Hydrothermal AFM and mixed-flow reactor studies of ZnS dissolution

C. SCHLUETER[1], G. JORDAN[1], O. POKROVSKY[2] AND W.W. SCHMAHL[1]

[1]Sektion Kristallographie, Departement für Geo- und Umweltwissenschaften, Theresienstr.41, 80333 München, Germany, (schlueter.christoph@googlemail.com, jordan@lmu.de, wolfgang.schmahl@lrz.uni-muenchen.de)
[2]LMTG-OMP CNRS, Univ. P. Sabatier, Toulouse, France, (oleg@lmtg.obs-mip.fr)

Sulfide minerals are the major contributors to acid mine drainage (AMD) and heavy metal release. While the weathering of iron sulfides has been studied intensively only little attention has been paid to the zinc sulfides. To understand the mechanisms and kinetics of sphalerite reactions in aqueous solutions, a combination of high resolution microscopy methods and chemical analytical methods proved to be perfect as it correlates nano-scale observations with macro-scale data.

Here, *in situ* hydrothermal AFM (HAFM) measurements and mixed-flow reactor experiments were conducted at pH 1-2 and a temperature of 125 °C. While HAFM measurements were performed on the (110) surfaces, sphalerite powder was used for mixed-flow reactor experiments.

Mixed-flow reactor experiments showed an initial maximum of zinc and sulfur release. This initial maximum in dissolution was followed by an exponentially decreasing part, which converted into a steady state after ca. 10,000-15,000 min. Within the accuracy of the data, the mixed-flow experiments revealed no incongruent or not stoichiometric dissolution. in situ HAFM measurements showed the formation of a thin altered layer on the surface during the initial state of dissolution followed by a development of facets.

From the mixed-flow reactor experiments it can be concluded that the leached layer observed in HAFM experiments can only be caused by a minimal shift in the chemical composition of the surface.

The HAFM experiments further showed the decomposition of the cleavage morphology into facets with three prominent orientations. These observations indicate that the observed initial maximum in zinc and sulfur concentration was caused by a change of the surface morphology from one morphology with high dissolution rates to another morphology with lower dissolution rates. As proved by SEM investigations, small particles on the crystals can be excluded as a reason for the observed rate maximum. Until now tip-surface convolution disabled crystallographic indexing of the facets by AFM. Indexing the facets via LEED remained difficult because the facets were not persistent while LEED sample conditioning. Further experiments are in progress.

In summary, the two different experimental approaches yielded complementary information which in combination allowed one to obtain a significantly more comprehensive understanding of the mechanisms and kinetics of sphalerite dissolution.

Architecture of phosphatic and calcitic brachiopod shell materials – A comparison.

W. W. SCHMAHL[1], C. MERKEL[1], E. GRIESSHABER [1], K. KELM[2] AND C.LUETER[3]

[1]Department for Earth and Environment, LMU Munich, Munich, Germany, (W.Schmahl@lrz.uni-muenchen.de)
[2]CAESAR Research Institute, Bonn, Germany, (K.Kelm@caesar.de)
[3]Museum für Naturkunde der Humboldt-Universität, Berlin, Germany, (Carsten.Lueter@museum.hu-berlin.de)

Brachiopods have developed shell materials employing the two principal mineral groups of hard biologic tissue: calcium carbonate and calcium phosphate, each with distinct hierarchical architecture. The “phosphatic” shells consist of a predominantly chitin fibrous matrix, which is reinforced by isometric hydroxyapatite or similarly sized amorphous Ca-phosphate particles attached to the fibres [1]. The fibre composit is not unlike vertebrate bone. A laminated structure is created by changing volume ratios of chitin and reinforcing particles. In contrast, the composit structure of calcitic brachiopod shells employs inorganic single-crystal fibres reinforced by thin intercrystalline and extremely thin intracrystalline organic membranes [2, 3]. The pronounced crystallographic texture of the fibres [2, 4] appears to originate from growth selection. Over lengths well exceeding hundred micrometers the fibres change crystallographic orientation continuously in the order of one degree. While the laminated organic fibre/inorganic nanoparticle strategy provides a degree of shell flexibility the inorganic fibre/polymer membrane composit provides a high stiffness and micro- and nanohardness.

References

[1] C. Merkel, E. Griesshaber, K. Kelm, R. Neuser, G. Jordan, A. Logan, W. Schmahl (2007), *J.G.R.- Biogeosci*. in press
[2] W.W. Schmahl, E. Griesshaber, R. Neuser, A. Lenze, R. Job, U. Brand (2004), *Eur. J. Mineral.* **16** 693-697
[3] E. Griesshaber, W. W. Schmahl, R. Neuser, T. Pettke, M. Blüm, J. Mutterlose, U. Brand (2007), *Am. Min.*, **9**, in press