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

Author(s):
Jung, Daniel Y.; Oganov, Artem R.

Publication Date:
2005-06

Permanent Link:
https://doi.org/10.3929/ethz-b-000032624

Originally published in:
Physics and chemistry of minerals 32[2], http://doi.org/10.1007/s00269-005-0453-z

Rights / License:
In Copyright - Non-Commercial Use Permitted
Daniel Y. Jung · Artem R. Oganov

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

Received: 20 September 2004 / Accepted: 26 January 2005 / Published online: 12 May 2005
© Springer-Verlag 2005

**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 3m) 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 (Irifune 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.
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) (Blochl 1994; Kresse and Joubert 1999; Blochl 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 2p⁶), 1.5 a.u. for silicon (core configuration 1s² 2s² 2p⁶) 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 2p⁶) 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 8×10⁻³ 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 8×8×8 (convergence of energy to within 7×10⁻⁵ eV/f.u.) for both CaO structures, 4×4×6 (convergence of energy to within 2×10⁻⁴ eV/f.u.) for the stishovite and the CaCl₂-structured phase, 4×4×4 (convergence of energy to within 2×10⁻³ eV/f.u.), for the α-PbO₂ structure.

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 Blochl (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.

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 r. Within the GGA, some nonlocality is introduced by taking into account also the gradient Vp 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).

### 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 r. Within the GGA, some nonlocality is introduced by taking into account also the gradient Vp 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).

---

¹ In the atomic units, the unit of length is 1 bohr = 0.529 Å
² 1 eV = 1.602 × 10⁻¹⁹ J = 96.485 kJ/mol
³ 1 f.u. = formula unit
and 4x4x4 (convergence of energy to within $2 \times 10^{-3}$ eV/f.u.) for the CaSiO$_3$ structures. For the SiO$_2$ and CaO structures, the convergence of energy differences due to $k$-points sampling are within $4 \times 10^{-3}$ eV/f.u., for CaSiO$_3$ perovskite it is within $1.5 \times 10^{-3}$ eV/f.u. All calculations were performed with primitive cells, except for CaSiO$_3$ perovskite, where all phases were considered in the 20-atom supercell common to all three perovskite variations considered here (this is to achieve maximum cancellation of the $k$-point sampling error for energy differences). All calculations were performed at zero Kelvin. The ions were relaxed with the conjugate gradients and the steepest descent methods.

The energy minimization procedure is iterative and proceeds until self-consistency within a prescribed tolerance ($10^{-6}$ eV per unit cell for electronic optimization and $10^{-4}$ eV per unit cell for ionic relaxation for the CaO, $10^{-9}$ eV per unit cell for electronic optimization and $10^{-6}$ eV per unit cell for ionic relaxation for the SiO$_2$ and the CaSiO$_3$).

We used the program EOS_1.0 (written by J.K. Dewhurst—http://physik.uni-graz.at/~kde/eos.html) to fit E-V data to the third order Birch-Murnaghan equation of state.

**Results**

For CaO, we explored the equations of state (Table 2) and the phase transitions from the NaCl-structured into the CsCl-structured phase. Phase transitions, which change the first coordination number, change the bulk modulus $K_0$ and its derivative $K'$ only modestly (Anderson and Liebermann 1970), whereas the effect is much clearer on phase transformations involving more efficient packing of the same coordination polyhedra. This can be seen when we look at the phase transformation for CaO, B1 and B2 do have almost equal $K_0$ and $K'$. The SiO$_2$ phase transformations change the $K_0$ and $K'$ much more clearer. For CaO we also did LDA calculations, but these were not as accurate as the GGA; see Table 3. As is typical for GGA calculations the volume is overestimated; apart from that the equation of state is also in agreement with previous studies, see Fig. 1 and Table 3. For SiO$_2$, we did all calculations with the GGA method. We found good agreement with previous studies. See Fig. 2 and Table 3.

There are different types of perovskites; the three most likely to form are included in this work: the ideal

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Equation of state of calculated structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOS third order BM</td>
<td>$V_0$ (Å$^3$)</td>
</tr>
<tr>
<td>This work CaO NaCl-type</td>
<td>28.31</td>
</tr>
<tr>
<td>This work CaO CsCl-type</td>
<td>25.37</td>
</tr>
<tr>
<td>This work SiO$_2$ stishovite-type</td>
<td>24.05</td>
</tr>
<tr>
<td>This work SiO$_2$ CaCl$_2$-type</td>
<td>24.03</td>
</tr>
<tr>
<td>This work SiO$_2$ $\alpha$-PbO$_2$-type</td>
<td>23.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Phase transitions of CaO and SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO: B1-B2</td>
<td>Pressure (GPa)</td>
</tr>
<tr>
<td>Theory: LDA</td>
<td>56</td>
</tr>
<tr>
<td>Theory: GGA</td>
<td>65</td>
</tr>
<tr>
<td>Exp: Jeanloz and Ahrens (1979)</td>
<td>65±5</td>
</tr>
<tr>
<td>SiO$_2$: stishovite-CaCl$_2$</td>
<td>Theory: GGA</td>
</tr>
<tr>
<td>Exp: Shieh et al. (2002)</td>
<td>50±3</td>
</tr>
<tr>
<td>SiO$_2$: CaCl$_2$-$\alpha$-PbO$_2$</td>
<td>Exp: Murakami et al. (2003)</td>
</tr>
<tr>
<td>Theory: GGA</td>
<td>98+(0.0095±0.0016)×T(K)</td>
</tr>
</tbody>
</table>

Fig. 1 Comparison of pressure against volume for CaO (1 f.u.), lines represent theoretical and symbols experimental data. This work: Solid line NaCl, dotted line CsCl; dash-dotted line NaCl, Habas et al. (1998); dashed line CsCl, Habas et al. (1998); squares Richet et al. (1988); + NaCl, Jeanloz et al. (1979); triangles CsCl, Jeanloz et al. (1979); × NaCl, Yamanaka et al. (2002); circles CsCl, Yamanaka et al. (2002)

Fig. 2 Comparison of pressure against volume for SiO$_2$ (1 f.u.), lines represent theoretical and dots experimental data. This work: Solid line stishovite, dotted line CaCl$_2$, dash-dotted line $\alpha$-PbO$_2$; + Ross et al. (1990); × Hemley et al. (1994); circles Andrault et al. (1998); dash-dotted line Karki et al. (1997)
cubic ($Pm\overline{3}m$) structure, the tetragonal ($I\overline{4}/mcm$) 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 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 $I\overline{4}/mcm$. 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. 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](image3)

![Table 4 Structures of the 20 atom cell of CaSiO$_3$ at 100 GPa](image4)

<table>
<thead>
<tr>
<th>Perovskite structure</th>
<th>Cubic $Pm\overline{3}m$</th>
<th>Tetragonal $I\overline{4}/mcm$</th>
<th>Orthorhombic $Pnam$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>0.500</td>
<td>0.500</td>
<td>0.500</td>
</tr>
<tr>
<td>Si</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>O</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>O 0.277</td>
<td>0.223</td>
<td>0.250</td>
<td>0.250</td>
</tr>
<tr>
<td>O 0.250</td>
<td>0.750</td>
<td>0.982</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 4 Enthalpy differences of CaSiO$_3$ (1 f.u.) between the tetragonal and the cubic (squares), orthorhombic and cubic (diamonds) structure](image4)
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 \textit{ab initio} methods fully and had to use models which introduced a certain amount of ambiguity. In the last 20 years, \textit{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 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 I$_4$/mcm structure to be the most stable, with $P4_2/mmc$ being the second most stable structure. We did further calculations on the three most promising perovskite structures of Caracas et al. (2005) ($P4_2/mmc$, I$_4/mmm$ and $P4/mmm$). At the pressures of the lower mantle, none of these structures had an enthalpy lower than the I$_4$/mcm perovskite structure examined above. Note that at high pressure, I$_4/mmm$ and $P4/mmm$ transform into the cubic (Pn 3 m) and $P4_2/mmc$ into I$_4/mcm$, $P4_2/mmc$, which had the lowest enthalpy of these three, had the same distortion in the $c/a$ ratio as the I$_4$/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).

### Table 5 Comparison of previous studies of CaSiO$_3$ with this work

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

$$D_H = \Delta H_{\text{CaSiO}_3} + \Delta H_{\text{SiO}_2} + \Delta H_{\text{CaO}}$$

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 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 ($Pnma$) 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 ($Pm\overline{3}m$) 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
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 trough 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 Ca$_2$O$_3$-type structure is not stable for CaSiO$_3$. CaSiO$_3$ perovskite appears to be stable throughout the lower mantle p-T regime.

Acknowledgments We thank W. Steurer, P. Schobinger-Papamantellos, S. Scandolo and G.D. Price for helpful discussions. Shigeaki Ono is thanked for sending us the preprint of his paper. G.D. Price is thanked for giving us the preprint of the paper “Equation of state and stability of CaSiO$_3$ under pressure” by Caracas et al. (2005). We gratefully acknowledge access to supercomputers at CSCS – Centro Svizzero di Calcolo Scientifico and the HP Superdome of ETH Zürich.

References


Ono S, Oganov AR, Ohishi Y (2005) In situ observations of phase transitions between perovskite and Ca$_2$O$_3$-type phase in MgSiO$_3$ and pyrolitic mantle composition. Earth Planet Sci Lett (submitted)


Shim SH, Duffy S, Shen G (2000a) The equation of state of CaSiO$_3$ perovskite to 108 GPa at 300 K. Phys Earth Planet Inter 120:327–338
Tamai H, Yagi T (1989) High-pressure and high-temperature phase relations in CaSiO$_3$ and CaMgSi$_2$O$_6$ and elasticity of perovskite-type CaSiO$_3$. Phys Earth Planet Inter 54:370–377