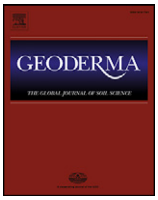
Geoderma 235–236 (2014) 329–333

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma



Mechanisms behind the ikaite-to-calcite phase transformation from molecular dynamics calculations

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ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form 20 July 2014
Accepted 27 July 2014
Available online 10 August 2014

Keywords:
Ikaite soil
Thermal expansion coefficient
X-ray diffraction
Phase changes

ABSTRACT

Since the discovery of ikaite ($CaCO_3 \cdot 6H_2O$) in Antarctic marine sediments and east Arctic polar oceans, studying the ikaite-to-calcite phase transformation above 100 K has attracted a lot of interest, both experimentally and theoretically. Despite intensive efforts, details about the thermal behavior and the mechanisms of the phase transformation of ikaite at ambient temperature are still ambiguous. To unlock the secrets of this rare and unstable mineral, we provide here a clear picture about the structural phase changes as well as the thermodynamic behavior of ikaite from 2 K to 400 K. The obtained results demonstrate the presence of an anisotropic thermal expansion character more pronounced above $T = 80$ K. Our X-ray diffraction patterns show that the structure of ikaite breaks down gradually during thermal expansion from 2 K to 200 K. At 200 K, it transforms into a vaterite-like structure, at short range, then further heating up to 300 K, leads the structure to be in the vaterite phase. However, at 338 K, the latest phase changes quickly to the calcite structure. Our data show that the thermal expansion coefficients of ikaite obtained from 2 K to 80 K increase with temperature, and are greater than those of ice (Ih). However, above $T = 100$ K, the situation is inverse and the relative expansion of ikaite is found to be smaller than that of ice. A larger volume thermal expansion is noticed from $T = 300$ K to 400 K, due to the contribution of extensive H bonds. These bonds allow greater flexibility of ikaite during expansion.

1. Introduction

Among hydrous phases of carbonate systems, ikaite is formed in environments where temperatures are close to 0 °C. The crystalline structure is characterized by hydrated calcium carbonate chains, which are aligned along the a-axis. These chains are linked together by hydrogen bonds and the calcium ions are 8-fold coordinated (Lennie et al., 2004). Ikaite has been determined to be stable at high pressure and low temperatures in an alkaline aqueous environment (Bischoff et al, 1993) and has been observed in bottom waters in fjords and on deep sea floors (Jansen et al., 1987). Marland (Marland, 1975) found ikaite stable only at pressures above 3 kbar (at 25 °C) relative to both calcite and aragonite. Experiments (Bischoff et al., 1993) show that at low temperatures, ikaite precipitates readily over calcite due to the fact that crystallization of anhydrous solids is in part limited to the rate of dehydration of the reactant ions.

Concerning the thermodynamic properties, the solubility trend of ikaite is opposite to calcite, aragonite, and vaterite, and it is more soluble than these minerals above 0 °C at atmospheric pressure. Nevertheless, ikaite transforms rapidly into calcite and vaterite at ambient temperature (Shaikh and Shearman, 1986).

Temperature appears to be the main factor in creating conditions suitable for ikaite precipitation. Previous X-ray powder diffraction experiments (Lennie et al., 2004) found that ikaite slowly decomposed to form both vaterite and calcite over the course of several hours at room temperature (Lennie et al., 2004). They show that the volume expansion rate from $T = 114$ to $T = 293$ K is intermediate between gypsum and ice. More recently, (Tang et al. (2009) clearly show the ikaite–vaterite transformation occurring when the hydrated phase is heated to room temperature or above. Their model explains the kinetic controls on vaterite formation, as well as the observed disorder and strain. Swainson and Hammon (2001, 2003) performed Neutron powder diffraction to measure only seven data ($T = 4$ K, 80 K, 160 K, 200 K, 240 K, 265 K and 270 K).

In order to elucidate the possibility of ikaite–vaterite or ikaite–calcite transformation under temperature effects, we propose here a complete nanoscale level study of the thermal expansion behavior of ikaite from 2 to 400 K. Using the molecular dynamics method (MD), we project to analyze in detail the structural changes as well as thermodynamic properties of ikaite such as the thermal expansion coefficients compared to experimental findings.

2. Description of potential model and molecular dynamics technique

Many forcefields have been developed to describe interactions in carbonate systems, especially for calcite ($CaCO_3$) (Archer et al., 2003;

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http://dx.doi.org/10.1016/j.geoderma.2014.07.021

De Leeuw and Parker, 1997, 1998; Fisler et al., 2000; Pavese, 1992; Pavese et al., 1996; Raiteri and Gale, 2010; Xiao et al., 2011). Parker et al. (1993), using an atomistic model, examined the surface precipitation and dissolution processes, while Fisler et al. (2000) used the shell model to simulate the rhombohedral carbonates and their point defects. Archer et al. (2003) developed a new empirical potential to study the first-order phase transition between calcite I and calcite II. The latest forcefield published by Xiao et al. (2011) for $CaCO_3$ derived a new set of forcefield parameters, which reproduces accurately the elastic and shear modulus for bulk aragonite crystal. Xiao et al. (2011) proposed a new forcefield to describe interatomic interactions for the bulk aragonite crystal in an aqueous and/or protein environment using the TIP3P water model (Jorgensen et al., 1983). Using this model, a recent work reports a nanoscale analysis to describe the morphology and surface stability of calcium carbonate polymorphs (Sekkal and Zaoui, 2013). The latter shows that Xiao's model is more appropriate for hydrated phases of calcite, which justifies its application in the present work.

The Xiao's model used Lennard–Jones (LJ) potentials rather than Buckingham potentials to describe all van der Waals interactions. It includes a LJ potential for the C – C interaction, which was neglected in Pavese's work (Pavese et al., 1996). For the covalent interactions between C and O in the carbonate ion, harmonic angular potentials and a dihedral potential were employed to restrain the O – C – O angle and carbonate plane, respectively. The total set of potential functions is:

$$
\begin{aligned}
V_{total} &= V_{nonbond} + V_{angle} + V_{dihedral} \\
&= \sum_{j=1}^{N-1}\sum_{i=j+1}^{N}\left\{\frac{e^2 z_i z_j}{r_{ij}} + \left(\frac{C_{12}}{r_{ij}^{12}} - \frac{C_6}{r_{ij}^{6}}\right)\right\} + \sum_{angle}\frac{1}{2}K_\theta(\theta-\theta_0) \\
&\quad + \sum_{plane} K_\psi(1-\cos 2\psi)
\end{aligned}
$$

where $z_i z_j$ are the atomic charges, θ is the O – C-angle, θ_0 is the equilibrium angle value of 120°, and ψ is the torsional angle of the $O_1 - C - O_2$ and $O_2 - C - O_3$ planes in carbonate. All forcefield parameters are listed in Table 1.

Molecular dynamics simulations have been performed using the DLPOLY program (Smith and Forester, 1999) in NPT ensemble where we keep pressure constant (equal to atmospheric value) whereas temperature varies from 2 to 400 K. The time step used for the derivation of motion equations is equal to 1 fs, then the simulation will be performed for 30 ns.

Table 1
Xiao's forcefield (Xiao et al., 2011) for aragonite and aragonite–water interactions. C_6, C_{12} are parameters for calcium, carbon and oxygen in $CaCO_3$ with a Lennard–Jones cut-off of 1 nm.

Aragonite		C_{12} (kJ/mol/nm^{12})	C_6 (kJ/mol/nm^6)
Pairwise LJ			
Ca	O_m	9.49×10^{-7}	0
C_m	C_m	4.61×10^{-6}	1.43×10^{-2}
C_m	O_m	9.04×10^{-10}	3.08×10^{-4}
O_m	O_m	5.94×10^{-7}	5.21×10^{-5}
Aragonite–water		C_{12} (kJ/mol/nm^{12})	C_6 (kJ/mol/nm^6)
Pairwise LJ			
Ca	O_w	8.85×10^{-7}	2.00×10^{-3}
C_m	O_w	5.91×10^{-6}	3.39×10^{-3}
O_m	O_w	2.07×10^{-6}	2.25×10^{-3}
O_m	H_w	7.98×10^{-9}	9.65×10^{-7}
Atomwise LJ			
Ca		2.52×10^{-7}	1.42×10^{-3}
C_m		1.44×10^{-5}	4.61×10^{-3}
O_m		1.77×10^{-6}	2.03×10^{-3}

$Z_{Ca}(e) = +1.668$; $Z_C(e) = +0.999$; $Z_O(e) = -0.889$.
K_θ (kJ/mol/rad^2) = 1852.
K_Ψ (kJ/mol) = 28.9.

In Table 2, we present the unit cell parameters (*a*, *b*, *c* and volume) of ikaite compared to experimental data from the database "American Mineralogist" data. We remark that the Xiao forcefield reproduces well the structure of ikaite since the errors are less than 3%.

3. Results

We report the structure and thermal expansion behavior of $CaCO_3 \cdot 6H_2O$ computed using MD calculations by heating gradually the $(7 \times 7 \times 7)$ supercell with size $(42.94 \times 42.94 \times 77.95)$ Å^3 between 2 K and 400 K. For each simulation, we have taken the last equilibrated system that we heated at a new given temperature. We equilibrate the system for 30 ns keeping pressure constant. In Fig. 1(a), (b) and (c), we present the equilibrated total energy, temperature and pressure with time for a given temperature $T = 277$ K.

When we handle calculations from the molecular dynamics method, the kinetic energy of the system is taken into account in the evaluation of the total energy. This energy is related to the velocity of the atoms and also to the temperature of the system (kinetic energy $= ½\, m_i V_i^2 = 3/2\, K_B T$, K_B is the Boltzman constant). Therefore, at a given temperature, there is a presence of a thermal agitation, so the equilibration phase of the system depends on the intensity of the disorder created. In the case of ikaite, it seems that 277 K creates a lot of disorder, so it needs too much time to equilibrate. Our results show that before 10 ns the system does not reach the equilibration phase, since the curves increase with time. It appears that from 10 ns to 30 ns, the system relaxes completely and reaches its equilibrium structure since the variation is quite linear.

In Figs. 2 and 3, we have plotted the variation of the unit cell parameters with increasing temperature from 2 to 420 K. From these figures we have deduced what we have called "phases" (1, 2, 3, 4).

In Fig. 2, we plot the variation of the relative lattice parameters along x, y and z directions with temperature. We notice that from 2 K to 70 K (phase 1) the variations of the lattice parameters *a*, *b*, *c* and β are small and look stable. Using the Graphical Display Interface for Structures program, GDIS, we have calculate the X-ray diffraction patterns with a wavelength of 1.5418 Å. The output atomic positions file is used to generate the theoretical diffraction patterns.

We may see from Fig. 4 the X-ray diffraction patterns calculated for phase 1 at 10 K and 60 K just before the structural phase transition. The structure of ikaite at 10 K and 60 K are qualitatively similar, and then no structural phase transformation has been noticed in that temperature range.

When heating ikaite gradually from 70 to 290 K, we can see that the variation of *a*, *b* and *c* is anisotropic and is found to be more pronounced along y and z rather than the x direction, which increases slightly with temperature. Our findings have the same trend as the experimental data of Swainson and Hammon (2001, 2003) who show the anisotropic thermal expansion of ikaite from 80 K to 290 K. From ambient temperature to 400 K, we notice that the variation is also anisotropic, larger and accompanied by fluctuations. We have therefore deduced three structural phases: phase 2 from 70 K to 170 K, phase 3 from 170 K to 290 K, and phase 4 from 290 K to 400 K. The same phases appear when plotting, in Fig. 3, the variation of β angle with temperature. Discrete points appear at $T = 70$ K, 170 K, and 290 K, which may reflect structural phase changes of ikaite under temperature effect.

Table 2
Structural properties of ikaite.

Mineral	Unit cell parameters	Xiao model	Experiments[a]	Δ(%)
Ikaite	*a* (Å)	8.93	8.79	0.70
	b (Å)	8.41	8.31	2.22
	c (Å)	11.13	11.02	1.06
	V (Å)	774.98	754.07	2.65

[a] Experimental data taken from the "American Mineralogist Database".