
Volume 298, Issues 3–4
1 October 2010
ISSN 0012-821X
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EARTH
& PLANETARY
SCIENCE LETTERS
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Earth and Planetary Science Letters 298 (2010) 427–433

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

High-pressure phase relations in the composition of albite $NaAlSi_3O_8$ constrained by an *ab initio* and quasi-harmonic Debye model, and their implications

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ARTICLE INFO

Article history:
Received 28 January 2010
Received in revised form 13 July 2010
Accepted 9 August 2010

Editor: L. Stixrude

Keywords:
ab initio simulation
albite
hollandite
meteorite
phase relation
quasi-harmonic Debye model

ABSTRACT

Phase relations in the composition of albite $NaAlSi_3O_8$ at pressures up to 40 GPa were constrained by a theoretical method that combines the *ab initio* calculation and quasi-harmonic Debye model. First, the *P-T* dependence of the thermodynamic potentials of the individual phase, stishovite (SiO_2; St), the calcium-ferrite type $NaAlSiO_4$ (Cf), jadeite ($NaAlSi_2O_6$; Jd) or the hypothetical hollandite-structured $NaAlSi_3O_8$ (Na-Holl) was derived. Our results are generally in consistent agreement with available experimental data and previous theoretical predictions. Second, the Gibbs free energy of the hypothetical Na-Holl phase was compared with that of the phase assemblage Jd + St (JS) or Cf + 2St (CS). Our results show that the Na-Holl phase is not a thermodynamically stable phase over the studied *P-T* conditions of 0–40 GPa and 100–600 K, which rules it out as a possible intermediate phase along the transition path from the JS phase assemblage to CS phase assemblage. Our calculations have predicted that the JS phase assemblage transforms into the CS phase assemblage at about 33.6 GPa at 0 K, and the Clayperon slope of this phase transition is about 0.014 GPa/K. This study implies that lingunite (Na-Holl), found in some meteorites, is not possibly a thermodynamically stable high-*P* phase, and the Cf phase probably plays an important role in maintaining the sodium budget and hosting the large-ion lithophile elements in the deep interior of the Earth.

1. Introduction

Feldspar is one of the most abundant minerals in the Earth's upper continental crust. It has been believed that numerous feldspars might have been carried from the Earth's surface down to the interior via the subduction process (Dupre and Allegre, 1983; Hofmann, 1997; Bozhilov et al., 1999), some of them even down to the core–mantle boundary (Hirose et al., 1999). Consequently the physical–chemical behaviors of feldspar at high pressures are potentially very important to the geodynamic process in the deep interior of the Earth, and have been investigated in a large number of studies both by high-*P* experimentation and by theoretical calculation (e.g., Birch and LeComte, 1960; Liu, 1978; Holland, 1980; Yagi et al., 1994; Liu, 2006; Tutti, 2007; Mookherjee and Steinle-Neumann, 2009).

Albite (Ab; $NaAlSi_3O_8$) is one of the few end members in the feldspar family, and its high-*P* behavior is obviously a prerequisite to the full understanding of the physical–chemical properties of feldspar at high pressures. So far it has been well accepted by the scientific community that Ab breaks down at about 2–3 GPa to the phase assemblage of Jd + Quartz (Qz; SiO_2), which subsequently turns into the phase assemblage Jd + Coesite (Coe) at ~3–4 GPa and then the phase assemblage Jd + St (JS hereafter) at ~9–10 GPa (Birch and LeComte, 1960; Liu, 1978; Holland, 1980). The JS phase assemblage might be stable up to ~23 GPa, and eventually directly change into the phase assemblage of Cf + 2St (CS hereafter) (Yagi et al., 1994; Liu, 2006); Cf is a high-*P* phase with the composition of $NaAlSiO_4$ and the structure of calcium ferrite (Liu, 1978; Yamada et al., 1983; Dubrovinsky et al., 2002). By ignoring any further phase transition of the SiO_2 phase, we can claim that the CS phase assemblage is stable up to at least 75 GPa (Tutti et al., 2000).

The current main debate about the phase relations of the composition $NaAlSi_3O_8$ at high pressures is whether the JS phase assemblage directly changes into the CS phase assemblage (Liu, 1978; Yagi et al., 1994; Liu, 2006; Tutti, 2007). The multi-anvil (MA) experiments by Yagi et al. (1994), Liu (2006) and Akaogi et al. (2010) suggested a direct phase transition whereas the diamond-anvil cell (DAC) experiments by Liu (1978) and Tutti (2007) proposed an indirect route via another phase assemblage Na-hollandite (Na-Hall; a phase with the composition of $NaAlSi_3O_8$ and the structure of hollandite). Although pure Na-Holl has never been successfully synthesized by using the MA press, there have been several lines of ambiguous evidence to support the experimental result of Liu (1978) and Tutti (2007). Firstly, for the composition of orthoclase (Or, the potassium counterpart of Ab; $KAlSi_3O_8$), there is a phase with the composition of $KAlSi_3O_8$ and the structure of hollandite (K-Holl) stable in a wide pressure interval from ~8 to 22 GPa (Kinomura et al., 1975; Urakawa et al., 1994; Yagi et al.,

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doi:10.1016/j.epsl.2010.08.008

1994; Liu, 2006), suggesting that Na-Holl might be stable at some pressures as well. Secondly, some shockwave experiments implied that Ab potentially transforms into Na-Holl at around 30 GPa Hugoniot pressure (Sekine and Ahrens, 1992). Thirdly, lingunite (natural hollandite with molar ratio Na/(Na + K) up to ~0.9) has been frequently found in many meteorites (e.g. Gillet et al., 2000; El Goresy et al., 2000; Tomioka et al., 2000; Kimura et al., 2000; Xie et al., 2001a,b; Jambon et al., 2002; Kimura et al., 2003; Chen et al., 2004; Ohtani et al., 2004; Beck et al., 2004), and its presence, plus the absence of Cf, has been used to constrain the peak shock pressure experienced by those meteorites (e.g. Gillet et al., 2000; Langenhorst and Poirier, 2000; Xie et al., 2001a,b).

The issue of the elusive Na-Holl is by no means trivial. If Na-Holl is stable at some pressures, due to the unique channel structure in the hollandite (Holl; Yamada et al., 1984) and the sodium-rich nature of the continental crust material of the Earth, it has the potential to carry many geochemically important large radius cations (such as Na, K, Ca, Sr and Rb) down to the interior of the Earth via the subduction process. This, in turn, might create in the mantle some reservoirs with distinctive geochemical signatures.

To investigate whether Na-Holl is a thermodynamically stable high-*P* phase or not, we here took a different technique by conducting theoretical simulations, rather than high-*P* experimentation.

2. Theoretical method

2.1. Details of ab initio simulation

Based on the density functional theory (DFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965), our *ab initio* simulations were performed with the generalized gradient approximation (GGA) incorporated with the planewave pseudopotential technique (PW-PP; Perdew et al., 1996). To reduce the computation load, ultrasoft pseudopotentials were used to replace core electrons. Energy cut-offs for the planewave basis of valence wavefunctions were chosen as 410 eV for Jd, Cf and Na-Holl, and 1500 eV for St. Since all the phases studied here are insulators, we adopted the simple Monkhorst–Pack scheme for the Brillouin-zone sampling (Monkhorst and Pack, 1976). The *k*-point meshes used in our calculation were 4×4×5 for Jd, 6×6×10 for St, 2×3×9 for Cf and 3×9×3 for Na-Holl. Careful tests on the cutoff energies and *k*-point meshes were conducted to ensure the numerical convergence of the calculated final energy.

The space group of Jd is C2/c (monoclinic), that of Cf Pbnm (orthorhombic) and that of St $P4_2$/mnm (tetragonal). Our computation cells for Jd, Cf and St contained 20 atoms, 28 atoms and 6 atoms, respectively. As to the case of Na-Holl, there was no any formal detailed description about its structure in the literature, so that a hypothetical crystal structure was built for it. In analogy to K-Holl, Na-Holl would potentially possess a tetragonal symmetry (I4/m). We firstly used the literature data to build the structure of K-Holl (Zhang et al., 1993), and then replaced K^+ with Na^+. During building the structures of Holl, different Al/Si ordering schemes were tested, and the energetically-favored ordering scheme was the one that the Al atoms take the diagonal sites in the Al(Si)-O octahedron. When Al substitutes for Si, the symmetry of Na-Holl is lowered from the tetragonal (I4/m) to the monoclinic (P2/m); this phenomenon has been well known to the scientists in the simulation research field. The experimentally-determined tetragonal symmetry for Holl represents a statistically-equilibrated (averaged, in another word) crystal structure with all possible Al-Si ordering schemes, all of which can be fully simulated, provided a substantial amount of computation time is available. Here we took the energetically-favored scheme (Al atoms residing on the diagonal sites in the Al(Si)-O octahedron) to forward our calculation. As will be clear later, this choice has little influence on the results reported here.

For all calculated phases, both equilibrium lattice parameters and internal coordinates were optimized by minimizing the Hellmann–Feynman force on the atoms and matching the stress on the unit cell to the target stress simultaneously. All the symmetries of the simulated phases were preserved during the optimization process.

2.2. Quasi-harmonic Debye model

To compare the relative stability of the phase assemblages of JS (Jd + St), CS (Cf + 2St) and Na-Holl, we first evaluated the Gibbs free energies of all individual phases, i.e. St, Jd, Cf and Na-Holl, using the quasi-harmonic Debye (QHD) model implemented in the Gibbs program (Blanco et al., 2004). Then, the Gibbs free energies of these different phase assemblages were arithmetically derived according to the phase proportion in the different phase assemblages for the composition $NaAlSi_3O_8$, and compared.

According to Maradudin et al. (1971), the disequilibrium Gibbs energy was presented as following:

$$G(V,P,T) = E(V) + PV + A_{\mathrm{vib}}(x,T),$$

where $E(V)$ is cohesive energy, P pressure, V volume, and A_{vib} vibrational Hemholtz free energy, respectively. A_{vib} is a function of temperature T and configuration parameter x, and can be represented by introducing the Debye model of the phonon density of states as below (Maradudin et al., 1971):

$$A_{vib}(\Theta,\mathrm{T}) = nkT\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln\left(1-e^{-\frac{\Theta}{T}}-D\left(\frac{\Theta}{T}\right)\right)\right],$$

where D, Θ and n are the Debye integral, Debye temperature and number of atoms per formula unit, respectively. D is defined as $D(y) = \frac{3}{y^3}\int_0^y \frac{x^3}{e^x-1}dx$. The Gibbs program is capable to evaluate the Debye temperature Θ, given the static energy–volume (E-V) relationship which is evaluated from the *ab initio* calculations. Eventually, G is minimized with respect to V by solving the following equation:

$$\left(\frac{\partial G(V,P,T)}{\partial V}\right)_{P,T} = 0.$$

Thermal equation of state $V(P,T)$ then can be obtained by V_{opt} that minimizes G. Similarly, other macroscopic properties at different P-T conditions can be derived as well.

3. Results

3.1. Structural parameters and thermodynamic stability at zero temperature

In Table 1, the derived unit-cell parameters of St, Jd, Cf and Na-Holl from our first-principles calculation are compared to the experimental results in the literature (Hemley et al., 1994). Also compared in Table 1 are the parameters of the equations of state; we derived our bulk modulus K_0 and its pressure derivative K_0' by fitting the P-V data from our simulation to the third-order Birch-Murnagham equation of state (Birch, 1978).

For St, the simulated unit-cell volume at zero temperature and pressure is slightly larger (about 2%, Table 1), compared to the experimentally-determined value at ambient condition; this is very typical with the GGA method (e.g. Ono et al., 2008). In addition, the P-V data (Figure 1a) agree very well with recent synchrotron measurements (e.g. Panero et al., 2003; Nishihara et al., 2005).

In the case of Jd, there have not been many high-*P* experimental data in the literature (Nestola et al., 2006; McCarthy et al., 2008), and the comparison between the experimental studies and our theoretical calculation is limited to about 10 GPa (Figure 1b). Firstly, the

Table 1
Comparison of the lattice parameters (a, b, c and β), bulk modulus (K) and its pressure derivative (K') of Cf, Jd, St and Na-Holl: experimentally-measured (ambient condition) vs. theoretically-calculated (zero P and zero T; this work).

Property	Theoretical	Experimental
Cf (space group: Pbnm; Z = 4)		
a_0 (Å)	10.5294	10.1546[a]
b_0 (Å)	8.8655	8.6642[a]
c_0 (Å)	2.8032	2.7385[a]
V_0 (Å^3)	261.67	240.93[a], 243.06[b]
K_0 (GPa)	176.67	220[b], 199[c]
K'	4.2	4.1[b], 4[c]
Jd (space group: C2/c; Z = 4)		
a_0 (Å)	9.55	9.418[d], 9.4242[e]
b_0 (Å)	8.65	8.562[d], 8.5657[e]
c_0 (Å)	5.28	5.219[d], 5.2242[e]
V_0 (Å^3)	415.06	401.2[d], 402[e]
β (°)	107.86	107.58[d], 107.578[e]
K_0 (GPa)	124	125[f], 134[e]
K'	3.66	5[f], 4[e]
St (space group: P4$_2$/mnm; Z = 2)		
$a_0 = b_0$ (Å)	4.2167	4.1801[g]
c_0 (Å)	2.6796	2.6678[g]
V_0 (Å)	47.642	46.6151[g]
K_0 (GPa)	270	301–315[h], 310[i]
K'	4.7	4.6[i]
Na-Holl (space group: P2/m; Z = 2)		
V_0 (Å^3)	238.667	236.118[j], 235.267[k]
K_0 (GPa)	158.1	
K'	4.06	

[a] Yamada et al. (1984).
[b] Dubrovinsky et al. (2002).
[c] Guignot and Andrault (2004).
[d] Prewitt and Burnham (1966).
[e] McCarthy et al. (2008).
[f] Zhao et al. (1997).
[g] Ross et al. (1990).
[h] Jiang et al. (2009).
[i] Andrault et al. (2003).
[j] Liu (1978).
[k] Tutti (2007).

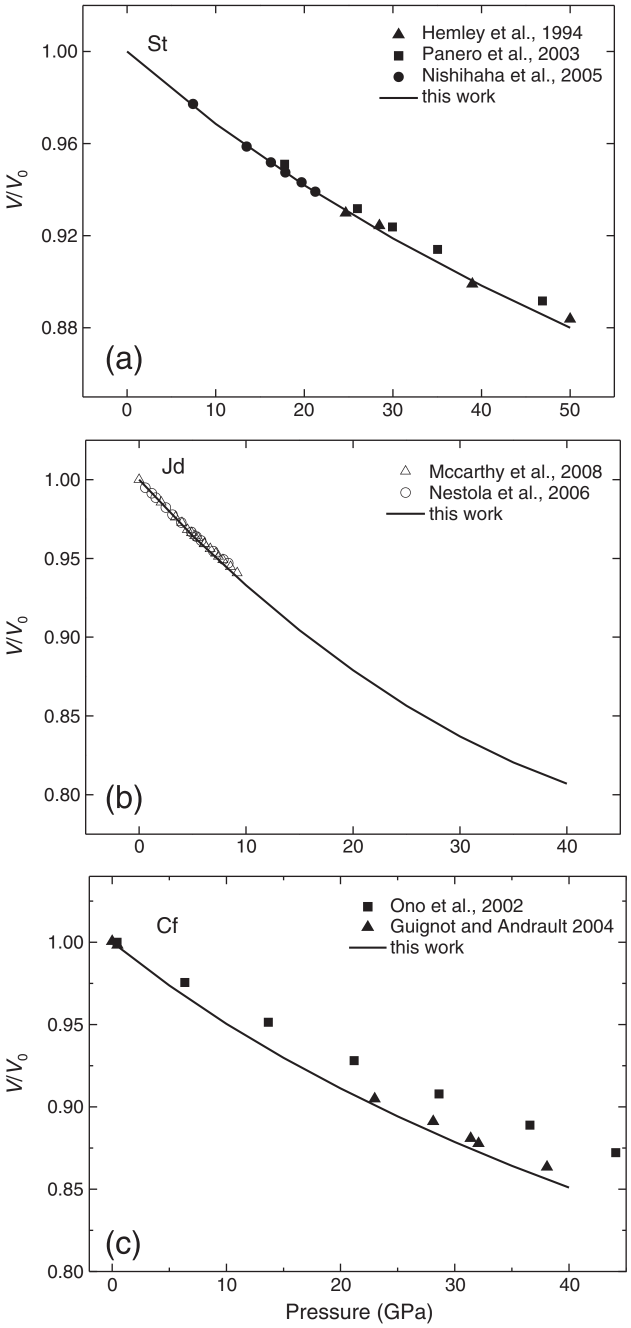

Fig. 1. Comparison of the theoretically-calculated (0 K) and experimentally-determined (300 K) compressional behaviors of St (a), Jd (b) and Cf (c).

simulated V_0 is relatively large (~3%; Table 1); again, this is typical with the GGA method (e.g. Ono et al., 2008). Secondly, the compressional behaviors determined by these three studies are very consistent, as illustrated in Figure 1b. Thirdly, the pressure dependences of the Na-O and Al-O bonds in Jd from McCarthy et al. (2008) and this work are almost identical (Figure 2); most our data deviate from the experimentally-determined trends less than 2.4%. It follows that our simulating scheme is appropriate to describe not only the bulk crystal compressional behavior but also the microscopic structure evolution under high pressures.

The compressional behavior of Cf obtained from our first-principles calculation agrees well with that from Guignot and Andrault (2004), but differs to that in Ono et al. (2002), as shown in Figure 1c. The starting material used by Ono et al. contained about 7.6 wt% FeO and 9.6 wt% MgO. It appears that the incorporation of these components into the Cf structure makes the Cf phase less compressible.

Being consistent with the nominally experimentally-determined values ($a_0 = 9.3$ Å and $c_0 = 2.73$ Å from Liu (1978); $a_0 = 9.302$ Å and $c_0 = 2.719$ Å from Tutti (2007)), our simulated lattice parameters for the hypothetical Na-Holl structure ($a_0 = 9.335$ Å and $c_0 = 2.73$ Å; Table 1) are smaller than those of the K-Holl structure (Yamada et al., 1984). This effect caused by the substitution of K by Na on the lattice parameters agrees with the theoretical calculation done by Caracas and Boffa Ballaran (2010). In comparison to the parameters of the equation of state of K-Holl ($K_0 = 180$–201 GPa with $K' = 4$; Nishiyama et al. (2005) and Ferroir et al. (2006)), the value of K_0 of Na-Holl ($K_0 = 158.1$ GPa and $K' = 4.06$) constrained by our simulation data up to 40 GPa is much smaller. This might be explained by the smaller ionic radius of Na$^+$, which perhaps makes the NaO$_8$ polyhedra more compressible. So far no experimentally-determined equation of state is available for the hypothetic Na-Holl.

The above comparison clearly shows that the simulated lattice constants and fitted equations of state for St, Jd and Cf are quite comparable with the experimental data, which validates our computational scheme. On this solid basis we can further investigate the high-P features of these phases at elevated temperatures.

At zero temperature, the relative thermodynamic stability of different phases or phase assemblages is determined by their relative enthalpies. Figure 3 plots our calculated enthalpy difference, as function of pressure, among the phase assemblages of CS, JS and hypothetic Na-Holl for the composition of NaAlSi$_3$O$_8$ (comparison between different phase assemblages made for the composition of NaAlSi$_3$O$_8$ hereafter).

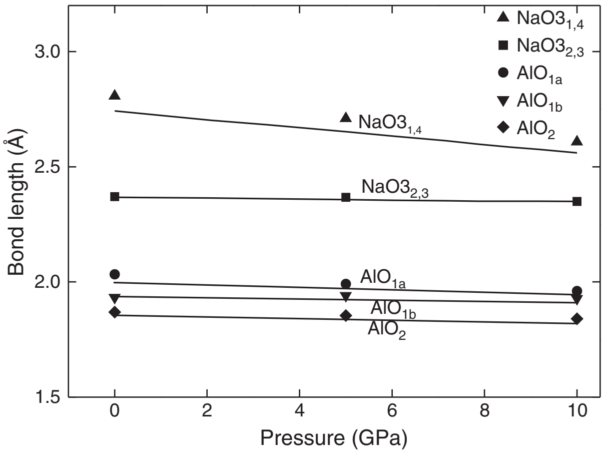

Fig. 2. Variation with pressure of the bond lengths of Na-O and Al-O in Jd. Solid lines stand for the experimental results (300 K; McCarthy et al., 2008) whereas symbols stand for the results from our *ab initio* simulation (0 K). The nomenclature scheme here follows that in Downs (2003).

Clearly shown in Figure 3 is that the enthalpy of the phase assemblage JS or CS is always substantially lower than that of Na-Holl at pressures above 1 atm, so that there is no chance for Na-Holl to be more stable than any of the two phase assemblages at high pressures. On the other hand, Figure 3 shows that the enthalpy difference between the phase assemblages JS and CS is negative at pressures lower than ~27 GPa, but becomes positive at high pressures, indicating a phase transition at approximately 27 GPa.

3.2. Compressional behavior at elevated temperatures

To examine our adopted quasi-harmonic Debye model, we calculated the compressibility of St and Jd at high temperatures, plotted the results along with the available experimental data in Figure 4.

The simulation for St was conducted at 0–40 GPa, and at two temperatures of 300 and 673 K. Figure 4a shows that the compressional data at different temperatures from Liu et al. (1999) and Nishihara et al. (2005) are well mixed, which can serve as a gauge to the quality of our simulation data. It can be seen in Figure 4a that our simulation generally reproduces well the low-temperature compression data. As temperature increases, however, the difference between the simulated results and the experimental observations becomes larger. For example, the difference between the theoretical and experiment V/V_0 ratios is ~0.3% at 5 GPa and ~0.8% at 15 GPa along the 300 K isothermal curve; but it becomes relatively large at high temperatures, ~0.7% at 5 GPa and ~1.5% at 15 GPa along the 673 K isothermal curve. This should be the indicator of the imperfectness of the Debye model at relative high temperatures.

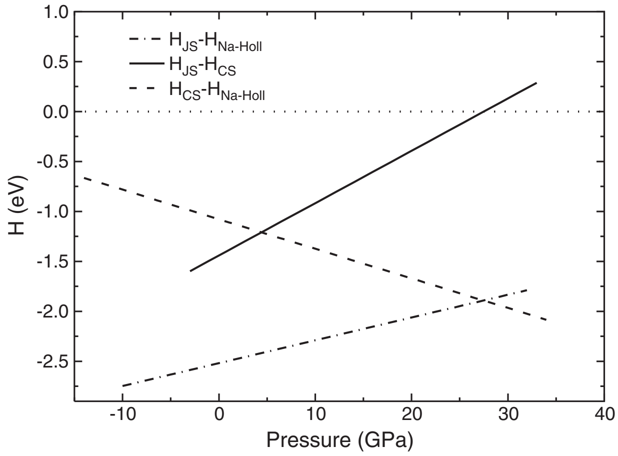

Fig. 3. Comparison of the enthalpies (0 K) of the phase assemblages of JS, CS and Na-Holl (for the composition $NaAlSi_3O_8$) at different pressures.

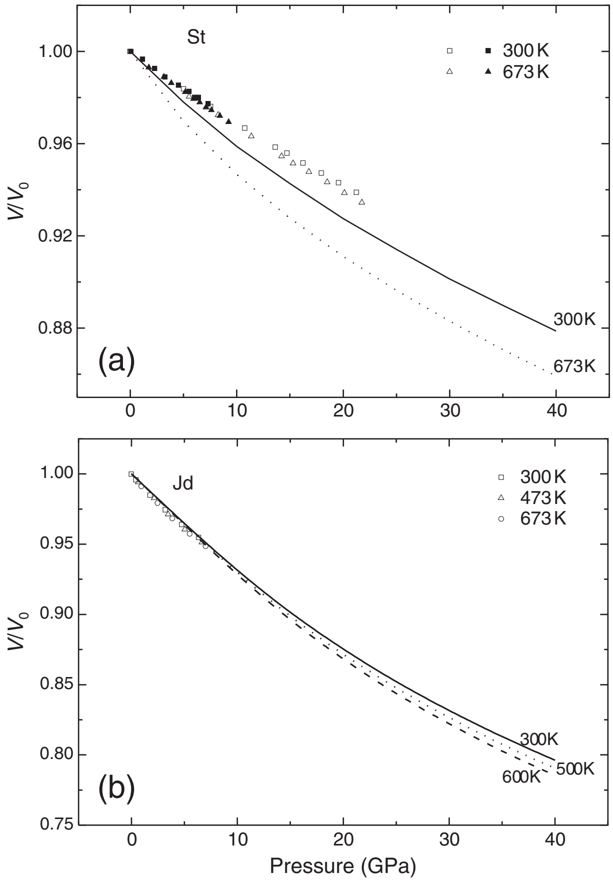

Fig. 4. Variation with pressure of the cell volume of St (a) and Jd (b) at different temperatures. Curves are from this investigation. In (a), the solid symbols represent the experimental data from Nishihara et al. (2005) while the empty ones represent the experiment data from Liu et al. (1999). In (b), the empty symbols represent the experiment data from Zhao et al. (1997).

As previously mentioned, available experimental data are still limited for Jd and more data at higher pressures are needed. Figure 4b shows that the experimental P-V/V_0 data at 300 and 673 K are almost indistinguishable, so that temperature is an unimportant factor in this issue (Zhao et al., 1997). Although a comparison as rigorous as that in the case of St is not possible, Figure 4b does tell us that the simulation results appear broadly consistent with the experimental observations.

As no experimental data seem to be available yet for the high P-T equation of state of Cf, there is no way to make any direct comparison.

3.3. Relative stabilities of JS and hypothetical Na-Holl, and CS and hypothetical Na-Holl at high temperatures

To address the question whether Na-Holl is a stable high-P phase or not, the total energy difference of the phase assemblages of JS and hypothetical Na-Holl, and that of the phase assemblages of CS and hypothetical Na-Holl phase for the P-T range of 0–40 GPa and 100–600 K are shown in Figure 5.

In Figure 5a, the large negative value of G_{JS}-$G_{Na\text{-}Holl}$ in the investigated pressure interval implies that the phase assemblage of JS is thermodynamically much more stable than the hypothetical Na-

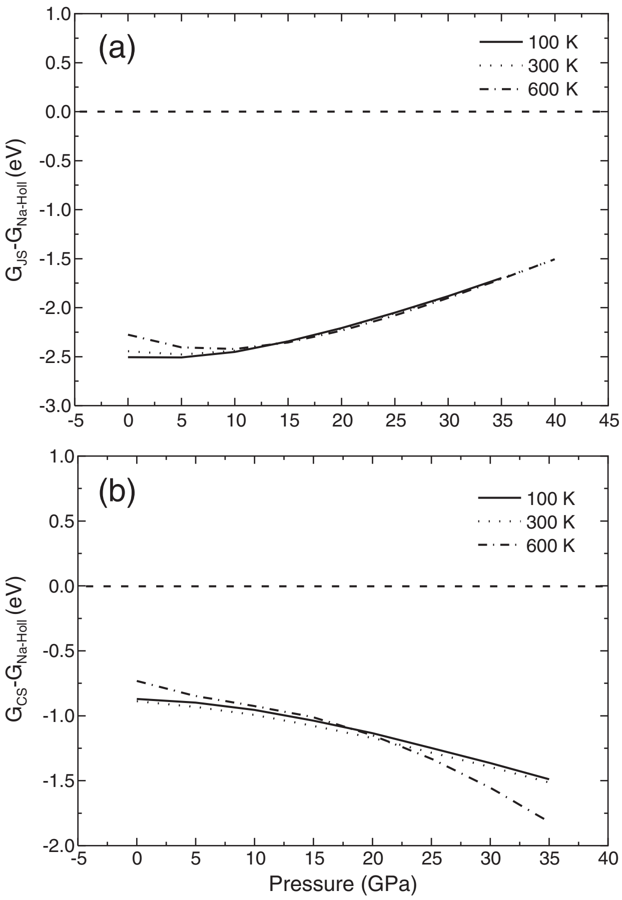

Fig. 5. Variation with pressure of the calculated Gibbs free energy difference of the phase assemblages of JS and Na-Holl (a), and of the phase assemblages of CS and Na-Holl (b) at 100, 300 and 600 K (for the composition $NaAlSi_3O_8$).

Holl phase. At pressures below 15 GPa, the variation of the Gibbs free energy difference with pressure at certain temperature is rather moderate; at higher pressures, however, the variation rate becomes slightly larger. On the other hand, the effect of temperature on the Gibbs free energy difference of these two phase assemblages at a given pressure is very small at pressures lower than 15 GPa, and completely negligible at higher pressures. This is important, and it means that the JS phase assemblage should still be much more stable than Na-Hall at much higher temperatures.

Similarly in Figure 5b, the phase assemblage CS is thermodynamically much more stable than the hypothetical Na-Holl at high temperatures for the studied pressure range. The high-*T* Gibbs free energy difference between the phase assemblages CS and Na-Holl at pressures higher than 20 GPa is always larger than 1 eV, and this difference positively correlates with pressure and temperature, so that the possibility for Na-Holl to be thermodynamically stable is further reduced. Figure 5b suggests that the best *P-T* conditions for Na-Holl to be stable would be low pressure and high temperature. To test this possibility, estimate has been made as follows: At 0 GPa, the energy difference of G_{CS}–$G_{Na\text{-}Holl}$ changes from −0.87 eV at 100 K to −0.73 eV at 600 K; assuming a constant changing rate, ~0.00028 eV/K, G_{CS}–$G_{Na\text{-}Holl}$ at 2000 K would be −0.34 eV, so that the phase assemblage CS would still be more stable than Na-Holl at such a high temperature.

From Figure 5a and b, it can be drawn that for the investigated *P-T* interval, Na-Hall is significantly less stable than any of the phase assemblages of JS and CS. In other words, Na-Holl is unlikely a thermodynamically stable phase at the studied *P-T* conditions.

3.4. Phase boundary between the phase assemblages of JS and CS

The energy difference between the phase assemblages JS and CS in the *P-T* range of 0–40 GPa and 100–600 K is shown in Figure 6. At pressures below ~35 GPa, G_{JS}–G_{CS} is negative, indicating the phase assemblage JS is more stable than the phase assemblage CS; at higher pressures, G_{JS}–G_{CS} becomes positive so that the phase assemblage CS is more stable. Specifically, the transition pressure from the low-*P* phase assemblage JS to the high-*P* phase assemblage CS is ~35 GPa at 100 K, ~37 GPa at 300 K and ~42 at 600 K, so that the change rate of the transition pressure is about 0.014 GPa/K, a value larger than those previous determinations (−0.001 GPa/K (Yagi et al., 1994), −0.0015 GPa/K (Tutti et al., 2000) and 0.0031 GPa/K (Akaogi et al., 2002)). With this change rate of the transition pressure, the transition pressure at 0 K should be ~33.6 GPa, a value higher than that constrained by the enthalpy calculation (Figure 3). This contrasting phenomenon is believed to be resulted from the fact that the zero-point vibration energy in the Gibbs free energy calculation does not approach zero whereas the enthalpy calculation is merely static.

Along with the literature data (Yagi et al., 1994; Tutti et al., 2000; Akaogi et al., 2002), the phase boundary of JS and CS constrained by our computation is shown in Figure 7. In general, the results from the high-*P* experiments (Yagi et al., 1994; Tutti et al., 2000) and thermodynamic calculation (Akaogi et al., 2002) are in mutual consistency (~22 GPa), but both contradict our simulation result (~35 GPa). What causes this overestimation of the transition pressure in our theoretical calculation (~50%) is currently unclear. Interesting enough, an overestimation of ~50% in the transition pressure of K-Holl to post K-Holl was also observed in the simulation done by Mookherjee and Steinle-Neumann (2009).

4. Discussion

Na-Holl (lingunite) has been found in many meteorites (e.g. Gillet et al., 2000; El Goresy et al., 2000; Tomioka et al., 2000; Kimura et al., 2000; Xie et al., 2001a,b; Jambon et al., 2002; Kimura et al., 2003; Chen et al., 2004; Ohtani et al., 2004; Beck et al., 2004), but the high-*P* experimental studies in history did not solve the issue whether Na-Holl is a thermodynamically stable phase or not (Liu, 1978; Yagi et al., 1994; Liu, 2006; Tutti, 2007). By performing some DAC experiments with the composition of Ab, Liu (1978) claimed that Na-Holl was stable from 21 to 24 GPa at 1000 °C, a result which was not

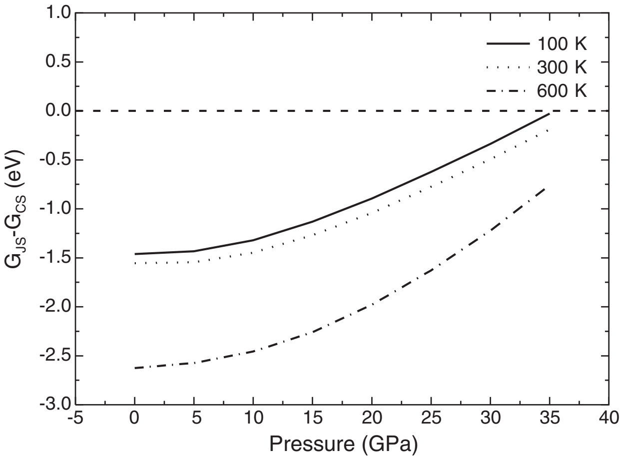

Fig. 6. Variation with pressure of the calculated Gibbs free energy difference of the phase assemblages of CS and JS at 100, 300 and 600 K (for the composition $NaAlSi_3O_8$). $G_{CS} - G_{JS} = 0$ indicates the phase transition between the two phase assemblages.

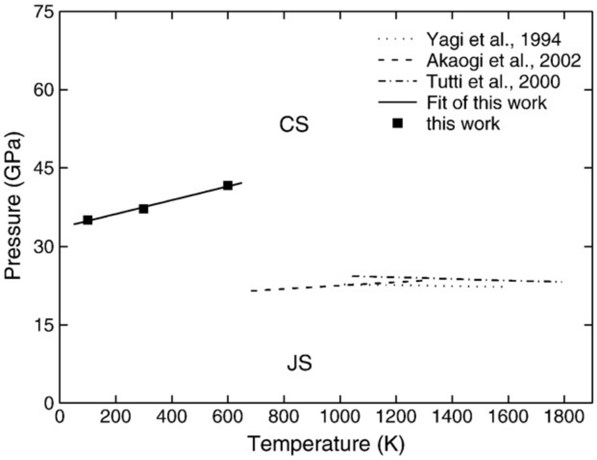

Fig. 7. *P-T* phase relation of the phase assemblages of JS and CS. Our data define a positive slope for the phase boundary. The two lines from Yagi et al. (1994) and Tutti et al. (2000) have slightly negative slopes while the one from Akaogi et al. (2002) has a slightly positive slope.

reproduced by the MA experiments in the same composition system at 22–23 GPa and 800–1200 °C (Yagi et al., 1994). Further, the negative message from Yagi et al. (1994) was extended to temperatures as high as 2400 °C by the MA experiments of Liu (2006; composition system Ab-Or; 22 GPa). However, the argument did not end there. Tutti (2007) recently conducted some DAC experiments with the composition of Ab, and one of them at 22.5 GPa and about 2000 °C showed a couple of X-ray diffraction peaks which potentially belonged to Na-Holl, a phenomenon almost exactly observed by Liu about 30 years ago (1978). Tutti speculated that the more rapid temperature-quenching in the laser-heated DAC experiments might help Na-Holl to preserve its structure down to the ambient temperature.

Our new approach of theoretical simulation adopted in this study suggests that Na-Holl is unlikely a thermodynamically stable phase. The Gibbs free energy of the phase assemblage of JS or CS is much lower than that of Na-Holl for a wide range of *P-T* conditions (Figure 5), indicating that Na-Holl is less stable. If this is correct, the origin of lingunite found in some meteorites is presently still a mystery, which probably can be concretely disclosed by shockwave experiments only.

The presence of Na-Holl and the absence of the Cf phase in the meteorites have been used to constrain the pressure of the shock events (e.g. Gillet et al., 2000; Langenhorst and Poirier, 2000; Xie et al., 2001a,b). This exercise, however, produced discrepant results; for instance, Na-Holl in the Tenham chondrite would suggest a peak pressure less than ~22 GPa while silicate perovskite would require the peak pressure of the impact event higher than 23 GPa (Tomioka and Fujino, 1997; Tomioka et al., 2000). On the ground that Na-Holl is not a thermodynamically stable phase, the discrepancy in the estimated peak pressures might be solved and Na-Holl was probably formed metastably at pressures much higher than 22 GPa. There has been indirect evidence to support this argument; in their recent synchrotron MA experiments, Kubo et al. (2010) observed that Jd can metastably nucleate from the partially/completely amorphous plagioclase in the stability field of CS. It follows that cautions must be taken in estimating the pressure of the shock event by using one or two high-*P* index phases.

If the peak pressures experienced by those lingunite-bearing meteorites were indeed much higher than 22 GPa, it would be very constructive to check if some of the grains with the composition of $NaAlSi_3O_8$ actually have the structure of the Cf phase. The impact might have changed the structure of Ab into that of Cf, but left the composition unchanged, just as it had done to the Jd phase in the meteorite Yamato 791384 (Kimura et al., 2000; Ohtani et al., 2004). In order to get better understanding to this process, several issues must be experimentally addressed: what composition ($NaAlSi_2O_6$ or $NaAlSi_3O_8$) the Jd phase observed in Kubo et al. (2010) has, how the Jd phase observed in those meteorites can simultaneously maintain the structure of Jd and the composition of $NaAlSi_3O_8$ (Kimura et al., 2000; Ohtani et al., 2004), and how easy the Cf phase can nucleate from the partially/completely amorphous plagioclase, as compared to the case of the Jd phase (Kubo et al., 2010).

Due to its special crystal structure (Zhang et al., 1993), hollandite has been regarded as one of the major carriers which can bring large quantities of incompatible, large-ion lithophile elements (e.g. Rb, Ba, Sr, K, Pb, La, Ce and Th) down into the mantle of the Earth via the subduction process of the continental crust (Prewitt and Downs, 1998). In this way, some compositional heterogeneities with distinctive geochemical signals, the EM-1 mantle end-member in particular (e.g. Hofmann, 1997), can be created in the mantle. The important role that hollandite plays in this process has been experimentally demonstrated by Rapp et al. (2008). Since Na-Holl is not a stable phase and the solubility of the component $NaAlSi_3O_8$ in K-Holl is very limited at *P-T* conditions experienced by the subducted continental crust material (Irifune et al., 1994; Yagi et al., 1994; Liu, 2006; Rapp et al., 2008; Wu et al., 2009), K-Holl might not be able to host all Na_2O. Indeed, Na-rich phases like majorite and Jd were observed in many high-*P* experimental studies at pressures up to ~24 GPa whereas the Cf phase was observed at still higher pressures (e.g. Irifune et al., 1994; Wu et al., 2009). In the structure of the Cf phase there is a channel running parallel to the *c*-axis, which might be able to host the large-ion lithophile elements (Ringwood, 1975); this could be very important to the trace element recycling and geochemical heterogeneity in the lower mantle since the Cf phase is stable at least up to 75 GPa (Tutti et al., 2000).

Acknowledgments

The authors thank Drs. Y. Fei, Z. Gong, Y. Zhang, L. Zhang and H. Zhen for providing valuable suggestions and comments on the project. Dr. M. Akaogi and another anonymous reviewer are thanked for constructive reviews. The study was financially supported by China Postdoctoral Science Foundation (20090450224) and National Natural Science Foundation of China (40872033 and 40704012). JD acknowledges the support from NSF (EAR-0757847).

References

Akaogi, M., Tanaka, A., Kobayashi, M., Fukushima, N., Suzuki, T., 2002. High-pressure transformations in $NaAlSiO_4$ and thermodynamic properties of jadeite, nepheline, and calcium ferrite-type phase. Phys. Earth Planet. Inter. 130, 49–58.

Akaogi, M., Haraguchia, M., Nakanishia, K., Ajiroa, H., Kojitani, H., 2010. High-pressure phase relations in the system $CaAl_4Si_2O_{11}$–$NaAl_3Si_3O_{11}$ with implication for Na-rich CAS phase in shocked Martian meteorites. Earth Planet. Sci. Lett. 289, 503–508.

Andrault, D., Angel, R.J., Mosenfelder, J.L., Le Bihan, T., 2003. Equation of state of stishovite to lower mantle pressures. Am. Mineral. 88, 301–307.

Beck, P., Gillet, P., Gautron, L., Daniel, I., El Goresy, A., 2004. A new natural high-pressure (Na, Ca)-hexaluminosilicate [$(Ca_xNa_{1-x})Al_{3+x}Si_{3-x}O_{11}$] in shocked Martian meteorites. Earth Planet. Sci. Lett. 219, 1–12.

Birch, F., 1978. Finite strain isotherm and velocities for single-crystal and polycrystalline NaCl at high pressures and 300 K. J. Geophys. Res. 83, 1258–1267.

Birch, F., LeComte, P., 1960. Temperature–pressure plan for albite composition. Am. J. Sci. 258, 209–217.

Blanco, M.A., Francisco, E., Luana, V., 2004. GIBBS: isothermal–isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model. Comput. Phys. Commun. 158, 57–72.

Bozhilov, K.N., Green II, H.W., Dobrzhinetskaya, L.F., 1999. Clinoenstatite in Alpe Arami peridotite: additional evidence of very high pressure. Science 284, 128–132.

Caracas, R., Boffa Ballaran, T., 2010. Elasticity of $(K, Na)AlSi_3O_8$ hollandite from lattice dynamics calculations. Phys. Earth Planet. Inter. 181, 21–26.

Chen, M., Xie, X., El Goresy, A., 2004. A shock-produced $(Mg, Fe)SiO_3$ glass in the Suizhou meteorite. Meteorit. Planet. Sci. 39, 1797–1808.

Downs, R.T., 2003. Topology of the pyroxenes as a function of temperature, pressure, and composition as determined from the procrystal electron density. Am. Mineral. 88, 556–566.

Dubrovinsky, L.S., Dubrovinskaia, N.A., Prokopenko, V.B., Le Bihan, T., 2002. Equation of state and crystal structure of $NaAlSiO_4$ with calcium-ferrite type structure in the conditions of the lower mantle. High Pres. Res. 22, 495–499.

Dupre, B., Allegre, C.J., 1983. Pb-Sr isotope variation in Indian Ocean basalts and mixing phenomena. Nature 303, 142–146.

El Goresy, A., Chen, M., Gillet, P., Dubrovinsky, L.S., 2000. Shock induced high-pressure phase transition of labradorite to hollandite "(Na_{47}-Ca_{51}-K_2)" in Zagami and the assemblage hollandite "(Na_{80}-Ca_{12}-K_8)"+Jadeite in L chondritis: constraints to peakshock pressures. Meteorit. Planet. Sci. 35, A51 (Supplement).

Ferroir, T., Onozawa, T., Yagi, T., Merkel, S., Miyajima, N., Nishiyama, N., Irifune, T., Ikegawa, T., 2006. Equation of state and phase transition in $KAlSi_3O_8$ hollandite at high pressure. Am. Mineral. 91, 327–332.

Gillet, P., Chen, M., Dubrovinsky, L., El Goresy, A., 2000. Natural $NaAlSi_3O_8$-hollandite in the shocked Sixiangkou meteorite. Science 287, 1633–1636.

Guignot, N., Andrault, D., 2004. Equations of state of Na-K-Al host phases and implications for MORB density in the lower mantle. Phys. Earth Planet. Inter. 143–144, 107–128.

Hemley, R.J., Prewitt, C.T., Kingma, K.J., 1994. High-pressure behavior of silica. In: Heaney, P., Gibbs, G.V., Prewitt, C.T. (Eds.), Reviews of Mineralogy. Mineralogical Society of America, pp. 41–81.

Hirose, K., Fei, Y., Mao, H.K., 1999. The fate of subducted basaltic crust in the Earth's lower mantle. Nature 397, 53–56.

Hofmann, A.W., 1997. Mantle geochemistry: the message from oceanic volcanism. Nature 385, 219–228.

Hohenberg, P., Kohn, W., 1964. Inhomogeneous electron gas. Phys. Rev. 136, B864–B871.

Holland, T.J.B., 1980. The reaction albite = jadeite + quartz determined experimentally in the range 600–1200 °C. Am. Mineral. 65, 129–134.

Irifune, T., Ringwood, A.E., Hibberson, W.O., 1994. Subduction of continental crust, terrigenous and pelagic sediments: an experimental study. Earth Planet. Sci. Lett. 126, 351–368.

Jambon, A., Barrat, J.A., Sautter, V., Gillet, P., Göpel, C., Javoy, M., Joron, J.L., Lesound, M., 2002. The basaltic shergottite Northwest Africa 856: petrology and chemistry. Meteorit. Planet. Sci. 37, 1147–1164.

Jiang, F., Gwanmesia, G.D., Dyuzheva, T.I., Duffy, T.S., 2009. Elasticity of stishovite and acoustic mode softening under high pressure by Brillouin scattering. Phys. Earth Planet. Inter. 172, 235–240.

Kimura, M., Suzuki, A., Kondo, T., Ohtani, E., El Goresy, A., 2000. Natural occurrence of high-pressure phases, jadeite, hollandite, wadsleyite and majorite-pyrope garnet, in an H-chondrite Y75100. Meteorit. Planet. Sci. 35, A87–A88.

Kimura, M., Chen, M., Yoshida, Y., El Goresy, A., Ohtani, E., 2003. Backtransformation of high-pressure phases in a shock melt vein of an H-chondrite during atmospheric passage: implications for the survival of high-pressure phases after decompression. Earth Planet. Sci. Lett. 217, 141–150.

Kinomura, N., Kume, S., Koizumi, M., 1975. Stability of $K_2Si_4O_9$ with wadeite type structure. In: Osugi, J. (Ed.), Proceeding of the 4th International Conference on High Pressure. Physical Chemistry Society of Japan, Kyoto, Japan.

Kohn, W., Sham, L.J., 1965. Self-consistent equations including exchange and correlation effects. Phys. Rev. 140, A1133–A1138.

Kubo, T., Kimura, M., Kato, T., Nishi, M., Tominaga, A., Kikegawa, T., Funakoshi, K., 2010. Plagioclase breakdown as an indicator for shock conditions of meteorites. Nat. Geosci. 3, 41–45.

Langenhorst, F., Poirier, J.P., 2000. 'Eclogitic' minerals in a shocked basaltic meteorite. Earth Planet. Sci. Lett. 176, 259–265.

Liu, L., 1978. High-pressure phase transformations of albite, jadeite and nepheline. Earth Planet. Sci. Lett. 37, 438–444.

Liu, X., 2006. 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. Earth Planet. Sci. Lett. 246, 317–325.

Liu, J., Zhang, J., Flesch, L., Li, B., Weidner, D.J., Liebermann, R.C., 1999. Thermal equation of state of stishovite. Phys. Earth Planet. Inter. 112, 257–266.

Maradudin, A.A., Montroll, E.W., Weiss, G.H., Ipatova, I.P., 1971. Theory of Lattice Dynamics in the Harmonic Approximation. Academic Press.

McCarthy, A.C., Downs, R.T., Thompson, R.M., 2008. Compressibility trends of the clinopyroxenes, and in-situ high-pressure single-crystal X-ray diffraction study of jadeite. Am. Mineral. 93, 198–209.

Monkhorst, H.J., Pack, J.D., 1976. Special points for Brillouin-zone integrations. Phys. Rev. B 13, 5188–5192.

Mookherjee, M., Steinle-Neumann, G., 2009. Detecting deeply subducted crust from the elasticity of hollandite. Earth Planet. Sci. Lett. 288, 349–358.

Nestola, F., Ballaran, T.B., Liebske, C., Bruno, M., Tribaudino, M., 2006. High-pressure behaviour along the jadeite $NaAlSi_2O_6$–aegirine $NaFeSi_2O_6$ solid solution up to 10 GPa. Phys. Chem. Mineral. 33, 417–425.

Nishihara, Y., Nakayama, K., Takahashi, E., Iguchi, T., Funakoshi, K., 2005. P-V-T equation of state of stishovite to the mantle transition zone conditions. Phys. Chem. Mineral. 31, 660–670.

Nishiyama, N., Rapp, R.P., Irifune, T., Sanehira, T., Yamazaki, D., Funakoshi, K., 2005. Stability and P-V-T equation of state of $KAlSi_3O_8$-hollandite determined by in situ X-ray observations and implications for dynamics of subducted continental crust material. Phys. Chem. Mineral. 32, 627–637.

Ohtani, E., Kimura, Y., Kimura, M., Takata, T., Kondo, T., Kubo, T., 2004. Formation of high-pressure minerals in shocked L6 chondrite Yamato 791384: constraints on shock conditions and parent body size. Earth Planet. Sci. Lett. 227, 505–515.

Ono, S., Hirose, K., Kikegawa, T., Saito, Y., 2002. The compressibility of a natural composition calcium ferrite-type aluminous phase to 70 GPa. Phys. Earth Planet. Inter. 131, 311–328.

Ono, S., Oganov, A.R., Brodholt, J.P., Vočadlo, L., Wood, I.G., Lyakhov, A., Glass, C.W., Côté, A.S., Price, G.D., 2008. High-pressure phase transformations of FeS: novel phases at conditions of planetary cores. Earth Planet. Sci. Lett. 272, 481–487.

Panero, W.R., Benedetti, L.R., Jeanloz, R., 2003. Equation of state of stishovite and interpretation of SiO_2 shock-compression data. J. Geophys. Res. 108 (2001JB001663).

Perdew, J.P., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868.

Prewitt, C.T., Burnham, C.W., 1966. The crystal structure of jadeite. Am. Mineral. 51, 956–975.

Prewitt, C.T., Downs, R.T., 1998. High-pressure crystal chemistry. In: Hemley, R.J. (Ed.), Reviews in Mineralogy. Mineralogical Society of America, pp. 283–317.

Rapp, R.P., Irifune, T., Shimizu, N., Nishiyama, N., Norman, M.D., Inoue, T., 2008. Subduction recycling of continental sediments and the origin of geochemically enriched reservoirs in the deep mantle. Earth Planet. Sci. Lett. 271, 14–23.

Ringwood, A.E., 1975. Composition and Petrology of the Earth's Mantle. McGraw-Hill, New York.

Ross, N.L., Shu, J.F., Hazen, R.M., 1990. High-pressure crystal chemistry of stishovite. Am. Mineral. 75, 739–747.

Sekine, T., Ahrens, T.J., 1992. Shock-induced transformations in the system $NaAlSi_3O_8$-SiO_2: a new interpretation. Phys. Chem. Mineral. 18, 359–364.

Tomioka, N., Fujino, K., 1997. Natural (Mg, Fe)SiO_3-ilmenite and -perovskite in the Tenham meteorite. Science 277, 1084–1086.

Tomioka, N., Mori, H., Fujino, K., 2000. Shock-induced transition of $NaAlSi_3O_8$ feldspar into a hollandite structure in a L6 chondrite. Geophys. Res. Lett. 27, 3997–4000.

Tutti, F., 2007. Formation of end-member $NaAlSi_3O_8$ hollandite-type structure (lingunite) in diamond anvil cell. Phys. Earth Planet. Inter. 161, 143–149.

Tutti, F., Dubrovinsky, L.S., Saxena, S.K., 2000. High pressure phase transformation of jadeite and stability of $NaAlSiO_4$ with calcium-ferrite type structure in the lower mantle conditions. Geophys. Res. Lett. 27, 2025–2028.

Urakawa, S., Kondo, T., Igawa, N., Shimomura, O., Ohno, H., 1994. Synchrotron radiation study on the high-pressure and high-temperature phase relations of $KAlSi_3O_8$. Phys. Chem. Mineral. 21, 387–391.

Wu, Y., Fei, Y., Jin, Z., Liu, X., 2009. The fate of subducted upper continental crust: an experimental study. Earth Planet. Sci. Lett. 282, 275–284.

Xie, X., Chen, M., Wang, D., 2001a. Shock-related mineralogical features and P-T history of the Suizhou L6 chondrite. Eur. J. Mineral. 13, 1177–1190.

Xie, X., Chen, M., Wang, D., El Goresy, A., 2001b. $NaAlSi_3O_8$-hollandite and other high-pressure minerals in the shock melt veins of the Suizhou meteorite. Chin. Sci. Bull. 46, 1121–1126.

Yagi, A., Suzuki, T., Akaogi, M., 1994. High pressure transitions in the system $KAlSi_3O_8$-$NaAlSi_3O_8$. Phys. Chem. Mineral. 21, 12–17.

Yamada, H., Matsui, Y., Ito, E., 1983. Crystal-chemical characterization of $NaAlSiO_4$ with the $CaFe_2O_4$ structure. Mineral. Mag. 47, 1277–1281.

Yamada, H., Matsui, Y., Ito, E., 1984. Crystal-chemical characterization of $KAlSi_3O_8$ with the hollandite structure. Mineral. J. 12, 29–34.

Zhang, J., Ko, J., Hazen, R.M., Prewitt, C.T., 1993. High-pressure crystal chemistry of $KAlSi_3O_8$ hollandite. Am. Mineral. 78, 493–499.

Zhao, Y., Von Dreele, R.B., Shankland, T.J., Weidner, D.J., Zhang, J., Wang, Y., Gasparik, T., 1997. Thermoelastic equation of state of jadeite $NaAlSi_2O_6$: an energy-dispersive Rietveld refinement study of low symmetry and multiple phases diffraction. Geophys. Res. Lett. 24, 5–8.