Contrib Mineral Petrol (2012) 164:1077–1081
DOI 10.1007/s00410-012-0802-0

DISCUSSION

Comment on "The beginnings of hydrous mantle wedge melting", CB Till, TL Grove, AC Withers, Contributions to Mineralogy and Petrology, DOI 10.1007/s00410-011-0692-6

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Received: 26 November 2011 / Accepted: 24 February 2012 / Published online: 14 September 2012

The paper by Till et al. (2011) reports new experiments on high pressure melting in the system (lherzolite + water). In comparison with earlier published work, several appropriate methods of phase characterisation and experimental techniques, have not been reported. A result is that the authors' conclusions are not substantiated for two important issues: the position in pressure, temperature (P, T) space of the hydrous vapour-saturated solidus and the compositions of near-solidus melts. The application of the experimental results to discussion of melting in the mantle wedge overlying subduction zones is therefore questionable.

With respect to the position of the vapour-saturated solidus, Grove et al. (2006) and Till et al. (2011) place the solidus at ~820 °C at 3–5 GPa, which is ~230 °C (3 GPa) to 500 °C (5 GPa) below the solidus inferred by Green et al. (2010, 2011) for the same HZ1 lherzolite composition, by Niida and Green (1999) on the compositionally near-identical MOR pyrolite composition and by Green (1972, 1973, 1976), Millhollen et al. (1974), Mengel and Green (1989), Wallace and Green (1991) and Fumagalli et al. (2009) on other lherzolite compositions. Grove et al. (2006) and Till et al. (2011) base the position of the solidus on the appearance of glass among the quench products and on a marked change in texture of the experimental charge at ~810 °C from 'fine-grained, uniform in porosity and homogeneous in texture' (inferred subsolidus) to 'coarser grained, mineralogically zoned, exhibit compaction of minerals in the bottom—and a gradient in porosity towards the top (hot) end of the charge' at temperatures above 810 °C, 3–5 GPa (inferred above-solidus). To support their interpretation, Till et al. (2011) publish low-magnification scanning electron microscope (SEM) images (Fig. 2 in Till et al. 2011) of their charges and plots of Mg# versus Temperature for minerals (Fig. 3 in Till et al. 2011). In the latter figure and in Electronic Supplementary Material of Till et al. (2011) there are no analyses from <840 °C (i.e. no 'subsolidus' mineral data) at 3.2 GPa, and the higher-temperature data suggest a solidus between 1020 and 1060 °C. The SEM images presented show an absence of poikiloblastic garnet in runs interpreted as 'subsolidus' at other pressures. The mineral analyses presented from five 'subsolidus' experiments show garnet with 17.3–24.9 wt % Al_2O_3 and 8–16.6 wt % CaO (Electronic Supplementary Material of Till et al. 2011). Compositions do not meet stoichiometric constraints, and natural lherzolite garnets are restricted to 4–6 wt % CaO. Similarly, orthopyroxene compositions are reported with 0.2–3.9 wt % CaO. Clinopyroxenes are reported with 12.5–20.7 wt % CaO and from below detection to

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This comment refers to the article available at 10.1007/s00410-011-0692-6.
An author's reply to this comment is available at 10.1007/s00410-012-0803-z.

Communicated by J. Hoefs.

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0.29 wt % Na_2O. The last number is important as these experiments are inferred to be subsolidus and water-saturated lherzolite with olivine + orthopyroxene + clinopyroxene + garnet + vapour. In this case with 10–15 modal % clinopyroxene (Grove et al. 2006; Green et al. 2011) as the only Na-bearing mineral, the clinopyroxene should contain >2 wt % Na_2O because of the bulk Na_2O content of 0.33 wt % in lherzolite HZ (Table 1 of Till et al. 2011). If the analyses of clinopyroxene are correct, then it implies that even at 760–800 °C at 3.6–6 GPa the vapour phase (>14.5 wt %) contains more than 80 % of the Na_2O in the charge.

The authors use 14.5 wt % water in their experiments, all added to the mix as brucite. After quenching, the low-temperature experiments immediately below the inferred solidus are reported to contain the subsolidus assemblage olivine + orthopyroxene + clinopyroxene + garnet + vapour. If this is correct, the capsule after quenching contains approx. 14.5 wt % or at least 30 vol. % liquid water. For experiments at >810 °C, this is consistent with the presence of water on opening the charge and with the highly porous, disaggregated olivine-rich and agglutinated pyroxene-rich inhomogeneity of the charges. At the high P, T run conditions, the volume percentage of vapour would have been similar, assuming density of the vapour phase is around 1 (Johnson and Walker 1993). However, Till et al. (2011) argue that because experiments from <810 °C do not show this highly porous, inhomogeneous texture, the textural change and the appearance of glass mark the water-saturated solidus. As noted previously, the low-magnification SEM images appear to show very fine-grained minerals with low porosity and questionable mineral compositions. We suggest an alternative explanation for the observations. Brucite is stable to ~850 °C at 1 GPa and ~1150 °C at 5 GPa (Johnson and Walker 1993). At the conditions of the experiments in question, brucite is stable under its own composition and its dehydration to release water (and enhance reaction rates) is dependent on reaction with other phases, particularly enstatite or free silica. Thus, samples are initially vapour-absent and reaction rates are controlled by solid-state diffusion. It is probable that at some temperature brucite will persist metastably in the starting mix. Also, the upper temperature stability limits of talc and antigorite are in the 700–850 °C range at high pressures, and these phases contain >10 wt % and 12 wt % water, respectively. If the 'subsolidus' experiments contain stable or metastable hydrous phases, then there may be little or no excess vapour phase. In view of the fine grain size of the run products and their unsuitability for electron microprobe analysis, characterisation of the run products by X-ray diffraction is necessary to eliminate the possibility that hydrous phases are modally important and to demonstrate the modal dominance of olivine, enstatite, clinopyroxene and garnet. In addition, high-magnification SEM, including on fractured surfaces, is desirable for such fine-grained run products (Fumagalli et al. 2009). The apparent absence of glass below 810 °C and the alternative reasons for this should be tested.

Till et al. (2011) observed fragmented glass films at temperatures above 810 °C and interpret this as quenched hydrous silicate melt, whereas Green et al. (2010, 2011) interpret similar glass 'froth' in experiments at and below 1000 °C as precipitate from an aqueous vapour phase. Importantly, Till et al. (2011) identify charges in which they can distinguish between vapour-phase quench and quench from hydrous silicate melt, in experiments in which vapour-saturated melts occur, that is, two fluid phases. In Fig. 6 (Till et al. 2011), SEM images show filaments or wisps of glass interpreted as quenched hydrous silicate melt, accompanied by olivine crystals and by spheres or bubbles of glass interpreted as precipitated from the vapour phase on quenching. Similar texture was also interpreted as silicate melt quench and vapour-phase quench by Adam et al. (1997). Accepting that this texture is correctly interpreted, the observations show that these conditions are below the second critical endpoint for the HZ1 composition and thus that there is a clear distinction between hydrous silicate melt and water-rich vapour. However, the authors present evidence for this texture only at 1060 and 1100 °C at 3.2 GPa and present no images showing this distinctive texture between 810 and 1060 °C nor at higher pressures. Based on the evidence actually presented by Till et al. (2011), the vapour-saturated solidus is between 1020 and 1060 °C at 3.2 GPa. This is consistent with the positioning of the solidus between 1000 and 1025 °C at 2.5 GPa and between 1200 and 1225 °C at 4 GPa by Green (1973), Green et al. (2010, 2011) and by Niida and Green (1999) at 1050 °C and 3 GPa (for the HZ lherzolite and MOR pyrolite compositions, respectively).

In interpreting these and related experiments, it is important to place this study in the wider context of prior work. If the Till et al. (2011) interpretation is correct and hydrous silicate melt is present above 810 °C, 3–5 GPa, then this melt has a composition such that it will have a liquidus temperature of 800–850 °C at 3–5 GPa and will crystallise olivine, orthopyroxene, clinopyroxene and garnet on or near its liquidus at those P, T conditions. There are sufficient studies of high pressure water-saturated melting of magmas from rhyolites to andesites to tholeiitic basalts and from kimberlites, olivine melilitites, olivine nephelinites, alkali olivine basalts to olivine tholeiites to establish that only alkali and silica-rich rhyolitic to rhyodacitic magmas have water-saturated liquidi at these low temperatures. However, their liquidus phases are clinopyroxene, garnet and quartz/coesite. Garnets have >9 wt % CaO and clinopyroxenes have high jadeite contents. These liquids are not complementary to lherzolitic residues. There are also many published studies of the phase relations of primitive mantle-derived basalts ("sensu lato") with water and water + CO_2, including liquidus temperatures, liquidus depression as a function of water content, and conditions for multiple saturation with olivine + orthopyroxene ± clinopyroxene ± garnet (i.e. consistent with melts derived from hydrous melting of lherzolite). In Fig. 1, we reproduce a figure (Green 1972) that summarises the melting behaviour of lherzolite at ~3 GPa as a function of melt fraction for a low water content in the source. For higher water contents, melt fractions increase at a given temperature (Fig. 3 in Green 1972) but melt compositions remain in equilibrium with lherzolitic to harzburgitic residues [see also discussion by Stalder (2012)]. Studies to that time and since have confirmed solidus temperatures for hydrous melting of lherzolite to lie between 970 and 1050 °C in the 1.5–3 GPa pressure range. The liquidus temperatures of 1000–1150 °C for vapour-saturated, alkali-rich, silica-undersaturated and nepheline normative magmas overlap with these values.

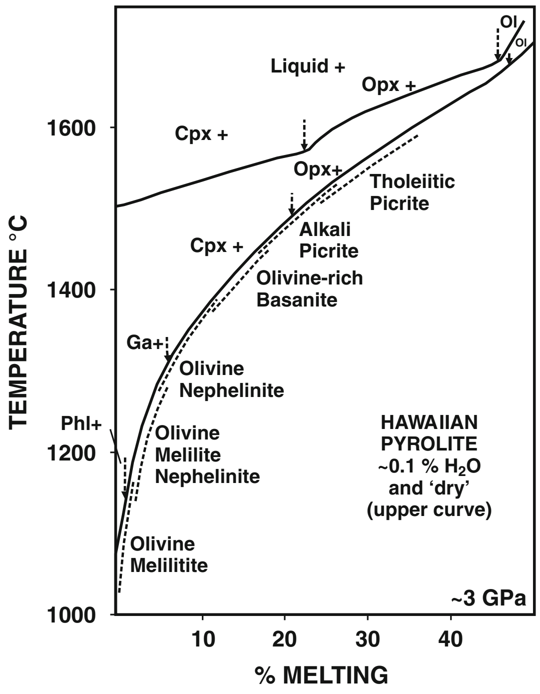

Fig. 1 Derived from Fig. 4 in Green (1972). The *upper solid curve* is a plot of melt fraction against temperature for anhydrous Hawaiian pyrolite composition at ~3 GPa, (i.e. at $P >$ pargasite stability at the solidus) also showing (*arrows*) progressive disappearance of clinopyroxene and orthopyroxene as residual phases with increasing melt fraction. The lower solid curve is the melting behaviour for Hawaiian pyrolite with ~1000 ppm water. The depression of the solidus by ~400 °C introduces both garnet and phlogopite as subsolidus phases, but phlogopite and then garnet are melted out at low melt fraction. The dashed lines link mantle-derived magmas of various petrological/geochemical types with melt fraction and changing residual phase assemblages. Note the alkali-rich and very silica-undersaturated liquids present at and near the solidus (water-saturated) and the transition through to tholeiitic picrite with decreasing water content and increasing melt fraction. The figure is based on experimental study of melting relations of Hawaiian pyrolite and of liquidus temperatures and phases of mantle-derived magmas, selected from the population of mantle-xenolith-bearing magmas together with inferred parental magmas for Hawaiian olivine tholeiites. These liquidus studies include the determination of liquidus depression of olivine-rich magmas for a given water content (Fig. 2 in Green et al. 2001). This relation effectively defines the ΔT between the two *solid curves* of Fig. 1 Till et al. (2011) do not relate their experimental study to this body of complementary information on compositions and petrogenesis of mantle-derived magmas

There is a strong element of déjà vu about the current debate. The study of Mysen and Boettcher (1975) used similarly high water contents to those used by Grove et al. (2006) and Till et al. (2011) and inferred similarly low solidus temperatures. It is referenced in both papers under discussion. However, because of the disagreement between this paper and the results of Kushiro et al. (1968), Green (1972, 1973) and Millhollen et al. (1974), a further study [Green (1976), not referred to by Grove et al. (2006) or Till et al. (2011)], was undertaken to address several issues:

(a) the use of crushed mineral mixes as starting materials [avoided by the Australian laboratories on the basis that fine crushing to <10 microns to ensure reactivity results in unavoidable contamination, particularly for garnet or spinel (Green and Ringwood 1967; Hensen and Green 1971; Raheim and Green 1974; among many authors)]: The use of mineral mixes as starting materials, the techniques of seeding with pre-synthesised, high or low pressure assemblages, and the presence of relict starting materials and of mineral zoning, have been well documented by many workers, but Till et al. (2011) in their use of a mineral mix to obtain compositions with low water content (0.7 wt %) make no reference to avoidance or evaluation of problems associated with this approach.

(b) the presentation of glass analyses, particularly high SiO_2 and low MgO glasses, as equilibrium melt compositions without recognition of the quench modification of interstitial melt: In Grove et al. (2006) and Till et al. (2011), there are no reversal experiments or other criteria to correct for quench modification of melt compositions. A further factor is the analysis for Na_2O in glass, recognising the potential volatilisation of Na with high beam currents and/or spot analyses by electron microprobe. Na_2O appears to be deficient in all experiments where mass balance calculations can be made. The issue of quench modification of equilibrium melts (olivine and nepheline normative i.e. silica-undersaturated) to yield analysable glass of quartz-normative character

> (i.e. silica-oversaturated) was more recently illustrated in dry melting of lherzolite mineral mixes (Baker et al. 1995). Their interpretation of quartz-normative melts was tested by reversal experiments (Falloon et al. 1997) and the initial interpretation corrected (Hirschmann et al. 1998). The current authors (Grove et al. 2006; Till et al. 2011) do not address this issue and are thus led to infer direct derivation of 'andesitic' melts as near-solidus melts from water-saturated melting in the mantle wedge setting— a model tested and rejected in the 1970s.

In response to the Mysen and Boettcher (1975) paper, Green (1976) repeated some of their experiments and observed persistence of relict minerals from the starting mix and quenched glass films from the water-rich (16–22 wt %) charges. Green (1976) reported further experiments on the 'pyrolite-minus-40 % olivine' composition, which located the solidus between 970 and 1000 °C at 1.5 GPa. The solidus was located on the basis of changes in Mg# and disappearance of pargasite at (2 GPa) or slightly above the solidus (1 and 1.5 GPa). Mysen and Boettcher (1975) presented many glass analyses of silica-oversaturated liquids, all from > 940 °C and pressures of 0.75–2.2 GPa and argued that these were equilibrium melts from water-saturated melting of lherzolite. Green (1973, 1976) addressed the quench-modified glass versus equilibrium melt debate by mass balance calculation of melt compositions in the (pyrolite-minus-olivine) composition, preparation of glasses matching these compositions and establishment of concordance between liquidus phases and temperatures of 'equilibrium melts' and residual phases of the (pyrolite-minus-olivine) composition at the same P, T. In contrast to this detailed assessment of the quenched glass issue, Grove et al. (2006) and Till et al. (2011) published one (1.2 GPa, 1020 °C) and two (1.6 GPa, 940 °C and 3.2 GPa, 1060 °C) analyses, respectively, of glass inferred to be quenched from hydrous silicate melt. None of these analyses is from experiments within the P, T range 3-5 GPa, 810–1000 °C, but all are silica–rich, very low in Na_2O and variable in MgO and CaO. In the light of earlier published work, it is necessary to test inferred equilibrium melt compositions by reversal and/or 'sandwich' technique experiments (Falloon et al. 1997; Davis et al. 2011). At least, the inferred equilibrium melt compositions must be compared with relevant studies of hydrous melting of different magma types, seeking closely matching liquidus temperatures and liquidus phases. In neither paper is there any discussion of the earlier work on quench modification of equilibrium melts nor reference to key papers on the topic.

An additional major difference between Grove et al. (2006), Till et al. (2011) and Green et al. (2010, 2011) is the stability of pargasite to 3 GPa in HZ lherzolite with water contents of <5 wt % approx. Till et al. (2011) conducted 6 experiments with 0.7 wt % water at 2.8 and 3.2 GPa, temperatures of 780–880 °C. In terms of the Niida and Green (1999), Green (1973), Fumagalli et al. (2009) and Green et al. (2010, 2011) studies, these experiments would be expected to contain pargasite at 2.8 GPa but not at 3.2 GPa. Till et al. (2011) report chlorite breakdown at 880 °C at both pressures but without detection of pargasite. Olivine, orthopyroxene, garnet, clinopyroxene and chlorite are present at both pressures below 860 °C. No analyses of phases are presented from these 6 experiments, and the difficulties of achieving reaction and equilibrium using natural mineral starting materials, alluded to previously, are not addressed by Till et al. (2011). A preferred interpretation of the observations and data presented is that in the experiments in which chlorite is present and thus there is no vapour phase, there has been no significant reaction at these temperatures and run times—and unreacted phases from the starting mix are preserved. In the higher-temperature experiments in which chlorite is absent, pargasite is expected to form at 2.8 GPa with the likely nucleation site at the interface of clinopyroxene and former chlorite. High-magnification elemental SEM mapping and X-ray diffraction are modern and 'old' techniques, respectively, which should be used to evaluate the alternative interpretations of these experiments. As presented in their paper, there is insufficient evidence to justify the authors' conclusion.

On the key issue of determination of the vapour-saturated solidus of lherzolite + H_2O as a function of P, T, the authors' conclusions are not convincing and alternative interpretations are preferred, based on their own and other published studies. Similarly, the authors do not present convincing evidence either for silica-oversaturated compositions of melt at and near the solidus or for limitation to the stability of pargasite at the mantle solidus to <2 GPa. In applying their inferred lherzolite + H_2O solidus to geophysical models of the subducted slab and mantle wedge environments, Grove et al. (2006) and Till et al. (2011) predict extensive melting of the mantle wedge. However, if the lherzolite + H_2O solidus has positive dP/dt at $P > 1.5$ GPa and is correctly located at ~1210 °C at 4 GPa and at ~1375 °C at 6 GPa (Green et al. 2010, 2011), then melting in the mantle wedge is much more restricted and melting of lherzolite + H_2O does not occur within the subducted lithospheric slab (c.f. Niida and Green 1999).

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