

## Interaction of Diopside and Jadeite with Potassium Chloride at 5 GPa

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Presented by Academician A.A. Marakushev July 7, 2006

Received July 12, 2006

DOI: 10.1134/S1028334X07050297

The alkali-enriched chloride inclusions found in diamonds [1–3] and olivines [4] from kimberlites provided new insight into the role of chloride components in the evolution of some mineral assemblages of the upper mantle. In some microinclusions from diamonds, chloride liquid often coexists with minerals of peridotite and eclogite assemblages. Products of reaction between them are observed in several cases [1–3]. According to the mineralogical thermobarometric data, these reactions proceeded at a pressure of ~5 GPa [1]. The deep-seated eclogite xenoliths also bear indications of the influence of fluids enriched in alkalis and chlorine. The alkali-rich glasses associated with djerdferite, sodalite, phlogopite, and sanidine are an example [5–7]. According to [5, 7], these processes could foster the crystallization of “metasomatic coated diamonds” [5, 7] suggesting a pressure of approximately 4.5–5.0 GPa. The participation of chloride liquids in metasomatic processes in the upper mantle is a highly attractive hypothesis, because these liquids are immiscible with silicate melts at a high pressure but can be a source of alkalis for these melts [8] and a medium for diamond growth [9, 10].

These data stimulate us to detailed experimental study of reactions between mantle minerals and chlorides under conditions of the upper mantle. Pyroxenes of the Di–Jd<sup>1</sup> series are the most interesting minerals in this respect, because they are the major components of omphacite, one of the main concentrators of alkalis in

the upper mantle. This communication presents the results of experimental study of the interaction of KCl with diopside, jadeite, and pyroxene Di<sub>65</sub>Jd<sub>35</sub>. Potassium chloride has been chosen, because this compound is the main supplier of chlorine to mantle liquids [1–3]. The runs were carried out at 5 GPa (average pressure determined with mineralogical barometry for the aforementioned mineral assemblages).

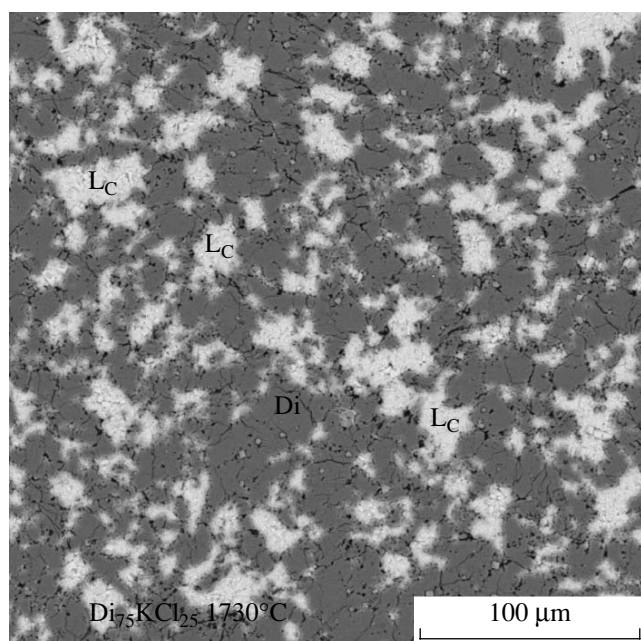
Glass (CaMgSi<sub>2</sub>O<sub>6</sub>), gel or glass (NaAlSi<sub>2</sub>O<sub>6</sub>), and crystalline KCl were used as starting materials. The experiments were performed on an anvil-with-hole apparatus with a toroidal-type cell made of lithographic limestone [11]. The starting mixtures were placed into Pt or Pt<sub>60</sub>Rh<sub>40</sub> capsules. The pressure in runs calibrated by standard phase transitions in Bi was set with an accuracy of ±0.2 GPa [11]. The temperature was controlled with an accuracy of ±20°C by the calibration curve (temperature versus current power) plotted with a Pt<sub>70</sub>Rh<sub>30</sub>/Pt<sub>94</sub>Rh<sub>6</sub> thermocouple. After the runs, the samples were studied with a CamScan MV2300 (VEGA TS 5130MM) electron microscope and the phase compositions were analyzed with a Link INCA EDS at the Laboratory of Electron Microscopy and Microprobe of the Institute of Experimental Mineralogy, Russian Academy of Sciences. SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, wollastonite, microcline, albite, and NaCl were used as standards for determination of Si, Mg, Al, Ca, K, Na, and Cl, respectively.

*The CaMgSi<sub>2</sub>O<sub>6</sub>–KCl join.* Despite the melting of chloride above 1500°C [13], readily identified on the basis of quenched aggregates of elongated KCl crystallites, run products containing as much as 50 wt % KCl lack any signs of interaction between the chloride melt and diopside up to 1730°C (Fig. 1). The composition of diopside did not change, but quenching products of the chloride melt contain as much as 0.15 wt % Si and 0.1–0.4 wt % Ca. In the absence of Mg, this implies insignificant incongruent dissolution of diopside in the KCl melt. We failed to constrain phase relations in the high-temperature region of this join. However, the phase relations between melting points of diopside (~1850°C [12])

<sup>1</sup> Mineral and phase abbreviations: (Cpx) clinopyroxene, (Ca-Ts) Tschermak Ca-molecule, (CEn) clinoenstatite, (Di) diopside, (Jd) jadeite, (KCl) potassium chloride, (K,Na)Cl solid solution, (Ks) kalsilite, (L<sub>C</sub>) chloride melt, (L<sub>S</sub>) silicate melt, and (San) sanidine.

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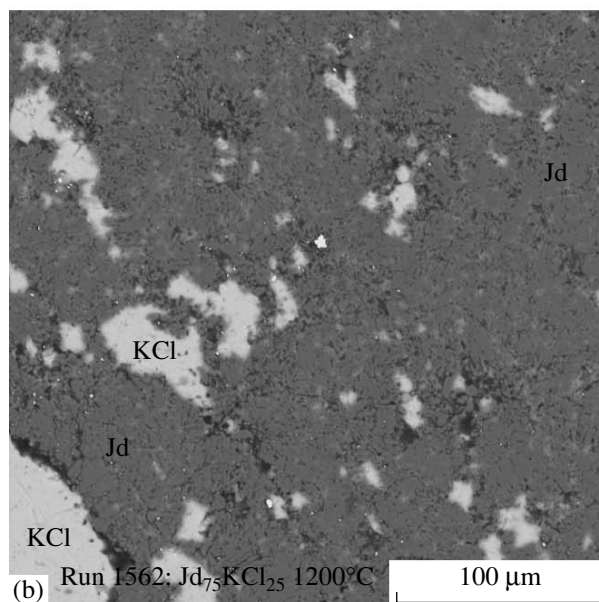
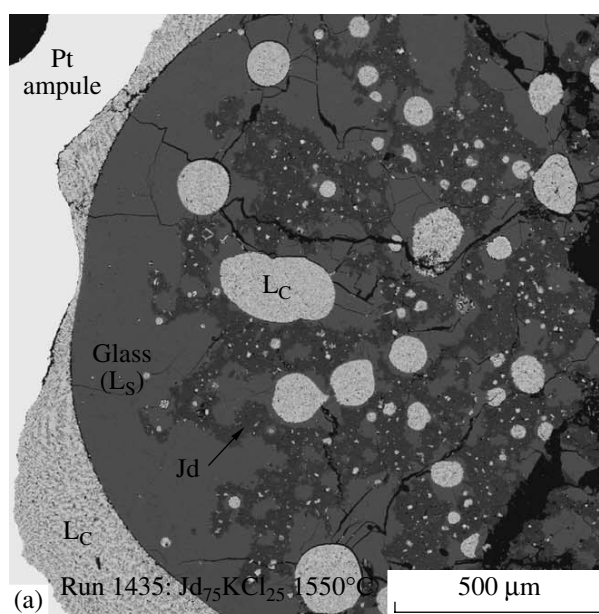
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**Fig. 1.** Diopside (Di) and KCl melt at 5 GPa. CamScan MV2300 BSE image.

and KCl (~1500°C [13]) show that the join is close in topology to a system with two immiscible liquids, where the liquidus temperature in the region of immiscibility is close to the melting temperature of the most refractory component (diopside). Below this temperature, diopside coexists with the chloride melt with a small amount of silicate constituent. This may imply that diopside and KCl melts are immiscible at a temperature above 1800°C.

*The NaAlSi<sub>2</sub>O<sub>6</sub>-KCl join.* The aluminosilicate glass was detected in this join in products of all runs except 1562 (Fig. 2a; table). The amount of glass decreases with a decrease in temperature and an increase in the Jd/KCl ratio. Chloride globules and jadeite crystals occur in the glass (Fig. 2a). The spherical or ellipsoidal globules vary in size from *n* to 250 μm even in the same sample. In some cases, the chloride material occurs as layers in the peripheral upper portions of capsules, indicating buoyancy of this material in the aluminosilicate melt during the runs. In the samples with abundant jadeite crystals, the globules acquire an irregular shape that mimics outlines of crystalline aggregates. However, they always include spherical menisci at the contact with glass. The globules consist of a fine-grained aggregate of KCl crystals. The presence of large (up to 20–30 μm) cubic crystals of Na–K chloride in globules against the background of the fine-grained mass of pure KCl suggests the separation of chlorides of K and K–Na during the chloride melt quenching. The large globules contain separate spherules of aluminosilicate glass up to 20 μm in diameter (“globule-in-globule” texture). The spherical shape of chloride globules and the globule-in-globule structure are character-



**Fig. 2.** Structural features of run products in the Jd–KCl join at 5 GPa. (a) Complete immiscibility of silicate and chloride melts: chloride globules in glass and layers of chloride melts on ampoule walls; (b) association of jadeite and KCl under subsolidus conditions. CamScan MV2300 BSE image.

istic indications of immiscibility of aluminosilicate and chloride melts under the run conditions. No other phases except jadeite and KCl have been found in the subsolidus region of this join at 1200°C (run 1562) (Fig. 2b). The status of chloride material in the products of this run remained ambiguous because of the absence of spherical chloride aggregates. Small crystals mainly composed of sodium chloride were occasionally detected at the contacts of KCl aggregates with the jadeite matrix.

Experimental conditions and average compositions of coexisting phases in products of runs at 5 GPa (Di–Jd–KCl system)

Component	1455 <sup>a</sup>			1456			1454			1433			
	Jd <sub>50</sub> KCl <sub>50</sub> , 1360°C, 60 min <sup>b</sup>			Jd <sub>75</sub> KCl <sub>25</sub> , 1360°C, 60 min			Jd <sub>75</sub> KCl <sub>25</sub> , 1400°C, 60 min			Jd <sub>50</sub> KCl <sub>50</sub> , 1500°C, 60 min			
	L <sub>C</sub> <sup>c</sup>	L <sub>S</sub>	Jd	L <sub>C</sub>	L <sub>S</sub>	Jd	L <sub>C</sub>	L <sub>S</sub>	Jd	L <sub>C</sub>	L <sub>S</sub>	Jd	KNC <sup>**</sup>
	7 <sup>d</sup>	7	1	2	6	3	5	6	6	4	8	9	1
SiO <sub>2</sub> (Si) <sup>e</sup>	0.10	53.38	59.38	0.13	53.80	59.40	0.08	54.47	59.79	0.13	52.13	59.38	0.00
Al <sub>2</sub> O <sub>3</sub> (Al)	0.08	21.08	25.84	0.00	20.97	25.51	0.09	21.69	25.22	0.03	20.95	25.04	0.00
Na <sub>2</sub> O (Na)	3.87	3.36	14.36	12.24	4.50	14.88	16.04	5.62	14.74	3.84	3.09	14.50	21.55
K <sub>2</sub> O (K)	46.46	17.66	0.05	34.67	16.01	0.07	32.24	14.90	0.19	46.46	17.71	0.05	31.53
Cl	49.78	1.71	0.00	51.49	1.66	0.02	54.03	1.80	0.06	49.56	1.60	0.02	54.37
Total	100.29	97.19	100.63	98.53	96.94	99.88	102.48	98.48	100.00	100.02	95.48	98.99	107.45

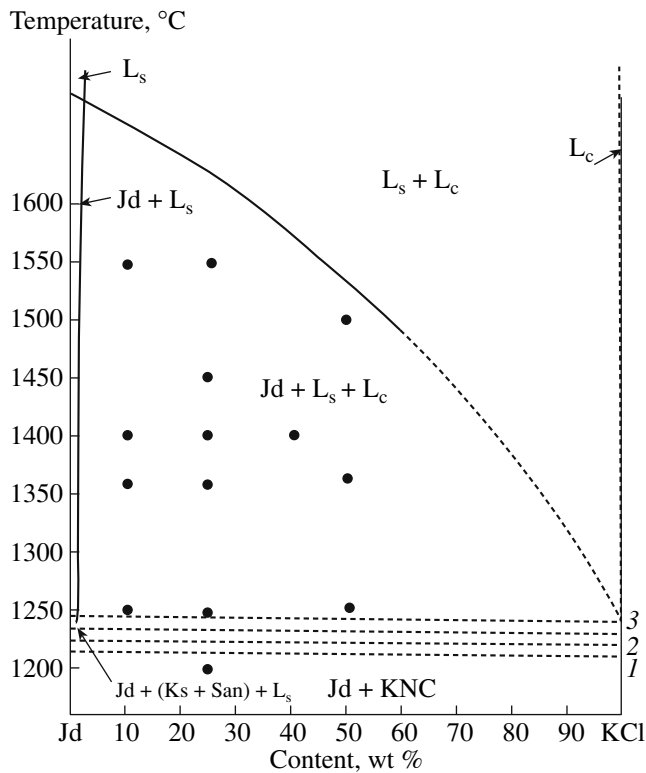
Component	1435			1436			1562		1541	
	Jd <sub>75</sub> KCl <sub>25</sub> , 1550°C, 45 min			Jd <sub>90</sub> KCl <sub>10</sub> , 1550°C, 45 min			Jd <sub>75</sub> KCl <sub>25</sub> , 1200°C, 120 min		Cpx <sub>80</sub> KCl <sub>20</sub> <sup>*</sup> , 1400°C, 60 min	
	L <sub>C</sub>	L <sub>S</sub>	Jd	L <sub>C</sub>	L <sub>S</sub>	Jd	Jd <sup>***</sup>	chloride <sup>****</sup>	L <sub>S</sub>	Cpx
	5	5	8	3	5	4	8	1	6	13
SiO <sub>2</sub> (Si)	0.11	54.00	59.49	0.11	52.89	59.79	60.92	0.05	53.37	55.05
Al <sub>2</sub> O <sub>3</sub> (Al)	0.05	21.16	25.19	0.07	22.45	24.98	26.09	0.06	13.93	4.87
MgO (Mg)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.30	16.36
CaO (Ca)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.43	21.38
Na <sub>2</sub> O (Na)	13.54	4.72	14.89	24.65	11.16	15.17	14.81	0.87	3.86	2.07
K <sub>2</sub> O (K)	34.89	15.62	0.04	17.66	6.53	0.04	0.64	50.17	12.74	0.15
Cl	53.01	1.82	0.05	55.15	2.29	0.01	0.24	47.61	2.72	0.01
Total	101.6	97.32	99.66	97.64	95.32	99.99	102.7	98.76	95.35	99.89

Note: (a) Hereinafter, run number; (b) run condition (proportion of components in the starting mixtures are given in wt %); (c) phase, (d) number of individual analyses; (e) analyses of silicate phases (glass and jadeite) are given in wt % of oxides (except Cl); analyses of chloride phases (in parentheses), in wt % of elements; (\*) Cpx–Di<sub>65</sub>Jd<sub>35</sub>; (\*\*) cubic crystal of K–Na chloride in a chloride globule, (\*\*\*) contaminated with potassium chloride, (\*\*\*\*) probably crystalline.

The concentrations of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in aluminosilicate melts (54–56 and 21–23 wt %, respectively) change slightly with variation of the Jd/KCl ratio in the starting mixtures. The stoichiometric composition of the melt is close to KAlSi<sub>2</sub>O<sub>6</sub> (table). The Na<sub>2</sub>O content increases with the Jd/KCl ratio in the starting mixtures. Depending on the composition of the starting material, the K<sub>2</sub>O content in the melt ranges from 14 to 20 wt %. The Na<sub>2</sub>O/K<sub>2</sub>O ratio is the main parameter that controls the Cl concentration in the melt. The melts obtained from the Jd<sub>90</sub>KCl<sub>10</sub> mixture are appreciably enriched in Cl (>2 wt %) at any temperature. This relationship is consistent with the data on Cl solubility in silicic melts at a moderate pressure [14]. The slight growth of Cl in the melt with an increase in temperature may also be related to the increase in Na<sub>2</sub>O concentration at a higher temperature as a result of more intense melting of jadeite. In general, the Cl concentration in melts of the Jd–KCl join at 5 GPa (1.5–2.3 wt %) is appreciably higher

than the Cl concentration in compositionally similar melts at a moderate pressure (see, for example, [14]). The Si content in chloride globules is not higher than 0.2 wt %, on average. The main variations in the composition of globules (chloride melt) are expressed in the distinct positive correlation between the Na/K ratio in globules and the Jd/KCl ratio in the starting mixture. No correlation between the Na/K ratio in the chloride melt and the temperature has been established.

The K<sub>2</sub>O content in jadeite crystals from run products above solidus does not exceed 0.1 wt % (table). In jadeite from run 1562 under subsolidus conditions, the average K<sub>2</sub>O content is 0.64 wt % (table). However, the presence of Cl indicates contamination of jadeite with KCl. Indeed, the recalculation of analyses of such jadeites shows that potassium is almost completely compensated by chlorine. Thus, the K<sub>2</sub>O concentration in these pyroxenes may be very low. However, the presence of even very small amounts of potassium in jadeite



**Fig. 3.** Tentative phase diagram for the Jd–KCl join at 5 GPa. The inferred phase boundaries are shown by dashed lines; boundaries based on experimental data (dots) are shown by solid lines. Inferred phase fields: (1) Jd + (Ks + San) + KNC; (2) Jd + (Ks + San) +  $L_c$ ; (3) Jd + (Ks + San) +  $L_s$  +  $L_c$ .

testifies to the formation of a limited  $KAlSi_2O_6$  solid solution as a result of K–Na exchange between aluminosilicate and chloride melts. As is evidenced from low Na contents in chloride (table), such an exchange occurs even under subsolidus conditions.

The composition of solid phases in the  $NaAlSi_2O_6$ –KCl join at 5 GPa shows that this join is a proxy of the multicomponent  $KAlSiO_4$ – $NaAlSiO_4$ – $SiO_2$ –KCl–NaCl system. However, no other phases except Jd and KCl have been detected under solidus conditions (Fig. 2b). The appearance of K–Na chloride under these conditions is a result of cation exchange between chloride and jadeite. This exchange becomes more intense with increasing temperature. However,  $KAlSi_2O_6$  is released as a high-K phase because of its strongly restricted solubility in jadeite. In the run products, this phase occurs above  $\sim 1250^\circ\text{C}$  as a potassium aluminosilicate melt. Nevertheless, the four-phase Jd + Ks + San + (K,Na)Cl assemblage may be expected in a temperature range of  $1200$ – $1250^\circ\text{C}$ . We failed to detect traces of this assemblage at 5 GPa, but this assemblage has been synthesized in preliminary runs at 4 GPa. Thus, the four-phase Jd + Ks + San + (K,Na)Cl assemblage is formed according to the reaction  $2Jd + 2KCl = Ks + San + 2NaCl$ . The exchange reactions, formation of four-phase assemblage, and appreciable solubility of chlorine in melts

explain the low temperature of the suggested solidus of the  $NaAlSi_2O_6$ –KCl join at 5 GPa (Fig. 3).

The possible occurrence of an aluminosilicate melt in the ternary  $CaMgSi_2O_6$ – $NaAlSi_2O_6$ –KCl system was confirmed by run 1541 (table). The euhedral Cpx crystals plunged into the glass ( $\sim 20$  vol. %) have been found in its products. The glass contains chloride globules pressed between Cpx crystals. The average jadeite content in Cpx is 14 mol %, which is approximately two times lower than the jadeite content in the starting mixture ( $Di_{65}Jd_{35}$ ). Clinopyroxene includes  $\sim 3$  mol % Ca–Ts and  $\sim 4$  mol % CEn. The average  $K_2O$  content in clinopyroxene is 0.15 wt %. Judging from the positive correlation of this component with aluminum,  $K_2O$  enters into Cpx as the  $KAlSi_2O_6$  end member. In the glasses from run 1541 with similar silica content, the contents of  $Al_2O_3$  and  $K_2O$  are lower relative to the melts from runs in the Jd–KCl join (table). The lower  $Al_2O_3$  and  $K_2O$  contents in the melt in run 1541 are compensated by the presence of CaO and MgO (table). The occurrence of these components provides a higher Cl concentration (up to 3 wt %) in this melt [14].

Thus, the performed experiments have demonstrated sharply distinct interactions of end members of the Di–Jd series with the KCl melt at 5 GPa. The introduction of KCl into the system virtually does not affect the temperature of diopside melting. It may be expected that similar relationships characterize systems with orthopyroxene and olivine. However, the results of our experiments do not allow prediction of interactions of chloride liquid with other Al-bearing minerals, e.g., with garnet. The interaction of a KCl melt with omphacite gives leads to the abrupt fall of its melting temperature as a result of intense K–Na exchange between chloride and silicate and to the formation of a melt enriched in K, Si, Al, and Cl. The composition of this melt is controlled by the Jd/Di ratio in the initial Cpx. These data show that eclogites are subjected to the influence of the KCl melt to a higher extent than peridotites and pyroxenites. Such an interaction produces alkaline melts enriched in Si and Al. Relicts of such melts occur in the products of partial melting of eclogite nodules [5–7] and associate with inclusions of eclogite minerals in diamonds [15]. These relicts often contain chlorine and associate with Cl-bearing minerals [5–7, 15]. However, much lower Cl concentrations in natural melts in comparison with synthetic counterparts show that the former melts did not reach the chlorine saturation limit; i.e., they did not coexist with the immiscible chloride liquid.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 07-05-00499, 05-05-64196, and 05-05-64101), the Foundation of the President of the Russian Federation for the Support of Young Scientists (project no. MK-969.2006.5) and Leading

Scientific Schools (project no. NSh-5338.2006.5), and the Presidium of the Russian Academy of Sciences (Program P-9-3 “Research of Materials under Extreme Conditions”).

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