University of Alberta

Effect of Chlorine on the Melting of the Subcratonic Lithospheric Mantle

by

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Abstract

 The presence of chlorine in the subcratonic lithospheric mantle (SCLM) has been evaluated by compiling the compositional data of fluid inclusions in fibrous diamonds. Chlorine associates with potassium, dissolving in water and forming a KCl-bearing brine with the $Cl/(Cl+H₂O)$ molar ratio of 0.05-0.68.

 To examine the effect of such a KCl-bearing brine on the melting behavior of the SCLM, we conducted experiments in the $Mg_2SiO_4-MgSiO_3-H_2O$ and $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems at 5 GPa and 1100-1700 °C. In the $Mg_2SiO_4-MgSiO_3-H_2O$ system, the solidus temperature of forsterite+enstatite is ~1230 °C. In the Mg₂SiO₄-MgSiO₃-KCl-H₂O systems with molar Cl/(Cl+H₂O) ratios of 0.2, 0.4 and 0.6, the solidus temperatures are \sim 1430 °C, \sim 1530 °C and \sim 1580 °C, respectively. The increase in the temperature of the solidus demonstrates that KCl elevates the solidus of the $Mg_2SiO_4-MgSiO_3-H_2O$ system. Therefore, KCl in the SCLM can prevent melting at the H_2O -saturated solidus, and a KCl-bearing fluid can be a robust agent for mantle metasomatism.

Acknowledgment

 Establishing the method of study and writing this thesis were not easy tasks, and I would like to express thanks to my supervisor, Dr. Robert W. Luth, a professor of Igneous Petrology and Experimental Geochemistry in the Department of Earth & Atmospheric Sciences at the University of Alberta, for giving me his continuous guidance, supervision and advice on this research. I am grateful for his wisdom and academic strength, and I will carry the knowledge gained into future studies.

 I would like to acknowledge Diane Caird, the Superpress and X-ray Technician in the Department of Earth & Atmospheric Sciences at the University of Alberta, for teaching me sample assembly and how to operate the Superpress. But more than that, I'd like to express appreciation for her motherly care while I was in the lab.

 I would like to acknowledge Dr. Sergi Matveev, the Microprobe Technician in the Department of Earth & Atmospheric Sciences at the University of Alberta, and Dr. Tom Chacko, a professor in the Department of Earth & Atmospheric Sciences at the University of Alberta, for helping me develop skills and solve problems when using the microprobe.

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Chapter 1. Introduction

 "Volatiles" in the petrological literature are constituents that are liquid or gaseous at normal Earth's surface conditions, and they mainly include H_2O , CO_2 and sulfur-bearing and halogen-bearing species (Luth, 2003). Present in the Earth's mantle, these constituents can have significant effects on the stability and physical-chemical properties of partial melts and the mantle (Dasgupta and Dixon, 2009; and references therein). Of these volatiles, halogens are rarely studied from mantle samples, and their effects on mantle processes are poorly constrained by experiments. Based on studies of fluid inclusions in fibrous diamonds (Johnson et al., 2000; Burgess et al., 2002; Burgess et al., 2009), chlorine has much higher concentrations than other halogens in the mantle-derived fluids, which indicates that chlorine is the dominant halogen in the upper mantle and may play a more significant role than fluorine, bromine or iodine.

 The existence of chlorine in the upper mantle has been documented in different tectonic settings over the past 30 years. In subduction zones, chlorine exists as solutes in subduction-related magmas (Perfit *et al.*, 1980; Poorter *et al.*, 1989; Kent et al., 2002) and as highly saline fluid inclusions in subduction zone metasediments (Philippot, 1993) and eclogite-facies rocks (Scambelluri and Philippot, 2001). In cratonic areas, the existence of chlorine in the upper mantle is evidenced by alkali chlorides in kimberlite groundmass (Kamenetsky *et al.*, 2004), chlorine-rich fluids trapped in fibrous diamonds (Izraeli et al., 2001; Tomlinson et al., 2006; Klein-BenDavid et al., 2007) and chlorine-bearing apatite and mica in mantle xenoliths (Smith *et al.*, 1981; Smith, 1981). In a Group Ι

kimberlite described as "exceptionally fresh" from the Udachnaya-East pipe in Siberia, alkali chlorides, alkali carbonates and sulfates (ratio 5:3:1) were found as >8 wt% of the groundmass (Kamenetsky *et al.*, 2004). A mantle origin of these chlorides and carbonates has been confirmed by Sr, Nd and Pb isotope studies (Kamenetsky *et al.*, 2004; Maas *et al.*, 2005). In fibrous diamonds from the Diavik mine in Canada, fluid inclusions can have chlorine contents up to 34.2 wt% (Klein-BenDavid *et al.*, 2007). In mantle xenoliths, chlorine content can be up to 1.0 wt% in apatite and 0.05 wt% in mica (Smith, 1981; Smith *et al.*, 1981).

 If widespread in the upper mantle, chlorine could potentially play important roles in affecting partial melting and metasomatism of the mantle and also in affecting physical-chemical properties of resulting melts or fluids. Experiments at pressures of <0.9 GPa show that chlorine reduces the activity of water in hydrous systems and increases the melting temperature of albite relative to the pure water case (Shmulovich and Graham, 1996). If this reduction of water activity still happens under high-pressure conditions, we anticipate that chlorine will increase the vapor-saturated solidus of hydrous peridotites and thereby prevent melting and stabilize water-rich fluids, which are effective agents for mantle metasomatism. Moreover, Keppler (1996) proposed that chloride would favor complexing with ions, such as Rb^{2+} , Ba^{2+} , Sr^{2+} and Pb^{2+} , rather than with more highly charged cations, such as Nb^{5+} and Ta^{5+} . Chemical transport by the chlorine-rich fluid will generate the relative enrichment of large ionic lithophile elements, such as Pb and U, and the relative depletion in high field strength elements, such as Nb and Ta, which has been invoked to explain the trace element pattern for calc-alkaline

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magmas in subduction zones where chlorine can be transported by subducted slab into the mantle and then released to the mantle wedge.

This thesis is composed of two sections. The first section (Chapter 2)

compiles compositional data of fluid inclusions in fibrous diamonds in order to

evaluate the composition of chlorine-bearing fluids in the subcratonic lithospheric

mantle. The second section (Chapter 3) reports the results of high pressure and

temperature experiments in the $Mg_2SiO_4-MgSiO_3-H_2O$ and

Mg₂SiO₄-MgSiO₃-KCl-H₂O systems to reveal the effects of chlorine on the

melting of the hydrous Earth's mantle.

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Chapter 2. Chlorine-bearing fluids in the subcratonic lithospheric mantle Introduction

 The presence of chlorine-bearing fluids in the subcratonic lithospheric mantle (SCLM) has been documented by fluid inclusions in fibrous diamonds (Izraeli et al., 2001; Tomlinson et al., 2006; Klein-BenDavid et al., 2007).

Because of their mechanical strength and chemical inertness, diamonds are probably the best material for transporting pristine fluid samples from the mantle to the surface (Navon et al., 1988). According to studies of syngenetic mineral inclusions in fibrous diamonds from both Koffiefontein in South Africa (Izraeli et al., 2004) and the Panda mine in Canada (Tomlinson et al., 2006), fibrous diamonds formed mainly at the pressure of 4-6 GPa and the temperature of 900-1200°C. Therefore, the fluids trapped in the diamonds can represent fluids at depths of 130-200 km in the SCLM.

 Compositions of the trapped fluids in the fibrous diamonds from different cratons have been reported by Schrauder and Navon (1994), Izraeli et al. (2001), Shiryaev et al. (2005), Tomlinson et al. (2006), Klein-BenDavid et al. (2006), Klein-BenDavid et al.(2007) and Klein-BenDavid et al. (2009). In the reported compositions, some components were analyzed but others were calculated based on various assumptions. Therefore, these data incorporate both analytical uncertainties and uncertainties associated with the assumptions inherent to the calculations, which introduces limitations in applying these data to reveal the compositions of fluids in the SCLM. Moreover, both H_2O and Cl have been found as common components in the trapped fluids and the $Cl/(Cl+H₂O)$ molar ratio

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may control the compositions of the trapped fluids, however, this $Cl/(Cl+H₂O)$ molar ratio has not been calculated in the previous studies.

 This chapter compiles the reported compositional data of fluid inclusions in fibrous diamonds and examines their limitations, with the aim to achieve a more accurate understanding of the compositions of chlorine-bearing fluids in the SCLM. Based on the more accurate understanding of compositions, the range of $Cl/(Cl+H₂O)$ molar ratio for the fluids is calculated in this chapter, which will guide the preparation of starting materials in the next chapter (Chapter 3).

Data compilation

 The compositions of sub-micrometer fluid inclusions have been reported in cubic fibrous diamonds, fibrous coats of octahedral diamonds and some undefined diamond fragments from Jwaneng in Botswana (Schrauder and Navon, 1994), Koffiefontein in South Africa (Izraeli et al., 2001), Brazil (Shiryaev et al., 2005), Diavik and Panda mines in Canada (Tomlinson et al., 2006; Klein-BenDavid et al., 2006; Klein-BenDavid et al., 2007) and Yakutia diamond field in Russia (Klein-BenDavid et al., 2006; Klein-BenDavid et al., 2009). Elements such as Si, Ti, Al, Cr, Fe, Mg, Ca, Ba, Sr, Na, K, P, S and Cl, were analyzed by electron probe microanalysis (EPMA) for individual inclusions. Volumes activated by the electron beam are bigger than inclusion volumes, and therefore the totals of the analyses are significantly lower than 100%. Schrauder and Navon (1994), being aware of the uncertainty arising from variable inclusion depths and the assumption of a uniform matrix, estimated precision of 10-40% for the various oxides in individual analyses and less than 10% for the sample averages. They

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also estimated that the accuracy of the results obtained by EPMA is in the range of 10-15% by comparing the EPMA data with proton-probe and neutron activation data of the same diamonds. Izraeli et al. (2004) estimated the EPMA precision and accuracy by examination of olivine microinclusions in clouds of fibrous diamonds. They estimated the precision to be better than \sim 15% by analyzing the same mineral inclusions at different dates and with different EDS systems, and they estimated the accuracy to be in the range of only a few percent for the most abundant elements by comparing the range of $Mg/(Mg+Fe)$ molar ratio and Si/(Mg+Fe) molar ratio of olivine microinclusions with those of large olivine inclusions in diamonds.

 Infrared absorption spectra of the fibrous diamonds were collected with Fourier transform infrared spectroscopy (FTIR). The absorption of the trapped materials in fluid inclusions was obtained after correcting the spectrum for baseline and diamond absorption. The most common bands after the corrections are those of carbonate and water. The $[CO₃]²/([CO₃]² + H₂O)$ molar ratio was estimated from the maximum height of net absorption bands of carbonate and water at \sim 1430 and \sim 3420 cm⁻¹ and Beer's law. The entire wafer thickness of diamond was sampled by IR spectroscopy, but it can be cancelled in calculating the $[CO₃]² / ([CO₃]² + H₂O)$ molar ratio, because the thickness is the same for both $[CO₃]²$ and H₂O for each analysis if assuming that H₂O and $[CO₃]²$ are in same inclusions. Because different absorption coefficients were used in the different studies, the $[CO₃]² / ([CO₃]² + H₂O)$ molar ratio has been recalculated in this thesis using consistent absorption coefficients ($\varepsilon_{\text{calcite}} = 250 \text{ L/mol cm}^{-1}$ (~1430 cm⁻¹)

(Navon et al., 1988), $\varepsilon_{\text{liquid water}} = 80 \text{ L/mol cm}^{-1} (3420 \text{ cm}^{-1})$ (Thompson, 1965), which are believed by Navon et al. (1988) to be representative of the absorption by the carbonate and hydrous species in the inclusions). As stated by Navon et al. (1988), absorption coefficients of other carbonates (for example, Na_2CO_3 , gaylucite) differ from that of calcite by less than 30%, and the water absorption coefficient is accurate to $\sim 30\%$ ¹.

 Based on results of a transmission electron microscopy study on four diamonds from Canada and Siberia, together with the tight range of composition detected by EPMA and the volatiles detected by FTIR, Klein-BenDavid et al. (2006) suggested that the fluids trapped in inclusions were uniform, dense and supercritical and then evolved to secondary phases, including crystallized minerals and low-density fluids, during cooling. Most elements in fluid inclusions are hosted in the crystallized minerals such as silicates, carbonates, phosphate, sulfates and chlorides, which is supported by the agreement of the composition of the whole inclusion to that of its daughter crystals (Klein-BenDavid et al., 2006). Based on these observations, Klein-BenDavid et al. (2006) postulated that Ca^{2+} , Mg^{2+} , Fe^{2+} , Ba^{2+} , Na^{+} and K^{+} were balanced by [Cl]⁻, [PO₄]³⁻ and [CO₃]²⁻ to form chloride, phosphate and carbonate and that Si^{4+} , Ti^{4+} and Al^{3+} were balanced by $O²$ to form silicates, and they calculated the $[CO₃]²$ content by the formula: $[CO_3]^2 = Ca^{2+} + Mg^{2+} + Fe^{2+} + Ba^{2+} + 0.5Na^+ + 0.5K^+ - 0.5[C1] - 1.5[PO_4]^3$. Based on studies of minerals crystallized from trapped fluids in more fibrous

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¹ The original paper states this accuracy to be "-30%". The assignment of accuracy as a negative percentage makes no sense; I believe the authors meant "~30%".

diamonds, Klein-BenDavid et al. (2007) assumed that Ti^{4+} , Ca^{2+} , Mg^{2+} , Fe^{2+} , Ba^{2+} , Na⁺ and K⁺ were balanced by [Cl]⁻, [PO₄]³⁻, [CO₃]²⁻ and [SiO₄]⁴⁻ and that $Si⁴⁺$ and $Al³⁺$ were associated with $Mg²⁺$, Fe²⁺ and K⁺ in proportions to form mica, and they changed the formula to be $[CO_3]^2 = 2Ti^{4+} + Ca^{2+} + Mg^{2+} + Fe^{2+} + Ba^{2+} +$ $0.5Na^{+} + 0.5K^{+} - 0.5[C1] - 1.5[PO₄]³⁻ - [SiO₄]⁴⁻. In this formula, [SiO₄]⁴⁻ is$ subtracted with the factor of 1, which implies for the silicates with the $(2Ti + Ca +$ $Mg + Fe + Ba + 0.5Na + 0.5K$ /Si molar ratio of 1, such as pyroxenes. Following the calculation of the $[CO₃]²$ content, the H₂O content can be calculated by using the $[CO₃]²$ content and the $[CO₃]² / ([CO₃]² + H₂O)$ molar ratio.

 In this thesis, only Si, Al, Fe, Mg, Ca, Na, K and Cl are considered (Table 2-1) because the other elements such as Ti, Cr, Ba, Sr, P and S are minor (<5mol% for each) and not always reported. These elements, together with the $[CO₃]² / ([CO₃]² + H₂O)$ molar ratio, are calculated into four components with a total of 100 mol%, including silica tetrahedron ($\text{[SiO}_4\text{]}^{4}$), carbonate ion ($\text{[CO}_3\text{]}^{2}$), chloride ion ([Cl]) and water molecule (H₂O), where $\left[SiO_4\right]^{4-} = Si^{4+}$, $\left[CO_3\right]^{2-} =$ $Ca^{2+} + Mg^{2+} + Fe^{2+} + 0.5Na^{+} + 0.5K^{+} - 0.5[Cl]$, [Cl] = [Cl], and H₂O = [CO₃]²⁻(1/ α -1) where $\alpha = [CO_3]^2$ /([CO₃]²⁻+H₂O) from FTIR.

Table 2-1. Original compositional data of fluid inclusions in fibrous diamonds. Table 2-1. Original compositional data of fluid inclusions in fibrous diamonds.

Note: C/CH represents $[CO_3]^2/([CO_3]^2+H_2O)$ molar ratio.

Note: C/CH represents $[CO_3]^2/([CO_3]^2+H_2O)$ molar ratio.

Table 2-1 (continued). Original compositional data of fluid inclusions in fibrous diamonds. Table 2-1 (continued). Original compositional data of fluid inclusions in fibrous diamonds.

Note: C/CH represents $\rm [CO_3]^2/([CO_3]^2+H_2O)$ molar ratio. Note: C/CH represents $[CO₃]²/([CO₃]² + H₂O)$ molar ratio.

Limitations

The calculation of $[CO₃]²$ in this thesis is based on the assumptions used by Klein-BenDavid et al. (2007) that Ti^{4+} , Ca^{2+} , Mg^{2+} , Fe^{2+} , Ba^{2+} , Na^{+} and K^{+} are balanced by [Cl]⁻, $[PO_4]^{3}$ ⁻, $[CO_3]^{2}$ ⁻ and $[SiO_4]^{4}$ - and that Si^{4+} and Al^{3+} are associated with Mg^{2+} , Fe²⁺ and K⁺ in proportions to form mica. This assumption considers that Mg^{2+} , Fe²⁺ and K⁺ not only combine with $[CO₃]^{2-}$ and $[Cl]^{-}$ but also combine with $\left[SiO_4\right]^4$, which is supported by the discovery of silicate minerals such as mica, pyroxenes and olivine in fluid inclusions. According to this assumption, the calculation of $[CO₃]^{2}$ should include the subtraction of $[SiO₄]^{4}$ with a factor. In the calculation by Klein-BenDavid et al. (2007), this factor is 1, which is only suitable for the fluid inclusions where the crystallized silicate minerals have the $(2Ti + Ca + Mg + Fe + Ba + 0.5Na + 0.5K)/Si$ molar ratio of 1. However, most crystallized silicate minerals in fluid inclusions do not have this molar ratio of 1. For example, quartz has this molar ratio of 0, and olivine has this molar ratio of 2. For fluid inclusions where the crystallized silicate mineral is only quartz, the calculation by Klein-BenDavid et al. (2007) will generate a negative value for $[CO₃]²$. Therefore, the calculation of $[CO₃]²$ in this thesis does not include the subtraction of $\left[\text{SiO}_4\right]^4$. Besides this, the calculation of $\left[\text{CO}_3\right]^2$ also does not consider the minor elements such as Ti, Cr, Ba, Sr, P and S.

Without subtracting $\left[SiO_4\right]^4$, $\left[CO_3\right]^2$ can be overestimated for Si-rich fluid inclusions, and H_2O can also be overestimated because H_2O is calculated from [CO₃]²⁻ using the formula: H₂O = [CO₃]²⁻(1/ α – 1). Therefore, the [Cl]⁻/([Cl]⁻ + H2O) molar ratio can be underestimated for Si-rich fluid inclusions because of the

overestimation of H_2O , and the $\text{[CI]} / (\text{[CI]} + H_2O)$ molar ratio for Si-rich fluid inclusions cannot represent their actual $Cl/(Cl + H₂O)$ molar ratio. However, the effect of not subtracting $[SiO_4]^4$ is negligible for Si-poor fluid inclusions. Furthermore, the neglect of Ti, Cr, Ba, Sr, P and S could cause uncertainty in the calculated $[CO₃]²$. For example, neglecting Ti, Cr, Ba and Sr underestimates $[CO₃]²$, and neglecting P and S overestimates $[CO₃]²$. Because these elements are minor in fluid inclusions and the underestimation and overestimation of $[CO₃]^{2-}$ can be cancelled by each other to some extent, the uncertainty caused by neglecting these elements is negligible. Therefore, the calculation without subtracting $\left[SiO_4\right]^4$ and without considering the minor elements can still yield a relatively accurate $Cl/(Cl + H_2O)$ molar ratio for the Si-poor fluid inclusions.

Table 2-2. Calculated composition of fluid inclusions in fibrous diamonds. Table 2-2. Calculated composition of fluid inclusions in fibrous diamonds.

Table 2-2 (continued). Calculated composition of fluid inclusions in fibrous diamonds. Table 2-2 (continued). Calculated composition of fluid inclusions in fibrous diamonds.

Composition of chlorine-bearing fluids

 Concentrations of the elements Si, Al, Fe, Mg, Ca, Na, K and Cl are calculated into molar percentages and shown in Table 2-2 and Figure 2-1. From the concentration of Cl, fluids in fibrous diamonds divide into high-Cl fluids and low-Cl fluids (Figure 2-1a and 2-1b, respectively), which are shown as the two peaks in the histogram of Cl mol% in Figure 2-2. The high-Cl fluids are rich in Cl and K but poor in Si, Mg and Ca, and they are from Diavik and Panda mines in Canada and Koffiefontein in South Africa. In contrast, the low-Cl fluids are poor in Cl but rich in Si, Mg, Ca and K, and they are from Brazil, the Diavik mine in Canada, Jwaneng in Botswana and Yakutia in Russia. The Cl/(Cl+K) molar ratio is around 0.6 for the high-Cl fluids but <0.35 for the low-Cl fluids, and the $K/(K+Na)$ molar ratio is >0.5 for all fluids (Figure 2-3). Overall, the concentration of elements indicates that fluids trapped in fibrous diamonds can be divided into the high-Cl fluids and the low-Cl fluids, and Cl is mainly associated with K.

The four components $[\text{SiO}_4]^4$ ⁻, $[\text{CO}_3]^2$ ⁻, $[\text{Cl}]$ ⁻ and H_2O are calculated and shown in Table 2-2 and projected in Figure 2-4. This projection of the four components shows that the high-Cl fluids, except those in fibrous diamonds from the Panda mine, fall along a line and the low-Cl fluids distribute close to the $[SiO₄]⁴$ - $[CO₃]²$ -H₂O plane. The fluid inclusions in the fibrous diamonds from the Panda mine fall between the line and the plane, which may be caused by mixing of different types of fluids. As listed in Table 2-2, the [Cl] /([Cl] + H₂O) molar ratio of the high-Cl fluids is 0.05-0.68, and the $\text{[CI]}/\text{([CI] + H₂O)}$ molar ratio of the low-Cl fluids is 0.01-0.25. Because the chlorine-rich fluids are poor in Si, the

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calculated $[CO₃]²$ and H₂O are not affected by the calculation without subtracting $[SiO₄]$ ⁴⁻ and therefore, their calculated [Cl] /([Cl] +H₂O) molar ratio would represent the actual $Cl/(Cl+H₂O)$ molar ratio of fluids. However, because the low-Cl fluids are rich in Si, the calculated $\text{[CI]}/\text{([CI] + H₂O)}$ molar ratio underestimates the $Cl/(Cl+H₂O)$ molar ratio of the fluids. Therefore, the $Cl/(Cl+H₂O)$ molar ratio of chlorine-bearing fluids in fibrous diamonds is more accurately represented by the $\text{[CI]} / \text{([CI]} + \text{H}_2\text{O})$ molar ratio of 0.05-0.68 for the high-Cl fluids.

 In previous works, Klein-BenDavid et al. (2007) concluded that there is a continuous compositional evolution between saline-HDFs and carbonatitic-HDFs by plotting the composition of fluid inclusions on the $(Si+Al)-(K+Na)-(Ca+Mg+Fe)$ triangular diagram, and, similarly, Safonov et al. (2007) also concluded a continuous compositional evolution between the Si-bearing chloride-carbonate brine and the chloride-bearing carbonatitic liquid by plotting compositions of fluid inclusions on the

 $(Si+Al+Ti+P)$ -Cl- $(Ca+Mg+Fe+Ba+Sr)$ triangular diagram. Because the high-Cl fluids in this thesis are equivalents to the saline-HDFs by Klein-BenDavid et al. (2007) and the Si-bearing chloride-carbonate brine by Safonov et al. (2007) and the low-Cl fluids in this thesis include the carbonatitic-HDFs by Klein-BenDavid et al. (2007) and the chloride-bearing carbonatitic liquid by Safonov et al. (2007), the division of high-Cl fluids and low-Cl fluids in this thesis is opposed to the continuous compositional evolution by Klein-BenDavid et al. (2007) and Safonov et al. (2007).

Figure 2-1. Concentrations of elements in fluid inclusions in fibrous diamonds.

Figure 2-2. Distribution of the concentration of Cl in fluid inclusions in fibrous diamonds.

Figure 2-3. Projection of Cl, K and Na in fluid inclusions in fibrous diamonds.

Figure 2-4. Projection of the calculated $[SiO₄]⁴$, $[CO₃]²$, $[Cl]$ ⁻ and $H₂O$ for fluid inclusions in diamonds.

Data are in Table 2-2. The formula to calculate $[CO₃]$ ² is in the text. The gray solid line is the regression of chlorine-rich fluid inclusions in diamonds from Diavik and Koffiefontein mines, which can be expressed as the equations: $[SiO_4]^4$ = $-0.0378H_2O + 4.5295$ ($r^2 = 0.73$), $[CO_3]^2 = -0.2387H_2O + 23.789$ ($r^2 = 0.78$) and $[Cl]^- = -0.7236H_2O + 71.682$ ($r^2 = 0.97$), and which intersects the $\text{[SiO}_4]^4$ - $\text{[CO}_3]^2$ - [Cl] plane at the point $\text{([SiO}_4]^4$, $\text{[CO}_3]^2$, [Cl]) = (4.5, 23.8, 71.7). The black solid line ties the point of the intersection and the H2O vertex, and it almost superposes the gray regressed line. Small black spheres on the black solid line show the water contents of 20, 40, 60, and 80 mol%.

This significant difference is due to considering H_2O as an end member in plotting, in this thesis. Klein-BenDavid et al. (2007) and Safonov et al. (2007) did not consider H_2O as an end member of fluid compositions in plotting, therefore, their results of plotting are equal to that of projecting the compositions of fluid inclusions from the "H₂O" vertex to the $\left[\text{SiO}_4\right]^4$ - $\left[\text{CO}_3\right]^2$ - $\left[\text{Cl}\right]$ " triangular plane in Figure 2-4. This projection can cause an intersection or connection of the group of high-Cl fluids and the group of low-Cl fluids in the $[SiO₄]⁴$ - $[CO₃]²$ - $[Cl]$ ⁻ triangular plane. Therefore, the division of high-Cl fluids and low-Cl fluids, revealed by plotting with considering $H₂O$ in compositions of fluid inclusions in this thesis, is more reliable than the continuous compositional evolution of fluids by Klein-BenDavid et al. (2007) and Safonov et al. (2007). This division is possibly caused by fluid immiscibility between the high-Cl fluids and the low-Cl fluids because both of these two kinds of fluid inclusions exist in fibrous diamonds from the Diavik mine in Canada.

Conclusion

 Fluids trapped in fibrous diamonds represent fluids in the SCLM, and they divide into high-Cl fluids and low-Cl fluids. Chlorine in the fluids is mainly associated with K and dissolves in H_2O with the $Cl/(Cl+H_2O)$ molar ratio of 0.05-0.68.

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Chapter 3. Effect of KCl on melting of the Mg2SiO4-MgSiO3-H2O system at 5 GPa

Introduction

 Chlorine has been found as a major constituent in fluids trapped in fibrous diamonds (Navon et al., 1988; Izraeli et al., 2001; Tomlinson et al., 2006; Klein-BenDavid et al., 2006; Klein-BenDavid et al., 2007). It is mainly associated with potassium, forming a KCl-bearing brine with the $Cl/(Cl+H₂O)$ molar ratio of 0.05-0.68 (see Chapter 2). Syngenetic mineral inclusions in the fibrous diamonds from Koffiefontein in South Africa and from the Panda mine in Canada revealed that these fibrous diamonds formed at pressures of 4-6 GPa and temperatures of 900-1200 \mathbb{C} (Izraeli et al., 2004; Tomlinson et al., 2006). The high end of this temperature range is above the anticipated water-saturated peridotite solidus of Grove et al. (2006). Because these fibrous diamonds originate from the subcratonic lithospheric mantle (SCLM), the KCl-bearing brine in fluid inclusions of these diamonds indicates the existence of KCl in the SCLM at the depth relevant to the pressure 4-6 GPa. KCl in the brine may reduce the activity of H_2O sufficiently to stabilize a fluid, rather than a melt, under these conditions.

 Chlorides have been shown to affect melting behavior at lower pressure. The melting of albite and dehydration of brucite in H_2O -NaCl fluids to 0.9 GPa and 700-900 $\mathcal C$ shows that NaCl increases the solidus temperature of albite+fluid relative to the pure water case by reducing the activity of water in hydrous systems (Shmulovich and Graham, 1996). The H₂O activity measurement in concentrated NaCl, KCl and KCl-NaCl solutions to 1.5 GPa and 550-900 \mathbb{C}

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shows that KCl reduces the activity of water more than NaCl does at the same condition (Aranovich and Newton, 1996; Aranovich and Newton, 1997;

Aranovich and Newton, 1998), which means that KCl can increase melting temperature more than the same amount of NaCl. However, whether this effect exists at high pressures, corresponding to the depth of the SCLM, is unknown. This study conducts experiments to examine the effect of KCl on melting of the $Mg_2SiO_4-MgSiO_3-H_2O$ system, a simple model for H_2O -bearing harzburgitic Earth's mantle, at 5 GPa ($\sim 160 \text{ km}$).

Experimental techniques

 Starting materials (Table 3-1) were prepared in four different compositions by mixing $Mg(OH)_2$ (\geq 95% purity), SiO₂ (99.999% purity) and KCl (99.999% purity) that were dried at 120°C for >12 h. Material 1 is a mixture of $Mg(OH)_2$ and $SiO₂$ in 3:2 molar proportion, generating the $Mg₂SiO₄-MgSiO₃-H₂O$ system with $Mg_2SiO_4/MgSiO_3$ molar ratio of 1 and water content of 18.3 wt%. Materials 2, 3 and 4, generated by mixing Material 1 (Mg:Si=1.5) with KCl in different proportions, have $Cl/(Cl+H₂O)$ molar ratios of 0.2, 0.4 and 0.6, respectively, which are consistent with those of chlorine-rich fluid inclusions in fibrous diamonds from the Diavik mine in Canada (Klein-BenDavid et al., 2007), ranging from 0.05 to 0.68 (see in Chapter 2). All starting materials were ground in an agate mortar under ethanol for 1 h and then dried at 120° C and stored in a desiccator. After this drying, the water content of Material 1 was checked by thermogravimetric analysis (Figure 3-1).

 Approximately 3-5 mg of the appropriate starting material was loaded into an open-ended Pt capsule for each experiment. After drying at 120° C for >12 h, the capsule was welded shut quickly, within 3 min, and compressed gently into a cylindrical shape in a steel die. The compressed capsules had a diameter of 1.5 mm and a length ranging from 1.0 to 2.3 mm.

All experiments were run in the 2000 ton uniaxial split-sphere multi-anvil apparatus in the C.M. Scarfe Laboratory for Experimental Petrology at the University of Alberta. The 18mm sample assembly with high-T stepped graphite furnace, described by Walter et al. (1995), was used in all experiments. A semi-sintered $MgO-5\%Cr_2O_3$ octahedron was used as a pressure cell, and the sample assembly was inserted in a cylindrical hole in the octahedron. A W_{95} Re₅-W₇₄Re₂₆ thermocouple was inserted axially into the cylindrical sample assembly, and it was in contact with the Pt capsule. Each sample assembly was dried at 120 °C for >10 h, then fired at 1000 °C in (2% H₂) N₂ gas flow for 1 h. The sample capsule was removed from the assembly for this latter step. After firing, the sample capsule was re-inserted in the assembly, and then the assembly was kept in 120° C until use. The dried sample assembly was placed in the octahedral cavity formed by triangular truncations of 11 mm of eight 32.5 mm edge-length WC-cubes. These cubes formed a big cube placed in the cubic cavity formed by six anvils of the uniaxial press. Calibrations of pressure and thermal gradient have been described in detail by Walter et al. (1995). The pressure calibration is accurate to within ± 0.5 GPa, and the thermal gradient of the high-T stepped graphite furnace is $+25^{\circ}$ C mm⁻¹, away from the furnace midline (Walter et al.,

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1995). Experiments were brought to 5 GPa, and then heated at ~70 $^{\circ}$ C s⁻¹ to 1100-1700 \degree C, and maintained at \pm 5 \degree C. No pressure correction to the emf of the thermocouple was applied. Durations for runs at $\leq 1600^{\circ}$ C were 8-12 h, and those for runs at $>1600^{\circ}$ C were 2 h. Experiments were quenched by turning off the power to the furnace, resulting in a temperature drop to $\langle 300^{\circ}$ C in 2-5 s, and then decompressed over 3 h. After the runs, the capsules were weighed and then punctured with a razor blade. The punctured capsules were dried at 120° C for >12 h and then reweighted. If there was no weight loss after the drying, the capsule was presumed to have leaked, and the experiment was repeated. The punctured capsules in successful experiments were boiled in distilled water for 20 min twice to remove water-soluble material, such as chloride, because the presence of this material caused plucking of run products during polishing. The boiled capsules were dried and mounted in an epoxy plug using Petropoxy 154. After mounting, sample mounts were ground, polished with progressively finer suspensions of alumina, ultrasonically washed and then dried at 120° C for >12 h before being coated with carbon.
Table 3-1. Starting materials.

Material 1 represents the $Mg_2SiO_4-MgSiO_3-H_2O$ system. Material 2, 3 and 4 represent the $Mg_2SiO_4-MgSiO_3-KCl$ - H_2O

systems with the Cl/(Cl+H2O) molar ratio of 0.2, 0.4 and 0.6, respectively.

Figure 3-1. Thermogravimetric analysis of starting material of $Mg_2SiO_4-MgSiO_3-H_2O$ system.

The total weight loss (Delta Y) of 18.58 wt% is close to the calculated water content of 18.31 wt% for the Material 1 in Table 3-1.

 Examination and analysis of the run products were carried out with the JEOL 8900R electron microprobe at the University of Alberta. The textural relationships between coexisting phases were examined using backscattered electron (BSE) imaging at least twice by repolishing the mounts. To examine the compositional changes at the solidus, the Ca contents of forsterite and enstatite were analyzed using 20 kV accelerating voltage, and the signal was detected by wavelength dispersive spectrometers with the PETH crystal. Because the Ca contents of forsterite and enstatite were much lower than that of diopside standard, the sample current for the diopside standard was 15 nA, and that for forsterite and enstatite samples was 150 nA. Counting time was 120 s on peaks and 60 s on background at each side. Si and Mg were also analyzed for the ZAF correction. In analyzing Ca, the detection limit and the standard deviation reported by microprobe were 5 ppm and ~10%, respectively. Potts (1986) pointed out that the reported detection limit (2 $\sigma_{\text{background}}$) is an over-optimistic estimate of the lower limit of detection and the limit of determination for quantitative measurement is 6 $\sigma_{\text{background}}$. Therefore, the limit of determination (6 $\sigma_{\text{background}}$) used in this thesis was calculated from the reported counts and counting time using the formula of Scott and Love (1983). The calculated limit of determination (6 $\sigma_{\text{background}}$) in analyzing Ca was 15 ppm. The EPMA analysis of run products is listed in the Appendix. **Results**

 Experimental conditions and results are summarized in Table 3-2. Because the fluids and melts are unquenchable, the texture of quenched phases cannot reveal the relationships, such as immiscibility, between the water/brine and

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silicate melts under experimental conditions. "Vapor" and "Liquid" are used to describe subsolidus fluids and suprasolidus melts, respectively. The solidus is determined by examining the amount of quenched phases and the change of Ca content in the primary phases. Because of the thermal gradient in the capsule, subsolidus vapor and suprasolidus liquid can appear in one capsule. According to the study of Walter et al., 1995, the thermal gradient for the high-T stepped graphite furnace is $+25^{\circ}$ C mm⁻¹ away from the furnace midline. Based on this thermal gradient, the temperature at the center of the capsule (*T'*) was corrected from the run temperature which was measured by a thermocouple at the top, and the temperature range (R) in the capsule was calculated from the inner height of the capsule.

 Textures of the run products are shown in Figure 3-2. For all systems, phases interpreted to be primary phases are equant to sub-equant and typically have large grain size, whereas quenched phases are subhedral to euhedral and typically display elongate prismatic habit. The primary phases in the $Mg_2SiO_4-MgSiO_3-H_2O$ system were typically smaller than those in $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems, and the quenched phases in the $Mg_2SiO_4-MgSiO_3-H_2O$ system are generally larger than those in $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems. In the $Mg_2SiO_4-MgSiO_3-H_2O$ system, primary forsterite and enstatite coexist in all runs; the quenched phases have compositions similar to enstatite and forsterite, and their amount increases abruptly at the run temperature of 1250° C. In Mg_2SiO_4 - $MgSiO_3$ -KCl-H₂O systems with $Cl/(Cl+H₂O)$ ratio of 0.2, 0.4 and 0.6, the primary phases changes

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from coexisting forsterite and enstatite at lower temperatures to only fosterite at higher temperatures; the quenched phases contain Si, Mg, K and Cl, and the amount of quenched phases increases abruptly at the run temperatures of 1450° C, 1600 °C and 1650°C, respectively. Quenched liquid (qL) and quenched liquid (qL) are very similar in texture, but they can be differentiated from the amount of quenched phases (Figure 3-2). The quenched phases in small amounts are determined as qV and those in large amounts are determined as qL. The quenched phases in moderate amounts are difficult to distinguish as either quenched vapor or quenched liquid, so they are noted as quenched vapor and liquid (qV/qL) . The coexistence of both vapor and liquid in one capsule is explained to be due to the existence of thermal gradient in the capsule.

	molar		$T({}^{\circ}\mathbb{C})$ Duration (h)	Results		T correction $({\cal C})$		Ca in Ol (ppm)				Ca in Opx (ppm)
Run #	$Cl/(Cl+H2O)$				T'	\boldsymbol{R}	N	Av	SD	N	Av	SD
3722	$\mathbf{0}$	1100	12	$En+Fo+V$	1080	14	27	30	11	26	191	11
3710	$\boldsymbol{0}$	1200	8	$En+Fo+V$	1178	12	20	29	7	15	220	29
3711	$\mathbf{0}$	1250	12	$En+Fo+V/L$	1229	12	10	49	8	τ	191	11
3709	θ	1300	8	$En+Fo+L$	1285	11	16	29	7	14	128	6
3755	$\boldsymbol{0}$	1350	12	$En+Fo+L$	1324	16	τ	26	8	10	143	19
3765	$\mathbf{0}$	1400	12	$En+Fo+L$	1379	9	15	74	43	18	160	26
3762	$\boldsymbol{0}$	1450	12	$En+Fo+L$	1428	11	12	71	37	19	256	97
3771	$\mathbf{0}$	1450	12	$En+Fo+L$	1425	11	48	26	6			
3770	$\mathbf{0}$	1500	12	$En+Fo+L$	1478	13	14	31	5	37	193	140
3715	0.2	1300	12	$En+Fo+V$	1277	18	11	28	6	16	234	9
3753	0.2	1300	12	$En+Fo+V$	1276	11	19	30	9	9	223	16
3721	0.2	1400	12	$En+Fo+V/L$	1377	18	48	26	6	33	195	11
3750	0.2	1450	12	$Fo+L$	1428	12	19	47	12			
3727	0.2	1500	12	$Fo+L$	1480	14	56	20	6			
3737	0.2	1600	12	$Fo+L$	1580	10	11	25	$\overline{4}$			
3761	0.2	1650	$\boldsymbol{2}$	L	1629	10						
3748	0.4	1400	12	$En+Fo+V$	1376	14	11	31	6	14	266	27
3728	0.4	1500	12	$En+Fo+V$	1476	17	28	37	$\overline{4}$	11	219	$\overline{7}$
3759	0.4	1550	12	$En+Fo+V/L$	1529	11	19	58	18	14	217	18
3744	0.4	1600	12	$Fo+L$	1584	8	26	31	11			
3763	0.4	1650	$\overline{2}$	$Fo+L$	1627	15	14	83	16			
3747	0.4	1700	$\sqrt{2}$	L	1676	13						
3754	0.6	1500	12	$En+Fo+V$	1475	12	6	30	5	9	261	20
3739	0.6	1600	10	$En+Fo+V/L$	1581	10	17	40	$\overline{7}$	9	250	60
3772	0.6	1650	$\boldsymbol{2}$	$Fo+L$	1624	12	57	26	5			
3740	0.6	1700	$\boldsymbol{2}$	$Fo+L$	1682	10	15	43	6			
3758	0.6	1700	\overline{c}	$Fo+L$	1677	11	16	40	$\overline{7}$			

Table 3-2. Experimental conditions and results.

Abbreviations: *T* temperature, *N* number of analysis, *R* temperature range in capsule, *Av* average, *SD* standard deviation, *En*

enstatite, *Fo* forsterite, *V* vapor, *L* liquid.

T correction is done by $T^* = T - \frac{1}{2}gh$ and $R = \frac{1}{2}gl$, where *g* is the thermal gradient in graphite furnace, *h* is the outer height

of capsule, and *l* is the inner height of capsule.

Figure 3-2. Backscattered electron images of run products.

A-D Run products of Mg₂SiO₄-MgSiO₃-H₂O system, primary phases are forsterite and enstatite. E-F Run products of the Mg2SiO4-MgSiO3-KCl-H2O system with Cl/(Cl+H2O) ratio of 0.2, subsolidus primary phases are forsterite and enstatite, suprasolidus primary phases are forsterite, and the enstatite/forsterite modal ratio decreases as the temperature increases. Abbreviations: *Pt*, platinum capsule, *Fo*, forsterite, *En*, enstatite, *qV*, quenched vapor, *qL*, quenched liquid. Black scale bars at left bottom represent 400 μm.

 For all systems, primary forsterite has Ca content of 20-83 ppm, and primary enstatite has Ca content of 128-226 ppm. The calcium in these experiments was probably derived from the reagent-grade $Mg(OH)$ ₂ starting material. In the $Mg_2SiO_4-MgSiO_3-H_2O$ system, forsterite has an obvious jump in Ca content around the temperature of 1229° C, and enstatite has a big drop in Ca content at the same temperature (Figure 3-3). In $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems with $Cl/(Cl+H₂O)$ ratio of 0.2, 0.4 and 0.6, forsterite has jumps in Ca content at temperatures of 1428° C, 1529° C and 1581° C, respectively (Figure 3-4).

 Abrupt increases in the amount of quenched phases and abrupt changes in Ca content of primary phases are interpreted to indicate the solidus, because transition from vapor to liquid will cause abrupt changes in the solubility of silicate in fluid and partitioning of trace elements between solid and vapor is different from that between solid and liquid. In the experiments on melting of peridotite- $CO₂$ system by Dasgupta and Hirschman (2006), the sodium content of the clinopyroxene dropped abruptly at the solidus, which suggests that the drop in content of minor element in pyroxene can indicate the position of solidus. In the $Mg_2SiO_4-MgSiO_3-H_2O$ system (Figure 3-3), the drop of Ca content in enstatite indicates the temperature of the solidus, and the jump of Ca content in olivine also happened at the same temperature. That forsterite and enstatite have different behaviors in changing Ca content at the temperature of solidus may be due to their different crystal structures, and both the drop of Ca content in enstatite and the jump of Ca content in olivine can be used in determine the solidus. Both the textural relationships and the Ca peaks give the same result for the

 $Mg_2SiO_4-MgSiO_3-H_2O$ system and the $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems with $Cl/(Cl+H₂O)$ molar ratio of 0.2 and 0.4. Solidus of the $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ system with $Cl/(Cl+H_2O)$ molar ratio of 0.6 cannot be determined from textural relationships because the quenched material collapsed when large amount of water-soluble material was removed, and it is only determined by the Ca peak of forsterite.

The temperature of the solidus changing with $Cl/(Cl+H₂O)$ molar ratio is shown in Figure 3-5. Above the solidus, both forsterite and enstatite coexist with melt in the $Mg_2SiO_4-MgSiO_3-H_2O$ system, which is consistent with a eutectic melting relationship of forsterite and enstatite at 5 GPa. In contrast, only forsterite coexists with melt in $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems, which may reveal the incongruent melting of enstatite.

Figure 3-3. Ca contents of forsterite (filled circle) and enstatite (open circle) in the Mg₂SiO₄-MgSiO₃-H₂O system as a function of temperature.

Error bars show temperature uncertainties in horizontal and 2 standard deviation of Ca content in vertical. The vertical line shows the inferred position of solidus. The big error bars for the Ca contents of forsterite and enstatite from high temperature experiments are because of the hardness in distinguishing primary phases from quenched phases.

Figure 3-4. Ca contents of forsterite in the Mg₂SiO₄-MgSiO₃-H₂O system and Mg₂SiO₄-MgSiO₃-KCl-H₂O systems. Error bars show 2 standard deviation of Ca content. Vertical lines show positions of solidi.

Figure 3-5. Phase relations of the Mg₂SiO₄-MgSiO₃-H₂O system and Mg₂SiO₄-MgSiO₃-KCl-H₂O systems at 5 GPa. The curve shows the relation between solidi and Cl concentrations.

Discussion

Chloride can significantly reduce H_2O activity in aqueous solutions, which was evidenced by measuring H_2O activity in NaCl, KCl and NaCl-KCl solutions by the brucite-periclase equilibrium (Aranovich and Newton, 1996; Shmulovich and Graham, 1996; Aranovich and Newton, 1997). The experiments by Aranovich and Newton (1997) revealed that the H_2O activity is nearly coincident with the square of its mole fraction in KCl solution at the pressure range from 4 to 15 kbar. Melting experiments of albite in NaCl solution by Shmulovich and Graham (1996) showed that the temperature of the vapor-saturated solidus of albite in a solution with NaCl mole fraction of 0.2 is \sim 100 °C higher than that in pure water at 9 kbar. Experiments on $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems at 5 GPa in this study (Figure 3-5) show that temperatures of solidi of the systems with the $Cl/(Cl+H₂O)$ molar ratio of 0.2, 0.4 and 0.6 are, respectively, \sim 200 °C, \sim 300 °C and \sim 350 °C higher than that with pure water, which indicates that chloride can also significantly reduce H_2O activity in aqueous solution at pressure relevant to depth of ~160km in the Earth's mantle. Therefore, chlorine in the SCLM, evidenced by fluid inclusions in fibrous diamonds, can inhibit melting of the mantle by reducing the H_2O activity in fluids, and the KCl-bearing fluids can be a robust agent of mantle metasomatism.

 The absence of primary enstatite under suprasolidus conditions in $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems may be due to the incongruent melting of enstatite. The incongruent melting of enstatite, discovered by Bowen and Andersen (1914) at 1 atm, has a significant bearing on the generation of

silica-saturated magmas from silica-undersaturated mantle rocks by partial melting or from silicate-undersaturated magmas by fractional crystallization (Kushiro et al., 1968), and thus potentially plays an important role in the Mg/Si differentiation of the planet. The incongruent melting of enstatite disappears at pressures higher than ~0.5 GPa under anhydrous conditions (Boyd et al., 1964) and at some pressure between 3 and 5.5 GPa under hydrous conditions (Kushiro et al., 1968; Inoue, 1994). The eutectic melting inferred in this study in the $Mg_2SiO_4-MgSiO_3-H_2O$ system at 5 GPa reveals that the incongruent melting of enstatite disappears at pressures less than 5 GPa. If the absence of primary enstatite under suprasolidus conditions in $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems is due to the incongruent melting of enstatite, it will mean that the chlorine-rich brine can make the incongruent melting of enstatite happen at the pressure of 5 GPa or more.

Conclusion

 KCl significantly elevates the solidus temperature of the $Mg_2SiO_4-MgSiO_3-H_2O$ system at 5 GPa by reducing the activity of H_2O in the fluid. This indicates that chlorine can prevent melting in the SCLM and the KCl-bearing fluids can be a robust agent of mantle metasomatism. In $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems, the absence of primary enstatite under suprasolidus conditions is probably due to the incongruent melting of enstatite, which needs to be defined by further experiments on the melting of the $MgSiO₃$ -KCl-H₂O system.

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Chapter 4. General Discussion and Conclusions

 The presence of chlorine in the subcratonic lithospheric mantle (SCLM) has been evaluated by compiling the compositional data of fluid inclusions in fibrous diamonds. It mainly associates with potassium, dissolving in water and forming a KCl-bearing brine with the $Cl/(Cl+H₂O)$ molar ratio of 0.05-0.68 mol%. To examine the effect of such a KCl-bearing brine on the melting behavior of the Earth's mantle, we conducted experiments in the $Mg_2SiO_4-MgSiO_3-H_2O$ and $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems at 5 GPa and 1100-1700 °C. In the $Mg_2SiO_4-MgSiO_3-H_2O$ system, the temperature of the fluid-saturated solidus is \sim 1230 °C, and both forsterite and enstatite coexist with the liquid under suprasolidus conditions. In the $Mg_2SiO_4-MgSiO_3-KCl-H_2O$ systems with molar $Cl/(Cl+H₂O)$ ratios of 0.2, 0.4 and 0.6, the temperatures of the fluid-saturated solidus are ~1430 °C, ~1530 °C and ~1580 °C, respectively, and only forsterite coexists with liquid under suprasolidus conditions. The increase in the temperature of the solidus demonstrates the significant effect of KCl on elevating the solidus of the $Mg_2SiO_4-MgSiO_3-H_2O$ system by reducing the activity of H_2O in the fluid. The change in the melting residues indicates that the incongruent melting of enstatite (enstatite $=$ forsterite $+$ silica-rich melt) could happen at pressures over 5 GPa in KCl-bearing systems, which needs to be verified by experiments on the $MgSiO_3$ -KCl-H₂O system in future work.

If KCl is present in the Earth's mantle, it will elevate the melting temperature of the H₂O-bearing mantle. In subduction zones, brine inclusions, with \sim 50 wt% NaCl and KCl, have been found in omphacite in eclogite (Scambelluri and

Philippot, 2001), which indicates the existence of chloride-rich brines in subducting slabs. Release of these brines, from subducting slabs to mantle wedges, will inhibit melting of the mantle wedges. In cratonic areas, fluid inclusions, with ~47 wt% KCl and NaCl, have been found in fibrous diamonds (Klein-BenDavid *et al.*, 2007), which indicates the existence of chloride-rich fluids in the diamond stability field of the cratonic mantle. These fluids will inhibit melting at the H2O-saturated solidus in the mantle, and the KCl-bearing brine can be a robust agent for mantle metasomatism at temperatures greater than that of the H2O-saturated solidus. Accordingly, the brine-bearing fibrous diamonds are inferred to form from fluid rather than melt in the SCLM.

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Run #	Analysis#	Phase	$MgO(wt\%)$	SiO ₂ (wt%)	$CaO(wt\%)$	Total (wt%)
3709	$LC3-1$	Fo	56.027	40.022	0.0038	96.053
3709	$LC3-2$	\rm{Fo}	54.814	41.515	0.0033	96.332
3709	$LC3-3$	En	39.339	59.713	0.0190	99.071
3709	$LC3-4$	En	38.564	59.424	0.0164	98.005
3709	$LC3-5$	En	37.989	58.777	0.0179	96.784
3709	$LC3-6$	En	39.330	57.759	0.0180	97.107
3709	$LC3-7$	En	38.469	57.237	0.0175	95.724
3709	$LC3-8$	En	38.005	58.020	0.0165	96.042
3709	$LC3-9$	Fo	52.589	39.617	0.0026	92.209
3709	$LC3-10$	Fo	49.574	39.690	0.0032	89.267
3709	$LC3-11$	Fo	49.974	41.070	0.0030	91.047
3709	$LC3-12$	En	37.197	58.304	0.0188	95.520
3709	$LC3-13$	En	37.139	59.185	0.0183	96.343
3709	$LC3-14$	En	39.216	60.001	0.0163	99.234
3709	$LC3-15$	En	39.937	61.031	0.0168	100.985
3709	$LC3-16$	En	39.969	59.925	0.0162	99.911
3709	$LC3-17$	En	40.183	60.432	0.0185	100.634
3709	$LC3-18$	En	40.173	60.448	0.0179	100.639
3709	LC3-19	En	39.443	59.216	0.0171	98.676
3709	$LC3-20$	F _o	55.249	42.112	0.0031	97.364
3709	$LC3-21$	Fo	47.822	37.529	0.0031	85.354
3709	$LC3-22$	Fo	54.906	43.307	0.0042	98.217
3709	$LC3-23$	Fo	54.451	41.216	0.0052	95.672
3709	$LC3-24$	Fo	53.831	42.644	0.0039	96.479
3709	$LC3-25$	Fo	53.932	41.960	0.0043	95.896
3709	$LC3-26$	Fo	52.279	40.467	0.0050	92.751
3709	$LC3-27$	Fo	54.593	41.903	0.0053	96.501
3709	$LC3-28$	\rm{Fo}	52.719	43.015	0.0059	95.740
3709	LC3-29	Fo	54.627	41.846	0.0047	96.478
3709	$LC3-30$	Fo	53.980	41.531	0.0050	95.516
3709	LC3-31	$\bf q$	39.091	57.950	0.0431	97.085
3709	LC3-32	$\bf q$	40.121	60.723	0.0453	100.890
3709	LC3-33	$\bf q$	39.519	58.801	0.0439	98.365
3709	LC3-34	$\mathbf q$	39.512	58.800	0.0493	98.362
3710	LC4-1	Fo	53.724	40.576	0.0027	94.303
3710	$LC4-2$	Fo	50.015	40.339	0.0045	90.359
3710	$LC4-3$	F _O	53.463	41.314	0.0060	94.783
3710	$LC4-4$	En	38.120	60.024	0.0272	98.172
3710	$LC4-5$	F _o	50.316	42.232	0.0048	92.553
3710	$LC4-6$	Fo	54.015	42.658	0.0031	96.676
3710	$LC4-7$	En	36.849	60.911	0.0263	97.787
3710	$LC4-8$	En	36.969	60.723	0.0278	97.721
3710	$LC4-9$	\rm{Fo}	53.967	43.200	0.0040	97.171
3710	$LC4-10$	\rm{Fo}	51.588	43.219	0.0041	94.811

Appendix. EPMA analysis of run products

Abbreviations: *En* enstatite in primary phase, *Fo* forsterite in primary phase, *q* quenched phases. Note: CaO (wt%) is calculated from counts reported by microprobe.