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Phase relations in the system $KAlSi_3O_8$–$NaAlSi_3O_8$ at high pressure–high temperature conditions and their implication for the petrogenesis of lingunite

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Abstract

Multi-anvil experiments have been made with the composition $(K_{0.2}Na_{0.8})AlSi_3O_8$ at 14–25 GPa and 1400–2400 °C. These experiments suggest that at subsolidus conditions the stable phase assemblages are hollandite-I + jadeite + stishovite (at pressures up to ~20 GPa), hollandite-II + jadeite + stishovite (at pressures between ~20 and ~24 GPa), and hollandite-II + calcium ferrite-type $NaAlSiO_4$ + stishovite (at pressures > ~24 GPa), where hollandite-I and hollandite-II are distinguished by their chemical compositions and phase diagram topology. The maximum $NaAlSi_3O_8$ in hollandite occurs at ~22 GPa, and its fraction is positively correlated to temperature, attaining a value of ~51 mol% at 2200 °C. At supersolidus conditions the solidus and liquidus phases around 14 GPa are hollandite-I and jadeite, respectively; at ~22 GPa, however, the solidus phase is jadeite while the liquidus phase is either stishovite or hollandite-II with a very low fraction of $NaAlSi_3O_8$. These experimental results therefore suggest that lingunite with the hollandite structure and ~90 mol% $NaAlSi_3O_8$, found in some meteorites, is a disequilibrium product. It is similarly proposed that the phase with the structure of jadeite but the composition of plagioclase, found along with lingunite, is also a disequilibrium phase.

Keywords: Hollandite; Jadeite; Lingunite; Meteorite

1. Introduction

At low pressures orthoclase $KAlSi_3O_8$ and albite $NaAlSi_3O_8$ form a complete solid solution (alkali feldspar) which is a major constituent mineral in the earth's crust. At pressures from ~9 to ~26 GPa $KAlSi_3O_8$ feldspar transforms to a high-pressure form with a hollandite structure (Holl-I; [1–8]). Recently Sueda et al. [8] and Ferroir et al. [9] demonstrated that at still higher pressures Holl-I transforms to hollandite-II (Holl-II) which has a monoclinic cell with *I*2/*m* space group. Interestingly, this new form of $KAlSi_3O_8$ back-transforms to Holl-I at ~20 GPa on release of pressure at room temperature [8]. In the case of $NaAlSi_3O_8$ feldspar, high-pressure experiments have produced controversial results [6,10], and the possibility of a high-pressure form with the hollandite structure has not

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been established beyond doubt (hereafter in this paper the word "hollandite" is loosely used for both Holl-I and Holl-II, of which only in situ method can definitely tell the difference). The experiments done by Liu [10] with a diamond cell showed that $NaAlSi_3O_8$ hollandite was stable at 20–23 GPa and 1000 °C while the experiments made by Yagi et al. [6] with a multi-anvil press suggested that the maximum $NaAlSi_3O_8$ in the hollandite solid solution at 20–23 GPa and 1000 °C was ~45 mol%. Thus it is unclear if there is a complete solid solution with the hollandite structure between $KAlSi_3O_8$ and $NaAlSi_3O_8$ at some pressures.

In sharp contrast to the experimental results mentioned above, lingunite, natural hollandite with molar Na/(Na+K) up to ~0.9, is frequently found to coexist with jadeite (Jd)+maskelynite/feldspathic glass in the shock veins of some L chondrites (Sixiangkou meteorite, [11]; Suizhou meteorite, [12–14]; Tenham meteorite, [15]; Yamato 791384, [16]), some H chondrites (Yamato 75100, [17]; Yamato 75267, [18]) and some Martian meteorites such as Zagami [19–21]. K_2O-rich hollandite, however, was found only in Zagami achondrite [22]. It has been argued that lingunite might have crystallized from the maskelynite/feldspathic glass at ~23 GPa and 2000 °C [11,23].

This experimental study has been carried out to assess if there is a *P–T* window where Na_2O-rich hollandite, or lingunite, exists under the condition of chemical equilibrium.

2. Experimental details

2.1. High pressure experiments

High-purity oxides (SiO_2 and Al_2O_3) and carbonates (K_2CO_3 and Na_2CO_3) were used to prepare the starting material of my experiments. These chemicals were firstly heated at 450 °C and 1 atm for 24 h to remove any possible water. The dried materials were then weighed, thoroughly mixed and ground under acetone in an agate mortar, and subsequently pelletized. This resulting product was then heated at 1050 °C and 1 atm for 24 h to remove CO_2, later melted at 1200 °C and 1 atm for 15 min, and finally quenched to make a glass. With an optical microscope and an electron microprobe in an EDS mode I checked the glass and found that the glass was optically clean (free of quench crystal and fluid inclusion) and compositionally homogeneous (close to the designed composition). Eventually this glass was ground, and then stored in an oven at 110 °C and room pressure during the course this study was carried out.

Experiments were made using a 2000-ton double stage multi-anvil apparatus at the Geodynamics Research Center of Ehime University. Tungsten carbide cubes with 3.0 mm truncated edge length (TEL) were used in all experiments reported here. Quenching method was adopted in the current study, with pressure applied first, temperature then increased to a target value, and experiment finally quickly quenched by turning off the electric power supply and unloaded slowly to ambient pressure. The pressure calibration for the 3.0 mm TEL cell was based on the electrical resistance changes associated with the phase transitions of ZnS, GaAs and GaP at room temperature. The uncertainty in the pressure measurement might be up to ~0.5 GPa. Temperature was measured by a $W_{97}Re_3$–$W_{75}Re_{25}$ thermocouple. The effect of pressure on the e.m.f. of the thermocouple was ignored. The uncertainty in the temperature measurement might be in the order of 50°.

The basic pressure cell arrangement in this study was generally the same as that described by Nishiyama and Yagi ([24]; Fig. 2) with the exceptions of different cell sizes and different capsule materials. In all experiments two samples were simultaneously run: one with the glass starting material of $(K_{0.2}Na_{0.8})AlSi_3O_8$ composition while the other with a glass starting material of $CaAl_2Si_2O_8$ composition (results to be reported elsewhere). The starting material in the experiment was contained by a platinum tube (OD=0.8 mm and ID=0.6 mm) or a rhenium tube (OD=0.7 mm and ID=0.5 mm; Table 1). The platinum tube was not welded but closed by crimping and pressing while the rhenium tube was closed at both ends by squeezing into them rhenium spacers (OD=0.5 mm and L=0.3 mm). The initial length of the capsule before an experiment was ~1.0 mm while the final length after the experiment was ~0.7 mm. The typical length of the recovered experimental material was ~0.4 mm in the experiments with platinum capsules while it was ~0.2 mm in those with rhenium capsules.

2.2. Analyzing methods

The experiment products were analyzed using an SEM in EDS mode with the working conditions of 15 kV, 0.885 nA and less than 1 μm beam spot. The collecting time for every analysis was 50 s. Only the experimental charge within a distance of 200 μm to the thermocouple was analyzed. I emphasize here that when there was no melt the phase assemblages in different parts of a capsule were always the same, and that the phase compositions were not very different, indicating a

Table 1
Experimental conditions and results

Run #	*P*	*T*	*t*	Phases observed
OS-1245	14	1400	26	Holl-I, Jd, St
OS-1253 [a]	14	1600	12	Holl-I, Jd, St
OS-1247	14	1800	7.5	Jd, St, Melt
OS-1278 [b]	14	2000	1	Jd, Melt
OS-1258	18	1600	12	Holl-I, Jd, St
OS-1261	18	1800	6	Holl-I, Jd, St
OS-1264	18	2000	4	Holl-I, Jd, St
OS-1279 [b]	18	2200	1.7	Holl-I, Jd, St
OS-1266	22	1600	29.4	Holl-II [c], Jd, St
OS-1262	22	1800	6.1	Holl-II, Jd, St
OS-1272	22	2000	5.3	Holl-II, Jd, St
OS-1378 [b]	22	2200	2	Holl-II, Jd, St
OS-1376 [b]	22	2400	0.2	Holl-II, St, Melt
OS-1274	25	1400	30	Holl-II, Cf, St
OS-1268	25	1600	41	Holl-II, Cf, St
OS-1263	25	1800	8	Holl-II, Cf, St
OS-1269	25	2000	4	Holl-II, Cf, St

P, pressure in GPa; *T*, temperature in °C; *t*, time in hour.
Holl-I, (K,Na)$AlSi_3O_8$ with hollandite structure; Holl-II, (K,Na)$AlSi_3O_8$ of monoclinic symmetry with *I*2/*m* space group; Jd, jadeite; St, stishovite; Cf, calcium ferrite-type $NaAlSiO_4$.

[a] Temperature controlled by input electrical power due to thermocouple failure.

[b] Rhenium capsule rather than platinum capsule was used.

[c] The structure of Holl-II isn't quenchable [8]. This study mainly relied on the extensive electron microprobe composition data to separate Holl-II from Holl-I (See text and Fig. 2 for more detailed discussion).

very small temperature gradient in the experiments, or an insignificant effect of temperature on the phase compositions, or both.

To check possible experimental contamination, I routinely analyzed for, besides SiO_2, Al_2O_3, Na_2O and K_2O, TiO_2, Cr_2O_3, MgO, FeO, MnO and CaO in all the present phases. These latter six oxides were essentially below the limits of detection. The water contents in the experiments were not checked, but trace amounts of H_2O should be expected since H_2O might moisten the small parts of the high pressure cell as they are being assembled [25]. Totals of the electron microprobe analyses are sometimes informative to the water contents of the present phases. In this study low totals of the EDS analyses for all phases were usually observed, but high totals were also not unusual. It is believed that the variation of the totals (typically 100±2%) mainly reflects the quality of sample-polishing rather than the water contents in these phases.

The experimental products were also checked by a micro-focus X-ray diffractometer (M18XHF), and all present phases except melt and Holl-II were confirmed.

3. Experimental results

In total 17 multi-anvil experiments were carried out: 14 subsolidus experiments and 3 supersolidus experiments. The conditions and results of the experiments are summarized in Table 1. In those subsolidus experiments the observed phases assemblages were Holl-I+Jd+stishovite (St) (at pressures up to ~20 GPa), Holl-II+Jd+St (at pressures between ~20 and ~24 GPa), and Holl-II+calcium ferrite-type $NaAlSiO_4$ (Cf)+St (at pressures>~24 GPa). Three different melt-bearing phase assemblages (Jd+St+melt, Jd+melt and Holl-II+St+melt) were observed in those supersolidus experiments. How Holl-I was differentiated from Holl-II will be discussed shortly.

Fig. 1 shows typical BSE images for the experimental products. Large and homogeneous crystals (Holl, Jd, St, and Cf-type $NaAlSiO_4$) have been synthesized because of the high experimental temperatures and long run times applied in this study. Consequently, accurate chemical analyses by electron microprobe can be easily made on the samples. In contrast, Liu [10] and Yagi et al. [6] did not report any BSE image, and they mainly relied on X-ray diffraction to characterize their fine-grained experimental products. The homogeneity of the phases is also supported by the composition data in Tables 2 and 3.

3.1. Phase compositions

The hollandite compositions at subsolidus conditions (Table 2) are summarized in Fig. 2. It is found that the Na/(Na+K) ratio of the hollandite is positively correlated to temperature at a certain pressure. Another feature shown in Fig. 2 is that the compositions of the hollandites are generally divided into two groups: a high-pressure group with higher Na/(Na+K) ratio and a low-pressure group with lower Na/(Na+K) ratio at similar temperatures. It is tentatively suggested that the hollandites in the high-pressure group have the Holl-II structure while the hollandites in the low-pressure group have the Holl-I structure according to the results of Sueda et al. [8]. Similar abrupt composition changes of Holl were previously observed under similar physical conditions for a K-rich basaltic composition, and a phase transformation was suggested to be the most likely reason [26]. In a similar way I assume that a phase transition between Holl-I+Jd+St and Holl-II+Jd+St takes place at ~20 GPa.

Jd, Cf and St were fully analyzed in all experiments although only those from OS-1266 and OS-1274 are listed in Table 3 as some examples. As expected, St

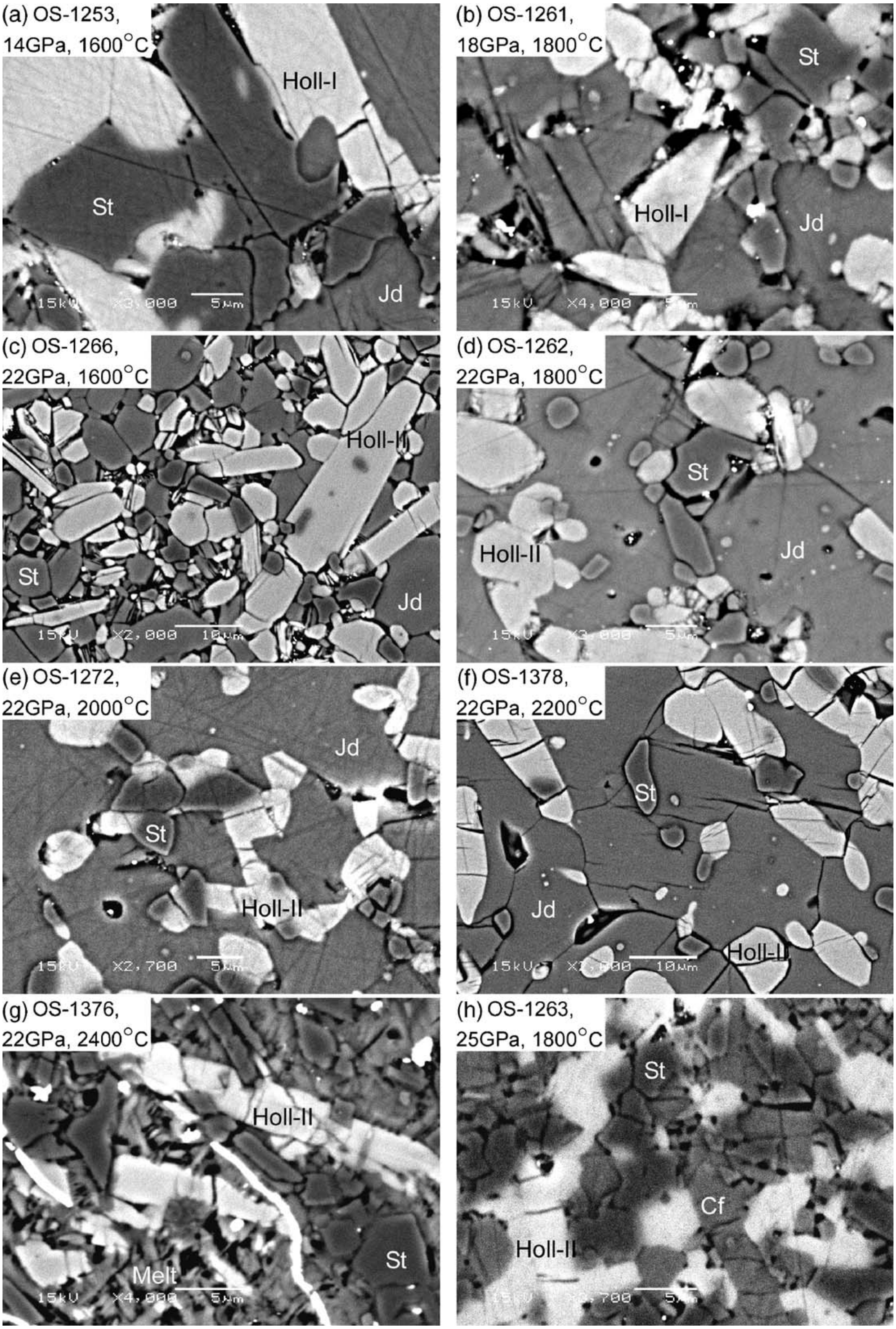
(a) OS-1253,
14GPa, 1600°C
Holl-I
St
Jd
15kV X3,000 5µm
(b) OS-1261,
18GPa, 1800°C
St
Holl-I
Jd
15kV X4,000 5µm
(c) OS-1266,
22GPa, 1600°C
Holl-II
St
Jd
15kV X2,000 10µm
(d) OS-1262,
22GPa, 1800°C
St
Holl-II
Jd
15kV X3,000 5µm
(e) OS-1272,
22GPa, 2000°C
Jd
St
Holl-II
15kV X2,700 5µm
(f) OS-1378,
22GPa, 2200°C
St
Jd
Holl-II
15kV 10µm
(g) OS-1376,
22GPa, 2400°C
Holl-II
Melt
St
15kV X4,000 5µm
(h) OS-1263,
25GPa, 1800°C
St
Cf
Holl-II
15kV X2,700 5µm

Table 2
Compositions of Holl-I and Holl-II

Run#	SiO_2	Al_2O_3	Na_2O	K_2O	Si	Al	Na	K	Total	Na/(Na+K)
OS-1245(11)[a]	64.45(54)[b]	18.33(23)	0.25(4)	16.98(43)	2.99(2)[c]	1.00(1)	0.02(0)	1.00(3)	5.02(2)	0.02(1)
OS-1253(15)	64.24(23)	17.98(14)	0.74(6)	17.04(21)	2.99(1)	0.99(1)	0.07(1)	1.01(1)	5.06(1)	0.06(1)
OS-1258(10)	64.34(28)	18.83(22)	1.88(20)	14.94(35)	2.97(1)	1.02(1)	0.17(2)	0.88(2)	5.04(1)	0.16(3)
OS-1261(10)	64.02(25)	19.23(25)	2.46(14)	14.28(22)	2.95(1)	1.04(2)	0.22(1)	0.84(1)	5.06(1)	0.21(2)
OS-1264(10)	64.62(31)	19.03(20)	1.57(11)	14.78(44)	2.97(1)	1.03(1)	0.14(1)	0.87(3)	5.01(2)	0.14(1)
OS-1279(10)	65.36(62)	18.81(44)	2.38(14)	13.45(33)	2.99(2)	1.02(2)	0.21(1)	0.79(2)	5.00(2)	0.21(2)
OS-1266(16)	64.83(24)	19.13(20)	3.26(27)	12.79(37)	2.97(1)	1.03(1)	0.29(2)	0.75(2)	5.04(2)	0.28(3)
OS-1262(15)	65.15(39)	19.23(29)	4.85(15)	10.76(26)	2.96(2)	1.03(2)	0.43(1)	0.62(2)	5.05(1)	0.41(2)
OS-1272(13)	65.82(73)	19.30(47)	4.83(14)	10.05(32)	2.98(2)	1.03(3)	0.42(1)	0.58(2)	5.01(2)	0.42(2)
OS-1378(11)	65.24(21)	19.95(27)	6.00(15)	8.81(23)	2.95(1)	1.06(1)	0.52(1)	0.51(1)	5.04(1)	0.51(2)
OS-1376(11)[d]	61.76(125)	24.37(127)	5.26(70)	8.61(68)	2.79(5)	1.30(7)	0.46(6)	0.50(4)	5.04(3)	0.48(10)
OS-1274(11)	63.85(97)	18.75(78)	1.53(48)	15.87(71)	2.96(4)	1.03(4)	0.14(4)	0.94(4)	5.06(4)	0.13(6)
OS-1268(12)	64.77(46)	19.00(30)	2.75(28)	13.47(43)	2.97(2)	1.03(2)	0.25(3)	0.79(3)	5.03(1)	0.24(4)
OS-1263(14)	65.00(55)	19.09(36)	4.23(25)	11.68(34)	2.97(2)	1.03(2)	0.37(2)	0.68(2)	5.05(2)	0.35(3)
OS-1269(15)	65.63(42)	19.34(25)	5.44(33)	9.59(44)	2.97(1)	1.03(2)	0.48(3)	0.55(3)	5.03(1)	0.46(4)

[a] The number in the parenthesis following the run number is the number of the electron microprobe analyses performed.

[b] 64.45(54) should be read as 64.45±0.54. All analyses were normalized to 100 wt.% before average and standard deviation were calculated.

[c] Cations calculated on the basis of 8 O per formula unit.

[d] Some contamination might occur in the analyses due to the small grain sizes (See Fig. 1).

contains neither Na_2O nor K_2O. Jd is essentially K_2O-free although diopside might host some (e.g. [27,28]). Irifune et al. [29] observed no potassium in Cf, and their observation is confirmed by this study (Table 3). It follows that a potassium-bearing phase, K_2O-rich hollandite as an example, is needed to host the trace amount of K_2O in the lower mantle.

3.2. Subsolidus phase relation

Fig. 3 shows the phase relationships of the system $KAlSi_3O_8$–$NaAlSi_3O_8$ at subsolidus conditions. At a certain temperature like 1400 °C, taken as an example, there are in total six univariant curves and two invariant points for the pressure range covered by the experiments reported here: BA (tentatively shown as a loop of Holl-I and Holl-II with different compositions), BC, BD and BE from invariant point B while DB, DF and DG from invariant point D.

For the composition of $KAlSi_3O_8$ Sueda et al. [8] and Ferroir et al. [9] concretely demonstrated a phase transition from Holl-I to Holl-II at ~24 GPa and 1400 °C. The *P–T* conditions of this phase transition were later roughly determined by Nishiyama et al. [30]. As $NaAlSi_3O_8$ is added into the system, the isothermally invariant phase assemblage Holl-I+Holl-II becomes univariant, and the invariant point A at 1400 °C probably splits into two points: one stands for the composition of Holl-I while the other for the composition of Holl-II. Since Holl-II can host more $NaAlSi_3O_8$ than Holl-I as discussed in the previous section (Fig. 2), the addition of $NaAlSi_3O_8$ should stabilize Holl-II to lower pressure, so that the transition pressure of Holl-I and Holl-II should be decreased as shown by the univariant composition loop AB, which meets other univariant curves BC, BD and BE at point B. It is emphasized here that the *exact position* and the *width* of the composition loop AB in the small pressure-composition window have not been experimentally defined yet.

The univariant curves BC, BD and DG are very interesting: to their left the divariant phase assemblages contain just one phase (Holl-I or Holl-II) while to their right the divariant phase assemblages contain three

Fig. 1. BSE images: (a) OS-1253 at 14 GPa and 1600 °C, (b) OS-1261 at 18 GPa and 1800 °C, (c) OS-1266 at 22 GPa and 1600 °C, (d) OS-1262 at 22 GPa and 1800 °C, (e) OS-1272 at 22 GPa and 2000 °C, (f) OS-1378 at 22 GPa and 2200 °C, (g) OS-1376 at 22 GPa and 2400 °C, (h) OS-1263 at 25 GPa and 1800 °C. The scale bar in (c) and (f) represents 10 μm, but it represents 5 μm in other images. The brightness of the solid phases is Holl-I/Holl-II>Jd/Cf>St. St always stands out of the surface of the sample due to its relatively high bulk modulus. Sometimes we can see Holl-I inclusion in St (a) or St inclusion in Holl-II (c). The textures of (g) and (h) look rather different: in the former case it is because of the melts and the quenching modification while in the latter case it is presumably due to the phase transition between Holl-II+Jd+St and Holl-II+Cf+St. Note that from the textures in these BSE images it is impossible to tell Holl-I from Holl-II. The small bright dots in some of the images are noble capsule material.

Table 3
Compositions of melts and some example solid phases

Phase	Melt(8) [a]	Melt(7)	Melt(6)	Jd(10)	St(6)	Cf(8)	St(6)
Run#	OS-1247	OS-1278	OS-1376	OS-1266	OS-1266	OS-1274	OS-1274
SiO_2	68.49(247) [b]	72.07(25)	63.05(80)	60.06(26)	98.29(21)	40.88(71)	98.32(35)
Al_2O_3	14.46(29)	15.20(18)	20.18(120)	25.28(19)	1.71(21)	37.63(41)	1.53(30)
Na_2O	3.43(30)	7.12(18)	13.59 (119)	14.65(27)	–	21.49(50)	–
K_2O	13.62(254)	5.60(15)	3.18(29)	–	–	–	–

[a] The number in the parenthesis following the name of the phase is the number of the electron microprobe analyses performed.

[b] 68.49(247) should be read as 68.49±2.47. All analyses were normalized to 100 wt.% before average and standard deviation were calculated.

phases (Holl-I+Jd+St, Holl-II+Jd+St or Holl-II+Cf+St). This phenomenon is caused by a composition degeneracy across the univariant boundaries BC, BD and DG: to their left the system consists of just two components ($KAlSi_3O_8$ and $NaAlSi_3O_8$) while to their right the system consists of four components (K_2O, Na_2O, Al_2O_3 and SiO_2).

For the $NaAlSi_3O_8$-rich portion of the system $KAlSi_3O_8$–$NaAlSi_3O_8$ two isothermally univariant curves (BE and DF) separating three divariant phase assemblages (Holl-I+Jd+St, Holl-II+Jd+St and Holl-II+Cf+St) were observed, compared to one univariant curve separating two divariant phase assemblages found by Yagi et al. ([6]; Holl+Jd+St and Holl+Cf+St). Because they neither applied synchrotron radiation in their experiments nor synthesized high quality samples for extensive electron microprobe analyses, it was impossible for Yagi et al. [6] to tell the difference of Holl-I and Holl-II.

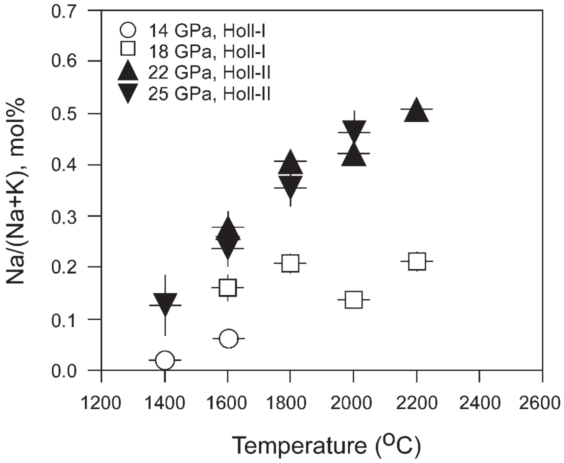

Fig. 2. Compositions of hollandites at subsolidus conditions. The hollandites at 14 and 18 GPa form a broad band, indicating a large effect of pressure on the Na/(Na+K) ratio. In contrast, the hollandites at 22 and 25 GPa plot on a narrow band, suggesting pressure is unimportant to the Na/(Na+K) ratio.

Considering the positive Clapeyron slope of the phase transition of Holl-I and Holl-II in the composition $KAlSi_3O_8$ [8,30], all the isothermally univariant curves in Fig. 3 should be shifted to higher pressures as temperature increases. This is apparently in agreement with the present experimental data.

Regarding the solubility of $NaAlSi_3O_8$ in the hollandite structure, Fig. 3 shows that at a given temperature pressure promotes the dissolution of $NaAlSi_3O_8$ into Holl-I but slightly reduces the proportion of $NaAlSi_3O_8$ in Holl-II [6], so that the

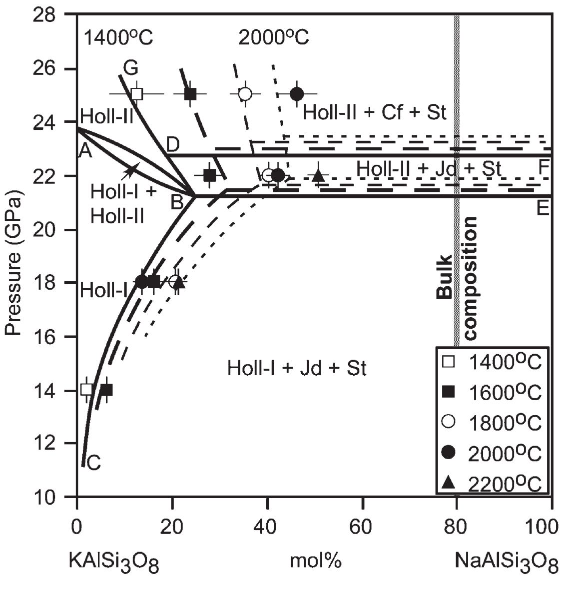

Fig. 3. A schematic P–X diagram of the system $KAlSi_3O_8$–$NaAlSi_3O_8$ at different temperatures lower than the solidi. The symbols represent the compositions of Holl observed in the experiments. The bulk composition used in the experiments is sketched as a very thick line in grey. The transition pressures of $KAlSi_3O_8$ Holl-I and $KAlSi_3O_8$ Holl-II at different temperatures are from [8]. For clearance, the compositional loops of Holl-I+Holl-II at other temperatures rather than 1400 °C are omitted. Although not defined yet, these compositional loops might have infinitesimal widths.

maximum $NaAlSi_3O_8$ in hollandite is reached at the isothermally invariant point where both Holl-I and Holl-II coexist with other solid phases. In the case at 1400 °C, for example, it is point B at ~25 mol% $NaAlSi_3O_8$ and ~21 GPa. This result is essentially consistent with the recent experimental study done by Akaogi et al. [31]. As temperature increases, all the univariant curves shift upright, resulting in higher transition pressure between Holl-I and Holl-II, and higher proportion of $NaAlSi_3O_8$ in hollandite. This shift caused by temperature increase, however, is very limited so that the transition pressure between Holl-I and Holl-II is just slightly dependent to temperature [30], and the proportion of $NaAlSi_3O_8$ increases to just ~51 mol% at a temperature of 2200 °C. It should be concluded that substantial amounts of $NaAlSi_3O_8$, as high as those found in lingunite, cannot be hosted by hollandite under equilibrium subsolidus conditions.

3.3. Partial melting at 14 and 22 GPa

Although the supersolidus experiments in the system $KAlSi_3O_8$–$NaAlSi_3O_8$ reported here are very limited, some important results can be derived from them. The two melt-bearing experiments at 14 GPa suggest that for the bulk composition used in the experiments the solidus phase is Holl-I while the liquidus phase is Jd (Table 1). The partial melting process starts at a temperature between 1600 and 1800 °C, but the compositions of the melts in equilibrium with Holl-I+Jd+St are unknown. A remarkable result from OS-1247 is that the melts coexisting with Jd and St are very poor in Na_2O (Table 3), suggesting that the melts in equilibrium with Holl-I+Jd+St at slightly lower degrees of partial melting lack Na_2O as well. Since the reaction at these low degrees of partial melting is *Holl-I + Jd + St → melt* as constrained by the phase composition data, the $NaAlSi_3O_8$ proportion in Holl-I at 14 GPa has to be very low, actually lower than in the melts, because the combination of Jd+St is essentially K_2O-free.

With Jd as the solidus phase the partial melting process of the system $KAlSi_3O_8$–$NaAlSi_3O_8$ at 22 GPa is fundamentally different from that at 14 GPa (Table 1). After the disappearance of Jd, Holl-II and St coexist with a melt phase which is compositionally rich in Na_2O (OS-1376; Table 3), as expected. The significant observation here is that even buffered by the Na_2O-rich melts, Holl-II still has a very low fraction of $NaAlSi_3O_8$ (Table 2), compared to the proportion of $NaAlSi_3O_8$ in lingunite. As the partial melting process progresses, the Na_2O content of the melts should be reduced, and consequently the proportion of $NaAlSi_3O_8$ in Holl-II should come down, suggesting that there is no stability field for $NaAlSi_3O_8$ hollandite at supersolidus conditions at 22 GPa.

4. Discussion

From his diamond cell experiments Liu [10] suggested that $NaAlSi_3O_8$ hollandite is stable in a small pressure range of 20–23 GPa at about 1000 °C. Identification of any possible hollandite-structure $NaAlSi_3O_8$ by X-ray diffraction in Liu [10], however, was complicated by overlap of the diffraction peaks of hollandite-structure $NaAlSi_3O_8$ with those of other phases. In fact, there were only two relatively weak peaks at very low angles which didn't overlap with the peaks of other phases (Table 1 in [10]).

The phase relations of the $NaAlSi_3O_8$ composition at high pressures were later revised by Yagi et al. [6] with a multi-anvil press, and direct transformation from Jd+St to Cf+St without the involvement of $NaAlSi_3O_8$ hollandite was observed at ~22.5 GPa and at temperatures up to 1200 °C. They also carried out experiments in the system $KAlSi_3O_8$–$NaAlSi_3O_8$ from 13 to 23 GPa at 1000 °C, which suggested a very limited solubility of $NaAlSi_3O_8$ in the hollandite structure under these physical conditions. On the bases of their experiments in both composition systems, Yagi et al. [6] suggested that the hollandite-structure $NaAlSi_3O_8$ detected by Liu [10] might be a minor phase synthesized at much higher temperature than 1000 °C in the local hot spots by the YAG laser heating.

In this study 17 multi-anvil experiments with the composition $(K_{0.2}Na_{0.8})AlSi_3O_8$ have been carried out from 14 to 25 GPa at very high temperatures, both below and above the solidus, to assess the solubility of $NaAlSi_3O_8$ in the hollandite structure. The results under subsolidus conditions generally agree with Yagi et al. [6] and Akaogi et al. [31] but clearly contradict Liu [10]. The results at supersolidus conditions also rule out any possible stability field for the hollandite-structure $NaAlSi_3O_8$.

The supersolidus phase relations of the system $KAlSi_3O_8$–$NaAlSi_3O_8$ at ~22 GPa determined in this study have been found in the intensively shocked basaltic Martian achondrite Zagami [22]. The typical composition of the primary feldspars in Zagami is $Ab_{47}An_{51}Or_2$ (An, $CaAl_2Si_2O_8$; [32,33]). According to my experimental results, if the influence of the An component was ignored, the equilibrium supersolidus phase assemblages should be $KAlSi_3O_8$-rich Holl+Jd+St+melt, $KAlSi_3O_8$-rich Holl+St+melt and $KAlSi_3O_8$-rich Holl/St+melt in the order of temperature increase. Remarkably, Zagami not only preserves the phase assemblage $KAlSi_3O_8$ Holl+omphacite (Jd-rich clinopyroxene)+St+melt, but also the partitioning of Na and K between $KAlSi_3O_8$ Holl and melt, with Na readily entering melt while K entering $KAlSi_3O_8$ Holl (Table 1 of [22]), exactly as what my experiments documented.

It is noted that some of the experimental results reported here are inconsistent with the lingunite-bearing assemblage (lingunite+Jd+maskelynite/feldspathic glass) found in some meteorites [11–21]. The typical composition of the primary feldspars in these meteorites is $Ab_{61-85}An_{8-13}Or_{2-8}$ [11–13,16], which is very close to the bulk composition used in my experiments if one ignores the An component. According to my experimental observations, the possible equilibrium phase assemblages are $KAlSi_3O_8$-rich Holl-I+Jd+St, $KAlSi_3O_8$-rich Holl-I+Jd+St+melt, Jd+St+melt and Jd+melt at relatively low pressures (up to ~20 GPa), and $KAlSi_3O_8$-rich Holl-II+Jd+St, $KAlSi_3O_8$-rich Holl-II+Jd+St+melt, $KAlSi_3O_8$-rich Holl-II+St+melt and $KAlSi_3O_8$-rich Holl-II/St+melt at relatively high pressures (from ~20 to 24 GPa). However, no St has been found out in the shock veins where lingunite coexists with maskelynite/feldspathic glass+Jd [11,17]. In addition, the compositions of both lingunite and maskelynite/feldspathic glass are almost identical to those of the primary feldspars, indicating disequilibrium partitioning of Na and K between lingunite and maskelynite/feldspathic glass. Moreover, Jd, with its structure confirmed by Raman spectroscopy [16,17,19], surprisingly, has a composition of plagioclase ($Ab_{83}An_{13}Or_4$; [16,17]). Thus it is tentatively suggested that this peculiar Jd and lingunite were metastably formed: the shock events severely pressured the primary feldspars, and abruptly changed their structures into those of K_2O-rich hollandite and jadeite, but left their chemical compositions unchanged because the shock durations were very short (e.g. ~4 s for the shock event recorded in Yamato 791384 in which lingunite and Jd with a composition of plagioclase have been found [16]). Since there was not any chemical reaction during this process, no St was formed. In addition, it should be pointed out that no shockwave experiments performed with feldspars of various compositions have documented the phase assemblage of lingunite+Jd+maskelynite/feldspathic glass (e.g. [34–37]), presumably due to the extremely short shock durations in the experiments (usually a few microseconds).

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