Z-contrast imaging and ab initio study on “d” superstructure in sedimentary dolomite

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ABSTRACT

Nano-precipitates with tripled periodicity along the c-axis are observed in a Ca-rich dolomite sample from Proterozoic carbonate rocks with “molar tooth” structure. This observation is consistent with previous description of d reflections. High-angle annular dark-field STEM imaging (or Z-contrast imaging) that avoids dynamic diffraction as seen in electron diffraction and high-resolution TEM imaging modes, confirms that d reflections correspond to nanoscale precipitates aligned parallel to (001) of the host dolomite. The lamellae precipitates have a cation ordering sequence of Ca-Ca-Mg-Ca-Ca-Mg along the c direction resulting in a chemical composition of Ca0.67Mg0.33CO3. This superstructure is attributed to the extra or d reflections, thus is referred to as the d superstructure in this study. The structure can be simply described as interstratified calcite/dolomite. The crystal structure of the d superstructure calculated from density functional theory (DFT) has a space group of P31c and has a and c unit-cell parameters of 4.879 and 16.260 Å, respectively, values between those of dolomite and calcite. The detailed structural characteristics and parameters obtained from ab initio calculations are also reported in this paper. The method of combining Z-contrast imaging and ab initio calculations can be used for solving structures of other nano-precipitates and nano-phases.

Keywords: Dolomite, d superstructure, Z-contrast imaging, density functional theory, molar tooth carbonate

INTRODUCTION

The dolomite (\(\text{CaMg(CO}_3\text{)}\)) structure has alternating \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) cation layers along the c-axis with the triangular \(\text{CO}_3^{2−}\) anion layers lying between two cation layers. Since the size of \(\text{Mg}^{2+}\) ions is smaller than that of \(\text{Ca}^{2+}\), the \(\text{CO}_3^{2−}\) layers are closer to \(\text{Mg}^{2+}\) layers. The lack of glides in the dolomite structure due to the cation ordering causes the occurrence of extra reflections (b reflections, h0l0, l = odd) in dolomite diffraction patterns compared to that of calcite (a reflections only) (Reeder 1992). Two additional reflections (c and d reflections) have been observed in natural sedimentary dolomite. Previously reported c reflections were interpreted as being a result of cation ordering within dolomite basal planes (Van Tendeloo et al. 1985). Our recent STEM work confirmed that the “c”-reflections could result from multiple diffraction between the host dolomite and twinned Mg-calcite nano-lamellae under TEM imaging and diffraction modes (Shen et al. 2013). The d reflection was first observed in Devonian dolomite samples by Wenk and Zenger (1983) and have been also found in ankerite samples (Reksten 1990). The d reflections occur as satellites around a and b reflections with diffraction vector -1/3 (000l)* and are usually streaking along c* direction (Wenk and Zenger 1983; Wenk and Zhang 1985; Van Tendeloo et al. 1985).

Dynamical diffraction in transmission electron microscopy (TEM) mode has been a major problem for structure determination as shown in previous work of analyzing “c” superstructures (Shen et al. 2013). The scanning transmission electron microscopy (STEM) method uses the high-angle annular dark-field (HAADF) detector to give the incoherent imaging, which eliminates most of the obvious effects of dynamical diffraction (Pennycook 2002). With the advantage of a spherical aberration corrector, the resolution of HAADF STEM or Z-contrast images is only limited by the size of the 1s Bloch state that is ~0.6–0.8 Å (Pennycook et al. 2000). The intensity of Z-contrast images depends on the atomic number of atoms through the ~Z 2 dependence of the Rutherford scattering cross-section, which thus provides chemical information for the material (Kirklan 1998; Pennycook et al. 2000). A study of microstructures in natural dolomite samples using Z-contrast images may help find answers to previous observations of superstructures and explore new microstructures in dolomite.

In addition to experimental studies in mineralogy, the application of ab initio calculations of crystal structure, phase stability, and physical properties of minerals at given pressure and temperature has increased in the past few years (Oganov et al. 2006; Barnard and Xu 2008; Chatterjee and Saha-Dasgupta 2010; Stackhouse et al. 2010). Density functional theory (DFT) uses the functional of electron density to solve the Schrödinger equation for a many electron system to acquire the minimum energy of the system (Sholl and Steckel 2009). This method can calculate the enthalpy of a system at 0 K and the corresponding structure. Since STEM work only provides topological information for the crystal structure, the use of the DFT method is needed in this study to calculate the detailed crystal structure of the d phase and confirm our model for the d superstructure by

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comparing the energetic stability of our model to another model proposed in literature.

The “molar tooth” structure refers to vertical and horizontal ribbons and blobs of fine-grained calcite in a dolomite host (Bauerman 1885). This structure has only been recognized in Mesoproterozoic and Neoproterozoic marine carbonate rocks with a few exceptions (Frank and Lyons 1998). The origin and the temporally limited occurrence of molar tooth carbonate have bewildered geologists for over a century (James et al. 1998; Pratt 1998; Meng and Ge 2002; Marshall and Anglin 2004; Pollock et al. 2006; Long 2007; Kuang et al. 2012). However, no previous work on the nanoscale mineralogy of carbonates with the “molar tooth structure” has been conducted. In this present study, STEM imaging and DFT calculations were combined to provide a complete crystallographic description of the d superstructure.

SAMPLES

The “molar tooth” carbonate samples were collected near Hungry Horse Dam, Montana, from outcrops of the Helena Formation of the Mesoproterozoic Belt Group (Frank and Lyons 1998). The sample HHL-00H was chosen for STEM analysis. In the hand specimen of HHL-00H (Fig. 1), the thin sinuous vertical and horizontal ribbons with width of ~0.2–1.5 cm intersect each other. The “molar tooth” is composed of clean and fine-grained calcite crystals with similar size (~10 μm). The “molar tooth” host has three major phases: dolomite, calcite, and quartz (Fig. 2). K-feldspar, illite, chlorite, rutile, and apatite are also present in the “molar tooth” host rock. The XRD powder analysis of the “molar tooth” host rock shows that the dolomite is cation-ordered with the presence of sharp (105) and (009) peaks. The dolomite has a composition of ~Ca1.02Mg0.98(CO3)2 based on the d104 value (2.890 Å) and the relationship between d104 values and MgCO3 content in ordered dolomite (Goldsmith and Graf 1958; Zhang et al. 2010).

METHOD

Specimens for STEM measurements were prepared by ion milling. Ion milling was performed with a Fischione 1010 ion mill operated at an accelerating voltage of 4 kV and an incident ion-beam angle of 10°, followed by gentler milling at an accelerating voltage of 2.6 kV and an incident angle of 10° to reduce surface amorphous material. The ion-milled samples were lightly carbon coated. The microstructures in the dolomite crystals were examined by using a spherical aberration-corrected FEG-STEM (Titan 80-200) operating at 200 kV at the University of Wisconsin-Madison. This instrument can image single atoms with ~0.1 nm or better spatial resolution in STEM mode. Probe current was set at 24.5 pA. Camera length for the image acquisition was set at 160 mm. Collection angle of the HAADF detector for acquiring the Z-contrast images ranges from 54 to 270 milliradians (mrad).

The DFT calculations were performed by using the Vienna ab initio simulation package (VASP) (Kresse and Furthmüller 1996). The general gradient ap-

FIGURE 1. (a)The outcrop shows the brittle deformation inside the carbonate layers with “molar tooth” structure. (b) Sinuous dark blue ribbons of fine crystallined calcite (“molar tooth”) exist in the dolomite host that is weathered into buff color. (c) Weathered surface of HHL-00H specimen. (d) “Molar tooth” becomes light color in fresh cut surface of HHL-00H specimen. (Color online.)

FIGURE 2. Powder XRD pattern of “molar tooth” host and “molar tooth” in sample HHL-00H. (Color online.)

FIGURE 3. TEM image shows that calcite inclusion that is free of modulations or strain contrast in Ca-rich dolomite host.
proximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE) parameters was employed (Perdew et al. 1996). The projector-augmented wave (PAW) method with an energy cutoff of 600 eV was used. A conventional hexagonal supercell of calcite derived structures including 30 atoms or 6 chemical formula units was used. We tested k-point convergence and a mesh of $3 \times 3 \times 1$ was found to be sufficient for the system. Two starting structures for the $d$ phase: one with calcite’s unit-cell parameters from experiments (Graf 1969) and another with dolomite’s (Beran and Zemann 1977). All the initial structures were optimized using the static energy minimization scheme, where both the shape and volume of the cell were allowed to relax. The structure with minimum energy calculated from the previous step was further calculated by ab initio molecular dynamics simulations at 10 K to better explore the local minimum. The powder and electronic diffraction patterns of calculated structures were generated by CrystalDiffract and SingleCrystal, respectively.

**High-resolution (S)TEM observations**

In TEM images, the modulated microstructures with strong strain contrast are prevalent through the “molar tooth” host dolomite. Calcite inclusions that are a common phenomenon in sedimentary dolomites can be easily recognized because of being free of modulations (Fig. 3). Diffuse streaks along $c^*$ occur in the electron diffraction pattern of the host dolomite (Fig. 4). Some maxima of the streaks are about one third of $d_{006}$ [Fig. 4, and also see diffraction patterns of Wenk and Zenger (1983); Wenk and Zhang (1985)]. According to the fast Fourier transform (FFT) patterns of different areas in the dolomite images, the streaks in the diffraction pattern come from the precipitates with linear features that are parallel to (001) (Fig. 5). However, the precipitates themselves are arranged in such a way that they are roughly parallel to (104). The observations above match the features of $d$ reflections that were first described by Wenk and Zenger (1983). It was proposed that the streaks parallel to $c^*$ could be from stacking disorder (Van Tendeloo et al. 1985).

The dark areas of the precipitates in the bright-field (BF) image under STEM mode become bright areas in the HAADF image (Fig. 6), which suggests higher Ca contents in the precipitates than the host dolomite. The occurrence of $d$ reflections in the FFT pattern of the HAADF image excludes the possibility that they are caused by multiple diffraction. In the HAADF of high magnification or Z-contrast image (Fig. 7), the alternating bright and dark layers along $c$ axis represent the alternating Ca and Mg layers in the normal dolomite structure. However, the dolomite precipitate has the cation sequence of Ca-Ca-Mg-Ca-Ca-Mg (Fig. 7). The FFT pattern of this domain shows that the $d$ reflections are attributed to this superstructure. This observation is different from the previous model for the $d$ superstructure in which every third Mg layer is replaced by a Ca layer producing a sequence of Ca-Mg-Ca-Ca-Ca-Mg (Wenk and Zhang 1985). But both sequences produce the same chemical stoichiometry of Ca$_{0.67}$Mg$_{0.33}$CO$_3$. However, the repetition along the $c$-axis is doubled in the previous model with respect to the observed Ca-Mg ordering in the Z-contrast image (Fig. 7).

Mg-bearing calcite precipitates are also observed in the dolomite (Fig. 8). Along the (020) trace, the calcite exsolution region has six consecutive Ca layers as opposed to the dolomite host that has alternating Ca and Mg layers. In the line profile of the calcite region, some Ca columns have slightly lower intensities than the pure Ca columns in the dolomite host, which suggests the existence of a small amount of Mg in this calcite precipitate (Fig. 8). This calcite exsolution is similar to Mg-calcite precipitates in Ca-rich dolomite (Shen et al. 2013).
Figure 7. High-magnification bright-field (a) and dark-field (b) STEM images of $d$ domains. Z-contrast (dark-filled) image shows that the Ca-rich precipitates have a cation sequence (bottom-right) of Ca-Ca-Mg-Ca-Ca-Mg along the $c$ axis as opposed to dolomite cation sequence as shown in the middle-right corner (b). The occurrence of streaking and splitting along $c^*$ (i.e., $d$ reflections) in the FFT patterns (bottom-left corner). 003 and 009 spots are from host dolomite, not from the $d$ superstructure, because the position of 003 halfway between 002 and 004 of the $d$ superstructure, and the position of 009 is halfway between 008 and 0010 of the $d$ superstructure. Noise-filtered Z-contrast image (c) shows enhanced cation sequences in the $d$ superstructure and dolomite host. Line profiles from line 1 (dolomite host) and 2 ($d$ superstructure) also illustrate the ordering of Ca and Mg atoms. (Color online.)

Figure 8. Z-contrast image shows calcite exsolution lamellae // (001) in dolomite host. The line profile 1 has six consecutive Ca columns along (T02) trace. The line profile 2 of the dolomite region shows the normal dolomite cation sequence of alternating Ca and Mg columns. The line profile 3 shows one repeat of $d$ superstructure. The lines with arrows show the boundaries between calcite and dolomite and between dolomite and $d$ superstructure. The atomic models for dolomite/calcite and dolomite/$d$ phase interfaces are shown at the bottom. Carbonate group are not shown proportionally to highlight the cations. (Color online.)
DFT CALCULATIONS

The structural parameters for the optimized d superstructure from DFT calculations are listed in Table 1. Tables 2 and 3 compare the calculated lattice parameters of dolomite and calcite structures with the reported experimental data. The calculated equilibrium volumes for both dolomite and calcite are slightly smaller than the reported data, the underestimated of the c parameter being the major contribution, but are still within the range of previous theoretical calculation data (see Tables 2 and 3). The calculated values are for the structures at 0 K. The reported experimental values were measured at ambient environment. Temperature could be a factor for the small discrepancy between calculated and measured the unit-cell volumes. A small discrepancy between calculated and experimental values of lattice parameters is not uncommon for DFT calculations and may result from the use of an approximate exchange-correlation potential (Hossain et al. 2011). Despite this discrepancy, the trend found in experimental data are maintained in our DFT calculations. The calculated d superstructure has an a parameter close to that of dolomite but has a c parameter closer to stoichiometric calcite.

### Table 1.

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<th>y</th>
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<th>Atom</th>
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<td>0.00000</td>
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<td>0.33333</td>
<td>0.34229</td>
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<td>0.62648</td>
<td>0.41719</td>
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Notes: a = 4.879 Å, c = 16.260 Å, V = 335.226 Å³. Space group = P31c (no. 159). C-O bond (Å) 1.294, 1.297; Ca-O bond (Å) 2.355, 2.374; Mg-O bond (Å) 2.086. CIF available.¹

### Table 2.

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<td>a (Å)</td>
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<td>c (Å)</td>
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<td>V (Å³)</td>
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<td>320.504⁴, 321.251⁴</td>
<td>308.623⁴, 335.409⁴, 329.248⁴</td>
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<td>1.233¹, 1.286⁴</td>
<td>1.286, 1.299⁴</td>
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<td>89.17, 90.83, 180</td>
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¹Graf (1969); ²Beran and Zemann (1977); ³Hossain et al. (2011); LDA functional was used; ⁴Hossian et al. (2011), GGA functional was used; ⁵Bakri and Zaoui (2011), fitted to Birch-Murnaghan equation of state.

### Table 3.

<table>
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<th>Lattice parameters</th>
<th>This work</th>
<th>Experimental</th>
<th>Theoretical</th>
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<td>c (Å)</td>
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<td>17.062¹</td>
<td>17.097¹, 15.902¹</td>
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<td>V (Å³)</td>
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<td>379.279³, 341.676³</td>
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<td>C-O bond (Å)</td>
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<td>1.286¹</td>
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<td>Ca-O bond (Å)</td>
<td>2.336</td>
<td>2.357¹</td>
<td>2.357¹</td>
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</table>

¹Graf (1969); ²Ayoub et al. (2011); ³Aydinol et al. (2007).

¹ Deposit item AM-14-717, CIF and Supplementary Data. Deposit items are stored on the MSA web site and available via the American Mineralogist Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

This finding is consistent with the observation from the diffraction patterns of the d superstructure that the difference between a parameters of dolomite and the d superstructure is smaller than that between c parameters, although the DFT calculations are unconstrained bulk structure calculations. This trend is reasonable because superstructure precipitates share the (001) interface with the host dolomite. Smaller differences in the a dimensions between the host dolomite and d superstructure would cause less strain at the interface.

The C-O bonds in CO₂ groups are rigid and the C-O distances in both experimental and calculation data are constant no matter what the actual composition of the carbonate mineral is. It is interesting to note that the C-O distances in the d superstructure are divided into two categories (Table 1): 1.294 Å when a CO₂ layer is between Ca²⁺ and Mg²⁺ layers along the c axis; and 1.297 Å when a CO₂ layer is in between two Ca²⁺ layers. DFT calculations predict slightly shorter Ca-O and Mg-O bonds in dolomite and calcite than experimental data (Tables 2 and 3). The Mg-O distance in the d superstructure increases from 2.069 Å in calculated dolomite to 2.085 Å. The C-O distance in the d superstructure differs depending on the oxygen positions; the Ca-O distances (2.374 Å) are larger when the oxygen ions are from CO₂⁺ group sitting in between Ca²⁺ and Mg²⁺ layers than those (2.355 Å) from CO₂⁺ group between two Ca²⁺ layers. This is because the CO₂⁺ layers are closer to Mg²⁺ layers than Ca²⁺ layers due to the smaller Mg²⁺ radius. The inversion center is missing in the d superstructure while the c glide is retained. The existence of (100) and (200) reflections in the diffraction pattern proves that it is not a rhombohedral unit cell, but a primitive hexagonal (Fig. 9c). Therefore, the space group is determined to be P31c (No. 159). The atom coordinates and symmetry equivalent positions of the d superstructure are reported in Table 1. The difference among the d superstructures of calcite and dolomite is illustrated in supplementary material.

The superstructure with cation sequence of Ca-Mg-Ca-Ca-Mg-Ca that was proposed to explain the d reflections was referred to as d structure (Wenk and Zhang 1985; Wenk et al. 1991) (see Fig. 9a). The calculated d structure has slightly larger unit-cell parameters (a = 4.883 Å and c = 16.281 Å) than the d superstructure indicated here. The enthapy of a unit cell of d structure is slightly higher than that of the d superstructure by 0.54 kJ/mol per MCO₃ unit. The previously proposed d structure is unstable with respect to the current d superstructure. The proposed d structure model was based on the assumption that overlapped diffraction patterns from host dolomite and d superstructure were from the precipitates only (Wenk and Zhang 1985). Careful examination of their diffraction pattern [Fig. 1a of Wenk and Zhang (1985)] and our FFT pattern (Fig. 9d), show that the position of 003 is not halfway between 002 and 004 of the d superstructure, and the position of 009 is not midway between 008 and 0010 of the d superstructure. The d superstructure does not have reflections with odd l due to its c glide. A powder X-ray diffraction pattern with d(00l) value of 2.930 Å for the d superstructure is also calculated (Fig. 10).

The observed intermediate phases are analogous to those locally ordered domains in mixed-layer clay minerals, such as interstratified chlorite/serpentine, chlorite/biotite, and chlorite/pyrophyllite minerals (Banfield and Bailey 1996; Xu and Veblen...
Figure 10. Calculated powder diffraction patterns of the d superstructure and stoichiometric dolomite (CuKα radiation). The peak of (105) in dolomite does not appear in the d superstructure phase. However, the peak of (106) in the d superstructure phase does not appear in dolomite. (Color online.)

1996; Xu et al. 1996; Wang and Xu 2006). The observed intermediate phase between calcite and dolomite may be described as interstratified calcite/dolomite, instead of δ-dolomite or d-dolomite.

Implications

The calculated energies of calcite [Ca(CO$_3$)$_2$], dolomite [CaMg(CO$_3$)$_2$], and d superstructure [Ca$_2$Mg(CO$_3$)$_3$] are 3620.64, 7132.37, and 10740.22 kJ/mol, respectively. The energy for the d superstructure [Ca$_2$Mg(CO$_3$)$_3$] is higher (~4.2 kJ/mol per MCO$_3$ unit) than the sum of the calculated energies from dolomite [CaMg(CO$_3$)$_2$] and calcite (CaCO$_3$) end-members. The d superstructures serve as a metastable phase with respect to the stoichiometric dolomite and calcite. The d superstructures have a maximum of 4 repeats of Ca-Ca-Mg along the c axis (<35 Å) in our sample and are only stable within dolomite host in the form of nano-precipitates. It is very difficult for extra Ca ions in the dolomite structure to diffuse through carbonate layers and to congregate to form lamellae parallel to the basal plane at low temperature (Wenk et al. 1991; Shen et al. 2013). This explains
all the reported occurrences of nano-precipitates of d-reflections in natural samples. Wenk et al. (1991) summarized the various proposed superstructures of Ca-Mg carbonates. By using Z-contrast imaging, we can image the cation ordering directly and propose a more accurate structure model. By using the DFT method, we can calculate the detailed structures and explore the energetics of these metastable nano- Phases. The methods may be applied to understand many other nano-phases, where there are challenges or artifacts by using other methods.

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