Mineralogy of Greigite Fe$_3$S$_4$

I. Letard[1], Ph. Sainctavit[1], N. Menguy[1], J.-P. Valet[2], A. Isambert[2], M. Dekkers[3] and A. Gloter[4]

[1]Laboratoire de Minéralogie - Cristallographie de Paris, Université Pierre et Marie Curie, 4, place Jussieu, F-75 252 Paris Cedex 05
[2]Institut de Physique du Globe de Paris, France
[3]Paleomagnetic Laboratory, Utrecht University, The Netherlands
[4]Laboratoire de Physique des Solides, Orsay, France

Abstract

Greigite Fe$_3$S$_4$ is one of the two natural magnetic iron sulphides. Its formula and structure make it the sulphide equivalent of magnetite Fe$_3$O$_4$, leading to frequent confusions between these two spinelles in paleomagnetic studies and possible wrong interpretation of some paleaomagnetization measurements.

We have carried out high resolution EELS experiments and recorded X-ray magnetic circular dichroic spectra at the iron L$_{2,3}$ edges on natural and synthetic samples. The natural samples present a core-shell structure of crystallized greigite surrounded by an amorphous iron oxide phase. The differences observed on the XMCD signal of Fe$_3$S$_4$ compared to Fe$_3$O$_4$ could be explained by the presence of iron vacancies, Fe$_3$S$_4$ being a lacunary iron sulphide.

1. Introduction

The study of rock magnetization gives information about the magnetic history of the Earth. Paleomagnetism, in association with other methods, allows to date precisely geological events like appearances and disappearances of animal species or to follow the movements of the lithospheric plates. Dating events thanks to this method is possible because the Earth magnetic field reverted its orientation several times at the geological scale of time.

Among the numerous iron-sulphide minerals, only two are ferrimagnetic, all the others being antiferromagnetic or having complicated magnetic structure (van Vleck paramagnetism). These two magnetic iron sulphides are pyrrhotite Fe$_7$S$_8$ and greigite Fe$_3$S$_4$. These minerals keep a print of the inversions of the Earth magnetic field. Thus their remanent magnetization is used as the starting point of paleomagnetic studies. Nevertheless, their electronic properties are not well known because they often occur as mixed phases and with an oxidized surface layer.

Fe$_3$S$_4$ is a sulphospinelle. Fe$_3$S$_4$ and magnetite Fe$_3$O$_4$ have the same cubic crystalline structure with octahedral and tetrahedral sites. They only differ by their anions. However, the repartition of Fe^{2+} and Fe^{3+} is not known in Fe$_3$S$_4$. Moreover, Fe$_3$S$_4$ presents a saturation magnetization by formula unit 2.5 times lower than Fe$_3$O$_4$ [1]. It has a different easy-magnetization axis ([100] instead of [111]) [2]. It shows no Verwey transition: whereas at temperature lower than 120 K, a distorsion of the cubic structure has been observed in Fe$_3$O$_4$, accompanied by a brutal decrease of the magnetic susceptibility, no such phenomenon has been seen on Fe$_3$S$_4$.

All these differences occur despite a similar crystal structure. Iron sulfiphides require a reducing environment. Iron should thus be mainly present as Fe^{2+}. But this would not be sufficient to account for the observed reduction of the magnetization. An other explaination for the reduced magnetization could be the presence of iron vacancies on the octahedral sites.

We have studied both natural and synthetic samples. The complexity of natural samples needs a preliminary observation by transmission electronic microscopy (TEM) associated with energy electron loss spectroscopy (EELS) in order to study the composition and crystalline structure of the sample and to investigate its stability on a period of time of several weeks. The study of the magnetic properties implies the use of X-ray absorption spectroscopy (XAS) and in particular X-ray magnetic circular dichroism (XMCD). To separate the contributions of Fe^{2+} and Fe^{3+} in the octahedral and tetrahedral sites, we followed an approch similar to that exposed in a companion paper by S. Brice-Profeta. However, in iron sulphides, the covalence of the bonds is stronger than in oxides. This implies that the multiplet structures are less visible than in oxides. In consequence, the selectivity of site and of oxidation state is less precise in sulphides than in oxides.

2. Samples description

The natural samples have been collected in the marine sediments uncovered by the errosion caused by the Crostolo River, Po Valley, Italy [3]. Fe$_3$S$_4$ is probably of biogenic origin, synthetized inside or around bacteria. Fe$_3$S$_4$ particles are separated from the sediment by a magnetic extraction in desoxygenized water. Using this method, we clear the sample from non-magnetic materials which can contain iron and disturb the XAS measurements. However, the resulting extracted sample may contain other magnetic particles among which some might bear iron.

We compared these natural biogenic samples to synthetic ones obtained by hydrothermal synthesis from Mohrs solution Fe(NH$_4$)$_2$(SO$_4$)$_2$ and sodium sulphide NaS$_2$ in desoxygenized water solution [4].

3. Experimental results

The TEM and EELS experiments have been carried out on the High Resolution TEM Akashi Topcon EM-002B of the LPS (Orsay, France) and on the 2010F Jeol microscope of the CP2M (Marseille, France). XAS measurements have been carried out on the SU23 beamline at LURE (Orsay, France) and on the BACH beamline at Elettra (Trieste, Italy). Spectra have been recorded at the iron L$_{2,3}$ edges.

3.1. *EELS: the core-shell structure of the particles*

The TEM study of the natural samples showed grains of about 50–200 nm wide, as presented in fig. 1. These grains are constituted of a core and a shell. The shell is about 10 nm thick when observed a few days after the extraction. It constitutes the totality of the grains after a few weeks. In the core, diffraction features appear clearly whereas the shell appears amorphous. We have recorded EELS spectra on both the core and the shell of several particles. We recorded spectra from a few eV after the
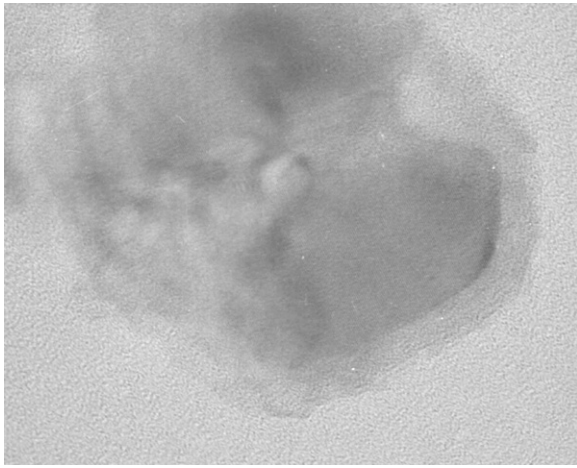
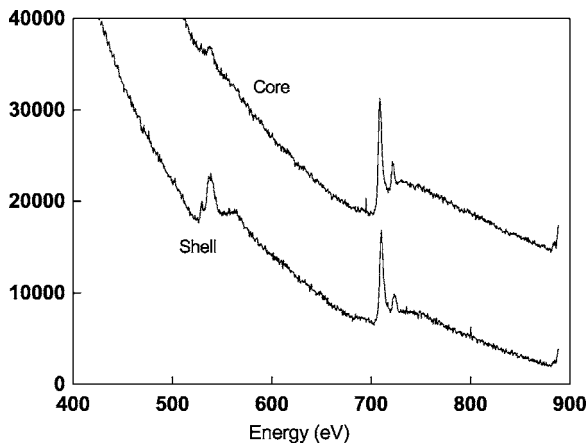Fig. 1. TEM picture of a grain of crystalline iron sulphide surrounded by a shell of amorphous iron oxide.

Fig. 3. Comparison of the iron $L_{2,3}$ edges spectra recorded by EELS respectively on the sulphur and on the oxide part of a particle and by XAS (fresh natural sample).

Fig. 2. EELS spectra recorded separately on the core and on the shell of a particle of natural Fe_3S_4: oxygen K-edge and iron $L_{2,3}$ edges.

Fig. 4. Isotropic and dichroic spectra recorded at 4.2 K in a magnetic field of $+/-2T$ on the natural and synthetic samples. The magnetization is saturated.

elastic feature to 900 eV. The O K-edge to Fe $L_{2,3}$ edges range is shown on fig. 2. The spectrum recorded on the core shows absorption at the S and at Fe $L_{2,3}$ edges and slight absorption at the O K-edge. On the contrary, the spectrum recorded on the shell presents strong absorption at the O K-edge and Fe $L_{2,3}$ edges but not at the S $L_{2,3}$ edges. The Fe $L_{2,3}$ edges feature is typical of spectra obtained on iron oxides. The shell is thus contituted of an amorphous iron oxide phase. An electron diffraction on the core confirms that this crystalline iron sulphide phase is greigite.

TEM observations on the synthetic samples have shown crystallized greigite particles of a few hundred nanometers wide. The synthetic particles were observed a few days after the synthesis and did not present any feature of oxidation. No measurement was carried out after a few weeks or months thus we have no idea of the way synthetic greigite oxidizes when aging.

EELS spectra have also been recorded with a better energy resolution on both the core and the shell of several particles. The spectra are shown on fig. 3. One can notice that the signal recorded on the sulphide part of the particle also contains the contribution of the surface. Indeed, to reach the core of the particle, the electron beam goes accross the oxide shell, which can contitute up to 20% of the explored volume depending on the oxidation rate of the particles.
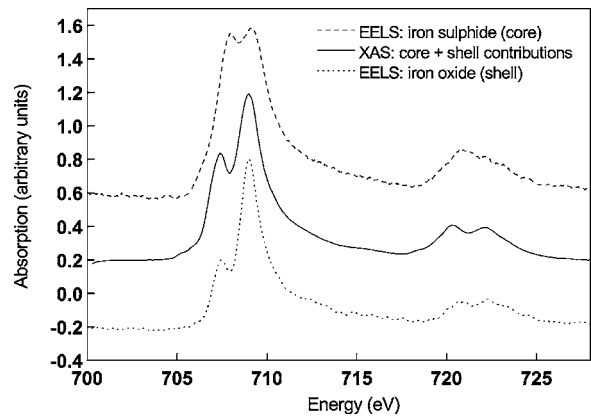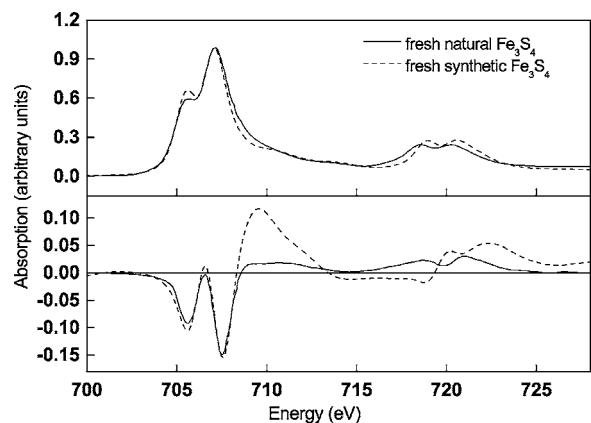
3.2. *XAS and XMCD*

Contrary to EELS, XAS and XMCD can give information on the magnetic properties. This spectroscopy does not bring as good spatial resolution as EELS, but brings a better energy resolution. The XAS spectra of natural greigite are the result of both contributions of the core and the shell of the particles (see fig. 3). In the same way, the XAS spectra of recently synthetized greigite is intermediate between the hematite spectra and the iron sulphur EELS spectra. It may be the result of a similar oxidation process that may yield a core-shell structure.

In order to determine the repartition between Fe^{3+} and Fe^{2+} in Fe_3S_4, we have recorded XMCD spectra on natural and synthetic Fe_3S_4. The signals are shown on fig. 4.

4. Interpretation

In samples as complexe as natural magnetic minerals, coupling the two techniques, EELS and XMCD, is necessary.

4.1. *Oxidation towards hematite*

XAS spectra on synthetic greigite have been recorded a few weeks after the synthesis and six months after. The isotropic spectra presented on fig. 5 show that the aging of greigite leads to an iron oxide very close to hematite α-Fe_2O_3, mineral containing only Fe^{3+} in octahedral sites. The spectrum of recently
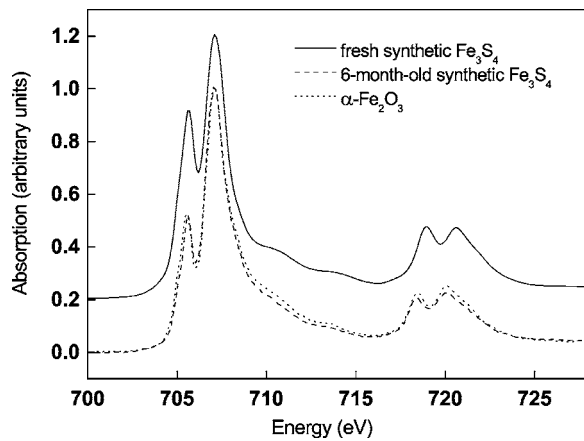
Fig. 5. XAS at iron $L_{2,3}$ edges spectra showing the evolution of synthetized Fe_3S_4 toward hematite.

synthetised Fe_3S_4 presents a stronger contribution for feature B. Fresh synthetic Fe_3S_4 shows dichroism (see fig. 4) whereas older synthetic Fe_3S_4 does not show any dichroic signal. Since the oxidized phases are stable, this result may evidence that the dichroic signal observed on fresh Fe_3S_4 is due to sulphide and not to oxide.

4.2. *No oxide contribution to the dichroic signal*

EELS spectra showed that the surrounding shell is contituted of amorphous iron oxide. This oxide probably leads to ferrihydrite or hematite α-Fe_2O_3. At 4 K, hematite is antiferromagnetic. The magnetic contribution of the shell to the spectra is thus a paramagnetic or antiferromagnetic contribution. Thus, whereas the isotropic spectra is the sum of oxide and sulphide contributions, the observed dichroic signal may be only due to the Fe_3S_4 core.

4.3. *Comparison between natural and synthetic samples*

The two samples present similar isotropic cross sections though XMCD signals are pretty different. We attribute the differences to various ratio of oxide *vs* sulphide contributions. The large positive bump after the L_3 edge is a clear sign of Fe-S hybridization. Fe_3S_4 structure can accomodate for various electronic and crystallographic modifications (Fe^{2+}/Fe^{3+} ratio or presence of vacancies) so that, even without spurious oxidation contributions, similar phases could yield quite different XMCD spectra. To illustrate this point, XMCD signals of γ-Fe_2O_3 and Fe_3O_4 are quite different although they are almost indistinguishable by diffraction techniques.

Compared to the dichroic signal obtained on Fe_3O_4 (presented on fig. 6), at the L_3 edge, the ratio of the two peaks is reverted: in Fe_3S_4, feature A is weaker than feature A′ and it is the contrary
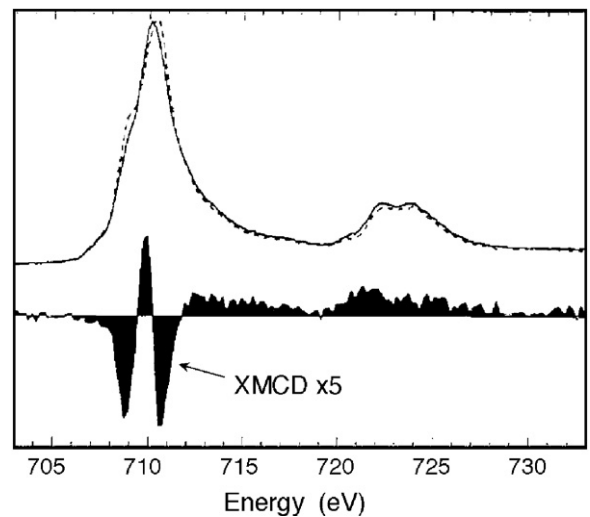

Fig. 6. Isotropic and dichroic spectra recorded on Fe_3O_4 [5].

in Fe_3O_4. This can be attributed to a contribution of Fe^{2+} in octahedral sites weaker in Fe_3S_4 than in Fe_3O_4.

5. Conclusion

EELS on natural greigite showed a core-shell structure composed of a core of well-crystalized Fe_3S_4 and a shell of amorphous iron oxide, possibly precursor of hematite α-Fe_2O_3. XMCD spectra more probably take into account only the sulphur contribution. The differences observed between the XMCD spectra of Fe_3S_4 and Fe_3O_4 can be explained by the presence of iron vacancies in Fe_3S_4 leading to a lacunary iron sulphide similar to the lacunary iron oxide maghemite γ-Fe_2O_3.

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