The equilibrium boundary of the reaction \( \text{Mg}_2\text{Al}_5\text{Si}_3\text{O}_{12} + 3\text{CO}_2 = \text{Al}_2\text{SiO}_5 + 2\text{SiO}_2 + 3\text{MgCO}_3 \) at 3–6 GPa

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**Abstract**

The stability of \( \text{CO}_2 \) fluid in the Earth’s mantle is restricted by the carbonation of rock-forming minerals. Among those, the reaction with garnet is of particular interest because it constrains the stability of \( \text{CO}_2 \) fluid in eclogites, whose minerals have been found in the \( \text{CO}_2 \)-bearing diamonds. In this work, we determined the equilibrium boundary for the reaction \( \text{Mg}_8\text{Al}_5\text{Si}_3\text{O}_{12} (\text{Prp}) + 3\text{CO}_2 (\text{fluid}) = \text{Al}_2\text{SiO}_5 (\text{Ky}) + 2\text{SiO}_2 (\text{Coe/Qz}) + 3\text{MgCO}_3 (\text{Mgs}) \) over the pressure interval 3–6 GPa using a multi-anvil press. Owing to the slow kinetics, the reaction was studied in both forward (left to right) and reverse (right to left) directions in experiments with durations extending up to 260 h. Our newly determined boundary is situated 3 GPa/950 ± 50 °C, 4.5 GPa/1150 °C, and 6 GPa/1350 ± 50 °C and has the equation \( P(\text{GPa}) = 0.0075 \times T \text{(°C)} - 4.125. \) The boundary crosses the graphite-to-diamond transition curve near 4.7 GPa and 1180 °C. Thus, the assemblage garnet + \( \text{CO}_2 \) fluid is stable in the diamond (Dia) stability field under \( P-T \) conditions of the continental geotherm with a heat flow of 41 mW/m².

**Keywords:** \( \text{CO}_2 \) fluid, pyrope, carbonation, garnet, phase relations, high pressure, multi-anvil experiments, Earth’s mantle

**Introduction**

The presence of \( \text{CO}_2 \) fluid during crystallization of some lithospheric diamonds is evidenced by findings of solid (Schrauder and Navon 1993; Chinn 1995; Barannik et al. 2021) and liquid \( \text{CO}_2 \) (Tomilenko et al. 2001; Smith et al. 2015) inclusions in natural diamonds. Systematic studies of \( \text{CO}_2 \)-bearing diamonds revealed inclusions of eclogitic minerals (Chinn 1995; Ragozin et al. 2002, 2009). However, the stability of \( \text{CO}_2 \) in the diamond stability field in eclogites (besides redox conditions) is restricted by carbonation reactions of clinopyroxene (Cpx) and garnet (Grt) (Hammouda and Keshav 2015) (Fig. 1).

It was experimentally shown that clinopyroxene, in the case of pure diopside (Di), is unstable with \( \text{CO}_2 \) in the \( P-T \) range of diamond stability (Luth 1995, 2006). However, the addition of iron to clinopyroxene expands its stability to the \( P-T \) conditions of lithospheric diamond formation (Martin and Hammouda 2011) (Fig. 1).

For a long time, conclusions about garnet stability with \( \text{CO}_2 \) were based on the work by Knoche et al. (1999) in which the reaction boundary:

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\text{Mg}_8\text{Al}_5\text{Si}_3\text{O}_{12} (\text{Prp}) + 3\text{CO}_2 = 3\text{MgCO}_3 (\text{Mgs}) + \text{Al}_2\text{SiO}_5 (\text{Ky}) + 2\text{SiO}_2 (\text{Coe})
\]

is situated at higher temperatures than most estimates for lithospheric diamond formation (Shirey et al. 2013; Stachel and Luth 2015) (Fig. 1). In the study by Knoche et al. (1999), several starting mixtures were employed. The most robust results were obtained using the oxide-carbonate (carb) starting mixture in experiments at 5.2 and 7.5 GPa and a duration of 4–6 h (Fig. 2a).

Recently, Bataleva et al. (2020b) reported new experimental data on the reaction boundary. They also used the oxide-carbonate starting mixture but in longer experiments with a duration extending up to 10–60 h (Fig. 2a). A comparison of these two studies shows that the reaction boundary shifts to lower temperatures as the run duration increases (Fig. 2). These observations and low conversion of the initial reagents into garnet indicate slow kinetics of the decarbonation reaction. Since in both works, the reaction was mainly studied only in the decarbonation direction; the established reaction boundaries may deviate to higher temperatures relative to the equilibrium one owing to slow kinetics.

To exclude kinetic factors and determine the equilibrium boundary, we investigated the reaction in both carbonation and decarbonation directions in multi-anvil experiments at 3–6 GPa, 900–1500 °C, and a duration of up to 260 h.

**Experimental procedure**

Two starting materials were employed to study the reaction from both sides. The first one (A) is a sandwich of natural pyrope powder, \( \text{Mg}_8\text{Fe}_{10}\text{Al}_5\text{Si}_3\text{O}_{12} \), and \( \text{Ag}_2\text{C}_2\text{O}_3 \) as a \( \text{CO}_2 \) source. The second one (B) is a mixture of reagent grade \( \text{SiO}_2 \), \( \text{Al}_2\text{O}_3 \), and natural magnesite (<0.1% impurities) from Brumado (Bahia, Brazil), blended in a molar ratio of 3:1:3. Prior to mixing the oxides were annealed at 1000 °C and magnesite at 300 °C for 1 h.

Experiments were run using a DLA-type 1500 ton press. Eight tungsten carbide cubes with 12 mm truncations were employed as anvils of the inner stage. Octahedra with an edge length of 20.5 mm with ground edges and corners made of semi-sintered \( \text{CaO-doped ZrO}_2 \) ceramics (Shatskiy et al. 2010) were employed as pressure media. The high temperature was generated using a tubular graphite heater 4.0/4.5 mm in inner/outer diameter.