Ab initio constant pressure molecular dynamics study of silicate perovskites

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Introduction

Silicate perovskites dominate the mineralogy of the Earth's lower mantle. Despite the progress made by *in-situ* high pressure/high temperature experiments in understanding their properties, these studies are still in their infancy and many outstanding problems are still unresolved (Hemley and Cohen, 1992). Fortunately *ab initio* quantum mechanical calculations have developed to such an extent that quantitatively accurate predictions of the physical and chemical properties of relatively complex solids can be made (Wentzcovitch *et al.*, 1993; Stixrude and Cohen, 1993). Particularly important, was the emergence of *ab initio* molecular dynamics (MD) (Car and Parrinello, 1985; Wentzcovitch and Martins, 1991), as it offers the prospect of enabling calculations at both simulated pressures and finite temperatures.

In this paper we exemplify the use of a newly developed constant pressure *ab initio* MD technique (Wentzcovitch *et al.*, 1993) to the study of silicate perovskites. The results are in outstanding agreement with the known low T/high P experimental data for these phases. Therefore we establish the viability of this approach by studying the behaviour of fully optimized structural geometries of MgSiO$_3$- and CaSiO$_3$-perovskite at 0 K and pressures up to 150 GPa.

Method

This technique is based on the combination of an improved version of the variable cell shape (VCS) MD (Parrinello and Rahman, 1980) with a conventional approach of *ab initio* MD (Wentzcovitch and Martins, 1991), in which
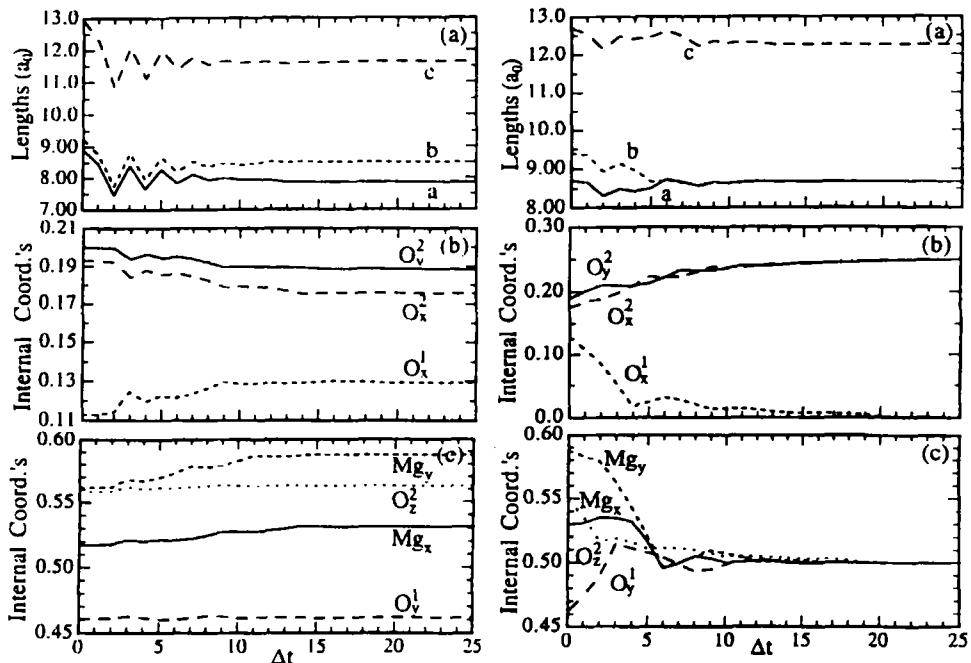

FIG. 1. Typical dynamical evolution of the a) lattice and b) and c) internal parameters of the *Pbnm* phase. In this example MgSiO$_3$ (left) and CaSiO$_3$ (right) have been subjected to an applied pressure of 150 GPa.
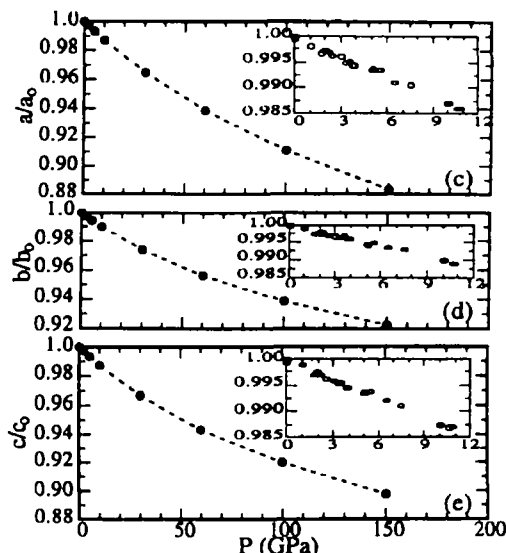
FIG. 2. Pressure dependence of reduced lattice parameters a/a_0, b/b_0, and c/c_0, of $MgSiO_3$-perovskite. a_0, b_0, c_0 are zero pressure values. The insets compare experimental results of Ross and Hazen (1990) (o) to ours ($\bullet$).

electronic structure and dynamics are dealt with independently. This VCS-MD (Wentzcovitch, 1991) is based on a Lagrangian formulation which promotes the components of the strain tensor to dynamical variables. The dynamics generated has the useful property of preserving a minimum space group symmetry along the trajectory, i.e. that of the initial condition. The MD then proceeds with the large time scale typical of classical simulations while quantum mechanical forces and stresses are obtained from fully self-consistent electronic structure calculations at every step of the dynamics. This is a plane-wave-pseudopotential algorithm in which the minimization of the Kohn-Sham (LDA) density functional is achieved by means of a standard self-consistency cycle, i.e. (iterative) diagonalization plus charge mixing. The number of plane-waves is allowed to vary as the cell shape alters, keeping the plane-wave energy cut-off constant. Furthermore we use soft and separable pseudopotentials (Troullier-Martins, 1991).

Results

The dynamics described above, has been used in a "damped' mode to obtain the equilibrium behaviour of certain phases under arbitrary pressures. A detailed description of this procedure can be found in Wentzcovitch *et al.*, 1993 and 1994. Typical structural optimizations are shown in Fig. 1, where the perovskite structures of $MgSiO_3$ and $CaSiO_3$-perovskites are determined at 150 GPa. At this pressure, $CaSiO_3$ is a cubic perovskite (5 atoms/cell), while $MgSiO_3$ is an orthorhombically distorted form with Pbnm space group (20 atoms/cell). The damped motion of all 10 structural parameters stops when internal forces vanish and internal stresses equilibrate the external pressure. Fig. 1 shows that it takes approximately 20 time steps to obtain the equilibrium value of all parameters. In $CaSiO_3$ the final parameters ($O_y^2 = O_x^2 = \frac{1}{4}$, $O_x^1 = 0$, $Mg_y = Mg_x = O_z^2 = O_y^1 = \frac{1}{2}$, $a = b = c/\sqrt{2}$) indicate a cubic structure. This is a special case of *Pbnm*.

This basic procedure has been used to determine the structural behaviour of both phases from 0 to 150 GPa. Detailed analysis of the results can be found in Wentzcovitch *et al.* (1994). Here we simply report the main results: 1) the calculated lattice parameters and the average Mg-O and Si-O bondlengths $MgSiO_3$-perovskite at 0 GPa are in extremely good agreement (1% smaller) with the experimental (room temperature) values, and so are 2) The calculated octahedral tilting angles are 1 degree larger than the experimental values. Both trends are expected for a 0 K calculation. 3) the calculated axial compressibilities of $MgSiO_3$ are displayed in Fig. 2, where the insets compare with the experimental results of Ross and Hazen (1990). The excellent agreement is apparent, and supports their findings that the *a* axis is the most compressive of all. This behaviour has been confirmed by the calculation of elastic constants of this mineral (Wentzcovitch *et al*, 1994), which indicates that C_{11} is smaller than C_{33}. 4) The calculated bulk modulus of $MgSiO_3$-perovskite is K = 259 GPa and its derivative K' = 3.9, while $CaSiO_3$-perovskite's is K = 254 GPa and K' = 4.4. $MgSiO_3$'s shear modulus is μ = 178 GPa. 5) $MgSiO_3$-perovskite is likely to remain orthorhombically distorted throughout the lower mantle, while $CaSiO_3$-perovskite will maintain a cubic symmetry

Conclusions

The outstanding agreement between the calculated and measured properties of $MgSiO_3$ and $CaSiO_3$ establish the viability of this approach to predict properties of silicate perovskites.In the foreseeable future, we expect computational processing speed to increase sufficiently that we will be able to use this methodology to perform finite temperature simulations under the conditions at which these phases occur within planetary interiors.