

Carbonation reactions in eclogites at high pressure: implications for carbonic fluids in the mantle

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Introduction

Carbonation reactions for olivine-bearing ultramafic rocks at conditions appropriate for the Earth's mantle have been extensively studied over the past three decades (cf. review by Luth *et al.*, 1993, and references therein). In these assemblages, the carbonation reactions invariably involve olivine reacting with CO₂. For example, carbonation in harzburgites (ol + opx) proceeds via: Enstatite + 2 Magnesite = 2 Forsterite + 2 CO₂. In lherzolites (ol + opx + cpx), carbonation would occur initially via: Dolomite + 2 Enstatite = 2 Forsterite + Diopside + 2 CO₂, with an exchange reaction between pyroxene and carbonate stabilizing magnesite at the expense of dolomite at higher pressure.

Eclogite, a garnet + clinopyroxene rock that lacks olivine, is well-represented in suites of mantle-derived xenoliths, and is inferred to be a significant lithology in the mantle. The above carbonation reactions for olivine-bearing assemblages won't work for these olivine-free assemblages, and little is known about possible carbonation reactions for these rocks. In a model (Fe-free) eclogite, an assemblage of cpx + gar + coes + Mg, Ca carbonate is observed (Luth, unpub. data). A carbonation reaction consistent with this assemblage would be: Dolomite + Coesite = Diopside + CO₂ (DCDV). This reaction is of interest aside from as a potential carbonation reaction for eclogites. With decreasing f_{O_2} , DCDV intersects the carbon-silicate-carbonate reaction: Dolomite + Coesite = Diopside + 2 Diamond/Graphite + O₂. This reaction may define the coexistence of elemental carbon and carbonate in eclogites and garnet pyroxenites (Luth, 1993).

The lower-pressure, quartz-bearing analog of DCDV has been studied in CO₂ and H₂O-CO₂ fluids (Egler *et al.*, 1976; Wyllie *et al.*, 1983; Slaughter *et al.*, 1975; Eggert and Kerrick, 1981; Jacobs and Kerrick, 1981; Lüttge and Metz, 1991, 1993). The DCDV reaction has not been studied experimentally to date. Its location in pressure-temperature space may be calculated with the internally-consistent thermodynamic databases of

Holland and Powell (1990) and Berman (1988, 1991). The two calculated curves are discrepant, markedly so at > 3 GPa, possibly resulting from the required extrapolation of the thermodynamic data to these conditions. Dalton and Wood (1993) found that these databases have difficulties reproducing reaction boundaries for carbonate-bearing reactions for peridotites, which were attributed to uncertainties in the thermochemical data for carbonates. The experimental determination of the DCDV reaction serves to constrain the stability of carbonate in eclogitic assemblages, and in addition will provide an informative test of the currently-available databases for a carbonation reaction not involving magnesite.

Experimental

Experiments were conducted at 3.5 to 6 GPa in the USSA-2000 split-sphere multiple-anvil apparatus in the C.M. Scarfe Laboratory of Experimental Petrology. The starting composition was a mixture of natural dolomite, synthetic diopside, and quartz. All experiments were run in sealed Pt capsules. Experiments were conducted in stepped graphite furnaces inserted into octahedral sample assemblies of 18 mm edge length. The duration of the experiments were 0.5–8 hr, depending on the temperature. The majority of the experiments were single stage, but the reaction was reversed at 5 GPa in two-stage experiments.

Results and discussion

The results agree well with the reaction boundary calculated from the Berman (1991) database. In contrast, the divergence of the Holland and Powell curve to lower temperatures with increasing pressure is not supported by the experimental data.

Fluids rich in CO₂ are unstable in the olivine-bearing peridotitic mantle at pressures greater than ~1.5 GPa. Reactions appropriate for peridotite, where CO₂ reacts either with olivine or with olivine + clinopyroxene, are not appropriate for olivine-free eclogite or pyroxenite assemblages. The reaction of CO₂ with clinopyr-

oxene to generate a dolomitic carbonate and coesite (DCDV) is feasible for eclogites and occurs at higher pressures than the carbonation reactions for peridotite. If DCDV is indeed the reaction by which eclogites carbonate, there is a depth interval of 30–50 km in the mantle where a CO₂-rich fluid is stable in eclogite or garnet pyroxenite, but is not stable in any neighboring peridotite. This conclusion may require modification if carbonation reactions involving garnet are important in eclogites. This possibility is currently under investigation.

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