The dry oxidation of tetragonal FeS$_{1-x}$ mackinawite

Abstract The gradual oxidation of dry mackinawite (tetragonal FeS$_{1-x}$) has been studied using X-ray diffraction (XRD), transmission electron microscopy (TEM), transmission Mössbauer spectroscopy (TMS) and X-ray photoelectron spectroscopy (XPS). The initial material and samples exposed to the air (5 min to 6 months) have been analysed. Diffraction patterns showed the slow disappearance of mackinawite with time with concomitant appearance of greigite (Fe$_3$S$_4$) and elemental sulphur (S(0)) as well as iron (oxyhydr)oxides, i.e. magnetite (Fe$_3$O$_4$) and probably goethite (α-FeOOH). After 6 months' air exposure, mackinawite and also greigite were entirely converted into elemental sulphur and iron (oxyhydr)oxide(s), indicating that greigite was an intermediate reaction product. Mössbauer spectra of samples oxidized in air appeared rather complex for interpreting what was easily conceivable in view of the association of several phases, as revealed by the diffraction patterns. The low-temperature Mössbauer spectrum obtained after 6 months air exposure was attributed to magnetite, although a mixture of magnetite and goethite was not completely excluded. XPS iron and oxygen data confirmed the formation of Fe(III) (oxyhydr)oxides at the surface after an induction period. Sulphur spectra demonstrated various oxidation states from S(II) (monosulphide) to S(VI) (sulphate) for the longest experiments. Mackinawite in these experiments reacted mainly with adsorbed O$_2$ to form elemental sulphur and magnetite. Additionally, sufficient sulphur was generated to react stoichiometrically with mackinawite to produce greigite. Finally, greigite, in the longest experiments, was transformed into elemental sulphur and magnetite.

Key words Iron sulphides · XPS · XRD · TEM · Mössbauer spectroscopy

Introduction

Pyrite (FeS$_2$) is by far the most abundant and widely occurring of the iron sulphide minerals encountered in sulphide ore deposits and in many metamorphic, igneous and sedimentary rocks. However, some other phases in the Fe–S system, like mackinawite and greigite, achieve great importance, although they are less common in their geological occurrence, due to their role as transient species in the formation of sedimentary pyrite at low temperatures (Berner 1964; Benning et al. 2000).

Mackinawite is a metastable sulphur-deficient iron (II) sulphide of composition FeS$_{1-x}$, where 0 < x < 0.07 (Vaughan and Craig 1978), so that it is also reported as Fe$_3$S$_8$ in the literature (Benning et al. 2000). It is an important constituent of anoxic sedimentary environments (Vaughan and Lennie 1991). The mackinawite structure (P4/mnm space group) consists of a distorted cubic-close-packed array of sulphur atoms with iron occupying some of the tetrahedral interstices (Taylor and Finger 1970). It may be synthesized experimentally either from the precipitation of aqueous ferrous iron (Rickard 1969; Patterson et al. 1997) or the reaction of metallic iron (Berner 1964; Lennie et al. 1995) with a sulphide solution.

Greigite, Fe$_3$S$_4$, the sulphur analogue of magnetite Fe$_3$O$_4$, has a similar inverse spinel structure that corresponds to the ideal formula [Fe$_{3+}$]$_{tetra}$ [Fe$^{3+}$]$_{octa}$ S$_4$ (Skinner et al. 1964), where the $Fd3m$ space group consists of sulphur in cubic close packing with 8 Fe$^{3+}$ in tetrahedral coordination and 8 (Fe$^{3+}$, Fe$^{2+}$) in octahedral coordination. Greigite is encountered in sediments and low-temperature hydrothermal deposits (Vaughan and Lennie 1991). Until now, all reports on greigite synthesis involve reactions with iron monosulphide “FeS” precursors such as mackinawite (Lennie et al. 1997; Benning et al. 2000).

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It is generally considered that the following reaction sequence is involved in the formation of pyrite nuclei: mackinawite → greigite → pyrite (Berner 1964; Lennie et al. 1997). Therefore, the first step of the conversion, i.e. the mackinawite-greigite transformation, occurs through an oxidation process. Some ferrous iron in the mackinawite structure becomes oxidized into ferric iron. However, the various studies have not completely elucidated the reaction mechanism, i.e. the crystallographic transformations and chemical reactions that occur during the two reaction steps. Since the geochemical understanding of mackinawite oxidation is mainly based upon wet chemical studies, difficulties arise probably from the oxidation state changes that occur in both crystalline and aqueous phases during the process. There is some uncertainty concerning the nature of the oxidant that drives the reaction, and the role of air in the mackinawite oxidation process is not completely elucidated. Berner (1964), in a study of iron sulphides formation from aqueous solutions at low temperature and atmospheric pressure, reported that air was necessary to the oxidation process. Rickard (1997) postulated that the mackinawite oxidation could occur in the absence of air. Horiuchi (1970) and Horiuchi et al. (1971) demonstrated that mackinawite in intimate contact with colloidal sulphur reacted on heating to produce greigite. More recently, Benning et al. (2000) also reported that the transformation mackinawite-pyrite via FeS and greigite transient species was possible only if oxygen or some other oxidant was present in the aqueous reaction medium.

In this study, we propose to examine in detail the mechanism of dry mackinawite oxidation in air at room temperature and atmospheric pressure. New data on the mackinawite oxidation process in air are presented. The techniques of investigation are X-ray diffraction (XRD), transmission electron microscopy (TEM), transmission Mössbauer spectroscopy (TMS) and X-ray photoelectron spectroscopy (XPS).

Materials and methods

Initial mackinawite: synthesis and sample preparation

Mackinawite synthesis was carried out under carefully controlled oxygen-free conditions. Accordingly, all reagents were prepared in a high-purity, nitrogen-purged Jacomex controlled-atmosphere glove box, using freshly boiled distilled water under N2 atmosphere. The synthesis was performed according to a method described by Lennie et al. (1995). Five g of iron wire was suspended in 500 cm3 of a 0.5-M acetic acid/acetate buffer (pH = 4.6). Partial dissolution of the iron wire by reaction with the acetate buffer (~3.5 h) evolved H2 gas and provided a reducing environment. Thirty cm3 of a 0.45-M Na2S solution was added to the reaction vessel. Black particles immediately precipitated. This suspension, containing the black particles, was allowed to stand open to the atmosphere for 24 h. The remnant of iron wire was removed and the supernatant discarded. The remaining mackinawite was washed and filtered several times with deionized and oxygen-free water before being freeze-dried. The structural properties of the initial mackinawite were checked using the techniques mentioned above.

To prevent any uncontrolled oxidation, the preparation of samples for analyses was conducted in the glove box and the samples were quickly transferred.

Oxidation experiments

Once the mackinawite sample was freeze-dried, it was naturally air-oxidized at room temperature for several months. It should be noted that oxidation experiments for XPS measurements were conducted with synthetic air, as the surface is very sensitive to contaminants. The oxidation progress was monitored periodically by examining samples at regular times of exposure to air (5 min to 6 months), using the same experimental techniques as for the initial freeze-dried mackinawite. In contrast to the initial mackinawite, no particular care for avoiding oxygen was necessary during sample preparation.

X-ray diffraction analysis (XRD)

Powder diffraction patterns were obtained from a classical powder diffractometer with transmission geometry, equipped with a Mo tube (quartz monochromator, Kα1 radiation, λ = 0.070930 nm) and a scintillation detector. The samples were filled into Lindemann glass tubes (1 mm diameter and 0.01 mm thick) and step-scanned from 2 to 40(2θ) using a step of 0.05(0). The angular resolution Γ (FWHM) was 0.04°. However, it was increased to 0.08° by the thickness of the Lindemann glass used.

Transmission electron microscopy (TEM)

A Philips CM20 transmission electron microscope operating at 120 or 200 kV and equipped with an energy-dispersive spectrometer was used to examine the initial mackinawite and the air-exposed samples. A suspension prepared in ethanol was dispersed onto an amorphous carbon-coated grid and loaded into the microscope chamber. Identification of initial mackinawite as well as its oxidation products was made from both selected-area electron diffraction patterns (SAED) and by energy-dispersive X-ray analysis.

Transmission Mössbauer spectroscopy (TMS)

The Mössbauer spectra were obtained by using a constant-acceleration Mössbauer spectrometer with a 50-mCi source of 57Co in Rh. The spectrometer was calibrated with a 25-µm foil of z-Fe at room temperature. The equipment at low temperatures consists of a closed-cycle helium Mössbauer cryostat with a vibrations insulation stand manufactured by Cryo Industries of America. Helium exchange gas was used to thermally couple the sample to the refrigerator, allowing variable temperature ranges from 12 to 300 K. Computer fittings were made using Lorentzian-shape lines with variable widths for taking into account spectral asymmetry. Measurements were performed at both room temperature and 12 K.

X-ray photoelectron spectroscopy (XPS)

Spectra were obtained with a VSW HA150 MCD electron energy analyser using a MgKα non-monochromatic source (1253.6 eV). Energy resolution was 0.8 eV. The base pressure inside the analytical chamber was of the order of 10⁻⁶ mbar. The energy scale was calibrated using the Au4f7/2 (84.0 eV) and Ag3d3/2 (368.2 eV) lines. Survey and narrow-region XPS spectra were obtained with an analyser pass energy of 90 and 22 eV, respectively. Raw spectra were Fourier-smoothed and fitted using a Shirley base-line and a Gaussian–Lorentzian peak shape. The background hydrocarbon C(1s) peak at 284.6 eV was adopted for checking the surface charging. Narrow region photoelectron spectra were obtained in order to achieve the chemical state information for iron, sulphur and oxygen.