data points are labeled with S86, E78, Eq 9, and the solid line represents the model Eq 9.

**Figure b**: Apparent molality of pure water at 0.5 GPa. Similar to Figure a, this graph also shows the relationship between temperature (°C) and apparent molality. The data points are labeled with B00, S01, Eq 9, and the solid line represents the model Eq 9.

**Figure c**: Apparent molality of pure water at 650 °C for a pressure range of 0 to 1.5 GPa. The graph includes data from B00, S01, this study, and the solid line represents the model Eq 9.

**Figure d**: Apparent molality of water-nitrate (H₂O-NaCl) system. The graph shows the relationship between pressure (GPa) and apparent molality, with data points for different temperatures and pressures at 650 °C. The models include This study, B00, and the solid line represents the model Eq 9.
Table 1. Forsterite solubility experiment measurements at 1GPa.

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<th>Expt. ID</th>
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<th>t (h)</th>
<th>H₂O in (mg)</th>
<th>NaCl in (mg)</th>
<th>X_{NaCl}</th>
<th>qtz in (mg)</th>
<th>xl in (mg)</th>
<th>xl out (mg)</th>
<th>IC in (mg)</th>
<th>IC out (mg)</th>
<th>m_{Fo} (mol/kg H₂O)</th>
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<td>0.000</td>
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</tbody>
</table>

Explanation: forsterite solubility (m_{Fo}) calculated from crystal weight change unless noted; “in” and “out” refer to weights before and after experiment; “xl”, crystal; “mid”, solubility is midpoint between values derived from crystal and capsule weight change; “vt”, vapor transport; “short”, insufficient run duration (see text). 1σ errors in weights given to three and four decimal places are respectively 0.002 and 0.0002 mg; errors in solubility (in parentheses) are propagated 1σ weighing errors in last decimal places.
### Table 2. Results of enstatite solubility experiments.

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<th>Expt. ID</th>
<th>T (°C)</th>
<th>P (GPa)</th>
<th>time (h)</th>
<th>H$_2$O in (mg)</th>
<th>NaCl in (mg)</th>
<th>NaCl qtz in (mg)</th>
<th>NaCl xl in (mg)</th>
<th>NaCl xl out (mg)</th>
<th>NaCl IC in (mg)</th>
<th>NaCl IC out (mg)</th>
<th>Apparent solubility (mol/kg H$_2$O)</th>
<th>$m_{Si}$ (mol/kg H$_2$O)</th>
<th>$m_{Mg}$ (mol/kg H$_2$O)</th>
<th>Notes</th>
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<td>0.251(12)</td>
<td>0.033(06)</td>
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<td>0.215(09)</td>
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<td>0.3294</td>
<td>1.2831</td>
<td>1.1657</td>
<td>59.395</td>
<td>59.301</td>
<td>0.268(04)</td>
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Explanation: Abbreviations and weight errors as in Table 1, except: “nd”, not determined; “+fo”, forsterite present; “-fo”, forsterite absent. All solubility entries are midpoints between those from crystal and inner capsule weight changes, except En-06 for which xl out could not be weighed. Where forsterite was present, apparent solubility assumes solute is SiO$_2$ only, and $m_{Si}$ and $m_{Mg}$ were calculated using Eqs. 3, 5 and 6 (see text). Numbers in parentheses are 1σ errors in final digits calculated numerically by Monte Carlo simulation (10,000 trials) based on weighing errors and errors in Eqs. 5 and 6; 1σ errors in NaCl are 2 to 4x10$^{-5}$ and are omitted.
Table 3. Results of diopside solubility experiments.

<table>
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<th>H2O in (mg)</th>
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<th>NaCl in (mg)</th>
<th>NaCl out (mg)</th>
<th>IC in (mg)</th>
<th>IC out (mg)</th>
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<th>Adjusted mSi (mol/kg H2O)</th>
<th>Adjusted mCa (mol/kg H2O)</th>
<th>Adjusted mMg (mol/kg H2O)</th>
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<td>gdi13</td>
<td>800</td>
<td>1.2</td>
<td>10</td>
<td>35.375</td>
<td>34.208</td>
<td>0.413</td>
<td>0.326</td>
<td>52.863</td>
<td>52.791</td>
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<td>gdi12</td>
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<td>1.5</td>
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<td>33.755</td>
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<td>0.720</td>
<td>54.050</td>
<td>53.947</td>
<td>0.0208(6)</td>
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<tr>
<td>gdi8</td>
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<td>36.666</td>
<td>36.695</td>
<td>0.487</td>
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<tr>
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<td>nd</td>
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<td>0.681</td>
<td>0.611</td>
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<tr>
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<td>31.380</td>
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<td>1.144</td>
<td>1.075</td>
<td>53.665</td>
<td>53.605</td>
<td>0.0141(8)</td>
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Explanation: Abbreviations and weight and solubility errors as in Tables 1 and 2, except: “xl only” indicates solubility determined by weight change of the crystals because inner capsule weight could not be determined due to partial welding to outer capsule. All solubility entries are midpoints between crystal and inner capsule results using “H2O in” unless not determined. Apparent solubility calculated assuming solute is CaSi1.5O4; mSi, mCa, and mMg are calculated using Eqs. 4 and 5 (see text). Numbers in parentheses are 1σ errors in final digits calculated numerically by Monte Carlo simulation (10,000 trials) based on weighing errors and error in Eq. 5; 1σ errors in XNaCl are 2 to 4x10⁻⁵ and are omitted.