

A. R. Oganov · J. P. Brodholt

## High-pressure phases in the $\text{Al}_2\text{SiO}_5$ system and the problem of aluminous phase in the Earth's lower mantle: *ab initio* calculations

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**Abstract** One of the main uncertainties in mineralogical models of the Earth's lower mantle is the nature of the aluminous mineral: it is not clear whether Al forms its own minerals or is mainly contained in  $(\text{Mg,Fe})\text{SiO}_3$ -perovskite. This question is very important, since it is known that if Al were mainly hosted by perovskite, it would radically change Fe/Mg-partitioning and phase equilibria between mantle minerals, and also alter many physical and chemical properties of perovskite, which is currently believed to comprise ca. 70% of the volume of the lower mantle. This, in turn, would require us to reconsider many of our geochemical and geophysical models for the lower mantle. This work considers the possibility of a  $\text{V}_3\text{O}_5$ -type structured modification of  $\text{Al}_2\text{SiO}_5$  to be the main host of Al in the lower mantle, as proposed by previous workers. We report *ab initio* calculations, based on density functional theory within the generalised gradient approximation (GGA) with plane wave basis set and nonlocal pseudopotentials. We consider polymorphs of  $\text{Al}_2\text{SiO}_5$  (kyanite, andalusite, sillimanite, and hypothetical  $\text{V}_3\text{O}_5$ -like and pseudo-brookite-like phases),  $\text{SiO}_2$  (stishovite, quartz) and  $\text{Al}_2\text{O}_3$  (corundum). Computational conditions (e.g., plane-wave energy cutoff, Brillouin zone sampling) were

carefully chosen in order to reproduce small energy changes associated with phase transitions between the  $\text{Al}_2\text{SiO}_5$  polymorphs. Good agreement of crystal structures, bulk moduli, atomisation energies and the phase diagram of  $\text{Al}_2\text{SiO}_5$  with experimental data was found. Strong disagreement between the calculated lattice parameters and density of  $\text{V}_3\text{O}_5$ -like phase of  $\text{Al}_2\text{SiO}_5$  and experimental values, assigned to it by previous workers, suggests that a  $\text{V}_3\text{O}_5$ -structured phase of  $\text{Al}_2\text{SiO}_5$  was never observed experimentally. In addition, we found that the most stable high-pressure assembly in  $\text{Al}_2\text{SiO}_5$  system is corundum + stishovite, and the value of the transition pressure at  $T = 0$  K (113 kbar) is in excellent agreement with experimental estimates (95–150 kbar). We explain the instability of octahedrally coordinated silicates of Al to decomposition on the basis of Pauling's second rule.

**Key words** Quantum-mechanical simulations · Phase equilibria

### Introduction

According to contemporary estimates (Table 1), Al is one of the most abundant elements in the Universe. Its significance becomes even greater in silicate phases, which constitute the Earth's crust and mantle. Oxide and silicate aluminous phases comprise a large part of the refractory "white inclusions" in carbonaceous chondritic meteorites, which are believed to represent primordial products of the condensation from the protosolar nebula. At the conditions of Earth's crust and upper mantle, Al is predominantly contained in silicate minerals – feldspars, zeolites, micas, amphiboles, pyroxenes, garnets, and frequently with a considerable degree of Al-Si disordering.

The Earth's deep interior is inaccessible, and all information about physical conditions, chemical and mineralogical composition of deep mantle and core comes from models based on geophysical measurements,

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Artem R. Oganov (✉)  
Department of Crystallography and Crystal Chemistry,  
Geological Faculty, Moscow State University,  
119899, Moscow, Russia

John P. Brodholt  
Department of Geological Sciences,  
University College London, Gower Street,  
London WC1E 6BT, UK  
E-mail: j.brodholt@ucl.ac.uk  
Fax: +44 (020)-7387-1612

*Present address:* A. R. Oganov  
Crystallography and Mineral Physics,  
Dept. of Geological Sciences,  
University College London,  
Gower Street, London WC1E 6BT, UK  
E-mail: a.oganov@ucl.ac.uk  
Fax: +44 (020)-7387-1612

**Table 1** Data on abundances of some chemical elements (in atoms per 1 atom Si)

Element	The Universe <sup>a</sup>	The whole Earth <sup>b</sup>	Earth's Crust <sup>c</sup>	Upper Mantle <sup>c</sup>	Lower Mantle <sup>c</sup>	Pyrolytic Homogeneous Mantle <sup>d,e</sup>
O	20.10	3.73	2.97	3.63	3.63	3.68
Na	0.06	0.06	0.12	0.03	2*10 <sup>-3</sup>	0.02
Mg	1.08	1.06	0.09	0.97	1.09	1.24
Al	0.08	0.09	0.36	0.17	0.06	0.12
Si	1	1	1	1	1	1
P	0.01	–	4*10 <sup>-3</sup>	6*10 <sup>-4</sup>	4*10 <sup>-5</sup>	4*10 <sup>-4</sup>
S	0.52	–	8*10 <sup>-4</sup>	6*10 <sup>-4</sup>	5*10 <sup>-5</sup>	2*10 <sup>-3</sup>
Ca	0.06	0.06	0.14	0.12	0.05	0.09
Cr	0.01	–	1*10 <sup>-4</sup>	5*10 <sup>-3</sup>	0.01	0.01
Fe	0.9	0.9	0.11	0.14	0.14	0.16
Ni	0.05	–	3*10 <sup>-5</sup>	3*10 <sup>-3</sup>	4*10 <sup>-3</sup>	3*10 <sup>-5</sup>

<sup>a</sup> Estimates of Anders and Ebihara (1982)

<sup>b</sup> Simple model based on cosmic abundances (Anderson 1989)

<sup>c</sup> Recalculated from data of Anderson (1989)

<sup>d</sup> Recalculated from (Ringwood 1991)

<sup>e</sup> It is still questionable whether the mantle is homogeneous, or

there is a chemical boundary between lower mantle and transition zone. If homogeneous, mantle should have pyrolytic composition. However, all models include significant amounts of Al in both lower and upper mantle.

knowledge of cosmic and meteoritic abundances of chemical elements, and *P-T*-phase diagrams of petrologically relevant systems. It is almost universally accepted that the most abundant minerals of the lower mantle are (Mg,Fe)SiO<sub>3</sub>-perovskite (ca. 70 vol.%), magnesiowüstite (Mg,Fe)O (ca. 20–25 vol.%), and CaSiO<sub>3</sub>-perovskite (ca. 5–10 vol.%). Although Al is even more abundant in the lower mantle than Ca (Table 1), not much is known about its mantle mineralogy. The lower mantle comprises 49.2 wt% (or 55.3 vol.%) of the whole Earth, and, therefore, mineralogical studies of this region are of a considerable importance for understanding physics and chemistry of the whole Earth. The mineralogy of Al is of particular interest, since if Al does not form a separate phase, it must be predominantly contained in (Mg,Fe)SiO<sub>3</sub>-perovskite. It has been shown that if it is the case, it would radically change Fe/Mg-partitioning and phase equilibria (Wood and Rubie 1996) between perovskite and magnesiowüstite, leading to significant enrichment of perovskite in Fe (especially in the form of Fe<sup>3+</sup>; McCammon 1997), and that would change dramatically many physical and chemical properties (e.g., electrical conductivity, thermodynamic, rheological and diffusional properties) of perovskite and the lower mantle as a whole. These changes would necessitate reconsideration of many geophysical and geochemical models for the lower mantle based on the properties of Al-free perovskite.

### Mineralogy of Al in the lower mantle

Based on the high-pressure experiments on pyrolytic material at 1800–1900 K and 23–28 GPa, Irifune (1994) has concluded that MgSiO<sub>3</sub>-perovskite should be the main host of Al in the lower mantle, being able to accommodate all Al present in the lower mantle. This closely corresponds to results of Liu (1977), who showed that up to 25 mol.% of Al<sub>2</sub>O<sub>3</sub> can be present in MgSiO<sub>3</sub>-based perovskite solid solution. However, many other

experimental studies (Madon et al. 1989; Irifune et al. 1991; Ahmed-Zaid and Madon 1991, 1995) reveal high-pressure aluminous phases that have been proposed to be the main hosts of Al in the lower mantle. In the earlier work, Irifune et al. (1991) proposed a high-pressure form of MgAl<sub>2</sub>O<sub>4</sub> with the CaFe<sub>2</sub>O<sub>4</sub> structure as the main Al-phase in the lower mantle; recently, Funamori et al. (1998) synthesised an even denser phase with the CaTi<sub>2</sub>O<sub>4</sub> structure, stable at higher pressures. Another candidate is a high-pressure modification of (Ca,Mg)Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub> with a hollandite-like structure (Madon et al. 1989).

Most attention has been paid to a possible high-pressure phase of Al<sub>2</sub>SiO<sub>5</sub>. Birle and Ehlers (1969) have studied high-pressure phase transition of Al<sub>2</sub>GeO<sub>5</sub> at 3.5 GPa and concluded that such a transition could occur in Al<sub>2</sub>SiO<sub>5</sub> at 15 GPa. Powder diffraction data on this phase did not allow the authors to identify the crystal structure of this new phase, although many of the diffraction lines can be indexed assuming the pseudobrookite structure (Oganov 1997). At the same time Ringwood and Reid (1969) showed that Al<sub>2</sub>GeO<sub>5</sub> decomposes to Al<sub>2</sub>O<sub>3</sub> + GeO<sub>2</sub> at high pressures and Liu (1974) found that a similar decomposition of kyanite into corundum (Al<sub>2</sub>O<sub>3</sub>) + stishovite (SiO<sub>2</sub>) at pressures 14–16 GPa and temperatures 1300–1700 K.

However, in the more recent works of Ahmed-Zaid and Madon (1991, 1995), a high-pressure form of Al<sub>2</sub>SiO<sub>5</sub> with the V<sub>3</sub>O<sub>5</sub>-type structure was found at 40–70 GPa and 2500 K. Lattice parameters were measured for this phase and, on the basis of these values and the composition, it was found that at atmospheric pressure the V<sub>3</sub>O<sub>5</sub>-type phase of Al<sub>2</sub>SiO<sub>5</sub> is 4.5% denser than the isochemical mixture of corundum and stishovite. The fact that this phase was formed as a high-pressure product in all studied samples of kyanite (Al<sub>2</sub>SiO<sub>5</sub>), anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), grossular (Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>) and pyrope (Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>), supported the idea that this phase might be the main host of Al in the lower mantle, comprising up to 5% of its volume. This is similar to the proportion of CaSiO<sub>3</sub>-perovskite and exceeds the vol-

ume of the Earth's crust by about 4 times! (This volume is sufficient to comprise a 125-km thick layer at depth of 2000 km or a 60-km thick layer at the surface of the Earth). More recent experiments on kyanite  $\text{Al}_2\text{SiO}_5$  (Gautron et al. 1997; Schmidt et al. 1997), however, have shown that this phase is not formed; instead, kyanite ( $\text{Al}_2\text{SiO}_5$ ) transforms into a mixture of corundum ( $\text{Al}_2\text{O}_3$ ) + stishovite ( $\text{SiO}_2$ ) at 25–75 GPa and  $T < 1900$  K according to Gautron et al. (1997) and at 14–17 GPa and 1300–2300 K according to Schmidt et al. (1997) and in close correspondence to earlier estimates (Liu 1974).

It is worth mentioning that quantum-mechanical simulations have already revealed many important insights into structure, dynamics and properties of the Earth's matter (Bukowinski 1994; Stixrude et al. 1998). Our work, employing the state-of-the-art quantum-mechanical *ab initio* simulation techniques, aims to check and rationalise contemporary experimental data and, therefore, to constrain possible variants of mineralogy of Al in the lower mantle of our planet.

In our calculations we consider simple oxides (corundum  $\text{Al}_2\text{O}_3$ , quartz and stishovite  $\text{SiO}_2$ ), and the modifications of  $\text{Al}_2\text{SiO}_5$ . The latter include both the observed (kyanite, andalusite, sillimanite) and the hypothetical phases, with octahedrally coordinated Al and Si:  $\text{V}_3\text{O}_5$ -like phase, proposed by Ahmed-Zaid and Madon (1991, 1995), and the pseudobrookite-like phase. The latter structure deserves attention because it is thermodynamically stable for many ternary transition-metal oxides (e.g., pseudobrookite  $\text{Fe}_2\text{TiO}_5$ , armalcolite  $\text{Ti}_2(\text{Fe},\text{Mg})\text{O}_5$ , karreroite  $\text{Ti}_2\text{MgO}_5$ , anosovite  $\text{Ti}_3\text{O}_5$ , tieilite  $\text{Al}_2\text{TiO}_5$ ,  $\text{Ti}_2\text{CoO}_5$ ,  $\text{Ga}_2\text{TiO}_5$ ,  $\text{Fe}_2\text{ZrO}_5$ ,  $\text{Sc}_2\text{TiO}_5$ ) and, presumably, was observed in high-pressure experiments on  $\text{Al}_2\text{GeO}_5$ . Figure 1 shows our theoretically calculated crystal structures of the hypothetical  $\text{V}_3\text{O}_5$ -like and pseudobrookite-like phases.

## Computational methodology

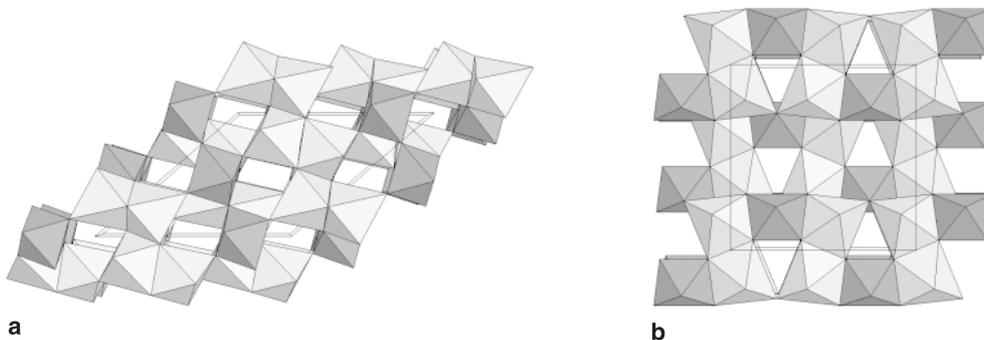
Depending on the number of atoms in the unit cell and the space group symmetry, the range in complexity of the calculations reported here varies from very simple (stishovite, space group  $P4_2/mnm$ , 6 atoms in the unit cell; quartz, space group  $P3_221$ , 9 atoms in the unit cell; corundum, space group  $R3c$ , 10 atoms in the unit cell)

through medium (pseudobrookite-like and  $\text{V}_3\text{O}_5$ -like phases, 16 atoms in the primitive unit cell, space groups  $Cmcm$  and  $C2/m$ , respectively) to quite complex ones (kyanite, andalusite, and sillimanite, 32 atoms in the unit cell, space groups  $P\bar{1}$ ,  $Pnmm$ , and  $Pbnm$ , respectively). Calculations on simple oxides were sufficiently small to be performed on a Silicon Graphics workstation; calculations on the silicate phases were performed on a 64-node parallel Cray T3E supercomputer in Edinburgh Parallel Computer Centre, atomic calculations were run on a Cray T3E in Manchester Computer Centre.

Our calculations were done with the VASP (Vienna *Ab initio* Simulation Package) code (Kresse and Furthmüller 1996a, b) and are based on density functional theory (Hohenberg and Kohn 1964; Kohn and Sham 1965) within the generalized gradient approximation (GGA; Wang and Perdew 1991) with valence electron wavefunctions being expanded in plane-wave basis set and all core electrons replaced by effective core pseudopotentials. All adopted pseudopotentials are non-local: norm-conserving pseudopotentials (Rappe et al. 1990) with partial core corrections (Louie et al. 1982) for Al and Si; non-normconserving (ultrasoft) pseudopotentials (Vanderbilt 1990) for O. Core region cutoffs are 0.96 Å for Al (valence configuration  $3s^23p^13d^0$ ), 0.95 Å for Si (valence configuration  $3s^23p^23d^0$ ), and 0.82 Å for O (valence configuration  $2s^22p^43d^0$ ). All these pseudopotentials are supplied with the VASP package.

$\text{Al}_2\text{SiO}_5$ -polymorphs are known to have very small energy differences ( $\sim 0.04$  eV per formula unit at ambient conditions); the resulting kinetic problems precluded precise experimental determination of the phase diagram of  $\text{Al}_2\text{SiO}_5$  for a long time (Zen 1969; Kerrick 1990). Therefore, care must be taken in order to reproduce these small effects correctly and reliably.

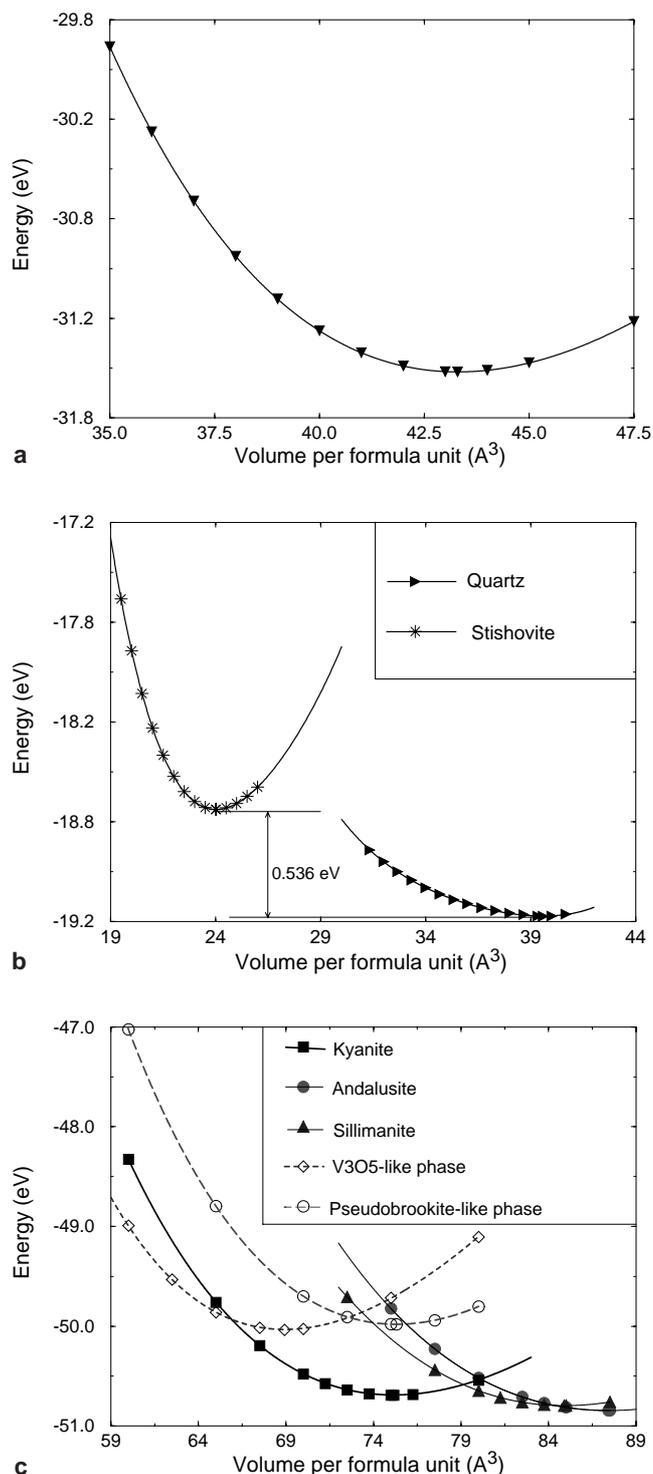
**Fig. 1a, b** Theoretically calculated crystal structures of the hypothetical high-pressure phases of  $\text{Al}_2\text{SiO}_5$ . Si-polyhedra are grey, Al-polyhedra are light grey. **a**  $\text{V}_3\text{O}_5$ -like structure. This structure is based on the hexagonal closest packing of oxygen atoms. Remarkable pairs of face-sharing octahedra tend to be occupied by Al rather than Si in order to reduce the cation-cation electrostatic repulsion (3<sup>rd</sup> and 4<sup>th</sup> Pauling's rules); this leads to the  $C2/c$  cation ordering shown here. **b** Pseudobrookite-like structure. This structure is not close packed, but contains only fragments ("islands") of close packing. Therefore, its density cannot be very high: it should be close to the density of the high-pressure  $\text{Al}_2\text{SiO}_5$ -melt. Interestingly, due to its topology, this structure in principle cannot be built from ideal Al-octahedra



A plane-wave cut-off energy of 800 eV proved very reliable (convergence to within  $6 \cdot 10^{-4}$  eV/atom) and computationally acceptable; this was used throughout all calculations. For Brillouin-zone sampling we used the Monkhorst-Pack scheme (Monkhorst and Pack 1976), and convergence of energy and stress with respect to the mesh density was tested for each mineral individually. k-point meshes used in our calculations, are  $4 \cdot 4 \cdot 4$  for corundum (10 symmetrically unique points) and stishovite (6 unique points),  $3 \cdot 3 \cdot 3$  for quartz (7 unique points), and  $2 \cdot 2 \cdot 2$  for all  $\text{Al}_2\text{SiO}_5$  phases (4 unique points for kyanite, 3 for  $\text{V}_3\text{O}_5$ -like phase, 2 for pseudobrookite-like phase, and 1 unique point for andalusite and sillimanite). Increasing these numbers did not lead to changes in total energy exceeding 0.01 eV per formula unit. The number of plane waves included in the calculation is roughly proportional to the unit cell volume, and for the most difficult cases – kyanite, andalusite, and sillimanite at equilibrium volumes – it was 15450, 17990, and 17430 plane waves per k-point, respectively.

The present calculations are static, performed in the athermal limit ( $T = 0$  K with no zero-point motion) with full symmetry-preserving relaxation of the lattice parameters and ionic positions. The energy minimisation procedure is iterative and proceeds until self-consistency within a prescribed tolerance ( $10^{-3}$  eV for ionic and  $10^{-4}$  eV for electronic relaxation). Stresses on the unit cell and forces on atoms, used for structure relaxation, are calculated from the charge density using the Hellmann-Feynman theorem. We used efficient constant-volume energy minimisation technique, which in VASP optimises all lattice parameters and ionic coordinates within the specified volume constraint. This technique reduces to minimum the effects of basis set incompleteness (e.g., basis set discontinuities during unit cell volume relaxation). As follows from the Hellmann-Feynman theorem, stresses and forces are more sensitive to errors due to incomplete convergence (of the wavefunction or of the atomic positions) than the energy: these errors, causing only second-order errors in the energy, lead to first-order errors in the stresses and forces. For quartz, which has loose structure with extremely flexible Si-O-Si tetrahedral linkages, errors due to incomplete convergence of atomic coordinates proved to be significant. Therefore, it may be more reasonable to obtain pressure indirectly, using thermodynamic formula  $P = -(dE/dV)$ , with fitted analytical  $E(V)$ -functions (we used 3<sup>rd</sup> and 4<sup>th</sup>-order polynomials). These analytical  $E(V)$ -curves, together with the original  $E(V)$ -datapoints, calculated by VASP, are shown on Fig. 2. The maximum difference found between the polynomial expansion and VASP points is 0.005 eV for all minerals considered, which is a good evidence for the high quality of our results. Typical differences for pressure are within 1–2 kbar (but for quartz they were larger by an order of magnitude).

There are three types of errors, affecting the precision our total energy calculations: (1) errors due to incomplete convergence with respect to the computational parameters (basis set incompleteness, limited Brillouin zone



**Fig. 2a–c** Calculated energy vs. volume curves. **a** Corundum, **b** Quartz and stishovite, **c**  $\text{Al}_2\text{SiO}_5$ -polymorphs (kyanite, andalusite, sillimanite,  $\text{V}_3\text{O}_5$ -like phase, pseudobrookite-like phase). Symbols indicate results of individual calculations, and lines are polynomial interpolations (*solid lines* real phases, *broken lines* hypothetical ones)

sampling, finite self-consistency thresholds), (2) pseudopotential errors, and (3) errors due to polynomial interpolations of the  $E(V)$ -curves. We estimate that the total energies are converged in all cases to within 0.02 eV

per formula unit. Our pseudopotentials are of very high quality (for O and Si it follows from the comparison with all-electron results – see below in Results section). The polynomial interpolation gives small (see above) random errors in the total energies. Most of the errors listed should be very well cancelled when calculating the energy differences between the phases.

One important quantity, which gives a direct check of ability of a computational method to simulate chemical bonding, is the binding (or atomisation) energy. Previous systematic study (Perdew et al. 1992), considering different exchange-correlation functionals, has shown good agreement between experimental and calculated (especially at the GGA level of theory) atomisation energies. In order to obtain absolute atomisation energies, we performed special calculations on atoms in their spin-polarised ground states using the same pseudopotentials, plane wave cutoff, and exchange-correlation functionals as before and large (15 Å side) primitive cubic unit cells. These calculations proved to be very demanding, since the basis set included over 173000 plane waves. It should be noted that the ground states for Al, Si and O were reproduced correctly. The atomic energies are converged to better than 0.01 eV/atom with respect to the unit cell size (this error is the same for all the polymorphs and, therefore, is cancelled exactly in the energy differences). Correction for the zero-point vibrational energy, necessary for rigorous calculations of the atomisation energy, was estimated in the ionic shell model with interatomic potentials (Sanders et al. 1984; Lewis and Catlow 1985) by means of GULP code (Gale 1997), diagonalising the dynamical matrix at 1000 reducible points of the Brillouin zone after complete structural relaxation.

## Results

Comparison between the calculated and experimental values of the equilibrium unit cell parameters and volumes, atomisation energies, bulk moduli,  $K_0$ , and their pressure derivatives  $K'$ , (which we obtained by fitting the Vinet equation of state (Vinet et al. 1989) to the calculated  $p(V/V_0)$ -points), is given in Table 2 together with theoretical data on the hypothetical phases of  $\text{Al}_2\text{SiO}_5$ . For the sake of brevity we do not list here atomic fractional coordinates, which are typically reproduced to within 0.001<sup>1</sup>. Theoretical predictions of atomisation energies are very good (underestimation by only about 1.1% (0.07 eV/atom) and 2.7% (0.17 eV/atom) without and with the zero-point energy correction, respectively). Theory overestimates the unit cell parameters and volume by a few percent; this noticeable error is typical for the GGA. However, when using reduced volumes ( $V/V_0$ ), equations of state are reproduced very well (Fig. 3).  $K_0$  and, frequently,  $K'$  are also in good agreement with experiment. The density differences between

phases are reproduced very accurately. The energy differences are more interesting (Table 3): it is interesting to observe that in absolutely all cases the lower-density phases (on the left hand sides of the reactions in Table 3) are relatively overstabilised. The underestimation of the atomisation energies (which correspond to the formation of condensed phases from a gas of infinitely separated atoms) by the GGA is the other side of the same effect. The reason for this error is, most probably, again in the limitations of the GGA. Tentatively, the forces, responsible for the overexpansion of structures in GGA, can also be responsible for the relative overestabilisation of polymorphs with more open structures. A direct consequence of this error is that in our calculations, in contrast to experiment, kyanite is not the thermodynamically stable phase at  $p = 0$  and  $T = 0$  K. Happily, application of pressure corrects this situation, increasing the relative stability of the denser polymorphs. As a result, the phase diagram of  $\text{Al}_2\text{SiO}_5$  (Fig. 4) is reproduced very well, all the calculated transition pressures being only ca. 20 kbar higher than the corresponding experimental values.

In recent all-electron study (Zupan et al. 1998), a similar effect of stabilisation of lower-density phases in GGA with respect to local spin density approximation (LSDA) was observed. It was concluded that both this effect and overexpansion of crystal structures in GGA are due to stabilisation of more inhomogeneous electron density distributions, characteristic of less dense structures, by gradient corrections. Results of all-electron calculations of Zupan et al. (1998) on quartz and stishovite (their structural parameters,  $K_0$  and  $K'$ ) are in excellent agreement with our pseudopotential study, highlighting the very high quality of the pseudopotentials used in our work.

Enthalpy vs pressure curves  $H(p)$ , calculated using fitted polynomial  $H(p)$ -curves, are represented on Fig. 5. From Figs. 2 and 5 it is obvious that the pseudobrookite structure cannot be thermodynamically stable for  $\text{Al}_2\text{SiO}_5$  and becomes increasingly less stable at high pressures. It can also be seen that kyanite, which in our simulations becomes the most stable phase at 19 kbar, transforms into the mixture of corundum and stishovite at 113 kbar (compare with 95 kbar extrapolated to  $T = 0$  K from experimental data of Schmidt et al. (1997) or 150 kbar from earlier estimates of Liu 1974).

$\text{V}_3\text{O}_5$ -like structure becomes more favourable than kyanite at 205 kbar, but appears to be less stable than corundum + stishovite assembly at all pressures in the range between 0 and 1500 kbar. Vibrational entropy is extremely unlikely to stabilise this phase at the temperatures of the Earth's mantle, since the enthalpy of its decomposition is quite large (−0.47 to −0.61 eV at 400 to 700 kbar and −0.83 eV at 1500 kbar). The maximum configurational entropy, assuming complete Al-Si disordering in octahedral sites,  $\Delta S_{conf}^{\max} = -3R[\frac{1}{3}\ln(\frac{1}{3}) + \frac{2}{3}\ln(\frac{2}{3})] = 15.87 \text{ J}/(\text{mol}\cdot\text{K})$ , can make the disordered  $\text{V}_3\text{O}_5$ -like phase stable to decomposition only at temperatures higher than  $T = 2900\text{--}5000$  K. Since Al-Si

<sup>1</sup> Full tables with comparison of the calculated and experimental atomic coordinates can be obtained from the authors

**Table 2** Phases in the Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system: theoretical results and experimental data**A. Simple Oxides****B. Known Al<sub>2</sub>SiO<sub>5</sub> polymorphs**

Property	VASP	Experiment	Property	VASP	Experiment
<b>Corundum</b> (space group $R\bar{3}c$ ; $Z = 6^a$ )			<b>Kyanite</b> (space group $P\bar{1}$ ; $Z = 4^a$ )		
$a_0 = b_0, \text{Å}$	4.811	4.7570 <sup>b</sup>	$a_0, \text{Å}$	7.185	7.1262 <sup>l</sup>
$c_0, \text{Å}$	13.072	12.9877 <sup>b</sup>	$b_0, \text{Å}$	7.916	7.8520 <sup>l</sup>
$V_0, \text{Å}^3$	259.77	254.52 <sup>b</sup>	$c_0, \text{Å}$	5.613	5.5724 <sup>l</sup>
$K_0, \text{GPa}$	233	254.4 <sup>c</sup> ; 258 <sup>d</sup>	$\alpha, ^\circ$	89.9	89.99 <sup>l</sup>
$K'$	3.99	4.275 <sup>c</sup> ; 4.88 <sup>d</sup>	$\beta, ^\circ$	101.1	101.11 <sup>l</sup>
$E_{\text{atom.}}, \text{eV}$	-31.518 (-31.04) <sup>e</sup>	-31.73 <sup>f</sup>	$\gamma, ^\circ$	106.0	106.03 <sup>l</sup>
<b>Stishovite</b> (space group $P4_2/mnm$ ; $Z = 2^a$ )			$V_0, \text{Å}^3$	300.64	293.60 <sup>l</sup>
$a_0 = b_0, \text{Å}$	4.229	4.1801 <sup>g</sup>	$K_0, \text{GPa}$	172	156 <sup>m</sup> ; 193 <sup>n</sup>
$c_0, \text{Å}$	2.687	2.6678 <sup>g</sup>	$K'$	4.01	5.6 <sup>m</sup> ; [4] <sup>n</sup>
$V_0, \text{Å}^3$	48.04	46.615 <sup>g</sup>	$E_{\text{atom.}}, \text{eV}$	-50.692 (-49.91) <sup>e</sup>	-51.27 <sup>f</sup>
$K_0, \text{GPa}$	265	306 <sup>g</sup> ; 313 <sup>h</sup>	<b>Andalusite</b> (space group $Pnnm$ ; $Z = 4^a$ )		
$K'$	4.88	2.8 <sup>g</sup> ; 6 <sup>h</sup>	$a_0, \text{Å}$	7.860	7.7980 <sup>l</sup>
$E_{\text{atom.}}, \text{eV}$	-18.687 (-18.40) <sup>e</sup>	-19.08 <sup>i</sup>	$b_0, \text{Å}$	7.956	7.9031 <sup>l</sup>
<b>Quartz</b> (space group $P3_221$ ; $Z = 3^a$ )			$c_0, \text{Å}$	5.592	5.5566 <sup>l</sup>
$a_0 = b_0, \text{Å}$	4.9943	4.91239 <sup>j</sup>	$V_0, \text{Å}^3$	349.68	342.45 <sup>l</sup>
$c_0, \text{Å}$	5.4979	5.40385 <sup>j</sup>	$K_0, \text{GPa}$	142	135 <sup>o</sup> ; 151 <sup>p</sup>
$V_0, \text{Å}^3$	118.76	112.933 <sup>j</sup>	$K'$	4.18	[4] <sup>o</sup> ; [4] <sup>p</sup>
$K_0, \text{GPa}$	44.3	37.12 <sup>k</sup>	$E_{\text{atom.}}, \text{eV}$	-50.844 (-50.07) <sup>e</sup>	-51.23 <sup>f</sup>
$K'$	3.20	5.99 <sup>k</sup>	<b>Sillimanite</b> (space group $Pbnm$ ; $Z = 4^a$ )		
$E_{\text{atom.}}, \text{eV}$	-19.224 (-18.92) <sup>e</sup>	-19.467 <sup>f</sup>	$a_0, \text{Å}$	7.555	7.4883 <sup>l</sup>
			$b_0, \text{Å}$	7.756	7.6808 <sup>l</sup>
			$c_0, \text{Å}$	5.795	5.7774 <sup>l</sup>
			$V_0, \text{Å}^3$	339.57	332.29 <sup>l</sup>
			$K_0, \text{GPa}$	159	171 <sup>p</sup>
			$K'$	2.70	[4] <sup>p</sup>
			$E_{\text{atom.}}, \text{eV}$	-50.795 (-50.01) <sup>e</sup>	-51.19 <sup>f</sup>

<sup>a</sup>  $Z$  is the number of formula units in the unit cell

<sup>b</sup> Kirfel and Eichhorn (1990)

<sup>c</sup> d'Amour et al. (1978)

<sup>d</sup> Dubrovinsky et al. (1998)

<sup>e</sup> Numbers in parentheses include the zero-point energy correction. In the ionic model, the V<sub>3</sub>O<sub>5</sub>-like phase spontaneously transformed into another structure, obstructing estimation of the zero-point energy correction for this phase

<sup>f</sup> Recalculated from (Olbricht et al. 1994)

<sup>g</sup> Ross et al. (1990)

<sup>h</sup> Sugiyama et al. (1987)

<sup>i</sup> estimated from the data (Olbricht et al. 1994) on quartz and the most recent data on  $\Delta H$  of quartz-stishovite transformation (0.384 eV) (Akaogi et al. 1995)

<sup>j</sup> Will et al. (1988)

<sup>k</sup> Angel et al. (1997).

<sup>l</sup> Winter and Ghose (1979)

<sup>m</sup> Comodi et al. (1997)

<sup>n</sup> Yang et al. (1997a).  $K'$  fixed equal 4

<sup>o</sup> Ralph et al. (1984).  $K'$  fixed equal 4

<sup>p</sup> Yang et al. (1997b).  $K'$  fixed equal 4

disordering is associated with local charge imbalance, it should significantly raise the enthalpy of this phase, shifting its stability field towards even higher temperatures not available in the Earth's mantle.

While stability considerations still leave some possibility for the V<sub>3</sub>O<sub>5</sub>-like phase to be stable at very high temperatures, consideration of lattice parameters and density lead us to the conclusion that this phase has never been synthesised. We predict (Table 3) that the V<sub>3</sub>O<sub>5</sub>-like phase should be 2.3% less dense than the corundum + stishovite mixture; this is in contradiction to the results of Ahmed-Zaid and Madon (1991), who found that their phase (identified as the V<sub>3</sub>O<sub>5</sub>-structured phase of Al<sub>2</sub>SiO<sub>5</sub>) was 4.5% denser than the oxide mixture. The difference in the unit cell volume of the V<sub>3</sub>O<sub>5</sub>-like phase between our calculations and results of Ahmed-Zaid and Madon (1991) is 11%, which is well beyond the errors of our method. Lattice parameters, obtained in the latter experiment, differ strikingly from

ours (Table 2); however, care must be taken since for monoclinic crystals (e.g., V<sub>3</sub>O<sub>5</sub>) three alternative settings of the coordinate system – “cell choices” (International Tables for Crystallography 1994) – are possible. Simple matrix transformations allow one to change cell choice. All these cell choices are listed in Table 2. Cell choice 2 resembles results of Ahmed-Zaid and Madon (1991) ( $a_0 = 8.478 \text{ Å}$ ,  $b_0 = 4.471 \text{ Å}$ ,  $c_0 = 6.782 \text{ Å}$ ,  $\beta = 104.25^\circ$ ;  $V_0 = 249.08 \text{ Å}^3$ ) more than the others, however, the differences, especially in the  $a_0$ -parameter, are irreconcilable. We believe, therefore, that the phase synthesised by Ahmed-Zaid and Madon (1991) is unlikely to be a V<sub>3</sub>O<sub>5</sub>-like polymorph of Al<sub>2</sub>SiO<sub>5</sub>.

We have also studied a variant of V<sub>3</sub>O<sub>5</sub>-like structure with space group  $P2/c$ , differing in the distribution of Al and Si in octahedral sites. In this structure, due to the symmetry lowering, there are four (instead of two) non-equivalent cationic positions. This variant can be produced from the  $C2/c$ -variant by exchanging positions of

### C. Hypothetical polymorphs of $\text{Al}_2\text{SiO}_5$

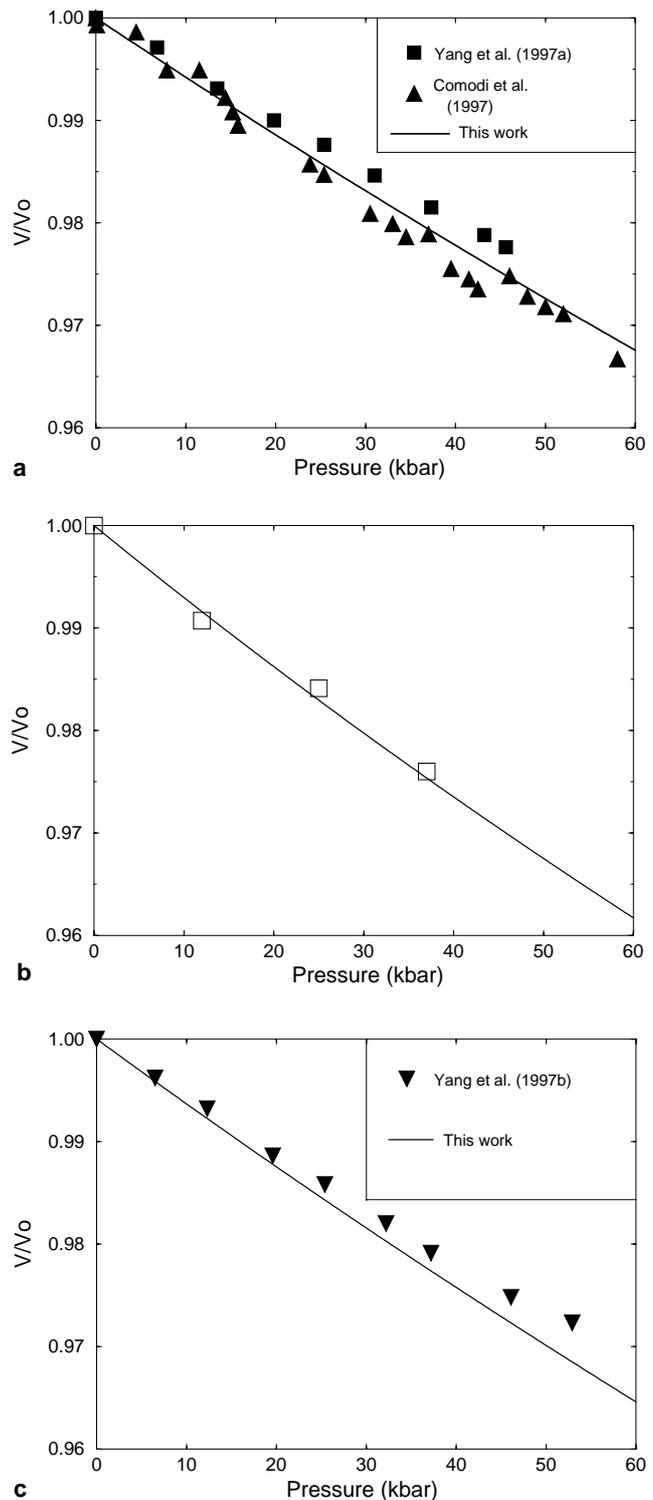
Property	VASP		
<b>Pseudobrookite-like phase</b>			
(space group $Cmcm$ ; $Z = 4^a$ )			
$a_0, \text{\AA}$	3.552		
$b_0, \text{\AA}$	9.261		
$c_0, \text{\AA}$	9.158		
$V_0, \text{\AA}^3$	301.26		
$K_0, \text{GPa}$	218		
$K'$	3.55		
$E_{\text{atom.}}, \text{eV}$	-49.982 (-49.23) <sup>c</sup>		
<b><math>\text{V}_3\text{O}_5</math>-like phase</b>			
(space group $C2/c$ ; $Z = 4^a$ )			
	Cell choice 1	Cell choice 2	Cell choice 3
$a_0, \text{\AA}$	9.474	9.312	6.676
$b_0, \text{\AA}$	4.705	4.705	4.705
$c_0, \text{\AA}$	9.312	6.676	9.474
$\beta, ^\circ$	137.98	109.51	112.11
$V_0, \text{\AA}^3$		275.68	
$K_0, \text{GPa}$		227	
$K'$		4.08	
$E_{\text{atom.}}, \text{eV}$		-50.038 <sup>c</sup>	

Si and one half of Al atoms. This structure is much higher in energy than the  $C2/c$ -variant ( $\Delta E = 0.23 \text{ eV}$ ) and somewhat less dense ( $\Delta V = 0.30 \text{ cm}^3/\text{mol}$ ). Therefore, it should not be expected as a candidate high-pressure phase. Its equilibrium lattice parameters are in a similarly striking disagreement with data of Ahmed-Zaid and Madon (1991). Quite large value of  $\Delta E = 0.23 \text{ eV}$  shows that the energy cost of Al-Si disordering in this structure is high.

Based on the data from the paper by Ahmed-Zaid and Madon (1991) and on the present results, we doubt that the Ahmed-Zaid and Madon's phase is at all a polymorph of  $\text{Al}_2\text{SiO}_5$ . The other variant, more consistent with the experimental unit cell volume, is  $\text{Al}_8\text{Si}_3\text{O}_8$  (isochemical mixture of corundum and stishovite at ambient pressure would have the molecular volume of  $239.6 \text{ \AA}^3$ ). It should be possible to determine what structure and composition match the experimental lattice parameters, using the newly developed genetic algorithms technique (Bush et al. 1995).

### Discussion

Using *ab initio* calculations, we have demonstrated that kyanite,  $\text{V}_3\text{O}_5$ -like and pseudobrookite-like phases of  $\text{Al}_2\text{SiO}_5$  are unstable with respect to decomposition into simple oxides, corundum ( $\text{Al}_2\text{O}_3$ ) and stishovite ( $\text{SiO}_2$ ) at high pressures. It was recently discovered that



**Fig. 3a-c**  $P(V)$ -equations of state. **a** Kyanite; **b** Andalusite. Empty squares experimental data of Ralph et al. (1984) corrected by Yang et al. (1997b); **c** Sillimanite. Solid lines theoretical results (present work)

both corundum and stishovite are not the most stable phases of the corresponding oxides at high pressures and should undergo phase transitions. Corundum is transformed into a phase with the  $\text{Rh}_2\text{O}_3(\text{II})$ -type

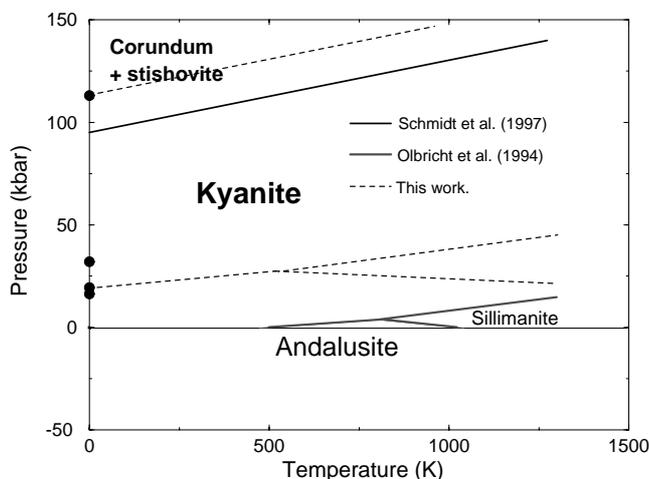
**Table 3** The energy and volume effects of mineral transformations at zero pressure: theory and experiment

Reaction	$\Delta E$ , eV	Experiment	$\Delta V_m$ , cm <sup>3</sup> /mol	Experiment
	VASP		VASP	
Andalusite $\rightarrow$ Sillimanite	0.05 (0.06) <sup>a</sup>	0.04	-1.5	-1.5
Andalusite $\rightarrow$ Kyanite	0.15 (0.16) <sup>a</sup>	-0.04	-7.4	-7.4
Quartz $\rightarrow$ Stishovite	0.54 (0.51) <sup>a</sup>	0.38 <sup>b</sup> ; 0.51 <sup>c</sup>	-9.4	-8.6
Andalusite $\rightarrow$ Corundum + Quartz	0.10 (0.11) <sup>a</sup>	0.03	-2.7	-3.3
Kyanite $\rightarrow$ Corundum + Stishovite	0.49 (0.46) <sup>a</sup>	0.46	-4.7	-4.6

<sup>a</sup> Numbers in parentheses include the zero-point energy correction, which proved to be small enough for the energy differences and was neglected in all our further calculations.

<sup>b</sup> Akaogi et al. (1995)

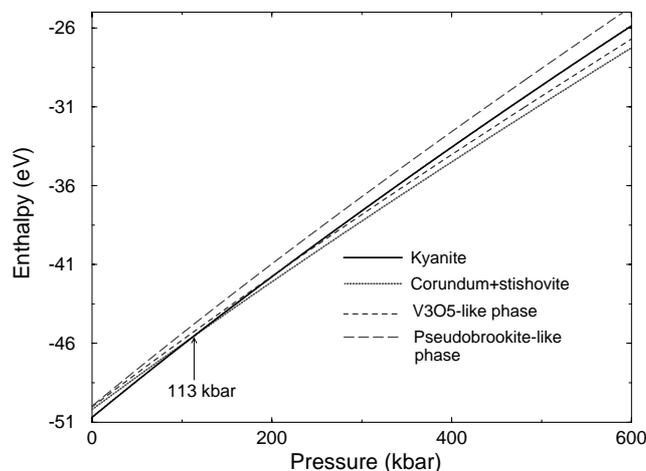
<sup>c</sup> Holm et al. (1967)



**Fig. 4** Phase diagram of  $\text{Al}_2\text{SiO}_5$ . Solid lines experimental data, filled circles calculated transition pressures at  $T = 0$  K, and broken lines were drawn through these points with experimental  $P(T)$ -slopes of equilibria kyanite-(corundum + stishovite), kyanite-andalusite, and kyanite-sillimanite. These data are sufficient to determine the  $P(T)$ -slope of andalusite-sillimanite equilibrium

structure at 80–100 GPa (experiment: Funamori and Jeanloz 1997; theory: Marton and Cohen 1994; Duan et al. 1998), and stishovite transforms into a phase with the  $\text{CaCl}_2$ -type structure at ca. 50 GPa (experiment: Kingma et al. 1995; theory: Karki et al. 1997); there are also theoretical predictions of further phase transitions for both minerals at higher pressures. All these phase transitions occur at much higher pressures than the decomposition of kyanite into corundum and stishovite and, therefore, do not change our calculated phase diagram, but only enhance our conclusion for very high pressures, where even more stable oxide phases appear.

Our results, concerning the hypothetical phases, can be rationalised in terms of classical crystal chemistry. It turns out that the  $\text{V}_3\text{O}_5$ -like phase does not satisfy Pauling's second rule (sum of the electrostatic bond valences on the anion should be equal to the anion's valence). It is easy to check that this rule cannot be satisfied by any composite phase in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system with octahedrally coordinated Al and Si. As has been shown by Brown (1992), structures that do



**Fig. 5** Calculated enthalpy vs pressure curves for kyanite and high-pressure candidate phases. Pressure of kyanite  $\rightarrow$  (corundum + stishovite) transformation is indicated by arrow

not satisfy the second Pauling's rule must undergo distortions, quantified by the modified Pauling's rule, proposed by Brown (1992). Apart from such electronic effects as Jahn-Teller effect, these distortions are usually destabilising. The distortion also results in an increase in the average bond lengths (the "distortion theorem" of Brown 1992, implied by the Brown's rule) that may decrease the density of the structure. In contrast to  $\text{V}_3\text{O}_5$ -like and pseudobrookite-like phases, corundum and stishovite satisfy Pauling's rule exactly. This partially explains the higher energy and lower density of the hypothetical  $\text{Al}_2\text{SiO}_5$ -phases with respect to the mixture of corundum and stishovite.

On the other hand, it is well known that the formation of complex oxides and silicates from the constituent oxides is favoured when cations differ significantly in the electronegativities (Urusov 1993) and ionic radii (e.g.,  $\text{MgO} + \text{SiO}_2 \rightarrow \text{MgSiO}_3$  due to significant differences in the electronegativities and ionic radii of Mg and Si). In other terms, the formation of the complex compounds is strongly favoured if the constituent components have different acid-base properties and can play different (crystal)-chemical roles. At high pressures both  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  adopt octahedral coordination and cannot play sig-

nificantly different structural roles anymore. As a result, pure Al-silicates are likely to break down, as in the case considered here. In contrast, aluminosilicates of large and electropositive cations (Ca, Mg, Na, K), e.g., the hollandite-like phase of  $(\text{Ca}, \text{Mg})\text{Al}_2\text{Si}_2\text{O}_8$ , or the high-pressure modifications of  $\text{MgAl}_2\text{O}_4$ , could be stable at the lower mantle conditions and present possible hosts of Al in the lower mantle, unless Al prefers to form  $(\text{Mg}, \text{Fe})(\text{Si}, \text{Al})\text{O}_3$ -perovskite solid solutions<sup>2</sup>.

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<sup>2</sup> Note, however, that both arguments (Pauling's second rule and acid-base properties of cations) are purely energetic and do not apply to the entropy. Therefore, although the octahedral Al-silicates are unfavoured energetically, they may be stabilised by the configurational entropy of Al-Si disorder at high temperatures. In the particular case of the  $\text{V}_3\text{O}_5$ -like modification of  $\text{Al}_2\text{SiO}_5$  we have shown that the mantle temperatures are insufficient to stabilise it. Generally, one can expect that Al-Si disordering in  $(\text{Mg}, \text{Fe})(\text{Si}, \text{Al})\text{O}_3$ -perovskite, with Al as a minor element, would produce greater net entropic effect than in any phase with both Al and Si as major components.

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