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ORIGINAL PAPER

Decomposition of kyanite and solubility of Al_2O_3 in stishovite at high pressure and high temperature conditions

**Xi Liu · Norimasa Nishiyama · Takeshi Sanehira ·
Toru Inoue · Yuji Higo · Shizue Sakamoto**

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Abstract In order to constrain the high-pressure behavior of kyanite, multi-anvil experiments have been carried out from 15 to 25 GPa, and 1,350 to 2,500°C. Both forward and reversal approaches to phase equilibria were adopted in these experiments. We find that kyanite breaks down to stishovite + corundum at pressures above ~15 GPa, and stishovite + corundum should be the stable phase assemblage at the pressure–temperature conditions of the transition zone and the uppermost part of the lower mantle of the Earth, in agreement with previous multi-anvil experimental studies and ab initio calculation results, but in disagreement with some of the diamond-anvil cell experimental studies in the literature. The Al_2O_3 solubility in nominally dry stishovite has been tightly bracketed by forward and reversal experiments; it is slightly but consistently reduced by pressure increase. Its response to temperature increase, however, is more complicated: increases at low temperatures, maximizes at around 2,000°C, and perhaps decreases at higher temperatures. Consequently, the Al_2O_3 solubility in dry stishovite at conditions of high temperature–high pressure is very limited.

X. Liu · N. Nishiyama · T. Sanehira · T. Inoue ·
Y. Higo · S. Sakamoto
Geodynamics Research Center,
Ehime University,
Matsuyama 790-8577, Japan

X. Liu (✉)
Department of Earth Sciences,
University of Western Ontario,
London, ON N6A 5B7, Canada
e-mail: xliu258@uwo.ca

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Introduction

Kyanite (Ky, Al_2SiO_5), commonly found in peraluminous eclogites and amphibolites, has been soundly demonstrated to be an important constituent phase for the materials of continental crust and pelagic sediment at pressures from ~1 to 16 GPa (Irifune et al. 1994; Schmidt et al. 2004). Its role at higher pressures, however, remains unclear. With some preliminary experiments in a Bridgman–anvil apparatus, Ringwood and Reid (1969) tentatively suggested that Ky appears stable up to 15 GPa and 1,000°C. Later Liu (1974) carried out experiments with a diamond-anvil cell (DAC), and demonstrated that Ky is stable up to ~16 GPa and then breaks down to an oxide mixture of stishovite (St) and corundum (Cor) at higher pressures, a result later confirmed not only by experimental studies with multi-anvil press (MA; Irifune et al. 1995; Schmidt et al. 1997), but also by ab initio calculation (Oganov and Brodholt 2000). On the other hand, some recent DAC experimental studies (Madon et al. 1989; Ahmed-ZaÏd and Madon 1991; Friedrich et al. 2004) argued that complicate aluminum silicates such as a V_3O_5-like phase of Al_2SiO_5 (Madon et al. 1989; Ahmed-ZaÏd and Madon 1991), a $Cr_2Ti_2O_7$-like phase of $Al_2Si_2O_7$ (Ahmed-ZaÏd and Madon 1991) and a phase of Al_2SiO_5 structurally related to Ky (Friedrich et al. 2004) might be stable at pressures up to ~70 GPa. Clearly more experiments with the Ky composition at high pressure–high temperature conditions are required before we can resolve this apparent discrepancy.

St, one of the major phases produced by the disproportionation of Ky, is obviously very important to the subducted MORB material at the mantle conditions (Irifune and Ringwood 1993; Kesson et al. 1994; Hirose et al. 1999; Wang and Takahashi 1999; Ono et al. 2001; Hirose and Fei 2002). Possibly it is also very important to the pyrolitic mantle, since Mg-perovskite, the most abundant phase in the lower mantle, probably breaks down to MgO and SiO_2 (e.g. Meade et al. 1995; Saxena et al. 1998), which was recently questioned frequently by ab initio simulations and high pressure experiments (e.g. Serghiou et al. 1998; Shim et al. 2001; Oganov and Ono 2004; Murakami et al. 2004). The physical and chemical properties of St thus might be very important to the geodynamics process between the subducted MORB material and the surrounding mantle material. It has been experimentally demonstrated that the six-coordinated Si in St can be replaced by Al via some charge-balanced substitution mechanisms (e.g. Pawley et al. 1993; Kesson et al. 1994; Gautron et al. 1996; Ono and Yasuda 1996; Hirose and Fei 2002; Chung and Kagi, 2002; Panero et al. 2003). Recent P–V–T studies of St with small amount of Al_2O_3 suggested that replacing Si by Al leads to lower bulk modulus (Liu et al. 1999; Ono et al. 2002a; Andrault et al. 2003; Lakshtanov et al. 2005). In order to rigorously assess how much the physical and chemical properties of St can be affected by the substitution of Al for Si, the question that has to be addressed in the first place is how much Al can be actually hosted in the St structure. Moreover, the solubility of Al_2O_3 is also critical to the incorporation of hydrogen by St since hydrogen is supposed to be coupled mainly with Al^{3+} through the substitution reaction of $Si^{4+} = Al^{3+} + H^+$ (Pawley et al. 1993; Chung and Kagi 2002; Panero et al. 2003).

In this high-pressure experimental study, we carried out MA experiments to investigate the decomposition of Ky and the solubility of Al_2O_3 in St at nominally anhydrous conditions.

Experiments

Experimental technique

Two types of starting materials with the composition of Al_2SiO_5 were used in this study: one was a simple mechanical mixture of pure quartz (Qz) and Cor while the other was pure Ky previously synthesized at 8 GPa and 1,400°C for 7 h using a 3,000-ton MA press. The initial materials of Qz and Cor were firstly heated at 1,000°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. Part of the mixture was directly used as the mechanically mixed starting material in our experiments while part of it was used to synthesize Ky. The Ky starting material was checked by X-ray, and Ky was confirmed to be the only presenting phase. The synthetic material was carefully crushed and thoroughly ground under acetone in an agate mortar. Both starting materials were kept in an oven at 110°C and 1 atm for later experimentation.

The experimental techniques used in this study were essentially identical to those reported in Liu (2006). Experiments were made on a 2,000-ton double stage MA apparatus. The second stage tungsten carbide anvils had a truncated edge length (TEL) of 3.0 mm. The quenching method was adopted, with pressure applied first, temperature then increased to a target value, and experiment finally quenched quickly by turning off the electric power supply and decompressed slowly to ambient pressure. The pressure determination 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. However, it should be noted that high temperatures in the experiments should slightly reduce the experimental pressures, according to our recent pressure calibration with the 3.0 mm TEL cell at 1,600°C (N. Nishiyama, unpublished data). The typical uncertainty in the pressure measurement might be in the order of 0.5 GPa. Temperature was measured by a $W_{97}Re_3$–$W_{75}Re_{25}$ thermocouple, with any possible effect of pressure on its e.m.f. ignored. The uncertainty in the temperature measurement might be in the order of ±50°C.

The basic cell arrangement in this research was also identical to that described by Liu (2006). In all experiments but one (OS-1219), platinum tube (OD = 0.8 mm and ID = 0.6 mm) was used to hold the experimental material. The platinum tubes in these experiments were not welded but closed by mechanical force. We used, in OS-1219, rhenium tube (OD = 0.7 mm and ID = 0.5 mm) with both ends closed 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 OS-1219 with rhenium capsules. In every experiment two samples ran simultaneously: *Sample 1* with the mechanical mixture of oxides while *Sample 2* with the synthetic kyanite.

Analyzing method

We analyzed the experiment products using a JEOL-8800 Superprobe in WDS mode with the working conditions of 15 kV, 5 nA and less than 1 μm beam spot. In order to reduce the possible effect of thermal gradient on the phase compositions, only the experimental charge within a distance of 200 μm to the thermocouple was analyzed. We emphasize here, however, that the compositions of the phases in different parts of a capsule were not very different, indicating a very small temperature gradient in our experiments, an insignificant effect of temperature on the phase compositions, or both.

To check possible experimental contamination, we routinely analyzed for, besides SiO_2 and Al_2O_3, TiO_2, Cr_2O_3, MgO, FeO, MnO, CaO, Na_2O and K_2O in St, Cor, and Ky. These eight oxides added to ~0.1 wt% in these phases and were subsequently ignored. In some experiments a few tiny grains of Na_2O-bearing phase/phases were observed. Due to the occasional presence of these grains in our experiments, the experimental charges were further checked for Na_2O using a SEM-Raman spectroscopic analyzer in EDS mode with a defocused beam. The concentration of Na_2O in the whole experimental charge was essentially below the detecting limit of EDS. Apparently these grains are essentially negligible to the main course here. Because there is no good way to analyze low amount of water (tens of ppm) in such small crystals (up to ~10 μm) as observed in this study, we did not check the water content in our experiments. However, trace amount of H_2O should be expected since H_2O readily moistens the small parts of the high-pressure cell as they are being put together (Irifune et al. 1995). Totals of the electron microprobe analyses are sometimes useful in estimating the possible incorporation of H_2O in experiments. In this study low totals of the WDS analyses for all phases were usually observed, but high totals were also not unusual. We believed the variation of the totals mainly reflects the quality of sample polishing rather than the water contents in the phases. Gautron et al. (1996) and Liu (2006) reached a similar conclusion. Cor is well known as a tough polishing material, but St, with a bulk modulus ~20% higher than that of Cor, is even harder (e.g. Léger et al. 1996).

The experimental products were also checked by a micro-focus X-ray diffractometer (M18XHF), and both St and Cor were concretely detected. The inadequate accuracy of the X-ray data, however, prevented us deriving any useful information on the effects of different compositions on the structures of St and Cor.

Experimental summary and equilibrium evaluation

Experimentation with the Al_2SiO_5 composition was demonstrated to be very difficult not only at low pressures (Kerrick 1990), but also at high pressures (Irifune et al. 1995; Schmidt et al. 1997) due to the sluggish nature of the reactions in the system. In order to overcome this kinetic problem, we made our experiments at very high temperatures with long running times. In addition, efforts were made to bracket the equilibria from two directions by using two different starting materials, as previously mentioned.

In this study 12 experiments with pressures from 15 to 25 GPa and temperatures from 1,350 to 2,500°C were carried out (Table 1). In all these experiments we observed St + Cor. In addition we observed small amounts of Ky in OS-1122 and OS-1153, and an unknown phase (temporarily termed as phase X here) in OS-1219. The compositions of St and Cor are listed in Table 2, and will be fully discussed shortly. While Ky was very homogeneous and essentially stoichiometric, phase X was very heterogeneous with 11.35 ± 1.58 wt% Al_2O_3 in it (9.77 ± 4.66 wt% from 10 analyses in *Sample 1* and 12.94 ± 5.11 wt% Al_2O_3 from 22 analyses in *Sample 2*), clearly different from the compositions of coexisting St and Cor. Due to their very low proportions, however, both Ky and phase X could not be detected by X-ray.

Figure 1 shows the textures of the experimental products. The phases in the samples with different starting materials are rather different: of plate in *Sample 1* while granular in *Sample 2*. This phenomenon presumably reflects different mechanisms by which these phases formed from the different starting materials. It is evident from Fig. 1 that large crystals were successfully synthesized in all these samples whatever the starting material was and whatever the experimental temperature was, so that electron microprobe analysis could be eventually conducted. This was not the case in the literature experimental studies in which good images and electron microprobe analyses were not available (Liu 1974; Irifune et al. 1995; Schmidt et al. 1997).

In order to fully assess the equilibrium state of our experiments, we collected a large number of electron microprobe analyses for all phases (Table 1). The very small standard deviations of the oxide components derived from these analyses (Table 2) strongly argue that phase equilibrium has been well established in the most experiments reported here, with the only exceptions of OS-1122 (*Sample 2* only), OS-1163 (*Sample 2* only) and OS-1219 (both *Sample 1* and *Sample 2*). The poor equilibrium state of *Sample 2* in OS-1122 can be

Table 1 Experimental conditions and results

Run no.	Pressure (GPa)	Temperature (°C)	Time (h)	Sample 1[a]	Sample 2[b]
OS-1122	15	1,350	8	St(3)[c], Cor(12), Ky(4)	St(14), Cor(16), Ky(3)
OS-1127	18	1,350	9	St(3), Cor(9)	St(7), Cor(19)
OS-1133	18	1,750	3	St(17), Cor(21)	St(16), Cor(20)
OS-1150	18	1,950	4	St(13), Cor(13)	St(18), Cor(16)
OS-1153	18	2,150	2	St(18), Cor(21), Ky(3)	St(29), Cor(21), Ky(3)
OS-1163	22	1,350	12	St(24), Cor(11)	St(11), Cor(12)
OS-1165	22	1,950	5.3	St(13), Cor(18)	St(24), Cor(18)
OS-1195	22	2,150	3	St(15), Cor(12)	St(15), Cor(11)
OS-1219[d]	22	2,500	0.5	St(21), Cor(22), ×(10)	St(26), Cor(22), ×(22)
OS-1186	25	1,350	18	St(16), Cor(12)	St(11), Cor(11)
OS-1191	25	1,950	5.5	St(14), Cor(13)	St(13), Cor(15)
OS-1192	25	2,150	3	St(12), Cor(16)	St(17), Cor(24)

[a] Mechanical mixture of oxides used as the starting material

[b] Sintered kyanite used as the starting material

[c] Name of the phase followed by the number of electron microprobe analyses in the parentheses

[d] Rhenium capsules used in this experiment. Temperature was estimated according to Fig. 1 of Zhang et al. (1993)

St stishovite, *Cor* corundum, *Ky* kyanite, *X* unknown phase

Table 2 Phase compositions of St and Cor

Run no.	Sample 1		Sample 2		Result 1		Result 2	
	St	Cor	St	Cor	St	Cor	St	Cor
OS-1122	1.14(82)[a]	0.32(20) [a]	4.11(127) [a]	1.28(79) [a]	2.62(148)[b]	0.79(40) [b]	1.74(17)[c]	0.65(7) [c]
OS-1127	0.92(60)	0.43(27)	1.51(24)	0.29(24)	1.21(30)	0.36(7)	1.21(25)	0.50(44)
OS-1133	2.22(37)	1.66(14)	2.33(22)	1.77(31)	2.27(5)	1.71(5)	2.42(39)	1.55(33)
OS-1150	1.41(38)	0.87(14)	5.29(98)	1.23(23)	3.35(194)	1.05(18)	2.45(15)	1.06(17)
OS-1153	0.76(50)	1.54(55)	2.44(19)	1.78(40)	1.60(76)	1.66(12)	2.29(12)	1.79(53)
OS-1163	0.53(38)	0.21(17)	5.07(215)	1.79(189)	2.80(227)	1.00(79)	1.42(2)	0.44(20)
OS-1165	1.15(16)	1.31(26)	4.70(83)	1.48(26)	2.93(178)	1.40(9)	2.00(55)	1.49(30)
OS-1195	0.69(35)	2.15(13)	1.96(40)	2.55(39)	1.33(64)	2.35(20)	1.57(6)	1.91(46)
OS-1219	0.67(37)	4.78(163)	2.85(64)	10.11(254)	1.76(109)	7.44(266)	1.65(2)	6.45(42)
OS-1186	0.16(13)	0.18(15)	1.49(49)	0.98(79)	0.83(67)	0.58(40)	0.72(23)	0.38(14)
OS-1191	0.76(24)	0.85(19)	1.44(28)	0.82(19)	1.10(34)	0.84(2)	1.33(10)	0.94(34)
OS-1192	1.41(23)	1.41(13)	1.86(51)	1.28(27)	1.64(23)	1.35(7)	1.63(26)	1.27(37)

[a] Average followed by one standard deviation based on the electron microprobe analyses; 1.14(82) read as 1.14 ± 0.82. Only the Al_2O_3 content in *St* and the SiO_2 content in *Cor* are listed here (in wt%). All electron microprobe analyses were normalized to 100 wt% before average and standard deviation were calculated

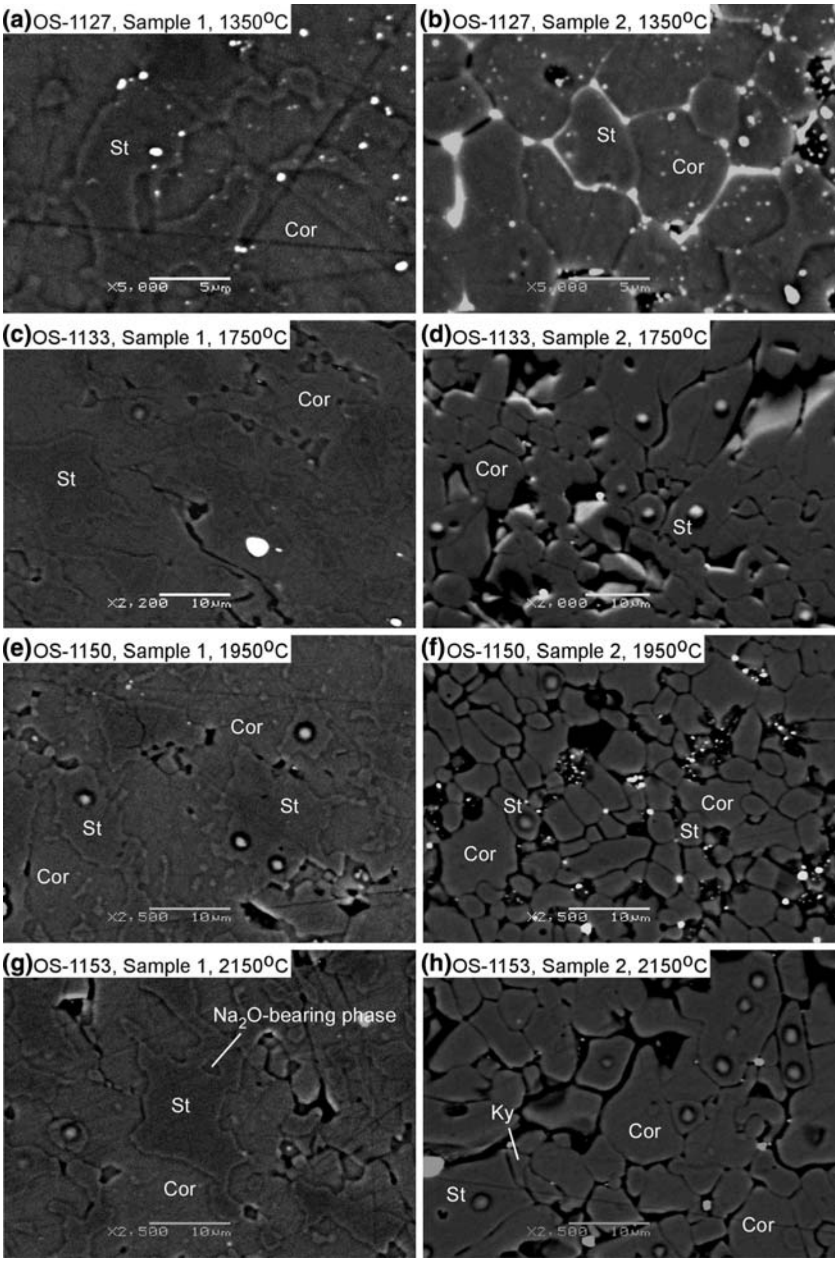
[b] Composition of the middle point of the averages observed in *Sample 1* and *Sample 2*; half of the composition gap regarded as one standard deviation

[c] Composition bracketed by *Sample 1* and *Sample 2*; middle point of the composition gap/overlap taken as the composition in equilibrium while half of the composition gap/overlap taken as one standard deviation (see Fig. 2 for an example)

well explained by the low experimental temperature and the slow reaction rate on the univariant curve of Ky + St + Cor. Low experimental temperature probably also explains the relatively poor equilibrium state in *Sample 2* of OS-1163. From the different equilibrium states of *Sample 1* and *Sample 2* in these two experiments, it can be concluded that the two different starting materials indeed affected the equilibrium-approaching processes. We believed that the relatively poor equilibrium in OS-1219 might be partly due to the high temperature gradient at the very high experimental temperature (~2,500°C) and partly due to the slow reaction rate on the univariant curve St + Cor + X (Table 1).

Figure 2 is an example which shows how well the phase compositions of St and Cor have been bracketed by the forward experiments and the reversal experiments. The very small composition gap/over-

Fig. 1 BSE images showing the textures of the experimental products at 18 GPa. The starting material used in *Sample 1* was the mechanical mixture of oxides while the starting material used in *Sample 2* was the synthetic Ky. The *scale bar* is 5 μm in **a** and **b** while it is 10 μm in others. *Sample 2* of OS-1127 was poorly polished and strong edge effect was observed. *St* always stands out due to its higher bulk modulus. It is unclear whether the Na_2O-bearing phase shown in **g** is melt or a solid phase. The bright spot on *St* caused by the electron beam might indicate trace amount of water in the experiments



lapping defined by the phase compositions from the forward approaching (*Sample 1*) and the reversal approaching (*Sample 2*) apparently indicates close equilibrium.

We used two methods to constrain the equilibrium compositions of St and Cor, as detailed in the notes of Table 2. It is evident that Result 2 is more internally consistent for the experiments at different physical conditions than Result 1, so that we will use Result 2 to make our argument hereafter. For all experiments, anyhow, good agreement on the phase compositions between Result 1 and 2 has been obtained (Table 2).

Results and discussions

Phase relation for the composition Al_2SiO_5 at high pressures and high temperatures

Our experiments, along with the literature results (Liu 1974; Madon et al. 1989; Ahmed-ZaÏd and Madon 1991; Irifune et al. 1995; Schmidt et al. 1997; Friedrich et al. 2004) are summarized in Fig. 3. The stability fields of andalusite and sillimanite at very low pressures are omitted because they are not presently relevant. The melting curve of St is from Zhang et al.

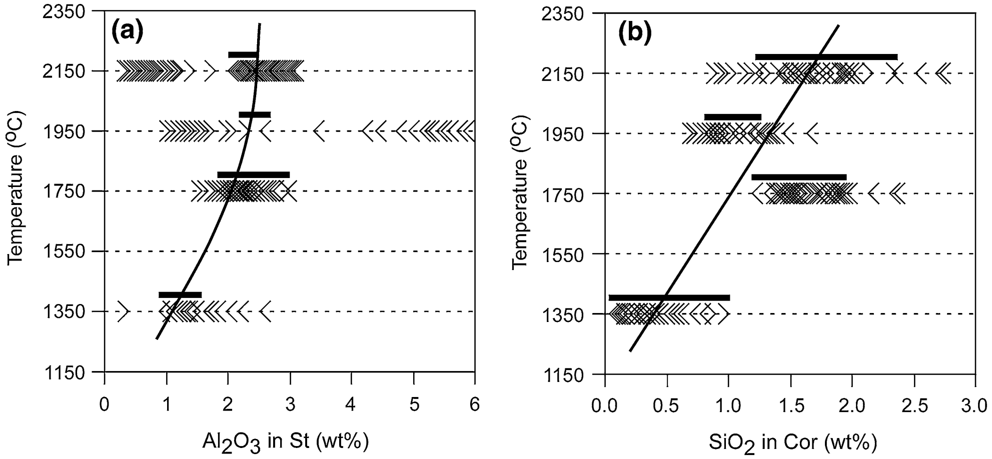


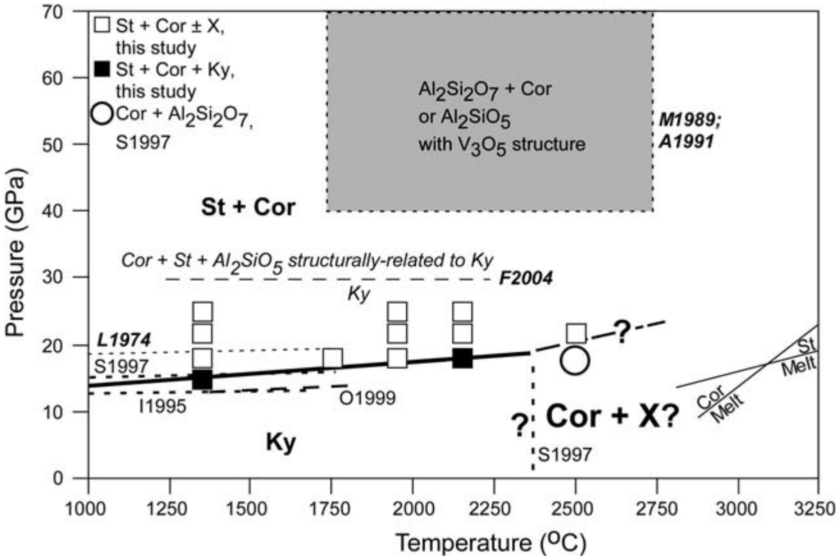
Fig. 2 Bracketed compositions of the phases in the experiments at 18 GPa. *Right angular brackets* composition data from *Sample 1*. *Left angular brackets* composition data from *Sample 2*. The small composition gap/overlapping is indicated by the *solid bar* above the symbols. The *curve* showing the effect of temperature on the phase composition is eye-fitted

(1993) and Shen and Lazor (1995) while that of Cor is from Shen and Lazor (1995) and Shen and Heinz (1998). Currently there are no data on the melting behavior of the composition Al_2SiO_5. In order to facilitate comparison, the result of the phase transition of Ky to St and Cor under hydrous conditions (Ono 1999) is also sketched in Fig. 3.

Apparently in Fig. 3 all MA studies suggest that Ky decomposes to form St + Cor at pressures of around 15 GPa both under nominally anhydrous conditions (Irifune et al. 1995; Schmidt et al. 1997; this study) and under hydrous conditions (Ono 1999), in spite of a minor difference of the P-T loci of the univariant curves of Ky + St + Cor. In particular, the results from this study and from Schmidt et al. (1997) are almost identical whereas those from Irifune et al. (1995) and Ono (1999) are nearly the same within the experimental uncertainties of *P*, *T* measurements.

As illustrated in Fig. 3, both this study and Schmidt et al. (1997) located the univariant curve of Ky + St + Cor at slightly higher pressures (~2 GPa) than Irifune et al. (1995) and Ono (1999). Since this study and Schmidt et al. (1997) were experimentally reversed and reached very good agreement, we can claim now that the *P*–*T* locus of the univariant curve of Ky + St + Cor has been firmly established. The small discrepancy between this study and Schmidt (1997), and Ono (1999) can be easily attributed to the effect of water. If there is water in the system, it should be hosted mainly by St (Rossman and Smyth 1990; Bell and Rossman 1992; Pawley et al. 1993; Chung and Kagi 2002; Panero et al. 2003), so that the stability field of St

Fig. 3 P-T diagram for the Al_2SiO_5 composition (phase relations at very low pressures omitted). L1974, Liu (1974); M1989, Madon et al. (1989); A1991, Ahmed-ZaÏd and Madon (1991); I1995, Irifune et al. (1995); S1997, Schmidt et al. (1997); O1999, Ono (1999); F2004, Friedrich et al. (2004). *Ky* kyanite; *St* stishovite; *Cor* corundum; *X* unknown phase. The potential univariant curves of Ky + Cor + X and St + Cor + X at very high temperatures have not been well defined yet



and Cor should be enlarged and the univariant curve of Ky + St + Cor should be shifted to lower pressure, according to thermodynamics reasoning. This is exactly what was observed in Ono (1999). Irifune et al. (1995) also presented both forward and reversal MA experiments although their result does not agree very well with the result defined by this study and Schmidt et al. (1997). This disagreement was firstly attributed by Schmidt et al. (1997) to possible inaccuracy in the temperature measurement via WC cubes in Irifune et al. (1995) and later explained by possible difference of inter-lab pressure calibrations (Ono 1999). The good agreement between Irifune et al. (1995) and Ono (1999), however, argues against the explanation made by Schmidt et al. (1997) because Ono (1999) did not measure temperatures via WC cubes. On the other hand, the minor disagreement between this study and Irifune et al. (1995) straightforwardly suggests that the explanation presented by Ono (1999) is implausible since both studies were carried out in the same lab with the same pressure scale. Here we would like to forward another explanation which might have brought forth the discrepancy between this study and Schmidt et al. (1997), and Irifune et al. (1995): the result of Irifune et al. (1995) was probably affected slightly by minor amounts of water whose role was clearly shown by the presence of hydrous phase egg in some of the experiments (Irifune et al. 1995; Schmidt 1995; Eggleton et al. 1978). The excellent agreement between Irifune et al. (1995; nominally dry) and Ono (1999; wet) is possibly another indicator of the influence of water in the MA experiments in Irifune et al. (1995).

Compared to the generally consistent results found in the MA experiments, the results from the DAC experiments displayed too much variation (Fig. 3). The early DAC experiments done by Liu (1974), remarkably, agreed very well with the MA experiments while the recent DAC experiments showed a very complicated picture (Friedrich et al. 2004). Friedrich et al. (2004) argued that Ky is stable up to 30 GPa and then breaks down to a phase assemblage of St + Cor + Al_2SiO_5 with a new structure closely related to Ky, although they observed that the X-ray peaks of Ky started to broaden at ~15 GPa. Considering the very short heating duration in the DAC experiments, we suggest that the peak broadening of Ky might represent a phase transition (Ky = St + Cor?), which somehow was kinetically hindered. It is also suggested here that the decomposition of Ky to St + Cor + Al_2SiO_5 with a new structure at ~30 GPa might be an experimental artifact caused by disequilibrium since one can have only three different phases along a univariant curve in a system of two components (here SiO_2 and Al_2O_3). Disequilibrium in Friedrich et al. (2004) was also manifested by the fact that St + Cor + Al_2SiO_5 with a new structure occurred as a divariant phase assemblage stable from 30 to 49 GPa and from 1,227 to 2,227°C. For a system with two components, a divariant phase assemblage can have only two phases according to the Gibbs phase rule.

Madon et al. (1989) and Ahmed-ZaÏd and Madon (1991) performed DAC experiments with the composition of Al_2SiO_5 as well. They found that from ~40 to 70 GPa the stable phase assemblage might be $Al_2Si_2O_7$ + Cor or Al_2SiO_5 with V_3O_5 structure (Fig. 3). Since the experimental pressures in their experiments were very different from those in other experimental studies, it is difficult to evaluate their experimental results. It should be noted, however, that their results do not agree with recent ab initio calculation (Oganov and Brodholt 2000). According to Oganov and Brodholt (2000), the most stable high-pressure phase assemblage for the composition Al_2SiO_5 is St + Cor and the transition pressure between Ky and St + Cor is ~11.3 GPa at –273°C, exactly what we have discovered in the MA experiments. One interesting issue of the DAC experiments done by Madon et al. (1989) and Ahmed-ZaÏd and Madon (1991) is that their result from ~40 to 70 GPa is actually very similar to the result of Run 1k-15 (18 GPa, ~2,500°C) from Schmidt et al. (1997; Fig. 3). Does this mean there was a huge overestimation of pressure in Madon et al. (1989) and Ahmed-ZaÏd and Madon (1991)? Same question was previously posed by Irifune et al. (1996).

It is evident from the above discussion that the phase relations of the composition Al_2SiO_5 at very high temperatures remain unclear (Fig. 3). Experiments made at 22 GPa resulted in melting the Re capsules and experimental charges. Recently, we successfully carried out some experiments at very high temperatures at 14 GPa and applied transmission electron microscopy to characterize the experimental products. The results will be reported elsewhere.

Effects of pressure and temperature on the Al_2O_3 content of St under anhydrous conditions

The Al_2O_3 contents in St bracketed out by our forward samples and reversal samples are plotted in Fig. 4. It is obvious that increasing pressure slightly but consistently reduces the Al_2O_3 content (Fig. 4a). The correlation between temperature and the Al_2O_3 content, however, is more complicate (Fig. 4b). The Al_2O_3 content in St firstly increases with temperature increase but reaches kind of maximum later. If we fit the data analytically, we may predict that the Al_2O_3 content will

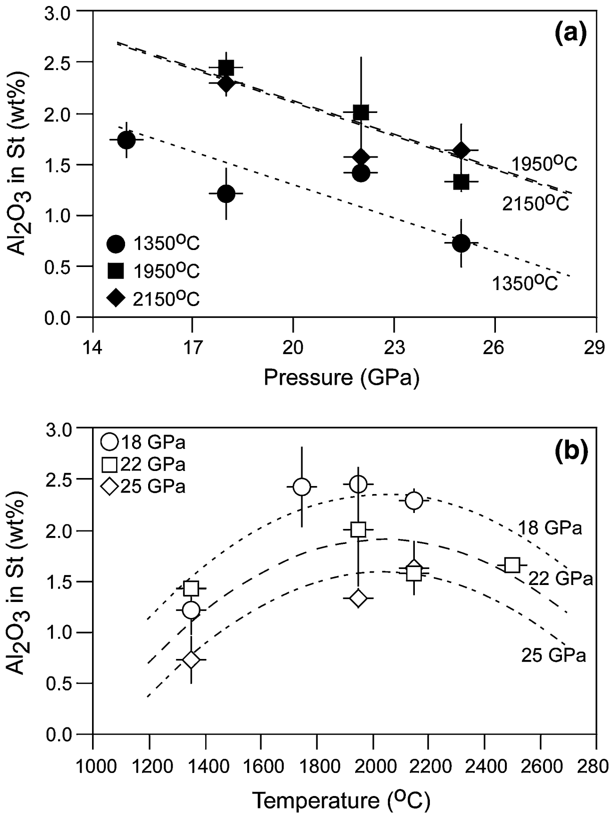


Fig. 4 Effects of pressure (**a**) and temperature (**b**) on the Al_2O_3 content in *St*. The uncertainty in the pressure measurement and the temperature measurement is assumed to be ±0.5 GPa and ±50°, respectively. The Al_2O_3 content in *St* has been fitted to the following second-degree polynomial by least-squares multiple linear regression: $[Al_2O_3] = -2.83(\pm1.81) \; -0.109(\pm0.023)P + 6.97 \times 10^{-3}(\pm 2x10^{-3})T - 1.7 \times 10^{-6}(\pm 5.5 \times 10^{-7})T^2$ with Al_2O_3 in wt%, P in *GPa* and T in °C. The difference between the observation in the experiments and the calculation with this polynomial is averagely 0.17 wt% Al_2O_3. The *lines* in **a** and the *curves* in **b** are drawn according to this polynomial

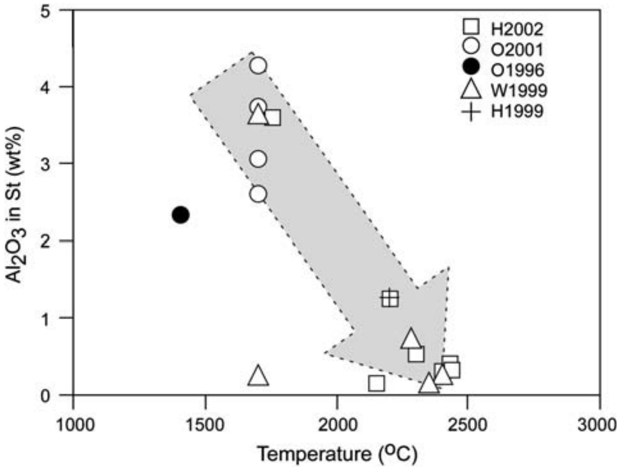


Fig. 5 Al_2O_3 in St for the MORB material under anhydrous condition. H2002, Hirose and Fei (2002); O2001, Ono et al. (2001); O1996, Ono and Yasuda (1996); W1999, Wang and Takahashi (1999); H1999, Hirose et al. (1999). One data with very low Al_2O_3 from Wang and Takahashi (1999) is probably an outlier

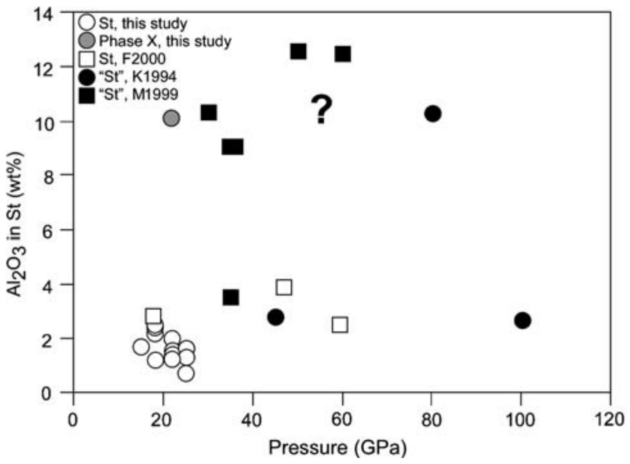


Fig. 6 High Al_2O_3 *"St"* from some laser-heated DAC experiments compared to our observations in the MA experiments. F2000, Funamori et al. (2000); K1994, Kesson et al. (1994); M1999, Miyajima et al. (1999). It should be noted that SiO_2 may take the $CaCl_2$ structure or the α-PbO_2 structure in the laser-heated DAS experiments at pressures above ~70 GPa (e.g. Kingma et al. 1995; Dubrovinsky et al. 1997; Andrault et al. 1998; Dubrovinsky et al. 2001; Ono et al. 2002b). Although it is unclear how these phase transitions affect the incorporation of Al_2O_3 into the SiO_2 phase, the question of dubious high Al_2O_3 *"St"* still holds. In order to facilitate comparison, *phase X* is also plotted

drop at very high temperatures. This kind of phenomenon is probably best explained by a phase transition (Fig. 3), as tentatively proposed by Schmidt et al. (1997). Alternatively, this complicated relationship between the temperature and the Al_2O_3 in St might indicate some difficulties in measuring temperature at very high temperatures where thermocouple wires might react with noble capsules to produce new alloys. The latter argument, however, is not supported by the composition data of Cor shown later in Fig. 8.

It is constructive to check what happens to the nominally dry stishovites in natural composition systems. The data for the MORB material from some literature studies are plotted in Fig. 5. Clearly, the Al_2O_3 content of St decreases quickly as temperature increases, from ~4 wt% at 1,700°C to ~0.2 wt% at 2,400°C. Due to the association of melts with very high temperatures in those experiments, however, it is not clear if the decrease of Al_2O_3 content in St is caused by partial melting or by high temperature.

Summarily we conclude that the Al_2O_3 content in anhydrous St at high temperature–high pressure conditions is very limited, probably just up to ~5 wt%.

In the literature, however, there are some data for “St” with Al_2O_3 content up to 13 wt% (Fig. 6). Kesson et al. (1994) attributed the high Al_2O_3 content to the large thermal gradient caused by laser-heating while Miyajama suggested their analyses might be affected by some small unknown inclusions (N. Miyajima, personal communication, 2004). Phase X observed in this study also has comparably high Al_2O_3 content, but highly possibly it is not a metastable phase, considering the much smaller thermal gradient and much longer experimental duration in the MA experiment than in the DAC experiments.

St and Cor at anhydrous and hydrous conditions

The compositions of St and Cor at anhydrous and hydrous conditions observed in the simple system Al_2O_3–SiO_2 ± CaO ± H_2O are plotted in Figs. 7, and 8, respectively. Generally, the Al_2O_3 contents in St under hydrous conditions are higher than our observations under anhydrous conditions. It is apparent in Fig. 7 that the Al_2O_3 content in St under anhydrous conditions is dependent to both temperature and pressure. In contrast, the Al_2O_3 content in St under hydrous conditions is mostly controlled by temperature, so that higher temperatures lead to higher Al_2O_3 contents and higher H_2O contents, as observed by Chung and Kagi (2002) and Panero et al. (2003). This phenomenon presumably reflects the difference in the mechanisms of incorporating Al_2O_3 into St under anhydrous and hydrous conditions. Under anhydrous conditions, the substitution reaction $Si^{4+} = Al^{3+} + 0.5O_{v}^{2+}$ should work; under hydrous conditions, another substitution reaction $Si^{4+} = Al^{3+} + H^{+}$ also takes place, as suggested by Pawley et al. (1993), Chung and Kagi (2002) and Panero et al. (2003). Apparently a larger effect of pressure on the mechanism of incorporating Al_2O_3 into St at anhydrous condition should be expected. This is because it becomes more difficult to create oxygen vacancy to maintain the charge balance, as the unit cell of St is getting more compacted by pressure increase. No significant effect of pressure on the Al_2O_3 solubility in the wet stishovites is indicated in Fig. 7, contradicting that suggested by recent first-principle calculation (Panero and Stixrude 2004).

SiO_2 uptake by Cor is very interesting. It seems likely the mechanisms of incorporating SiO_2 in Cor under anhydrous and hydrous conditions are rather similar since all dry and wet corundums are plotted in the same trend (Fig. 8), probably reflecting the negligible solubility of H_2O in Cor (Rossman and Smyth 1990). Another interesting point in Fig. 8 is that the effect of pressure on the SiO_2 content in Cor at high temperatures is much larger than that at low temper-

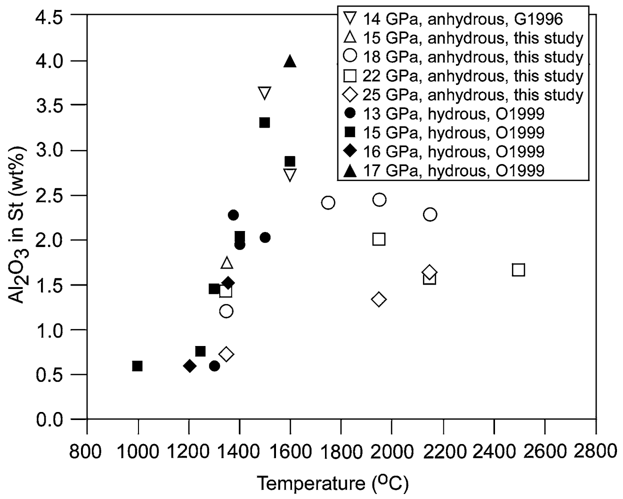


Fig. 7 Al_2O_3 in *St* under hydrous and nominally anhydrous conditions in the system SiO_2-Al_2O_3 ± CaO ± H_2O. G1996, Gautron et al. (1996); O1999, Ono (1999). The phase assemblages of the experiments from Gautron et al. (1996) are garnet + St + CAS while those from Ono (1999) are St + Cor + fluid/phase egg/topaz-OH, so that in all cases the Al_2O_3 content in St is univariant at specific temperature or pressure. One data from Gautron et al. (1996) shows high Al_2O_3, presumably indicating the presence of water

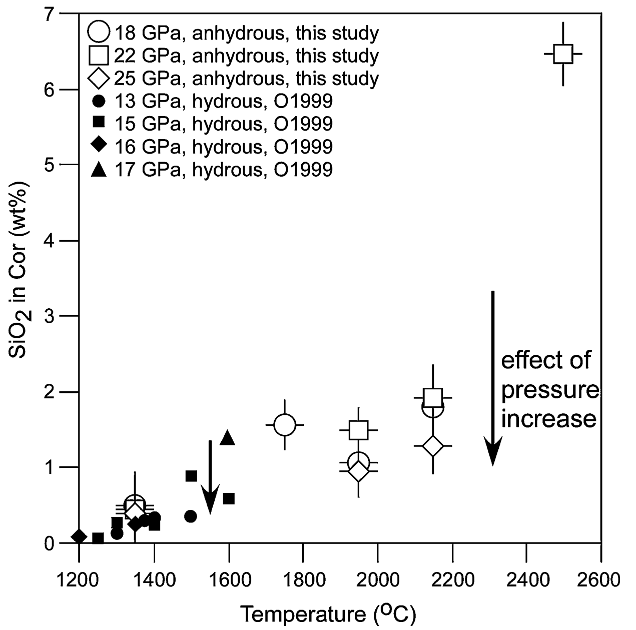


Fig. 8 SiO_2 in Cor under hydrous and nominally anhydrous conditions in the system SiO_2–Al_2O_3 ± H_2O. O1999, Ono (1999). The phase assemblages of the experiments from Ono (1999) are St + Cor + fluid/phase egg/topaz-OH. The effect of pressure increase on the SiO_2 content in Cor is, as indicated by the *arrows*, very small at low temperatures but very large at high temperatures

atures. As temperature increases, the unit cell of Cor is more expanded so that a larger effect of pressure should be expected.

Conclusions

The conclusions drawn from the current work are:

1. Phase equilibrium data collected in our MA experiments suggest that Ky indeed breaks down to St + Cor at pressures ~15 GPa, dependent to temperatures, and the phase assemblage of St + Cor is stable at least up to 25 GPa.
2. The Al_2O_3 content in nominally anhydrous St is constantly suppressed by pressure increase. Its response to temperature, however, is more complicated: initially increases at low temperatures, peaks at around 2,000°C, and perhaps decreases at higher temperatures. Consequently, the Al_2O_3 solubility in dry stishovite under conditions of high temperature–high pressure is very limited.
3. The Al_2O_3 contents in anhydrous St and hydrous St are very different, and have different responses to *P–T* change, suggesting that the mechanisms of incorporating Al into the structures of anhydrous St and hydrous St are different. Under dry conditions, Al^{3+} is mainly coupled with oxygen vacancy to replace Si^4+ while it is mainly coupled with hydrogen under wet conditions.

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