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The mechanism and kinetics of the uptake of CO_2, SO_2, HNO_3 and HCl on calcite ($CaCO_3$) at ambient temperature: the importance of adsorbed water on mineral dust

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All experimental observations of the uptake of the four title compounds on calcite using a low pressure flow reactor are consistent with the reactivity of the reactive bifunctional surface intermediate Ca(OH)(HCO_3) that has been proposed in the literature. The uptake of CO_2 and SO_2 occurs on specific adsorption sites of crystalline $CaCO_3$(s) rather than by dissolution in adsorbed water, H_2O(ads), that is present under the experimental conditions. SO_2 primarily interacts with the bicarbonate moiety whereas CO_2, HNO_3 and HCl all react first with the hydroxyl group of the surface intermediate. Subsequently, the latter two react with the bicarbonate group to presumably form $Ca(NO_3)_2$ and $CaCl_2 2H_2O$ thereby releasing CO_2 as a reaction product. The effective equilibrium constant of the interaction of CO_2 with calcite in the presence of H_2O(ads) is $\kappa = \Delta CO_2/((H_2O(ads)[CO_2])$ = 1.62x10^3 bar^{-1} where ΔCO_2 is the quantity of CO_2 adsorbed on $CaCO_3$ at a given quantity of adsorbed water, H_2O(ads). The excess solubility for CO_2 and SO_2 exceeds the normal Henry's law solubility in H_2O(ads) by more than six and eight orders of magnitude, respectively. The reaction mechanism involves a weakly-bound precursor species which is reversibly adsorbed and undergoes rate-controlling concurrent reactions with both functionalities of the surface intermediate. The initial uptake coefficients γ_0 on calcite powder depend on the abundance of H_2O(ads) under the present experimental conditions and are on the order of 10^{-4} for CO_2 and 0.1 for SO_2, HNO_3 and HCl with γ_{ss} being significantly smaller than γ_0 for HNO_3 and HCl thus indicating partial saturation of the

uptake. At 33% rh and 300K there are 3.5 layers of H_2O adsorbed on calcite which reduces to a fraction of a monolayer of weakly- and strongly-bound water upon pumping and/or heating.