

## FT-IR spectroscopy of thin film water on solid surfaces

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Infrared (IR) spectra of liquid water was measured by using attenuated total reflectance (ATR)-IR method. Effects of solid surface on neighbouring liquid water were evaluated by changing incident angle of IR beam (variable angle ATR) with an ATR crystal of Ge (refraction index,  $n=4$ ). Depth of penetration ( $D_p$ ) of IR beam varies from about 200 nm to 1000 nm. The change in OH stretching band around  $3400\text{ cm}^{-1}$  with  $D_p$  was quantitatively interpreted.

We measured as well IR spectra of synthetic oxides and hydroxides, both in transmission through KBr pellets and diffuse reflectance on powders, to obtain basic informations on OH species on solid surfaces.

Interaction of liquid water with solid surfaces was then assessed by ATR-IR microspectroscopy with thin film water sandwiched between ATR crystals ( $\text{ZnSe}$ ,  $n=2.4$ ) and different solid plates.

The final set of experiments was performed on the first prototype of near-field IR spectrometer. This apparatus allowed us to get, at nanometric scale, IR spectra of liquid water (-OH absorption band) confined between grain boundary of polycrystalline silica (agate) sample.

Results were interpreted in the frame of "hard" water concept (Nakashima, 1998), where IR absorption band of liquid water shifts from typically  $3430\text{ cm}^{-1}$  down to typically  $3200\text{ cm}^{-1}$  (Ice at  $0^\circ\text{C}$ :  $3250\text{ cm}^{-1}$ ). Such hardness accounts for the capability of this adsorbed water to persist at the grain boundary up to consolidated metamorphic rocks (Ito and Nakashima, 2002). Comparisons were also made with IR OH bands of different aqueous solutions, affected by the nature of dissolved species with increasing/decreasing "hard" water components (Masuda et al., 2003). Since ubiquitous distribution of thin film water in geomaterials is expected, its potential significance in water-rock interface geochemistry should be highlighted.

### References

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## The mineral-specific thermodynamic sorption database RES<sup>3</sup>T: Concept description, implementation, and application towards contaminated systems

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### Database design and implementation

RES<sup>3</sup>T – the Rossendorf Expert System for Surface and Sorption Thermodynamics – is a digitized thermodynamic sorption database utilizing surface complexation models (SCM). It is mineral-specific and can therefore also be used for complex models of solid phases such as rocks or soils. As to the knowledge of the authors there is no such digital thermodynamic database for surface complexation equilibria existent worldwide, despite of the vast amount of available data.

Data records comprise of mineral properties, specific surface area values, characteristics of surface binding sites and their protolysis, sorption ligand information, and surface complexation reactions. An extensive bibliography is also included, providing links not only to the above listed data items, but also to background information concerning surface complexation model theories, surface species evidence, and sorption experiment techniques.

An integrated user interface helps users to access selected mineral and sorption data, to extract internally consistent data sets for sorption modeling, and to export them into formats suitable for other modeling software. It assists the identification of critical data gaps, the evaluation of existing parameter sets, consistency tests and the establishing of selected reference data sets.

RES<sup>3</sup>T is implemented as a relational database under MS ACCESS. The database is intended for an international use and is currently converted into a WWW-based version.

### Application example

A system for illustrating the current blind predictive capabilities of SCM using the RES<sup>3</sup>T database is the  $\text{Cu}^{2+}$  sorption onto iron oxyhydroxides. To keep the number of parameters at a minimum, the Diffuse Double Layer model was selected to account for electrostatics. The calculation was performed with the FITEQL code, version 3.2. The respective SCM parameters from RES<sup>3</sup>T were the binding site density for the minerals, the surface protolysis constants, and the brutto stability constants for all relevant surface complexes. The model prediction almost always represented the experimental values for the sorbed amount of  $\text{Cu}^{2+}$ , expressed as conventional distribution coefficients  $K_d$  as required by PA software.

### Reference

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