Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

High-pressure transformations of CaC_2O_5 – the full structural trend from double $[CO_3]$ triangles through the isolated group of $[CO_4]$ tetrahedra to framework and layered structure

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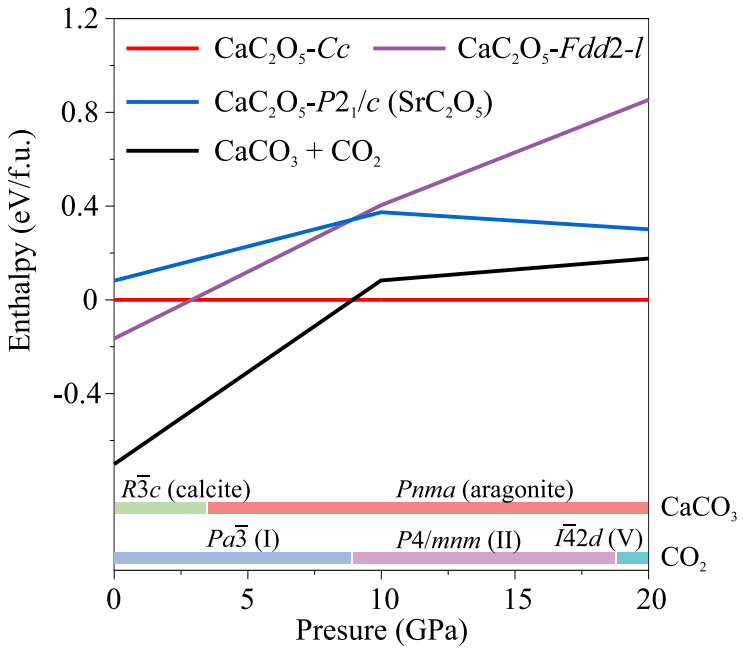

Figure S1: Enthalpy-pressure dependence for the structures of CaC_2O_5 and ($CaCO_3$ + CO_2) mixture.

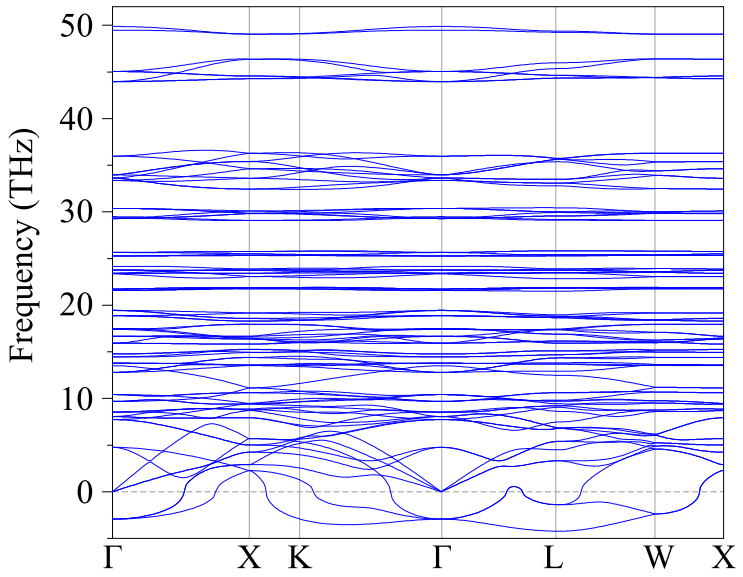

Figure S2: Phonon dispersion curves of the predicted CaC_2O_5-$Fd\bar{3}m$ at 25 GPa and 0 K.

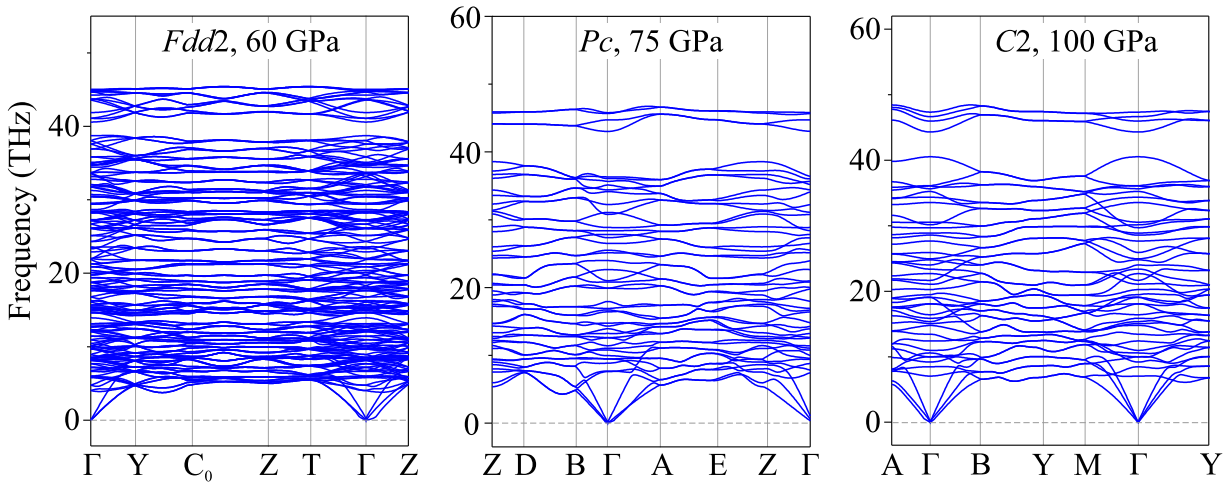

Figure S3: Phonon dispersion curves of the previously predicted structures CaC_2O_5-*Fdd*2, *Pc*, and *C*2.

Table S1: CaC_2O_5 structures introduced in the current study.

Space group	Pressure (GPa)	Lattice parameters (Å, deg)			Atom	Coordinates		
						x	y	z
Cc (#9)	15	$a = 7.435$	$b = 10.421$	$c = 4.589$	Ca1	0.249	0.144	-0.052
		α=90.00	β=121.19	γ=90.00	C1	0.616	0.117	0.757
					C2	-0.035	0.114	0.233
					O1	0.151	0.075	0.346
					O2	0.544	0.188	0.497
					O3	0.410	0.325	-0.088
					O4	0.031	0.426	0.407
					O5	0.331	0.411	0.398
$I\bar{4}2d$ (#122)	50	$a = 7.165$	$b = 7.165$	$c = 10.148$	Ca1	0.533	0.250	0.125
		α = 90.00	β=90.00	γ = 90.00	C1	-0.014	0.336	0.332
					O1	0.149	0.329	0.252
					O2	-0.023	0.189	0.405
					O3	0.000	0.000	0.839
C2-l (#5)	50	$a = 12.019$	$b = 6.936$	$c = 6.936$	Ca1	0.750	0.378	0.039
		α = 90.00	β=125.25	γ = 90.00	Ca2	0.000	0.667	0.500
					Ca3	0.000	0.588	0.000
					C1	-0.041	0.294	0.692
					C2	0.791	0.111	0.375
					C3	0.209	0.144	0.292
					C4	0.541	0.461	0.275
					O1	-0.039	0.128	0.210
					O2	0.289	0.128	0.540
					O3	0.377	0.453	0.476
					O4	0.877	0.302	0.778
					O5	0.128	0.279	0.552
					O6	0.628	0.477	0.203
					O7	0.032	0.445	0.754
					O8	0.718	0.099	0.150
					O9	0.282	0.156	0.214
					O10	0.468	0.310	0.190
$Fd\bar{3}m$ (#227)	50	$a = 10.146$	$b = 10.146$	$c = 10.146$	Ca1	0.500	0.500	0.500
		α = 90.00	β=90.00	γ = 90.00	C1	0.207	0.207	0.207
					O1	-0.035	0.125	0.125
					O2	0.280	0.280	0.280

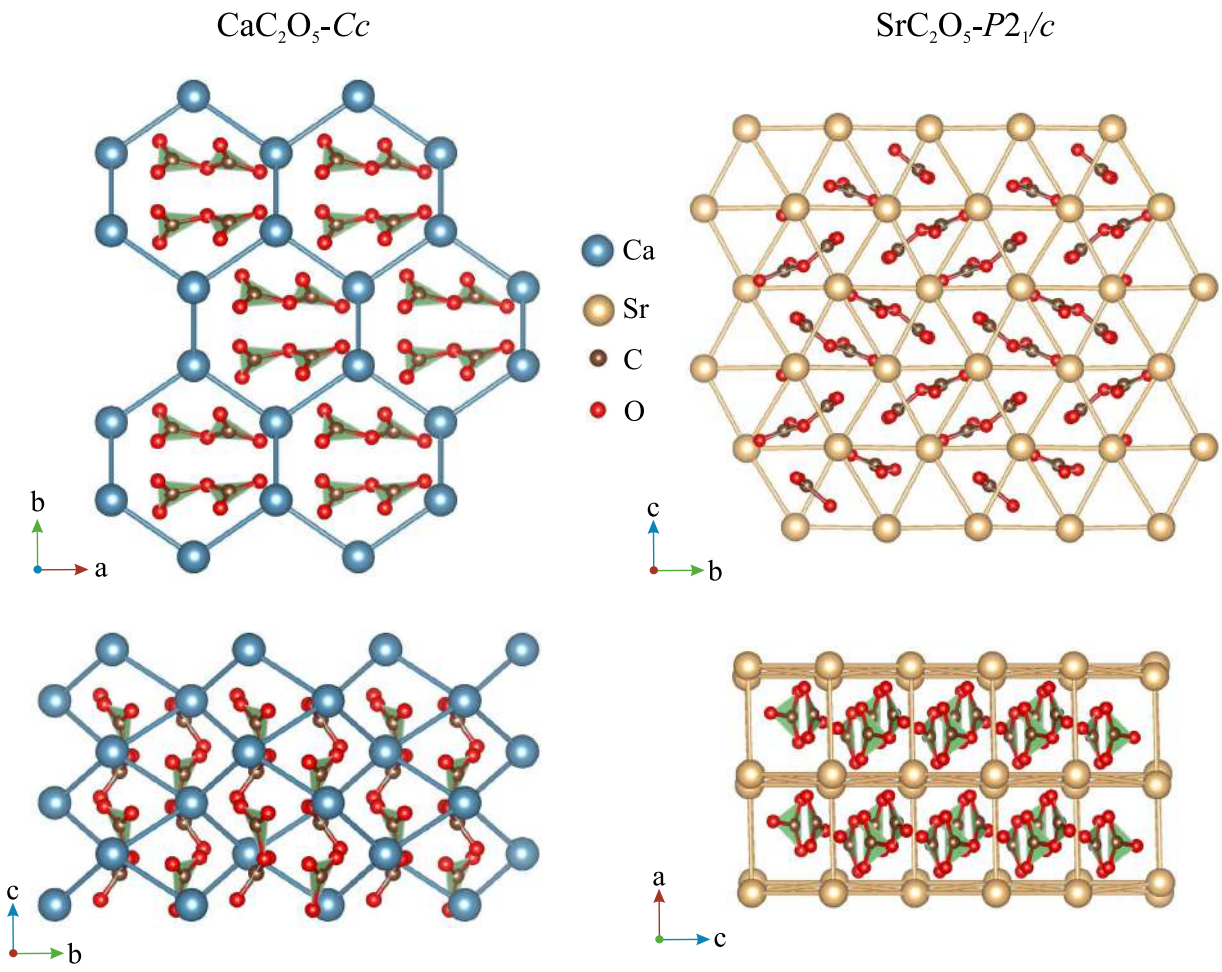

Figure S4: Comparison of Ca- and Sr-pyrocarbonate structures at 15 GPa.

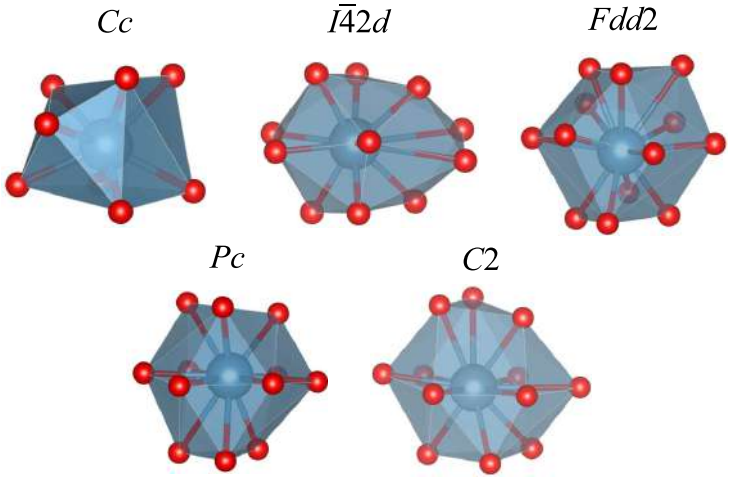

Figure S5: Comparison of Ca-polyhedra of CaC_2O_5 modifications.

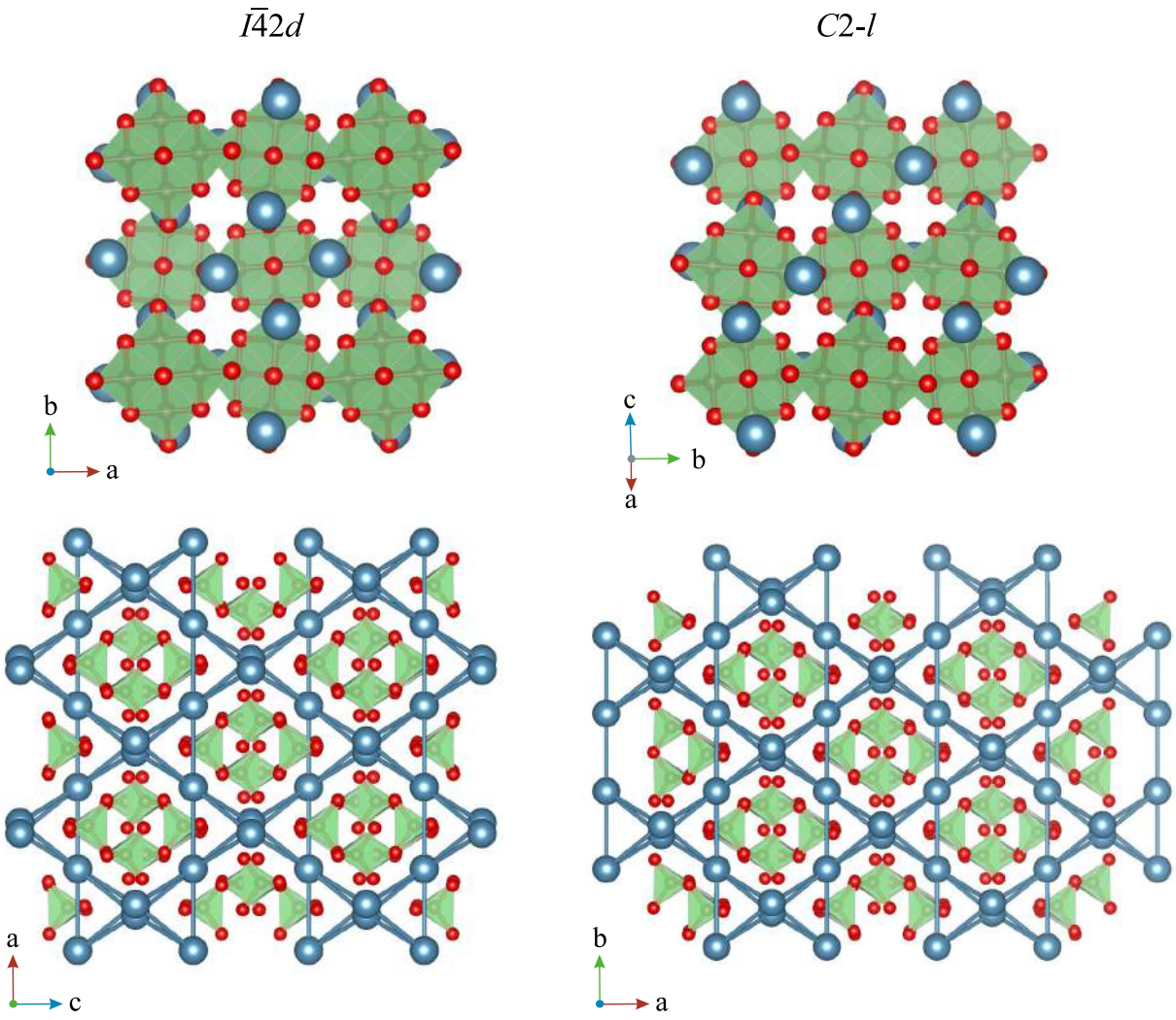

Figure S6: Comparison of $I\bar{4}2d$ and $C2$-l structures at 25 GPa.

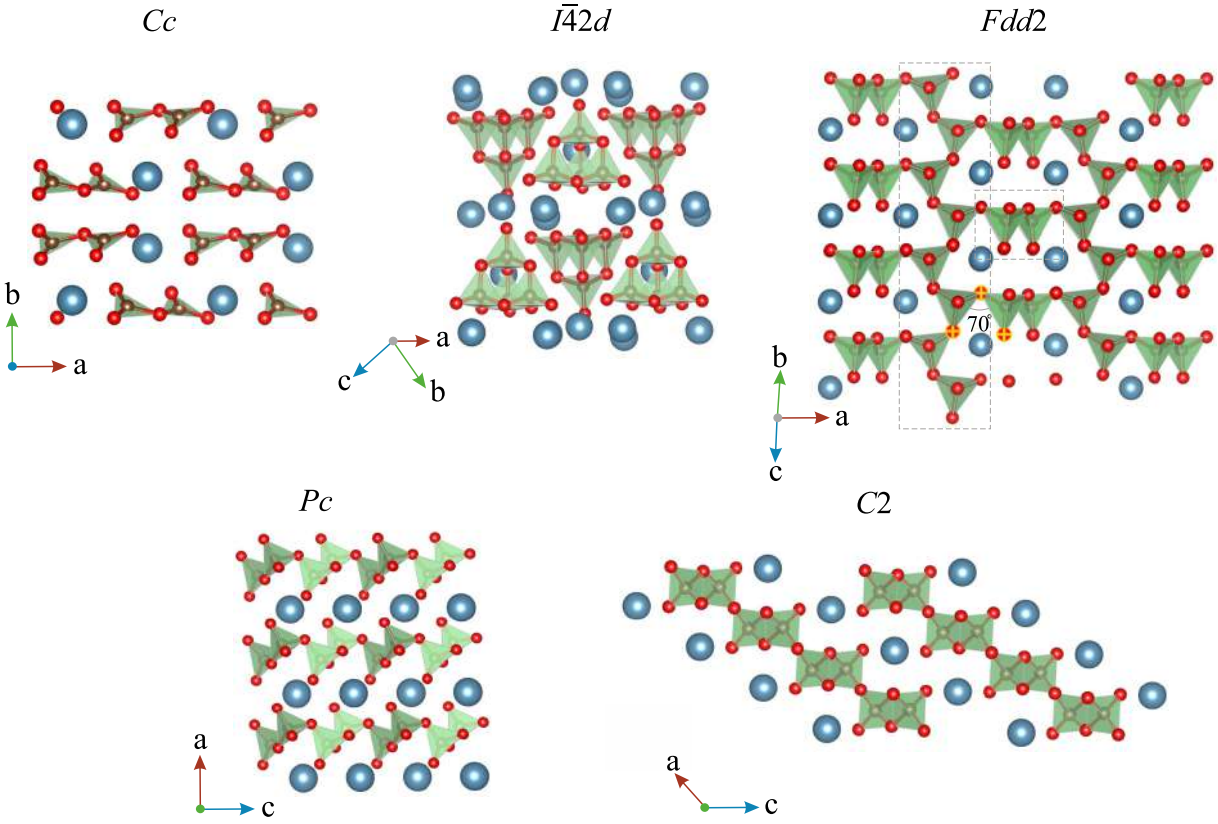

Figure S7: Crystal structure of the CaC_2O_5 polymorphic modifications.

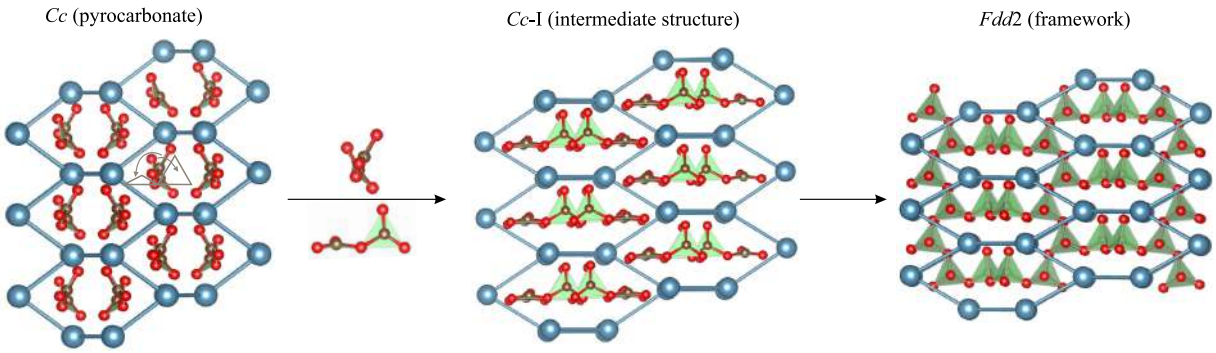

Figure S8: Transformation mechanism of reconstruction of pyrocarbonate CaC_2O_5-*Cc* into a framework carbonate CaC_2O_5-*Fdd*2.

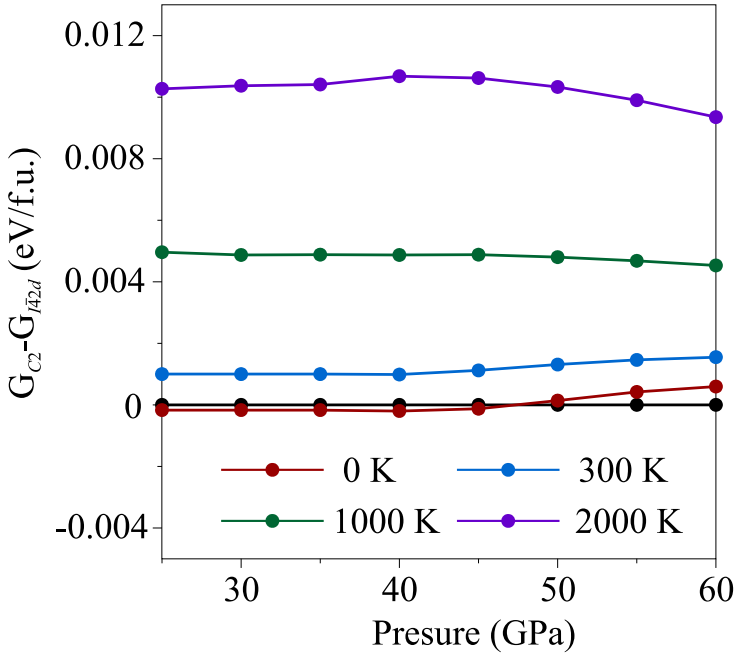

Figure S9: Relative difference between the Gibbs free energies of structures CaC_2O_5-$I\bar{4}2d$ and CaC_2O_5-$C2$-I.

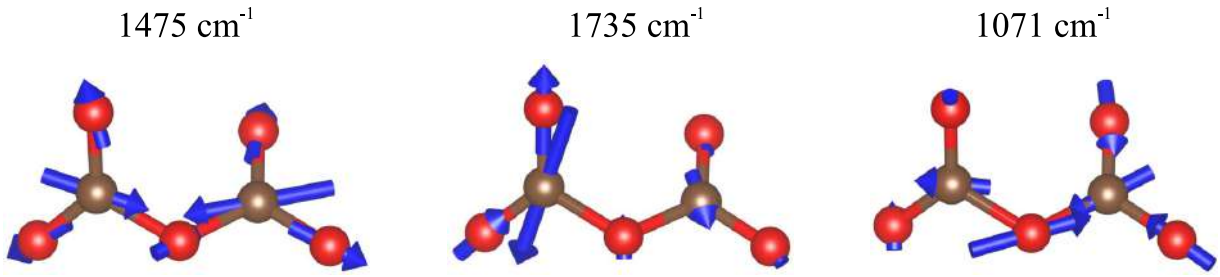

Figure S10: Displacement patterns in Raman modes of CaC_2O_5-Cc at 1475 cm^{-1}, 1735 cm^{-1}, and 1071 cm^{-1} at pressure of 15 GPa

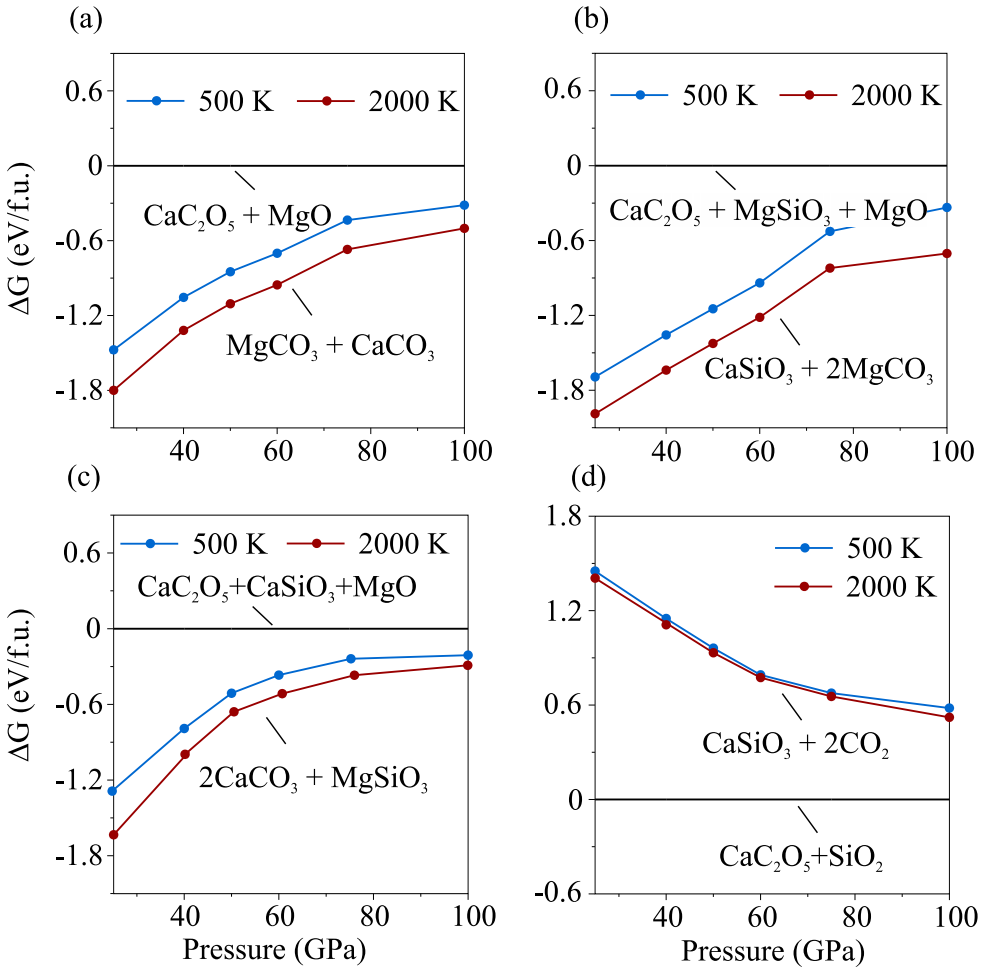

Figure S11: Relative Gibbs free energies as a function of pressure, at several temperatures, for reactions: $CaC_2O_5 + MgO = MgCO_3 + CaCO_3$ (a), $CaC_2O_5 + MgSiO_3 + MgO = CaSiO_3 + 2MgCO_3$ (b), $CaC_2O_5 + CaSiO_3 + MgO = 2CaCO_3 + MgSiO_3$ (c), and $CaC_2O_5 + SiO_2 = CaSiO_3 + 2CO_2$ (d).