

## Dolomite III: A new candidate lower mantle carbonate

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[1] Dolomite is a major constituent of subducted carbonates; therefore evaluation of its phase stability and equation of state at high pressures and temperatures is important for understanding the deep Earth carbon cycle. X-ray diffraction experiments in the diamond anvil cell show that  $\text{Ca}_{0.988}\text{Mg}_{0.918}\text{Fe}_{0.078}\text{Mn}_{0.016}(\text{CO}_3)_2$  dolomite transforms to dolomite-II at  $\sim 17$  GPa and 300 K and then upon laser-heating transforms to a new monoclinic phase (dolomite-III), that is observed between 36 and 83 GPa. Both high-pressure polymorphs are stable up to 1500 K, indicating that addition of minor Fe stabilizes dolomite to Earth's deep-mantle conditions. **Citation:** Mao, Z., M. Armentrout, E. Rainey, C. E. Manning, P. Dera, V. B. Prakapenka, and A. Kavner (2011), Dolomite III: A new candidate lower mantle carbonate, *Geophys. Res. Lett.*, *38*, L22303, doi:10.1029/2011GL049519.

### 1. Introduction

[2] Studies of the high pressure-temperature properties of carbon-bearing minerals are essential to understand carbon storage in the Earth's mantle and therefore the mantle's role in the global carbon cycle. Due to its low solubility in mantle silicates, carbon is mostly stored as accessory minerals such as graphite/diamond and/or carbonates [e.g., *Isshiki et al.*, 2004; *Oganov et al.*, 2006; *Dasgupta and Hirschmann*, 2010]. The presence and state of carbon in the Earth's mantle can strongly affect a number of physical and chemical properties [e.g., *Jana and Walker*, 1997; *Dasgupta et al.*, 2006; *Gaillard et al.*, 2008]. Geochemical and petrologic evidence suggests that carbon is subducted mainly as carbonate [e.g., *Wood et al.*, 1996; *Plank and Langmuir*, 1998].

[3] Dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , is one of the dominant crustal carbon-bearing minerals. At low pressures, its structure is similar to that of calcite, with Mg substituting for Ca in alternating layers. Below 7 GPa and at temperatures of 800–1300 K, it decomposes into aragonite plus magnesite [*Martinez et al.*, 1996; *Sato and Katsura*, 2001; *Shirasaka et al.*, 2002]. However, a shock-wave study identified a rate-dependent low- to high-density phase transition of dolomite at  $\sim 27$  GPa [*Grady et al.*, 1976]. An infrared spectroscopy study of (CaMg) dolomite [*Santillán et al.*, 2003] showed evidence of a phase transformation to a calcite-III-like structure (called dolomite-II) at  $\sim 20$  GPa and 300 K. Theoretical studies predict that trigonal  $\text{CO}_3$ -based structures will trans-

form to tetrahedral  $\text{CO}_4$ -based structures at high pressures [*Oganov et al.*, 2006, 2008; *Panero and Kabbes*, 2008; *Arapan and Ahuja*, 2010; *Minch et al.*, 2010].

[4] The dolomite structure permits significant substitution of  $\text{Fe}^{2+}$  for Mg [*Davidson*, 1994], and ferrous iron is indeed observed in carbonate material associated with crustal and mantle petrologic processes [e.g., *Shibuya et al.*, 2007; *Zedgenizov et al.*, 2009]. Fe-bearing carbonates have been shown to undergo pressure-induced spin transitions at deep Earth conditions [*Lavina et al.*, 2009, 2010a, 2010b], and recently, a new high-pressure structure of Mg-Fe carbonate has been discovered [*Boulard et al.*, 2011]. The coupled redox processes of carbon and iron can add additional complexity to this system [*Dasgupta and Hirschmann*, 2010]. In this study, we have investigated the high-pressure phase stability and compression behavior of an iron-bearing dolomite in the laser-heated diamond anvil cell up to 83 GPa and 1700 K using synchrotron-based X-ray diffraction techniques. We studied the phase stability of Fe-dolomite at conditions relevant to the Earth's lower mantle, identified the structure of its high-pressure phase, and determined its P-V equation of state.

### 2. Experimental Procedure

[5] Our starting material is a natural Fe-dolomite from Windham, Vermont. The composition,  $\text{Ca}_{0.988}\text{Mg}_{0.918}\text{Fe}_{0.078}\text{Mn}_{0.016}(\text{CO}_3)_2$ , was determined by electron microprobe in the Department of Earth and Space Sciences, University of California, Los Angeles. The sample was ground to a fine powder and a powder X-ray diffraction pattern was obtained, determining ambient pressure and temperature values of the lattice parameters to be  $a_0 = 4.8126(8)$  Å,  $c_0 = 16.0413(18)$  Å. High-pressure measurements were conducted using symmetric diamond anvil cells equipped with two 200  $\mu\text{m}$  diamonds. The powder sample was mixed with 5 wt.% Pt as the pressure calibrant and laser absorber [*Fei et al.*, 2007]. The sample was loaded into the diamond anvil cell and maintained under vacuum with Re gasket before loading with a Ne pressure medium. All the diamond anvil cell experiments were performed at the GSECARS beamline of the Advanced Photon Source, Argonne National Laboratory, including double-sided laser heating of the pressurized samples, and room temperature X-ray diffraction before and after heating.

[6] In a first set of experiments, a sample was loaded in the diamond cell, and compressed at ambient temperatures. Diffraction patterns were collected every 2–3 GPa. At 17 GPa, the sample was then laser-heated to 1400–1700 K, and a diffraction pattern was obtained after heating. In a second set of measurements, a sample was compressed to 45 GPa and then laser-heated to  $\sim 1500$  ( $\pm 100$ ) K. Diffraction patterns were obtained before and after heating. The

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sample was then pressurized to 83 GPa at room temperature. Upon compression, the sample was laser-annealed every 5–8 GPa, and X-ray diffraction patterns were obtained after each compression and heating step. This sample was then decompressed to 26 GPa. During decompression, the sample was laser-annealed to ~1500 K every 5–10 GPa. Ambient temperature diffraction patterns were obtained after every annealing step.

### 3. Results: Structure and Phase Stability

[7] The powder X-ray diffraction patterns of the starting material (Figure 1) revealed the existence of a secondary phase, galena (PbS), which is commonly associated with carbonates. This minor phase did not react with Fe-dolomite at the investigated pressure-temperature range based on the collected diffraction patterns at high pressure-temperature (Figure 1 and Figure S1 in the auxiliary material).<sup>1</sup> A change in the dolomite diffraction pattern was observed at ~17 GPa and 300 K, in which most of the diffraction peaks split into doublets (Figure 1). Previous work had shown that Fe-dolomite decomposes into magnesite plus aragonite [Martinez *et al.*, 1996], yet the obtained diffraction patterns cannot be explained by the decomposed phases [Isshiki *et al.*, 2004; Oganov *et al.*, 2006, 2008; Panero and Kabbes, 2008; Boulard *et al.*, 2011]. Following Santillán *et al.* [2003], we identify this high pressure phase as Fe-dolomite-II. Phase II remains stable after heating to ~1600–1700 K at pressures between 27 and 31 GPa (Figure 2). Further increasing the annealing temperature above 1700 K leads to its decomposition to aragonite and magnesite (Figure 2), as observed by Martinez *et al.* [1996].

[8] In the second set of experiments, Fe-dolomite was compressed to ~17 GPa at room temperature and again transitioned to the dolomite-II phase. We then increased the pressure to 41 GPa at 300 K. When laser-heated to 1500 K, the diffraction pattern immediately changed, indicating another phase transformation to a new high-pressure phase, Fe-dolomite-III (Figure 1). The same diffraction pattern is observed in situ during laser heating and also after temperature quench. The diffraction pattern of phase III is characterized by the presence of two peaks with high *d*-spacings near 6.08 and 3.89 Å (corresponding to  $2\theta = 3.15^\circ$  and  $4.92^\circ$  respectively) (Figure 1). The observed new diffraction pattern cannot be explained by magnesite, siderite, post-aragonite and/or a mixture of oxides. This new phase was shown to be stable during compression to 83 GPa and 1500 K (Figures 2 and S1). We further decompressed the cell with laser-heating up to 1500 K, showing that the new phase remained stable at least down to 36 GPa and 1500 K. Further decompression led to a pressure drop to 26 GPa at 300 K where the new phase was still stable, yet heating the sample upon 1500 K and 26 GPa leads to a decomposition into aragonite and magnesite. Observation of two carbonates in decompression suggests that the high pressure phase observed has indeed the composition of dolomite. Future study is needed to investigate if this new phase can be quenched to ambient conditions.

[9] Fe-dolomite is expected to behave similarly to dolomite at high pressure-temperature. Our observed phase transition

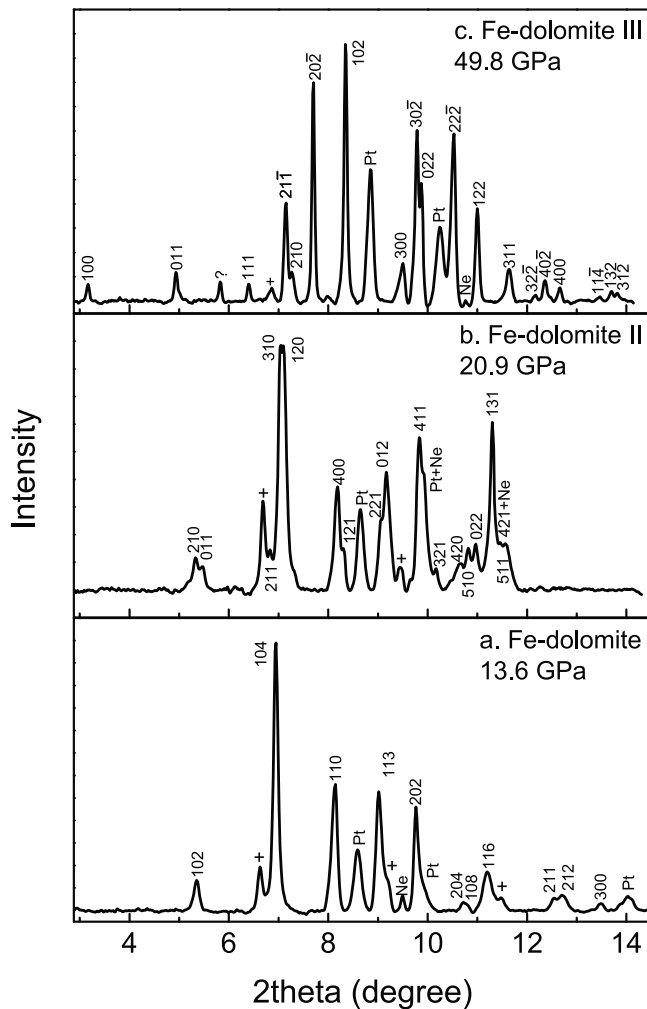
from Fe-dolomite to Fe-dolomite-II occurs at a slightly lower pressure (17 GPa) than that for iron-free dolomite (~20 GPa) [Santillán *et al.*, 2003]. This difference may be due either to the presence of Fe in our sample, or to the stiff pressure medium used by Santillán *et al.* [2003]. Based on the higher intensity of our diffraction pattern, Fe-dolomite-II can be indexed into an orthorhombic cell (Figure 1 and Table S1) in contrast to the earlier study's assignment of the calcite-III (monoclinic) structure. For Fe-dolomite phase III, most of the observed peaks can be explained with a monoclinic unit cell with  $\beta = 108.3^\circ$ , except a weak peak near 3.28 Å (Figure 1 and Table S1). In this case, the crystal symmetry decreases from trigonal for Fe-dolomite to orthorhombic for phase II, to monoclinic for phase III. The variation of symmetry with pressure is consistent with the experimental observations and theoretical predictions for other carbonates, such as calcite and magnesite [Oganov *et al.*, 2006, 2008; Panero and Kabbes, 2008]. However, alternative indexing the diffraction peaks for both Fe-dolomite-II and -III are possible. Future studies are required to identify the crystal structure of each phase.

### 4. Discussion: Equation of State and Spin Transition

[10] The 300 K unit cell volumes for Fe-dolomite, phase II (orthorhombic unit cell) and phase III (monoclinic unit cell) are shown in Figure 3. The transition from dolomite to phase II is accompanied by a 15% decrease in the unit cell volume, and the transition from phase II to phase III is accompanied by a ~8% decrease. X-ray diffraction patterns were collected on phase III upon compression between 45 and 83 GPa and upon decompression down to 26 GPa. In the range where they overlap, the compression and decompression results are in good agreement. However, during decompression we observed a ~2% drop in the unit cell volume of phase III at ~47 GPa (Figure 3b). Similar-scale discontinuities were also observed at the same pressure in each of the lattice parameter *a*, *b*, and *c* of phase III (Figure S2). This volume drop can arise from either a structural phase transformation, or a spin transition. Since we observe no qualitative change in the diffraction pattern, we interpret our observations as a pressure-induced spin transition in the Fe-bearing dolomite-III phase. Spin transitions have been predicted [Shi *et al.*, 2008] and observed [Mattila *et al.*, 2007; Lavina *et al.*, 2009, 2010a, 2010b] in high pressure Fe-bearing carbonates, resulting in volume reductions up to 10% for Fe-end member siderite.

[11] Fitting the Fe-dolomite (low pressure) pressure-volume data using the third-order Birch-Murnaghan equation of state (EoS) yields:  $K_0 = 94.1(\pm 0.4)$  GPa,  $V_0 = 321.77(\pm 0.06)$  Å<sup>3</sup> with  $K'_0 = 4$  (fixed) for Fe-dolomite. The obtained incompressibility for Fe-dolomite is consistent with the reported value for dolomite [Ross and Reeder, 1992; Martinez *et al.*, 1996]. The EoS of phase II could not be determined from current dataset because of its limited pressure range. For low spin phase III, We obtained  $K_0 = 184 (\pm 4)$  GPa,  $V_0 = 231.8(\pm 0.7)$  Å<sup>3</sup> with  $K'_0 = 4$  (fixed) and for high spin  $K_0 = 164(\pm 8)$  GPa,  $V_0 = 239.2 (\pm 1.5)$  Å<sup>3</sup> with  $K'_0 = 4$  (fixed). Both compression and decompression results were used in the fitting for high spin phase III. Strong tradeoffs between  $K_0$  and  $K'_0$  (Varying  $K'_0$  by  $\pm 0.5$  will produce up to 15%

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2011GL049519.

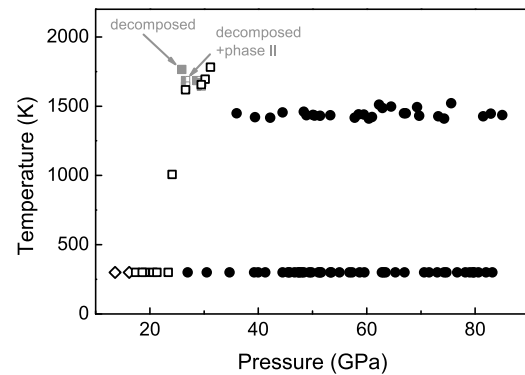


**Figure 1.** High-pressure, ambient temperature X-ray diffraction (wavelength = 0.3344 Å). (a) Fe-dolomite in trigonal symmetry; (b) Fe-dolomite-II in orthorhombic symmetry; (c) Fe-dolomite-III in monoclinic symmetry. The + symbol indicates X-ray peak positions corresponding to the secondary phase PbS.

change in  $K_0$  and 1.3% in  $V_0$ .) and an unknown value of  $V_0$  for phase III generate large uncertainties in these values.

## 5. Implications for Carbonate Storage in the Earth's Mantle

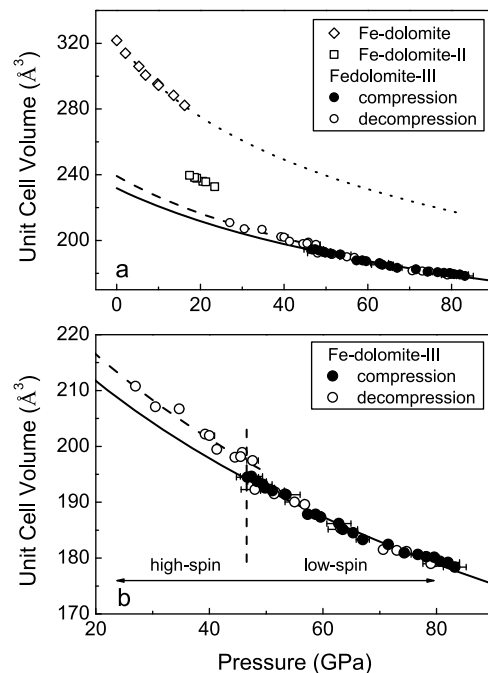
[12] Previous experimental studies have shown that dolomite is a low-pressure but relatively high-temperature phase and breaks into magnesite plus aragonite at pressure-temperature conditions relevant to the Earth's upper mantle [e.g., *Martinez et al.*, 1996; *Shirasaka et al.*, 2002]. As a result, dolomite is normally not considered as a potential carrier to transport carbon to the Earth's deep interior. Here we showed that only 8 mol% substitution of Fe for Mg stabilize Fe-dolomite up to 17 GPa at low temperatures, and the higher pressure phases of II and III are stable at high temperatures as well as high pressures. This indicates that if Fe-bearing dolomite can be transported in the cooler parts of subduction slabs to the transition zone, the high pressure carbonate phases may be stable storage mechanisms for carbonate in the mid-to-



**Figure 2.** Temperature-pressure range of this study indicating the stability of Fe-dolomite. Open diamonds: Fe-dolomite in trigonal symmetry; open square: Fe-dolomite-II; half-filled grey squares: Fe-dolomite II plus decomposed aragonite and magnesite; solid grey squares: aragonite and magnesite; solid circles: Fe-dolomite-III.

deep mantle. Additionally, the pressure-induced spin transition increases the stability of Fe in deep Earth minerals. This work suggests that a small amount of Fe stabilizes the carbonate phase in the deep Earth, with implications for the coupled Fe-carbon redox system for the deep Earth.

[13] The presence of Fe-dolomite in the Earth's mantle, including its high-pressure phases, has significant geophysical implications—whether as part of a stable accessory mineral phase, or as part of a carbon-rich mantle petrology. Such carbonates may react with Mg-perovskite and  $\text{SiO}_2$  rich basalts in the subduction slabs or decompose into other



**Figure 3.** Unit cell volume as a function of pressure for Fe-dolomite. Diamonds and dotted line: trigonal Fe-dolomite; squares: Fe-dolomite-II; solid circle and line: Fe-dolomite-III in compression; open circle and dashed line: Fe-dolomite-III in decompression.

carbonates or oxides at higher temperature conditions [e.g., Martinez *et al.*, 1996; Shirasaka *et al.*, 2002; Takafuji *et al.*, 2006; Oganov *et al.*, 2008]. Chemical reactions and/or decomposition in some cases may lead to the production of free CO<sub>2</sub>. The presence of CO<sub>2</sub> fluid in the lower mantle can largely lower the melting point, induce partial melting, and thus influence the mantle's chemical differentiation and help interpret the observed lower velocity region in the upper mantle [e.g., Presnall *et al.*, 2002; Dasgupta and Hirschmann 2010].

[14] In conclusion, we have studied the high pressure-temperature behavior of Fe-dolomite, Ca<sub>0.988</sub>Mg<sub>0.918</sub>Fe<sub>0.078</sub>Mn<sub>0.016</sub>(CO<sub>3</sub>)<sub>2</sub>, using synchrotron X-ray diffraction. Trigonal Fe-dolomite is undergoes a pressure-induced phase transition to orthorhombic Fe-dolomite-II at 17 GPa and 300 K, and is stable up to 1500 K. We observed another high-pressure phase, Fe-dolomite-III, stable between 36 and 83 GPa up to 1500 K in a monoclinic structure. The observed high-pressure polymorphs, Fe-dolomite-II and -III, may be capable of delivering carbon to the Earth's deep interior. Additional experiments are needed to solve the structure of dolomite-III, examine the potential effects of Fe substitution on the phase transition, and determine the redox properties of Fe-bearing carbonate in the Earth's mantle.

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