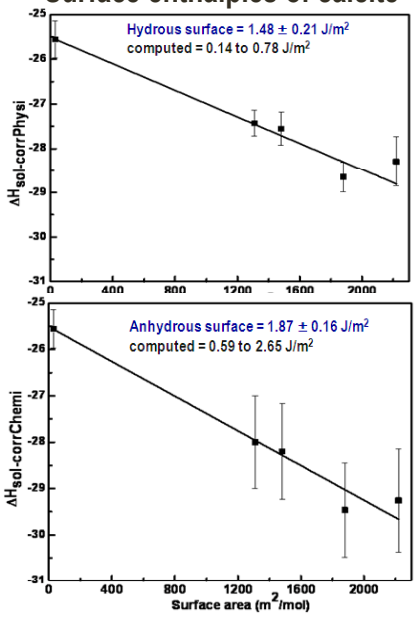
The energetics of nanophase calcite

Surface energy of nanocalcite determined by isothermal acid solution (ΔH_{sol}) and water adsorption (ΔH_{H2Oads}) calorimetry

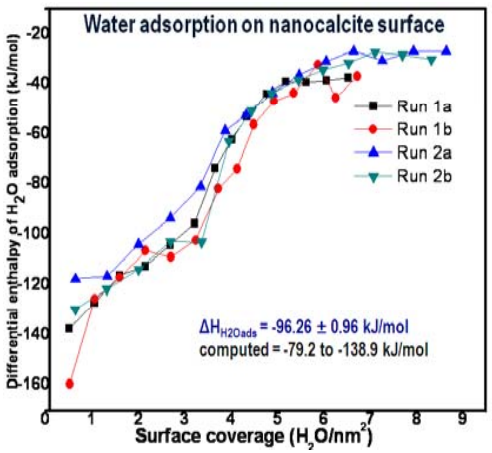
***Sample characterization:** XRD, TEM, BET, TGA, & ICP-MS*

nano calcite	Particle size (nm)			ΔH_{sol}
Composition	XRD	TEM	BET	(kJ/mol)
$Ca_{0.996}Mg_{0.004}CO_3 0.052 H_2O$	74 ± 2	92 ± 2	117.8 ± 1.0	-28.67 ± 0.34
$Ca_{0.99}Mg_{0.01}CO_3$ 0.055 H_2O	42 ± 2	133 ± 4	169.0 ± 2.3	-27.45 ± 0.29
$Ca_{0.99}Mg_{0.01}CO_3$ 0.038 H_2O	36 ± 2	119 ± 3	150.6 ± 2.6	-27.57 ± 0.37
$Ca_{0.99}Mg_{0.01}CO_3$ 0.069 H_2O	28 ± 2	65 ± 2	99.8 ± 0.4	-28.32 ± 0.56
$Ca_{0.984}K_{0.016}CO_3$ (bulk)	>100	5000	7000 ± 100	-25.56 ± 0.41

Surface enthalpies of calcite



Water–calcite interface characterization by water adsorption calorimetry



Enthalpy of chemisorbed water on nanocalcite surface = ΔH_{H2Oads} = -96.26 ± 0.96 kJ/mol & water coverage on surface = 5.01 ± 0.63 H_2O per nm²

- $CaCO_3$ precipitation in a geologic CO_2 repository occurs in confined micro/nanopores of the sandstone aquifer. In this nanoscale regime, the order of thermodynamic stability of $CaCO_3$ polymorphs could be inverted due to surface area induced energy crossovers.
- The difference in the measured solution enthalpies (ΔH_{sol}) for the nanophase and bulk calcite samples stems from the increased surface areas of the nanophase samples.

$$\Delta H_{sol\text{-}bulk} = \Delta H_{sol\text{-}corr\ nano} + SA * \gamma$$

Enthalpies corrected for physically ($\Delta H_{sol\text{-}corr\text{-}physi}$) or chemisorbed ($\Delta H_{sol\text{-}corr\text{-}chemi}$) water where SA = surface area of nanocalcite (m²/mol); γ = surface enthalpy (J/m²)

- From the calorimetric data, the surface energies of calcite were determined as ***1.48 ± 0.21 and 1.87 ± 0.16 J/m²*** for hydrous and anhydrous surfaces. These values are larger than predicted from computational models for idealized calcite surface because the synthetic samples contain a range of planes and defect structures.

Forbes, Radha, Navrotsky
Geochimica et Cosmochimica Acta 75, 7893 (2011)