Equations of state and elasticity of brucite and portlandite at high temperatures and pressures from classical atomistic simulations

Tararushkin E V [1,@] and Kalinichev A G [1,2]

[1)] *National Research University Higher School of Economics, Myasnitskaya 20, Moscow 101000, Russia, etararushkin@hse.ru*

[2)] *Institut Mines-Telecom Atlantique, 4 Rue Alfred Kastler, Nantes 44300, France*

INTRODUCTION

Brucite, $Mg(OH)_2$, and portlandite, $Ca(OH)_2$, have a similar hexagonal layered crystal structure that is held together by hydrogen bonding between the hydroxyl groups of the opposing layers. The thermodynamic and elastic properties of such minerals at high temperatures and pressures are of great importance for fundamental geochemistry and geophysics. The ClayFF force field [1-3] has been originally developed for classical atomistic computer simulations of clays and their hydrated interfaces under ambient conditions.

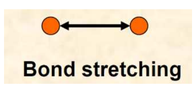
The total potential interaction energy of ClayFF force field

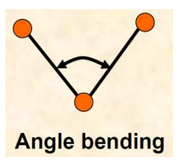
$$E_{Pot} = E_{Bond\ Stretch} + E_{Angle\ Bend} + E_{Coulm} + E_{vdW}$$

$$E_{vdW} = \sum_{i \neq j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \qquad E_{\mathrm{Coulm}} = \frac{e^2}{4\pi\varepsilon_0}\sum_{i \neq j}\frac{q_i q_j}{r_{ij}}$$

Non-bonded interactions (van der Waals and electrostatic)

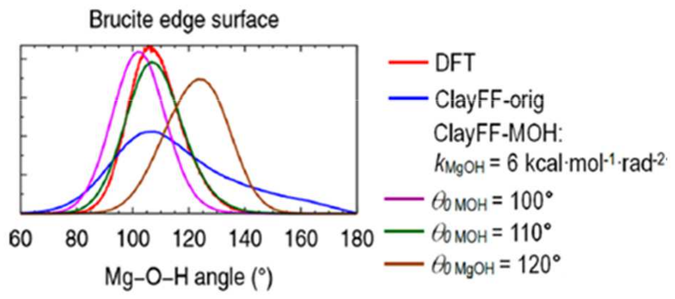
$$E_{Bond\ Stretch} = D_0\left[1 - e^{-\alpha(r-r_0)}\right]^2 \qquad E_{Angle\ Bend} = k_2(\theta_{ijk} - \theta_o)^2$$





Modified ClayFF force field

Recently there was a modification of the ClayFF force field that introduced an additional metal-O-H (M-O-H) angle bending term (ClayFF-MOH), parameterized by a simple harmonic function [4, 5]. The new ClayFF modification allows for a much more accurate modeling of the edges of mineral particles and their hydrated interfaces by explicitly accounting for the bending of M−O−H angles of the metal hydroxides.



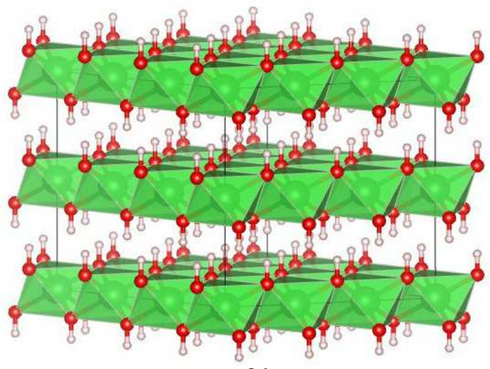
Magnesium−O−H angle distributions for the brucite [5]

Research objectives:

- The main objective of present work is to use the new ClayFF parameters for brucite and portlandite and to test their applicability and predictive capabilities over the wide ranges of temperature and pressures, well beyond the conditions of their original parameterization
- Comparison of the two versions of the ClayFF force field with each other and with available experimental and theoretical data

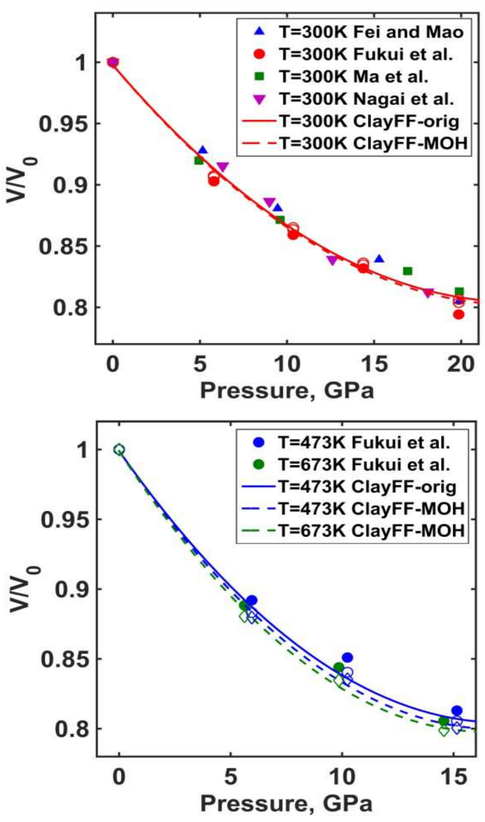
ATOMISTIC MODELS AND RESULTS

Structural models: ideal unit cell was used as the initial building block for a supercell containing 968 units (11 × 11 × 8 along *a*, *b*, *c* cell vectors respectively) for both brucite and portlandite. As a result, the simulation supercell contains of 4840 atoms. Periodic boundary conditions were then applied in all three dimensions of supercell. For ClayFF-orig and ClayFF-MOH, the supercell was the same. LAMMPS simulation package [6] was used to perform the MD simulations.

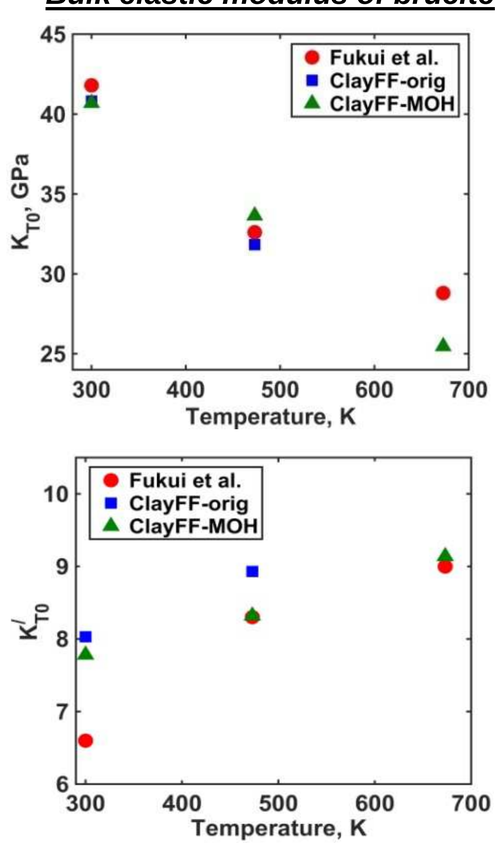


Layers of brucite
Mg – green, O – red, H – white

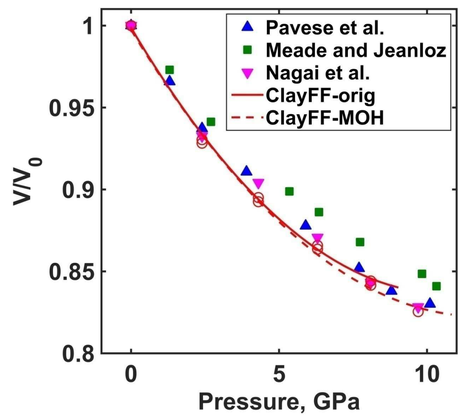
Compressibility of brucite



Bulk elastic modulus of brucite



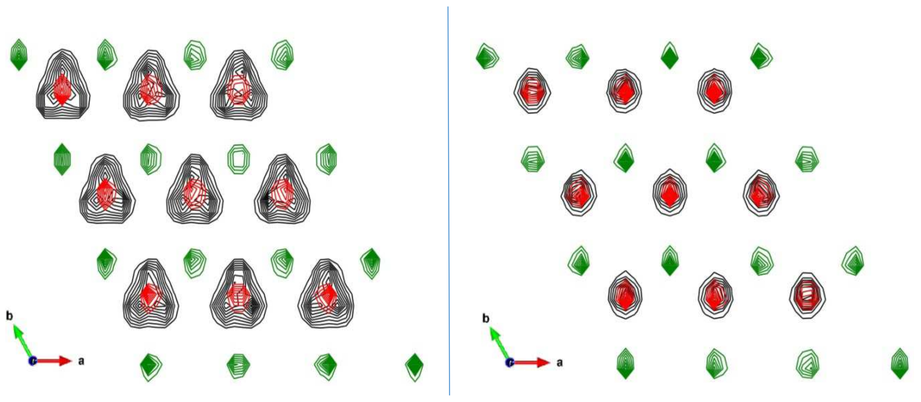
Compressibility of portlandite (T=300K)



Bulk elastic modulus of portlandite (T=300K)

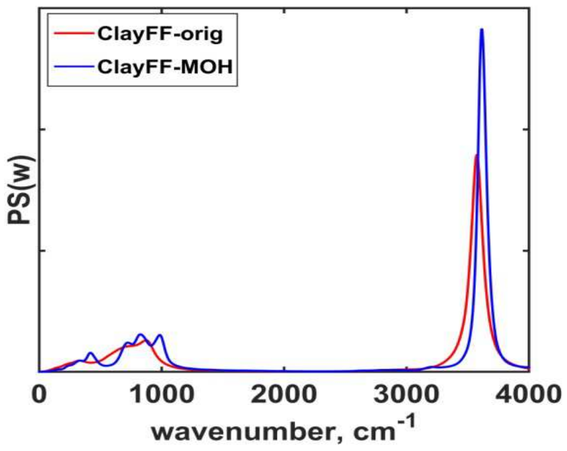
K_{T0} GPa	K'_{T0}	Source
25.6	7.6	ClayFF-orig
24.1	8.2	ClayFF-MOH
34.2	5.2	Pavese et al.
37.8	5.2	Meade and Jeanloz
31.2	4.9	Nagai et al.

Contour maps of atomic densities

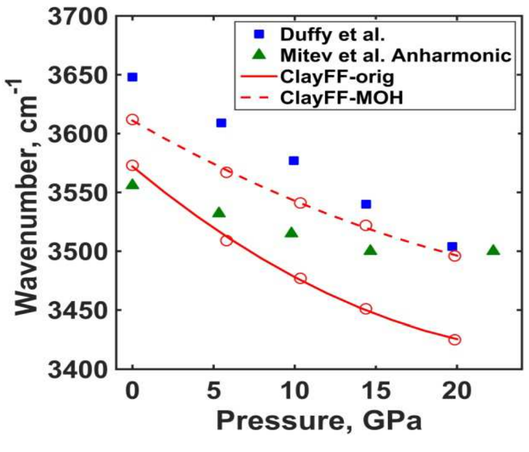


Contour maps for portlandite for normal conditions.
Ca – green, O – red, H – black
Localization of hydrogen atoms is observed for ClayFF-MOH force field.

Power spectra of atomic vibrations



Power spectra for brucite for normal conditions.



Calculated and experimental OH stretching peak positions at room temperature for brucite.

Conclusions

- Elastic and vibrational properties of brucite and portlandite in a wide range of temperatures and pressures are reproduced when simulated by both versions of the ClayFF force field with acceptable deviations from the experimental data
- Fixing the angle in metal-O-H bending term made it possible to simulate materials at higher temperatures and pressures than without fixation. For example, brucite was successfully simulated by ClayFF-MOH force field at T=673K and P=5.62GPa
- The simulation results showed that for the application of the new more accurate ClayFF-MOH force field leads to the formation of a stronger hydrogen bonds in the interlayer spaces of brucite and portlandite, which leads to a more stable structure of materials at higher temperatures and pressures

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Reference

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