A synchrotron radiation laboratory for environmental studies

J. GÖTTLICHER[1] , R. STEININGER[1], U. KRAMAR[2], J. MAJZLAN[3], G. NEHRKE[4] AND N. ZÖGER[5]

[1]Forschungszentrum Karlsruhe, Institute for Synchrotron Radiation, Synchrotron Radiation Source ANKA Karlsruhe, Germany (joerg.goettlicher@iss.fzk.de)
[2]Institute of Mineralogy und Geochemistry, Universität Karlsruhe (TH), Forschungszentrum Umwelt (FZU), Karlsruhe, Germany
[3]Institute of Mineralogy and Petrology Albert-Ludwig-University of Freiburg, Freiburg, Germany
[4]Alfred Wegener Institute for Polar and Marine Research, Bremerhaven; Germany
[5]TU-Wien, Atominstitut d. oesterr. Universitaeten, Wien, Austria

Samples required to solve Earth and environmental questions are often complex (e.g., weathered minerals and rocks, contaminated soils, lake and dump sediments). They consist of mixtures of mineral phases (often with micrometer particle sizes), microbes, and in some cases living tissues or are only available in scarce amounts of tiny particles (exhaust particles, precipitations in extreme environments). Elemental distribution, spatially resolved chemical speciation and mineral phase identification are helpful to uncover relationships between mineral phases, main and trace elements and finally to comprehensively understand natural and anthropogenic affected systems. Such problems can be addressed by a combination of microfocused synchrotron X-ray techniques as they have been setup with the Synchrotron Radiation Laboratory for Environmental Studies at ANKA. The lab consists of a microfocus X-ray beamline (SUL-X) that enable elemental mapping using X-ray fluorescence analysis (XRF), chemical speciation with X-ray absorption spectroscopy (XAS) and mineral phase determination by X-ray diffraction (XRD), successively at the same sample position. Moreover, the laboratory is supplemented with an infrared microscope (SUL-IR) at an edge radiation IR beamline.

First measurements during the commissioning period of SUL-X comprise localization and speciation of arsenic in natural iron minerals for water treatment and in weathering rims of sulfides in tailing impoundments by microfocused XRF analysis and X-ray absorption near edge structure (μ-XANES) spectroscopy. Selected area XRD has been used to identify mineral formations in sea water ice. μ-XRD and μ-XANES spectroscopy is applied to characterize lead in human bone junctions.

To meet the demand of speciation of low Z elements like Al, Si, P, S for environmental questions, it is planned to offer XAS at energies down to the Al K edge (1.5keV).

Microstrain and structural defects in the magnesian calcite skeleton of the Crown of Thorns starfish

HERIBERT A. GRAETSCH

Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, D-44780 Bochum, Germany (heribert.graetsch@rub.de)

Sea stars have a magnesium calcite ($Ca_{1-x}Mg_xCO_3$) skeleton made up of small ossicles which form an open meshwork supporting the body. In spite of their spongy morphology, the skeletal parts are single crystals as in other echinoderms (sea urchins, sea lilies, sea cucumbers and brittle stars). The skeletons are metastable formations as their composition often lies within the miscibility gap between calcite and dolomite. The Crown of Thorns starfish (CoT) was chosen for this x-ray diffraction study for its extraordinary high magnesium content of $x = 0.17$. The name is for the large number of long spikes. The high Mg content indicates an average water temperature of the habitat of about 29°C.

The x-ray powder reflections of CoT are slightly broadened with respect to those of quartz which was used as internal standard. A Williamson Hall plot indicates that the broadening is almost entirely due to microscopic strain caused by lattice imperfections rather than to small crystallite size. Annealing experiments suggest that the microstrain can only partly be explained by the different sizes of Mg^{2+} and Ca^{2+} cations incorporated in the calcite lattice. A single crystal structure refinement revealed the presence of vacancies on cation sites and misoriented CO_3 groups.

After annealing at 300°C, the appearance of few weak extra reflections indicate the beginning of the exsolution of high-magnesium calcite to low-magnesium calcite and calcian dolomite.

Annealing at lower temperatures (100 - 200°C) causes some changes of the microstructure which show up in the diffraction patterns. The lattice parameters expand slightly on increasing temperature of the heat treatment [1]. Simultaneously, the broadening of the x-ray powder reflections is reduced indicating less microstrain. Single crystal structure refinements show a reduction of vacancies and smaller atomic displacement parameters suggesting some healing of structural defects.

Annealing at about 250°C, however, causes an increase of the reflection broadening indicating larger microstrain introduced by newly formed lattice imperfections. Additional weak diffuse intensity was found close to the strongest reflections which can be ascribed to Huang scattering caused by the occupation of interstitial lattice sites. The formation of interstitials seems to be an intermediate step before at higher temperatures unmixing of the solid solution begins.

Reference

[1] Richter, D.K. (1984), *Bochumer geologische und geotechnische Arbeiten*, **15**, Bochum, 310p