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CARBONATED ECLOGITE AT 3.5-5.5 GPA – THE EFFECT OF THE CAPSULE MATERIAL ON SOLIDUS TEMPERATURES

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We experimentally investigated a nominally anhydrous, K-bearing, altered MORB composition GA1 + 10% CaCO₃ (GA1cc), from 1050-1400°C and 3.5-5.5 GPa. This composition (see Table in the abstract 10IKC-081) models deep subduction of carbonated oceanic crust, the major process for replenishment of the earth's deep carbon cycle. All experiments were conducted in 1.27 cm diameter end-loaded Boyd-England type piston-cylinder apparatuses in the Research School of Earth Sciences, The Australian National University with two types of capsules: "Pt with inner graphite (Pt-Gr)" and "Au-Pd". A 200 ton press was employed for the experiments at 3.5 and 4.5 GPa, while for 5 and 5.5 GPa experiments an ultrahigh pressure 500 ton piston-cylinder press was used.

The observed phase assemblages were used to construct an experimental P-T phase diagram (Fig. 1).

The subsolidus phase assemblages for both sets of experiments (Pt-Gr and Au-Pd) consist of clinopyroxene, garnet, carbonate, rutile, K-Feldspar, coesite (at 4.5 and 5.0 GPa) and apatite (observed only in the Pt-Gr subsolidus run). The textures observed in the experiments change dramatically with the degree of melting. Above-solidus experiments contain quenched partial melts which differ in two sets of runs. In Pt-Gr runs the partial melts can be subdivided into four types. With increasing temperature at any given pressure they are: low-degree siliceous melts,

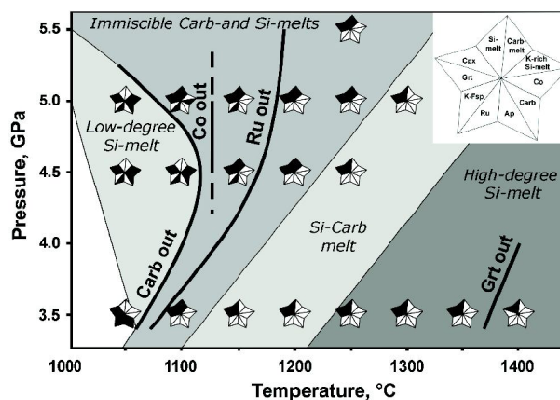


Figure 1. Experimental P-T phase diagram for GA1cc in Pt-Gr capsules. Si-melt – silicate melt, Carb-melt – carbonate melt, Si-Carb melt – silicate-carbonate melt, Carb – solid carbonate, Co – coesite, Ru – rutile, Grt – garnet, Cpx – clinopyroxene, Ap – apatite, K-Fsp – K-feldspar. K-rich Si-melt (in the legend) is identical in composition to the field of the Low-degree Si-melt on the diagram.

coexisting silicate and carbonate melts, silicate-carbonate melts and high-degree silicate melts. In Au-Pd runs the melts evolve from low-degree carbonatitic to siliceous at higher degrees of melting.

MELTING CHARACTER IN NOMINALLY ANHYDROUS EXPERIMENTS IN A PT-GR CAPSULE

Melts exhibit various textures and compositions depending on the degree of melting. **Low-degree siliceous melts** were detected only



in runs at 4.5 and 5.0 GPa at 1050-1100°C and 1050°C respectively. Such melt quenches into small patches of homogenous glass and either occupies a small region around and within the carbon spheres or is non-uniformly distributed throughout the run material. These melts have low totals (80-90%) and high content of silica and potassium (roughly 58-60 wt.% SiO₂ and 9-11% K₂O), which made them similar to K-feldspar composition.

Two coexisting carbonate and silicate melts (Fig. 2a-d) were observed at all pressures at low-intermediate degrees of melting. The temperature interval of two coexisting melts expands with pressure and varies from around 50°C at 3.5 GPa to around 150°C at 5.0 GPa. This corresponds to only one run at 1100°C at 3.5 GPa, two runs – 1150 and 1200°C at 4.5 GPa and four runs 1100-1250°C at 5.0 GPa. The only run at 5.5 GPa and 1250°C also produced two coexisting liquids.

The two coexisting melts can either form separate pools within a carbon sphere (Fig. 2a-d), or be interstitial to the residual silicate grains on the edge of the capsule with higher degrees of melting. Carbonate-immiscible melt forms

irregular shapes and is usually heterogeneous and patchy compared to the subsolidus carbonate crystals formed at lower temperatures.

The proportion of carbonate and silicate melts within the heterogeneous area can differ significantly. If a random melt pocket composed of silicate and carbonate liquids is considered, then any of the following scenarios can be applied: silicate melt > carbonate melt, carbonate melt > silicate melt (Fig. 2d), and approximately equal amounts of both melts (Fig. 2b). With the increase of temperature at the same pressure, the amount of silicate melt pools increases.

The two coexisting melts, present at temperatures above the low-degree alkali-rich siliceous melting field always exhibit carbonate and silicate compositions. Although the carbonate melts seem to be similar in composition to solid carbonate, they can be clearly distinguished from it. First, the melts have much lower Mg# and lower Ca#. Also, the addition of minor elements is very useful for the distinction as the carbonate melts have high Ti, P and K contents (up to 3.98 wt.% TiO₂, 1.46 wt.% Na₂O, 3.30 wt.% P₂O₅ and 3.00 wt.% K₂O), whereas in the subsolidus carbonate these elements are much less abundant (often below detection limits).

The SEM-EDS totals of carbonate immiscible melts are very low (about 55-65%), because of the large amount of carbonate component. In some cases small grains of quenched apatite are present within the melt. All calcitic carbonate melts have fairly high Fe and Mg contents (5.83-9.72 wt.% FeO and 3.02-4.73 wt.% MgO). SiO₂ contents can vary within a wide range (from 0.59 to 17.5 wt.% SiO₂) and tend to increase with increasing temperature. At higher temperatures the carbonate and silicate melt compositions approach each other and the proportion of silicate melt increases.

The coexisting silicate melts display significantly higher microprobe totals than coexisting carbonate-rich melts (75-90 wt.%). These melts are usually K-rich (2.67-10.2 wt.%

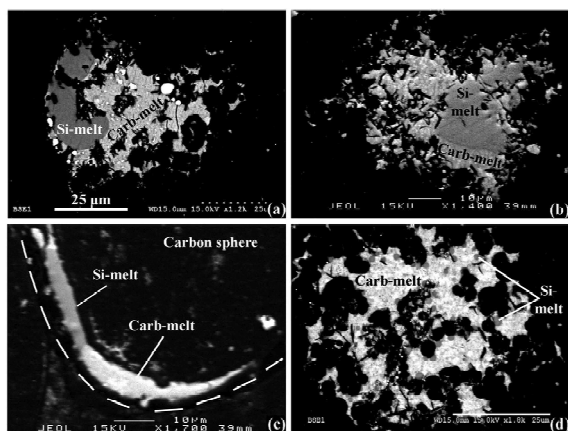


Figure 2. BSE images of the immiscible melts (IM): silicate (dark grey) and carbonate (light grey). (a) Run G1150_4.5 (should be read as GA1cc at 1150°C and 4.5 GPa) and (b) Run G1150_5. IM within carbon sphere. Bright crystals are quenched Ru. (c) Run G1100_5. IM around the carbon sphere. (d) Run G1100_3.5. Small round ocelli of silicate melt inside the pool of carbonate melt inside the carbon sphere.



K₂O) and resemble the compositions of low-degree siliceous melts. However, with increasing temperature, the silicate melts become less potassic and more magnesian and calcic. The Fe and Mg contents of these melts are less than in coexisting carbonate melts, while Na₂O is higher. Summarizing the compositions of coexisting carbonate and silicate melts: K, Al and to a lesser extent Na tend to be concentrated in silicate melts; whereas P, Mg, Fe, Ca are incorporated into the carbonate melts. Mn partitions into garnet and is present in all the melts in very low abundances.

Immiscible liquids in the experiments show regular compositional trends with increasing temperature (Fig. 3). The data obtained in this study are in very good agreement with all the other data on alkali-poor carbonated eclogites, although compared to the other studies, silicate and carbonate immiscible melts at lower temperatures in GA1cc are very strongly shifted toward the Si+Al and Ca+Mg+Fe apices at Figure 3.

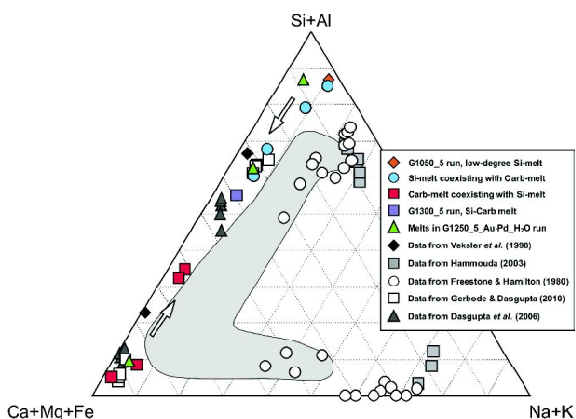


Figure 3. Immiscible melts compositions in this and other studies. Black symbols indicate compositions obtained in this study for the experimental runs in Pt-Gr capsule at 5 GPa: diamond – low-degree K-rich melt, circles – immiscible silicate melts, squares – immiscible carbonate melts, crossed square – silicate-carbonate melt, triangle – IM in G1250_5_Au-Pd-H₂O run. Colourless symbols represent the compositions of IM obtained in other studies. Grey area represents the field of Cl-poor fluid and melt inclusions from Siberian pipes after Zedgenizov et al. (2010). Arrows show the change in melt compositions in this study with increasing temperature. All the elements are given in moles, molar (SiO₂+Al₂O₃), molar (CaO+MgO+FeO), molar (Na₂O+K₂O). Data from Freestone & Hamilton (1980), Veksler et al. (1998), Hammouda (2003), Dasgupta et al. (2006), Gerbode & Dasgupta (2010), Kiseeva et al. (2011).

Silicate-carbonate melts were detected at intermediate degrees of melting at all pressures. They occur in two runs at 1150 and 1200°C at 3.5 GPa, in one run at 1250°C at 4.5 GPa and in one run at 1300°C and 5.0 GPa. Tiny (5 μm) fragments of silicate-carbonate melts tend to be spread randomly in small, isolated patches throughout the capsule (Fig. 4). The interpretation of this texture is that initially the melt contained rather high amounts of dissolved volatile components, presumably mostly CO₂ or carbonate (> 30-40 wt.%). Upon quenching, CO₂ separated from the silicate liquid and dispersed the melt throughout significant volumes of the graphite capsule. The polishing of these sorts of runs was particularly difficult due to the resulting vesiculation and fragmentation of graphite capsules.

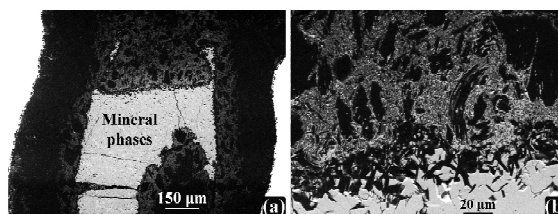


Figure 4. BSE image of experimental run G1200_3.5. (a) Silicate-carbonate melt spread throughout the capsule. Mineral phases are Grt and Cpx. (b) enlargement of image area shown in (a).

To check this hypothesis, a capsule-piercing procedure while determining the outcome using gas chromatography was undertaken. The G1200_3.5 run was reproduced. The capsule was pierced post-run under vacuum into a gas chromatograph and the spectrum revealed a CO₂ peak, consistent with the above interpretation. No H₂O peak was detected, although some H₂O may be present dissolved in the quenched melts.

It is inferred therefore that all the other melts that formed between the liquid immiscibility field and distinctly separated silicate melts pools, produced CO₂ fluid on quenching. Therefore compositionally these dispersed melts are defined as silicate-carbonate. The definition is used



because melts contain significant amount of both silicate and carbonate components.

High-degree silicate melts were observed only at 3.5 GPa at high and very high degrees of melting, which corresponds to the temperatures higher than 1250°C. These melts quench to separate pool of quenched glass at one end of the capsule (Fig. 5) and are inferred to contain significant dissolved CO₂ (< 12%, based on mass balance calculations and the EDS analysis totals).

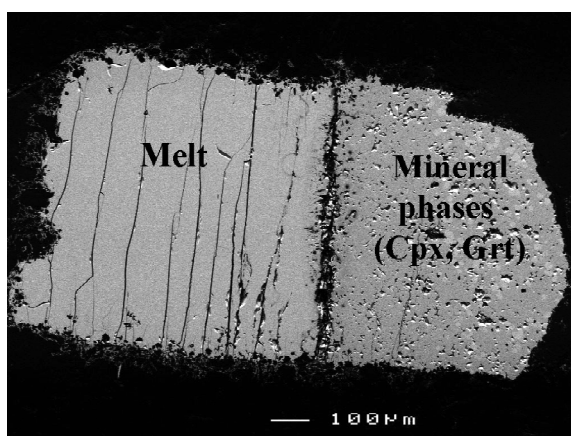


Fig. 5. BSE image of experimental run G1350_3.5. Melt pool and mineral phases segregated to different parts of the capsule.

MELTING CHARACTER IN NOMINALLY ANHYDROUS EXPERIMENTS IN AAU-PD CAPSULE

Five additional experiments at 5 GPa with the identical starting composition and temperatures to the 5 GPa Pt-Gr experiments, were performed in Au-Pd capsules with no inner graphite. The run at 1200°C crystallized a sub-solidus phase assemblage, with clinopyroxene, garnet, rutile, calcitic carbonate, coesite and K-feldspar. No melt was detected. At this pressure, the estimated solidus based on the Pt-Gr encapsulated runs is below 1050°C. Therefore an apparent 200°C increase in solidus temperature is observed in the Au-Pd encapsulated experiment relative to the Pt-Gr experiment. First melt appeared at 1225°C and was of carbonatitic

composition. This melt has a heterogenous texture and contains quenched carbonate and other crystals. At this temperature no more solid carbonate or K-feldspar was detected, although tiny (< 1 μm) K- and Al-rich patches were occasionally observed along garnet-clinopyroxene grain boundaries. Their fine grain size precluded accurate determination of their composition. Although the possibility that they are residual K-feldspar crystals is not ruled out, it is suggested that they are more likely to be metastable K-rich phases quenched from the K-rich carbonatitic melt.

With an increase in the degree of melting, no liquid immiscibility was detected and melts evolved towards more siliceous compositions.

MELTING CHARACTER IN HYDROUS EXPERIMENT IN AAU-PD CAPSULE

One experiment was performed with the addition of free water. The run conditions were 1250°C at 5.0 GPa with about 10 wt.% H₂O estimated.

There are three distinct melts in the G1250_5_Au-Pd_H₂O run: carbonate and silicate immiscible melts which occur interstitial to mineral phases (Fig. 6), and a high fraction of silicate melt, which occupies about half of the capsule. The formation of high-degree silicate-melt is accounted for by the thermal gradient and is due to the large capsule length. On the other hand, it allows the comparison of immiscible and high-degree silicate melts. Because of the small size of the pocket with two immiscible melts, it is not possible to obtain the precise composition for some elements (Ca, Mg for silicate immiscible melt and Si for carbonate-immiscible melt). Nevertheless, these melts follow the general trend of the melt evolution with temperature in Pt-Gr experiments. Thus, this experiment confirms that low-degree silicate-rich melt and coexistence of immiscible silicate-rich and carbonate-rich melts at higher degree of melting in the Pt-Gr

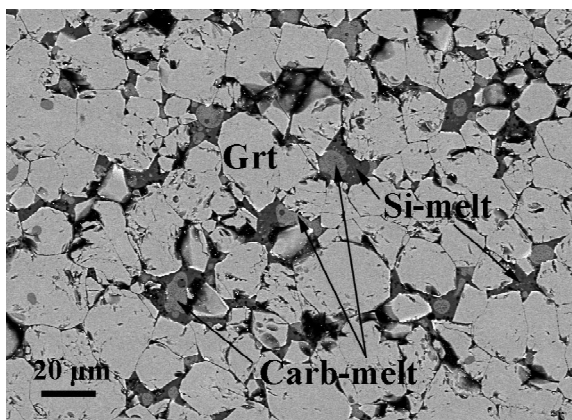


Figure 6. Figure 2.3. BSE images of the IM: Run G1250_5_Au-Pd_H₂O. IM pool within the crystalline grains of Grt.

experiments are probably explained by unavoidable contamination of the sample by the penetration of H₂O or hydrogen.

Thus, the most striking results from this study are (1) the differences in near solidus melts between the experiments conducted using the different capsule materials (potassic siliceous melt in Pt-Gr versus carbonatite melt in Au-Pd) and (2) the significant difference of approximately 130°C between the estimated carbonate solidus temperatures at 5.0 GPa in experiments conducted using Pt-Gr capsules and those using Au-Pd capsules. Further the possible reasons for these contrasting melting behaviours are explored.

Although extensive efforts were made to minimize hydration of mixes and experimental components during preparation of the assemblies, it is likely that during the relatively long-duration runs, hydrogen diffused into the Pt capsules and produced H₂O (Brooker *et al.*, 1998) by reaction with CO₂ or FeO. To test this hypothesis FTIR spectrometry was applied and 0.87 wt.% H₂O in the quenched glass from run G1400_3.5 was measured, which suggests presence of about 0.5 wt.% H₂O in the experiments. In order to minimise the effect of hydrogen penetration into the capsule and hydration of the sample, experiments were made in Au-Pd capsules. Au-Pd capsules permit less H diffusion than Pt under experimental

conditions (Hall *et al.*, 2004; Nishihara *et al.*, 2006). The dramatic difference between the results in two different capsules with GA1cc apparently indicates either different permeability of Pt and Au-Pd for H or possible redox reactions caused by the presence of graphite in the Pt capsules. Elevated permeability of Pt capsule has also been observed by Laporte *et al.* (2004).

Thus, the silicate solidus temperature at any investigated pressure for the Pt-Gr capsule experiments is one of an infinite array of H₂O-undersaturated solidi, which decrease in temperature with increasing H₂O content from the inferred anhydrous GA1cc carbonate solidus (the Au-Pd experiments) towards the H₂O-saturated solidus of GA1cc as determined by Yaxley & Green (1994).

This assumption has been proved by the experiment in a Au-Pd capsule with deliberately added H₂O, in which two immiscible carbonate and silicate melts were formed at 5 GPa and 1250°C and the degree of melting was near 50%. This demonstrates that liquid immiscibility for GA1cc composition at 3.5-5.0 GPa is valid only for the high H₂O/CO₂ (~ e'' 0.1) ratios in the system.

Although many studies have proved the depression of the eclogitic silicate solidus under hydrous conditions, to author's knowledge, the current study is the first demonstration that the carbonate solidus under the influence of minor amounts of water in the system is also lowered in temperature. This can have a major impact on melting relations of carbonate eclogite inferred to be present in the mantle.

CONCLUSIONS

- 1) Based on the comparison between solidus temperatures and subduction geotherms the H₂O-undersaturated carbonated eclogite would survive along typical subduction P-T paths without melting.
- 2) Both silicate and carbonate solidi of carbonate-



bearing H₂O-undersaturated eclogite within cratonic pressures are at lower temperatures than the wet-solidus of a peridotite. According to average mantle geotherm, at 5 GPa carbonate-bearing H₂O-undersaturated eclogite will not survive equilibration with mantle temperatures and will start melting.

- 3) The lowest-degree melts for H₂O-undersaturated carbonate-bearing MORB compositions at 3.5-5.0 GPa are K-rich highly siliceous liquids (broadly trachyandesite-phonolite), which have not yet been reported in any previous experimental studies of carbonate eclogites.
- 4) Liquid immiscibility is a result of the presence of minor H₂O in the system. It was observed at all the pressures in a narrow melting interval (13-18%) and over a temperature interval expanding with pressure from about 50°C at 3.5 GPa to > 150°C at 5 GPa.
- 5) Intermediate- to high-degree melts for both anhydrous and H₂O-saturated compositions are Si-undersaturated silicate-carbonate melts (36-45 wt.% SiO₂) containing substantial dissolved CO₂ (up to about 21% CO₂).
- 6) In contrast to previous reports, the SiO₂ content of the melt can decrease with increasing degree of melting. This occurs in H₂O-undersaturated systems all the way through to until the closure of the immiscibility gap and can explain the variation of fluid and melt inclusions in Cl-free (or Cl-poor) diamonds.

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