Supplementary Materials: Fluorine incorporation into calcite, aragonite and vaterite $CaCO_3$: Computational chemistry insights and geochemistry implications

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Table S1: The influence of dispersion corrections. Three sets of the energies for the various substitution mechanisms are shown: without van der Waals correction, using optPBE-vdW and using D2-vdW, for each of the four substitution mechanisms considered and for each of the three polymorphs considered. Units are kJ/mol ($CaCO_3$).

method	calcite				aragonite				vaterite			
	Ca-site	C-site	O-site	CaF_2	Ca-site	C-site	O-site	CaF_2	Ca-site	C-site	O-site	CaF_2
none	42.1	40.4	13.6	-12.1	41.4	39.1	8.1	-14.6	35.8	32.5	6.0	-15.1
optPBE-vdW	43.2	39.2	13.2	-11.8	42.8	37.5	7.0	-14.4	37.6	31.4	5.0	-15.2
D2-vdW	45.2	41.2	12.5	-13.9	45.8	38.8	7.1	-10.6	38.3	32.1	5.3	-13.1

Table S2: Focusing on the O-site substitution, we get the results as re-listed here, which allows us to check on the influence of dispersion corrections on our observations. With or without dispersion correction the relative energy differences between substituted and non-substituted structures do not vary and again we still see that vaterite $<$ aragonite $<<$ calcite for the O-site substitution Units are kJ/mol ($CaCO_3$).

method	defect energy change			energy difference	
	calcite	aragonite	vaterite	$\Delta(calcite - aragonite)$	$\Delta(calcite - vaterite)$
none	13.63	8.05	6.04	5.6	7.6
optPBE-vdW	13.51	7.37	5.63	6.1	7.9
D2-vdW	27.32	22.24	19.71	5.1	7.6

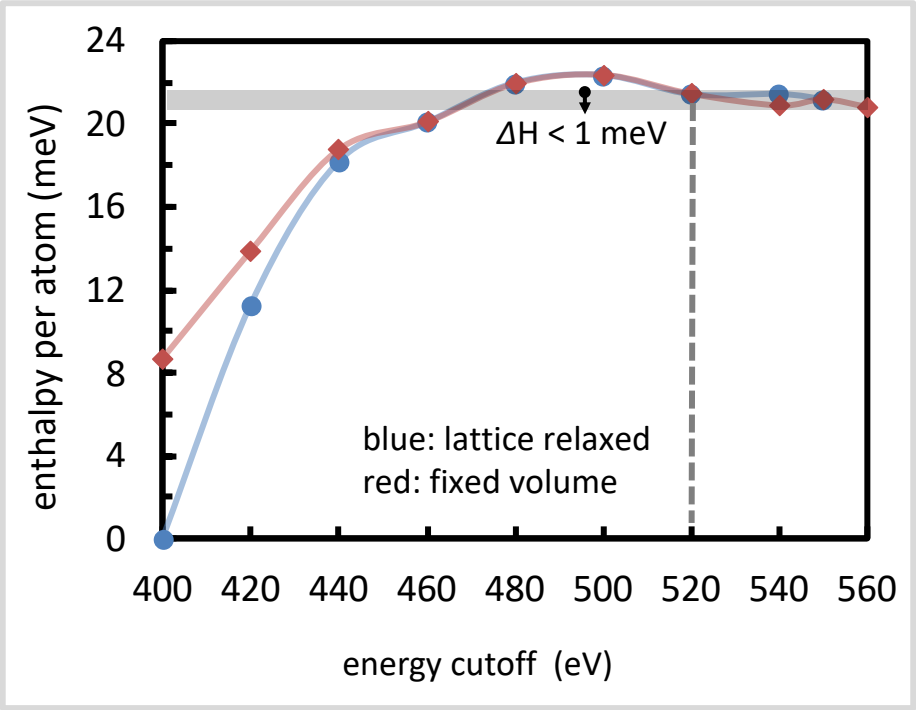

Figure S1: The level of convergence of atomic energies, in F-bearing aragonite. As we can tell from the figure, 520 eV is sufficient to get a reliable enthalpy H (H $\lessapprox$ 1 meV), while the default value by VASP (400 eV) does not give sufficiently accurate energy in this system.