

## Epitaxy of calcite on dolomite and kutnahorite (104) surfaces

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Carbonate minerals with dolomite-type structure show an anomalous reactivity in aqueous environments. Two examples of this are the complex dissolution paths of kutnahorite,  $\text{Mn,Ca}(\text{CO}_3)_2$ , in pure water [1] and the growth inhibition of dolomite,  $\text{Mg,Ca}(\text{CO}_3)_2$ , from supersaturated aqueous solutions at ambient conditions, i.e. “the dolomite problem” [2]. Key to resolving the problems linked to the reactivity of these minerals is the systematic investigation of the interaction between their surfaces and aqueous solutions with various compositions and saturation states [3,4].

Here we present Atomic Force Microscopy (AFM) observations of the epitaxial growth of calcite on dolomite and kutnahorite (104) faces at room temperature. Growth was promoted by immersing freshly cleaved dolomite and kutnahorite crystals into highly supersaturated aqueous with respect to calcite ( $20 < \beta_{\text{calcite}} = [a(\text{Ca}^{2+}) \cdot a(\text{CO}_3^{2-}) / K_{\text{sp,calcite}}] < 100$ ). Epitaxial growth of calcite occurs by both the spreading of thin layers and the nucleation and growth of oriented three-dimensional islands on (104) substrates. While the growth of calcite thin films is highly anisotropic, the nucleation of 3D-islands occurs preferentially on step edges. This indicates relatively large substrate-overgrowth interfacial energies. Moreover, sequences of AFM images of 3D-islands show that spiral growth on simple or multiple screw dislocations is frequent. The presence of such dislocations can be related to the accommodation of lattice-misfit strains as epitaxial growth proceeds. Additional information provided by recording lateral (friction) forces during the scan with increasing loading forces indicates low adhesion forces between 3D-islands and (104) substrates.

Our AFM observations show that the epitaxial growth of calcite on dolomite and kutnahorite (104) surfaces is a complex phenomenon that leads to the formation of surface patterns at the nanometric scale. The development of such patterns is discussed considering the factors that control the epitaxial growth modes, i.e. Frank-Van der Merwe, Volmer-Weber and Stranski-Krastanov [5].

[1] Mucci (2004) *Aquatic Geochemistry* **10**, 139-169. [2] Lippmann (1973) *Sedimentary carbonate minerals*, Springer-Verlag, 228 pp [3] Hu, Grossie & Higgins (2005) *American Mineralogist*, **90**, 963-968. [4] Higgins & Hu (2005) *Geochimica et Cosmochimica Acta*, **69**, 2085-2094. [5] Chernov (1984) *Modern Crystallography III*, Springer-Verlag, 517 pp.

## Next generation of *in situ* chemical analysis of Titan aerosols via laser desorption mass spectrometry

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Laser desorption mass spectrometry is an attractive analytical tool for the search for organics in space flight missions. Laser desorption provides complementary information to that obtained via the more ubiquitous methods like pyrolysis GC-MS and EGA because it provides molecular information without the need for sample heating. It is also well suited to space flight missions due to the relative ease (or complete lack) of sample preparation. Many mass analyzers have been used in previous missions, such as time-of-flight and quadrupole mass spectrometers, but ion traps in particular have the potential to operate at higher pressures with lower power requirements. One such space flight mission in the development phase is the Mars Organic Molecule Analyzer (MOMA), aboard the joint NASA/ESA rover ExoMars set to launch in 2018. There, Martian soil core samples from a depth of ~2 meters will be interrogated by either pyrolysis gas chromatography or laser desorption mass spectrometry in ambient atmospheric conditions. The mass analyzer is a linear ion trap, capable of providing chemical structural analysis via tandem mass spectrometry (MS/MS). A similar mass spectrometer can also be used for analysis of atmospheric particulates, if collected or concentrated properly. Potential applications could include the analysis of Titan's atmospheric components or deposited organic material on the surface.

To better understand the instrumental response to Titan-like aerosols, a series of aerosol analogs have been generated via far-UV irradiation of relevant Titan precursors. Aerosols are collected and deposited onto a sample plate interfaced to a commercial version of the MOMA instrument (Thermo MALDI LTQXL). By exploring different aerosol precursors, we are able to test sensitivity of the instrument to different chemical characteristics of the aerosol, including pure hydrocarbons, nitrogen-containing compounds, and large aromatic structures. We will present mass spectrometric results for the range of synthesized analog aerosols; for example, we will compare the spectra of benzene-sourced aerosol to those sourced from the nitrogen-heteroatom equivalent pyridine. These results will highlight the compatibility of the laser desorption method to give abundant molecular and fragment ions for these classes of compounds. Further, the results from the commercial instrument will be compared to analyses utilizing the prototype MOMA instrument, currently in development.