Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Table S.I.1.- k-points utilized in the DFTcalculations of $Ca(CO_3)_{1-x}(AO_4)_xO_3$ polymoprhs.

Concentration, x	Aragonite	Calcite	Vaterite *P6₃/mmc*	vaterite *Ama2*
0	6 x 4 x 6	6 x 6 x 6	6 x 6 x 6	4 x 4 x 6
0.25	4 x 4 x 4	--	4 x 6 x 4	--
0.167	--	4 x 4 x 2	--	--
0.125	2 x 4 x 4	--	--	4 x 4 x 4
0.083	--	4 x 4 x 2	2 x 4 x 4	--
0.063	4 x 2 x 4	--	--	4 x 2 x 4
0.056	--	--	2 x 2 x 2	--
0.042	--	2 x 2 x 1	--	--
0.031	2 x 2 x 2	--	--	4 x 2 x 2
0.028	--	--	2 x 2 x 2	--
0.021	2 x 2 x 2	2 x 2 x 1	--	2 x 2 x 2

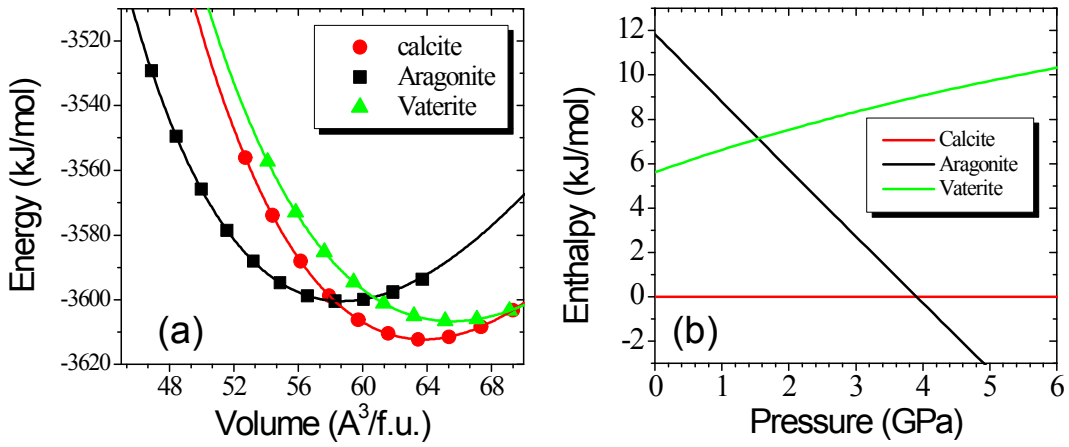

Figure S.I.1.- (a) Calculated total energy *vs* volume curves of the $CaCO_3$ polymorphs; calcite (red) Aragonite (black) and vaterite (green). Symbols correspond to the DFT calculated data, and lines show the fitting to the Murnagham equation of state. (b) Calculated enthalpy *vs*. pressure for the $CaCO_3$ polymorphs.

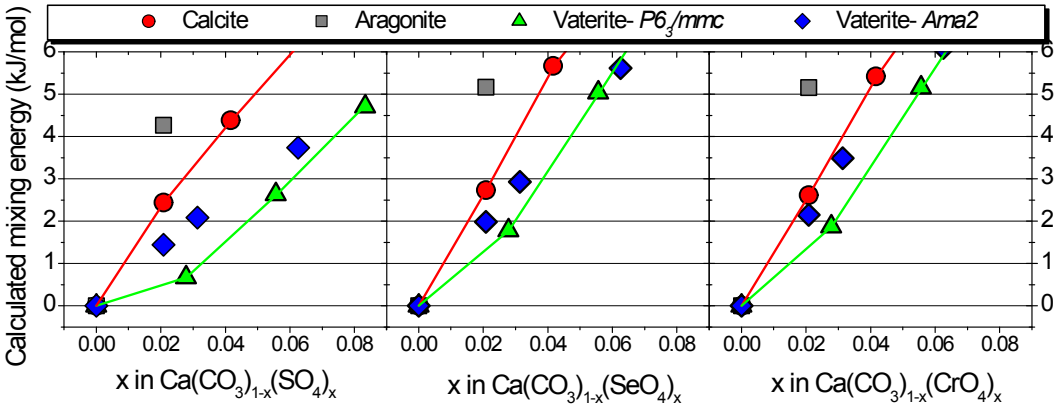

Figure S.I.2.- Same as **Figure 3** in main text: Calculated mixing energies of $Ca(CO_3)_{1-x}(AO_4)_x$ in the crystal structures of calcite (red circles) aragonite (grey squares) and Vaterite-P63/cmm (green triangles) and vaterite-Ama2 (blue diamonds). Lines are guide to the eye.

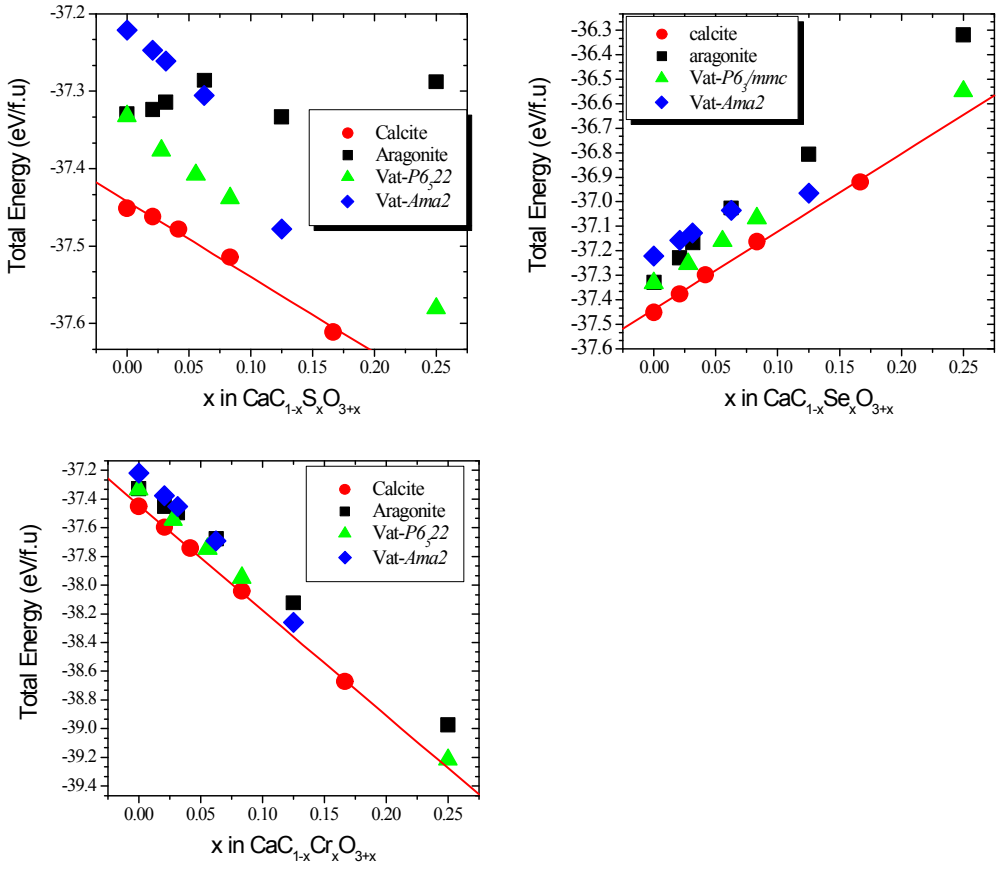

Figure S.I.3.- Calculated total energy *vs* concentration of the $Ca(CO_3)_{1-x}(AO_4)_xO_3$ polymorphs; calcite (red circles), aragonite (black squares), vaterite *P6₃/mmc* (green triangles) and vaterite *Ama2* (blue diamonds). **Figure 4** in main text is constructed taking the energy difference between the calculated DFT data and the linear fitting of the calcite energy, Ecalcita = $a + bx$ (red lines) where the parameters, a and b, are estimated by the method of least squares. Correlation factors of the linear fittings are $R_S = 0.993$, $R_{Se} = 0.999$, $R_{Cr}=1$