

Wettability alteration of calcite surface induced by ion exchange

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The interaction of water and organic molecules with mineral surfaces controls a range of processes in nature and industry. The thermodynamic property, surface tension, helps describe these interactions. We investigated the change in water affinity for a calcite (CaCO_3) {10.4} surface where Ca^{2+} and CO_3^{2-} ions were sequentially replaced with Mg^{2+} and SO_4^{2-} , in the bulk solid and at the surface, which is a system of broad interest, for biomineralisation, oil production, and many others. We used electronic structure calculations based on density functional theory (DFT).

Mg^{2+} substitution for Ca^{2+} is favored but only when SO_4^{2-} ions are present and MgSO_4 incorporates preferentially as ion pairs at the fluid-calcite interface. Mg incorporation weakens organic molecule adhesion, while strengthening water adsorption (Fig. 1). Thus, Mg^{2+} substitution renders the calcite surface more water wet, or hydrophilic, making it less favourable for organic compound attachment. We estimated the change in calcite surface tension after ion exchange and determined the resulting change in macroscopic wettability. When only 10% of surface Ca is replaced by Mg, contact angle changes dramatically, i.e. 40 - 70°, converting a hydrophobic surface to a mixed wet surface. Producing magnesium calcite is a simple trick organisms can use for controlling calcite growth and the process helps explain why oil recovery from carbonate reservoirs is enhanced when both Mg^{2+} and SO_4^{2-} are present in the pore water.

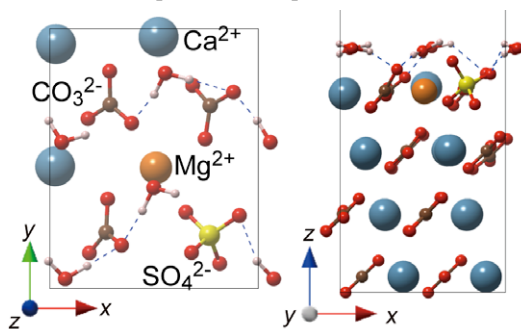


Figure 1: The lowest energy configuration for four water molecules on a calcite {10.4} surface with substitution by a Mg SO_4 ion pair. (Left) Top view. (Right) Side view.

Characterization and Surface Reactivity of Natural and Synthetic Magnetites

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Magnetite is an Fe(II/III) oxide mineral that occurs naturally and potentially as small particles with significant surface reactivity, and although much work is reported on synthetic material [1,2], little work exists for natural samples. The goal of the present work was to carefully characterize four natural magnetite samples from an iron ore deposit [3] and two synthetic commercial reference samples, and to compare their surface characteristics and reactivity with the aim of evaluating their geochemical behavior towards adsorption of environmentally relevant ions, as well as their potential for use as environmental remediation sorbents. In addition, their As(V) adsorption behavior was determined at pH 6, and was analyzed as related to the surface characteristics and particle aggregation behavior determined.

The analyses revealed high magnetite purity in the natural samples, and specific surface areas (SSA) ranging from 1 to 8 m^2/g . Small alumino-silicate impurities were found in natural magnetites, apparently occurring at the particle surfaces and significantly lowering the magnetite isoelectric point. All samples are composed of aggregates of 39-52 nm magnetite particle units, but highly aggregated with very large size dispersions. The synthetic sample with the smallest particle size (30 nm in average - 39 m^2/g) showed its entire surface area available for adsorption, despite its highly aggregated state observed, suggesting an open and highly dynamic aggregate framework. The other larger samples showed more complex aggregation behavior, which produced: (1) a widely variable As(V) adsorption behavior with no clear predictable pattern among samples; and (2) a large decrease of the As(V) adsorption maxima with increasing solids concentration (Cs) imposed in the experimental set-up for any one particular sample. Therefore, we recommend high caution in using the BET-SSA and Cs parameters when performing experimental adsorption work with micro-sized magnetite.

[1] Das *et al.* (2010) *J. Radioanal. Nucl. Chem* **285**, 447-454.

[2] Ilton *et al.* (2010) *Environ. Sci. Technol.* **44**, 170-176.

[3] Rivas *et al.* (2009) *Earth Planets Space* **61**, 151-160.