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Elemental distribution between diamondite-forming carbonatite melts and syngenetic minerals under experimental conditions

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Trace element abundances in silicate mantle minerals (garnets and clinopyroxenes) present in natural diamondites (Kurat and Dobosi, 2000; Dobosi and Kurat, 2002) indicated that carbonatitic melts were likely involved in the formation of diamondites and associated silicates. In support of these findings, we succeeded in experimental diamondite formation from carbon dissolved in completely miscible eclogite-carbonatite melts.

Experimental conditions and compositions

Graphite of spectral purity was used in the experiments as a heater with 5 mm outer and 3 mm inner diameters. The experimental charge was placed inside the heater - within the inner isothermal zone – and also outside (a layer of 2.2 mm thick) the heater, where a steady state temperature gradient zone was developed during the experiment within a 300 - 350 $^{\circ}$ C interval. (Fig. 1). Details are given by Litvin et al. (2003), Litvin et al. (2004), Litvin et al. (2005).



Fig. 1 Fig. 1 BSE image of run #1719: 1: isothermal central zone, 2: graphite heater, 3: fine-grained reaction zone 4: pyrophylite holder.



Starting materials for our experiments at 8.5 GPa were homogeneous mixtures of eclogite (ECL), carbonates (CARB) and a cocktail of trace elements (TE). The composition of the model clinopyroxene-garnet eclogite is given in Table 1. The carbonate consists of a mixture of 25% K_2CO_3 50% MgCO₃ and 25% CaCO₃. The charges were doped with 2% of a suite of trace elements (Li, Rb, Cs, Sr, Ba, Sc, Y, Ti, Zr, Hf, Nb, Ta, Cr, Mo, W, Mn, Fe) and REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). The final mixture for run #1719 has the composition ECL₂₉CARB₆₉TE₂

The run products were analyzed using a Cameca SX100 microprobe.

Table 1. Starting composition of model clinopyroxenegarnet eclogite for run #1719.

Oxide	SiO ₂	Al_2O_3	Feo	MgO	CaO	Na ₂ O	Total
cpx	52.22	8.01	3.35	14.88	19.79	1.75	100.00
gt	39.23	22.19	8.51	24.08	5.98	-	100.00

Results and discussion

The run products in zone 1 are carbonates and glasses. The zone 3 can be divided into 3 concentric zones. Zone 3a consists of a 100 mµ thick belt of solely garnet (Fig 2). The second part of this zone consists of coexisting well-crystallized garnet, clinopyroxene and carbonate (dolomite), and glass.



Fig. 2. Detailed BSE image of zone 3 divided into three subzones: zone 3a, zone 3b, and zone 3c.

The following zone 3b consists of clinopyroxene that forms aggregates in a matrix of carbonate (calcite) and glass. In the outermost zone 3c, clinopyroxene disappears and only glass and carbonate (calcite) coexist.

The carbonates in zone 1 are dolomite with 5.0 wt% FeO, SiO2 ranging from 0.24 to 0.74 wt%, Al2O3 from 0.34 to 0.60 wt% and K2O from 0.66 to 1.17 wt% and calcites with low FeO (0.42 wt%) and high Al2O3 and K2O up to 7.5 and 1.8 wt%, respectively. The Mg# of glass in this zone varies from 88.9 to 91.6.

Garnet from the zone 3a is homogeneous with composition Alm9Py73Gross18 and the clinopyroxene is diopside with Mg# ranging from 94.0 to 95.2. In this zone the carbonate is magnesite with CaO content ranging from 0.49 to 1.4 wt%, FeO from 2.7 to 3.7 wt%. and K2O being below detection limit. A striking feature of this zone is the absence of glass.

In zone 3b, garnet disappears and clinopyroxene is dominating. Its composition is that of a diopside and is similar to that of the diopside from zone 3a. Carbonate is mainly calcite and only traces of magnesite and dolomite. The glass composition changed rapidly and the Mg# dropped to 67.

The final zone 3c consists mainly of calcite and glass with Mg# ranging between 33 and 25.

In general, the MgO content of the glass correlates negatively with FeO and CaO (Fig. 3). In the zone 1 glasses are very MgO-rich (up to 35 wt%), whereas in the outer zone 3c the MgO content decreases dramatically to 2.5 wt%.

The fact that the run products in the isothermal zone 1 consist of carbonate (dolomite, calcite and/or their solid solutions) suggests that carbonate is the liquidus phase.

Microprobe analyses on the products of the experiment #1719 with the composition $ECL_{29}CARB_{69}TE_2$ reveal the crystallization sequence in the T=1650 to ~ 1300 °C interval. The quench procedure produced in the core, where the highest temperature was reached (T=1650°C), only silicate-carbonatitic glass and



dolomitic carbonates. Due to the thermal gradient towards the outer part of the vessel, subsolidus garnet is followed by clinopyroxene and magnesite. The chemical composition of co-existing garnet-clinopyroxene pairs yield for P = 8.5 GPa equilibrium temperatures between 1350 and 1400 °C.

At these high run P-T conditions the entire Ti is partitioned into garnet, whereas the clinopyroxene is Ti-free, which indicates that, compared to the neighboring elements Eu and Dy in the spidergrams, the commonly observed and pronounced negative Ti anomaly in clinopyroxenes is the effect of preferential partitioning into garnet (Ntaflos et al., 2007). A striking feature of clinopyroxenes is the relatively high concentration of potassium (K₂O range from 0.10 -0.20 wt%), suggesting that the main repository for K at high pressures is - beside carbonates - the clinopyroxene - in support of previously done experiments observations and on natural clinopyroxenes



Fig. 3. MgO content in carbonatitic glass correlates negatively with FeO and CaO contents. The glass composition is changing from MgO-rich in the zone 1 to MgO-poor in the zone 3c.

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