

Multi-element 2D analysis of drilling cores containing mining residues using LIBS and chemometric analysis

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Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy that uses a laser-generated plasma to ablate, atomize, and excite material from a sample surface. LIBS has potential for rapid non-destructive and in-situ geochemical analysis. However, quantitative analysis with LIBS, especially of heterogeneous materials, is very challenging; matrix effects and plasma variations influence the LIBS signal. These limitations have successfully been overcome using multivariate chemometric methods and repetitive measurements in other applications [e.g. 1].

This study tries to estimate limits of detection and accuracy for multi-element LIBS analysis of drilling cores containing mining residues (Harz, Germany) with the LIBS system described below. The LIBS system uses a Nd:YAG 50 mJ 1064 nm laser and an Echelle spectrograph with CCD detector (285-960 nm, resolution 28-94 pm). On the drilling cores, nine meter in total and each one cut in halve, 1000 x 12.5 mm large surface strips were measured, representing 20000 individual (5 accumulated laser shots each) LIBS measurements. Over 100 alternating layers consisting of sludge, Pochsand or wall rock were found; all layers were sampled and analysed by XRF as reference samples. A calibration model was developed with Partial Least Square Regression (PLSR) analysis.

A qualitative LIBS analysis based on characteristic emission lines for heavy metals and major elements has shown, that significant chemical differences may exist between layers. Inside a layer of sludge or wall rock, the LIBS signal appears to be relatively constant. On the other hand, Pochsand layers that consist of very coarse sand appear to be very heterogeneous; heavy-metal enrichment is clearly related to distinct particles. Multivariate chemometric analysis on the relatively homogeneous layers is currently applied to build and test calibration models for a quantitative interpretation of the LIBS measurements.

[1] Sirven *et al.* (2006) Anal. Chem. 78, 1462-1469.

H₂O-adsorption at the (100)-pyrite surface: Forcefield simulation studies supporting GIXRD-experiments

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It is of great importance to study mineral-adsorbate interfaces, because in natural processes mineral surfaces are able to function as templates for the ordering of organic molecules and water. The periodically ordered surface atoms induce an ordering of the adsorbates, so that specific chemical reactions can take place near surfaces. The (100)-pyrite (FeS₂) surface plays an important role in many environmental, biological and mineralogical processes, e.g. in acid mine drainage processes and in the Iron-Sulphur world scenario, that describes one possibility for the origin of life [1].

The structure of the (100)-FeS₂-H₂O interface was determined with grazing incidence X-ray diffraction experiments under environmental conditions, previously [2]. An adsorption model for H₂O at the (100)-FeS₂ surface was determined including three adsorption layers in a distance of 1.9(1)Å, 3.0(3)Å and 5.4(4)Å to the surface, a transitional zone of partial ordered H₂O molecules and H₂O molecules that occupy vacancies of the topmost FeS₂-layer.

Here we report about molecular dynamic (MD) simulations of the H₂O-adsorption on the (100)-FeS₂ surface, carried out with the program package Materials Studio 5.0, particularly the program "Adsorption locator", from Accelrys Inc. Using the forcefield COMPASS27 we confirmed the experimental achieved adsorption model of H₂O. Additionally we determined the orientation of H₂O-molecules within the adsorption layers, the exact positioning of the H-atoms and we get information about the influence of the H₂O-density on the ordering within the adsorption layers. The comparison of the experiment and different MD simulations is well suited to get detailed information about the atomic structure of the (100)-FeS₂-H₂O-interface and to get information about interface systems under perfect adsorption conditions compared to interface systems exposed to higher entropy.

[1] G. Wächtershäuser, C. Huber (1998), Science 281 670-672. [2] S. Meis, U. Magdans, X. Torrelles (2011), Acta Cryst. A67, C338-C339.