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Melting relations in the chloride–carbonate–silicate systems at high-pressure and the model for formation of alkalic diamond–forming liquids in the upper mantle

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Abstract

The experiments in the model system $CaMgSi_2O_6$–(Na_2CO_3, $CaCO_3$)–KCl are performed at 5 GPa and 1400–1600 °C in order to study the phase relations, including liquid immiscibility, in the chloride–carbonate–silicate systems with application to alkali and chlorine-rich liquids preserved in kimberlitic diamonds. Experiments in the boundary joins of the system demonstrated that both the carbonate–silicate and chloride–carbonate melts are homogeneous; while high-temperature (above 1800 °C) liquid immiscibility is assumed for the chloride–silicate join of the above system. Addition of silicate component into the chloride–carbonate melts and chloride component into the carbonate–silicate melts results in splitting of the homogeneous liquids into the immiscible chloride–carbonate brine and carbonate–silicate melt. Carbonate–silicate and chloride–carbonate branches of the miscibility gap converge within the carbonate-rich region of the system. Regular temperature evolution of the shape and size of the miscibility gap is deduced. With decreasing temperature, the convergence point moves toward more Si-rich compositions, expanding fields of homogeneous chloride–carbonate silica-saturated melts. This effect is governed by the precipitation of the silicate phases even from silica-bearing chloride–carbonate melts. In addition, experiments revealed regular evolution of both Cl-bearing carbonate–silicate melt and Si-bearing chloride–carbonate brine toward the low-temperature chlorine–bearing carbonatitic liquid with decreasing temperature. These trends are similar to the evolution of the melt and brine inclusions in some diamonds from Botswana, Brazil, Canada, and Yakutia, indicating their growth during cooling. The model for interaction of the chloride–carbonate brine with the mantle rocks is developed on the basis of the present experimental data. This model is applied to the chlorine-enriched kimberlites of the Udachnaya–East pipe.

Keywords: High-pressure experiment; Chloride–carbonate–silicate melts; Liquid immiscibility; Mantle; Diamonds; Kimberlites

1. Introduction

Role of chlorine and alkali chlorides in the formation of mantle rocks is traditionally considered to be negligible (e.g., [1]). Nevertheless, data on compositions of micas, amphiboles, and, especially, apatites from the upper mantle rocks indicate their interaction with fluids enriched in chlorine (e.g. [2–5]). Chlorine-rich fluid inclusions have also been observed in the upper mantle rocks [2,6]. Kimberlites, which are assumed to be derivatives of the most deep-seated mantle melts [7,8],

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provide direct mineralogical and geochemical evidences on presence of alkali chloride compounds during their evolution. Halite and sylvite are known both in groundmass [9] and in secondary melt inclusions in olivine [10] of some fresh Yakutian kimberlites. Recent Sr, Nd, and Pb isotopic study [11] provided strong evidence for primary magmatic origin of alkali chlorides and carbonates in these kimberlites [11]. The deep-seated origin (>4 GPa) of alkali-rich chloride–carbonate liquid as a derivate of kimberlitic magma is supported by the study of primary melt inclusions in olivines from unaltered kimberlites of the Udachnaya–East pipe, Yakutia [12]. The estimated chlorine content of the kimberlite melt, that produces chlorine–carbonate liquid, could be above 7 wt.% [12]. This concentration is much higher than the chlorine solubility in mantle-derived basaltic melts (e.g. [13,14]).

Further evidence for the activity of alkalic Cl-bearing liquids during the evolution of some deep-seated assemblages is provided by the compositions of alkaline (mostly high-potassic) liquid inclusions in diamonds from kimberlites. Four compositional groups of these liquids are distinguished in diamonds from Africa, Canada, Brazil, Yakutia, and India (Fig. 1): (1) alumino–silicate melt inclusions [15–20]; (2) carbonate–silicate melt inclusions [21–27]; (3) carbonate melt inclusions [23,25,27–30]; (4) chloride–carbonate brine inclusions [29–33]. The composition of the brine inclusions in diamonds [29,30,32,33] closely resembles the composition of chloride–carbonate inclusions in kimberlitic olivines [11,12]. Concentration of Cl in the carbonate–silicate inclusions reaches 1.5 wt.% [21–24]. The carbonate-rich inclusions contain 6–12 wt.% of Cl [27–30]. Chlorine in the carbonate–silicate and carbonate inclusions shows a distinct positive correlation with K at negative correlation both with Si and Al (e.g. [22,29,30]). Correlation between K and Cl was previously reported for diamonds from Yakutia, Africa, and Canada, which were analyzed by the proton microprobe, neutron activation method, and step heating techniques [18,34–36]. This correlation implies that KCl is the major chlorine contributor to composition of the above inclusions [30]. Burgess and Turner [36] estimated chlorine content of 2–5 wt.% in the mantle-derived fluid, which is in a good agreement with compositions of carbonate–silicate and carbonate melt inclusions in diamonds. The chloride–carbonate brine inclusions are apparently concentrated in cores of diamond crystals and associated both with eclogitic and peridotitic mineral assemblages [29,32,33]. Locally, products of reactions between mantle minerals and brines are observed in single inclusions in diamonds [26,30,33]. Assemblage of brine and mineral inclusions allow determination of P–T conditions for their entrapment: 4.6–5.1 GPa and 1000–1200 °C [26,32,33]. These data imply that diamond growth was coeval with an influx of alkali-rich chloride–carbonate liquids, which arrived from the greater depths.

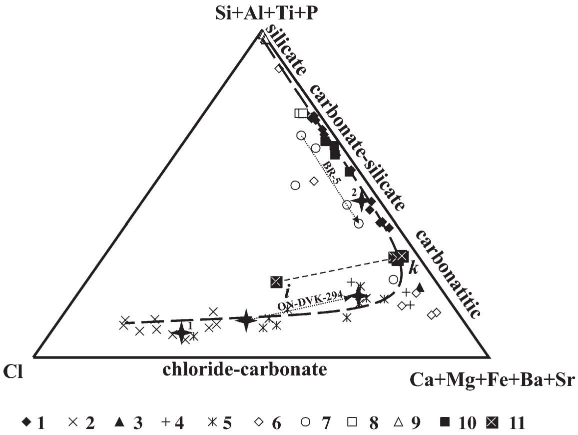

Fig. 1. Variations in compositions of the melt and fluid inclusions in diamonds from kimberlites of (1) Zaire and Botswana [22], (2, 3) Koffiefontein pipe, South Africa [26,32]; (4) Yubileinaya pipe, Yakutia [25,28,30]; (5) Diavik mine, Canada [29,30]; (6) diverse Yakutian pipes (O. Navon, pers. comm.); (7) Brazil [27]; (8) Aikhal pipe, Yakutia [17]; (9) Mir pipe, Yakutia [16,19], as well as (10) from alluvial Indian diamonds (O. Navon, pers. comm.). (11) average composition of chloride–carbonate inclusion in olivine (i) and host kimberlites (k) from the Udachnaya–East pipe, Yakutia ([11,12], A. Sobolev, pers. comm.). Alkalis are omitted in the diagram since their addition masks behavior of chlorine. Long-dashed thick line illustrates a specific shape of the immiscibility gap in the chloride–carbonate–silicate melts deduced from the composition of the inclusions. Short-dotted thin line shows a tie-line connecting compositions of chloride–carbonate inclusion in olivine (i) and host kimberlites (k) from the Udachnaya–East pipe, Yakutia, implying their liquid immiscibility relations. Black stars show average compositions of liquids in three diamonds from the Diavik mine [30]: 1 — brine inclusion in diamond ON-DVK-272; 2 — carbonate–silicate melt inclusion ON-DVK-281. Dotted arrows illustrate evolution of average compositions of melt inclusions in diamond BR-5 [27] and ON-DVK-294 [29,30].

Fig. 1 demonstrates regular variations of chlorine in the melts included in diamonds. The data points form two continuous trends along the silicate–carbonate and carbonate–chloride joins [37]. The continuous trend between the silicate and carbonatitic melts is also recorded in compositional variation of the melts inclusions within single diamond crystals [22,27]. Chlorine positively correlates with content of the “carbonate” end-member [22,27]. Brine inclusions from the Koffiefontein pipe [32,33] and the Diavik mine [29,30] also form continuous trends along the chloride–carbonate join. These trends converge near the “carbonate” (Ca + Mg + Fe + Ba + Sr) apex of the diagram