Phase relations of carbonated eclogite under upper mantle PT conditions - implications for carbonatite petrogenesis

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Introduction

It has been suggested that carbonated eclogite could act as an upper mantle source for some crustally emplaced carbonatites (Treiman and Essene 1983; Nelson *et al.* 1988). Relative to mid-ocean ridge basalts, carbonatites have low ε_{Nd}, high $^{87}Sr/^{86}Sr$, and radiogenic Pb-isotopes, and are similar to ocean island basalts (OIBs) (Nelson *et al.* 1988). These characteristics have been linked to the emplacement of previously subducted oceanic lithosphere into the source regions of OIBs and carbonatites, after long term storage (1-2 Ga) in the mantle (Hofmann and White 1982; Nelson *et al.* 1988; Hofmann 1997).

Yaxley and Green (1994) demonstrated experimentally that during subduction of carbonate-bearing garnet amphibolite and eclogite (modelling altered oceanic crust), carbonate behaves as a residual, refractory phase forming part of an eclogitic residue in equilibrium with hydrous, highly siliceous partial melts (rhyodacites to dacites). Thus, if carbonate is a constituent of altered oceanic basalt, it is likely to survive subduction into the upper mantle without melting or decarbonation, although it is also sensitive to reduction to graphite or diamond.

However, the high pressure behaviour of residual carbonate in residual anhydrous eclogite from which a highly siliceous melt fraction was extracted during a previous episode of subduction, is currently inadequately constrained by experiment. Carbonate in many basaltic compositions will crystallise at high pressures as calcite-dolomite solid solution [$(cc-dol)_{ss}$] (Yaxley and Green 1974). Irving and Wyllie (1975) have demonstrated the presence of a minimum melt on the $CaCO_3$-$CaMg(CO_3)_2$ join, and the locus of these minimum melts in PT-space lies very close to the soldii of typical oceanic basalt compositions (*eg*, Green 1982; Yaxley and Green *submitted*). The presence of FeO and Na_2O in natural compositions is expected to lower the temperature of minimum melting of $(cc-dol)_{ss}$ to below that of the basalt solidus. Coupled with the fact that refractory residual basalt compositions, which crystallise quartz- or coesite-free eclogite at high pressures, are likely to have higher solidus temperatures than typical oceanic basalt compositions, there is the possibility of a high pressure field for carbonatite melt in equilibrium with ga + cpx, at temperatures below the silicate solidus. Accordingly, we have examined the high pressure phase relations of a carbonate-bearing composition (EC1) chosen to crystallise garnet (ga) + clinopyroxene (cpx)+ calcite-dolomite solid solution (but not free SiO_2), under eclogite facies PT conditions.

Experimental techniques

Composition EC1 contained 30.1 wt% SiO_2, 11.7 wt% Al_2O_3, 19.4 wt% CaO, 12.4 wt% MgO, 10.1 wt% FeO, 0.9 wt% Na_2O and 15.4 wt% CO_2. A starting mix with this composition was made from sintered oxides and carbonates. FeO was added as synthetic fayalite. The EC1 mix was encapsulated in

graphite-lined Pt capsules. Runs were conducted at 3.5 GPa in a standard $^1/2$" piston cylinder apparatus, using NaCl-pyrex sleeves and a graphite heater.

Experimental Results

At P=3.5 GPa and T≤1215°C, EC1 crystallised sub-solidus assemblages of ga + cpx + (cc-dol)$_{ss}$. At 1250 and 1275°C super-solidus assemblages of ga + cpx + (cc-dol)$_{ss}$ + carbonate melt formed. At 1300°C, carbonate liquid co-existed with ga + cpx residue.

With increasing temperature, the mole fraction of calcite increased at the expense of the mole fraction of dolomite in unmelted carbonate, and the mole fraction of pyrope increased at the expense of grossular in garnet. For example, carbonate crystallised at 1000°C had the composition $CC_{57}Mag_{35}Sid_8$ and co-existed with garnet with composition $Gr_{28}Py_{42}Alm_{30}$. Carbonate crystallised at 1275°C had the composition $CC_{86}Mag_{12}Sid_2$, and co-existed with garnet with composition $Gr_{22}Py_{51}Alm_{27}$. Ca/Mg values for cpx's did not vary systematically with temperature.

Carbonate melts exhibited clear quench textures, and a strong tendency to segregate from the ga + cpx ± carbonate residues and form a layer at the top of the capsule during the run. These melts were calcio-dolomitic compositions, and contained 3-4 wt% SiO_2, 0.4-1.0 wt% Al_2O_3, and about 65 mol% calcite, 25 mol% magnesite and 10 mol% siderite. Na_2O-contents in the carbonate melts varied from 2.8 to 1.6 wt% with increasing temperature from 1250 - 1300°C. Partition coefficients for Na between cpx and melt (cpx/melt) were ≈0.2 at 1250 and 1275°C. Mg#'s [atomic Mg/(Mg+ΣFe)] of the carbonate melts varied from 68.3 - 73.3, and were similar to the Mg# of EC1 (68.8).

Discussion

A new and significant result of this reconnaisance experimental study is that carbonated eclogite can yield carbonatite melts at temperatures below the eclogite's silicate solidus. This supports suggestions based on trace element abundances and isotopic compositions of carbonatites (eg; Nelson et al. 1988) that ancient, recycled, altered (carbonate-bearing) oceanic crust is a potential source for some crustally emplaced carbonatites.

For composition EC1, carbonatite melt can form at 3.5 GPa at between 1215 and 1250°C, temperatures well above the carbonate solidus for pyrolite + CO_2 (Falloon and Green 1990). If ambient fO_2 is sufficiently high to stabilise carbonate, carbonatite melt derived from high pressure partial melting of a discrete body of carbonated eclogite in the peridotitic upper mantle, could rapidly segregate from the eclogitic source at low melt fractions, and percolate into the surrounding peridotite. The melt will re-equilibrate with peridotitic phases, forming sodic dolomitic carbonatite melt, with increased Mg# (up to ≈85) (nb; this behaviour contrasts with that exhibited by low degree, highly siliceous melts of eclogite [dacites], which react out of existence with peridotite wall-rock, essentially by replacing olivine with enstatite [Yaxley and Green, submitted]).

The carbonate melt will continue to percolate upwards until it intersects the reaction opx + dol = cpx + ol + CO_2 at around 2.0 GPa, whereupon decarbonation reactions will result in replacement of peridotitic

aluminous enstatite with sodic clinopyroxene, driving lherzolitic or harzburgitic lithosphere towards magnesian wehrlite (Green and Wallace 1988). This metasomatic style has been extensively documented in some spinel peridotite xenoliths (*eg;* Yaxley *et al.* 1991; Rudnick *et al.* 1993). Continued influx of metasomatising carbonatite could armour lithospheric wall rock with wehrlitic material, preventing further reaction, and allowing access of carbonatites to shallower depths, and leading ultimately to crustal emplacement (Dalton and Wood 1993; Sweeney *et al.* 1995).

Eclogite compositions with higher Na_2O and FeO contents than EC1 are expected to have carbonate solidii at lower temperatures than EC1. Future experimental studies will be aimed at more completely delineating the PT fields for, and compositions of, carbonatite melts in equilibrium with EC1 and other eclogitic compositions (varying Ca/Mg values, Na and/or Fe abundances, for example).

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