Mineralogy of reactive iron as driving force for microbial activity in marine sediments

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Goals of the session
We report on the second experimental session of a new experiment focussed on the mineralogy and redox state of reactive and reduced iron in marine sediments. During the previous experimental session in December 2009, we measured XANES spectra at the Fe K-edge of 19 Fe-containing minerals and 30 marine sediment samples from several environmental settings and with different iron content. The purpose of the second session was focussed on (1) increasing our library of standard mineral spectra, (2) producing standard spectra of amorphous and dissolved iron compounds, (3) complete measurements of marine sediment samples and compare spectra to the additional standard spectra, and (4) experimentally test effects of iron leaching from silicates and the effect of free sulphide on a range of different iron (hydr)oxides and iron-rich silicates.

Beamline and settings
We used the A1 beamline at the DORIS III facility. XANES spectra at the Fe K-edge were measured at the A1 beamline in fluorescence mode with a PIPS detector. The beam size on the samples was 5 mm horizontal x 0.8 mm vertical. The beam was appropriate for producing characteristic Fe XANES spectra of the studied sediment samples and standard materials.

Sample preparation
Samples and standards were prepared using several different methods. In order to evaluate effects of the preparation method, selected samples were prepared using several of the described methods simultaneously.

Standard minerals were measured as entire fragments when available or as pellets. The pellets were manufactured by compressing cellulose powder containing approximately 100 mg of finely ground sample material. Also, most sediment samples were air-dried and prepared as pellets. Some of the anoxic samples were anaerobically dried, ground and formed into a pellet using the press that is located in the anaerobic chamber.

Wet sediment samples were filled in a sample holder and covered with kapton foil. Wet standards, such as solutions of Fe-salts or suspensions were filled headspace-free into a cryo-vial with screw cap.

Anoxically-stored wet sediments were sub-sampled, loaded on a sample holder and sealed with kapton foil in an anaerobic chamber. Samples were stored in the anaerobic chamber until the beamline was ready for measurement, then immediately transferred to vacuum chamber of the beamline.

Completed measurements
During our beamtime, we recorded XANES spectra of about 30 different Fe-containing minerals (standards) including liquid standards of 1M Fe(II)Cl₂ and 100 mM Fe(III)citrate.

In addition to the bare standards we experimentally tested 12 different standard minerals for interaction with free sulphide and the formation of Fe-sulphide coatings. For this purpose, the minerals were incubated in anoxic solutions of 100 M NaS₂ in 10 mM carbonate buffer. After shaking the experiments for 3 weeks, the sulphate was nearly consumed in some of the samples
indicating the formation of Fe-sulphides. Also a possible leaching effect during submarine basalt weathering was simulated with basalt and two mafic silicate minerals, enstatite and hypersthen.

The following sediment samples from the several locations were analysed:
- Black Sea (3 samples, anoxic)
- Eastern Equatorial Pacific (4 samples, air dried)
- Bering Sea (10 samples, anoxic)
- Arctic sea, Svalbard (7 samples, anoxic)
- CO₂ storage site, Ketzin (14 samples, air dried as pellets)
- North Pond, North Atlantic (MSM 11/1 expedition) (3 samples, wet sediment)
- Miocene Monterey Formation, California (5 samples, pellets)

Results

Standard Minerals
Most XANES spectra at the Fe K-edge were clearly distinct from the blank sample holder, thus are over the detection limit. From the liquid samples, however, only the most concentrated solutions produced good-quality XANES spectra. The diverse standard minerals show clearly distinct spectra, as described in the literature [1], [2].

Fe in marine sediments
The spectra from these sediments from Bering Sea, Black Sea, and Peru Margin measured during the previous session in 2009, have been evaluated to show that the dominant form of iron is clay minerals, either chlorite or smectite group minerals, dependent on the location. Only the black sea samples revealed the presence of sulphides.

Sediments at the base of a 420 m thick sedimentary sequence at Ocean Drilling Program (ODP) Site 1226, in the Eastern Equatorial Pacific, show the presence of Fe-oxyhydroxides. These precipitates likely formed as a secondary phase during reoxidation of Fe due to inflow of oxic seawater along the basalt/sediment interface. This finding demonstrates that Fe-oxidation is an ongoing process that is probably driven by microbial activity within deeply buried sediments.

Several XANES spectra were produced from Fe-rich sandstone of the Triassic Schilfsandstein Formation. This porous sandstone is currently used as reservoir for subsurface CO₂ storage near the city of Ketzin (Germany). The high Fe content may play an important role for chemical interaction of the (acidic) CO₂ with the rock and may have a significant effect on the long-term behaviour and stability of the reservoir. The XANES spectra show that the dominating Fe phase is a Fe (hydr)oxide. This mineral fraction is below detection limit in the X-ray diffraction, such that we previously assumed most Fe is in the form of less reactive sheet silicates. Based on the XANES data we know now that the Fe is in a reactive form that can be easily leached by the CO₂.

Further evaluation of the large dataset, including the additional sites and re-evaluating some of the previous sample runs using the new selection of standard minerals is currently in process.

Publications in progress

References