The refractory nature of carbonate during partial melting of eclogite: evidence from high pressure experiments and natural carbonate-bearing eclogites

G.M. Yaxley
D.H. Green
H. Klápová

Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia
Department of Petrology, Charles University, Albertov 6, Prague, Czech Republic.

Introduction

The importance of trace amounts of volatile phases in mantle processes has been well established in recent years. The presence of H_2O $\pm$ CO_2 can significantly alter melting relations in peridotite and the nature of the primary melts produced. Carbonate-bearing hydrous peridotites are capable of yielding dolomitic carbonatite as the low melting fraction at $\approx$930°C near 2 GPa (Wallace and Green 1988). However, melting relations of carbonate-bearing hydrous mafic compositions (quartz-bearing eclogite) have not been determined and may be quite different to peridotite because of the much lower silicate solidus in hydrous, mafic compositions ($\approx$700°C at 2 GPa). This is of importance as many altered ocean-floor basalts contain calcitic carbonate as a low temperature alteration phase. Subduction of such material has the potential to transport carbonate into a high pressure-temperature regime. The behaviour of carbonate under these conditions is currently constrained by early simple system studies (e.g. Huang *et al.*, 1980) which showed that decarbonation or melting of carbonate would not occur under the PT regime encountered in a slab. This early work did not determine the stability of carbonate in the presence of partial silicate melting. In order to elucidate this, high pressure piston-cylinder experiments were performed using a complex natural composition representative of altered oceanic basalt to which had been added carbonate of varying compositions.

Experimental procedures

A series of magnesite-periclase-graphite-buffered (MPG) piston-cylinder experiments was performed on the 1.27 cm apparatus at the University of Tasmania. The altered oceanic basalt composition (GA1) was made from analytical-grade reagents and pre-synthesized with excess H_2O (2.0 GPa, 700°C) to produce a quartz + rutile-bearing garnet amphibolite. Splits of this material were then mechanically blended with 10 wt% calcite, 10 wt% magnesite or 5 wt% calcite + 5 wt% magnesite, and run at pressures of 1.5–3.5 GPa and temperatures of 700–1000°C. MPG buffering using the double capsule technique ($Ag_{75}Pd_{25}$ inner; Pt outer capsules) ensured that f_{O_2} was sufficiently high to prevent graphite formation at the expense of carbonate in the runs.

Experimental results

Experiments using the GA1 + 10% calcite bulk composition revealed that at low pressure-high temperature conditions (1.5 GPa, T $\geqslant$ 850°C; 2.0 GPa, T $\geqslant$ 950°C) decarbonation occurred producing amphibole + omphacitic clinopyroxene $\pm$ garnet + melt + CO_2-rich fluid assemblages. However, at all other super-solidus PT conditions investigated (T > 700°C at P = 1.5–3.5 GPa) residual carbonate was stable as part of a rutile-bearing eclogite assemblage in equilibrium with broadly dacitic to andesitic melts. Carbonate also formed part of the sub-solidus assemblages (700°C at 1.5 and 3.0 GPa). This constitutes the first experimental demonstration of the refractory nature of carbonate in an eclogitic residue in equilibrium with highly siliceous melts. That most model geotherms for subducting slabs (eg; Oxburgh and Turcotte, 1976; Peacock *et al.*, 1994) traverse the carbonate stability field suggests that carbonate can be recycled from crust to mantle via subduction in agreement with many recent studies (eg; Hauri *et al.*, 1993; Trull *et al.*, 1993; Zhang and Zindler, 1993). Such subduction can occur with the carbonate-eclogite acquiring a particular 'refractory residue' signal through loss of those volatile components fractionated into hydrous silicic melt.

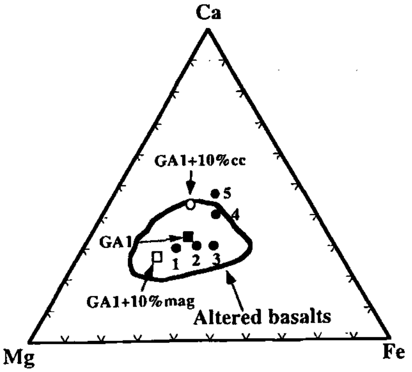

FIG. 1. Ca-Mg-Fe ternary plot showing some compositions considered in this study including GA1, GA1 + 10% calcite, GA1 + 10% magnesite and the carbonated eclogites. 1 = H321, 2 = H323, 3 = K670, 4 = H324 and 5 = D521. The 'altered basalts' field contains > 50 analyses of altered oceanic basalts, averaged to calculate GA1.

The equilibrium carbonate composition depended on pressure, temperature and bulk composition. In GA1 + 10% calcite runs, carbonate was Fe-bearing dolomite in equilibrium with grossular-rich garnet at low T and high P ($T < 850°C$, $P \geqslant 2.5$ GPa: eg; $CC_{52}Mag_{37}Sid_{11}$ + $Gr_{35}Py_{18}Alm_{47}$ at 3.0 GPa, 700°C). Increasing T or decreasing P rapidly stabilized Mg-calcite + more pyrope-rich garnet (eg; $CC_{89}Mag_7Sid_3$ + $Gr_{33}Py_{29}Alm_{38}$ at 3.0GPa, 900°C, and $CC_{63}Mag_{24}Sid_{13}$ + $Gr_{22}Py_{50}Alm_{28}$ at 2.0 GPa and 700°C), suggesting the exchange equilibrium calcite + pyrope = dolomite + grossular runs to the right with increasing P and decreasing T. Runs conducted with GA1 + 10% magnesite at 3.0 GPa and 850 and 900°C indicated that the exchange equilibrium dolomite + pyrope = grossular + magnesite is pushed to the right by decreasing temperature. A single run conducted at 3.0 GPa and 900°C using GA1 + 5% calcite + 5% magnesite contained no residual carbonate. This may be a result of minimum melting relations on the $CaCO_3$–$MgCO_3$ join (Irving and Wyllie 1975).

Discussion

The major findings of this study are that carbonate-bearing rutile eclogite residue can exist in equilibrium with dacitic to andesitic melts under the range of PT conditions imposed on altered oceanic crust during subduction. In Ca-rich bulk compositions (similar to GA1 + 10% calcite) the low pressure equilibrium assemblage would be Mg-calcite + pyrope-rich garnet. At high pressures dolomite + grossular-rich garnet would be the equilibrium assemblage. In more Mg-rich bulk compositions (similar to GA1 + 10% magnesite) the lower pressure assemblage is dolomite + pyrope-rich garnet and the high pressure assemblage is Ca-magnesite + grossular-rich garnet. Intermediate bulk compositions (similar to GA1 + 5% magnesite + 5% calcite) may yield carbonatite melt, or carbonated silicate melt $\pm$ CO_2-rich fluid, but this is yet to be experimentally demonstrated.

Natural evidence for the above behaviour of eclogite + carbonate systems is provided by a suite of carbonate-bearing eclogites from the Bohemian Massif in the Czech Republic (Klápová 1990). These samples exhibit a variety of carbonate compositions and corona textures, and bulk-rock geochemistries. For example, samples H323, H321 and K670 have the most magnesian bulk-rock geochemistry (Figure 1) and contain magnesite (Mg# = 81–85) $\pm$ calcite (Mg# = 27 at core to 79 at rim) cores surrounded by thin rims of dolomite (Mg# = 83–87), associated with garnet. Garnet is Py-poor and Gr-rich in the cores (eg; $Gr_{27}Py_{10}Alm_{63}$ in K670). It is inferred that the calcite cores are pre-eclogitic (low Mg#) and have been (partially or completely) replaced by magnesite which has approached equilibrium with garnet cores under eclogite facies conditions. This prograde metamorphic path, was followed by a near-isobaric heating event which resulted in formation of the dolomite rims on the magnesite $\pm$ calcite cores. The dolomite rims are believed to have approached equilibrium with the garnet rims, which are Gr-poor and Py-rich (eg; $Gr_{17}Py_{24}Alm_{59}$ in K670).

In contrast, samples H324 and D521 have more calcic bulk-rock compositions (Figure 1) and contain dolomite cores (Mg# = 84) surrounded by thin rims of calcite (Mg# = 83). In these samples, it is inferred that dolomite replaced pre-eclogitic calcite during prograde metamorphism and that the dolomite cores have approached equilibrium with adjacent garnet cores under eclogite facies conditions. Again, a heating event at eclogitic pressures resulted in formation of the high Mg# calcite rims. Formation of high pressure dolomite instead of magnesite in equilibrium with garnet cores is inferred to be a response to varying bulk compositions (Fig. 1) rather than attainment of higher pressures by the magnesite-bearing group.

Veins of quartz + rutile + paragonite + amphibole + zoisite cross-cut the Bohemian Massif eclogites and may indicate siliceous partial melt segregations. Hence, the natural rocks provide an excellent parallel to the experimental study, in that they demonstrate the stability of carbonate in the subduction regime, and its behaviour as a refractory phase during partial melting.