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Letter

Dolomite-IV: Candidate structure for a carbonate in the Earth’s lower mantle

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Abstract

We report the crystal structure of dolomite-IV, a high-pressure polymorph of Fe-dolomite stabilized at 115 GPa and 2500 K. It is orthorhombic, space group Pnma, a = 10.091(3), b = 8.090(7), c = 4.533(3) Å, V = 370.1(4) Å3 at 115.2 GPa and ambient temperature. The structure is based on the presence of threefold C3O9 carbonate rings, with carbon in tetrahedral coordination. The starting Fe-dolomite single crystal during compression up to 115 GPa transforms into dolomite-II (at 17 GPa) and dolomite-IIIb (at 36 GPa). The dolomite-IIIb, observed in this study, is rhombohedral, space group R3, a = 11.956(3), c = 13.626(5) Å, V = 1686.9(5) Å3 at 39.4 GPa. It is different from a previously determined dolomite-III structure, but topologically similar. The density increase from dolomite-IIIb and dolomite IV is ca. 3%. The structure of dolomite-IV has not been predicted, but it presents similarities with the structural models proposed for the high-pressure polymorphs of magnesite, MgCO3. A ring-carbonate structure match with spectroscopic analysis of high pressure forms of magnesite-siderite reported in the literature, and, therefore, is a likely candidate structure for a carbonate at the bottom of the Earth’s mantle, at least for magnesitic and dolomitic compositions.

Keywords: Carbonate, high-pressure structure, tetrahedral ring-carbonate, single crystal

Introduction

Minor and trace elements in the Earth’s mantle play an important role in geochemical processes. In recent years, there has been a particular interest in the understanding of the

behavior of carbon in the inner Earth. It is estimated that 90% of bulk-Earth carbon is hidden in deep reservoirs (Hazen and Schiffries 2013). A significant fraction is very likely in the core, stored in intermetallic phases, such as Fe_3C or Fe_7C_3, as suggested by the composition of iron meteorites (Anders 1964) and as recently found within super-deep diamonds (Smith et al. 2016). In the upper and lower mantle, carbon may be present as elemental carbon (diamond), dissolved in fluids (e.g., CH_4, CO_2), or as carbonate minerals. The occurrence of carbonate as inclusions in diamonds (Berg 1986; Howell et al. 2012) indicates that the coexistence of reduced and oxidized carbon form is possible.
Carbonates undergo polymorphic phase transitions; therefore, the search for the possible structures adopted by carbonates at high pressures and temperatures, still unclear (Hazen et al. 2012), is an important issue to be addressed. Computational and experimental work suggest a rich polymorphism of carbonates and their transformation at extreme conditions into complex

structures featuring tetrahedrally coordinated carbon (Arapan et al. 2007; Oganov et al. 2008, 2013; Boulard et al. 2011). However, a full ab initio experimental determination of the structure of a carbonate with tetrahedrally coordinated carbon and ABO3 stoichiometry has still not been achieved. We have previously applied synchrotron single-crystal diffraction on a multigrain sample after red-ox reaction of a natural Mg-siderite (Merlini et al. 2015), and successfully determined the crystal structure of a new carbonate, Mg2Fe2(C4O13), whose stoichiometry deviates from that of ABO3, adopted by calcite, magnesite, and dolomite. The results indicate that, from a methodological point of view, it is possible to perform accurate single-crystal X-ray diffraction and ab initio structure determination in non-ideal situations, with a conventional single-crystal diffraction approach. From a crystal chemistry point of view, the Mg2Fe2(C4O13) structure confirms the coordination increase from three- to fourfold for carbon and the pressure-induced polymerization of carbonate units.

Here, we report a novel experimental work on

Fe-dolomite studied above megabar{{AU:OK?}} pressures and lower mantle temperatures, with the main aim to determine a crystal structure of a carbonate with ABO3 stoichiometry. Few attempts in stabilizing a single crystal of HP-magnesite have been not successful. In previous studies (Mao et al. 2011; Merlini et al. 2012a), it was observed that dolomite compositions above 40 GPa can exist as single phases at mantle pressures and temperatures in contrast to the decomposition into a mixture of aragonite/post-aragonite and magnesite seen in pure CaCO3. We selected a sample with the same composition (Merlini et al. 2012a) for the experiment, i.e., Ca(Mg0.6Fe0.4)(CO3)2, expecting that also at a higher pressure a single phase could be maintained, possibly without undergoing a red-ox reaction. The presence of Fe in the sample is fundamental for the possibility of heating, by coupling an infrared laser to the electronic structure of iron that is capable of absorbing the laser radiation. For comparison, the compression behavior of pure dolomite was also investigated up to 100 GPa pressures.

Materials and methods

Natural samples of Fe-dolomite from La Mure (Isere, France) were used in the current experiment, similar to the sample used in a previous study (Merlini et al. 2012a). A pure sample of dolomite from Bazena (Italy) was also used.
Microprobe analysis was performed at the Earth Science Department (University of Milano, Italy), and the results indicate a stoichiometry of $Ca(Mg_{0.6}Fe_{0.4})(CO_3)_2$ for Fe-dolomite, and pure dolomite composition, $CaMg(CO_3)_2$, for the other sample used. High-pressure experiments were performed at the ID09A high-pressure beamline at ESRF (Grenoble, France). We used the standard beamline setup with a monochromatic beam of 0.4139 Å with a section of 10 × 10 μm^2 on the sample.
The diamond-anvil cell used mounted two beveled diamonds, one with a 150 µm diameter cullet and the second with 120 µm diameter cullet, bevel out of 350 µm with 9° angle. The gasket was made of Re, pre-indented to a thickness of 35 µm and drilled by spark-erosion. The sample was a single crystal of ca. 10 × 10 × 5 μm^3, deposited on a diamond face in such a way that only a fraction of an edge was actually touching the diamond. The pressure medium, Ne, therefore surrounded the crystal, acted as an insulating layer, and prevented any chemical reaction between

sample and diamonds. The high-pressure ramp, data reduction and analysis follow the established protocols for the beamline (Merlini and Hanfland 2013). Structure solution was achieved with the charge-flipping algorithm (Oszlányi and Suto 2010) and Fourier-difference analysis, using Super-Flip (Palatinus and Chapuis 2007) and Jana software (Petrícek et al. 2014). The unit-cell volume data were fitted to second- and third-order Birch-Murnaghan EoS (BM-EoS; Birch 1947; Angel 2000) using the EOS-FIT5.2 program (Angel 2000). The BM-EoS parameters were simultaneously refined using the data weighted by the uncertainties in P and V.

Results

Fe-dolomite high-pressure behavior: Compressibility and phase transitions

During the compression of the single crystal of Fe-dolomite, we observe at 17 GPa the second-order dolomite–dolomite-II phase transition. The low-pressure data were fitted to a second-order BM equation of state and the results (Table 1 and Supplementary1 data) are in agreement with the data previously reported (Merlini et al. 2016). The dolomite-II structure was solved with a charge flipping algorithm. The results confirm the model previously reported by Merlini et al. (2012a). It is a distortion of the dolomite structure, associated by the rotation of carbonate groups. It presents a crystallographic group-subgroup relation between dolomite and dolomite-II, similar to the calcite–calcite-II transition (Merrill and Bassett 1975). Above 36 GPa, a first-order transition with volume discontinuity is observed. The unit-cell parameters (Table 1) of the high-pressure polymorph are different from those reported for dolomite-III (Merlini et al. 2012a), despite the similar composition of Fe-dolomite used in this and the previous studies (Merlini et al. 2012a). We refer to this new polymorph as dolomite-IIIb. The structure solution for Fe-dolomite-IIIb was readily achieved with a charge flipping algorithm. It crystallizes in rhombohedral symmetry (space group R3) with lattice parameters a ~11.956 and c ~13.626 Å at 39.4 GPa. Its topology is similar to that of calcite, i.e., NaCl-type connection, with carbonate groups differently oriented in the unit cell instead of the parallel arrangement as in calcite and dolomite. The tilting of carbonate groups causes an increased coordination number for the cation sites and a noticeable density increase (Fig. 1). We observe high-pressure behavior similar to that of calcite, where a few different polymorphs can be detected in the same pressure range (Merlini et al. 2012b, 2014). This can be explained by the similar energy of several carbonate polymorphs as shown by computational studies (e.g., Oganov et al. 2008) in several predicted metastable structures.

The volume data for Fe-dolomite-IIIb up to Mbar pressures, fitted with a second-order BM EoS, result in a bulk modulus K0 = 91.0(9) GPa and an extrapolated volume at ambient pressure of 104(1) Å3, i.e., a density of 3.146 g/cm3, which is 3.7% higher than that of the R3c ambient-pressure structure. The diffraction data for dolomite-IIIb at 115 GPa can still be indexed and fitted with the same structure model.

Dolomite high-pressure behavior: Compressibility and phase transitions

During the compression of pure dolomite, we observed the dolomite–dolomite-II transition between 14 and 18 GPa. The dolomite-II structure is the same dolomite-II structure observed for the Fe-bearing dolomite. Dolomite-II is observed to be stable up to 40 GPa. Above 41 GPa, a new triclinic structure is formed. It is labeled as dolomite-IIIc, and crystallizes in a triclinic unit cell, which differs from those of dolomite-III and dolomite-IIIb (Table 1 and Supplementary1 materials). Any attempt to solve the structure in the centrosymmetric P1 space group failed, suggesting the possibility of a non-centrosymmetric symmetry. The similarity of dolomite-IIIc volume with dolomite-III and IIIb, and, especially, the geometrical relationship between the lattice of dolomite-IIIc and dolomite-II, suggests a unit-cell content of eight formula unit [i.e., CaMg(CO3)2; Z = 8]. Unfortunately, the number of observed diffractions is not sufficient to allow structure solution and refinement with 350 variables. The diffraction patterns collected up to 100 GPa are indexed with the same triclinic unit cell. The volume data for dolomite-III fitted to a BM EoS lead to an extrapolated bulk modulus and volume per formula unit at ambient pressure of K0 = 92(6) GPa and V0 = 105(1) Å3, i.e., with an ambient-pressure density of 2.94 g/cm3, 3.5% higher than that of dolomite. No other phase transitions are observed within the P-range investigated. A comparison of the volume of dolomite-IIIc and Fe-dolomite-IIIb polymorphs (supplementary data) indicates that Fe-dolomite-IIIb has a significantly lower molar volume.

Deposit item AM-17-96161, CIF and Supplemental Material. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2017/Sep2017 data/Sep2017_data.html).

Table 1. Lattice parameters, structural data, and elastic data for the different polymorphs of Fe-dolomite and dolomite

P (GPa) Annealing Phase Unit-cell a,b,c (Å); Space group Formula, Z Second-order BM-EoS

T (K) a, ß, . (°); V (Å3) K0 (GPa), V0/Z (Å3)

0.001 298 Fe-dolomite 4.8165(2), 4.8165(2), 16.079(1); R3 Ca(Mg0.6Fe0.4)(CO3)2, Z = 3 91.7(10), 107.7(3)

 90, 90, 120; 323.0(3)

15.58 298 Fe-dolomite-II 4.7293(19), 5.6217(15), 7.282(3); P1 Ca(Mg0.6Fe0.4)(CO3)2, Z = 2 83(3), 108.1(3)

 103.84(3), 89.74(3), 91.62(3); 187.90(1)

36.81 298 Fe-dolomite-IIIb 12.010(3), 12.010(3), 13.700(5); R3 Ca(Mg0.6Fe0.4)(CO3)2, Z = 21 91(9), 104(1)

 90, 90, 120; 1711.34(5)

115.18 2500 Fe-dolomite-IV 10.091(3), 8.090(7), 4.533(3); Pnma Ca(Mg0.6Fe0.4)(CO3)2, Z = 6 150(25), 92(1)

 90, 90, 90; 370.1(4)

0.001 298 Dolomite 4.8078(2), 4.8078(2), 16.008(1); R3 CaMg(CO3)2, Z = 3 95(1), 106.9(3)

 90, 90, 120; 320.4(3)

18.16 298 Dolomite-II 4.714(3), 5.574(2), 7.232(4); P1 CaMg(CO3)2, Z = 2 76(3), 110(1)

 103.57(4), 89.49(5), 91.62(4); 184.6(2)

41.5 298 Dolomite-IIIc 4.455(3), 11.239(6), 13.714(11);

Possibly P1 CaMg(CO3)2, Z = 8 92(6), 105(1)

111.13(6), 91.29(6), 89.77(5); 640.3(8)

Dolomite-IV crystal structure

The presence of iron in the natural Fe-dolomite crystal allowed laser heating. The sample was annealed at 2500 °C at 120 GPa for 5 min. After a thermal quench, X-ray diffraction showed that the crystal transformed into a multigrain sample. Single-crystal spots were visible in the diffraction images, and with the aid of a reciprocal space visualizer, an orthorhombic lattice was successfully identified that was able to index most of the diffraction peaks. Inspection of the inter-planar distances (d) of the non-indexed peaks indicates that no other periodicities occur; however, the d values of non-indexed spots match those of the indexed peaks. The multigrain sample, therefore, is likely a single phase. The unit-cell constants are a = 10.091(3), b = 8.090(7), c = 4.533(3) Å, and V = 370.1(4) Å3 at 115.2 GPa and ambient temperature. The structure solution and refinement was successfully performed in the orthorhombic Pnma space group. Dolomite-IV is a ring carbonate. Its main feature is the presence of corner-sharing tetrahedral CO_4 units in threefold rings (Fig. 2). The cations form distorted eightfold and 10-fold coordination polyhedra. The multiplicities {{auth: okay?}} of the two cation sites are different, and this suggests a disordered cation distribution among the two sites. It was impossible to recover the sample after pressure release, because the diamonds broke during decompression. A few pressure points have also been collected on decompression, in the pressure range 70–115 GPa. The volume data were fitted to a second-order BM-EoS, leading to a bulk modulus $K_0 = 150(25)$ GPa and an ambient-pressure volume of 92(1) Å3 per formula unit. The ambient-pressure density increases by 13% compared to that of dolomite-III. The density increase calculated at 115 GPa is 1% higher. The normalized volume (per formula units) compared to the normalized volume of dolomite-IIIb indicates a density increase of about

1.5% (Fig. 3).
This is consistent with a transformation without compositional change. The structure, in terms of unit cell and symmetry, does not match any predicted structure. However, the ring-carbonate topology is similar to the predicted stable structures of $MgCO_3$ (Oganov et al. 2008; Pickard and Needs 2015).

Discussion and implications

The search for possible host structures of carbonates has stimulated computational and experimental work in the last 10 years. One major outcome is the prediction (Arapan et al. 2007; Oganov et al. 2006, 2008, 2013; Pickard et al. 2015; Boulard et al. 2015) and the experimental verification of the coordination change of carbon in carbonates by crystal structure determination (e.g., Merlini et al. 2015) and spectroscopic analysis (e.g., Boulard et al. 2011, 2015). Tetrahedral carbonate units can polymerize, and a comparison with silicates may suggest that the high-pressure crystal chemistry of carbonates could reproduce the variability observed in ambient structures of silicates.

However, as has been pointed out by computational work (i.e., Oganov et al. 2013), the energy of C_2O_7 groups as a function of C-O-C angles presents two marked minima, preventing all the flexibility observed in silicates, where the energy curve is more flat. In the dolomite-IV ring-carbonate structure, we observe two C-O-C angles of ~119°, close to the predicted ~123.6°. The third C-O-C angle, which completes the threefold ring, is ~104°. Ring-carbonates are predicted as stable phases for $MgCO_3$ composition (Oganov et al. 2008; Pickard et al. 2015). Few different polymorphs have been calculated, but all of them present the topology observed experimentally, based on layers of rings where apical O atoms in neighboring layers point in opposite directions. The experimental data reported here add an interesting insight into the crystal chemistry of carbonates at extreme conditions. For the first time, it has been stabilized in mixed composition, almost in the middle of the compositional diagram $CaCO_3$-$MgCO_3$-$FeCO_3$. The cation crystal sites, two with different multiplicities, indicate that Ca, Mg, and Fe are statistically distributed. The ring-carbonate structure can accommodate the strain arising from the variable size of Ca, Mg, and Fe cations, and this observation is different, for example, if compared to silicate Ca- and Mg-perovskite at high pressure, where the two end-members do not mix. A ring-carbonate, therefore, represents a good candidate for a carbonate structure stable at lower mantle conditions, in an Mg-rich environment. The dolomite-IV structure does not have any analogues among the main silicates, except for walstromite mineral, $BaCa_2Si_3O_9$ (Dent Glasser and Glasser 1968), and the walstromite-type high-pressure polymorph of $CaSiO_3$, which could be found only as inclusions in super-deep diamonds (Joswig et al. 2003; Anzolini et al. 2016).

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Figure 1. Structure of Fe-dolomite-IIb viewed down [001] and down [010], and reconstruction of reciprocal plane a*b* using experimental X-ray data collected at 60 GPa. (Color online.)

Figure 2. Crystal structure of dolomite IV and projection of b*c* reciprocal space layers from experimental X-ray data collected at 115 GPa after high-temperature annealing. (Color online.)

Figure 3

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Figure 3. Experimental volume data (normalized per formula units, V/Z) for Fe-dolomite polymorphs. The second-order EoS for Fe-dolomite-IIIb and -IV polymorphs are also plotted. (Color online.)