

## The role of carbonated eclogite in kimberlite and carbonatite petrogenesis

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### Introduction

The exotic and rare rock types – kimberlites and carbonatites are undoubtedly of mantle origin and are sometimes considered to be genetically related, but the compositions of their parental melts and melting conditions are still widely debated.

There are several models for kimberlite and carbonatite formation, each of which includes high pressure partial melting of either mantle peridotites or eclogites, as the most likely source rocks. Many workers have investigated the peridotite model, favouring a metasomatised peridotite source. However, similar to many ocean island basalts, carbonatites and kimberlites often exhibit the so-called HIMU isotopic signature, which has been related to the presence in the magmas' sources, of recycled oceanic crust, i.e. eclogite. Thus, a component in the source of kimberlitic and carbonatitic melts may be carbonate-bearing eclogite, reflecting a heterogeneous component in the mantle derived from recycling during subduction of oceanic crust.

The aim of this study is to investigate the behaviour of carbonate-bearing eclogite in upper-mantle conditions and to test its possible involvement in the mantle sources of kimberlite and related magmas. The first part of our investigation aims to locate the solidus positions and partial melt compositions as functions of bulk compositional parameters such as SiO<sub>2</sub> and CO<sub>2</sub> contents, Ca/Mg, Na<sub>2</sub>O/CO<sub>2</sub>, etc. The starting experimental composition (GA1) is an average "altered" MORB composition, calculated from about 80 whole rock analyses of dredged and drilled altered material first published by Yaxley and Green (1994).

### Methods

Altered oceanic crust typically contains a few per cent of calcite, formed during hydrothermal alteration. Ten percent was added to the preliminary experiments to facilitate detection of carbonate in the runs. GA1 was prepared as a synthetic sintered oxide mix, and most experiments were done with a glass prepared from it, to which 10% CaCO<sub>3</sub> was added (GA1+10%cc). The second mix – Volga is GA1 minus 6.5% SiO<sub>2</sub>, to which 10% CaCO<sub>3</sub> was also added (Volga+10%cc).

Experiments at 3.5 and 4.5 GPa were run in standard 200T piston-cylinder presses, while a 500T, ultra-high pressure piston-cylinder press was used for runs at  $\geq 5$  GPa. Experiments were run at 3.5–5 GPa and the temperatures from 1150 to 1400°C.

In all experiments graphite capsules sealed in 2.3 mm OD Pt capsules were used. In some runs graphite spheres were placed at the bottom of the capsules as a melt trap. Assemblies were standard, salt-Pyrex sleeves with straight graphite heaters and MgO spacers. Experimental capsules were heated to 600 °C with minimal pressure in order to soften the Pyrex before temperature and pressure were increased simultaneously up to the desired conditions.

Recovered capsules were mounted in epoxy and polished in kerosene; aqueous polishing media were avoided in order to prevent possible loss of H<sub>2</sub>O-soluble carbonates. After the sample was exposed, it was impregnated with epoxy in an attempt to retain the fragile material during polishing.

The run results were analyzed with a HITACHI 4300 SE/N FESEM and JEOL 6400 at the ANU Electron Microscopy Unit, using EDS detectors for quantitative analysis of mineral phases. Analytical conditions were: accelerating voltage 15kV, beam current 1nA and counting time 100s. Melt compositions were usually analyzed with a broad area scan in order to decrease the influence of heterogeneity on the measured compositions.

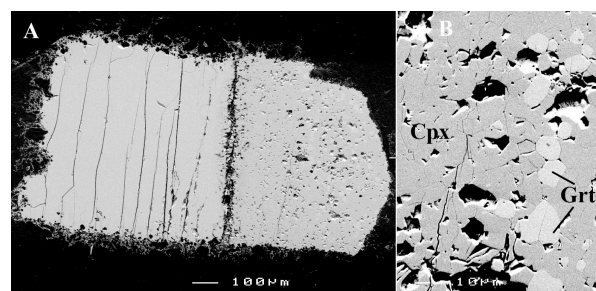


Fig. 1. Backscattered electron image of the run products of GA1 + 10%cc, 1350 °C, 3.5 GPa. **A.** Melt (left) and solid phase (right). **B.** Magnified view of part of the solid material in **A**, showing clinopyroxene (Cpx) and garnet (Grt) crystals.

## Results

Experimental runs after quenching usually contained the three phases: garnet, clinopyroxene and melt (Fig. 1). In GA1 + 10%cc 1200 °C and 5 GPa experiments coesite (Co), potassium feldspar (K-Fspar) and rutile (Ru) were also observed.

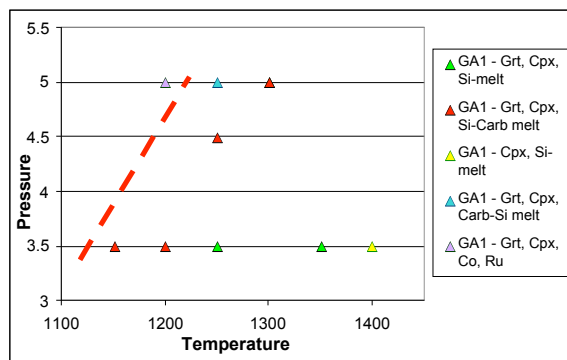


Fig. 2. Results of experiments with GA1+10%cc. Approximate solidus is shown by the red dashed line.

Garnet compositions vary between almandine (30-40 mol%), grossular (25-40 mol%) and pyrope (25-50 mol%). The pyrope component usually increases with increasing temperature, while the almandine component decreases with increasing temperature. The grossular component is 10% higher than in garnets crystallised under similar PT conditions from the carbonate-free GA1 composition (Spandler et al., 2008), and remains almost constant at about 30 mol.%, increasing slightly with pressure. Interestingly, in the lower SiO<sub>2</sub> Volga runs, the pyrope component is usually higher and the almandine component lower than in GA1, whereas the grossular component remains similar at ≈30 mol.%. The spessartine component is minor, around 0.8-1.2 mol.%. TiO<sub>2</sub> contents in all the garnets are around 0.5-1.3 wt.%.

Clinopyroxene is the major mineral in all GA1+10%cc and Volga+10%cc experiments being also a liquidus phase (Fig.3).

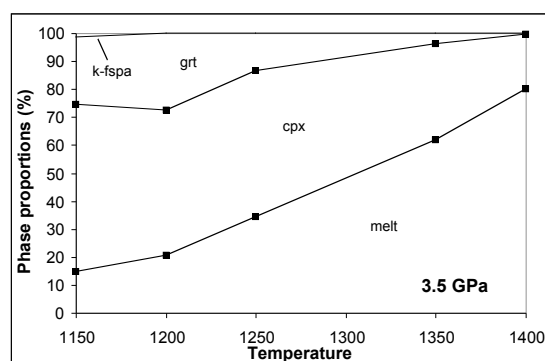


Fig. 3. Phase proportions for GA1+10%cc at 3.5 GPa pressure. The sole liquidus phase is Cpx.

Clinopyroxene compositions are similar to those reported in other experimental studies of dry, carbonate-free eclogite (Yaxley & Green, 1998,

Pertermann & Hirschmann, 2003, Spandler et al., 2007) but contain much more calcium and less iron.

Several types of melt were observed in our experiments. A large melt fraction (>30%) of silicate melt is present in higher temperature runs ( $T \geq 1250$  °C). In these cases the silicate melt segregated to form a pool at one end of the capsule (Fig. 1, A). CaO/SiO<sub>2</sub> ratio in this form of melt usually varies between 0.2-0.3, slightly increasing with temperature. The totals are about 88-92%, suggesting 8-12% CO<sub>2</sub> dissolved in the melt. At  $T = 1200$  to  $1300$  °C and 3.5 GPa in both GA1+10%cc and Volga+10%cc experiments we did not observe distinct melt pools. Instead tiny particles of incompatible-element rich material (ie K-rich and P-rich) are distributed throughout much of the graphite capsule (Fig. 4). Often the graphite capsule was vesiculated or fragmented. It was difficult to measure precisely the composition of this material because of its heterogeneity, but most of the analysis show totals at about 50-75%, suggesting the presence of carbonate.

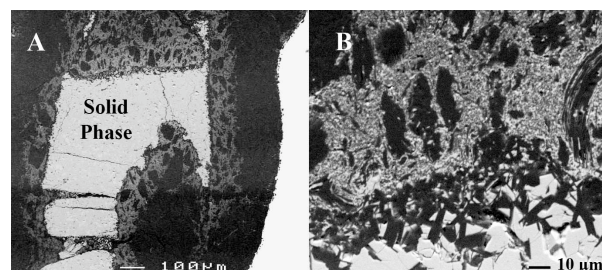


Fig. 4. Backscattered electron image of GA+10%cc 1200°C, 3.5 GPa run material. A. Solid phases represented by Grt and Cpx crystals. B. Magnified area of melt distributed within the capsule. Melt is in contact with residue.

Capsule piercing of some of these runs into a gas chromatograph detected significant CO<sub>2</sub>-fluid. Water was not detectable.

In some experiments at higher pressures (4.5 and 5 GPa) quenched melt patches containing a heterogeneous mixture of carbonates and silicates were observed. (Fig. 5.).

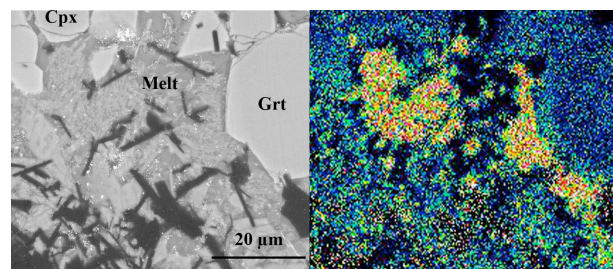


Fig. 5. Backscattered image (left) and Ca X-ray map (right) of the GA1+10%cc, 1250 °C and 5 GPa run.

A distinct field of carbonate melt (CaO/SiO<sub>2</sub> ≈ 3.5) was observed in Volga+10%cc experiment at 1250 °C and 4.5 GPa conditions.

The amount of incompatible minor elements in melt decreases with temperature, with the exception of a 1150-1200 °C temperature interval (Fig. 6).

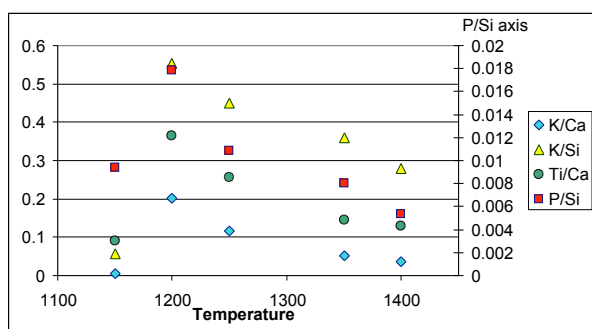


Fig. 6. Distribution of incompatible elements within the melt using GA1+10%cc composition at 3.5 GPa.

## Discussion and conclusions

We have experimentally determined phase and melt compositions of an anhydrous eclogite + 10% carbonate, represented by starting mix GA1 and Volga. Because of the high carbonate-content, it has lower solidus temperatures than other volatile-free eclogite compositions recently examined experimentally.

The solidus for GA1+10%cc at 3.5 GPa is below 1150°C. At 5 GPa the solidus is estimated to be at about 1225°C. Thus the solidus is much lower than that of the carbonate-free GA1, (between 1230 and 1260 °C at 3.5 GPa and 1300 °C at 5 GPa) (Spandler et al.) (Fig. 2).

We observe a continuum of liquid compositions with increasing temperature, from low degree (near solidus) melts rich in carbonate with a minor silicate component (eg at 5 GPa, 1250°C; Fig. 5), to higher degree melts containing higher silica contents but retaining significant carbonate, and finally to very high degree siliceous melts with several wt% dissolved CO<sub>2</sub>.

This reflects progressive change in the style of melting with increasing temperature. At low degrees of melting, liquids are dominated by components derived from the carbonate, which likely reflects minimum melting on the calcite-magnesite join (Yaxley and Brey 2004), with additional contributions from accessory, low temperature melting point phases, apatite, K-feldspar, coesite and rutile. The minor element compositions of these melts are buffered by these phases; hence Ti, K and P abundances increase with temperature over this melting range. These phases are eliminated at ~ about 20% melting at 3.5 GPa. The low degree carbonatitic melts quenched to complex heterogeneous patches of integrown carbonate and silicate phases (Fig. 5).

At moderate degrees of partial melting, the melt is carbonate-rich but now contains significant silicate components. Melting is dominated by components derived from residual garnet + clinopyroxene. On quenching, this melt rapidly exsolved significant CO<sub>2</sub>-rich fluid which mechanically disrupted and vesiculated the run material and low-strength graphite capsule. Hammouda (2003) attributed similar observations in some of his melting experiments on a

carbonate eclogite composition to a decarbonation reaction:



described by Luth (1995). Based upon our investigation, we consider that it is more likely to relate to decarbonation on quenching.

At high degrees of melting, the liquid is dominated by siliceous components derived from breakdown of garnet and clinopyroxene with the carbonate component being increasingly diluted. This results in siliceous melts with several wt.% dissolved carbonate, which quenched to glass.

The glasses are usually low in silica (35-48% SiO<sub>2</sub>), which decreases with increasing pressure. Low amounts of incompatible elements in glass at 1150 °C and 3.5 GPa are due to dilution by components from the earlier melted accessory phases by Si, Al, Mg and Fe-rich components from breakdown of garnet and clinopyroxene.

Carbonate-rich melts formed from a low degree of eclogite melting will infiltrate neighbouring peridotite, resulting in metasomatism and refertilization. Our next aim is to investigate how these melts would interact with peridotite and compare the outcomes with melt compositions that may be parental to kimberlites

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