Novella, D., Dolejš, D., Myhill, R., Pamato, M. G., Manthilake, G., & Frost, D. J. (2017). Melting phase relations in the systems $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ and $\text{MgSiO}_3\text{-H}_2\text{O}$ and the formation of hydrous melts in the upper mantle. *Geochimica et Cosmochimica Acta*, 204, 68-82.
<https://doi.org/10.1016/j.gca.2016.12.042>

Peer reviewed version

Link to published version (if available):
[10.1016/j.gca.2016.12.042](https://doi.org/10.1016/j.gca.2016.12.042)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via Elsevier at <http://www.sciencedirect.com/science/article/pii/S0016703717300054> . Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

1 **Melting phase relations in the systems $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ and $\text{MgSiO}_3\text{-H}_2\text{O}$ and the**
2 **formation of hydrous melts in the upper mantle**

3

4 Davide Novella ^{a,b,c*}, David Dolejš ^{d,e}, Robert Myhill ^{a,f}, Martha G. Pamato ^{a,g}, Geeth
5 Manthilake ^{a,b} and Daniel J. Frost ^b

6

7 ^a Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, D-95447
8 Bayreuth, Germany

9 ^b Laboratoire Magmas et Volcans, Université Blaise Pascal, 5 Rue Kessler, 63038
10 Clermont-Ferrand, France

11 ^c Lawrence Livermore National Laboratory, Livermore, California 94550, USA

12 ^d Institute of Petrology and Structural Geology, Charles University, Albertov 6, CZ-12843
13 Praha 2, Czech Republic

14 ^e Present address: Institute of Earth and Environmental Sciences Albert-Ludwigs-
15 University of Freiburg, Albertstrasse 23b, D-79104, Freiburg, Germany

16 ^f Present address: School of Earth Sciences, University of Bristol, Queens Road, BS8
17 1RJ, Bristol, UK

18 ^g Present address: Department of Earth Sciences, University College London, Gower
19 Street, WC1E 6BT, London, UK

20

21 *Corresponding author. E-mail: dn345@cam.ac.uk; Tel: +44 1223 768327

22 Present address: Department of Earth Sciences, University of Cambridge, Downing
23 Street, CB2 3EQ, Cambridge, UK

24 **Abstract**

25 High-pressure and high-temperature melting experiments were conducted in the systems
26 $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ and $\text{MgSiO}_3\text{-H}_2\text{O}$ at 6 and 13 GPa and between 1150 to 1900 °C in order to
27 investigate the effect of H_2O on melting relations of forsterite and enstatite. The liquidus
28 curves in both binary systems were constrained and the experimental results were
29 interpreted using a thermodynamic model based on the homogeneous melt speciation
30 equilibrium, $\text{H}_2\text{O} + \text{O}^{2-} = 2 \text{OH}^-$, where water in the melt is present as both molecular H_2O
31 and OH^- groups bonded to silicate polyhedra. The liquidus depression as a function of
32 melt H_2O concentration is predicted using a cryoscopic equation with the experimental
33 data being reproduced by adjusting the water speciation equilibrium constant. Application
34 of this model reveals that in hydrous MgSiO_3 melts at 6 and 13 GPa and in hydrous
35 Mg_2SiO_4 melts at 6 GPa, water mainly dissociates into OH^- groups in the melt structure.
36 A temperature dependent equilibrium constant is necessary to reproduce the data,
37 however, implying that molecular H_2O becomes more important in the melt with
38 decreasing temperature. The data for hydrous forsterite melting at 13 GPa are
39 inconclusive due to uncertainties in the anhydrous melting temperature at these
40 conditions. When applied to results on natural peridotite melt systems at similar
41 conditions, the same model infers the presence mainly of molecular H_2O , implying a
42 significant difference in physiochemical behavior between simple and complex hydrous
43 melt systems. As pressures increase along a typical adiabat towards the base of the upper
44 mantle, both simple and complex melting results imply that a hydrous melt fraction
45 would decrease, given a fixed mantle H_2O content. Consequently, the effect of pressure

on the depression of melting due to H₂O could not cause an increase in the proportion, and hence seismic visibility, of melts towards the base of the upper mantle.

Keywords: olivine, enstatite, phase equilibria, hydrous melting, cryoscopic equation, water speciation.

1. Introduction

The effect of H₂O on the formation of silicate melts underlies a number of igneous processes taking place within the Earth's mantle. H₂O has an important influence on the generation of magmas at subduction zones being both a metasomatic agent of the arc magma source region and responsible for the high degrees of melting that produce these magmas (e.g. Tatsumi et al., 1986). The lithospheric mantle shows abundant evidence for metasomatism by H₂O-bearing melts (e.g. Menzies and Hawkesworth, 1987; Erlank et al. 1987) and several exotic magma types such as kimberlites and lamproites are likely formed, at least in part, as a result of H₂O lowering the mantle solidus (e.g. Kushiro et al., 1968; Kawamoto and Holloway, 1997; Sokol et al., 2013). H₂O induced melting of the deep mantle has also been proposed to explain a number of geophysical observations such as the Earth's seismic low velocity zone (Lambert and Wyllie, 1970; Mierdel et al., 2007) and possible low velocity layers present on top of the transition zone (Tauzin et al., 2010) and immediately below it (Schmandt et al., 2014). Recently, it was proposed that H₂O-induced melts would tend to migrate in the lower mantle, and transfer H₂O from ultramafic to mafic lithologies, as a result of the difference in H₂O storage capacities of these rock types (Pamato et al., 2015).

69

70 In order to understand the production of hydrous melts in the Earth's mantle it is
71 important to constrain how H₂O affects the melting behaviour of mantle materials. In this
72 regard, a number of studies have been performed to quantify the effects of H₂O on
73 lowering melting temperatures and increasing melt yields in natural mantle rock systems
74 (Mysen and Boettcher, 1975; Hirose and Kawamoto, 1995; Gaetani and Grove, 1998;
75 Balta et al., 2011; Tenner et al., 2012b; Novella et al., 2014). Determining the effect of
76 H₂O on melting in natural chemical systems is challenging, however, due to the large
77 number of chemical components that are potentially influenced by H₂O. These
78 determinations are further complicated by a number of other instrumental factors, such as
79 control of oxygen fugacity, attainment of equilibrium, H₂O and FeO loss from
80 experimental capsules and the difficulty in determining the H₂O contents of melts
81 (Brooker et al., 1998; Liu et al., 2006; Tenner et al., 2012b; Novella and Frost, 2014).

82

83 It has long been appreciated that the effects of H₂O on silicate melts can be more easily
84 quantified by examining melting behavior in simple systems (Kushiro et al, 1968;
85 Kushiro and Yoder, 1969; Kushiro, 1972; Hodges, 1973, 1974). From results of
86 experiments in simple systems such as Mg₂SiO₄-SiO₂-H₂O, Kushiro (1972) proposed, for
87 example, that hydrous mantle partial melts would be more SiO₂-rich compared to dry
88 melts. Studies in simple systems can also be used to quantify the effect of H₂O on mineral
89 melting at high pressures and experiments have been performed up to conditions
90 equivalent to those in the mantle transition zone (Kushiro and Yoder, 1969; Luth, 1993;
91 Inoue, 1994). While relatively detailed melting phase relations on hydrous forsterite

(Kushiro and Yoder, 1969; Hodges 1973) and enstatite (Kushiro and Yoder, 1969; Kushiro et al., 1968) exist up to 3 GPa, phase relations at higher pressures are more sparse and show less mutual agreement. Luth (1993) and Inoue (1994) investigated the melting behavior of forsterite with 17-20 wt% H₂O up to pressures of 12 and 15.5 GPa, respectively, although the two studies are in poor agreement. In addition, Inoue (1994) also studied the phase relations of hydrous enstatite and an intermediate Mg/Si ratio composition to similar pressures. However, in this previous study more emphasis was placed on determining the conditions of the hydrous solidus rather than quantifying the effect of melt H₂O content on the melting temperature.

Recently, several studies on natural multicomponent systems have proposed generalized models for the effects of H₂O on peridotite melting temperatures (Medard and Grove, 2008; Tenner et al., 2012a). While such models are quite successful in reproducing the experimental observations, they make assumptions concerning both the thermodynamic data and the mechanism by which H₂O dissolves in melts that can be more easily tested using results on simplified systems. In simplified systems additional constraints are also provided by calorimetric measurements such as those performed to determine the entropy of melting (Bottinga, 1985; Navrotsky et al., 1989; Richet et al., 1993; Tangeman et al., 2001). One advantage of examining experiments in simple systems is that treatment with relatively simple thermodynamic models should provide a firmer basis for understanding hydrous melting on a physicochemical level (Burnham, 1975; Silver and Stolper, 1985) and can be used to examine how the effect of H₂O on melting may be further modified by pressure.

115

116 The goal of this study is to determine the melting phase relations in the systems Mg_2SiO_4 -
117 H_2O and MgSiO_3 - H_2O at upper mantle conditions. In particular, we investigate the H_2O
118 contents of melts in equilibrium with forsterite and/or enstatite as a function of
119 temperature at high pressure by bracketing the location of the hydrous liquidus curves.
120 The experimental data are analysed using thermodynamic models to provide insight into
121 the H_2O dissolution mechanism and its effects at high pressures. Results are presented for
122 both systems at 6 and 13 GPa corresponding to ~ 180 and ~ 390 km depth in the mantle,
123 and temperatures ranging between 1150 to 1900 °C.

124

125 **2. Experimental and analytical details**

126 Two sets of compositions were prepared for experiments in the systems Mg_2SiO_4 - H_2O
127 and MgSiO_3 - H_2O . In the system Mg_2SiO_4 - H_2O , starting compositions were mixed from
128 two end-member compositions: Mg_2SiO_4 (forsterite) synthesized from high purity oxides,
129 MgO and SiO_2 , and a 2:1 molar mixture of $\text{Mg}(\text{OH})_2$ (brucite) and SiO_2 . The pure
130 forsterite was synthesized by firing the oxides at 1500 °C for 2 hours and then grinding
131 the sintered mix for 1 hour under ethanol. This firing and grinding process was repeated 4
132 times. The 2:1 brucite-silica mixture corresponds to a composition of Mg_2SiO_4 with 20.4
133 wt% H_2O in the bulk. In order to prepare this end member, brucite and SiO_2 were dried
134 overnight at 120 °C and 1000 °C, respectively. The calculated amount of each component
135 was then weighed, ground for 1 hour under ethanol and dried under an infrared lamp. By
136 varying the mass proportions of the end member compositions a range of mixtures were
137 prepared with variable H_2O content but with a constant stoichiometry of $\text{Mg}/\text{Si} = 2$ (Table

1). All mixtures with water contents less than 20.4 wt% were prepared by grinding the weighed proportions of dry forsterite and forsterite with 20.4 wt% bulk H₂O for 30 minutes under ethanol, and then drying. Before each mixture was prepared the forsterite end-member was dried at 1000 °C for one hour and the water-bearing forsterite end-member was dried overnight at 120 °C. This approach was also followed for the preparation of starting mixtures in the system MgSiO₃-H₂O. In this case, an end-member 1:1 molar mixture of brucite and SiO₂, corresponding to a composition of MgSiO₃ with 15.2 wt% bulk H₂O, was initially prepared (Table 1). The dry end-member MgSiO₃ was prepared from high purity oxides MgO and SiO₂ and the dry and hydrous end-members were mixed in different mass proportions to obtain the compositions given in Table 1. Once prepared, all final mixtures were stored in a furnace at 120 °C to limit the adsorption of water.

150

151 Platinum or platinum/rhodium multi-chamber capsules were fabricated from 2 mm
152 diameter Pt or Pt/Rh (Pt₉₀Rh₁₀) rods cut into 1 mm long sections. The resulting discs were
153 spark eroded on one surface, obtaining rows of 4 to 6 chambers per disc with the
154 chambers being 0.25 mm in diameter and approximately 0.66 mm deep. Each chamber
155 was loaded with a different starting powder such that H₂O contents increased across the
156 row of chambers. Sample powders were packed into each chamber using a tungsten-
157 rhenium needle. When packed sufficiently the chambers remained full even when air was
158 blown over the surface. Blowing air removed extraneous sample powders from chambers
159 that had not yet been loaded. The Pt capsules were closed by placing a second Pt disc
160 0.25 mm thick on top of the chambers, which was held closed under pressure. When
161 Pt/Rh capsules were employed the open extremities of the chambers were closed by
162 placing on top 6 foils of Pt/Rh with total thickness of ~0.25 mm.

163

164 High pressure and high temperature experiments were carried out using a multianvil
165 apparatus installed at the Bayerisches Geoinstitut (BGI). The experiments were
166 performed in an 18/11 assembly, with an 18 mm edge length Cr₂O₃-doped MgO
167 octahedral pressure medium and 11 mm WC-anvil corner truncations. Experiments at 6
168 GPa were performed using a 500 tonne Walker-type multi anvil press and a 5000 tonne
169 Kawai-type multianvil press. The experiments at 13 GPa were carried out only with the
170 5000 tonne multianvil apparatus. The pressure calibration at 6 GPa was performed using
171 the CaGeO₃ garnet to perovskite phase transition (Ross et al, 1986) for the 500 tonne
172 multianvil apparatus, while the pressure calibration described by Frost et al. (2004) was

employed for the experiments performed with the 5000 tonne press. A stepped graphite heater was used in the experiments at 6 GPa, while for those performed at 13 GPa a stepped LaCrO_3 heater was employed. Temperatures during the experiments were monitored using a $\text{W}_{97}\text{Re}_3\text{--W}_{75}\text{Re}_{25}$ (D type) thermocouple inserted within an alumina sleeve. The thermocouple junction was in contact with the base of the spark eroded capsules, ~ 0.5 mm from the sample chambers, with an estimated temperature uncertainty of 50°C (Frost et al., 2004). However, higher uncertainty (100°C) is considered for experiments where the thermocouple reading failed and temperature was determined based on power-temperature calibrations. A $25\text{ }\mu\text{m}$ thick foil of rhenium was placed on the top of the capsule in order to avoid direct contact between the capsule and the thermocouple junction. The maximum temperature fluctuation during the experiments was $\pm 5^\circ\text{C}$. The capsule was surrounded by MgO spacers and sleeves. Each experiment was first pressurised over 4 hours then heated in ~ 15 minutes to target temperature where it remained for up to 30 minutes depending on target temperature. Once completed, the experiment was quenched by turning off the power supply to the graphite/ LaCrO_3 heater, and decompression was carried out over approximately 15 hours.

After each experiment, the Pt or Pt/Rh sample disk was recovered, mounted in epoxy and polished in the absence of water. Due to the high porosity of the charges, impregnation with either epoxy resin or superglue was often required in order to avoid loss of material during the polishing. Once the samples were polished, phase identification and chemical analyses were carried out using a JEOL-JXA-8200 electron microprobe (EMPA) at the BGI. Conditions of 15 kV and 15 nA for the accelerating voltage and beam current,

respectively, were adopted in all the analyses, using a beam diameter of $\sim 1\ \mu\text{m}$. Standards for SiO_2 and MgO were forsterite and enstatite, respectively, and all the analyses were processed following the ZAF corrections.

Raman spectroscopy was conducted on some of the experimental charges to confirm the nature of the mineral phases produced. The analyses were performed using a LABRAM Raman spectrometer installed at the BGI and operating with a He-Ne laser with 632 nm red-line wavelength. Analyses were performed with a total of 3 spectrum collections and an accumulation time of 15 seconds each.

3. Results

Sections of typical experimental runs are shown in Fig. 1. At both pressures of 6 and 13 GPa melts quenched to produce a fine intergrowth of crystals. However, crystals that were solid phases during heating of the experiments were easily distinguished from the quenched crystals based on their euhedral character and grain size. In some experiments quenched areas with different grain sizes and crystallite shapes could be observed that might be interpreted as separate coexisting liquids, or vapour (Fig. 1a). Given that the H_2O contents of the charges are relatively low for fluid-saturated conditions to be encountered (e.g. Mibe et al., 2002), it seems more likely that these differences in texture result from local differences in nucleation and growth during quenching of the experiments. All quench textures are consistent with an origin as H_2O -bearing melts rather than aqueous fluids. This distinction is made based on the quench crystal density

compared to previous studies performed at lower temperatures where a sub-solidus aqueous fluid phase was encountered (Mibe et al. 2002).

Sections were ground by hand to over half way through the sample chambers to verify the absence of crystals in experiments interpreted to have encountered superliquidus conditions. Continual checks were made during grinding to examine for crystals that might not otherwise appear in the final section. Some samples were ground more than 80% through to ensure that no crystals were present in the charge. The small size of the sample chambers should ensure that thermal gradients across the samples are minimal. The large relative size of the metal capsule should also help to relax thermal gradients. Based on measurements performed in similar assemblies using two pyroxene thermometry (Brey et al., 1990), the thermal gradients within each chamber are estimated to be $<20^{\circ}\text{C}$.

Several experiments were performed at the same conditions but with different heating durations in order to assess H_2O loss from the Pt capsules during the experiments. Two experiments loaded with the same starting mixtures were performed at 6 GPa and 1400°C for 5 and 30 minutes, respectively, and in both cases the resulting assemblages in each of the sample chambers were identical. At 13 GPa the same result was obtained in two experiments performed at 1450°C . These observations imply that significant loss of H_2O does not occur in experiments with run durations up to 30 minutes at temperatures up to 1450°C . However, it was observed that in some experiments performed at higher temperatures ($>1650^{\circ}\text{C}$), run durations greater than 30 minutes led to substantial

crystallisation, likely due to H₂O loss from the Pt capsule. Therefore, experiments performed above 1650 °C were held at target temperature for 5-20 minutes only.

3.1 Experimental results at 6 GPa

Experimental conditions and phase assemblages of the runs performed at 6 GPa for both Mg₂SiO₄-H₂O and MgSiO₃-H₂O systems are summarized in Table 2. In the forsterite-H₂O system, experiments were performed from 1250 to 1650 °C (Fig. 2). In some runs performed at 1250 °C crystals of enstatite were also observed, possibly suggesting incongruent melting at these conditions. However, this observation is not in agreement with the experimental results of Inoue (1994), which indicate the transition from congruent to incongruent melting of forsterite in the system Mg₂SiO₄-H₂O to occur between 7.7 and 12 GPa. Rather than incongruent melting, the appearance of enstatite is possibly due to slight variations of certain starting mixtures from the Fo-H₂O join, which would be more visible at high degrees of crystallization. Our data suggest that the invariant curve Fo + En = Liquid is passing very close to the fo-H₂O line and possibly crossing it (Fig. 3), explaining the observed phase relations (Table 2). In experiments conducted at temperatures above 1250 °C, the run products contained either forsterite and melt or melt only, implying congruent melting. The run with the highest H₂O content (20.4 wt%) produced crystals in equilibrium with quenched melt at 1250 °C, hence it had not yet reached the liquidus temperature (Table 2). However, at temperatures higher than 1250 °C, most experiments had one or more chambers that contained a supraliquidus product that comprised only quenched melt. At 1400 °C, for example, forsterite crystals coexisting with melt were produced in charges with H₂O contents of 7.9, 9.7, 13.8 wt%,

but the run with 18.3 wt% H₂O contained only hydrous melt (Fig. 1b, Table 2). The proportion of crystals in each of these runs decreases in agreement with the lever rule as the crystal-melt region is crossed as a function of H₂O content in the system. No interpretation of these proportions is made, however, as it may be inaccurate due to the particular sample section obtained during polishing.

In the MgSiO₃-H₂O system, experiments were carried out from 1050 °C to 1650 °C, with starting mixtures containing up to 15.2 wt% H₂O (Table 2, Fig. 4). All run products contained enstatite and melt or melt only, indicating that melting occurred congruently over the entire temperature range. In one experiment (V704, Table 2) a tiny crystal of forsterite was found as an inclusion in a large enstatite crystal, but this was most likely a consequence of chemical inhomogeneity in the starting mixture. The enstatite liquidus is bracketed at 1650 °C at ~10 wt% H₂O and at 1500 °C at ~15 wt% H₂O.

3.2 Experimental results at 13 GPa

Experimental conditions and phase assemblages observed at 13 GPa for both systems Mg₂SiO₄-H₂O and MgSiO₃-H₂O are summarized in Table 3. Experiments were performed between 1300 and 1900 °C. In the Mg₂SiO₄-H₂O system, forsterite was found to melt incongruently to an assemblage containing enstatite, forsterite and hydrous melt at temperatures below 1600 °C (Fig. 5). However, the congruent forsterite liquidus could be bracketed at 1700 °C between 13.8 and 20.4 wt% H₂O and at 1900 °C between 5 and 13.8 wt % H₂O (Table 3). At 1300 °C, for example, the formation of forsterite in equilibrium with melt was observed at the highest bulk water contents (20.4 wt%), while enstatite was

also crystallized at lower bulk H₂O contents. This is possibly due to the fact that the univariant Fo + En = Liquid curve has moved closer to the Fo-H₂O join and small variations within the bulk composition causes enstatite to crystallize (Fig. 3). At 1500 °C, the Mg₂SiO₄ plus 5 wt% H₂O starting mixture produced forsterite and melt along with minute crystals of MgO (estimated to be <1 vol%). The lower temperature of this experiment compared to others where MgO was not observed implies that the MgO crystals most likely formed due to a slight inhomogeneity in the starting mixture, rather than an incongruent melting reaction. As we do not observe the presence of MgO in any other of the experiments it is likely that the Fo + Per = Liquid univariant curve crosses the Fo-H₂O join at lower H₂O contents than studied (Fig 3), which can be then roughly constrained using the study of Presnall and Walter (1993).

In the system MgSiO₃-H₂O, enstatite melted congruently at 1900 °C and the liquidus curve was bracketed at this temperature between 4.3 and 10 wt% H₂O (Fig. 6). However, in some of the experiments performed between 1300 and 1700 °C, the formation of small crystals of stishovite occurred along with enstatite and melt, in agreement with observations of Yamada et al. (2004) at 13.5 GPa. The presence of stishovite may be due to the fact that En + St + L univariant curve has moved near to the En-H₂O join, or even crossed it (Fig. 3). This phase, however, was observed only as a minor component, ~2 vol %, and is, therefore, not expected to cause significant departures from the determined phase relations. Additionally, the enstatite liquidus curve was bracketed at 1700 °C between 6.2 and 11.8 wt% H₂O. At 1600 °C, the most H₂O-rich charge (15.2 wt% H₂O)

produced an assemblage of enstatite plus melt, which constrains the minimum H₂O concentration of the liquidus melt at this temperature.

4. Discussion

4.1 Model for hydrous melting of Mg₂SiO₄ and MgSiO₃

A number of studies have examined the melting point depression of silicate minerals as a function of H₂O content in the melt using the cryoscopic equation (e.g. Silver and Stolper 1985; Medard and Grove, 2008; Hirschmann et al., 2009; Myhill et al., 2016). For Mg₂SiO₄ at the liquidus, for example,

$$\ln a_{\text{Mg}_2\text{SiO}_4}^{\text{melt}} = \frac{-\Delta_m G^\circ}{RT} \quad (1)$$

where $\Delta_m G^\circ$ is the standard state Gibbs free energy of melting of pure forsterite (see Appendix) and $a_{\text{Mg}_2\text{SiO}_4}^{\text{melt}}$ is the activity of the Mg₂SiO₄ component in the binary Mg₂SiO₄-H₂O melt. At temperatures below the pure forsterite melting point, $\Delta_m G^\circ$ can be determined by integrating the entropy of melting of pure Mg₂SiO₄, $\Delta_m S^\circ$, between the temperature of interest, T , and the anhydrous melting point, T_m . Assuming that $\Delta_m S^\circ$ is constant with temperature, Eq. (1) becomes:

$$\ln a_{\text{Mg}_2\text{SiO}_4}^{\text{melt}} = \frac{\Delta_m S^\circ (T - T_m)}{RT} \quad (2)$$

330

331 The standard entropies of melting for Mg_2SiO_4 and MgSiO_3 solid phases have been
332 derived from calorimetric measurements at 1 bar (e.g. Navrotsky et al. 1989; Richet et al.,
333 1993) and expressions for $\Delta_m S^\circ$ at higher pressures can be determined from data on the
334 anhydrous melting curves combined with equations of state for solid and liquid Mg_2SiO_4
335 or MgSiO_3 (see Appendix).

336

337 Use of the cryoscopic equation requires a plausible relationship between the activity and
338 concentration of silicate species in the hydrous melt, which will depend on the H_2O
339 concentration in the melt and its dissolution mechanism. Empirical molecular mixing of
340 Mg_2SiO_4 or MgSiO_3 and H_2O does not produce a sufficient depression of the liquidus to
341 explain the experimental data and it has long been recognized that upon dissolution in
342 silicate melts H_2O dissociates into hydroxyl groups bonded to the silicate framework
343 (Burnham 1975, 1979, 1994; Stolper, 1982; Silver and Stolper, 1989; Zotov and Keppler,
344 1998), i.e.

345

347

348 Spectroscopic analyses indicate that both molecular H_2O and OH^- groups are present in
349 silicate melts (e.g. Stolper, 1982, Dixon and Stolper, 1995), and their properties are
350 temperature-dependent (Nowak and Behrens, 1995; Zotov and Keppler, 1998). Silver and
351 Stolper (1985) proposed a thermodynamic model to describe the effects of H_2O
352 speciation on the activity of silicate melt components. They assumed that all three species

(H₂O, O²⁻ and OH⁻) mix ideally following a homogeneous melt equilibrium (Eq. 3). The activity of the silicate component, $a_{\text{Mg}_2\text{SiO}_4}^{\text{melt}}$, is related to the mole fraction of non-protonated oxygen atoms in the melt, $X_{\text{O}^{2-}}^{\text{melt}}$, through the expression

$$a_{\text{Mg}_2\text{SiO}_4}^{\text{melt}} = (X_{\text{O}^{2-}}^{\text{melt}})^r \quad (4)$$

where r is the number of oxygen atoms available for protonation and mixing per formula unit of silicate, with the chosen formula unit being consistent with the value of $\Delta_m S^\circ$. Setting $r=4$ for Mg₂SiO₄ or 3 for MgSiO₃ implies that H can bond to any of the oxygen atoms in the silicate melt structure.

The extent of H₂O dissociation in the silicate melt (Eq. 3) is described by the equilibrium constant K ,

$$K = \frac{(X_{\text{OH}^-}^{\text{melt}})^2}{X_{\text{H}_2\text{O}}^{\text{melt}} X_{\text{O}^{2-}}^{\text{melt}}}$$

(5)

Following mass balance,

$$X_{\text{H}_2\text{O}}^{\text{melt}} = X_{\text{H}_2\text{O}}^{\text{melt}} + 0.5 X_{\text{OH}^-}^{\text{melt}} \quad (6)$$

374 where $X_{\text{H}_2\text{O}^{\text{tot}}}^{\text{melt}}$ is the total mole fraction of H₂O in the silicate-H₂O melt. Solving Eqs. (5)

375 and (6) simultaneously, subject to the closure constraint

376

$$377 \quad X_{\text{H}_2\text{O}}^{\text{melt}} + X_{\text{OH}^-}^{\text{melt}} + X_{\text{O}^{2-}}^{\text{melt}} = 1 \quad (7)$$

378

379 yields mole fractions of all three species in the hydrous melt. Substituting Eq. (5) and (6)

380 into Eq. (7) yields

381

$$382 \quad X_{\text{H}_2\text{O}^{\text{tot}}}^{\text{melt}} = 1 - X_{\text{O}^{2-}}^{\text{melt}} + \frac{KX_{\text{O}^{2-}}^{\text{melt}} - \sqrt{(KX_{\text{O}^{2-}}^{\text{melt}})^2 + 4KX_{\text{O}^{2-}}^{\text{melt}} - 4K(X_{\text{O}^{2-}}^{\text{melt}})^2}}{4} \quad (8)$$

383

384 which is evaluated for the fraction of non-protonated oxygen atoms in the melt. The

385 corresponding activity of the silicate melt component is calculated from Eq. (4) and the

386 liquidus temperature is then defined by Eq. (2). In order to compare the results of the

387 model with experimental data, $X_{\text{H}_2\text{O}^{\text{tot}}}^{\text{melt}}$ can be converted to $w_{\text{H}_2\text{O}^{\text{tot}}}^{\text{melt}}$, the mass fraction of

388 H₂O dissolved in the melt using,

389

$$390 \quad w_{\text{H}_2\text{O}^{\text{tot}}}^{\text{melt}} = \frac{X_{\text{H}_2\text{O}^{\text{tot}}}^{\text{melt}} M_{\text{H}_2\text{O}}}{X_{\text{H}_2\text{O}^{\text{tot}}}^{\text{melt}} M_{\text{H}_2\text{O}} + (1 - X_{\text{H}_2\text{O}^{\text{tot}}}^{\text{melt}}) \frac{M_{\text{sil}}}{r}}$$

391 (9)

392

where $M_{\text{H}_2\text{O}}$ is the molar mass of water (18.015 g/mol) and M_{sil} is the molar mass of the silicate formula unit.

4.1.1 Liquidus depression at 6 GPa

Fig. 2 shows the experimental results for the forsterite liquidus as a function of melt H_2O content at 6 GPa compared to liquidus calculations using several limiting cases of the thermodynamic model. The thermodynamic data used to determine the anhydrous melting point of Mg_2SiO_4 and $\Delta_{\text{m}}S^\circ$ at the pressure and temperature of interest are listed in Table A (see Appendix and Supplementary Material).

Three different curves for the Mg_2SiO_4 liquidus are shown calculated for different values of the dissociation equilibrium constant, K . If all H_2O is completely dissociated to OH^- ($K = \infty$), the experimental data at the lowest temperatures are in poor agreement with the model as the experimental liquidus becomes less depressed at high H_2O contents. On the other hand, if all H_2O is dissolved in the molecular form ($K = 0$), the predicted liquidus curve is not in agreement with experimental data at any H_2O concentration. The change in slope of the experimental liquidus implies that K is not constant over the range of experimental temperatures, but must change from a high or infinite value (>50) above 1400 °C to <10 below 1300 °C, i.e. molecular H_2O becomes more important as the H_2O saturated solidus is approached. Variations in K with temperature can be described using the function,

$$\ln K = \frac{a}{T} + b, \quad (10)$$

416

417 which mimics the enthalpic and entropic contributions to K . The experimental data do not
418 provide sufficient constraints to determine the a and b coefficients in Eq. (10) uniquely
419 due to their high correlation. Values of $a \sim -7000$ K and $b \sim 5.6$ are in reasonable
420 agreement, however, with the data and their uncertainties. A different set, $a = -8000$ K
421 and $b = 8$, recently proposed for alkaline basalt by Lesne et al. (2011) based on
422 spectroscopic measurements would also just fit the experimental uncertainties, but start to
423 diverge at temperatures below 1300 °C. The experimental data can only be used to imply
424 a qualitative, strong dependence of K on temperature. Independent *in-situ* spectroscopic
425 data would be required to provide a more accurate estimate of this dependence.

426

427 Although the model is relatively simple, improvements that would provide a significantly
428 better fit to the experimental data are relatively limited, without making the model
429 completely empirical. For example, a slightly better agreement between the liquidus
430 curve and the experimental data at ~1450 °C can only be achieved by decreasing the
431 standard entropy of forsterite melting at 1 bar, which is already near the lower limit
432 derived from calorimetric studies (see Appendix). Non-ideal mixing can be included in
433 the model, however, a simple symmetric mixing parameter between the Mg_2SiO_4 and
434 H_2O components produces no significant improvement of the fit. In addition, such terms
435 have been shown to be unnecessary to describe the effect of H_2O on melting at lower
436 temperatures, where non-ideal effects should be even more important (Silver and Stolper,
437 1985).

438

We further compare our experimental results with the model of Tenner et al. (2012a), which is based on the limiting case where all H₂O dissolves as OH⁻. In Fig. 2, the liquidus is calculated according to this model using the same thermodynamic data as above and assuming $r = 4$ (random protonation of all oxygen atoms), which is analogous to using a single-oxygen formula unit for the silicate end-member (Tenner et al. 2012a; their Eqs. 9 and 11). The predicted liquidus is substantially different from that obtained from the Silver and Stolper (1985) model with $K = \infty$, although both models should be equivalent in describing the liquidus depression when H₂O dissolves completely as OH⁻. The difference arises in the conversion relationships for the mass fraction of H₂O by Silver and Stolper (1985) and Tenner et al. (2012a). To bring these two models to numerical consistency, the following relationship would have to be used to calculate the mole fraction of OH⁻ in the melt from the H₂O mass fraction,

$$X_{OH^-}^{melt} = 2 \frac{w_{H_2O^{tot}}^{melt} / M_{H_2O}}{w_{H_2O^{tot}}^{melt} / M_{H_2O} + (100 - w_{H_2O^{tot}}^{melt}) / M_{sil}}, \quad (11)$$

rather than the conversion equation proposed by Tenner et al. (2012a). The model of Tenner et al. (2012a) has been found to quite accurately reproduce the liquidus of experiments performed in natural complex systems when silicates are mixed on a 3-oxygen formula basis. However, the model does not reproduce data on Mg₂SiO₄ at 6 GPa, regardless of the silicate molecular unit considered, providing an independent confirmation that H₂O upon dissolution in silicate melt incompletely dissociates to OH⁻.

A further complexity in the model would be to consider the possibility that not all of the oxygen atoms in the melt structure are available for protonation but, for example, $r = 1$ or 2 per 4-oxygen formula unit (silicate polyhedron) due to local avoidance or ordering principles. This consideration raises two issues, however. First, it would imply a maximum limit for H_2O solubility in the melt, which appears to be not the case. Second, if the number of oxygen sites, which are accessible for proton bonding became an adjustable parameter and were allowed to change, for example, with the H_2O concentration, the resulting fit parameters would be highly correlated with K . These parameters cannot be meaningfully constrained without an independent estimate of K . Therefore, the Silver and Stolper (1985) model with temperature-dependent speciation in the melt supported by current estimates for $\Delta_m S^\circ$ of forsterite and the pressure-temperature melting curve of anhydrous forsterite appears to provide an adequate and well-constrained approximation of the experimental data.

In Fig. 4 experimental results bracketing the $\text{MgSiO}_3\text{-H}_2\text{O}$ liquidus at 6 GPa are compared with the same set of models as described above. The model that considers complete dissociation to OH^- ($K = \infty$) agrees with experimental data at the highest temperatures investigated (above 1600 °C). At lower temperatures, the experimental data again imply a shallower liquidus slope that is not consistent with the complete dissociation of H_2O into OH^- . On the other hand, mixing with molecular H_2O only ($K = 0$) results in a liquidus curve far outside of the experimental uncertainties. A model that considers variation of K with temperature (Eq. 10) fulfils the constraints imposed by the experiments, although a large range of parameters in this equation can provide an

adequate fit to the data. The curve in Fig. 4 was calculated with values of $a = -6000$ K and $b = 4.5$ with K decreasing from ~ 7 at 2100°C to ~ 2 at 1300°C . In addition, two models from Tenner et al. (2012a) that assume mixing of silicate molecules with 1- and 3-oxygen formula units, respectively, are shown in Fig. 4. The model of Tenner et al. (2012a) based on 1-oxygen per formula unit predicts values within the experimental uncertainties. However, these authors find the best agreement with melting data using natural peridotite composition when a 3-oxygen silicate molecule is assumed but, as shown in Fig. 4, this is in poor agreement with the data in this simple $\text{MgSiO}_3\text{-H}_2\text{O}$ subsystem.

Both enstatite and forsterite melting experiments at 6 GPa can be described by Silver and Stolper (1985) models that assume mixing of H on all silicate oxygen atoms and a temperature-dependent dissociation of H_2O , which proceeds towards complete OH^- formation above $\sim 1400^\circ\text{C}$. It is interesting to note that the mass fraction (wt %) of H_2O in the liquidus melt at a given temperature is nearly identical at 6 GPa for both MgSiO_3 and Mg_2SiO_4 over the entire temperature range.

4.1.2 Liquidus depression at 13 GPa

In Fig. 5 experiments bracketing the $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ liquidus at 13 GPa are shown and compared to the same models as described for the results at 6 GPa. The melting of pure Mg_2SiO_4 becomes incongruent above 10 GPa, with Mg_2SiO_4 reacting to produce MgO and melt at the solidus (Presnall and Walter, 1993). Upon the addition of H_2O to the system, melting becomes congruent between $1700\text{-}1900^\circ\text{C}$ (Table 3). For the purpose of

modelling the forsterite liquidus, thermodynamic data for congruent Mg_2SiO_4 melting at lower pressures have been extrapolated using the melt model of de Koker and Stixrude (2009) to 13 GPa. Models using complete dissociation into OH^- by Silver and Stolper (1985) with $K = \infty$ and by Tenner et al. (2012a) do not reproduce the experimental data (Fig. 5). The best agreement with the experimental liquidus is found for the limiting case of no dissociation, that is, mixing of molecular H_2O ($K = 0$ or 0.2). There are, however, larger inherent uncertainties in performing this evaluation at 13 GPa arising from the melting temperature assumed for anhydrous Mg_2SiO_4 . Although the thermodynamic model of de Koker and Stixrude (2009) used here provides some theoretical justification for the extrapolation, the resulting dramatic change predicted in the H_2O speciation most probably arises from resulting inaccuracies in the temperature of metastable forsterite melting. By assuming an anhydrous melting temperature that is 250 °C higher than predicted by the anhydrous melting model, the temperature-dependent model for K calibrated at 6 GPa for Mg_2SiO_4 can be equally applied at 13 GPa. We conclude, therefore, that it is more likely that the anhydrous melting temperature is in error, than that there is a dramatic shift in H_2O speciation at high pressure. This highlights the problems of examining melting point depression in incongruent systems, which are likely to be even more complex for natural multicomponent systems such as mantle peridotite melts.

For MgSiO_3 , the liquidus depression at 13 GPa is consistent with the Silver and Stolper (1985) model for nearly complete dissociation to OH^- in the melt (Fig. 6). While this is in contrast to Mg_2SiO_4 at the same pressure, it is in better agreement with the experimental

results at 6 GPa. Introducing a temperature dependence to K is not justified by the data, within the experimental uncertainties. A molecular H_2O model is far outside of the experimental constraints, however, as is the model of Tenner et al. (2012a).

4.2 The effect of pressure on liquidus depression due to H_2O in simple and complex silicate systems

The liquidus depression under hydrous conditions in comparison to the anhydrous melting point is shown for both the $\text{MgSiO}_3\text{-H}_2\text{O}$ and $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ systems at 6 and 13 GPa in Fig. 7. Experimental data of Kushiro et al. (1968) for $\text{MgSiO}_3\text{-H}_2\text{O}$ at 1 GPa and between 1375 and 1525 °C are used in order to provide an additional comparison; a value of $K = 0.5$ in the Silver and Stolper (1985) formulation provides a good fit to these data. For MgSiO_3 , pressure enhances the influence of H_2O in depressing the melting temperature in line with thermodynamic estimates for the entropy of fusion and the anhydrous melting curve of MgSiO_3 . The effect of pressure on the water-driven melting point depression of MgSiO_3 is best explained by an increase in the dissociation of H_2O with increasing pressure, with essentially no molecular H_2O being involved above 1400 °C, at pressures of 6 GPa and higher.

For the $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ binary, however, there is an apparent decrease in the effect of H_2O on liquidus depression between 6 and 13 GPa. As discussed above this is most likely caused by an underestimate in the metastable melting temperature of anhydrous Mg_2SiO_4 , which melts incongruently above 10 GPa. If the anhydrous melting temperature is assumed to be 250 °C higher at 13 GPa, then the effect on liquidus depression is reversed.

This implies that the extrapolated melting curve for Mg_2SiO_4 is incorrect. The Silver and Stolper (1985) model with values of $K = \sim 0.2$ at 2100 °C and approaching 0 at 1300 °C successfully reproduce experimental data of Hodges (1974) at 3 GPa in the forsterite- H_2O system. Data at 3 GPa show lower melting temperature depression in comparison to those at 6 GPa, is in agreement with the pressure trend observed in the enstatite- H_2O system and further suggesting a positive effect of pressure on melting temperature depression.

In Fig. 7, data for the liquidus depression due to H_2O for melts of natural peridotite composition are shown from Tenner et al. (2012a) at 3.5 GPa and Novella and Frost (2014) at 6 GPa. The depression of melting due to H_2O is much smaller for these complex melts compared to either of the simple systems at the same pressure. This difference is partly due the lower anhydrous liquidus temperatures of the natural multicomponent melts. As indicated by Eq. (2) the magnitude of the liquidus depression should increase with the anhydrous melting temperature, as observed in all experiments. In Fig. 7 these data are fitted using a Silver and Stolper (1985) model with molar mass of 37 g/mol per single-oxygen formula unit and a $\Delta_m S^\circ = 0.4 \text{ J/(K}\cdot\text{g)}$ (Tenner et al., 2012a; Kojitani and Akaogi, 1997). A constant value of $\Delta_m S^\circ$ in Eq. (2) is assumed at all pressures and temperatures and the anhydrous melting temperatures are taken from Walter (1998). The best correspondence with experiments at 3.5 GPa requires a temperature dependent value of K , which starts near unity close to the anhydrous melting temperature but decreases to effectively zero below 1200 °C. Although there is only one data point available at 6 GPa the depression of melting is consistent with a similar model as at 3.5 GPa, with the only difference being the anhydrous melting temperature. The

Silver and Stolper (1985) model, therefore, implies a much smaller extent of H₂O dissociation into OH⁻ and a greater proportion of molecular H₂O in multicomponent melts when compared to simple systems. This difference may have several origins, however. First, the value of $\Delta_m S^\circ$ employed for peridotite melt is poorly constrained as it is derived from calorimetric measurements in the CaO-MgO-Al₂O₃-SiO₂ system at 1 bar (Kojitani and Akaogi, 1997) and it may not suitably account for the effects of pressure and composition. Second, it is possible that certain components present in the natural peridotite melt compositions, such as Al₂O₃, cause a reduction in the effect of H₂O on the configurational entropy of the melt. As a result of such distinct behaviour, the effect of H₂O on melting in such simple systems may be quite far away from that in complex mantle melts.

Although the justification as to how the melt OH⁻ mole fraction is calculated is somewhat unclear in the model of Tenner et al. (2012a), particularly in relation to the Silver and Stolper (1985) model, it is interesting to note that it does closely predict the liquidus depression for complex peridotitic melts at both 3.5 and 6 GPa. The model is based on a 3-oxygen melt described by Eq. (11) and it predicts curves identical to those shown in Fig. 7 using the Silver and Stolper (1985) model for the natural peridotite data at 3.5 and 6 GPa. Although only empirical in its nature, it tends to numerically mimic decreasing protonation of the oxygen sites in the silicate melt structure, and it produces a good fit to the natural multicomponent data with fewer adjustable parameters. As there seems to be no clear justification to the way in which the OH⁻ mole fraction is derived in the Tenner et al. (2012a) model, the predictive capacity may be a coincidence.

599

600 **4.2.1 Hydrous melts along adiabatic temperature gradient**

601 A number of seismic observations appear to show evidence for low shear wave velocities
602 at the base of the upper mantle above the 410 km discontinuity (e.g. Song et al., 2004;
603 Vinnik et al., 2009; Jusbinken et al., 2010; Tauzin et al., 2010). These observations have
604 been proposed to result from the presence of low degree volatile-bearing melts at these
605 depths (Bercovici and Karato, 2003). Assuming that the upper mantle has a constant H₂O
606 content, it might be possible to explain the visibility of H₂O induced melting at the base
607 of the upper mantle if pressure enhances melt productivity at these conditions. One way
608 that this might occur is if less H₂O were required to stabilise melts with increasing
609 pressure.

610

611 In Fig. 7 the speciation model of Silver and Stolper (1985) using a temperature-dependent
612 value of K varying between ~ 1 and 0 at 3.5 and 6 GPa is extrapolated to 13 GPa by
613 assuming an anhydrous melting temperature of 1900 °C at this pressure (Takahashi,
614 1986). The model by Tenner et al. (2012a) would predict an identical liquidus depression.
615 The results of this extrapolation are given in Fig. 8, which shows the H₂O content in
616 MgSiO₃, Mg₂SiO₄ and peridotite melts determined at upper mantle adiabatic temperatures
617 (potential temperature ~ 1350 °C).

618

619 With increasing pressure the amount of H₂O required to stabilize Mg₂SiO₄ melt along a
620 mantle adiabat increases quite substantially between 6 and 13 GPa. This means that for a
621 system with a fixed H₂O content, the percentage of melt will decrease towards conditions

of the base of an upper mantle. This effect would work in conjunction with an increase in the forsterite-melt H₂O partition coefficient with pressure (see Hirschmann et al., 2009; Novella et al., 2014), which would also act to decrease the percentage of melting for a given bulk H₂O concentration. By contrast, the H₂O content of a MgSiO₃ melt appears to actually decrease slightly between 6 and 13 GPa, which could in theory lead to an increase in the percentage of melting for a fixed H₂O content. However, the decrease in melt H₂O content is small and this effect would be counteracted by an increase in the enstatite-melt partitioning coefficient with pressure, calculated from the literature (Rauch and Keppler, 2002; Yamada et al., 2004; Withers and Hirschmann, 2007; Withers et al., 2011) and melt H₂O content from this study. Peridotite melts are also predicted to require more H₂O to be stable at higher pressures, although the H₂O concentrations tend to vary very little towards the base of the upper mantle similar in fact to MgSiO₃. This analysis indicates that there is no evidence for increasing melt productivity due to H₂O towards the base of the Earth's upper mantle, although it has to be recognised that there is some uncertainty as the results for peridotite are being extrapolated above 6 GPa.

In order for the proportion of hydrous melting to increase and therefore be seismically more visible towards the base of the upper mantle, the bulk mantle at these conditions would need to be significantly enriched in H₂O. Such a localized enrichment in H₂O at this depth would require an effective fractionation process to maintain high H₂O concentrations at this depth. Bercovici and Karato (2003) proposed that hydrous melts formed under these conditions may be neutrally buoyant and, therefore, separate from the upwelling mantle and concentrate to form a low-velocity zone. Such a separation will

depend on melt density, which in turn will depend on the melt H₂O concentration. Melt density experiments by Matsukage et al. (2005) favour such a scenario, although their H₂O concentrations (~6 wt%) are approximately 50 % of those estimated in this study for natural peridotitic melts at the bottom of the upper mantle (Fig. 8). Following the density systematics of Jing and Karato (2009), partial melts in equilibrium with peridotite at 13 GPa should be much less dense than the surrounding mantle if the H₂O contents in the melt are close to those predicted here (Fig. 8).

Acknowledgements

Hubert Schulze, Raphael Njul, Stephan Übelhack, Heinz Fischer, Detlef Krausse and Sven Linhardt are kindly acknowledged for their technical support. The present study was supported by the Elitenetzwerk Bayern international graduate school “Structure, Reactivity and Properties of Oxide Materials”. D.N. further acknowledges funding from the French Government Laboratory of Excellence initiative n°ANR-10-LABX-0006, the Région Auvergne and the European Regional Development Fund. This is Laboratory of Excellence ClerVolc contribution number xx. D.D. would like to acknowledge personal support by the Czech Science Foundation Project Nr. 210/12/0986. We thank associate editor Mike Toplis and Mike Walter and an anonymous reviewer for comments that significantly improved the manuscript.

Appendix: Thermodynamic relations and parameters

The Mie-Grüneisen equations of state (EOS) were employed to determine the Gibbs energy of melting ($\Delta_m G^0$) of forsterite and enstatite required for the cryoscopic equation

in the $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ and $\text{MgSiO}_3\text{-H}_2\text{O}$ binaries. Expressions to define the Gibbs energy for Mg_2SiO_4 and MgSiO_3 were taken from Stixrude and Lithgow-Bertelloni (2011) for solids and from de Koker and Stixrude (2009) for liquids and are based on the fundamental thermodynamic relation between the Helmholtz energy (F) and the Gibbs energy:

$$G(P, T) = F(V, T) + PV, \quad (\text{A.1})$$

where V is the volume, P is the pressure and T is the temperature. The Helmholtz energy at elevated pressure and temperature is obtained by stepwise integration from ambient conditions ($T_0 = 298.15$ K, $P_0 = 101325$ Pa) *via* isothermal compression at reference temperature (c) and isochoric heating (th), which accounts for the effect of thermal vibrations:

$$F(V, T) = F(P_0, T_0) + \Delta F_c(T_0) + \Delta F_{th}(V). \quad (\text{A.2})$$

The contribution to the Helmholtz energy due to isothermal compression (ΔF_c) was calculated from the third-order Birch-Murnaghan EOS (Murnaghan, 1937; Birch, 1947; e.g. Poirier, 2000):

$$\Delta F_c(T_0) = 9K_0V_0 \left[\frac{f^2}{2} + \frac{af^3}{3} \right]. \quad (\text{A.3})$$

The EOS is based on the finite strain theory, where the finite strain (f) and the factor a are calculated as follows:

$$f = \frac{1}{2} \left(\frac{V_0}{V} \right)^{2/3} - 1 \quad (\text{A.4})$$

and

$$a = \frac{3}{2} (K'_0 - 4) . \quad (\text{A.5})$$

In this formulation, K_0 and V_0 correspond to the bulk modulus and the volume, respectively, at the reference pressure and temperature, and K'_0 is the first pressure derivative of the bulk modulus at reference conditions. The volume (V) of the phase at the pressure and temperature of interest was found in order to satisfy the following relation:

$$P = P_c + P_{th} , \quad (\text{A.6})$$

where

$$P_c = 3K_0 f (2f + 1)^{5/2} (1 + fa) . \quad (\text{A.7})$$

711 The equations of state for thermal pressure (P_{th}) and calculation of the relevant
 712 thermodynamic properties differ for liquid and solid phases. For the liquid phases, the
 713 thermal pressure is defined by

$$715 \quad P_{th} = \frac{\gamma}{V} c_v (T - T_0) \quad (A.8)$$

716
 717 where c_v is the isochoric heat capacity, and γ , representing the Grüneisen parameter, is a
 718 function of volume as follows

$$720 \quad \gamma = \gamma_0 + \gamma' \left[\frac{V}{V_0} - 1 \right] \quad (A.9)$$

721
 722 where γ_0 is the Grüneisen parameter at the reference conditions and γ' is its first
 723 derivative with respect to the volume. The thermal contribution to the Helmholtz energy
 724 (ΔF_{th}) of a liquid is then defined by:

$$725 \quad \Delta F_{th}(V) = -S_0(T - T_0) - c_v \left[T \ln \left[\frac{T}{T_0} \right] - (T - T_0) \right] - c_v (T - T_0) (\gamma_0 - \gamma') \ln \left[\frac{V}{V_0} \right] + (\gamma - \gamma_0) \quad (A.10)$$

729 where S_0 is the standard entropy of the substance at a reference state chosen to be
 730 consistent with literature data as described above (see Table A).

731

For the solid phases, a slightly different approach was used starting with the calculation of the volume at the pressure and temperature of interest (V). The thermal pressure of the solid phase was determined using an expression for the Debye thermal energy (E_{th}), that is,

$$P_{th} = \frac{\gamma}{V} [E_{th}(V, T) - E_{th}(V, T_0)] \quad (A.11)$$

and, in this case, the Grüneisen parameter is calculated as

$$\gamma = \gamma_0 \left(\frac{V}{V_0} \right)^{q_0}, \quad (A.12)$$

where q_0 is a constant, and the thermal internal energy (E_{th}) is defined by the Debye model for the lattice vibrational energy

$$E_{th} = 9nRT \left(\frac{T}{\theta} \right)^3 \int_0^{\frac{T}{\theta}} \frac{t^3}{e^t - 1} dt, \quad (A.13)$$

where R is the universal gas constant, n is the number of atoms per formula unit, $t = \theta/T$, with the Debye temperature (θ) calculated as

$$\theta = \theta_0 e^{\frac{\gamma_0 - \gamma}{q_0}}. \quad (A.14)$$

753

754 The corresponding expression for the thermal Helmholtz energy (F_{th}) of the solid phases,
755 defined as the Debye approximation of the quasi-harmonic vibrational density of states, is
756 as follows:

757

758
$$F_{\text{th}}(V) = 9nRT \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \ln(1 - e^{-t}) t^2 dt . \quad (\text{A.15})$$

759

760 The thermal contribution to the Helmholtz energy (ΔF_{th}) of the solid phases between the
761 reference temperature (T_0) and that of interest (T) at the constant volume of interest (V), is
762 found by difference:

763

764
$$\Delta F_{\text{th}}(V) = F_{\text{th}}(V, T) - F_{\text{th}}(V, T_0) . \quad (\text{A.16})$$

765

766 The thermodynamic properties employed in the calculations of the Gibbs energy for solid
767 and liquid Mg_2SiO_4 and MgSiO_3 are summarized in Table A and are based on previous
768 compilations by de Koker and Stixrude (2009) and Stixrude and Lithgow-Bertelloni
769 (2011) for liquid and solid phases, respectively. The Helmholtz energy for liquid
770 substances at reference conditions (F_0) was empirically calculated from the room pressure
771 melting temperatures as explained by Liebske and Frost (2012). The reference state
772 volumes (V_0) and entropies (S_0) for the liquid end-members were slightly altered
773 compared to those reported by de Koker and Stixrude (2009) in order to obtain better
774 agreement with the experimental melting temperatures and to be consistent with
775 calorimetric data for the enthalpy of melting of MgSiO_3 and Mg_2SiO_4 (Navrotsky et al.,

1989; Richet et al., 1993). Specifically, the thermodynamic data of Mg_2SiO_4 liquid of de Koker and Stixrude (2009) had to be modified such that the value of $\Delta_m S^\circ$ for forsterite at 1 bar was consistent with 52.7 J/(K·mol) proposed by Navrotsky et al. (1989). This is at the lower end of the range of values reported in the literature, which vary from 70 to 47.5 J/(K·mol) (Bottinga, 1985; Navrotsky et al., 1989; Richet et al., 1993; Tangeman et al., 2001). Values for the standard heat capacity and volume of Mg_2SiO_4 liquid were then also adjusted to bring the model into agreement with experimental data on the melting curve of Mg_2SiO_4 (Davis and England, 1964; Kato and Kumazawa, 1985; Presnall and Walter, 1993).

References

- Balta J.B., Asimow P.D. and Mosenfelder J.L. (2011) Hydrous, low-carbon melting of garnet peridotite, *J. Petrol.* **52**, 2079–2105.
- Bercovici D. and Karato S.-I. (2003) Whole-mantle convection and the transition-zone water filter. *Nature* **425**, 39–44.
- Brey G.P., Köhler T. and Nickel K.G. (1990) Geothermobarometry in four-phase lherzolites I. Experimental Results from 10 to 60 kb. *J. Petrol.* **31**, 1313–1352.
- Birch F. (1947) Finite elastic strain of cubic crystals. *Phys. Rev.* **71**, 809–824.
- Bottinga Y. (1985) On the isothermal compressibility of silicate liquids at high pressure. *Earth Planet. Sci. Lett.* **74**, 350–360.
- Brooker R., Holloway J. and Hervig R. (1998) Reduction in piston cylinder experiments: the detection of carbon infiltration into platinum capsules. *Am. Mineral.* **83**, 985–994.

799 Burnham C.W. (1975) Water and magmas; a mixing model. *Geochim. Cosmochim. Acta*
800 **39**, 1077–1084.

801 Burnham, C.W. (1979) The importance of volatile constituents. In: *The Evolution of the*
802 *Igneous Rocks* (ed. H.S. Jr. Yoder). Princeton Univ. Press, Princeton, NJ. pp. 439–
803 482.

804 Burnham, C.W. (1994) Development of the Burnham model for prediction of H₂O
805 solubility in magmas. In: *Volatiles in Magmas* (eds. M.R. Carroll and J.R.
806 Holloway). Reviews in Mineralogy **30**, Mineralogical Society of America,
807 Washington D.C.

808 Dalton, J.A. and Presnall, D.C. (1997) No liquid immiscibility in the system MgSiO₃-
809 SiO₂ at 5.0 GPa. *Geochim. Cosmochim. Acta* **61**, 2367–2373.

810 Davis B.T.C. and England J.R. (1964) The melting of forsterite up to 50 kilobars. *J.*
811 *Geophys. Res.* **69**, 1113–1116.

812 de Koker N. and Stixrude L. (2009) Self-consistent thermodynamic description of silicate
813 liquids, with application to the shock melting of MgO periclase and MgSiO₃-
814 perovskite. *Geophys. J. Internat.* **178**, 162–179.

815 Dixon J.E. and Stolper E.M. (1995) An experimental study of water and carbon dioxide
816 solubilities in mid-ocean ridge basaltic liquids. Part II: Applications to degassing.
817 *J. Petrol.*, **36**, 1633–1646.

818 Erlank E.J., Waters F.G., Hawkesworth C.J. Haggerty S.E., Allsopp H.L., Rickard R.S.
819 and Menzies M. (1987) Evidence for mantle metasomatism in peridotite nodules
820 from Kimberly pipes, South Africa. In: *Mantle Metasomatism* (eds. M.A. Menzies
821 and C.J. Hawkesworth). Academic Press, London, pp. 313–361.

- 822 Frost D.J., Poe B.T., Tronnes R.G., Liebske C., Duba A. and Rubie D.C. (2004) A new
823 large-volume multianvil system. *Phys. Earth Planet. Int.* **143–144**, 507–514.
- 824 Gaetani G.A. and Grove T.L. (1998) The influence of water on melting of mantle
825 peridotite. *Contrib. Mineral. Petrol.* **131**, 323–346.
- 826 Hirose K. and Kawamoto T. (1995) Hydrous partial melting of lherzolite at 1 GPa: the
827 effect of H₂O on the genesis of basaltic magmas. *Earth Planet. Sci. Lett.* **133**,
828 463–473.
- 829 Hirschmann M.M., Tenner T., Aubaud C. and Withers A.C. (2009) Dehydration melting
830 of nominally anhydrous mantle: The primacy of partitioning. *Phys. Earth Planet.*
831 *Int.* **176**, 54–68.
- 832 Hodges F.N. (1973) Solubility of H₂O in forsterite melt at 20 kbar. *Carnegie Inst.*
833 *Washington Yearb.* **72**, 495–497.
- 834 Hodges F.N. (1974) The solubility of H₂O in silicate melts. *Carnegie Inst. Washington*
835 *Yearb.* **73**, 251–255.
- 836 Inoue T. (1994) Effect of water on the melting phase-relations and melt composition in
837 the system Mg₂SiO₄-MgSiO₃-H₂O up to 15 GPa. *Phys. Earth Planet. Int.* **85**, 237–
838 263.
- 839 Jasbinsek, J.J., Dueker, K.G. and Hansen, S.M. (2010) Characterizing the 410 km
840 discontinuity low-velocity layer beneath LA RISTRA array in the North American
841 Southwest. *Geochem. Geophys. Geosys.* **11**, doi:10.1029/2009GC002836.
- 842 Jing Z. and Karato S-I. (2009) The density of volatile bearing melts in the Earth's deep
843 mantle: The role of chemical composition. *Chem. Geol.* **262**, 100–107.

844 Kato T. and Kumazawa M. (1985) Melting and phase relations in the system Mg_2SiO_4 -
845 MgSiO_3 at 20 GPa under hydrous conditions. *J. Geophys. Res.* **91**, 9351–9355.

846 Kawamoto T. and Holloway J.R. (1997) Melting temperature and partial melt chemistry
847 of H_2O -saturated mantle peridotite to 11 GPa. *Science* **276**, 240–243.

848 Kojitani H. and Akaogi M. (1997) Melting enthalpies of mantle peridotite: calorimetric
849 determinations in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ and application to magma
850 generation. *Earth Planet Sci. Lett.* **153**, 209–222.

851 Kushiro I. (1972) Effect of water on the composition of magmas formed at high
852 pressures. *J. Petrol.* **13**, 311–334.

853 Kushiro I. and Yoder H.S.Jr. (1969) Melting of forsterite and enstatite at high pressures
854 and hydrous conditions. *Carnegie Inst. Washington Yearb.* **67**, 153–158.

855 Kushiro I., Yoder H.S.Jr. and Nishikawa, M. (1968) Effect of water on the melting of
856 enstatite. *Geol. Soc. Am. Bull.* **79**, 1685–1692.

857 Lambert I. B. and Wyllie P. J. (1970) Low-velocity zone of the Earth's mantle; incipient
858 melting caused by water. *Science* **169**, 764–766.

859 Lesne P., Scaillet B., Pichavant M., Iacono-Marziano G. and Beny J.M. (2011) The H_2O
860 solubility of alkali basaltic melts: an experimental study. *Contrib. Mineral. Petrol.*
861 **162**, 133–151.

862 Liebske C. and Frost D.J. (2012) Melting phase relations in the MgO-MgSiO_3 system
863 between 16 and 26 GPa: Implications for melting in Earth's deep interior. *Earth*
864 *Planet Sci. Lett.* **345–348**, 159–170.

- 865 Liu X., O' Neill H.St.C., and Berry A.J. (2006) The effects of small amounts of H₂O, CO₂
866 and Na₂O on the partial melting of spinel lherzolite in the system CaO-MgO-
867 Al₂O₃-SiO₂±H₂O±CO₂±Na₂O at 1.1 GPa. *J. Petrol.* **47**, 409–434.
- 868 Luth R.W. (1993) Melting in the Mg₂SiO₄-H₂O system at 3 to 12 GPa. *Geophys. Res. Let.*
869 **20**, 233–235.
- 870 Matsukage K.N., Jing Z. and Karato S-I. (2005) Density of hydrous silicate melt at the
871 conditions of Earth's deep upper mantle. *Nature* **438**, 488–491.
- 872 Médard E. and Grove T.L. (2008) The effect of H₂O on the olivine liquidus of basaltic
873 melts: experiments and thermodynamic models. *Contrib. Mineral. Petrol.* **155**,
874 417–432.
- 875 Menzies M.A. and Hawkesworth C.J. (1987) *Mantle metasomatism*. Academic press,
876 London.
- 877 Mibe K., Fujii T. and Yasuda M. (2002) Composition of aqueous fluid coexisting with
878 mantle minerals at high pressure and its bearing on the differentiation of the
879 Earth's mantle. *Geochim. Cosmochim. Acta* **66**, 2273–2285.
- 880 Mierdel K., Keppler H., Smyth J.R. and Langenhorst F. (2007) Water solubility in
881 aluminous orthopyroxene and the origin of Earth's asthenosphere. *Science* **315**,
882 364-368.
- 883 Murnaghan, F. D. (1937) Finite deformations of an elastic solid. *Amer. J. Math.* **49**, 235–
884 260.
- 885 Myhill, R., Frost, D.J. and Novella, D. (2016) Hydrous melting and partitioning in and
886 above the mantle transition zone: insights from water-rich MgO-SiO₂-H₂O

887 experiments. *Geochim. Cosmochim. Acta*,
888 <http://dx.doi.org/10.1016/j.gca.2016.05.027>.

889 Mysen B.O. and Boettcher A.L. (1975) Melting of hydrous mantle I. Phase relations of
890 natural peridotite at high pressures and temperatures with controlled activities of
891 water, carbon dioxide, and hydrogen, *J. Petrol.* **16**, 520–548.

892 Navrotsky A., Ziegler D., Oestrike R. and Maniar P. (1989) Calorimetry of silicate melts
893 at 1773 K - measurement of enthalpies of fusion and of mixing in the systems
894 diopside-anorthite-albite and anorthite-forsterite. *Contrib. Mineral. Petrol.* **101**,
895 122–130.

896 Novella D. and Frost D.J. (2014) The composition of hydrous partial melts of garnet
897 peridotite at 6 GPa: implications for the origin of group II kimberlites. *J. Petrol.*
898 **5**, 2097–2124.

899 Novella D., Frost D.J., Hauri E.H., Bureau H., Raepsaet C. and Roberge M. (2014) The
900 distribution of water between nominally anhydrous peridotite and melts in the
901 Earth's upper mantle. *Earth Planet Sci. Lett.* **400**, 1–13.

902 Nowak M. and Behrens H. (1995) An in situ near infrared spectroscopic study of water
903 speciation in haplogranitic glasses and melts. *Fifth Silicate Melt Work-shop*
904 *Program and Abstracts*, La Petite Pierre, France.

905 Pamato M., Myhill, R., Boffa Ballaran T., Frost D.J., Heidelbach F. and Miyajima N.
906 (2015) Lower-mantle water reservoir implied by the extreme stability of a
907 hydrous aluminosilicate. *Nature Geoscience* **8**, 75–79.

908 Poirier J.P. (2000) Introduction to the physics of the Earth interior. 2nd ed, Cambridge
909 University Press, Cambridge.

910 Presnall D.C. and Walter M.J. (1993) Melting of forsterite, Mg_2SiO_4 , from 9.7 to 16.5
 911 GPa. *J. Geophys. Res.* **98**, 19777–19783.

912 Rauch, M. and Keppler, H. (2002). Water solubility in orthopyroxene. *Contrib. Mineral.*
 913 *Petrol.* **143**, 525–536.

914 Richet P., Robie R.A. and Hemingway B.S. (1993) Entropy and structure of silicate
 915 glasses and melts. *Geochim. Cosmochim. Acta* **57**, 2751–2766.

916 Ross N.L., Akaogi M., Navrotsky A., Susaki J., and McMillan P. (1986) Phase
 917 transformations among CaGeO_3 polymorphs (wollastonite, garnet, and perovskite
 918 structures): studies by high-pressure synthesis, high-temperature calorimetry and
 919 vibrational spectroscopy and calculation. *J. Geophys. Res.* **91**, 4601–1696.

920 Schmandt B., Jacobsen S.D., Becker T.W., Liu Z. and Dueker K.G. (2014) Dehydration
 921 melting at the top of the lower mantle. *Science* **344**, 1265–1268.

922 Silver L.A. and Stolper E.M. (1985) A thermodynamic model for hydrous silicate melts.
 923 *J. Geol.* **93**, 161–178.

924 Silver L.A. and Stolper E.M. (1989) Water in albitic glasses. *J. Petrol.* **30**, 667–709.

925 Sokol A.G., Kupriyanov I.N., Palyanov Y.N., Krunk A.N. and Sobolev N.V. (2013)
 926 Melting experiments on the Udachnaya kimberlite at 6.3–7.5 GPa: Implications
 927 for the role of H_2O in magma generation and formation of hydrous olivine.
 928 *Geochim. Cosmochim. Acta* **101**, 133–155.

929 Song, A.T-R., Helmberger, D.V. and Grand, S.P. (2004) Low-velocity zone atop the 410-
 930 km seismic discontinuity in the northwestern United States. *Nature* **427**, 530–533.

931 Stixrude L. and Linthgow-Bertelloni C. (2011) Thermodynamics of mantle minerals – II.
 932 Phase equilibria. *Geophys. J. Int.* **184**, 1180–1213.

- 933 Stolper E. (1982) Water in silicate glasses: an infrared spectroscopy study. *Contrib.*
 934 *Mineral. Petrol.* **81**, 1–17.
- 935 Takahashi E. (1986) Melting of dry peridotite KLB-1 up to 14 GPa: implications on the
 936 origin of peridotitic upper mantle. *J. Geophys. Res.* **91**, 9367–9382.
- 937 Tangeman J.A., Lange R., and Forman L. (2001) Ferric-ferrous equilibria in K₂O-FeO-
 938 Fe₂O₃-SiO₂ melts. *Geochim. Cosmochim. Acta* **65** 1809–1819.
- 939 Tatsumi Y., Hamilton D.L. and Nesbitt R.W. (1986) Chemical characteristics of fluid
 940 phase released from a subducted lithosphere and origin of arc magmas: Evidence
 941 from high-pressure experiments and natural rocks. *J. Volcan. Geotherm. Res.* **29**,
 942 293–309.
- 943 Tauzin B., Debayle E. and Wittlinger G. (2010) Seismic evidence for a global low-
 944 velocity layer within the Earth's upper mantle. *Nature Geoscience* **3**, 718–721.
- 945 Tenner T.J., Hirschmann M.M. and Humayun M. (2012a) The effect of H₂O on partial
 946 melting of garnet peridotite at 3.5 GPa. *Geochem. Geophys. Geosys.* **13**,
 947 doi:10.1029/2011GC003942.
- 948 Tenner, T.J., Hirschmann, M.M., Withers, A.C. and Ardia, P. (2012b) H₂O storage
 949 capacity of olivine and low-Ca pyroxene from 10 to 13 GPa: consequences for
 950 dehydration melting above the transition zone. *Contrib. Mineral. Petrol.* **163**,
 951 297–316.
- 952 Vinnik, L., Oreshin, S., Kosarev, G., Kiselev, S. and Makeyeva, L. (2009) Mantle
 953 anomalies beneath southern Africa: evidence from seismic S and P receiver
 954 functions. *Geophys. J. Int.* **179**, 279–298.

955 Walter M.J. (1998) Melting of garnet peridotite and the origin of komatiite and depleted
 956 Lithosphere. *J. Petrol.* **39**, 29–60.

957 Withers, A.C. and Hirschmann, M.M. (2007) H₂O storage capacity of MgSiO₃ clino-
 958 enstatite at 8–13 GPa, 1100–1400 °C. *Contrib. Mineral. Petrol.* **154**, 663–674.

959 Withers, A.C., Hirschmann, M.M. and Tenner, T. (2011) The effect of Fe on olivine H₂O
 960 storage capacity: consequences for H₂O in the Martian mantle. *Am. Mineral* **96**,
 961 1039–1053.

962 Yamada A., Inoue T. and Irifune T. (2004) Melting of enstatite from 13 to 18 GPa under
 963 hydrous conditions. *Phys. Earth Planet. Int.* **147**, 45–56.

964 Zotov N. and Keppler H. (1998) The influence of water on the structure of hydrous
 965 sodium tetrasilicate glasses. *Am. Mineral.* **83**, 823–834.

966

967 **Figure captions**

968 **Fig. 1:** Backscattered electron (BSE) images of experiments performed at 6 GPa in the
 969 Mg₂SiO₄-H₂O system. The bright material is the Pt capsule. Grey crystals (50 to 100 µm
 970 across) of forsterite can be easily distinguished from the fine grain quenched melt. **(a):**
 971 figure corresponds to experiment V649 (Table 2) where in order from left to right are
 972 sample chambers containing starting mixtures of Mg₂SiO₄ plus 5, 10, 15 and 20.4 wt%
 973 H₂O in the bulk. The third chamber from the left shows two quench textures in the same
 974 charge with different fibrous grain sizes, likely formed due to differences in nucleation
 975 and crystal growth (see text). **(b):** BSE image of experiment V660 (Table 2) where, from
 976 left to right, starting mixtures of Mg₂SiO₄ with 7.9, 9.7, 13.8 and 18.3 wt% H₂O (bulk)
 977 were employed.

Fig. 2: Phase diagram of the $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ system at 6 GPa showing experimental data and models for the liquidus curves (described in the text). Data points determined in this study are displayed by black and grey symbols (Table 2) while data from Luth (1993) at 6 GPa and Inoue (1994) at 5.5 GPa are shown by blue and green symbols, respectively. Data from Luth (1993) and Inoue (1994) were determined for bulk compositions of Mg_2SiO_4 plus 20.4 wt% H_2O but are plotted at slightly higher H_2O content to aid visibility. The liquidus at approximately 20 wt% H_2O is ~ 200 °C lower than reported by Inoue et al. (1994) at 5.5 GPa but is in agreement, within uncertainty, with the data of Luth (1993) at 6 GPa. The plotted liquidus curves are all constrained by the dry melting temperature of forsterite at 6 GPa reported by Kato and Kumazawa (1985). Details regarding the different curves are reported in the text. Uncertainties of 1 wt% in the melt composition and 50-100 °C for the temperature of the experiments (see text) are displayed by the error bars.

Fig. 3: Indicative ternary phase diagrams in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$. Phase relations are tentatively constrained at 6 (top) and 13 (bottom) GPa by the experimental results reported in this study and the literature. Starting compositions in the forsterite- H_2O and enstatite- H_2O joins are plotted as black circles, on a molar basis. Fo: forsterite; En: enstatite; Per: periclase; St: stishovite; L: liquid (or melt). The dashed line indicates the $\text{Fo} + \text{En} = \text{L}$ reaction curve while the dotted lines show the possible location of the $\text{Fo} + \text{Per} = \text{L}$ (toward MgO corner) and $\text{En} + \text{St} = \text{L}$ (toward SiO_2 corner) curves.

Fig. 4: The depression of the MgSiO_3 liquidus curve at 6 GPa as a function of melt H_2O content. Data points determined in this study (Table 2) are displayed by black symbols while green symbols are from Inoue (1994), plotted at slightly higher H_2O content to aid

visibility. Uncertainties of 1 wt% in the melt composition and 50-100 °C for the temperature of the experiments (see text) are displayed by the error bars. Curves describing the liquidus determined by different models as described in the text are also shown. The liquidus curves are all constrained by the dry melting temperature of enstatite at 6 GPa reported by Kato and Kumazawa (1985).

Fig. 5: Melting phase relations in the $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ system at 13 GPa. Uncertainties of 1 wt% in the melt composition and 50-100 °C for the temperature of the experiments (see text) are displayed. The dry melting temperature of forsterite at 13 GPa was calculated to be 2200 °C by extrapolation of the equations of state of de Koker and Stixrude (2009).

Fig. 6: The melting phase relations in the $\text{MgSiO}_3\text{-H}_2\text{O}$ system at 13 GPa. Uncertainties of 1 wt% in the melt composition and 50-100 °C for the temperature of the experiments (see text) are displayed. The dry melting temperature of enstatite at 13 GPa was calculated to be 2250°C using the model of de Koker and Stixrude (2009). Values of $a = -8000$ K and $b = 8$ were employed in the calculation of constant K (red line).

Fig. 7: The depression in the hydrous melting temperature as a function of H_2O for $\text{MgSiO}_3\text{-H}_2\text{O}$ (black lines), $\text{Mg}_2\text{SiO}_4\text{-H}_2\text{O}$ (green lines) and natural (blue lines) melt compositions between 1 and 13 GPa. Hydrous garnet peridotite melt compositions are from Tenner et al. (2012a) at 3.5 GPa (red dots) and Novella and Frost (2014) at 6 GPa (grey square). The blue curves are fitted to these data, as described in the text.

Fig. 8: Melt H_2O contents as a function of pressure determined at 3.5, 6 and 13 GPa and at temperatures corresponding to a mantle adiabat (1350 °C, 1400 °C and 1500 °C, respectively). Peridotite data are taken from the curves shown in Fig. 7.