

Study of surfaces of Al_2SiO_5 minerals by Lateral Force Microscopy

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Kyanite, sillimanite and andalusite (Al_2SiO_5) are polymorphic minerals which traditionally have been used as geobarometers and geothermometers. However, P-T determinations using Al_2SiO_5 minerals are problematic. Transformations between Al_2SiO_5 polymorphs involve breaking strong Si–O and Al–O bonds. This, combined with the small free energy differences between polymorphs, makes difficult to determine the P-T fields of these minerals, which usually persist as metastable phases [1].

The aim of this work is to study the nanotribological properties of kyanite, sillimanite and andalusite surfaces and their relationship with different Si–O and Al–O bonds schemes. We measured friction on Al_2SiO_5 cleavage surfaces immersed in water using a lateral force microscope (LFM) at RT. Lateral deflection signals along different crystallographic directions were measured and converted into frictional forces after an adequate calibration [2]. While frictions measured at the microscale on different Al_2SiO_5 surfaces were compared, $10 \times 10 \text{ nm}^2$ frictional maps provided detailed structural information (see Figure). The methodology and preliminary results presented here represent a new approach to the study of the Al_2SiO_5 polymorphs.

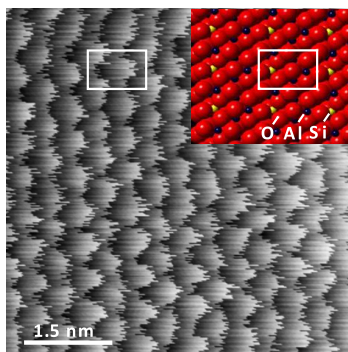


Figure: LFM image of kyanite (100) face showing the surface lattice. The inset shows the kyanite surface structure.

[1] Putnis, A. (1992) *Introduction to mineral sciences*. 457 pp.

[2] Noy et al (1995) *J. Am. Chem. Soc.* **117**, 7943.

Nanotribology of mineral surfaces in aqueous environments

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Investigations on the structure of mineral surfaces are fundamental to gain a better understanding of their reactivity. The latest developments in surface sensitive techniques and, in particular, in atomic force microscopy (AFM), have provided interesting information on the terminations of mineral faces at the nanoscale. Despite this, nanotribology studies of mineral surfaces are still scarce. Recent works have, however, demonstrated that friction measurements performed with lateral force microscopy (LFM) can be used to obtain detailed crystallochemical and crystallophysical information on mineral surfaces [1-3].

Here we present friction measurements conducted on carbonate, sulphate and silicate mineral surfaces using LFM operating in water. Measured friction forces at the nanoscale are typically in the range of 10 nN and they were found to vary with the crystallographic direction. In all cases, crystal lattices could be resolved and the surface unit cells were measured. On the surfaces studied no reconstruction nor relaxation phenomena were observed.

Our LFM measurements were extended to study epitaxial overgrowths on mineral surfaces [4]. Frictional maps allowed us to resolve substrate and overgrowth surface lattices and to determine epitaxial relationships. Furthermore, by increasing the vertical force of the LFM, we removed overgrown islands attached on the substrates. Depending on the mismatch between overgrowth and substrate lattices, different shear strengths for overgrowth detachment in the range of 5 to 150 MPa were calculated.

The results that we present here demonstrate that LFM in liquid is a very suitable technique to study mechanical properties of mineral surfaces and epitaxial phenomena at a molecular scale.

[1] Shindo *et al* (1999) *Physical Chemistry Chemical Physics*, **1**, 1597-1600. [2] Pina *et al* (2012) *Physical Review B*, **85**, 073402 [3] Cubillas & Higgins (2009) *Geochemical Transactions*, **10**,7. [4] Pina *et al* (2012) *Mineralogical Magazine*, **76**, 2235.