Report of the workshop: Magnetic Methods in Biogeochemistry

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Purpose:

In our project we are interested in the suffidation of ferric (hydr)oxides in the presence and absence of DOM in the anoxic aquifers. We will investigate the mechanisms and kinetics of solid-phase transformations associated with this reaction, such as formation of pyrite and transformation of ferric (hydr)oxides induced by Fe(II) generated from oxidation of sulfide at the mineral surface, using modern analytical instrumentation, particularly Moessbauer spectroscopy which is quite sensitive of iron mineral. Electron microscopy is usually the choice for detailed observation. Many new techniques have been developed in the electron microscopy field, in which we are interested. The workshop, including four main parts: Field trip, Moessbauer spectroscopy, electron microscopy and Environmental magnetism provides an opportunity to learn these modern analytical techniques and leads us to apply them into our research.

Schedule:

The whole workshop is well considered and filled with lectures and practicals. The second day(Mai 27th) we had a field trip to a marine sediment area and learned some field works. The following three days we gained some knowledge of principle of Moessbauer spectroscopy and the practical, we learned to used sofeware(M-fit) do some calibration and fitted our own samples. From Mai 30th to June 4th we spent our time in Center for Electron Nanoscopy (CEN) of Technical University of Denmark (DTU). Here we have learned all techniques applied in electron microscopy and how to perform our experiment and operate SEM and TEM during practical. The last part we gained the basic knowledge of environment magnetism.

Result:

Field trip:

During the field trip we've learn samples preservation. For those samples which contain sulfide species protection from oxidation must be applied. There are several choices, including applying different plastic bags and glove bags. However, oxygen can still go through the plastic, samples, therefore, may be partially oxidized. For this reason, samples should be carefully selected when they are measured.

Moessbauer spectroscopy

One of the most important parameters for defining the usefulness of a Moessbauer transition is the fraction (f-value) of gammas which are emitted and absorbed without recoil. Each different mineral has its particular f-value, which, at the same time shows a temperature dependence.

There are only approximately eight Moessbauer transitions which can be carried out at room temperature, including ^{57}Fe(14.4keV), which is the most convenient Moessbauer nuclide. However, improved spectra at low temperature of these eight elements are still necessary, particularly for organic compounds. All the remaining higher energy transitions require low temperature.

Three kinds of hyperfine interactions which are observed are important in a Moessbauer spectrum: the isomer shift, the electric quadrupole interaction and the magnetic dipole interaction or hyperfine splitting.
Some relaxation effects should be considered when one analyzes Moessbauer spectra. The main three principal types of are spin-spin relaxation, spin-lattice relaxation and superparamagnetism. The first two are important in dilute paramagnets and the last in fine particle, magnetically ordered materiasl.

Electron microscopy:
Electron microscopes includes SEM, TEM, STEM and STM/AFM(scanning tunneling microscopy/ atomic force microscopy). We've learned the principle of electron microscopy, and at the same time did the practical. The electron microscopy is a type of microscopy that uses an electron beam to illuminate the specimen and create a magnified image of the specimen. Electron beam is created by using certain electron sources, including thermionic emission source and field emission source. The latter source is a sharp tungsten tip, thus has a higher brightness and higher intensity. And electrons are extracted by a high electric field. Here high vacuum is necessary.
When electron beams hit the specimen, electron scattering occur, including elastic and inelastic scattering. The scattered electron is most likely to be forward scattered, but there is a small amount of backscattered. And secondary electron can be emitted when ions beams hit the surface of the specimen.
In case of SEM, secondary electrons are detected to form normal SEM images. Because secondary electrons have low energy, typically only a few eV, they are only emitted from the top 5 to 50nm of the specimen, the images are therefore surface specific. Backscattered electrons are also detected by using a detector around the objective pole piece. This collects electrons scattered upwards from the specimen. Backscattered electrons have much higher energy because of elastic scattering, and can be emitted from the top to 300nm of the specimen. But due to the amount of backscattered electrons is quite small the resolution of images is quite low.
Most forward scattered electrons are detected in TEM. That means, the specimen should be as thin as possible(<100nm). They are mostly transparent to electrons so that Most of the electrons go straight through. The imaging of TEM has very little contrast at low magnification. Normally an objective aperture is used around the central beam to increase the contrast and exclude all the diffracted beams. This gives a bright-field image, in which the contrast is diffraction contrast. In bright-field image, strongly diffracting areas are dark. If the reflections that are selected do not include the unscattered beam, then the image will appear dark wherever no sample scattering to the selected peak is present, as such a region without a specimen will appear dark. This is known as a dark-field image. Here, strongly diffracting areas are bright. The bright-field and dark-field images show general microstructure, crystallography and grain sizes of the mineral, together with diffraction patterns mineral phase can be identificated. Ring diffraction pattern, which is analogous to X-ray powder diffraction, can identify phases in localized areas.
Other techniques are applied in TEM such as high resolution image, EDX, EELS, tomography which does well in 3D reconstruction, holography which measure magnetism of mineral, STEM which applies both SEM and TEM. High resolution image is applied to identify nano-particles and atomic structure, together with diffraction patterns. X-ray spectroscopy(EDX/EDS) determine compositions of element of a specified area, but the result cannot be fully convinced. Low energy

of electron beam should be applied when measuring with EDX to increase the precision of measurement. Similarly, Electron energy-loss spectroscopy(EELS) allows to apply particular energy values, which can be associated with the way the electron has interacted with the sample. This normally results in chromatic aberration. EELS is therefore characteristic of elements present. It is able to measure most of element (except H, He and Li) and deduce chemical state from shape of edge as well. Electron energy-loss maps basic on EELS allow determining different phase, for example, if iron oxides' shell around mackinawite. But it becomes difficult if the composition of the phases is similar.

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