

Supporting Information

Merlini et al. 10.1073/pnas.1201336109

SI Text

The lattice for dolomite-II reported in the text ($a = 4.7211$ $b = 5.5367$ $c = 7.1583$ $a_l = 103.333$ $b_e = 89.588$ $g_a = 92.79$ Vol = 181.85 at 19.5 GPa) and that of (1) are 'reducible' to an identical subcell lattice with a volume of approximately 60 \AA^3 . 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) → common sublattice)

$1 \ 0 \ 0 \ 0 \ 2/3 \ -1/3 \ 0 \ 1/3 \ 1/3$ (for triclinic → 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 $\sim 180 \text{ \AA}^3$), this implies that an effective Z for this sublattice (volume $\sim 60 \text{ \AA}^3$) is $2 * 1/3$ and the effective Z for the

lattice of (1) (volume $\sim 240 \text{ \AA}^3$) is $2 * 1/3 * 4 = 8/3$ (2.666). The equivalent volume for a $Z = 3$ lattice, is therefore approximately $\sim 240 \text{ \AA}^3 / (2.666) * 3 = \sim 270 \text{ \AA}^3$, 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

1. Mao Z, et al. (2011) Dolomite III: A new candidate lower mantle carbonate. *Geophys Res Lett* 38:L22303.

N	h	k	l	2 θ Obs	2 θ 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.

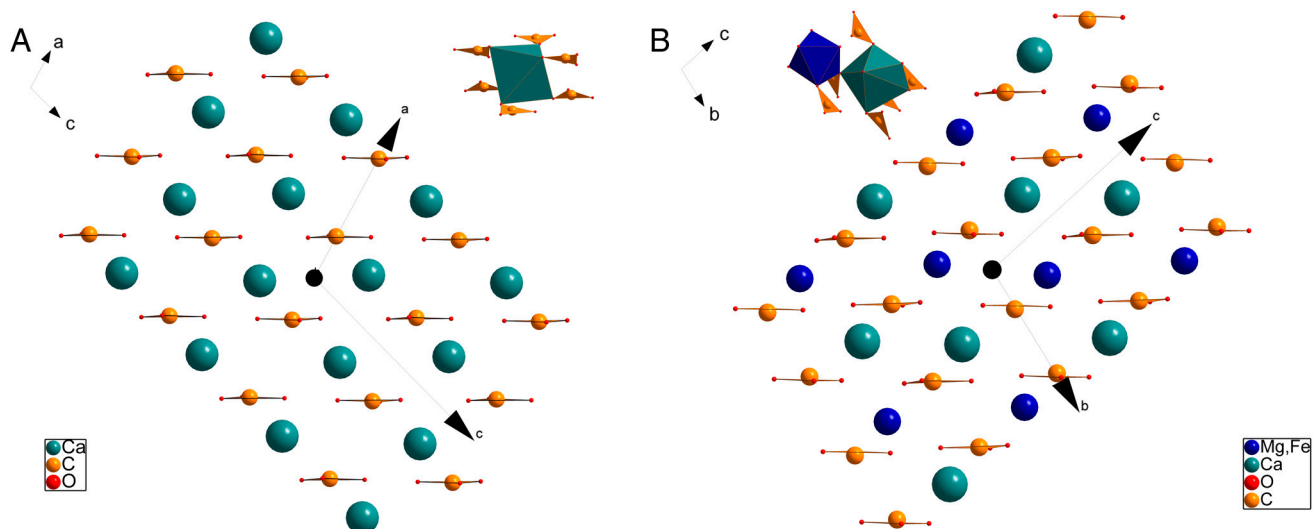


Fig. S1. Comparative crystal structures of CaCO_3 -II (1) (*left*) and dolomite-II (*right*). Barring the different chemistries, the structures of dolomite-II and monoclinic calcite-II are essentially identical. The ordered substitution of $(\text{Mg}_{0.6}\text{Fe}_{0.4})$ over one-half of the Ca^{2+} sites in calcite-II is sufficient on its own to reduce the overall symmetry of the unit cell to $P\bar{1}$ 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 O_3 plane, as per NaClO_3 (2) and also seen in dolomite-III, are insufficient to cause this reduction of lattice symmetry, while the atoms remain otherwise equivalent. The $P\bar{1}$ 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 coordinations: C.N. 8 for Ca site, and C.N. 6 for (Mg,Fe) sites.

- Merrill L, Bassett WA (1975) The crystal structure of CaCO_3 δ III, a high-pressure metastable phase of calcium carbonate. *Acta Crystallogr* B31:343–349.
- 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.

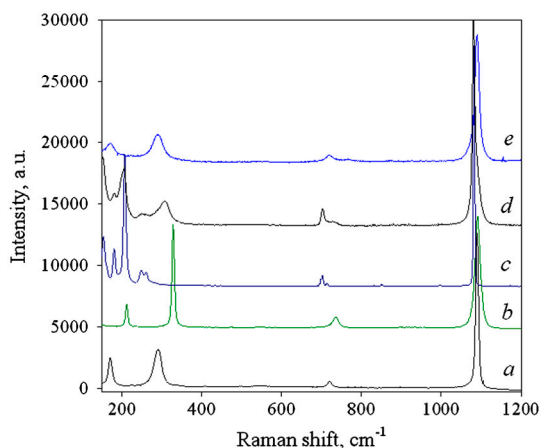


Fig. S2. Raman spectra from loadings of dolomite and other possible components: (A) starting material, dolomite $\text{CaMg}_{0.6}\text{Fe}_{0.4}(\text{CO}_3)_2$; (B) magnesite MgCO_3 ; (C) aragonite CaCO_3 ; (D) material recovered after heating of dolomite at 26(1) GPa and 2050(100) K; and (E) material 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 CaCO_3 -rich (recovered as aragonite) and MgCO_3 -rich (recovered as magnesite) phases (spectrum "d"), heating at 72 GPa does not lead to decomposition (spectrum "e").

