Water structure at the structurally heterogeneous calcite surface

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The calcite surface has been subject of numerous simulation studies. These studies have generally focused on simulations of perfectly flat calcite surfaces, and in particular the dominant (10-14) face. In both natural environments and in experiments, the calcite surface is of course not atomically flat, and surface roughness is expected to have an effect on the reactivity of the surface sites. Indeed, it has been shown that trace elements differentially incorporate into the calcite surface depending on surface structure [1], while this differential reactivity is not at all captured in the current macroscopic surface chemical models [2,3]. The aim of this work is to obtain information on the interactions of water molecules with the different surface sites present in etch pits and on growth terraces at the calcite (10-14) surface. Results show that the local environment around the structurally distinct sites differs significantly, with the formation of more calcium–water bonds and H-bridges at less-coordinated sites, while the bond length of the metal-hydroxyl site does not vary with position at the surface. Temperature changes over the range of 300 to 340 K does not affect the local environment of the surface groups.

The information obtained in this study is crucial for the improvement of the existing macroscopic surface model for the reactivity of calcite [2]. This mineral surface structural model for calcite was developed using the Charge Distribution MUltiSite Ion Complexation (CD–MUSIC) modelling approach [4] to describe the chemical structure of carbonate mineral-aqueous solution interfaces. The high sensitivity of the model toward parameters describing hydrogen bridging and bond lengths at the mineral-water interface, currently limits the predictive application of the calcite CD–MUSIC model.

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Mass-independent Cd isotope fractionation during evaporation

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Modern mass spectrometry is capable to reveal mass-independent isotope fractionations (MIF) for many heavy elements [1].

Here, we investigate mass-independent Cd isotope fractionations that result from the evaporation of liquid Cd into vacuum. Three residues from evaporation display large mass-dependent Cd isotope fractionations with $1000\ln\alpha$ ranging from -23.2 to -48.3 ‰ for ^{110}Cd/^{114}Cd relative to the starting material [2]. These samples were repeatedly analyzed at high precision using a Neptune MC-ICP-MS, with ion beam intensities typically larger than 20V for ^{114}Cd and analysis times of about 30 minutes. Deficits ranging from 8 to 28 ppm were well resolved for ^{111,113,116}Cd/^{114}Cd. The accurate quantification of the MIF requires that the mass-dependence of the evaporation induced isotope fractionation is accurately corrected. This was facilitated using the generalized power law and normalization to ^{110}Cd/^{114}Cd of the starting material. Note, that the mass-dependence for evaporation was found to be intermediate between that expected to describe kinetic and equilibrium fractionation [2, 3].

MIF for ^{111}Cd, ^{113}Cd and ^{116}Cd scales with deviations from a trend between nuclide mass and mean-squared nuclear charge radii defined by the other five Cd isotopes, thus suggesting that the MIF is due to nuclear volume effects. The preferential evaporation of ^{111}Cd, ^{113}Cd and ^{116}Cd may result from their more tightly bond 5s electrons that are thus not as easily delocalized and hence form weaker metallic bonds in the liquid. Our results are in accord with previous work [4] on the evaporation of Hg, another group 12 element.

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