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Origin of Cl-bearing silica-rich melt inclusions in diamonds: Experimental evidence for an eclogite connection

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ABSTRACT

Melting phase relations of a model chloride- and carbonate-bearing eclogite have been studied at 7.0–10.5 GPa and 1200–1675 °C. The mineral assemblage coexisting with partial melts is garnet, omphacite, kyanite, and coesite or stishovite. At temperatures of 1200–1400 °C, the partial melt has an SiO_2-poor, Cl-bearing carbonatite composition. With increasing temperature, it becomes progressively SiO_2 rich, and at temperatures of 1500–1700 °C contains as much as 53 wt% SiO_2. The compositions of the melts are comparable with those of silicic end members of inclusions in fibrous and/or cloudy diamonds worldwide, implying that they may be produced via chemical reactions of alkalic chloride-carbonate liquids with mantle eclogites. Our experiments reproduced the trends of the compositional variations of the fluid or melt inclusions within eclogitic diamonds, and thus suggest a reliable model for their origin.

INTRODUCTION

Various sources of information indicate that chlorine can locally accumulate in the upper mantle, as recorded by (1) melt and fluid inclusions in diamonds and other mantle minerals (Izraeli et al., 2001, 2004; Frezzotti et al., 2002; Misra et al., 2004; Klein-BenDavid et al., 2004, 2006, 2007; Zedgenizov et al., 2007), (2) fresh chloride-rich kimberlites (Kamenetsky et al., 2004, 2009; Maas et al., 2005), and (3) chlorine enrichment of carbonatite volcanics (Keller and Spettel, 1995; Stoppa et al., 1997; Dawson, 1998). The presence of water-rich chloride-carbonate inclusions in kimberlitic diamonds implies that Cl-rich brines were trapped at pressures of 4.5–7.0 GPa (Izraeli et al., 2001, 2004). Recent findings of halite and sylvite in presumably transition zone diamonds (Wirth et al., 2009) indicate that Cl-bearing media can accumulate even at deeper mantle levels.

Three major end members can be defined among fluid and melt inclusions observed in fibrous diamonds worldwide (Klein-BenDavid et al., 2007): (1) hydrous silicic, enriched in SiO_2, Al_2O_3, and H_2O; (2) carbonatitic, enriched in carbonate, CaO, MgO, and FeO; and (3) hydrous saline, enriched in Cl, K, Na, and H_2O. The carbonatite end member was further subdivided into high- and low-Mg carbonatite components (Klein-BenDavid et al., 2009; Weiss et al., 2009). Klein-BenDavid et al. (2007) explained the miscibility gap between saline and hydrous-silicic end members by fractionation of carbonate from a parental Cl-bearing carbonatite melt. This immiscibility was confirmed experimentally at 5 GPa; however, the proposed trend of melt evolution has an opposite direction from a parental Si-rich carbonate-chloride–bearing melt toward immiscible Cl- and carbonate-bearing compositions (Safonov et al., 2007, 2009). Both the experimental modeling and trace element data on diamond-hosted fluids reveal that interaction of mantle peridotites and eclogites with the chloride-carbonate fluid or melt can explain nearly the whole range of Cl-bearing carbonate-silicate and carbonatite melts observed as inclusions in diamonds (Safonov et al., 2007; Weiss et al., 2009). In particular, formation of hydrous silicic inclusions is believed to be related to eclogitic assemblages, based on the observation of associated mineral inclusions of coesite, omphacite, eclogitic garnet, and rutile (Weiss et al., 2009).

Litasov and Ohtani (2009a) experimentally demonstrated that partial melting of carbonate-chloride–bearing peridotite can explain the origin of carbonatitic inclusions in diamonds and their possible connections with Cl-bearing kimberlites (see Kamenetsky et al., 2004, 2009). They found significant changes in melt composition with increasing degree of melting in the peridotite-carbonate-chloride system at 7–16 GPa, from carbonatitic to moderately Si rich compositions, and suggested a closure of the miscibility gap between silicate-carbonate and chloride-carbonate melts at high pressures. No systematic study of the system eclogite-carbonate-chloride has been performed so far. In this study, we report melting phase relations for a chloride- and carbonate-bearing eclogite. We have deduced an evolution of the partial melts in equilibrium with an eclogite assemblage and applied these data to the origin of the silicic fluid or melt inclusions in diamonds.

EXPERIMENTAL METHODS

The starting material was an oxide mixture representing an average mid-oceanic ridge basalt (MORB) composition (Pertermann and Hirschmann, 2003) simplified to the CaO-MgO-Al_2O_3-SiO_2 system via the procedure of O'Hara (1968): 4.0 wt% of CO_2 was added as $MgCO_3$ and $CaCO_3$ (adjusting the proportion of MgO and CaO) and 3.0 wt% Cl was added as a mixture of NaCl and KCl in molar ratio 3:2 (Table 1). Starting charges were placed in welded Pt capsules.

A Kawai-type 3000 t multi-anvil apparatus installed at Tohoku University, Japan, and equipped with tungsten carbide anvils (5 mm truncated edge length) was used for the experiments. Semi-sintered zirconia was used as the pressure medium and a cylindrical $LaCrO_3$ heater was used as the heating element. A boron nitride spacer was placed between the capsule and heater. Temperature was measured with a $W_{97}Re_3$–$W_{75}Re_{25}$ thermocouple located at the center of the furnace. The details of pressure calibration and temperature gradient measurements were reported by Litasov and Ohtani (2009a, 2009b, 2010).

After the runs, samples in Pt capsules were cut at the middle, mounted into epoxy, and polished using fine-grained sandpaper and oil-based diamond paste. Compositions of phases after runs were measured with electron microprobe (JEOL Superprobe, JXA-8800L) at the Geophysical Laboratory, Carnegie Institution of Washington. Crystalline phases were analyzed using an acceleration voltage of 15 kV and a beam current of 15 nA, whereas quenched melts were analyzed with defocused beam and a beam current of 1–5 nA. Backscattered electron images of the samples were obtained using a field emission scanning electron microscope (JEOL JSM 6500F at the Department of Terrestrial Magnetism of Carnegie Institution of Washington).

RESULTS AND DISCUSSION

The phase relations during melting of the chloride- and carbonate-bearing eclogite were investigated at 7.0 and 10.5 GPa and 1200–1675 °C (Table 1). Garnet (50–60 modal percent, mod%), clinopyroxene (10–16 mod%), coesite or stishovite (1–15 mod%), and kyanite (2–4 mod%) were the crystalline phases in all runs. Coesite or stishovite modal abundance decreases drastically in high-temperature runs. Garnet is a pyrope-grossular-majorite solid solution. Clinopyroxene contains 37–66 mol% of jadeite, 1–7 mol% of Ca-Eskola component, and 0.12–0.29 wt% of K_2O.

Melts were present in all runs. Quenched Cl-bearing carbonatite (carbonate-chloride) melt as spongy aggregates of dendritic crystals was

TABLE 1. RUN CONDITIONS AND COMPOSITIONS OF THE MELTS IN THE SYSTEM ECLOGITE-CARBONATE-CHLORIDE

Sample	Starting mixture	K-354	K-355	K-398	K-379	K-385	K-358	K-352	K-360	K-381
Pressure (GPa)		7.0	7.0	7.0	7.0	10.5	10.5	10.5	10.5	10.5
Temperature (°C)		1200	1300	1400	1550	1300	1400	1500	1600	1675
Time (min)		360	360	360	30	360	360	240	240	60
Melt (%)		9.0	11.5	14.0	25.0	8.5	11.0	14.0	18.0	30.0
SiO_2	49.80	11.72 (0.72)	24.77 (1.32)	38.52 (1.18)	53.25 (1.05)	16.69 (1.27)	22.49 (1.25)	29.72 (1.14)	38.35 (2.16)	50.90 (1.33)
Al_2O_3	16.40	1.54 (0.11)	4.74 (0.30)	8.23 (0.89)	10.72 (0.96)	0.80 (0.24)	1.83 (0.37)	2.74 (0.23)	4.94 (0.52)	6.42 (0.56)
MgO	13.24	4.18 (0.12)	2.24 (0.16)	4.55 (0.54)	2.51 (0.24)	1.03 (0.21)	1.34 (0.22)	1.58 (0.37)	1.79 (0.47)	1.51 (0.24)
CaO	11.04	24.27 (2.54)	20.17 (1.75)	10.22 (0.54)	7.79 (0.69)	20.26 (1.63)	22.72 (1.59)	22.65 (0.82)	18.43 (1.30)	14.55 (0.41)
Na_2O	1.58	2.56 (0.53)	2.56 (0.37)	1.85 (0.26)	1.59 (0.15)	0.95 (0.19)	1.15 (0.20)	1.15 (0.16)	1.59 (0.25)	2.07 (0.15)
K_2O	1.60	5.73 (0.69)	6.51 (0.59)	3.35 (0.30)	4.14 (0.15)	3.48 (0.39)	5.89 (0.77)	7.73 (0.59)	7.21 (1.84)	5.27 (0.29)
CO_2	4.00	45.00 (2.41)	34.90 (1.72)	30.00 (2.10)	16.34 (1.52)	47.50 (2.27)	37.10 (1.84)	29.20 (0.92)	22.00 (2.56)	13.70 (1.16)
Cl	3.02	6.52 (1.16)	5.29 (1.02)	4.29 (0.84)	4.71 (0.70)	11.94 (0.75)	9.72 (0.84)	6.78 (0.56)	7.32 (1.49)	7.27 (0.72)
O^-	0.68	1.47	1.19	0.97	1.06	2.69	2.19	1.53	1.65	1.64

Note: Melt compositions are in weight percent. Coexisting phases are garnet, clinopyroxene, kyanite, and coesite (stishovite at 10.5 GPa). CO_2 content is calculated from total deficit of microprobe analyses. Standard deviations (10–30 points per sample) are shown in parentheses.

observed in the products of low-temperature runs, i.e., 1200–1400 °C at 7 GPa and 1300–1600 °C at 10.5 GPa (Fig. 1). In the high-temperature runs (1550 °C at 7 GPa and 1675 °C at 10.5 GPa), the melts form an interstitial glass with abundant spherical voids representing former gas bubbles at both pressures and presumably quenched coesite crystals at 7 GPa (Fig. 1). The degree of partial melting estimated from mass balance gradually increases with temperature, but does not exceed 30%. The SiO_2 content in the melts increases with temperature from 12 to 53 wt% at 7 GPa and from 17 to 51 wt% at 10.5 GPa. Taking into account quenched coesite, the SiO_2 content in the melt at 7 GPa could be as high as 55–56 wt%. The Al_2O_3 content increases simultaneously from ~1 wt% to 6–10 wt% at both pressures. These SiO_2 and Al_2O_3 contents of melt are significantly higher than those for the eclogite-CO_2 system at similar degrees of melting (Yaxley and Green, 1994; Litasov and Ohtani, 2010). The CO_2 content (estimated from total deficit of oxides in microprobe analyses) decreases from 45 to 47 wt% to 13–17 wt%. As a result, with increasing temperature the melt composition changes gradually from chloride-carbonate to essentially alumino-silicate with lower content of dissolved carbonate components. This trend of melt evolution from carbonatite to Si-rich carbonated melt is consistent with that in the Cl-free carbonated eclogite systems (Hammouda, 2003; Yaxley and Brey, 2004; Dasgupta et al., 2004; Litasov and Ohtani, 2010); however, the maximum SiO_2 contents (>50 wt%) observed in our

work were not achieved in continuous melting sequences and comparable degrees of melting (below 30%) in any starting mixtures.

The SiO_2-rich melts (49–57 wt%) coexisting with relatively refractory carbonates were observed as a result of low-degree melting of a CO_2-H_2O–bearing eclogite at 2.5 GPa and 750–850 °C (Yaxley and Green, 1994), melting of the comparable system at 5–6 GPa and 1150–1300 °C (Hammouda, 2003), and during melting of the eclogite-H_2O system (50–60 wt% SiO_2) at 4–6 GPa and 900–1300 °C (Kessel et al., 2005). Although these melts can be consistent with silicic end-member inclusions in diamonds, they do not form continuous compositional trends toward carbonatite with increasing or decreasing temperature. Silicic inclusions in diamonds contain a significant amount of H_2O (in the range of 10–20 wt%; e.g., Weiss et al., 2010), and the effect of H_2O should be tested experimentally. In our study, it was shown that silicic to carbonatite compositions can be obtained in the H_2O-free eclogitic system. The exact effect of H_2O on the obtained melting relations is not known at present; however, it can be argued that H_2O will significantly decrease temperature stability of silicic melts, while barely changing the melt compositions. It is known that SiO_2 and Al_2O_3 have enhanced solubility in both H_2O and H_2O-NaCl fluids (e.g., Newton and Manning, 2000, 2006).

Figure 2 illustrates that the essentially silicate melts produced in the high-temperature sets of our experiments are projected close to the
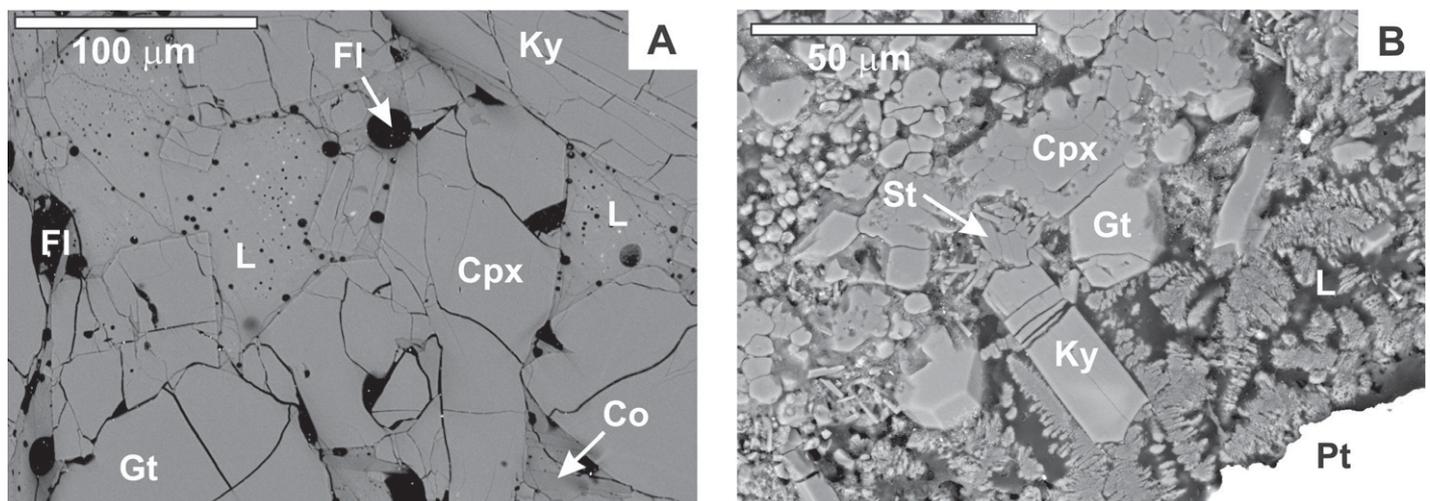

Figure 1. A: Backscattered electron (BSE) image of alumino-silicate glass (L) with abundant fluid bubbles (Fl) at 7.0 GPa and 1550 °C. Cpx—clinopyroxene, Gt—garnet, Ky—kyanite, Co—coesite. B: BSE image of chloride- and carbonate-bearing dendritic aggregates (L) at 10.5 GPa and 1300 °C, coexisting with Cpx, Gt, Ky, and Co, or stishovite (St). Pt—platinum capsule.
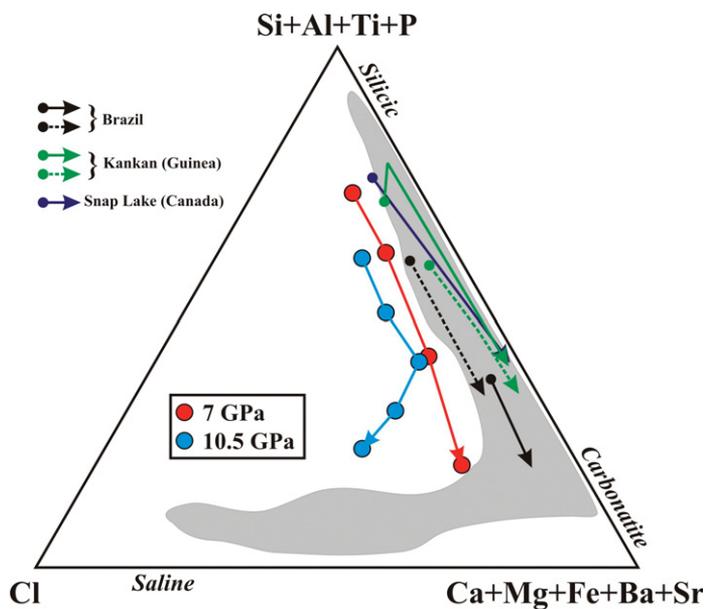
Figure 2. Evolution of melts produced in system eclogite-carbonate-chloride at 7.0 and 10.5 GPa in comparison with core-to-rim changes of fluid compositions in diamonds from Brazil (Shiryaev et al., 2005; black solid and dotted arrows), Kankan, Guinea (Weiss et al., 2009; green solid and dotted arrows), and Snap Lake, Canada (A. Logvinova, 2010, personal commun.; blue arrow). Gray field shows range of compositions of fluid or melt inclusions in diamonds worldwide (see compilation in Safonov et al., 2009).

compositional range of the silicic inclusions in diamonds. Weiss et al. (2009) argued that the silicic melts preserved in eclogitic diamonds from Guinea and Yakutia are near solidus melts produced by low-degree melting of carbonate-bearing eclogite in the presence of aqueous fluid. Following the experimental results of Hammouda (2003), they suggested that during progressive melting, partial melts would evolve from silica-rich toward carbonate-rich compositions. As shown here, this cannot be the case, and in this mechanism only silicic inclusions can be formed. Our data show that the range from SiO_2-rich to carbonatite melts can be produced at relatively low degree of melting (<30%) of eclogite interacting with the H_2O-free chloride-carbonate melt. The direction of the trends for the melt evolution in the system eclogite-carbonate-chloride is similar to that deduced from the system peridotite-carbonate-chloride (Litasov and Ohtani, 2009a), supporting a general scheme of phase relations and melt evolution in chloride-carbonate-silicate systems (Safonov et al., 2007, 2009). These trends are consistent with the core-to-rim compositional zoning of the melt inclusions in eclogitic diamonds from Kankan (Guinea; Weiss et al., 2009), Snap Lake (Canada; A. Logvinova, 2010, personal commun.), and Brazil (Shiryaev et al., 2005), indicating that these diamonds may grow during cooling of the diamond-forming system. As pointed out by Shiryaev et al. (2005) and Weiss et al. (2009), observed compositional zoning in diamonds is not continuous; instead, two to three distinct zones through the diamond were recorded. However, these zones can still show progressive evolution from silicic to carbonatitic compositions in a continuous process with repeated melt impregnation and/or heating events. According to estimates by Navon (1999), fibrous diamonds typically formed shortly before kimberlite eruptions.

The appearance of a range of primary fluid and mineral inclusions in diamonds suggests that the inclusions are parts of diamond-forming media in natural environments. The H_2O-CO_2–dominated nature of the fluid reveals oxidized conditions for diamond formation. Diamond crystallization can occur by the reaction of this fluid with a reduced eclogite

matrix, which is expected to be equilibrated at fO_2 stability of diamond at 5–6 GPa (e.g., Frost and McCammon, 2008). The original substrate would contain diamond, which acts as a carbon source for crystallization of newly formed fibrous crystals. This is clear from the fact that many fibrous and cloudy diamonds contain octahedral or other shape-transparent cores (e.g., Weiss et al., 2009). Alternatively, diamond can be formed by reduction of carbonate-chloride melt by the modified decarbonation reactions with eclogite minerals, for example, coesite + kyanite + carbonate (Ca, Mg) = garnet + diamond + O_2. Crystallization of diamond will be controlled by saturation of the diamond-forming medium with carbon and by the reducing capacity of matrix eclogite relative to the oxidizing capacity of carbonate-chloride–bearing melt. In experiments, diamond nucleation occurs at carbonate/silicate weight ratios of ~1 and an H_2O/silicate ratio of ~0.1. Various chloride-carbonate-H_2O media are also favorable for diamond crystallization (Palyanov et al., 2007). The effect of chlorine on diamond nucleation in the silicate-bearing systems is not yet established.

It is important to discuss the origin of bubbles in the high-temperature Si-rich melts. The chlorine content of the melt increases with increasing pressure (Table 1). At each pressure, chlorine content is the highest in the low-temperature chloride-carbonate melts. It decreases gradually with increasing degree of melting due to dilution by silicate components of starting eclogite and becomes approximately constant at above 1400 °C at 7 GPa and above 1500 °C at 10.5 GPa. In the high-temperature runs we assume the presence of an immiscible chloride-bearing phase. This phase could be fluid or melt concentrating CO_2, Cl, Ca, Na, and K, with low contents of silica and alumina. Taking into account the numerous empty bubble-like voids within the glass (Fig. 1), the presence of a CO_2-rich fluid is more likely than an immiscible carbonate-chloride melt, which usually forms large globules (Safonov et al., 2007, 2009). Possible formation of CO_2 bubbles during quenching cannot be excluded, as the largest voids are usually, but not always, associated with the grain boundaries. This fluid may originate from a gradual decarbonation of the carbonate-chloride melt during its interaction with crystalline silicate phases. According to the experimental data of Knoche et al. (1999), the equilibrium 2 magnesite and/or aragonite + kyanite + 2 coesite or stishovite = garnet + 2 CO_2, relevant to our run assemblage, strongly shifts to the right side at temperatures above 1400 °C at 7 GPa and above 1550 °C at 10.5 GPa. This reaction presumably proceeds at lower temperatures in the presence of the chloride-carbonate liquid. Active decarbonation of the melt and reaction with coesite or stishovite explains a rapid increase of silica content in the partial melts even at a relatively low degree of melting (i.e., 30%). Thus, the melting of the chloride-carbonate–bearing eclogite can be represented by the following scheme: coesite + carbonate-chloride melt → silicate melt + CO_2-rich fluid. As a result, the alkali- and chlorine-rich silicate melt forms.

In summary, our experiments in the eclogite-carbonate-chloride system reproduced the compositional trends from silicic to carbonatite fluid or melt inclusions observed in fibrous and/or cloudy diamonds worldwide. We can argue that the typical crystallization sequences include formation of silicic melt via interaction of eclogite with carbonate-chlorine (+H_2O) melt followed by fractionation of coesite or stishovite, which are common syngenetic inclusions, and formation of SiO_2-poor carbonatite melts. The key role of chlorine in this process is emphasized. The role of H_2O, which is one of the major components in diamond fluids, should also be examined in future experiments.

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