Supporting Information

Merlini et al. 10.1073/pnas.1201336109

SI Text

DN A S

DNAS A The lattice for dolomite-II reported in the text (a = 4.7211 b = 5.5367 c = 7.1583 al = 103.333 be = 89.588 ga = 92.79 Vol = 181.85 at 19.5 GPa) and that of (1) are *'reducible'* to an identical subcell lattice with a volume of approximately 60 Å³. This, then, is one-quarter of (1)'s lattice volume and one-third of the lattice volume reported herein.

Matrices for such a transformation are:

 $0\ 0\ 1\ \frac{1}{2}\ 0\ 0\ 0\ \frac{1}{2}\ 0$ (for (1) \rightarrow common sublattice)

1 0 0 0 2/3 -1/3 0 1/3 1/3 (for triclinic \rightarrow common sublattice) They result in a pseudo-tetragonal 4.49 4.69 2.81 90 90 90 lattice.

Given that the triclinic lattice reported (demonstrable by crystal structure solution and refinement) has Z = 2 (volume ~ 180 Å³), this implies that an effective Z for this sublattice (volume ~ 60 Å³) is 2 * 1/3 and the effective Z for the

 Mao Z, et al. (2011) Dolomite III: A new candidate lower mantle carbonate. Geophys Res Lett 38:L22303. lattice of (1) (volume ~ 240 Å³) is 2 * 1/3 * 4 = 8/3 (2.666). The equivalent volume for a Z = 3 lattice, is therefore approximately ~240 Å³/(2.666) * 3 = ~270 Å, on the line extending from the dolomite-I compression, at about 20 GPa, with no, or little, volume change on transition from dolomite-I to dolomite-II.

An alternative possibility of indexing dolomite-II, from data in (1), is:

V = 188.6, M20 = 10.5, Cell = 7.212 5.743 4.69 90 90 103.82 Wavelength: 0.33440

Angular Tolerance: 0.150 Nb of calculated lines: 118 Nb of observed lines: 18 Nb of indexed lines: 18

N	h	k	I	20 Obs	20 Calc	Dif
1	0	-1	1	5.332	5.340	-0.008
2	-2	0	0	5.462	5.474	-0.012
3	-2	0	1	6.832	6.833	-0.001
4	-2	1	1	7.036	7.037	-0.001
5	-2	-1	0	7.121	7.127	-0.006
6	0	0	2	8.183	8.177	0.005
7	2	1	1	8.320	8.218	0.103
8	-1	1	2	9.041	9.040	0.001
9	3	0	1	9.186	9.178	0.009
10	-2	0	2	9.836	9.845	-0.010
11	-3	2	1	10.160	10.227	-0.068
12	-4	1	0	10.663	10.674	-0.011
13	1	-3	1	10.821	10.830	-0.009
14	-4	0	0	10.962	10.960	0.002
15	-1	-3	0	11.302	11.296	0.006
16	4	-2	0	11.476	11.467	0.010
17	-3	0	2	11.598	11.601	-0.003
18	0	0	3	12.281	12.279	0.002

The worst reflection in the fit is the (211), which may be associated with a PbS reflection.



Fig. S1. Comparative crystal structures of CaCO₃-II (1) (*left*) and dolomite-II (*right*). Barring the different chemistries, the structures of dolomite-II and monoclinic calcite-II are essentially identical. The ordered substitution of ($Mg_{0.6}Fe_{0.4}$) over one-half of the Ca²⁺ sites in calcite-II is sufficient on its own to reduce the overall symmetry of the unit cell to $P\overline{1}$ and to result in a dolomite-II-like lattice and site distribution. Equally, the increase in multiplicity required by the site symmetry in the higher $P2_1/c$ structure of calcite-II necessitates that all divalent cation sites are symmetrically (and chemically) equivalent. Other effects, such as the displacement of C from the O₃ plane, as per NaClO₃ (2) and also seen in dolomite-III. are insufficient to cause this reduction of lattice symmetry, while the atoms remain otherwise equivalent. The $P\overline{1}$ symmetry of dolomite-II is also compatible with significant local distortion of the two dissimilar cation sites. As a consequence, dolomite-II presents two different coordinatons: C.N. 8 for Ca site, and C.N. 6 for (Mg,Fe) sites.

- 1. Merrill L, Bassett WA (1975) The crystal structure of CaCO3 öllP, a high-pressure metastable phase of calcium carbonate. Acta Crystallogr B31:343–349.
- 2 Meyer D, Gasperin M (1973) Étude structurale d'une phase haute température instable du chlorate de sodium. [Structural study on a high-temperature instable phase of Sodium Chlorate]. Bulletin de la Société Française de Minéralogie et Crystallographie 96:18–20, French.



Fig. S2. Raman spectra from loadings of dolomite and other possible components: (A) stating material, dolomite $CaMg_{0.6}Fe_{0.4}(CO_3)_2$; (B) magnesite MgCO₃; (C) aragonite CaCO₃; (D) material recovered after heating of dolomite at 26(1) GPa and 2050(100) K; and (E) material recovered after heating of dolomite at 72 (2) GPa and 2350(100) K. While laser heating at 26 GPa resulted in decomposition of the dolomite on CaCO₃-rich (recovered as aragonite) and MgCO₃-rich (recovered as magnesite) phases (spectrum "d"), heating at 72 GPa does not lead to decomposition (spectrum "e").



Fig. S3. Phase relations in $CaMg_{0.6}Fe_{0.4}(CO_3)_2$ as identified in this study by in situ single crystal X-ray diffraction at ambient temperature (vertical lines), and examination of recovered after laser heating in DACs samples by Raman spectroscopy (white and green circles) and X-ray diffraction (red circle). Decomposition of $CaMg_{0.6}Fe_{0.4}(CO_3)_2$ was observed upon heating at pressure below ~35 GPa (white circles). Two lower mantle geotherms are reported, with data taken from (1) (A) and (2) (B).

1. Brown JM, Shankland TJ (1981) Thermodynamic properties in the earth determined from seismic profiles. Geophys J R Astron Soc 66:579–596.

2. Anderson OL (1982) The Earth's core and the phase diagram of iron. Phil Trans R Soc Lond A306:21-35.

Run	P (GPa)	Results	Volume/Z	Note
S1	0	Dolomite-I	53.55(2)	
S1	0.18(5)	Dolomite-I	53.48(2)	
S1	0.99(5)	Dolomite-I	52.96(2)	
S1	5.11(5)	Dolomite-I	50.93(2)	
S1	9.43(5)	Dolomite-I	49.39(2)	
S1	19.53(5)	Dolomite-II	45.48(2)	
S1	24.47(5)	Dolomite-II	44.12(2)	
S1	29.65(5)	Dolomite-II	42.91(2)	
S1	34.34(5)	Dolomite-II	41.88(2)	
S1	39.88(5)	Dolomite-III	39.76(2)	
S1	44.91(5)	Dolomite-III	39.19(2)	
S1	49.87(5)	Dolomite-III	38.43(2)	
S1	0	Dolomite-I	53.60(2)	Pressure quench
S2	1.42(5)	Dolomite-I	52.96(2)	
S2	13.47(5)	Dolomite-I	47.80(2)	
S2	17.55(5)	Dolomite-II	46.24(2)	
S2	23.04(5)	Dolomite-II	44.61(2)	
S2	28.25(5)	Dolomite-II	43.37(2)	
S2	31.44(5)	Dolomite-II	42.70(2)	
S2	34.41(5)	Dolomite-II	41.88(2)	
S2	37.64(5)	Dolomite-III	40.39(2)	
S2	38.3(5)	Dolomite-III	40.04(2)	
S2	43.45(5)	Dolomite-III	39.42(2)	
S2	47.85(5)	Dolomite-III	38.83(2)	
S2	52.44(5)	Dolomite-III	38.21(2)	
S2	56.03(5)	Dolomite-III	37.58(2)	
S2	59.96(5)	Dolomite-III	36.77(2)	
S3	13.47(5)	Dolomite-I	47.88(2)	
S3	17.55(5)	Dolomite-II	46.08(2)	
S3	34.41(5)	Dolomite-II	41.94(2)	
S4	0	Dolomite-I	54.0(1)	Laser heated, melted at 2600 K and
				43 GPa and quenched; XRD
S5	26(2) GPa, 2050(100) K	Aragonite+magnesite		Raman on quench product
S6	32(2) GPa, 2350(100) K	Aragonite+magnesite		Raman on quench product
S7	46(2) GPa, 2150(100) K	Dolomite-I		Raman on quench product
S8	55(3) GPa, 2100(100) K	Dolomite-I		Raman on quench product
S9	72(3) GPa, 2200(100) K	Dolomite-I		Raman on quench product

Table S1. Experimental run list

Table S2. Summary of single crystal refinement for the dolomite-II structure, with data collected at 34.4 GPa

Total number of reflections	284 0.0582
R1 _{all}	0.0686
wR	0.0691
wR _{all}	
no. parameters	42
GooF	5.27

Table S3. Summary of single crystal refinement for the dolomite-III structure, with data collected at 56 GPa

856
0.0684
0.0984
0.0724
0.0742
161
4.69

Table S4. Synoptic table with features of high pressure dolomite phases reported in different works (1, 2)

	Santillan et al., 2003 CaMg(CO ₃) ₂		Mao et al., 2011 Ca(Mg _{0.92} Fe _{0.08})(CO ₃) ₂		This study Ca(Mg _{0.6} Fe _{0.4})(CO ₃) ₂	
Dolomite-I	CaMg(CO ₃) ₂ -I (0-20 GPa)	Calcite-like structure	Ca(Mg _{0.92} Fe _{0.08})(CO ₃) ₂ -I (0–17 GPa)	Calcite-like	Ca(Mg _{0.6} Fe _{0.4})(CO ₃) ₂ -I (0–17 GPa)	Calcite-like
Dolomite-II			Ca(Mg _{0.92} Fe _{0.08})(CO ₃) ₂ -II (17–35 GPa)	~15% density increase on I/II transition reported; ~0% density increase with Z corrected	Ca(Mg _{0.6} Fe _{0.4})(CO ₃) ₂ -II (17–35 GPa)	~0% density increase on I/II transition
Dolomite-III	CaMg(CO ₃) ₂ -II (20–50 GPa)	CaCO ₃ -III like features; ~4% density increase on transition; large hysteresis	$\begin{array}{c} {\sf Ca}({\sf Mg}_{0.92}{\sf Fe}_{0.08})({\sf CO}_3)_2\text{-III} \\ (3580\ {\sf GPa}) \end{array}$	quench from HP/HTFe high/low spin transition at ~50 Gpa; no decomposition after laser heating	Ca(Mg _{0.6} Fe _{0.4})(CO ₃) ₂ -III (35–65 GPa)	~4% density increase on II/III transition; no decomposition after laser heating

Mao Z, et al. (2011) Dolomite III: A new candidate lower mantle carbonate. *Geophys Res Lett* 38:L22303.
Santillan J, Williams Q, Knittle E (2003) A high-pressure polymorph of CaMg(CO3)2. *Geophys Res Lett* 30:1054.

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