

## Supporting information

The formation of Mg-orthocarbonate through  
the reaction  $\text{MgCO}_3 + \text{MgO} = \text{Mg}_2\text{CO}_4$  at  
Earth's lower mantle  $P - T$  conditions

Pavel N. Gavryushkin <sup>\*1,2</sup>, Dinara N. Sagatova<sup>1,2</sup>, Nursultan  
Sagatov<sup>1</sup>, and Konstantin D. Litasov<sup>3</sup>

<sup>1</sup>*Sobolev Institute of Geology and Mineralogy, Siberian Branch of  
Russian Academy of Sciences, prosp. acad. Koptiyuga 3, 630090  
Novosibirsk, Russia*

<sup>2</sup>*Novosibirsk State University, Pirogova 2, Novosibirsk 630090,  
Russia*

<sup>3</sup>*Vereshchagin Institute for High Pressure Physics RAS, 108840,  
Troitsk, Moscow, Russian Federation*

## Details of the computational methods

**Crystal structure predictions.** The crystal structure prediction calculations using USPEX were performed at 25, 50, and 100 GPa for 1-4 formula units per unit cell. The size of the first generation in the calculations was equal to 65 structures. 60% of the structures with the lowest enthalpy were selected after the optimization and then used for the production of the next generation. A new generation was produced as follow: 35% of all structures were generated by heredity, 20% - by atomic mutation, 10% – by lattice permutation, and 35% – randomly. In average 38-44 generations have been produced and relaxed at each pressure. Using AIRSS about 4000-4200 structures were randomly generated and optimized at 50 GPa, and those with the lowest enthalpy were selected.

The total energies and forces were calculated by solving the Schrödinger equation based on projector augmented plane-wave implementation of density functional theory using VASP package [1, 2]. Exchange correlation effects were

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<sup>\*</sup>Electronic address: [gavryushkin@igm.nsc.ru](mailto:gavryushkin@igm.nsc.ru), [p.gavryushkin@g.nsu.ru](mailto:p.gavryushkin@g.nsu.ru); Corresponding author

treated in the generalized gradient approximation (GGA) with Perdew-Bürke-Ernzerhof scheme [3]. Pseudopotentials with  $2p^63s^2$  (Mg\_sv),  $2s^22p^2$  (C), and  $2s^22p^4$  (O) electrons have been used.

In all crystal structure prediction calculations, medium-quality optimization was performed using the conjugate gradient. The medium quality settings were as follows: plane-wave cutoff energy — 420 eV; Monkhorst-Pack k-point sampling grid of spacing —  $0.5 \text{ \AA}^{-1}$ ; Gaussian smearing with parameter  $\sigma = 0.2 \text{ eV}$ . The most promising predicted structures were then optimized at various pressures with higher accuracy: the cutoff energy — 600 eV, k-point sampling grid of spacing —  $0.25 \text{ \AA}^{-1}$ , and  $\sigma = 0.1 \text{ eV}$ .

**Thermodynamic properties.** Phonon dispersions and free energy calculations were performed using the Phonopy package [4]. Real-space force constants were calculated using supercell method and finite-displacement method, with a  $2 \times 2 \times 2$  supercell for MgO,  $\text{MgCO}_3$ - $R\bar{3}c$ , and  $\text{Mg}_2\text{CO}_4$ - $Pnma$ ,  $1 \times 1 \times 1$  for  $\text{MgCO}_3$ - $C2/m$ , and  $2 \times 2 \times 1$  for  $\text{Mg}_2\text{CO}_4$ - $P2_1/c$ . Helmholtz free energies were computed at 8 volumes (starting from 0 GPa to 150 GPa) for MgO and  $\text{MgCO}_3$ - $R\bar{3}c$ , at 6 volumes (50-150 GPa) for  $\text{MgCO}_3$ - $C2/m$ , at 7 volumes (15-150 GPa) for  $\text{Mg}_2\text{CO}_4$ - $Pnma$ , and at 7 volumes (40-150 GPa) for  $\text{Mg}_2\text{CO}_4$ - $P2_1/c$ , then corrected for thermal expansion using the quasi-harmonic approximation, resulting in Gibbs free energies in both pressure regimes. In this case, high quality settings were used: the cutoff energy — 800 eV, k-point sampling grid of spacing —  $0.2 \text{ \AA}^{-1}$ , and  $\sigma = 0.05 \text{ eV}$ .

**Melting temperature.** We perform ab initio molecular dynamic simulations to determine the melting curve using Z-method, which has been proven successful to predict melting temperature in several systems. The pseudopotentials for Mg, C, and O were the same as in the crystal structure prediction calculations. We used plane-wave cutoff of 450 eV, and the Brillouin zone was sampled only with the  $\Gamma$  point. Simulations were performed in the NVE ensemble, using supercell of  $\text{Mg}_2\text{CO}_4$ - $Pnma$  with 224 atoms, for two volumes of 57.465 and 60.982  $\text{\AA}^3/\text{f.u.}$  For each volume the system was simulated for 10000-14000 steps with the time step of 1.0 fs for different initial kinetic energy in order to construct an isochoric curve T vs P.

**Elastic properties.** The elastic constants  $C_{ij}$  were evaluated using the stress-strain method  $\sigma_i = C_{ij}\epsilon_j$ . Four different strains ( $\pm 0.01$  and  $\pm 0.02$ ) were applied in each distortion and the resulting stress-strain values were then fitted. Obtained elastic constants then used to calculate the elastic moduli. In order to compute elastic moduli, we apply the Voigt-Reuss-Hill approximation [5,6]. In this approach, the actual effective modulus for a system is approximated by the arithmetic mean of the two well-known bounds for single-crystals according to Voigt [7] and Reuss [8]. The mathematical formulation is provided below.

For  $\text{MgCO}_3\text{-}R\bar{3}c$  :

$$B_V = \frac{1}{9} [2(C_{11} + C_{12}) + 4C_{13} + C_{33}],$$

$$B_R = \frac{C^2}{M},$$

$$B = B_{VRH} = \frac{B_V + B_R}{2}.$$

$$G_V = \frac{1}{30} (M + 12C_{44} + 12C_{66}),$$

$$G_R = \frac{5}{2} \left[ \frac{C^2 C_{44} C_{66}}{3B_V C_{44} C_{66} + C^2 (C_{44} + C_{66})} \right],$$

$$G = G_{VRH} = \frac{G_V + G_R}{2},$$

where

$$M = C_{11} + C_{12} + 2C_{33} - 4C_{13}^2,$$

$$C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2.$$

For  $\text{Mg}_2\text{CO}_4\text{-}Pnma$ :

$$B_V = \frac{1}{9} [C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})],$$

$$B_R = \Delta [C_{11}(C_{22} + C_{33} - C_{23}) + C_{22}(C_{33} - 2C_{13}) - 2C_{33}C_{12} + C_{12}(2C_{23} - C_{12}) \\ + C_{13}(2C_{12} - C_{13}) + C_{23}(2C_{13} - C_{23})]^{-1},$$

$$B = B_{VRH} = \frac{B_V + B_R}{2}.$$

$$G_V = \frac{1}{15} [C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})],$$

$$G_R = 15 \{ 4 [C_{11}(C_{22} + C_{33} + C_{23}) + C_{22}(C_{33} + C_{13}) + C_{33}C_{12} - C_{12}(C_{23} + C_{12}) \\ - C_{13}(C_{12} + C_{13}) - C_{23}(C_{13} + C_{23})] / \Delta + 3 \left[ \frac{1}{C_{44}} + \frac{1}{C_{55}} + \frac{1}{C_{66}} \right] \}^{-1},$$

$$G = G_{VRH} = \frac{G_V + G_R}{2},$$

where

$$\Delta = C_{13}(C_{12}C_{23} + C_{13}C_{22}) + C_{23}(C_{12}C_{13} - C_{23}C_{11}) + C_{33}(C_{11}C_{22} - C_{12}^2).$$

In the following formulas, subscript  $V$  denotes the Voigt bound,  $R$  denotes the Reuss bound, and  $VRH$  denotes the Voigt–Reuss–Hill average.

The isotropic wave propagation velocities in the material can then be evaluated from the bulk and shear moduli and the density,  $\rho$ , as follows

$$V_p = \sqrt{\frac{B + \frac{4}{3}G}{\rho}}, \quad V_s = \sqrt{\frac{G}{\rho}}.$$

There are many descriptions of anisotropy named the compression anisotropy ( $A_B$ ) and the shear anisotropy ( $A_G$ ) which represent the percentage of the bulk modulus and shear modulus, correspondingly, and the universal anisotropy index. They can be obtained as follows:

$$\begin{aligned} A_B &= \frac{B_V - B_R}{B_V + B_R}, \\ A_G &= \frac{G_V - G_R}{G_V + G_R}, \\ A^U &= 5\frac{G_V}{G_R} + \frac{B_V}{B_R} - 6. \end{aligned}$$

If  $A_B$ ,  $A_G$ , and  $A^U$  are equal to zero, phase turns to isotropic crystal.  $A_B$  and  $A_G$  could vary from 0 to 1 (i.e from 0 to 100 % anisotropy).

## Results

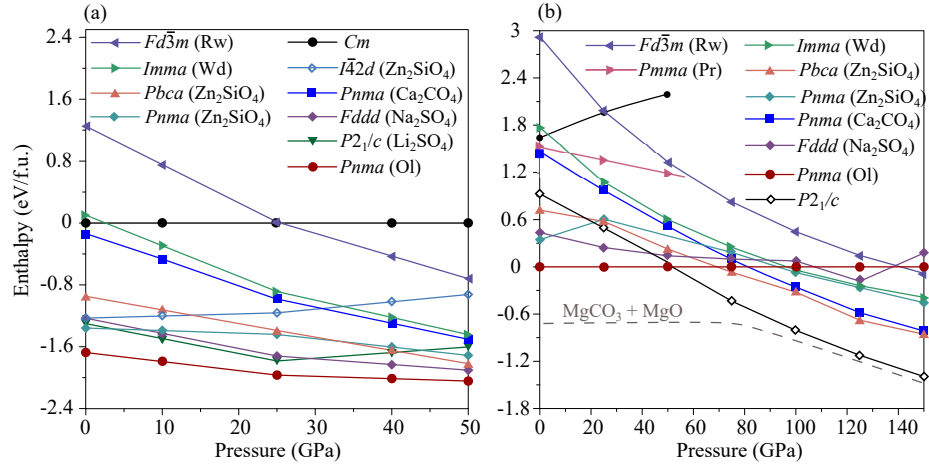


Figure S1: Enthalpy-pressure dependencies of the predicted  $\text{Mg}_2\text{CO}_4$  structures in the pressure range 0–50 GPa (a) and 0–150 GPa (b). The grey dashed line represent relative enthalpy of the  $(\text{MgCO}_3 + \text{MgO})$  mixture. In legend, isostructural compounds are indicated in brackets: Rw – ringwoodite, Wd – wadsleyite, Pr – poirierite, Ol – olivine

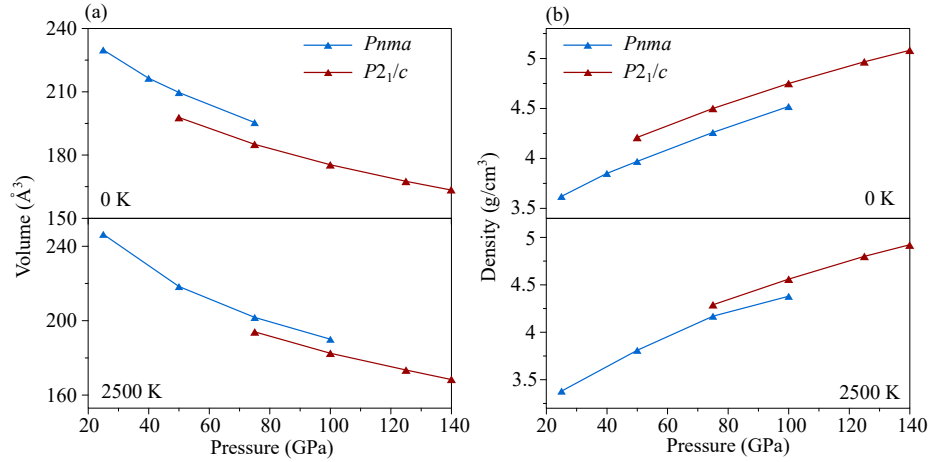


Figure S2: Volume (a) and density (b) dependencies of pressure for  $\text{Mg}$ -orthocarbonate.

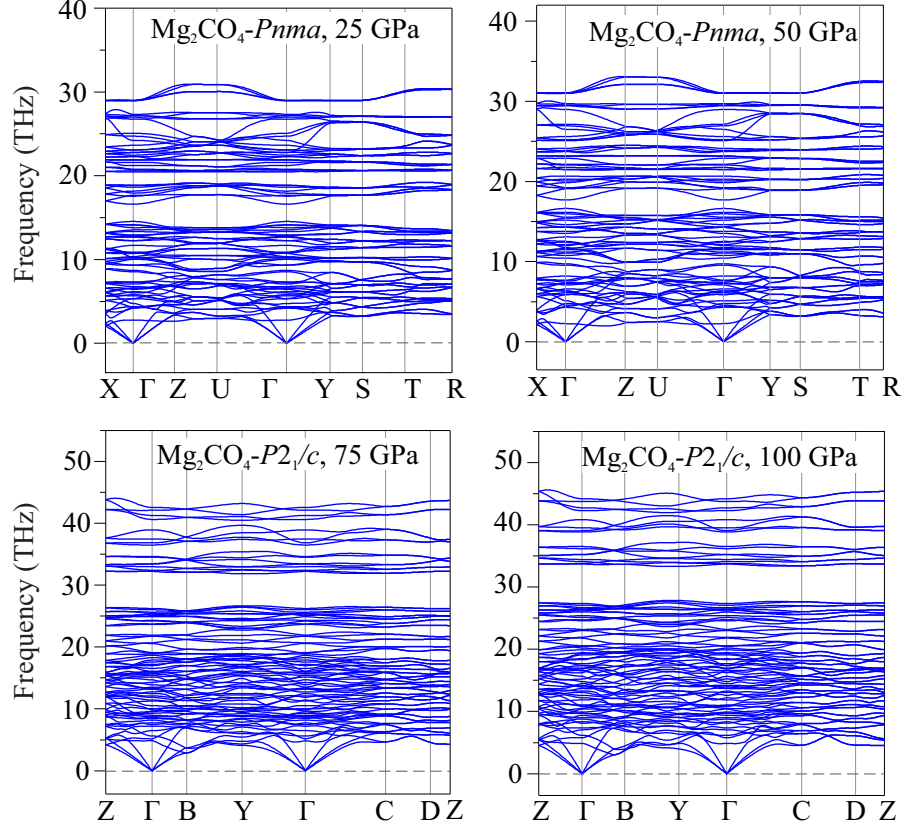


Figure S3: Phonon dispersion curves of  $\text{Mg}_2\text{CO}_4$ - $Pnma$  and  $\text{Mg}_2\text{CO}_4$ - $P2_1/c$  at 25 GPa, 50 GPa, 75 GPa, and 100 GPa.

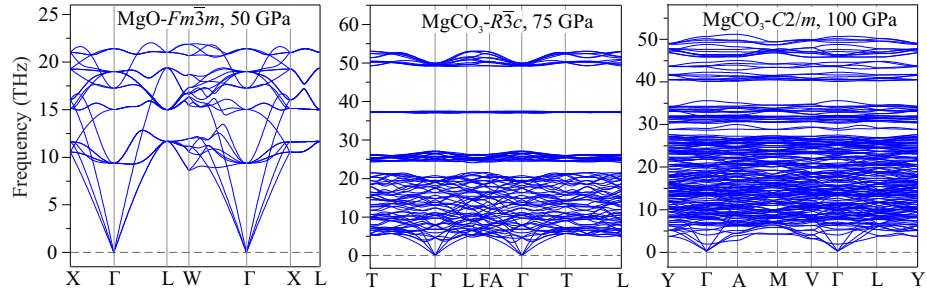


Figure S4: Phonon dispersion curves of  $\text{MgO}$  at 50 GPa,  $\text{MgCO}_3$ - $R\bar{3}c$  at 75 GPa, and  $\text{MgCO}_3$ - $C2/m$  at 100 GPa.

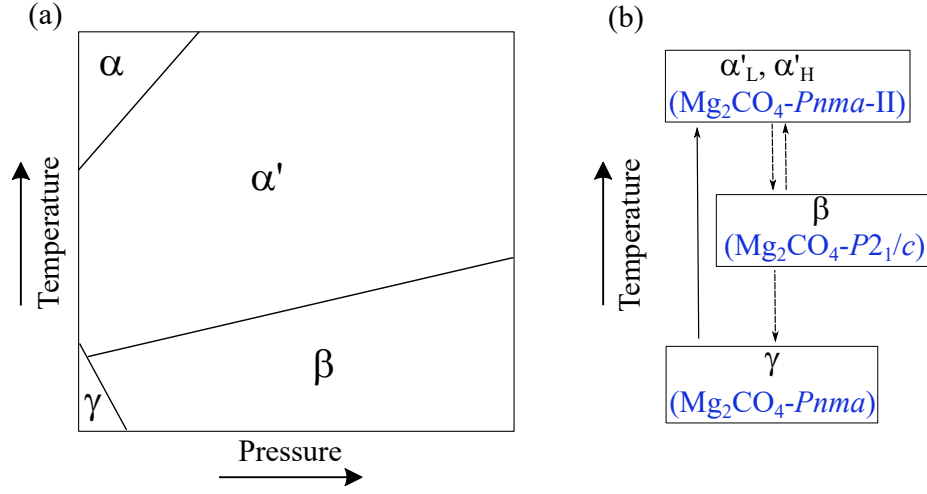


Figure S5: Schematic  $P-T$  phase diagram of  $\text{Ca}_2\text{SiO}_4$  according to [9] (a) and corresponding sequences of phase transitions realised on heating at ambient pressure (b). Dashed line corresponds to metastable phase transitions, solid line — to stable transitions.

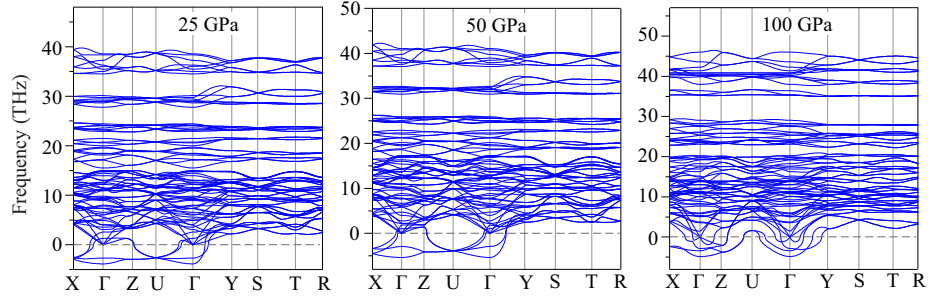


Figure S6: Phonon dispersion curves for dynamically unstable phase of magnesium orthocarbonate,  $\text{Mg}_2\text{CO}_4\text{-Pnma-II}$  at 25 GPa, 50 GPa, and 100 GPa.

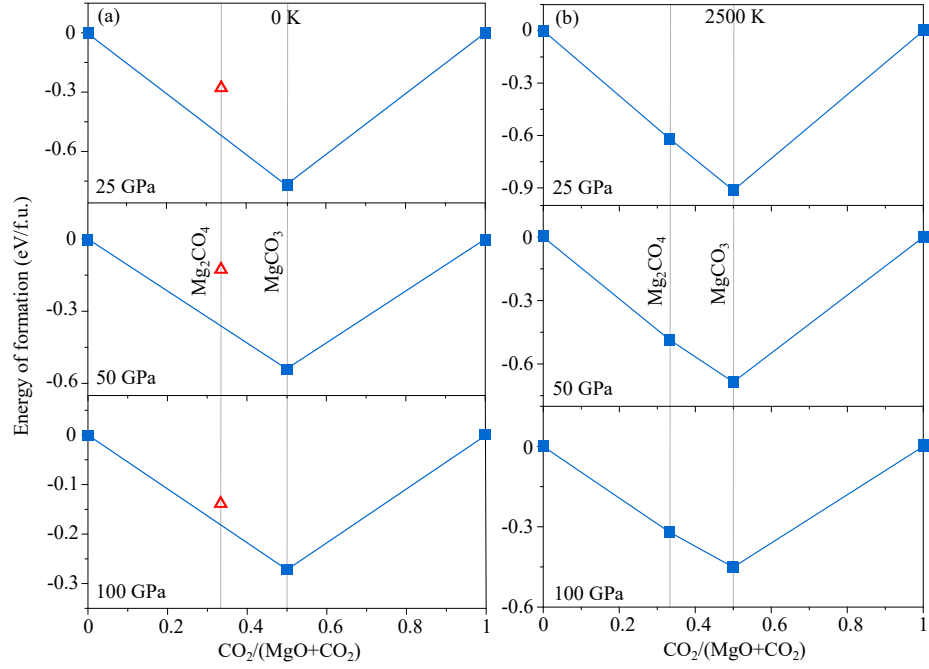


Figure S7: Thermodynamic convex hulls for MgO-CO<sub>2</sub> system at 0 GPa, 50 GPa, and 100 GPa and 0 K (a) and 2500 K (b). Blue filled squares denote stable structures, and red open triangles — metastable ones.

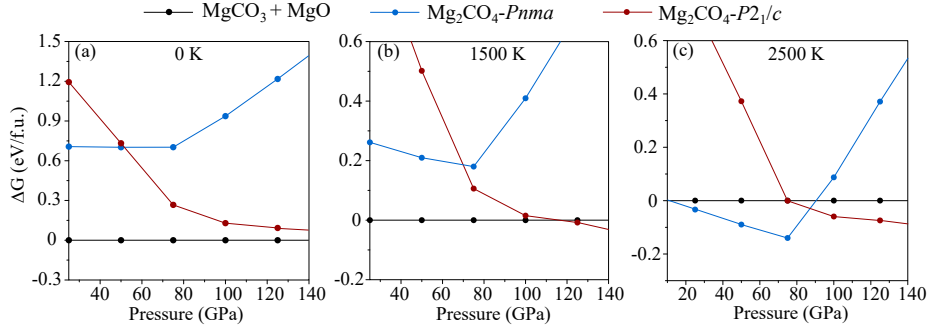


Figure S8: The relative Gibbs free energies as function of pressure for  $\text{Mg}_2\text{CO}_4 = \text{MgCO}_3 + \text{MgO}$  reaction at 0 K (a), 1500 K (b), and 2500 K (c).



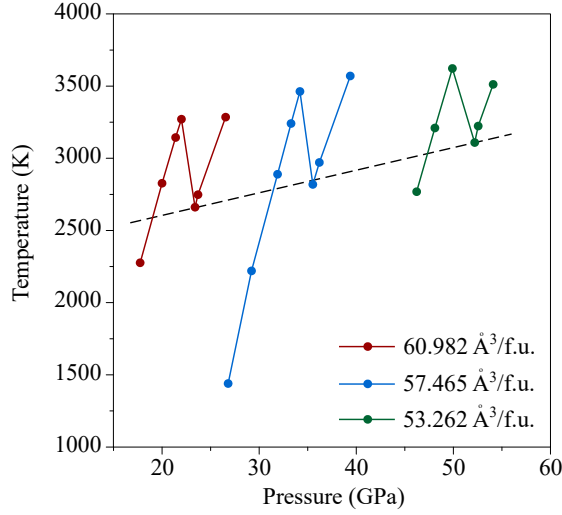


Figure S9: The Z isochores for  $\text{Mg}_2\text{CO}_4\text{-Pnma}$  at volumes  $53.252 \text{ \AA}^3/\text{f.u.}$ ,  $57.465 \text{ \AA}^3/\text{f.u.}$  and  $60.982 \text{ \AA}^3/\text{f.u.}$  shown by blue and red lines, respectively.

Table S1: Calculated elastic constants  $C_{ij}$  (GPa) of  $\text{MgCO}_3\text{-R}\bar{3}c$  and  $\text{Mg}_2\text{CO}_4\text{-Pnma}$  at 50 GPa and 0 K.

Phase	$C_{11}$	$C_{12}$	$C_{13}$	$C_{22}$	$C_{23}$	$C_{33}$	$C_{44}$	$C_{55}$	$C_{66}$
$\text{Mg}_2\text{CO}_4\text{-Pnma}$	375.9	272.6	234.5	497	253.4	572.9	170.6	161.3	124.4
$\text{MgCO}_3\text{-R}\bar{3}c$	543.9	239.5	230.6	543.9	230.6	352.4	122.4	122.4	152.3

Table S2: Calculated density  $\rho$  ( $\text{kg/m}^3$ ), bulk modulus  $B$  (GPa), shear modulus  $G$  (GPa), compression  $V_p$  (km/s) and shear  $V_s$  (km/s) velocities, compression anisotropy  $A_B$ , shear anisotropy  $A_G$ , and universal anisotropy  $A^U$  indexes of  $\text{Mg}_2\text{CO}_4\text{-Pnma}$  and  $\text{MgCO}_3\text{-R}\bar{3}c$  at 50 GPa and 0 K.

Phase	$\rho$	B	G	$V_p$	$V_s$	$A_B$	$A_G$	$A^U$
$\text{Mg}_2\text{CO}_4\text{-Pnma}$	3951.72	324.3	131.3	11.24	5.77	0.0165	0.0425	0.4772
$\text{MgCO}_3\text{-R}\bar{3}c$	3798.67	307.8	125.9	11.19	5.76	0.0256	0.0226	0.2838

## References

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## Crystallographic information files for the predicted structures