# Scientific Report for FIMIN - Short Visit Grant 3394
# Phase transitions of nanocrystalline iron sulfides

## Purpose of the visit

The purpose of visiting the research group of Prof. Liane G. Benning was to synthesize ad characterize freshly precipitated and heated iron sulphide samples. We planned to study the phase transitions between amorphous mackinawite and mackinawite, and also between mackinawite and greigite. As I started to incorporate other ions into makcinawite previously, I wanted to do the experiments with and without Ni ions as well and heat the samples in anaerobic conditions at different temperatures for different periods, and study the fate of the Ni ions during the phase transitions. At the University of Leeds (in the School of Earth and Environment, within the research group of Prof. Liane Benning) both significant expertise with iron sulphides and sophisticated instrumentation for their study exist.

## Work carried out

I prepared 23 samples (using the reagents thioacetamide, sodium hydroxide, nickel chloride and ferrous sulphide). I worked with 2 concentrations of $Ni^{2+}$, and I synthesized a set of samples without Ni ions as well. The freshly precipitated iron-sulfides were poorly crystalline mackinawites, so in order to study the phase-transitions and the fate of the Ni ions during the phase transitions, I had to heat the samples in a reactor in oil bath or in an oven. Since the phase transitions are very slow at room temperature, the transformations were accelerated by using higher temperatures. As I wished to know how the temperature affects the speed of the transformation, I heated the samples to 3 different temperatures (120/150/170°C) for 3 different periods (2/5/12 hours). As the iron sulphides are extremely sensitive to oxygen, I carried out the experiments in an anaerobic chamber.
For the characterization we used X-Ray Powder Diffracion and SEM techniques, and we plan to analyze the samples using TEM and SAED methods.

## Main results

We found that the crystallization process can be sped up by heating, but above 120 degrees pyrrhotite appeared, even though we expected the presence of crystalline mackinawite and the appearance of greigite ($Fe_3S_4$). The syntheses were succesful in the sense that there were no iron oxide phases beside the iron sulphides, but we must determine how the transformations took place at different temperatures after various periods of heating.

The samples with and without Ni do not differ significantly neither in view of the diffractograms nor of the SEM pictures, but further analyses are required using ICP and TEM measurements to determine the concentration of Ni ions that remained in solution and elemental maps of the samples will be obtained using electron energy-filtered imaging, in order to understand the distribution of Ni in the iron sulphide.

Apart from having more than 20 new samples - which shows that these 10 days I spent in Leeds were very efficient - I studied a lot from that group, especially from Prof. Liane Benning. Beside many tiny things I learnt how to work with an anaerobic chamber and I was introduced to Scanning Electron Microscopy.

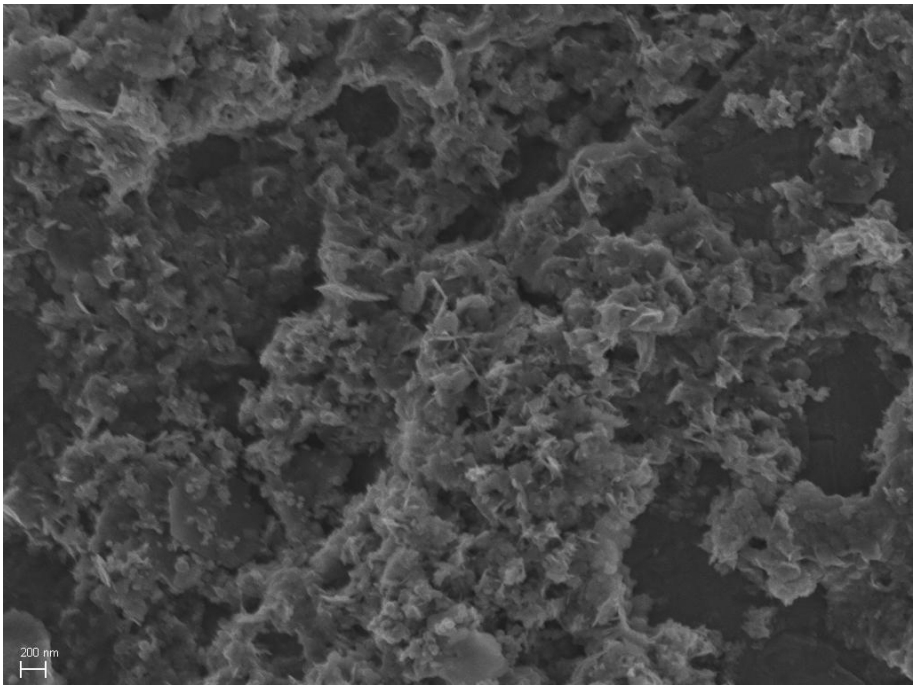


Fig. 1. SEM picture of a freshly precipitated poorly crystalline mackinawite

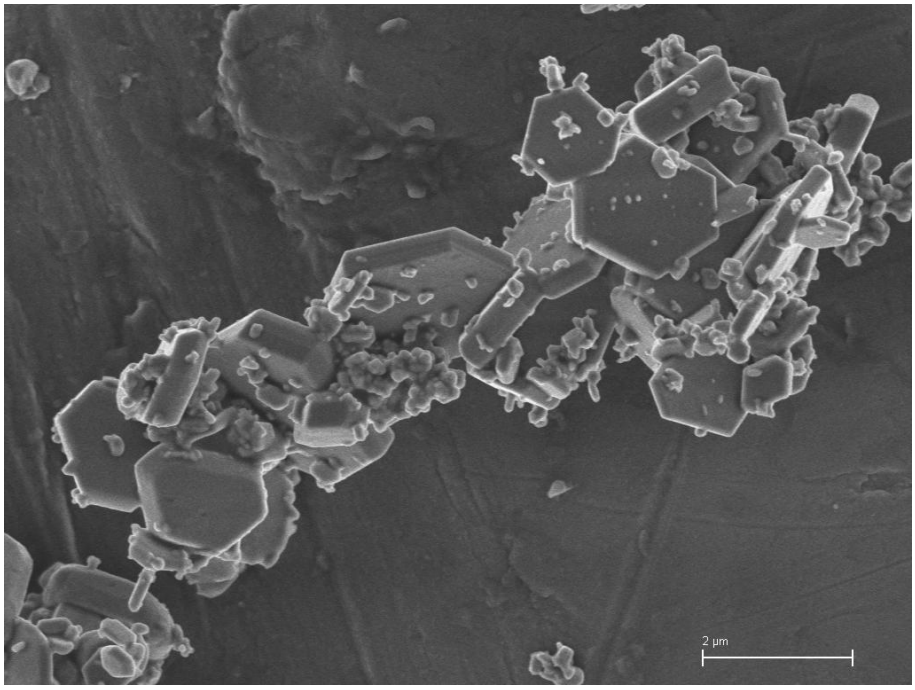


Fig. 2. SEM picture of a heated sample (170°C for 2 hours), hexagonal pyrrhotite crystals appeared frequently near the mackinawite phase

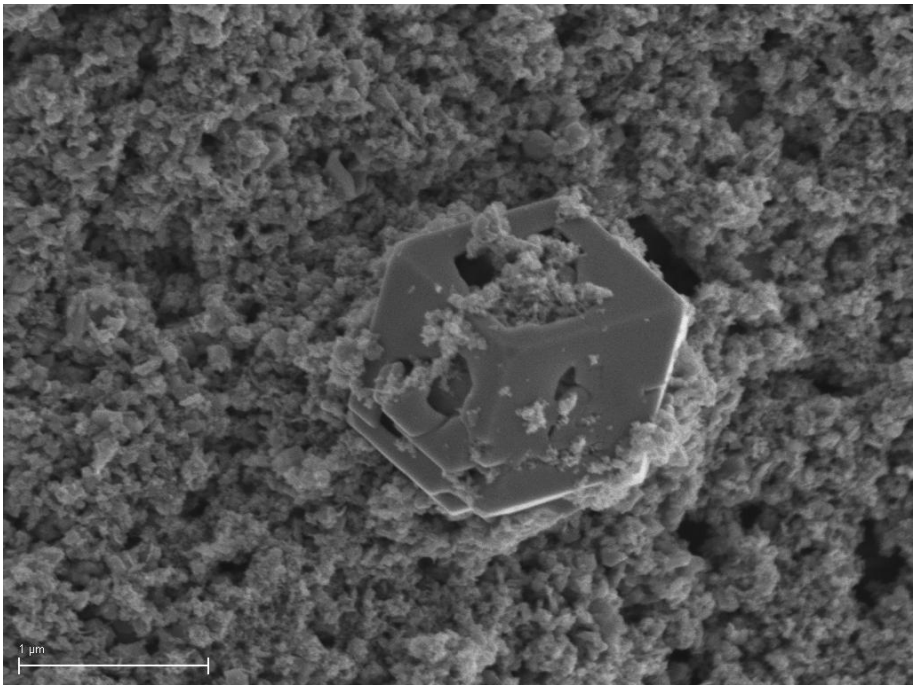


Fig. 3. SEM picture of a non-identified, cubic crystal that was very abundant in heated samples and consists mainly of iron and sulfur according to the EDS spectra, but further analyses are needed to determine its phase

## Future collaboration

Possibilities of further collaboration have been offered by Prof. Liane G. Benning.

## Projected publications

The results obtained from the short visit in Leeds will be presented on a poster for the IMA2010 conference (21-27 August 2010, Budapest), and at least one article will be prepared in the near future.

Veszprém, 15th of July 2010

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