The influence of H₂O on mantle wedge melting

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Abstract

The solidus and near-solidus melting behavior of a primitive undepleted peridotite composition has been determined over a pressure range of 1.2–3.2 GPa at H₂O saturated conditions. Vapor-saturated melting (melting in the presence of an H₂O-rich supercritical fluid) begins at 940 °C at 1.2 GPa and the solidus temperature decreases continuously to 860 °C at 2 GPa and 800 °C at 3.2 GPa. This solidus is similar to the lower temperature results of previous investigations. The temperature discrepancies found in earlier studies could be a result of short run times used in several studies and the slower kinetics of olivine vs. diopside melting. The solidus phases include olivine, orthopyroxene, high-Ca clinopyroxene and Al-rich phases that change from spinel+amphibole (1.2–1.8 GPa) to spinel+chlorite over the pressure range of 2–2.4 GPa. Above 2.4 GPa garnet+chlorite+ilmenite are present along with olivine+orthopyroxene+clinopyroxene on the solidus. Chlorite may be a stable phase at the base of the mantle wedge and it may play a role in the onset of flux melting. Ilmenite might play a role in the development of HFSE depletions in arc magmas. Flux melting of the mantle wedge above the subducting oceanic lithosphere begins when an H₂O-rich component (either fluid or melt) released from the slab ascends within the overlying mantle. As it ascends into the mantle wedge the H₂O triggers melting at the vapor-saturated solidus at a depth shallower than the wedge–slab interface. Melting continues as the melt ascends into shallower, hotter overlying mantle. Melting in this part of the wedge occurs at vapor-undersaturated conditions because the H₂O content of the melt is continually diluted as the melt ascends through the wedge, dissolving and re-equilibrating with shallower, hotter mantle. Final equilibration with the mantle wedge occurs at shallow depths near the top of the wedge. A model of this process is developed using the vapor-saturated phase relations as a starting point.

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1. Introduction

In subduction zone settings, mantle melting occurs in response to the addition of an H₂O-rich component released from the subducted oceanic lithosphere. Arc magmas [1–4] inherit their high H₂O contents from this process. Melting might be initiated at the vapor-saturated solidus [5] near the base of the wedge at high pressure. The H₂O-rich melt that is initially produced continuously reacts with overlying hotter, shallower mantle, diluting the magmatic H₂O content as the melt ascends [6]. To understand this process one needs to know the melting behavior of the mantle in the presence of excess H₂O and this study re-examines this melting process. Previous determinations of the solidus differ significantly, resulting in more than a 200 °C difference in the vapor-saturated solidus temperature over the pressure range of 2.5–3 GPa [7]. This study presents new experimental data, compares them with the results of the four previously published experimental studies, and critically reevaluates the wet peridotite solidus. Results of this study are similar to those of earlier investigators who

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found lower melting temperatures for the peridotite solidus [8]. We use our results along with evidence from experimental studies of primitive arc magmas to model the mantle wedge melting processes and the evolution of primitive arc magmas.

### 2. Experimental methods

#### 2.1. Starting materials

The experiments (Table 1) use a synthetic oxide mix with the composition of Hart and Zindler’s primitive mantle [9]. This composition (Table 2, top row) was prepared by mixing high purity oxides or metasilicates and FeO was added by mixing metallic iron and hematite in the appropriate molar proportions. Brucite, Mg(OH)₂, was synthesized from high purity MgO [5,10,11] and used as the source for MgO and H₂O. The H₂O present in brucite (∼31 wt.%) allowed the incorporation of ∼14.5 wt.% H₂O in the starting mix.

#### 2.2. Experimental procedures

All of the experiments were carried out at the MIT Experimental Petrology Laboratory in a 0.5” solid medium piston cylinder apparatus [12] using the hot piston-in technique [13]. The pressure medium was BaCO₃, and pressure was calibrated against the reaction: anorthite+gehlenite+corundum=Ca-tschermak pyroxene [14]. Pressures are thought to be accurate to ±50MPa. Temperature was monitored and controlled using W₉₇Re₃–W₇₅Re₂₅ thermocouples with no correction applied for the effect of pressure on the thermocouple EMF. Temperatures are thought to be accurate to ±10 °C. The sample was positioned in the center

| Expt. | P (GPa) | T (°C) | Duration (hours) | H₂O present? | Phases | ol | opx | cpx | sp | gar | ilm | amph | chl | melt | r² | %Fe loss (or gain) | QUILF T (K) | fO₂ (ΔQFM) |
|-------|--------|--------|-----------------|---------------|--------|----|-----|-----|----|-----|-----|------|-----|-----|-----|-----|---|-----------------|--------------|-----------|
| B993  | 1.2    | 930    | 73.1            | yes           | xxxx   | x  | x   | x   | x  |     |     |      |     |      |     |     | 0.10| −2.8            | 1327 (22)    | −1.0       |
| B985  | 1.2    | 950    | 48.0            | yes           | xxxx   | x  | x   | x   | x  |     |     |      |     |      |     |     | 0.11| −5.0            | 1362 (54)    |           |
| B804  | 1.2    | 980    | 50.0            | yes           | xxxx   | x  |     | x   | x  |     |     |      |     |      |     |     |     | −2.8            | 1327 (22)    | −1.0       |
| B810  | 1.2    | 1000   | 54.3            | yes           | 0.48   | 0.33| 0.08| 0.01| 0.10|     |     |      |     |      |     |     | 0.07| −2.8            | 1327 (22)    | −1.0       |
| B814  | 1.2    | 1020   | 54.3            | yes           | 0.58   | 0.21| 0.09| 0.01| 0.11|     |     |      |     |      |     |     | 0.11| −5.0            | 1362 (54)    |           |
| B816  | 1.2    | 1100   | 25.0            | no            | 0.44   | 0.40| 0.14| 0.02|     |     |     |      |     |      |     |     |     | −5.0            | 1362 (54)    |           |

* A large amount of melt was present in these charges, but could not be analyzed. n.a.=not analyzed.
of the graphite heater near the hot spot, and the thermocouple was positioned above the sample in the cooler upper part of the furnace. A correction of +20 °C was added to the thermocouple temperature. This temperature difference was obtained by direct measurement using offset thermocouples. We also mapped out the thermal gradient in our run assembly using the kinetics of the MgO+Al₂O₃=MgAl₂O₄ reaction [15]. We found that the hot spot in the furnace is 20 °C hotter than the thermocouple temperature and located at the top of our sample capsule 2 mm from the thermocouple junction. Over the length of the silicate sample (∼1 mm) the temperature drops by 10 °C. Thus, the hottest part of the sample container is at the top of the charge, and the temperature is 10 °C lower at the bottom.

Au capsules were used for all of the experiments. The Au capsules were fabricated from 0.43” long Au tubes with a 0.01” wall thickness. The Au tube was triple-crimped, welded on one end and then flattened to make a uniformly thick capsule top. About 0.04 g of the starting material was loaded into the capsule. The bottom of this capsule was again triple-crimped and welded shut with an arc welder. This welded capsule was flattened in a die to produce a final capsule length (∼0.15”) similar to that of our conventional anhydrous graphite capsule assemblies. The resulting product was a small capsule that could be welded shut and still retain the 14.5 wt.% H₂O added as brucite. These capsules were centered in graphite furnaces in the same manner utilized in our conventional experimental assemblies [16]. Experiments were pressurized to 1 GPa at room temperature, and then the temperature was raised to 865 °C at 100 °C/min (if the final experimental temperature was <865 °C, the final experimental temperature was achieved during this step). The experiment was held at these conditions for 6 min, then the pressure was increased to the desired value and the temperature was raised to the final run conditions at 50 °C/min. The sample was held at isothermal conditions for the duration of the experiment (Table 1). Experimental durations ranged from 25 to 148 h. At the end of the experiment the sample was quenched by turning off the power. A hole was made in the capsule using a small diameter hand drill, and the presence or absence of water was noted (Table 1). After this step the capsule was sliced using a diamond saw, dried out, vacuum-impregnated in epoxy and polished for further examination.

2.3. Analytical methods

Back scattered electron (BSE) images and wavelength dispersive X-ray elemental maps of the polished run products were collected with a JEOL JXA-733 Superprobe at Massachusetts Institute of Technology. An electron beam rastering and/or x–y stage translation technique (depending on the size of the image) was used to obtain large area spatial representations of the samples [17]. Secondary electron images of fractured surfaces of the sample were obtained using a JEOL 6320 field emission SEM at the Massachusetts Institute of Technology. These images and maps were extremely useful in examining the distribution of minerals in the sample, detecting the beginning of melting and to identify points for conventional spot analysis by wavelength dispersive spectrometry (WDS).

The experimental products were analyzed by WDS with the MIT five-spectrometer JEOL 733 Superprobe. The on-line data reduction utilized the CITZAF correction package [18]. The atomic number correction of Duncumb and Reed, Heinrich’s tabulation of absorption coefficients, and the fluorescence correction of Reed were used to obtain a quantitative analysis [18]. Analyses of mineral and quenched liquid products are presented in Table 2. All analyses were performed with a 15 kV accelerating voltage and a 10 nA beam current. Spot size was 1 μm for the mineral analyses. Elements in the crystalline phases were measured for up to 40 s, depending on abundance level. In one experiment the glass phase was analyzed using a 10 μm beam size. Most of the Na in the glass was lost in the first second of counting (see Experimental results), despite the short counting time used for Na (5 s).

3. Experimental results

3.1. Mineral phase relations

The results of the experiments are shown on a pressure–temperature plot in Fig. 1. In all of the plotted experiments olivine + orthopyroxene + high Ca-clinopyroxene (oliv+opx+cpx) are present. The symbols and boundaries demarcate the stability fields of aluminous and/or hydrous minerals that were stable along with oliv+opx+cpx. Fig. 2A, B shows a high pressure subsolidus (2 GPa, 850 °C) experiment where super-critical vapor coexisted with crystals. Fig. 2C shows the texture in a lower pressure experiment (1.2 GPa, 1020 °C, B814) when melt and a super-critical vapor phase are present. At 1.2 GPa amphibole + spinel are present, with amphibole disappearing above 1010 °C. Above 1.7 GPa and 980–1000 °C amphibole breaks down and spinel becomes the stable aluminous phase. Garnet and spinel coexist in a small P–T region above the solidus between 2 and 2.4 GPa and between 880 and 1000 °C. Above approximately 2.2 GPa on the solidus, garnet becomes the only anhydrous aluminous phase to coexist with oliv+opx+cpx (Fig. 3). At the lowest temperatures (780–840 °C) and highest pressures
Table 2
Analyses of selected experiments

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Number below each oxide is one standard deviation of mean of replicate analyses.
(a) Glass composition lost Na₂O during the analysis. The composition was recalculated by adding Na₂O to achieve mass balance.
(b) Pyroxenes in this sample were small and very difficult to analyze. The analyses represent single points of pyroxenes with lowest, Al and Ti contents.
investigated (2.8 and 3.2 GPa) magnesian chlorite [19,20] and geikielite–ilmenite solid solution (Table 2) coexist with garnet, oliv, opx and cpx near the solidus (Fig. 4).

3.2. Detection of melt

Two criteria were used to determine the presence of melt: (1) the presence of visible interstitial melt and (2) the simultaneous occurrence of variations in modal abundance in minerals in the charge along with regions of melt + crystal segregation. The textural characteristics of the sample and the appearance of the quenched melt changes over the range of pressures investigated. In the pressure range of 1.2–2.0 GPa (Fig. 2C) the minerals form an open diktytaxitic network that was filled by supercritical H2O and pockets of melt blebs (up to 10 μm in size) that are trapped between grain boundary junctions. At higher pressures (>2 GPa) the porosity of the open crystal network decreases and the most common appearance of melt was as small bubble-filled regions that were ubiquitously present in the entire charge, but preferentially concentrated in the upper (hotter) portion of the charge with garnet, oliv, opx and cpx near the solidus (Fig. 4).

Fig. 1. Vapor-saturated phase equilibria for the Hart and Zindler [9] primitive mantle composition. Symbols show phases present in addition to olivine + orthopyroxene + clinopyroxene. Grey curve is the vapor-saturated solidus.

determined by looking at broken pieces of the experiments with an SEM. Fig. 5 shows the quenched melt in the upper olivine+opx-rich zones of the charge in sample C260 (2.8 GPa, 910 °C).

At constant pressure, the lowest temperature (unmelted) experiments are texturally unzoned, with a homogeneous distribution of phases throughout the charge (Fig. 2A). With increasing temperature the charge (melt-bearing experiments) is no longer texturally homogeneous and porosity decreases from the hottest part (top) to the coldest part (bottom) of the charge (there is a 10 °C thermal gradient in the charge). We attribute this textural zonation to a thermal compaction effect [21] facilitated by the presence of melt, the small thermal gradient (∼10 °C) and the long experimental run times. The low temperature reactant phases segregate to the cooler bottom of the sample, and the high temperature liquid + solid product phases segregate to the hotter top. This modal segregation does not occur when only crystals + vapor are present, either because the entropy reduction driving force is not high enough between the hot and cold ends or the element transport rates are not fast enough. In the modally zoned melted experiments clinopyroxene tends to concentrate in the cold end of the sample as clearly revealed in the Ca X-ray images (Figs. 3D and 4B). Olivine and melt (and the open pore space—formerly occupied by supercritical H2O vapor) concentrate in the hot part of the charge (Figs. 3 and 4). The phases remain chemically homogeneous throughout the charge.

Samples that had not undergone melting also have very distinctive textural characteristics. Subsolidus experiments (Fig. 2A,B) show the characteristic uniformity in the distribution of phases throughout the charge. The textures of the minerals in the subsolidus experiments are also distinctive. Euhedral needles of pyroxene extend into a uniformly distributed open pore space (Fig. 2B) throughout the entire experimental charge.

As summarized in Fig. 1 and Table 1, the vapor-saturated solidus that would be inferred from these experiments is at 940 °C at 1.2 GPa, 865 °C at 2 GPa and 800 °C at 3.2 GPa within an uncertainty of ±15 to 20 °C. The vapor saturated solidus shown in Fig. 1 is extrapolated to the 0.01 MPa dry solidus, according to the predictions of [22,23] for the Hart and Zindler peridotite composition. At 0.01 MPa, H2O solubility in the melt would be negligible.

3.3. Mineral textures

The mineral shapes and textural characteristics of these experiments are a response to the nucleation and growth of the product phases from an oxide starting mix in the presence of H2O. Olivine grew as equant, euhedral to subhedral crystals in all charges and ranged in size...
from 10 to 100 μm (Figs. 2–5). Orthopyroxene and clinopyroxene grew as elongate prismatic crystals that ranged in dimension from 20 by 100 μm in higher temperature experiments (Figs. 2 and 4C) to needle-like laths with high aspect ratios and widths of 1–10 μm (Fig. 4C) in the lowest temperature experiments. Amphibole crystallized as well developed euhedral crystals up to 100 μm in longest dimension (Fig. 2D) that poikilitically enclose the olivine and pyroxene in high temperature experiments. Spinel was present as small subhedral to euhedral crystals that were rarely larger than 2 μm in diameter. Garnet always grew as large subhedral crystals (up to 500 μm in diameter, Figs. 3 and 4) that poikilitically enclosed oliv+opx+cpx. Garnet nucleated in all parts of the capsule regardless of the presence or absence of melt (Figs. 3E and 4A).

### 3.4. Mineral and melt composition

Multiple mineral grains were analyzed (Table 2) in the experimental charges to assess the extent to which the oxide starting mix had reacted to a set of homogeneous silicate products. In BSE images all phases appear to be compositionally uniform and homogeneous, and this observation is reinforced by the lack of compositional variability measured by analyzing multiple mineral grains. Olivine and orthopyroxene are the most chemically homogeneous phases and Fe and Mg are very homogeneous with variations in the means of replicate analyses that range from <1 to 2% relative. The minor element contents of pyroxenes show slightly more variation. The large poikilitic phases (amphibole and garnet) are also compositionally homogeneous, despite their large size. Spinel was difficult to analyze because of its small grain size and it showed the largest compositional variations. The phase compositions vary from sample to sample in response to variations in temperature, pressure and melt composition. Despite the variability in minor element contents of pyroxenes and in spinel in individual samples, a variation can be identified with increases in melt fraction and temperature of the sample.

Melt could be analyzed only in one experiment (e.g., B814, Table 2, Fig. 2C) because in most experiments, it
was present as micron-thick bubble walls in a quenched melt froth making it impossible to analyze with the electron microprobe. The melt in B814 is a high-Al2O3 andesite (57 wt.% SiO2, 22.4% Al2O3). The high SiO2 content of this melt and its occurrence with olivine in the hotter end of the charge is consistent with a peritectic melting reaction:

\[
\text{opx} + \text{cpx} + \text{spinel} = \text{olivine} + \text{melt}
\]

Although melt compositions could not be determined in the higher pressure experiments, the association of olivine + liquid is present up to 2.8 GPa, suggesting that melts remains SiO2 rich. In the 3.2 GPa experiments orthopyroxene joins olivine and melt, suggesting that the first melt becomes olivine-normative at higher pressures [24].

We do not think that the quenched melt that we observe is an SiO2-enriched fluid phase that formed below the solidus. The solubility of SiO2 in H2O at these conditions in the presence of olivine and orthopyroxene is very low [25,26], and our expectation is that a quenched fluid phase would produce spherical blebs of an SiO2-rich component by unmixing from a dominantly fluid phase.

3.5. Oxygen fugacity

The oxygen fugacity of the spinel-bearing experiments was estimated using the olivine–orthopyroxene–spinel oxygen geobarometer [27]. The predicted values lie between −1 to +2 log units around the QFM buffer with an average of +0.8 log units above QFM (Table 1). Thus, the \( f_{O2} \) of these experiments is similar to the \( f_{O2} \) values inferred for the mantle wedge above subduction zones [28].

Fig. 3. Melt-bearing near-solidus experiment C260 (910 °C and 2.8 GPa). Hot end of the sample faces up. (A) Back-scattered electron (BE) image showing gold capsule with concentration of olivine+melt at top of charge. Black regions are porosity, previously vapor-filled. (B) BE image of close-up of melt and olivine at top of charge. (C) Large area BE image showing edges of Au capsule (bright regions) and poikilitic garnet (gt) crystals throughout the sample. (D) Large area Ca WDS X-ray image showing compaction of clinopyroxene toward bottom. (E) Large area Al WDS X-ray image highlighting the garnet crystals, present near the top and near the bottom of the charge.
3.6. Approach to equilibrium

The experiments reported here are synthesis experiments, no reversal-type experiments have been performed. Demonstration of equilibrium through a reversal experiment would be difficult (if not impossible) for an assemblage of phases with this compositional complexity. However, we will demonstrate that reaction among coexisting solids has proceeded sufficiently so that the coexisting minerals have approached near equilibrium values, and that the results are meaningful for investigating the systematics of peridotite melting. Three sets of observations indicate a close approach to equilibrium: (1) the growth of compositionally homogeneous, chemically unzoned minerals, (2) the achievement of 2-pyroxene temperatures between coexisting orthopyroxene and high-Ca clinopyroxene (opx + cpx) that are similar to the experimental conditions and (3) maintenance of constant bulk composition.

As discussed above, the silicate minerals produced in these experiments are compositionally uniform, even when they are large, as in the case of garnet and amphibole. The combination of using oxide starting mixes, H2O and the long duration of the experiments has led to the development of homogeneous experimental products. This has also been the conclusion of other experimental studies on dry peridotite melting [5,29] that compared the compositions of minerals using experiments that used both oxide and natural crystalline starting materials. In these dry experiments the oxide mixes grew more uniform products, whereas the mineral grains in the natural peridotite experiments retained compositional heterogeneities for much longer; even after the longest experiment durations [29].

For all of the experiments that were analyzed we calculated a 2-pyroxene temperature using the QUILF thermometer [30]. The temperatures predicted by QUILF are summarized in Table 1. Of the 10 experimental charges

![Image](https://example.com/image.png)

**Fig. 4.** Melted near-solidus experiment D151 (840 °C and 3.2 GPa). Hot end of the sample faces up. (A) Back-scattered electron (BE) image of the entire sample. Au is black with white fringe as a result of image processing. Melt + bubble layer is visible at top of the charge. Poikilitic garnet (gt) is distributed throughout the charge. (B) Large area Ca WDS X-ray image showing gradation in cpx abundance away from the melt + olivine rich layer near the hot end. (C) Close up BE image near top of the charge.
analyzed, all but 3 predict the experimental temperatures within 1 sigma of the uncertainty in the estimate, and the other 2 are close, and would probably approach the experimental value more closely, if more analyses were made of the minerals. The exception is one of the lowest temperature experiments analyzed (D151). In this experiment it was not possible to obtain good quality analyses of the pyroxenes. The width of the pyroxene grains (Fig. 4C) is on the order of the electron beam size, and melt coating the grain edges interferes in the X-ray generation. Thus, the close correspondence of the experimental and estimated temperatures is judged to be sufficient evidence that the experiments approached equilibrium.

An approach to equilibrium requires that there be no loss or gain of mass between the starting material and the enclosing capsule. The analyzed experiments were mass balanced and with the exception of the highly melted experiment (B816, 1100 °C, where the melt phase was not analyzed) have low sum of squares of the residuals (<0.25). Also, the gain or loss of Fe to the enclosing capsule was calculated (Table 1) and was generally less than 5 wt.% relative. The element that did not mass balance well was Na, and this is because it is concentrated in the melt or fluid phase. For the melt analysis of B814 (w/Na2O in Table 2), the result of the mass balance calculation was used to restore Na2O in the liquid. We do not know whether some Na2O was also partitioned into the super-critical fluid, and this restored value should be viewed as a maximum amount.

4. Discussion

4.1. Comparison with previous experimental studies

Four prior experimental studies investigated the lower-pressure vapor saturated melting of peridotite [8,31–34]. The earliest studies were made when the piston cylinder technique was in its infancy. The experiments of Kushiro et al. [33,34] and Millhollen et al. [32] were carried out in either Pt or Mo capsules, run durations were short (from 5 min to 3 h) and H2O was added as a liquid to a starting material of natural peridotite powder. Green [31] utilized AgPd alloy capsules with experimental run times of up to 6 h and 10 wt.% H2O was added to an oxide starting material. All three of these studies reached a similar conclusion for the melting behavior of peridotite. Their results show a curved concave-up P–T boundary with a minimum melting temperature of about 1000 °C at 2.5–3 GPa (Fig. 6A). Mysen and Boettcher [8] used AgPd alloy capsules but with much longer experimental run times of up to 64 h and their starting material of natural peridotite powder contained 20–30 wt.% H2O. Their melting behavior differs substantially from the three other experimental studies. The melting point depression is significantly greater and reaches a minimum at 800 °C at 3 GPa (Fig. 6A). Mysen and Boettcher [8] used AgPd alloy capsules but with much longer experimental run times of up to 64 h and their starting material of natural peridotite powder contained 20–30 wt.% H2O. Their melting behavior differs substantially from the three other experimental studies. The melting point depression is significantly greater and reaches a minimum at 800 °C at 3 GPa (Fig. 6A) and is most similar to results of the present study.

The reason for the apparent discrepancy in results may be that the higher melting point experiments were all run for very short times, perhaps too short for melting of the natural minerals to be observed. Experimental studies have shown that the melting kinetics of olivine are significantly slower than those of diopside under similar temperature–pressure conditions [35]. Kinzler and Grove [22] found that this could explain discrepancies in basalt–peridotite sandwich melting experiments where olivine persisted with pyroxene and melt outside its equilibrium stability range. The melting behavior observed in the previous vapor-saturated peridotite experiments that found a higher
temperature solidus may be similarly influenced by melting kinetics. The solidus depression in the older short duration experiments is most similar to that observed for pure diopside [36,37] (the mineral that melts faster) while the solidus depression found in the longer duration experiments [8] is more similar to that observed for the vapor-saturated melting of forsterite [38,39]. At 2 GPa, the melting point depression in diopside caused by the presence of H₂O is ~200 °C less than that observed for forsterite. A possible explanation of the high solidus temperature of the short duration experiments is that they were too short for equilibrium melting to occur. At the lowest temperature (e.g. 800 °C, 3 GPa), melting rates for diopside and olivine are so slow that neither phase melted during the short run time. Also, temperatures are too low for disequilibrium melting of diopside (the mineral with the fastest melting kinetics) to occur. At higher temperatures (1000 °C) diopside melted significantly during the experiment: some olivine may have melted as well. Enough disequilibrium melting occurred so that the melt could be observed in the run product. Thus, the melts in these experiments were not in equilibrium with the other mineral phases and the solidus determined was not the equilibrium solidus.

Another factor in two of the early studies was the use of Pt and Mo capsules. These containers are now known to lose H₂O rapidly by diffusion of H₂ through the capsule and to interact with the silicate starting material. It is possible that H₂O loss and Fe loss also influenced the experimental results. The expected effect on the solidus would be to move it to higher temperatures. The experimental results presented here are in close agreement with those obtained by Mysen and Boettcher [8]. We conclude that both sets of experiments provide a more accurate characterization of the vapor-saturated melting behavior of peridotite. Both studies used experimental durations significantly longer than the studies that found a higher temperature solidus. Both used capsule material that is inert to exchange of Fe with the starting material and both also added significant amounts of H₂O to the starting material, which may have facilitated the observation of the appearance of the first melt.

4.2. Phase equilibrium controls on melting in subduction zones

4.2.1. Amphibole stability in hydrated mantle peridotite

The amphibole stability in our experiments is most similar to that found by Mysen and Boettcher [8]. As discussed by Wyllie [40] and Niida and Green [41] peridotite bulk composition (alkalis and titanium contents) as well as oxygen fugacity influence the upper temperature and pressure limits of amphibole stability. The upper pressure limit of amphibole in this study (<2 GPa, Fig. 1) is at the low pressure end of the range found in previous investigations [40,41], and our peridotite also has the lowest Na₂O and TiO₂ of the ones that have been used in amphibole stability studies. Vapor-saturated melting in the presence of amphibole occurs from 940 °C at 1.2 GPa to 880 °C at 1.7 GPa.

4.2.2. Chlorite as a stable phase on the peridotite solidus

A high pressure chlorite phase has been found in mantle-analog [19] and in natural peridotite compositions [20]. We find a similar phase coexisting with melt at the peridotite solidus from 2 to 3.2 GPa (Figs. 1, 2B,

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Fig. 6. (A) Water-saturated peridotite solidus comparison. M&B=[8] K&K, S&A=[33,34], M=[32], G=[31], K&G=[23]. (B) Comparison of vapor-saturated melting of peridotite, with that of MORB basalt and terrigenous sediment. Basalt melting (dashed grey lines) from L&W [47] and L et al. [46]. Sediment melting studies (dashed black lines) are P&S [48] and N et al. [49].

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and 4)C, Table 2). This hydrous phase contains 12 wt.% H2O and is potentially stable at the peridotite solidus during mantle wedge melting. If so, then H2O released from the slab into the overlying mantle wedge at P>2 GPa (~60 km) may be stored as chlorite that can be advected to greater depths by descending mantle flow at the base of the wedge. This hydrated mantle will be heated and then dewatered when chlorite breaks down, releasing its water and initiating hydrous melting.

4.2.3. Ilmenite as a residual phase—HFSE depletions

The low temperatures of the wet peridotite solidus result in a significant decrease in the solubility of “other” components (CaTi2Al2O6, CaAl2SiO6, CaCrAlSiO6, etc.) in high-Ca pyroxene. The consequence is the saturation of another oxide phase that is an ilmenite–geikielite solid solution (D151, Table 2). This oxide phase is a potential reservoir for high field strength elements (HFSE, e.g., Zr, Nb and Ta) [42] and its presence may lead to retention of HFSE elements during melting in arc systems [43]. In this case the HFSE retention would be a consequence of melt/mantle residue partitioning of these elements at the initiation of H2O saturated peridotite melting, and not a consequence of melting of subducted oceanic crust.

4.2.4. The source of H2O for melting of the mantle wedge

In the following discussion we assume that H2O is in abundance at the onset of melting in the mantle wedge. The dehydration of hydrous minerals in subducted oceanic lithosphere may be the source and H2O may be supplied from hydrated sediment, basalt or mantle lithosphere [6,44]. Also, serpentinized mantle lithosphere underlying the top-most sediment and basalt layers of subducted lithosphere can be an important reservoir that fuels vapor-saturated flux melting. Recent observations of serpentine formation at the locus of plate bending in the fore arc [45] indicate that serpentine can form at depths of 25 km within the subducted lithospheric mantle. Chlorite-bearing hydrated mantle above the slab may also carry H2O into the melt generation zone. H2O is supplied to the wedge by hydrous mineral breakdown throughout the subducted lithosphere wherever hydrous minerals become unstable. The vapor-saturated solidus of peridotite is compared to that of basalt [46,47] and sediments [48,49] from previous experimental studies in Fig. 6B. The solids are separated by ~100 °C at pressures relevant to subduction zone melting. This depth is chosen as that corresponding to the average depth range to the slab–wedge interface in modern subduction zones (100–125 km). If the subducted basalt or sediment is heated sufficiently melting will occur. The resulting siliceous and H2O-rich melt (~30 wt.% H2O) would encounter solid mantle as it ascended into the overlying wedge, crystallize, converting olivine to orthopyroxene, and producing an alkali and trace element enriched supercritical fluid that would equilibrate with peridotite [6].

4.3. Mantle wedge melting processes

In the following discussion the vapor-saturated phase relations for peridotite are used as a starting point to develop a model of mantle wedge flux melting. The model assumes that the first melt generated along the base of the wedge is vapor-saturated, and that melting will occur everywhere above the slab where temperature exceeds the vapor-saturated solidus. After this melt forms and ascends into the wedge, melting will continue at H2Oundersaturated conditions. This simplifying assumption neglects the potential controls that might exist on the release of H2O into the mantle wedge [50]. At present we do not have a complete characterization of the melting behavior of natural hydrous mantle peridotite. However, we do understand that H2O has a large influence on melting [44,51] characterized by a large temperature lowering effect that spreads melting out over a larger temperature interval. Thus, while realizing that there are complexities we are not accounting for in the model, a simplified melting model exploring the general influence of variations in H2O may reveal some features that could be important in arc melt generation in the mantle wedge.

4.3.1. A simplified peridotite melting model

The relationship between melt H2O content, temperature and pressure is approximated by taking advantage of the results of thermodynamic models for simple silicate–H2O binary systems developed by Silver and Stolper [52]. Their model accounts for speciation of H2O in the melt phase and its influence on melting behavior. Their prediction for the temperature–composition (T–XH2O) liquidus surface has been modified for natural peridotite. The input parameters needed are the H2O content of the vapor-saturated solidus (XH2O) and an approximation of the dry peridotite melting behavior. We use the phase relations determined here (Fig. 1) along with measured H2O solubility vs. pressure in forsterite–H2O [38,39] to predict the peridotite–melt boundary in T–P–XH2O space. The expression is:

\[
7290^\circ P - 810^\circ T - 24600^\ast H_2O + 1093500 = 0
\]  

where T is in °C, P is in kilobars and H2O content is in wt.%. The dry peridotite melting temperatures are reasonable approximations of sub-liquidus partial
melts of peridotite taken from [22,24] and the simplified melting boundary is essentially the liquidus in a binary system that extends from a eutectic-like vapor-saturated solidus to a dry liquidus (Fig. 7). This model represents the liquidus as a planar surface in $T$–$P$–$X_{H2O}$. This is the shape of the liquidus surface predicted by the Silver and Stolper model [52] for Diopside–$H2O$ and Albite–$H2O$.

The fraction of melt produced at the vapor-saturated solidus ($F_{init}$) is assumed to be 2.5 wt.% This is an unknown parameter and the distribution of $H2O$-rich fluid at the base of the mantle wedge may influence the initial melt fraction [50]. Estimates of equilibrium melt fraction for anhydrous melts in olivine-rich aggregates range from <0.1 to 2.5 wt.% interstitial melt [53] and up to 8–9 wt.% in olivine+pyroxene-bearing water-saturated systems [54]. We chose the value of 2.5 wt.% because it yields melts of comparable melt fractions ($F$=0.17–0.20) to melting amounts inferred by experimental petrology [6].

The first melt generated along the base of the wedge is vapor-saturated (P1, T1, Fig. 7). After this melt forms and ascends into the overlying mantle it continues to react and melt its surroundings. It will evolve along the $H2O$ undersaturated peridotite liquidus surface (Eq. (1)). The variation in melt fraction is calculated by determining the amount of crystalline material that needs to be dissolved in order to bring the melt at a higher temperature and lower pressure (P2, T2 in Fig. 7) into equilibrium with the surrounding solids ($\Delta F2$ in Fig. 7). At P2, T2 the amount of melt ($F_{P2, T2}$) is given by:

$$F_{P2, T2} = \left( \frac{X_{init} - X_{P2, T2}}{X_{init}} \right) / X_{init} + F_{init}$$

where $X_{P2, T2}$ is the equilibrium $H2O$ content of the vapor-undersaturated melt on the crystal +melt boundary at P2, T2. P2 and T2 are specified by knowing the thermal structure of the wedge, thereby allowing estimation of $X_{P2, T2}$. The melting process continues and the melt ascends again to shallower depths, encounters hotter mantle (P3, T3) and melts ($\Delta F3$ in Fig. 7). At each step the amount of melt can be estimated by calculating the amount of solid that needs to dissolve at the shallower, hotter depth to bring the melt into equilibrium with the enclosing mantle minerals:

$$\Delta F_n = \left( \frac{X_{n-1} - X_n}{X_{n-1}} \right) / X_{n-1},$$

where $X_n = f(T, P)$.

The $H2O$-rich melts would be very buoyant would leave the base of the wedge and ascend into the overlying mantle by porous flow or by coalescing into small upward moving diapirs [55]. Grove et al. [6,44] discuss the possible mantle flow mechanisms and favor reactive porous flow as the flux melting process. In either case, the melt or melt + crystal diapirs must come into thermal equilibrium with the surrounding mantle. We assume a reactive porous flow mechanism and also assume that the melt does not lose $H2O$ to the surrounding mantle as it ascends (essentially a closed system for $H2O$, a reasonable assumption since only nominally anhydrous phases are stable in the wedge).

The system is open to exchange of heat and all other elements between the melt and surrounding mantle. The
melt is a relatively small mass distributed in grain boundaries and is thermally overwhelmed by its surroundings.

4.3.2. Pressure–temperature variations in the mantle wedge

The temperature distribution in the mantle wedge shown in Fig. 8 is taken from a numerical study by Kelemen et al. [56]. The exact temperature distribution, spacing of isotherms and maximum temperature achieved in the

4.3.3. A flux melting model

The model flux melting process is mapped into the mantle wedge thermal model in Fig. 8. Melting has not been calculated at depths >108 km. This cut off is arbitrary, but it is assumed that below some depth H$_2$O will no longer be supplied to the overlying mantle wedge. Also, for the thermal model used in Fig. 8, the vapor-saturated solidus is at the wedge–slab interface at 108 km depth. Vertical melting paths are calculated from 108 km depth to 55 km on the slab interface. This shallower depth corresponds to the depth above which vapor-saturated melting no longer occurs, because the overlying mantle is too cool to exceed solidus temperatures. The base of the shaded region in Fig. 8 marks the part of the wedge that is above the vapor-saturated solidus. Above that melting is vapor-undersaturated. The melt fraction increase is shown in Fig. 8A and the melt H$_2$O content is shown in Fig. 8B. The H$_2$O content of the first vapor-saturated melt is calculated to be 28 wt.% at 108 km and 20 wt.% at 60 km (Fig. 8B). A very H$_2$O-rich melt is predicted in a thin sliver at the base of the melting regime. Melt fraction is low all along the base and H$_2$O content drops as initial pressure of melting decreases. Melt fraction increases toward the hotter center of the mantle wedge. The maximum amount of melting (10–15 wt.%) occurs in the hot core of the mantle wedge that ranges from 40 to 63 km depth and H$_2$O contents of these melts vary from 3 to 5 wt.%. These melt fractions and H$_2$O contents are consistent with evidence from experimental petrology [6,44]. Melting of the overlying wedge at progressively shallower depths occurs at lower temperatures and produces lower extents of flux melting with higher H$_2$O contents. The maximum amount of melting in the hot core of the mantle wedge in this region (30–40 km depth) is 3–5 wt.% and the H$_2$O contents of these melts vary from 10 to 15 wt.%.

The upper hatched region in Fig. 8A represents the part of the mantle with a normal thermal gradient and the hatched region is extended from the hot core up to the minimum depth and temperature of the vapor-saturated solidus. The melt passes into this part of the mantle, cools
and reacts further with the mantle by dissolving olivine and crystallizing orthopyroxene [58] and increase melt H2O content. Alternatively, melts might pool, coalesce and ascend as diapirs evolving further by adiabatic melting processes.

4.4. Summary

In summary, our re-evaluation of the melting of peridotite in the presence of excess H2O finds a solidus that is much lower (by ~ 200 °C at 3 GPa) than reported by some early experimental studies. The discrepancy in results is probably the result of short run times used in these early studies. Chlorite is a stable and abundant phase on the vapor-saturated peridotite solidus from 2 to 3.2 GPa and could be a potentially important reservoir for H2O. The near-solidus peridotite assemblage contains 16 wt.% chlorite and could hold ~ 2 wt.% H2O. The new phase diagram also allows the description of reactive porous flow flux melting in the mantle wedge. Melts produced by this process will undergo most of their melting at shallow mantle depths in the hottest part of the wedge. The maximum amount of melt (~ 15 wt.%) is in the hottest part of the mantle wedge over a depth range of 40–60 km.

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