Supplementary information

Synthesis of calcium orthocarbonate, Ca_2CO_4-*Pnma* at *p, T*-conditions of Earth's transition zone and lower mantle

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Table S1. Crystallographic information of low- and high pressure orthorhombic Ca_2CO_4-*Pnma*.

P (GPa)	20.1(2)	89.0(8)
T_{max}(K)[a]/ *t* (min)	1830(150)/ 5	2500(250)/ 5
$T_{collection}$(K)	298(2)	298(2)
a, b, c (Å)	6.263(5), 4.896(4), 8.524(15)	5.917(5), 4.456(4), 7.934(14)
V (Å^3)	261.4(4)	209.2(4)
ρ (g/cm^3)	3.967(3)	4.959(2)
Z	4	4
F(000)	312	312
Theta range (˚)	2.35-16.63	1.78-14.98
Completeness to d = 0.8 Å (%)	23.92	42.30
Index ranges	-6 < h < 7	-7 < h < 7
	-8 < h < 8	-5 < k < 6
	-16 < h < 15	-7 < l < 10
No. of measured/independent reflections (I>3σ(I))	589/277(214)	589/280(181)
R_{int}	0.0548	0.0632
R1/wR2[b] (I>3σ(I))	0.0552/0.0591	0.0474/0.0451
R1/wR2(all data)	0.0644/0.0609	0.0819/0.0513
No. of parameters	26	26

[a]Data collection was performed on temperature quenched samples.

[b]Due to the limited amount of available reflections, nearly all displacement parameters of the atoms were refined in the isotropic approximation. However, it was possible to refine the displacement parameters of Ca anisotropically.

Table S2. Crystallographic data of Ca_2CO_4-*Pnma* at 20 and 89 GPa as obtained after refinement.

20.1(2) GPa

Atoms	Site	*x*	*y*	*z*	*U*iso
Ca1	4*c*	0.4912(4)	0.25	0.31247(17)	0.0054(9)[a]
Ca2	4*c*	0.1495(4)	0.25	0.59222(17)	0.0074(9)[a]
O1	4*c*	0.8092(13)	0.25	0.4293(6)	0.0066(10)
O2	8*d*	0.8073(10)	0.4810(9)	0.6551(4)	0.0079(8)
O3	4*c*	0.5098(13)	0.25	0.5843(6)	0.0072(10)
C	4*c*	0.7297(17)	0.25	0.5803(8)	0.0050(12)

89.0(8) GPa

Atoms	Site	*x*	*y*	*z*	*U*iso
Ca1	4*c*	0.4845(3)	0.25	0.3198(4)	0.0060(6)[a]
Ca2	4*c*	0.1458(3)	0.25	0.5999(3)	0.0072(7)[a]
O1	4*c*	0.8119(10)	0.25	0.4179(12)	0.0066(13)
O2	8*d*	0.8171(7)	0.4924(8)	0.6525(7)	0.0048(8)
O3	4*c*	0.5056(9)	0.25	0.5950(11)	0.0065(13)
C	4*c*	0.7375(14)	0.25	0.5751(16)	0.0044(15)

[a]Displacement parameters of Ca atoms were refined anisotropically.

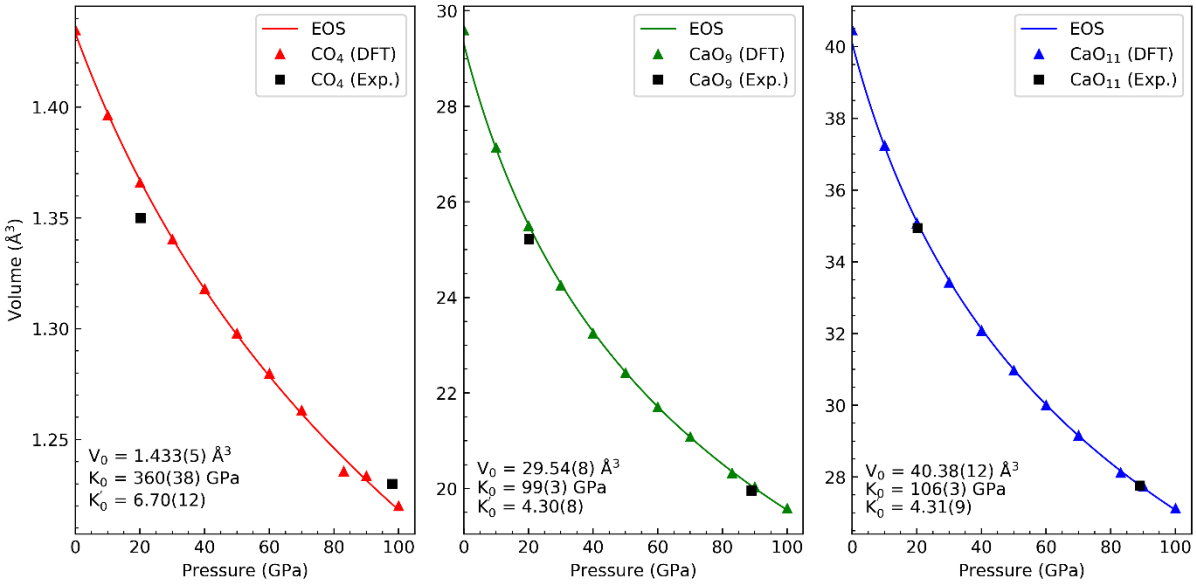

Figure S1. Pressure-dependence of the polyhedra volumes of Ca_2CO_4-*Pnma*. The DFT data were fitted using a third-order Birch-Murnaghan EOS (Gonzalez-Platas et al., 2016; Birch, 1947) using the *EoS-FIT7-GUI* program (Gonzalez-Platas et al., 2016).

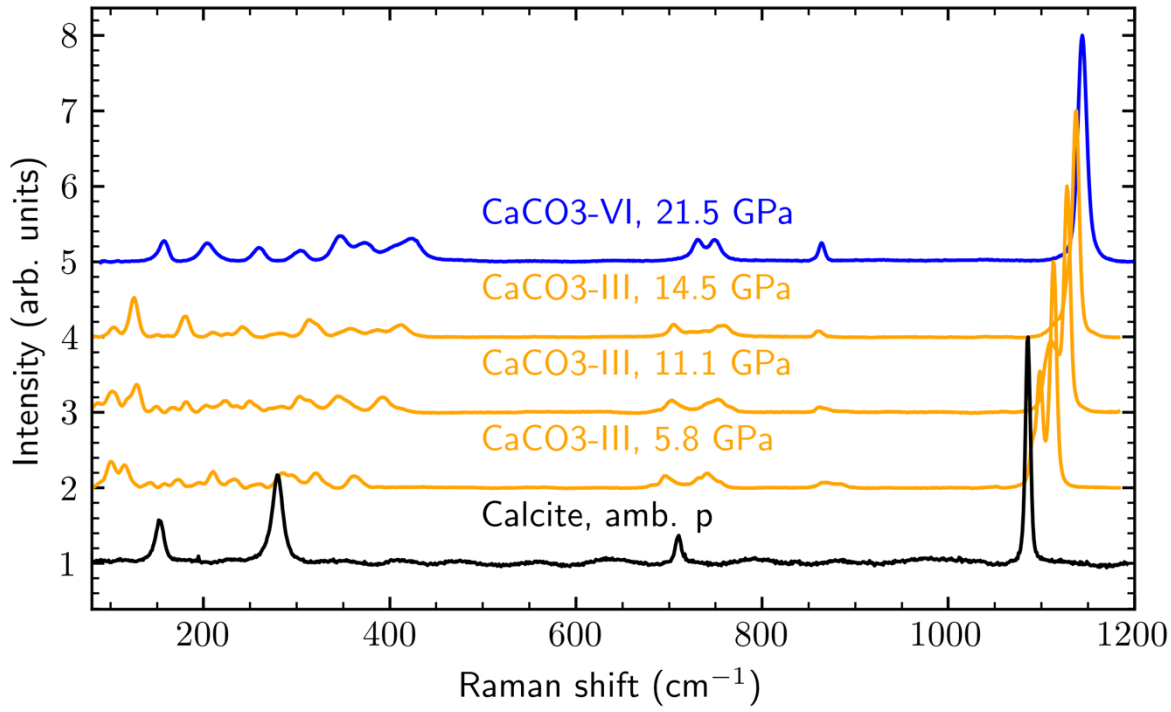

Figure S2. Raman spectra of $CaCO_3$ high pressure polymorphs measured upon compression.

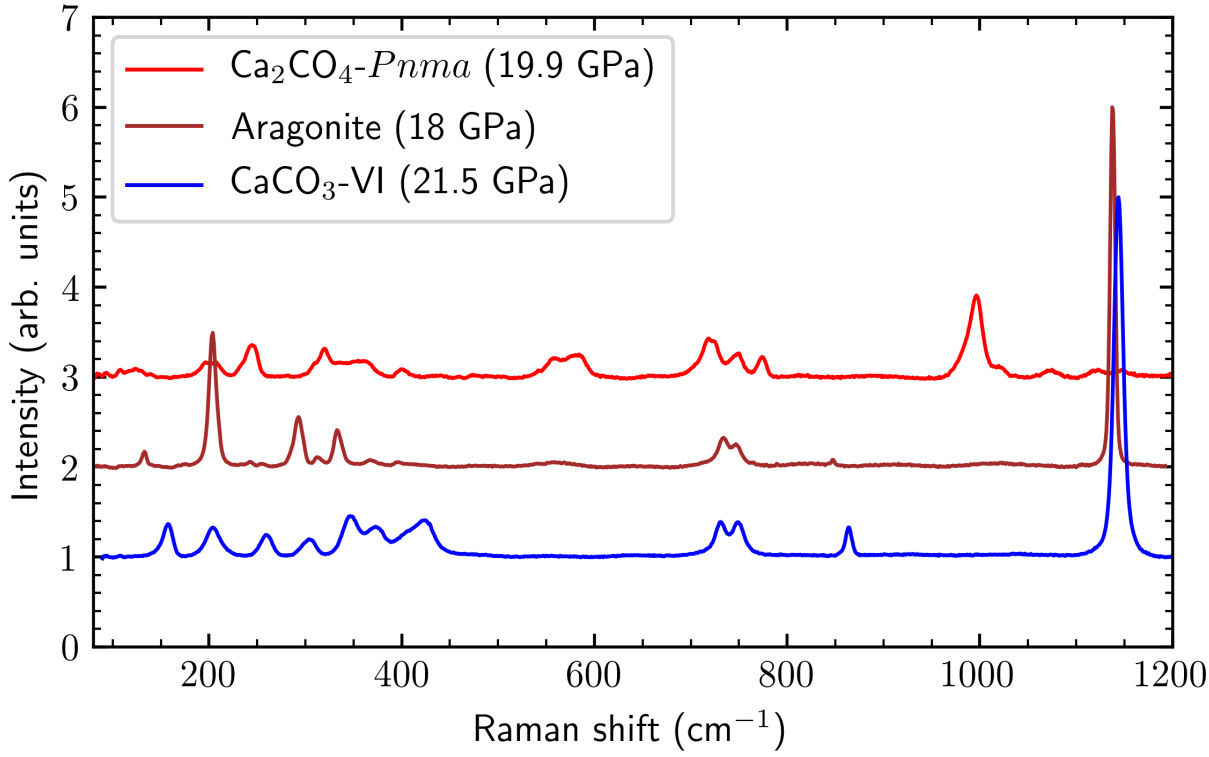

Figure S3. Comparison of Raman spectra of Ca_2CO_4-*Pnma* (temperature quenched from~ 2255 K), $CaCO_3$-VI and aragonite (Bayarjargal et al., 2018) measured at similar pressures.

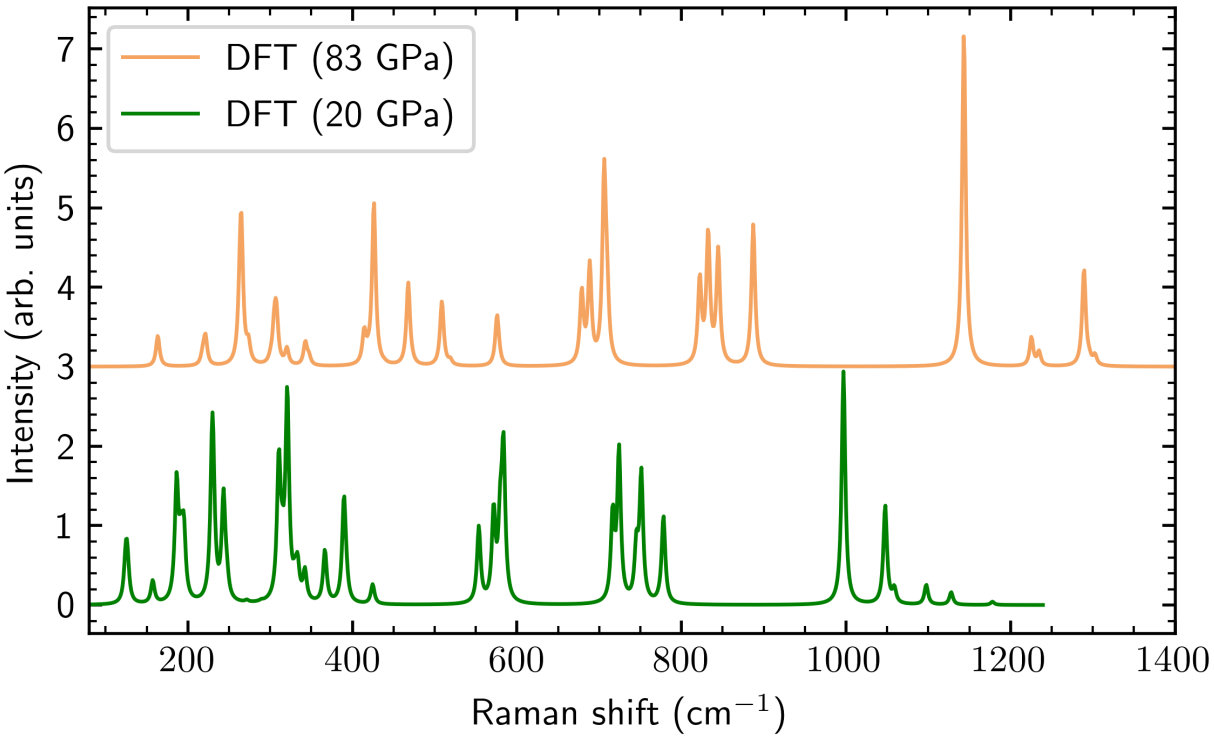

Figure S4. Theoretical Raman spectra of Ca_2CO_4-*Pnma* at 20 and 83 GPa. The calculated frequencies were multiplied by a scaling factor of 1.04.

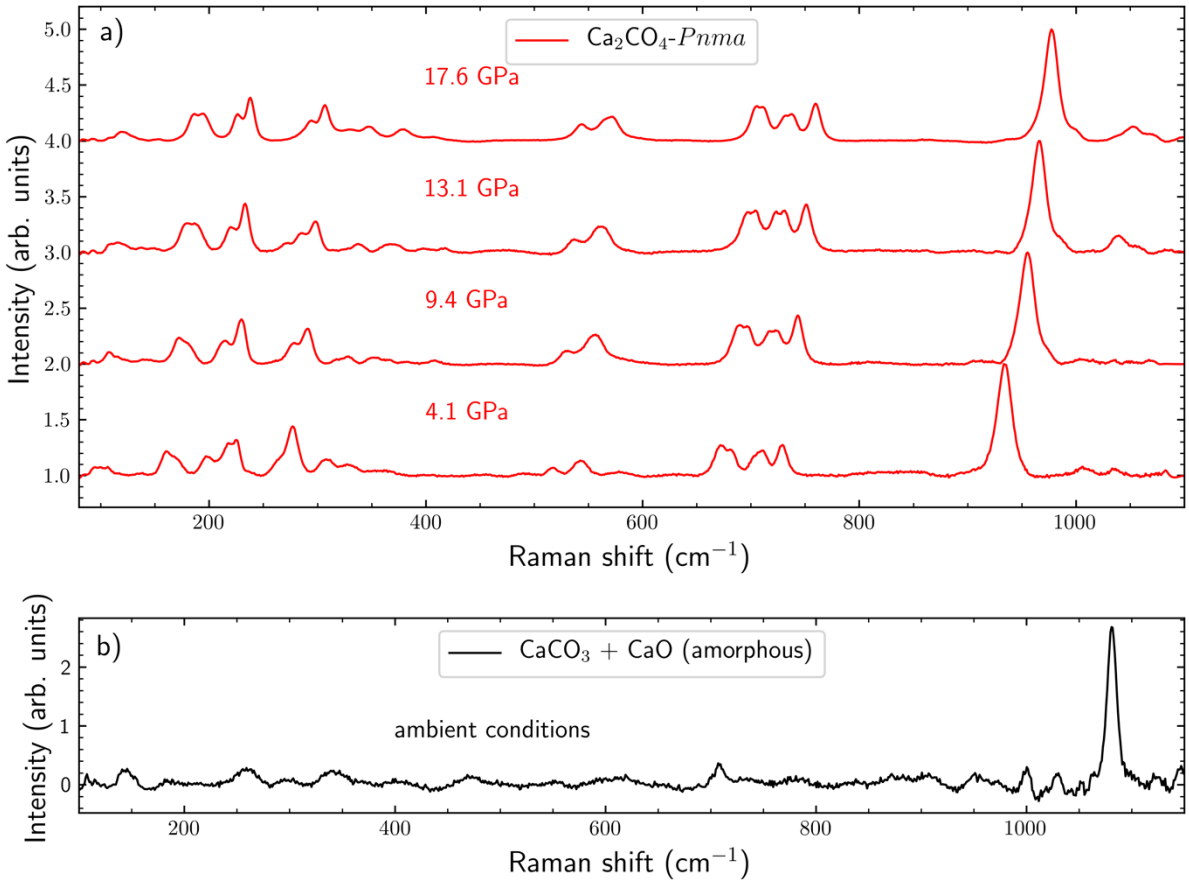

Figure S5. a) Experimental Raman spectra of Ca_2CO_4-*Pnma* obtained upon cold decompression. **b)** Experimental Raman spectrum of amorphous $CaCO_3$ + CaO.

Table S3. List of experimental and theoretical data in chronological order of acquisition.

	Method	Pressure (GPa)	Temperature (K)	Observed Phase	a (Å)	b (Å)	c (Å)	V (Å)^3
Experimental								
BX-90	SC-XRD	89.0(8)[d]	2500(250)[a]	Ca_2CO_4 ($Pnma$)	5.917(5)	4.456(4)	7.934(14)	209.2(4)
	SC-XRD	93.2(8)	amb. T	Ca_2CO_4 ($Pnma$)	5.831(3)	4.529(5)	7.811(10)	206.3(5)
	SC-XRD	79.1(6)[b]	amb. T	Ca_2CO_4 ($Pnma$)	5.955(2)	4.51(6)	7.902(8)	212.2(3)
	SC-XRD	69.4(5)[b]	amb. T	Ca_2CO_4 ($Pnma$)	5.969(4)	4.601(4)	7.932(11)	217.8(5)
BA1	Raman	0.27(2)	amb. T	$CaCO_3$ (Calcite $R\bar{3}c$)				
	Raman	7.5(2)	amb. T	$CaCO_3$-III ($P\bar{1}$)				
	Raman	13.6(4)	amb. T	$CaCO_3$-III ($P\bar{1}$)				
	Raman	22.8(2)	amb. T	$CaCO_3$-VI ($P\bar{1}$)				
	Raman/SC-XRD	20.1(2)[d]	1830(150)[a]	Ca_2CO_4 ($Pnma$)	6.263(5)	4.896(4)	8.524(15)	261.4(4)
	SC-XRD	15.7(2)[b]	amb. T	Ca_2CO_4 ($Pnma$)	6.343(7)	4.9577(11)	8.661(2)	272.4(5)
	SC-XRD	10.8(2)[b]	amb. T	Ca_2CO_4 ($Pnma$)	6.351(7)	5.022(2)	8.776(3)	279.9(2)
BA2	Raman	amb. p	amb. T	$CaCO_3$ (Calcite $R\bar{3}c$)				
	Raman	0.55(3)	amb. T	$CaCO_3$ (Calcite $R\bar{3}c$)				
	Raman	5.8(1)	amb. T	$CaCO_3$-III ($P\bar{1}$)				
	Raman	11.1(2)	amb. T	$CaCO_3$-III ($P\bar{1}$)				
	Raman	14.5(3)	amb. T	$CaCO_3$-III ($P\bar{1}$)				
	Raman	21.5(2)	amb. T	$CaCO_3$-VI ($P\bar{1}$)				
	Raman	19.9(4)	2255(250)[a]	Ca_2CO_4 ($Pnma$)				
	Raman	17.6(4)[b]	amb. T	Ca_2CO_4 ($Pnma$)				
	Raman	13.1(5)[b]	amb. T	Ca_2CO_4 ($Pnma$)				
	Raman	9.4(3)[b]	amb. T	Ca_2CO_4 ($Pnma$)				
	Raman	4.1(2)[b]	amb. T	Ca_2CO_4 ($Pnma$) + Amorphous $CaCO_3$ + CaO				
	Raman	amb. p[b]	amb. T					
Theory	DFT	0	0	Ca_2CO_4 ($Pnma$)	6.485	5.134	9.086	302.51
	DFT	10	0	Ca_2CO_4 ($Pnma$)	6.366	5.004	8.765	279.20
	DFT (Raman)[c]	20	0	Ca_2CO_4 ($Pnma$)	6.282	4.898	8.559	263.37
	DFT	30	0	Ca_2CO_4 ($Pnma$)	6.215	4.812	8.400	251.22
	DFT	40	0	Ca_2CO_4 ($Pnma$)	6.156	4.740	8.273	241.40
	DFT	50	0	Ca_2CO_4 ($Pnma$)	6.102	4.680	8.166	233.19
	DFT	60	0	Ca_2CO_4 ($Pnma$)	6.055	4.627	8.071	226.10
	DFT	70	0	Ca_2CO_4 ($Pnma$)	6.010	4.580	7.989	219.91
	DFT (Raman)[c]	83	0	Ca_2CO_4 ($Pnma$)	5.954	4.521	7.885	212.86
	DFT	90	0	Ca_2CO_4 ($Pnma$)	5.932	4.501	7.846	209.46
	DFT	100	0	Ca_2CO_4 ($Pnma$)	5.897	4.466	7.785	204.98

[a] Experiments were conducted after quenching to ambient temperature.
[b] Data obtained after pressure release.
[c] Theoretical Raman spectra were calculated.
[d] Solved and refined structure. BA = Boehler Almax DAC type.

References cited

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