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Recrystallization Processes Involving Iron Oxides in Natural Environments and *In Vitro*

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Additional information is available at the end of the chapter

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1. Introduction

Research of nano-size phases through electron microscopy and especially through high resolution electron microscopy enables to observe the morphology of each nano-sized crystal or short range ordered phase, that are usually not detected by other methods. Moreover, lattice fringes of the precursor and the product differ from each other but the original crystal size and morphology remain. The main object of this chapter is to demonstrate the advantages of using electron microscopy in detecting recrystallization processes and possible identification of the precursors.

Nano sized iron oxides are very common minerals in various environments. Various phases of iron oxides crystallize in natural environments of rocks, sediments and soils. Some of the iron oxides form directly either from melts or from solutions; others are formed by recrystallization processes of a precursor through dehydroxylation, dissolution/precipitation, oxidation or aggregation involving internal rearrangement within the structure of the precursor. Another formation pattern involves recrystallization of iron-bearing minerals crystallized under anaerobic conditions which are exposed to air. The Fe^{2+} of these iron bearing minerals is then oxidized and hydrolyzed into iron oxyhydroxides.

By using a high resolution electron microscopy, the morphology of newly formed iron oxides can be observed. Moreover, in some cases it is also feasible to detect the precursor's morphology. The newly formed end products are identified by electron diffraction and their chemical compositions are obtained by point analyses; hence, impurities that result from the initial phases can be detected. In most of the samples presented in this chapter, the fine fraction was checked with a High Resolution Transmission Electron Microscopy (HRTEM) using a JEOL FasTEM 2010 electron microscope equipped with a Noran energy dispersive spectrometer (EDS) for microprobe elemental analyses. Other pictures were obtained using

a scanning electron microscope JEOL, JXA-8600 and a High Resolution Scanning Electron Microscope Sirion.

The iron oxides studied were found in various natural environments (Figure 1) including:

- recent precipitates in hyper-saline sediments in the Dead Sea Area;
- coating quartz grain in sand dunes and soils under the east Mediterranean climate in Israel;
- sediments of hydrothermal hyper-saline environment of the Red Sea;
- marl layers exposed in the Judean hills;

Other phases were synthesized in a NaCl solution under varying conditions.

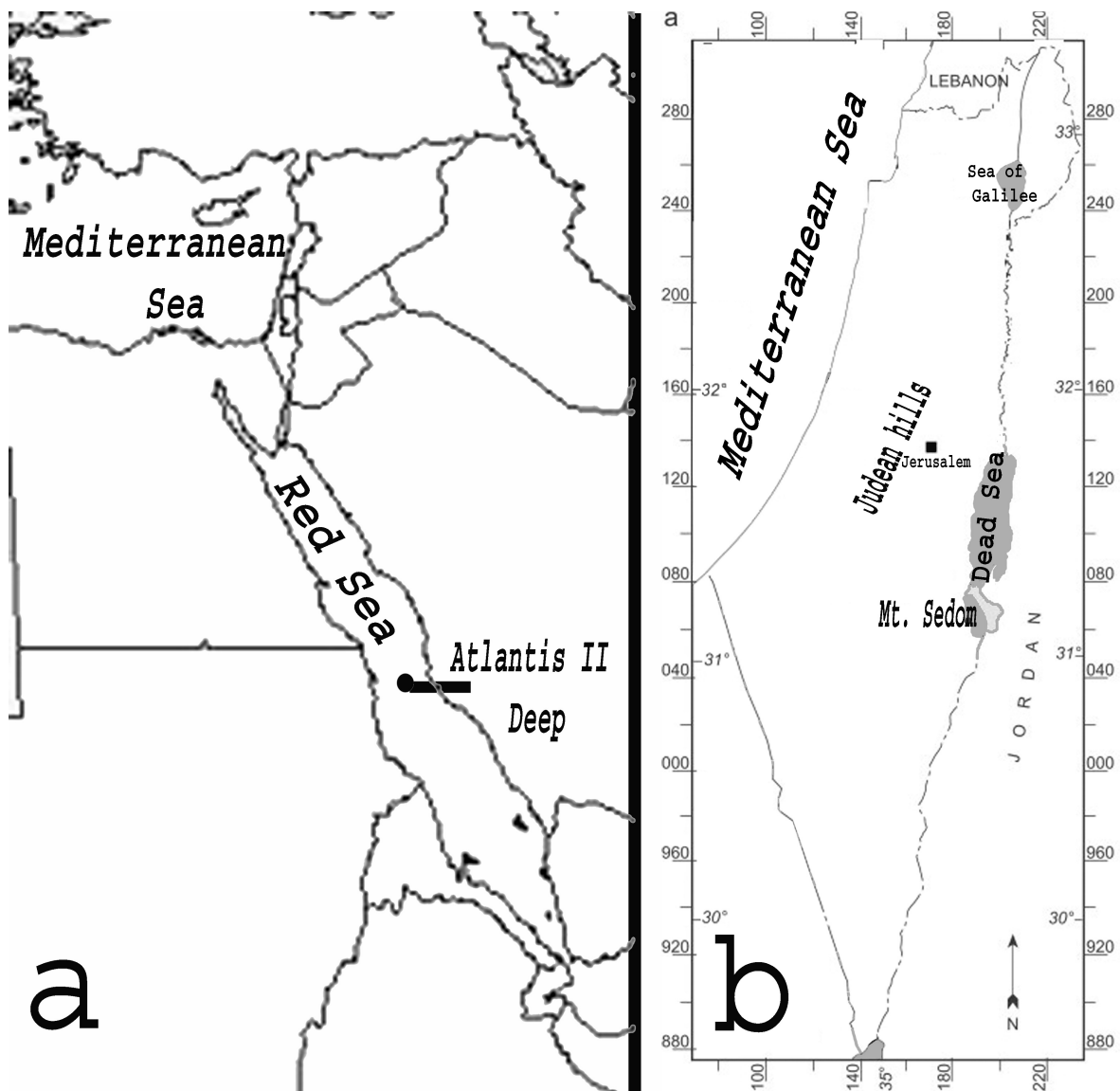


Figure 1. a) Middle East map with Atlantis II Deep located in the Red Sea. b) Israel map with location of Mt. Sedom near the Dead Sea and Judean hills. Samples were also collected along the Mediterranean Sea coast.

2. Results and discussion

Short range ordered 2-line ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) is one of the precursors of other iron oxides. It initially precipitates due to Fe^{2+} oxidation and its crystal growth is hindered by the presence of silicate or soil organic matter. Its structural inner order can clearly be visible in HRTEM images. A selected area electron diffraction pattern shows 2 bright rings at 0.15 and 0.25nm. (Figure 2).

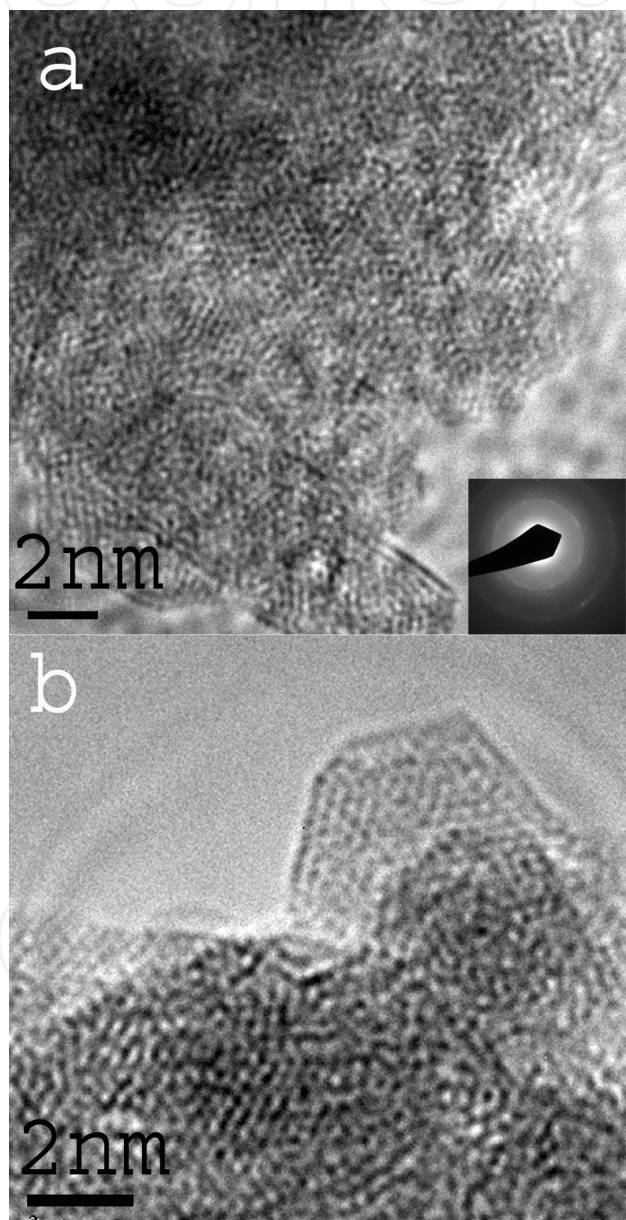


Figure 2. a) High resolution images of short range ordered ferrihydrite preserved within halite crystals in the hyper-saline environment at the Dead Sea. The initial stage of recrystallization into a stable phase can be observed at the lower part of the image. Two bright rings at 0.15 and 0.25nm in SAED were obtained. b) A short range ordered pattern was observed in other crystals of ferrihydrite.

2.1. Recrystallization of ferrihydrite into akaganéite in a hyper-saline environment

Akaganéite (β -FeOOH) usually precipitates directly at acidic conditions with the presence of Cl (Cornell & Schwertmann, 2003). In the Dead Sea area close to Mount Sedom salt diaper, a hyper-saline brine discharges in a small spring. As the dissolved Fe^{2+} ions of the spring are exposed to air, ferrihydrite precipitates as an initial iron oxide (Figure 2) and the crystallites are preserved within halite crystals. Dissolution of the halite crystals and its reprecipitation at acidic conditions and elevated Cl concentration enables a recrystallization process into akaganéite crystallites, and they are preserved again within the newly formed halite crystals. Tiny crystallites of akaganéite preserve their initial ferrihydrite precursor's morphology and exhibit a well-crystallized pattern observed through a high resolution transmission electron microscope (Figure 3).

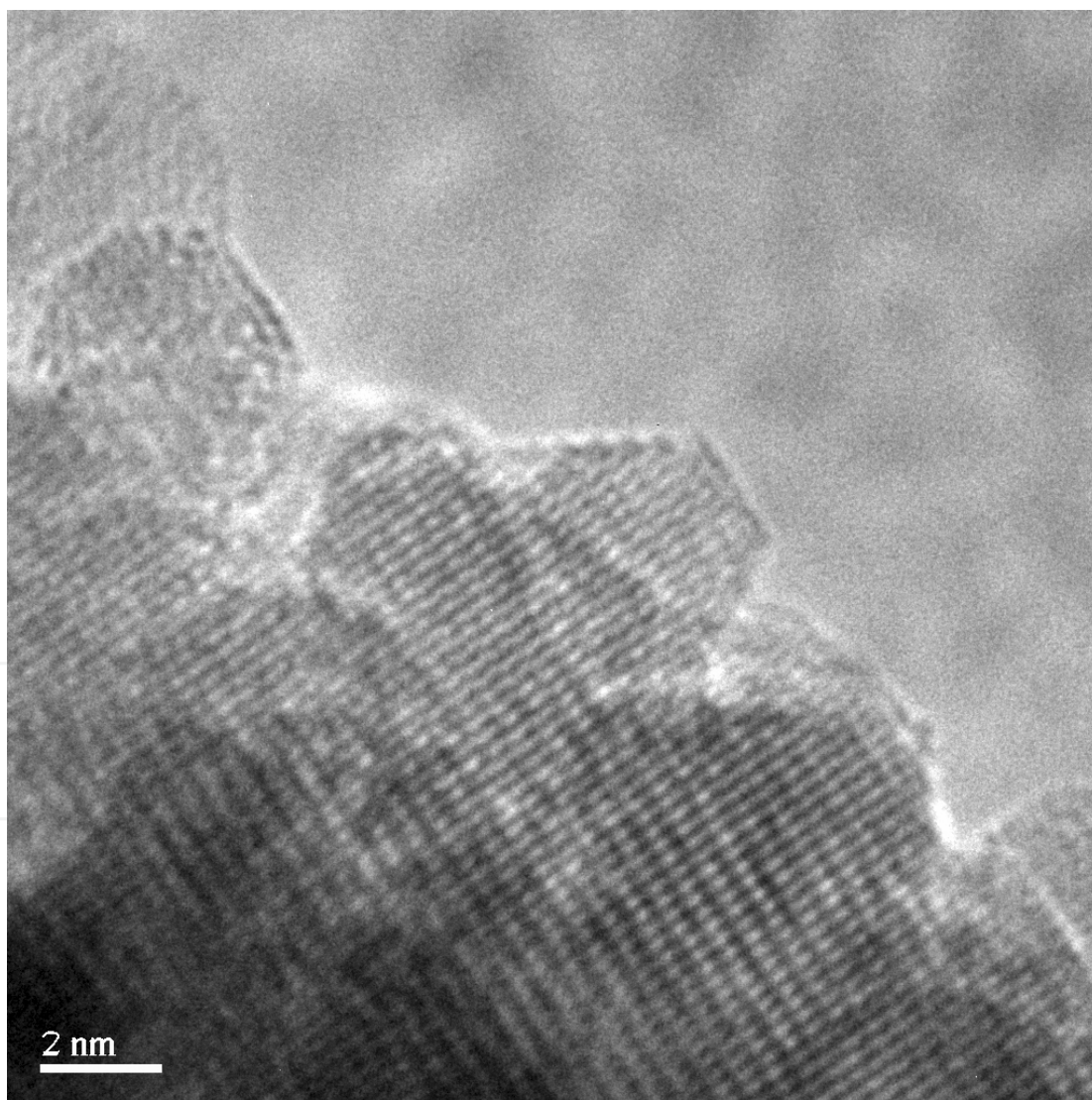


Figure 3. A high resolution image of akaganéite crystallites that present a recrystallization product of ferrihydrite in a hyper-saline environment in the Dead Sea area.

2.2. Recrystallization of ferrihydrite into hematite and goethite in sand dunes and soils

Quartz grains are blown inland along the eastern Mediterranean coastline and form sand dunes. A Mediterranean climate, namely a long hot dry season and a mild winter with a November–March annual precipitation of 400–600 mm (Saaroni et al., 2010) enables the piling up of additional clay minerals that are not washed away but adhere to the quartz grains and then serve as a surface for additional precipitation and recrystallization of iron oxides. Precipitation of these iron oxides causes reddening (rubification) of the quartz grains.

Ferrihydrite is the initial phase formed and it serves as the precursor for hematite ($\alpha\text{-Fe}_2\text{O}_3$) or goethite ($\alpha\text{-FeOOH}$) (Figure 4). Recrystallization of ferrihydrite into other iron oxides requires aerobic conditions in a warm climate with a wet and dry season that enables formation of more stable iron oxides. Hematite is formed during the dry season due to aggregation process that includes short range crystallization within a ferrihydrite aggregate (Cornell & Schwertmann, 2003). Dissolution and reprecipitation processes are usually involved in goethite formation. Yet the presence of clay minerals prevented complete drying of the iron oxides, and precipitation of goethite preserved the initial morphology of the ferrihydrite crystallites.

2.3. Recrystallization into hematite from other iron bearing minerals

Small grains of ilmenite (FeTiO_3) are transported along with quartz grains to the eastern coast of the Mediterranean Sea. As they are exposed to the Mediterranean climate, they recrystallize into tiny grains of hematite with Ti impurities resulting from their initial precursors. The recrystallization process is feasible since both minerals ilmenite and hematite share the same crystallographic system and even the same space group. Sometimes ilmenite and hematite even form a solid solution. By using electron microscopy, it is possible to observe the initial ilmenite grain along with the secondary hematite crystals that result from the recrystallization process. The precursor and the recrystallized tiny hematite crystals remain close to each other since they are all kept within clay minerals. SA-ED detects ilmenite crystal, and point analyses obtained from the large crystal and the surrounding tiny crystals show that the large ilmenite grain lost most of its iron to the hematite crystallites; however, some of the Ti precipitated within the hematite crystals as an impurity. Other elements shown in the point analyses resulted from the surrounding clay minerals (Figure 5).

Pyrite (Fe_2S) crystals precipitated within Cretaceous marl layers of the Judean hills probably under anaerobic conditions. Oxidation of these crystals yielded pseudomorphic recrystallization into tiny crystals of hematite preserving the initial pyrite large cubic crystal. Using a higher resolution image enabled the observation of small hexagonal plates of hematite crystallites (Figure 6); hence, pyrite served as a precursor for hematite crystals.

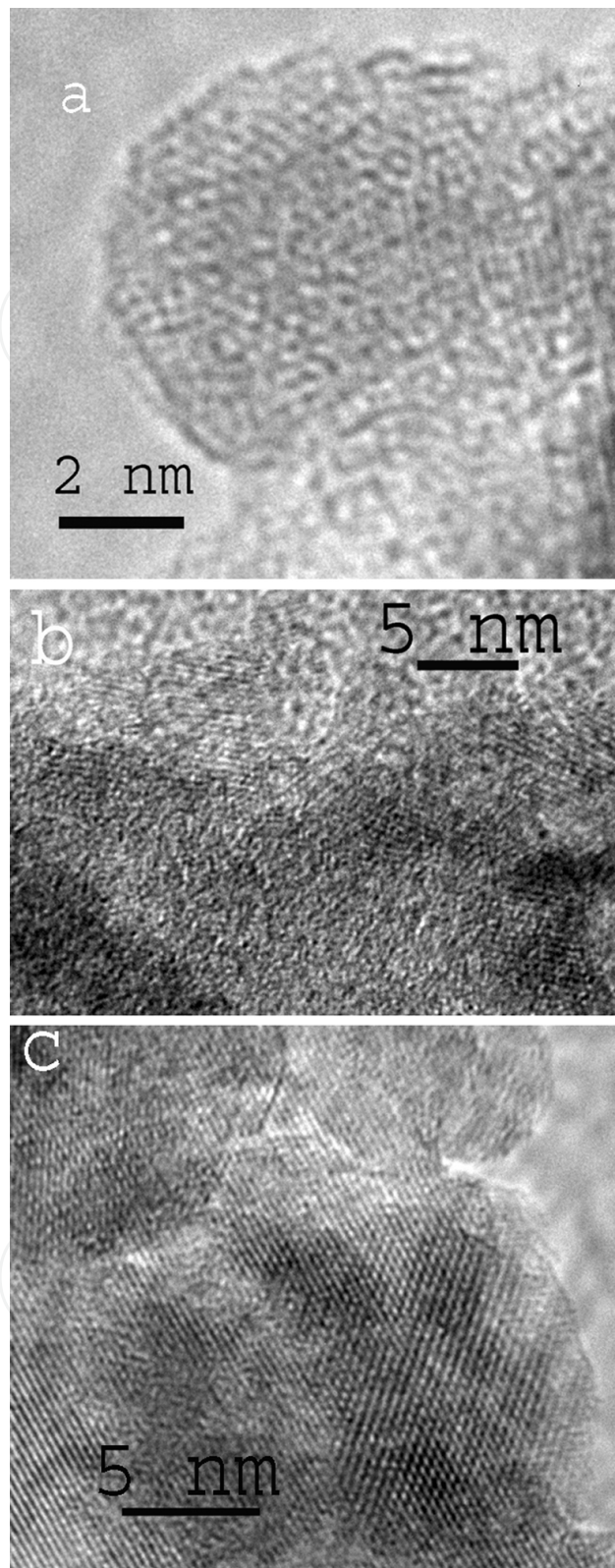


Figure 4. High resolution images of a) A short range ordered ferrihydrite; b) goethite crystals preserving ferrihydrite morphology; c) Hematite tiny crystals preserving the initial morphology of ferrihydrite.

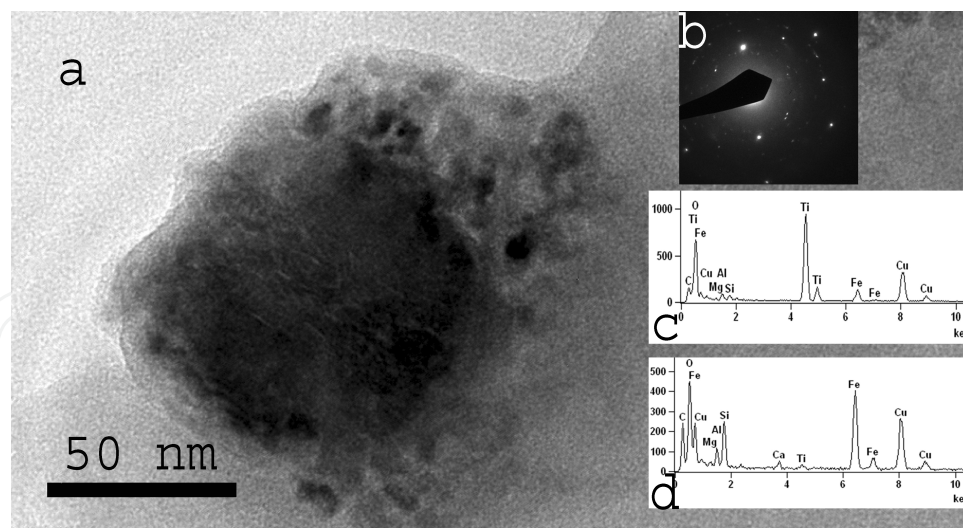


Figure 5. a) An ilmenite grain surrounded by tiny hematite crystals kept within clay minerals; b) SAED of ilmenite crystal; c) Point analysis of ilmenite crystal that went through some dissolution causing Fe removal from the grain into surrounding hematite crystallites; d) Point analysis of hematite crystallites showing a Ti impurity.

2.4. Recrystallization processes in a hydrothermal hyper-saline environment in the Atlantis II Deep, Red Sea

Iron oxides and short range ordered Si-Fe phases precipitate within the hydrothermal brine of the Atlantis II Deep, in the Red Sea (Taitel-Goldman, 2009). Multi-domain goethite is usually formed at elevated Na^+ concentration (Cornell & Giovanoli, 1986). Most of the goethite crystals found in the Atlantis II Deep exhibit multi-domainic character. Appearance of multi-domainic hematite crystals in the Atlantis II Deep was quite rare, yet, some were found in the sediments, probably resulting from the recrystallization process of a multi-domainic goethite precursor (Figure 7).

Rounded particles of short range ordered Si-Fe phase (suggested name: singerite) ($\text{SiFe}_4\text{O}_6(\text{OH})_4\text{H}_2\text{O}$) were identified for the first time in the sediments of the Atlantis II Deep (Taitel-Goldman et al., 1999 ; Taitel-Goldman & Singer, 2002). This short range ordered phase is usually metastable and transforms into a more stable phase of iron rich clay mineral like nontronite (Figure 8).

2.5. Recrystallization in vitro of green rust into magnetite

Magnetite ($\text{Fe}^{2+}\text{OFe}^{3+}_2\text{O}_3$) mainly crystallizes in magmatic rocks or precipitates in a mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ solution in aqueous alkaline systems. Formation of magnetite involves an initial stage of either green rust ($\text{Fe}^{3+}_x\text{Fe}^{2+}_y(\text{OH})_{3x+2y-z}\text{A}_z$; $\text{A}=\text{Cl}, 1/2\text{SO}_4$) or hexagonal flakes of $\text{Fe}(\text{OH})_2$ that gradually oxidizes into green rust and then recrystallizes into magnetite crystals (Cornell & Schwertmann, 2003). At elevated temperatures and salinities, less oxygen is available for the oxidation of the dissolved Fe^{2+} , leading to magnetite (mixed Fe^{2+} and Fe^{3+} phases) precipitation. Synthesis was performed in NaCl matrix solutions (4M and 5M) that were kept in a water bath at 70°C and 80°C. N_2 was bubbled through the solutions for 20 minutes to remove dissolved oxygen. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ salt was chosen for the Fe^{2+} solutions to

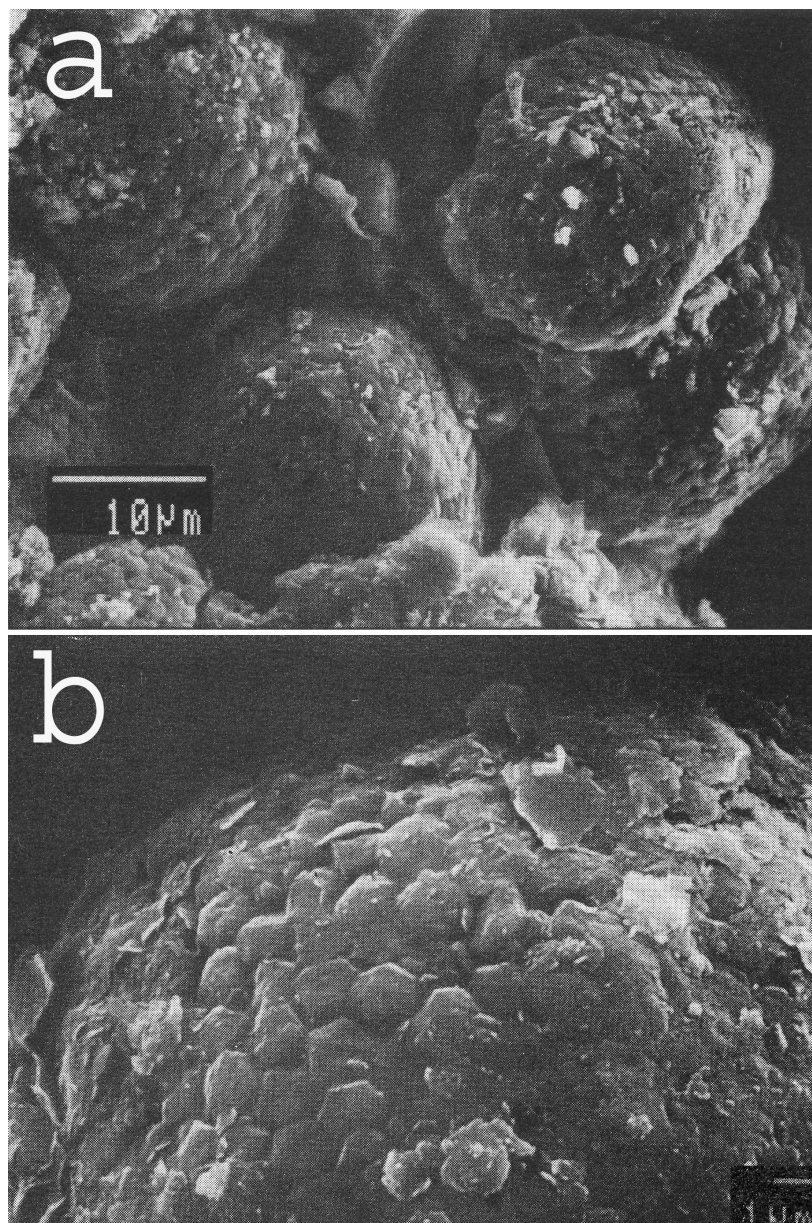


Figure 6. Scanning electron micrograph of tiny hexagonal plates of hematite crystals formed by recrystallization of large cubic pyrite crystals. a) The cubic morphology of pyrite was preserved. b) A close observation of tiny hematite crystallites.

yield a concentration of 0.06M. Fe oxidation was carried out by introducing air at flow rates of 25ml/l, which was monitored with a flow meter, and was kept stable during the 3h of synthesis. Buffering of the pH was obtained by adding a small amount of NaOH (1M). It appears that the pH has a major effect on the kinetics of recrystallization; hence, in samples that were prepared in a highly alkaline solution, transformation into magnetite was quicker, leading to preservation of the precursor. Usually, the recrystallization process yields a cubic morphology of magnetite but due to very fast oxidation and the recrystallization process, the crystals formed preserve the hexagonal morphology of green rust that was observed with a high resolution scanning electron microscope (Figure 9).

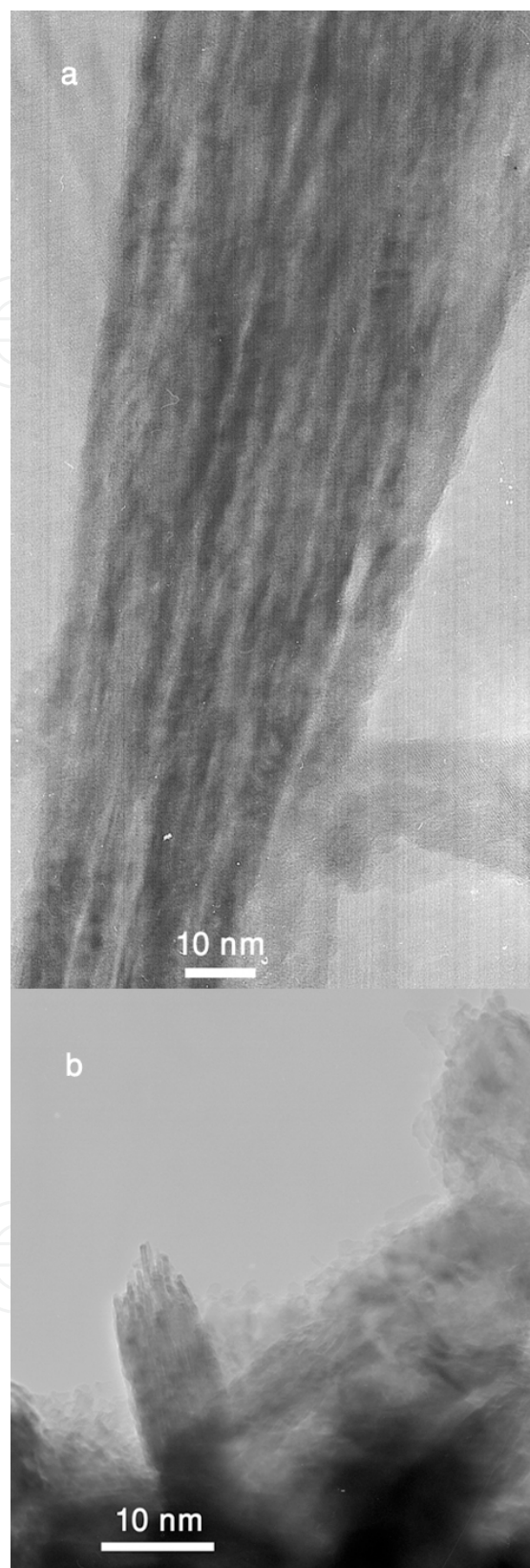


Figure 7. Iron oxides observed in the hyper-saline sediments of the Atlantis II Deep in the Red Sea. a) Multi-domainic goethite; b) Multi-domainic hematite that was formed in a recrystallization process probably from goethite.

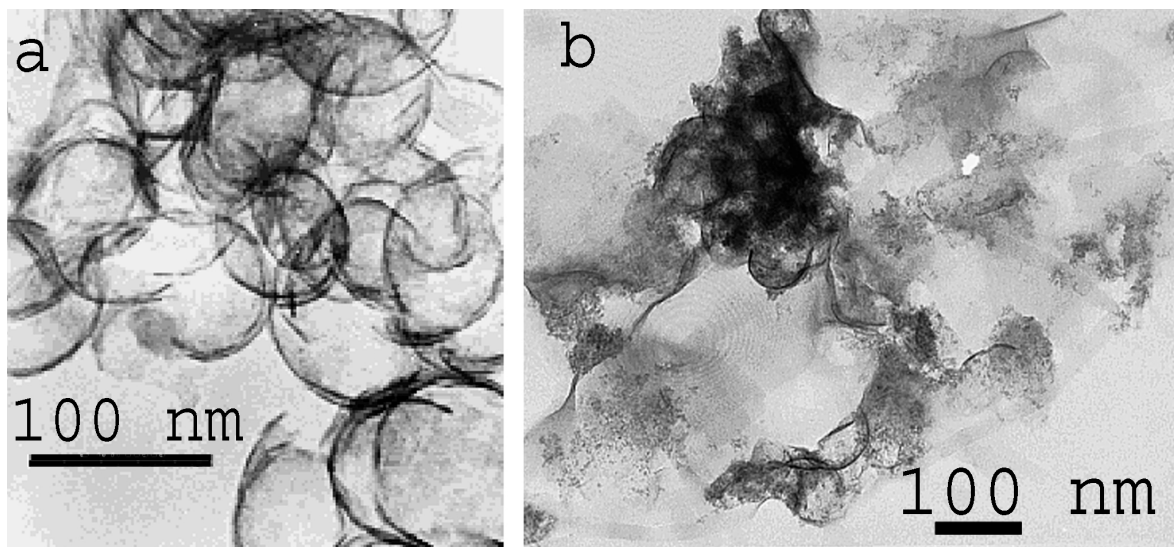


Figure 8. a) A cluster of rounded particles of a short range ordered Si-Fe phase (singerite); b) Disintegration and recrystallization of singerite into iron-rich clay mineral (nontronite).

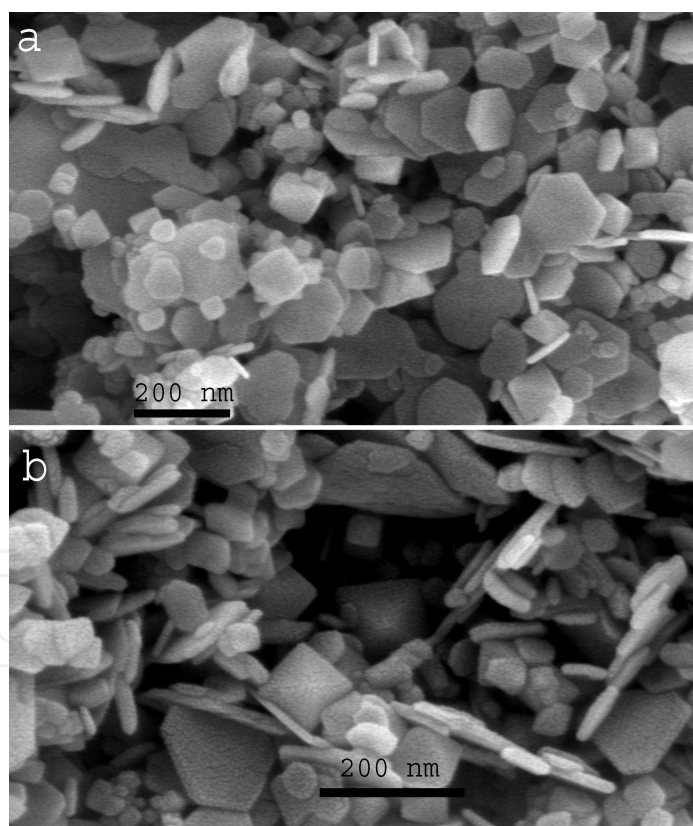


Figure 9. A high resolution scanning electron microscope image of synthesized magnetite in varying conditions. Plates appear in both images due to quick recrystallization from green rust or $\text{Fe}(\text{OH})_2$ plates. Samples were synthesized at a) 70°C pH 9.4 and a solution of 4M NaCl b) 60°C pH 10.2 and in a 5M NaCl solution.

3. Conclusions

Iron oxides are not the only minerals formed by recrystallization processes. However, their abundance, small crystallite size, quick formation patterns that often involve preservation of their precursor enables their observation through various electron microscopes of the morphology or impurities from the precursor.

In this chapter it was shown that the initial morphology of ferrihydrite is preserved in recrystallization into more stable phases like goethite, akaganéite and hematite. It was also shown that hematite can be formed through several recrystallization processes from other iron oxides or iron bearing minerals.

In some cases, slow recrystallization process is captured within the sample leading to observation both the decomposing precursor and the newly formed product. For example transformation of singerite into nontronite clay mineral or ilmenite into hematite.

Author details

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