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***Ab initio* study of the high-pressure behavior of CaSiO₃ perovskite**

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Abstract Using density functional simulations, within the generalized gradient approximation and projector-augmented wave method, we study structures and energetics of CaSiO₃ perovskite in the pressure range of the Earth's lower mantle (0–150 GPa). At zero Kelvin temperature the cubic (*Pm* $\bar{3}m$) CaSiO₃ perovskite structure is unstable in the whole pressure range, at low pressures the orthorhombic (*Pnam*) structure is preferred. At 14.2 GPa there is a phase transition to the tetragonal (*I4/mcm*) phase. The CaIrO₃-type structure is not stable for CaSiO₃. Our results also rule out the possibility of decomposition into oxides.

Keywords *Ab initio* · CaSiO₃ perovskite · Decomposition · Phase transition · SiO₂ · CaO · Post-perovskite structure

Introduction

CaSiO₃ perovskite is thought to constitute between 6 wt% and 12 wt% of the Earth's lower mantle (Irfune 1994; O'Neill and Jeanloz 1990; Ita and Stixrude 1992) and is the third most abundant phase after (Mg,Fe)SiO₃ perovskite (~70%) and magnesiowüstite (Mg,Fe)O (~20%), under the assumption that the lower mantle is pyrolytic. It is, however, very difficult to perform detailed structural studies at lower-mantle pressures (up to 136 GPa) in the laboratory. A feasible solution to these

problems is to use quantum-mechanical simulations. Here we investigate the structural stability of CaSiO₃ at high pressures. These results are important for the understanding of the physics and chemistry of the mantle phase; its phase stability, elasticity, and its ability to incorporate other cations such as Mg, Fe, and Al, for example, will be affected by its structure. Phase transitions in lower-mantle constituents have important implications for the understanding of recent seismological observations of reflective features within the lower mantle near 700, 900, 1,200 and 1,700 km depths (Vinnik et al. 2001). These observations might indicate the presence of previously unpredicted phase transitions (e.g., CaSiO₃-perovskite phase transition in the lower mantle, Stixrude et al. 1996), sharply bounded compositional heterogeneities, transition of the Fe²⁺ from high-spin to low-spin or the decomposition of perovskites.

The structure of CaSiO₃ perovskite in the pressure regime of the lower mantle is disputed (Table 1); some claim it to be cubic with no detectable deviations of the diffraction pattern from cubic symmetry (Mao et al. 1989; Wang et al. 1996). Theoretical studies based on ionic models (Wolf and Jeanloz 1985; Wolf and Bukowski 1987), periodic Hartree-Fock (Sherman 1993), pseudopotential density functional theory calculations (Wentzcovitch et al. 1995; Warren et al. 1998) have supported this picture. However there are studies which find the cubic structure to be unstable. First-principles simulation based on linearized augmented plane wave (LAPW) with the local density approximation (LDA) (Chizmeshya et al. 1996; Stixrude et al. 1996), LDA muffin-tin calculations (Magyari-Köpe et al. 2002a, b), synchrotron X-ray diffraction (Shim et al. 2002) and variationally induced breathing model calculations (Akber-Knutson et al. 2002) support this picture. There is almost no doubt that even if the cubic phase is dynamically unstable at low temperatures, at mantle temperatures it will be stabilized by entropy. However, the ability to reproduce the small structural distortion (or its absence) is an interesting test of theoretical methods.

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Table 1 Comparison of previous studies of CaSiO₃ with this work

Author	Structure	Method
Wentzcovitch et al. (1995)	Cubic	LDA pseudopotential calculation
Chizmeshya et al. (1996)	Cubic is dynamically unstable tetragonal	LDA linearized augmented plane wave
Stixrude et al. (1996)	Cubic is dynamically unstable at all pressures; tetragonal	Linearized augmented plane wave linear response calculations with LDA
Warren et al. (1998)	Cubic	LDA pseudopotential calculation
Shim et al. (2000b)	Cubic; but could be tetragonal if ratio change $c/a < 0.7\%$	Energy dispersive X-ray diffraction in diamond anvil cell
Magyari-Köpe (2002a)	Orthorhombic	LDA muffin-tin calculations
Magyari-Köpe (2002b)	Orthorhombic	LDA muffin-tin calculations
Shim et al. (2002)	Tetragonal	High-resolution synchrotron energy dispersive X-ray diffraction in diamond anvil cell
Akber-Knutson et al. (2002)	Orthorhombic	Variationally induced breathing method
Ono et al. (2004); Kurashina et al. (2004)	Low temperature: tetragonal, high temperature: cubic	In situ X-ray in laser heated diamond anvil cell
This study	Orthorhombic up to 14.2 GPa, then tetragonal	Density functional theory with GGA-PAW method

Another possibility, which has been considered so far, is that CaSiO₃ could form the CaIrO₃ structure, recently found to be stable for MgSiO₃ (Oganov and Ono 2004; Murakami et al. 2004).

This work is the first *ab initio* study to investigate the decomposition of CaSiO₃ perovskite in the pressure range of the lower mantle. This decomposition was suggested as a possibility by Yamanaka et al. (2002). Our calculations are based on the generalized gradient approximation (GGA; Perdew et al. 1996) and the all-electron projector augmented wave (PAW) (Blöchl 1994; Kresse and Joubert 1999; Blöchl et al. 2003) method, which is a very accurate method for solving the total energy problem. Previous theoretical studies were concerned with decomposition of related materials: MgSiO₃ perovskite (Oganov and Price 2005), MgAl₂O₄ (Catti 2001) and Al₂SiO₅ (Oganov and Brodholt 2000).

Computational methodology

Present calculations have been performed with the VASP code (Kresse and Furthmüller 1996). Local density approximation (LDA) and generalized gradient approximation (GGA) (Perdew et al. 1996) have been used for comparison. Within the LDA, the exchange-correlation energy density at the point r is calculated using only the electronic density at point ρ . Within the GGA, some nonlocality is introduced by taking into account also the gradient $\nabla\rho$ of the electronic density. LDA typically overestimates the cohesive energies and lattice parameters are underestimated (1%). GGA improves the description of the core electrons and the total energies and energy differences are better than with the LDA. However, the bond lengths are overestimated (~1%). Phase transition pressures are usually underestimated by several GPa within the LDA, and are very close to the experimental values (or slightly higher) in the GGA (Zupan et al. 1998; Oganov and Brodholt 2000). For a more detailed view on this topic, see Oganov et al. (2002).

The projector augmented wave is a mix between pseudopotential and all-electron method. The big advantage of this method is the accuracy of an all-electron method at the low cost of a pseudopotential method. The interested reader is referred to Blöchl (1994), Kresse and Joubert (1999) and Blöchl et al. (2003). The use of the combined GGA-PAW method enables us to do, firstly, more accurate *ab initio* calculations on energies and structure than with the LDA and, secondly, to do this with a reasonable amount of computer power.

In all calculations, we used the following PAW potentials for the GGA method: Core region cut-off is 2.3 a.u.¹ for Ca (core configuration 1s² 2s² p⁶), 1.5 a.u. for silicon (core configuration 1s² 2s² p⁶) and 1.52 a.u. for oxygen (core configuration 1s²). For the LDA calculations, the potentials are: Core region cut-off is 2.3 a.u. for Ca (core configuration 1s²), 1.6 a.u. for silicon (core configuration 1s² 2s² p⁶) and 1.52 a.u. for oxygen (core configuration 1s²).

A plane wave cut-off energy of 500 eV² for all calculations proved to be reliable (convergence of energy to within 5×10^{-2} eV per f.u.,³ convergence of pressure to within 0.3 GPa) and computationally acceptable. More important is that the energy differences converge to within 8×10^{-4} eV per f.u. which allow us to do precise calculations. For the 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 structure individually. The convergence of pressure for all structures was better than 0.2 GPa. The k -point meshes used here are $8 \times 8 \times 8$ (convergence of energy to within 7×10^{-5} eV/f.u.) for both CaO structures, $4 \times 4 \times 6$ (convergence of energy to within 2×10^{-4} eV/f.u.) for the stishovite and the CaCl₂-structured phase, $4 \times 4 \times 4$ (convergence of energy to within 2×10^{-3} eV/f.u.), for the α -PbO₂ structure

¹In the atomic units, the unit of length is 1bohr = 0.529 Å

²1 eV = 1.602×10^{-19} J = 96.485 kJ/mol

³f.u. = formula unit

cubic ($Pm\bar{3}m$) structure, the tetragonal ($I4/mcm$) distorted case and finally the orthorhombic ($Pnam$) structure. Figure 3 shows the structures in z and x directions. The structure types depend only on the tilting of the octahedra. The cell and the coordinates of the asymmetric unit are shown in Table 4.

We optimized the structures and calculated enthalpies at pressures from 0 GPa to 150 GPa. Figure 4 shows the enthalpy difference (relative to cubic structure) versus pressure. This gives us an orthorhombic structure at low pressures. The phase transition to tetragonal takes place at 14.2 GPa. However, we note that at low pressures the two are energetically very similar. The cubic structure is never stable in the whole pressure range.

Table 1 shows some results from earlier measurements and calculations. In present calculations the difference between the orthorhombic phase and the cubic one is 13 meV/f.u. at 0 GPa and 16 meV/f.u. between

Table 4 Structures of the 20 atom cell of CaSiO_3 at 100 GPa

Perovskite structure			
Cubic $Pm\bar{3}m$			
Cell (Å) (4.667/4.667/6.600)			
Ca	0.500	0.000	0.250
Si	0.000	0.000	0.000
O	0.000	0.000	0.250
Tetragonal $I4/mcm$			
Cell (Å) (4.644/4.644/6.664)			
Ca	0.500	0.000	0.250
Si	0.000	0.000	0.000
O	0.000	0.000	0.250
O	0.277	0.223	0.000
Orthorhombic $Pnam$			
Cell (Å) (4.660/4.691/6.573)			
Ca	0.500	0.500	0.250
Si	0.000	0.500	0.500
O	0.000	0.535	0.250
O	0.250	0.750	0.982

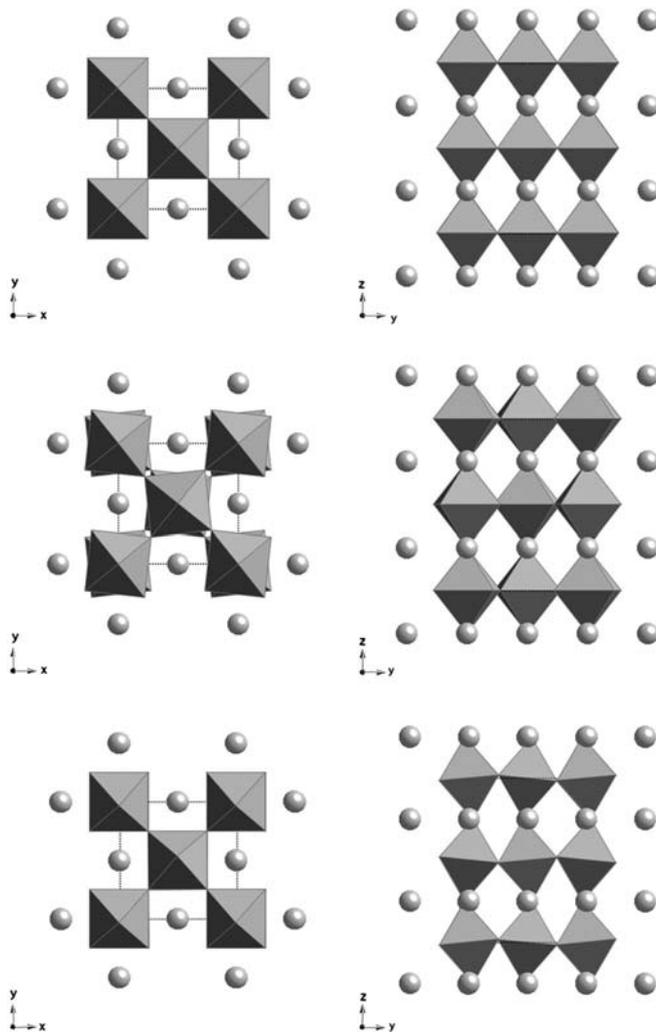


Fig. 3 CaSiO_3 perovskite: cubic, tetragonal and orthorhombic structure, in z direction on the left and in x direction on the right. Calcium can be seen as balls, whereas the oxygen and the silicon form octahedra

tetragonal and cubic phase at 80 GPa. Magyari-Köpe et al. (2002b) found the difference to be 63 meV/f.u. between orthorhombic and cubic at 0 GPa and Stixrude et al. (1996) calculated 27 meV/f.u. between tetragonal and cubic at 80 GPa. The tetragonal distortion in our calculation shows a c/a ratio of 1.012–1.017, rising with pressure (c in the ratio above is from the primitive setting, this is equal to the c of our 20-atom supercell divided by $\sqrt{2}$). Shim et al. (2002) found a c/a ratio of 0.993–0.996. Ono et al. (2004) found a c/a ratio of 0.997–0.993, diminishing with pressure. Thus, we see a contradiction between theory and experiment regarding the sign of the distortion. In our calculations the c -axis is bigger than a , because the a axis can only become smaller with the tilting of the silicate octahedra for $I4/mcm$. However, both theory and experiment indicate a tetragonal distortion increasing slightly with pressure.

The fact that Magyari-Köpe et al. (2002) used a different method to get the orthorhombic structure in their calculations might be the source of the discrepancy in enthalpy difference (63 meV/f.u. at 0 GPa). Calculations

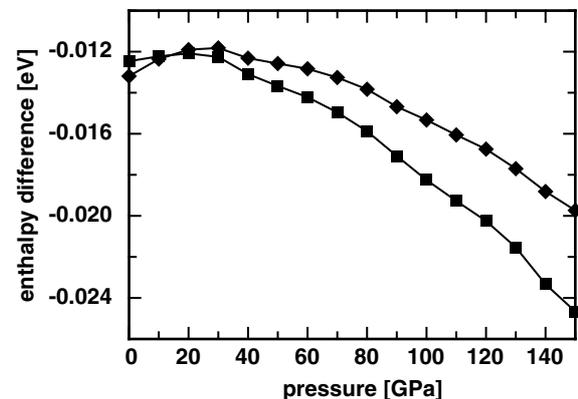


Fig. 4 Enthalpy differences of CaSiO_3 (1 f.u.) between the tetragonal and the cubic (squares), orthorhombic and cubic (diamonds) structure

with the LDA gave us a slightly larger enthalpy difference: our LDA calculations result in about 16 meV/f.u. at 0 GPa and at 80 GPa the LDA enthalpy difference is 24 meV/f.u., which is close to the 27 meV/f.u. from Stixrude et al. (1996). As in the results of Stixrude et al. (1996) the enthalpy difference is so small that a temperature corresponding to the lower mantle can induce a phase transition to the cubic structure. Latest experiments (Ono et al. 2004, Kuurashina et al. 2004) show a tetragonal structure at low temperatures and a cubic structure at high temperatures.

Third order Birch-Murnaghan equation of state fitting of our results gave a good agreement with other experimental and theoretical studies; see Table 5. The results concerning the V_0 of Wolf and Jeanloz (1985) and Wolf and Bukowinski (1987) are higher than the rest. This can be explained by the fact that they did not use *ab initio* methods fully and had to use models which introduced a certain amount of ambiguity. In the last 20 years, *ab initio* methods have increased their accuracy and power to predict structures in the same degree as the methods and the computer power have advanced.

Figure 5 shows the volume versus pressure equation of state. Our GGA calculations tend to overestimate the volume whereas LDA calculations underestimate the volume. The experimental points lie in between these lines. One exception is the dashed-dotted line in the p-V graph (Wentzcovitch et al. 1995), which diverges at high pressures from the other calculations. Although Wentzcovitch et al. (1995) used pseudopotentials with partial core correction, their result performs badly versus the all-electron methods, reflecting the difficulties in constructing reliable pseudopotentials for Ca.

The question why most of the previous studies differ in the structure of CaSiO_3 perovskite may be answered by the fact that the enthalpy differences are really small. They are in the meV range (1 meV corresponds to about 11.6 K). Additionally, the structural distortion from the ideal cubic case is also small, the c/a ratio differs from 1 only by about one or two percent. Many errors and uncertainties, such as approximations used for

Table 5 Comparison of previous studies of CaSiO_3 with this work

EOS third order BM	V_0 (\AA^3)	K_0 (GPa)	K'
Theory			
Wolf and Jeanloz (1985)	56.13	269.5	3.86
Wolf and Bukowinski (1987)	55.74	263	4.13
Wentzcovitch et al. (1995)	46.15	254	4.4
Chizmeshya et al. (1996)	45.62	227	4.29
Akber-Knutson et al. (2002)	45.90 ± 0.02	228 ± 2	4.3 ± 0.1
Magyary-Köpe et al. (2002b)	45.69	216	4.82
This work orthorhombic	46.90	219.16	4.08
This work tetragonal	46.89	219.04	4.08
Experiment			
Tamai and Yagi (1989)	45.58 ± 0.07	352 ± 10	4
Mao et al. (1989)	45.37 ± 0.08	281 ± 4	4
Wang et al. (1996)	45.58 ± 0.04	232 ± 8	4.8 ± 0.3
Shim et al. (2002)	45.58	255 ± 5	4
Ono et al. (2004)	45.38	248 ± 8	4

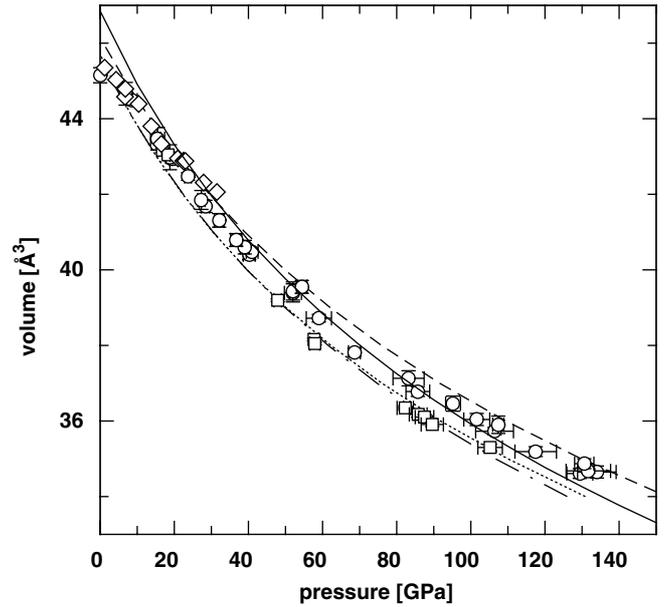


Fig. 5 Pressure versus volume with third order Birch-Murnaghan equation of state fitting compared with other studies, lines represent theoretical and dots experimental data. *Solid line* this work; *squares* Shim et al. (2000a); *diamonds* Tamai and Yagi (1989), *circles* Mao et al. (1989), *dotted line* Magyary-Köpe et al. (2002b); *dash-dotted line* Chizmeshya et al. (1996); *dashed line* Wentzcovitch et al. (1995)

theoretical or nonhydrostatic pressure present in experimental work, can lead to altered results.

The c/a ratio lower than one of Ono et al. (2004) and Shim et al. (2002) may indicate that they found a different tetragonal structure. Caracas et al. (2005) also examine different structures of CaSiO_3 perovskite using density functional theory. Like us, they found the $I4/mcm$ structure to be the most stable, with $P4_2/nmc$ being the second most stable structure. We did further calculations on the three most promising perovskite structures of Caracas et al. (2005) ($P4_2/nmc$, $I4/mmm$ and $P4/mbm$). At the pressures of the lower mantle, none of these structures had an enthalpy lower than the $I4/mcm$ perovskite structure examined above. Note that at high pressure, $I4/mmm$ and $P4/mbm$ transform into the cubic ($Pm\bar{3}m$) and $P4_2/nmc$ into $I4/mcm$. $P4_2/nmc$, which had the lowest enthalpy of these three, had the same distortion in the c/a ratio as the $I4/mcm$ structure.

The recently found post-perovskite structure type CaIrO_3 (Oganov and Ono 2004, Murakomi et al. 2004) is energetically favored for MgSiO_3 at high pressures. We also did calculations for a post-perovskite phase in CaSiO_3 , but the CaIrO_3 phase is not stable for CaSiO_3 with an enthalpy difference of 0.45–0.75 eV per formula unit; see Fig. 6. This is big enough to say that this phase does not occur. In fact, the incorporation of Ca into MgSiO_3 was found to shift the region, where the MgSiO_3 post-perovskite phase can exist, to higher pressures (S. Ono, A.R. Oganov, Y. Ohishi, submitted).

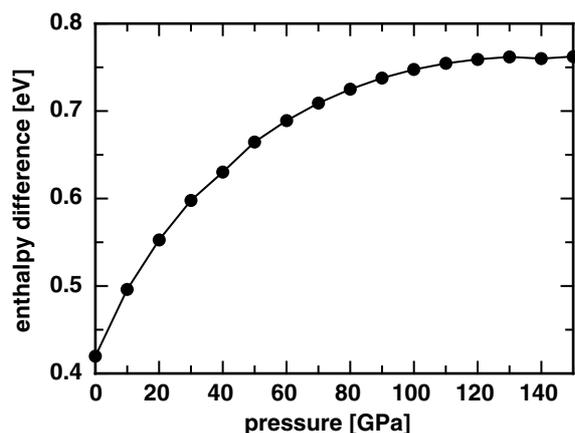


Fig. 6 Enthalpy difference of the post-perovskite structure minus the $I4/mcm$ perovskite structure

Decomposition of CaSiO_3 into CaO and SiO_2

Once all the enthalpies of the different structures are known, it is straightforward to get the enthalpy of decomposition. The enthalpy of decomposition is given by:

$$\Delta H = -H_{\text{CaSiO}_3} + H_{\text{SiO}_2} + H_{\text{CaO}}.$$

As one can see, in Fig. 7, the line never drops below zero, the CaSiO_3 -perovskite is stable in the pressure range of 0–150 GPa. CaSiO_3 -perovskite is stable by more than 0.2 eV at zero pressure and when above 65 GPa it is stable by more than 1.65 eV. Errors due to finite k -point sampling and basis set are two orders of magnitude smaller than these values and are thus insignificant.

It is almost certain that CaSiO_3 perovskite changes to the cubic structure at high temperatures. The question is, does temperature also influence the decomposition and if so, at which temperature would the decomposition

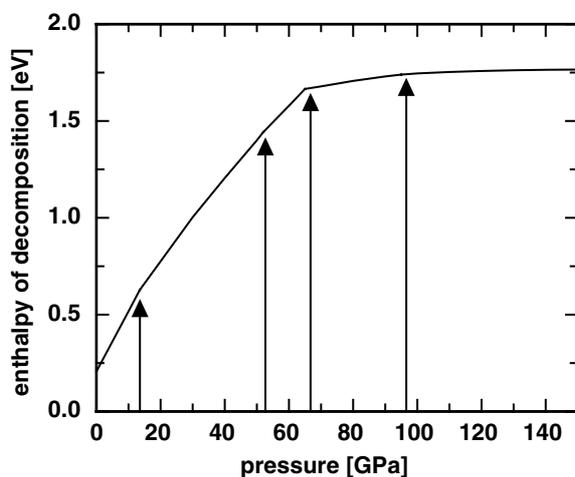


Fig. 7 Enthalpy of decomposition of CaSiO_3 (1 f.u.) in CaO and SiO_2 . Each arrow points at a phase transition

take place? The entropy of decomposition $\Delta S = \Delta H/T_{\text{dec}}$ necessary for decomposition to occur at mantle temperatures (2,000–4,000 K) is unrealistically high. Temperature in the lower mantle can reach 4,000 K and this gives us for an enthalpy difference of 1.7 eV an entropy difference of 41 J/mol K. This is not a reasonable value to occur, even more when compared with other values, e.g., MgSiO_3 $\Delta S = -5.3$ J/mol K (Oganov and Price 2005), which is much smaller and has an opposite sign.

Yamanaka et al. (2002) suggested the possibility for CaSiO_3 perovskite to decompose at higher pressures because of the lower volume of the oxides. But present results show that CaSiO_3 perovskite has a lower or equal volume in this pressure range of the lower mantle (see Fig. 8). This also points to the fact that there is no decomposition.

Conclusion

Simulations based on density functional theory within the generalized gradient approximation and the projector-augmented wave method are capable of achieving high accuracy for calculating small enthalpy differences, they perform very well for phase transition pressure determination.

The enthalpy of each structure in the pressure range of 0–150 GPa has been calculated using an *ab initio* total energy PAW method. This gives us for the CaSiO_3 perovskite an orthorhombic ($Pnam$) structure up to the phase transition at 14.2 GPa and from there upwards a tetragonal ($I4/mcm$) structure. It is possible to have temperature-induced phase transition to the cubic ($Pm\bar{3}m$) phase because of the small enthalpy difference of 12–20 meV, (Stixrude et al. 1996). This is also in agreement with Ono et al. (2004) and Kurashina et al. (2004) who show experimental tetragonal structures at low temperature and cubic structure at high temperatures.

The question of the different c/a ratio of Ono et al. (2004) and Shim et al. (2002) remains. Our tetragonal

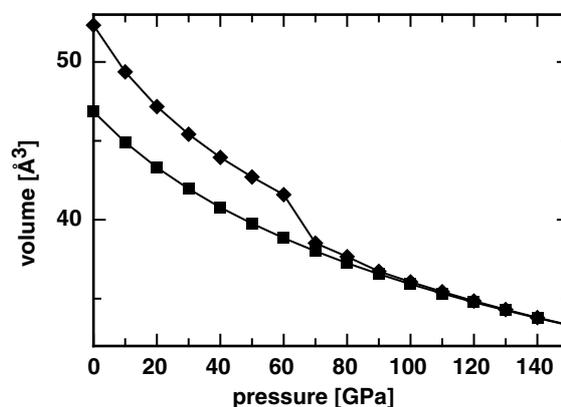


Fig. 8 Comparison of volumes: *Diamonds* represent the volume of one CaO plus one SiO_2 molecule and the *squares* represent the volume of one CaSiO_3 (1 f.u.)

structures of the lowest enthalpy have a $c/a > 1$. Currently, our group is exploring the possibility to resolve the controversy.

Further, the decomposition of the CaSiO_3 perovskite into SiO_2 and CaO has been looked at, and we showed that CaSiO_3 perovskite is stable through the whole mantle pressure range. This holds true even if we take impurities into account, the decomposition enthalpy is so big. The seismic velocity discontinuities thus cannot be caused by the decomposition of CaSiO_3 perovskite. We find that the post-perovskite CaIrO_3 -type structure is not stable for CaSiO_3 . CaSiO_3 perovskite appears to be stable throughout the lower mantle p-T regime.

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