MAGNETIC MONITORING OF THERMAL ALTERATION FOR NATURAL PYRITE AND GREIGITE

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Abstract

Pure pyrite and greigite and pyrite/greigite mixtures were submitted to Curie balance experiments. The magnetic monitoring of the alteration of pyrite with temperature shows that at about 500°C magnetite always appears and can alter afterwards to hematite depending on the experimental conditions. Therefore, an increase of magnetisation due to the magnetite suggests the presence of pyrite in the studied samples. Samples with a pyrite/greigite mixture show minimum magnetisation during heating at 400°C, and its subsequent immediate increase. The increase of magnetisation is much higher in samples dominated by pyrite than in samples dominated by greigite. This behaviour can allow identification of pyrite in a pyrite/greigite mixture. Alteration with temperature of pyrite and greigite, which implies the appearance of magnetic minerals, can be used in magnetic and environmental studies.

Key words: magnetic mineralogy, pyrite, greigite, Curie balance.

1. INTRODUCTION

Iron sulphides are present in magmatic, metamorphic and sedimentary rocks. Some of these, such as greigite (Fe₃S₄) and monoclinic pyrrhotite (Fe₇S₈), are ferrimagnetic and are able of carry a remanent magnetisation. They are thus of interest in various magnetic studies. Others, such as pyrite (FeS₂) and hexagonal pyrrhotite (Fe₉S₁₀), are
paramagnetic at ambient temperature; nevertheless, their alterations during heating imply the appearance of magnetic minerals. It is therefore very important to recognise them and their products of transformation in natural conditions in order to identify better the natural remanent magnetisation carriers of rocks. Also in palaeomagnetic studies the transformation of sulphide during heating may strongly alter the magnetic signal. The thermomagnetic behaviour of hexagonal pyrrhotite, which changes just above 200°C into monoclinic pyrrhotite, has already been studied (Schwarz, 1975; Soffel, 1977; Bennett and Graham, 1980; Rochette et al., 1990; Dekkers, 1990; Horng et al., 1992). Pyrite, after Differential Thermal Analysis (DTA), changes during heating into iron oxides (e.g., Bollin, 1970). High resolution DTA of pyrite under oxidative conditions after Bollin (Fig. 1) shows an exothermal transformation at about 540°C. The transformation starts at about 440°C, and continues with several steps to 540°C. The result of this transformation is hematite. Nevertheless, under conditions of poor air circulation it was established that the depletion of oxygen and the transformation of intermediate products can occur. Therefore, it is possible to follow its transformation during thermomagnetic experiments, as made by Kruczyk (1983), and in this way indirectly identify this mineral in studied rocks.

The presence of pyrite in sedimentary rocks is an important indicator of the environment. Indeed, if pyrite is of early diagenetic origin, its presence, as the presence of greigite, indicates the conditions in which the authigenesis was taking place – condi-
tions related to the bacterial degradation of organic matter in anoxic, sulphate reducing environments (sediment, water column) with sufficient quantities of dissolved iron; see for instance: Berner et al., (1979), Berner (1980); Curtis (1987), Roberts and Turner (1993). Greigite is quite easily detectable now in sediments because of its magnetic properties, and particularly the thermomagnetic behaviour due to mineralogical changes (Krs et al., 1992); nevertheless, its presence must be confirmed by other analyses such as X-ray diffraction (XRD); see Snowball and Torii (1999) for review of bibliography.

In this paper, results of thermomagnetic experiments are presented on pure pyrite and greigite, and also on a pyrite/greigite mixture. The implications of their alteration with temperature can be used in various magnetic studies as for example for sedimentary rocks discussed here.

2. MATERIAL, METHODS AND RESULTS

Pure pyrite and greigite from the Department of Earth Sciences in Orsay collection, both of natural origin and identified by X-ray diffraction (Fig. 2), were submitted to the Curie balance experiments. Three samples of fresh pyrite were heated to 700°C during 25 min, 1 hour and 2 hours. The last two samples of pyrite, pulverised and stored for several months before analysis and called subsequently “altered samples”, were heated to 700°C for 1 hour. Greigite and mixtures of pyrite and greigite in the proportions based on mass (greigite to pyrite: 3/1, 1/1, and 1/3), were heated to 650°C during 25 min. The thermomagnetic behaviour of these samples was determined on a horizontal force translation balance in atmosphere, in a magnetic field of 0.375 T, linear temperature increase from room temperature and immediate linear cooling back.

The thermomagnetic behaviour of all analysed pyrite samples is typical at first for paramagnetic material and presents very low magnetisation (Fig. 3a-e). At about 440°C magnetisation increases to 540°C and then decreases sharply at 580°C to almost 0 (samples heated 25 min and 1 hour: Fig. 3a-d) or to a low value and decreases finally to almost 0 just before 700°C (Fig. 3e). In these samples, the increase of magnetisation occurs continuously (Fig. 3a, b, d), or stepwise around 520°C and at 540°C (Fig. 3c, e). The curves for altered material (Fig. 3d, e) are not fully repeatable, as the conditions of chemical transformation during experiment might vary slightly. On cooling, we observe in samples heated quickly a very strong increase of magnetisation (Fig. 3a, b), which starts at 580°C. In one of the two altered samples of pyrite, the increase of magnetisation during cooling occurs in two steps, at 680°C and near 500°C (Fig. 3d). In the sample heated for 2 hours, the increase of magnetisation during cooling starts near 680°C (Fig. 3c) and is much lower than in the first two experiments. These experiments show that pyrite changes during heating always into magnetite between 440°C and 540°C. Depending on experimental conditions (time of heating)
Fig. 2. X-ray diffraction pattern obtained for pure pyrite and greigite from the Department of Earth Sciences in Orsay collection: pyrite (upper panel), and greigite (lower panel). P – pyrite, G – greigite, Q – quartz (Siemens generator, tube of X-ray with Co anthi-cathode and INEL CPS 120 curved detector).
and/or the degree of alteration of pyrite, this change is stepwise or continuous and afterwards the oxidation can continue towards maghemite into hematite.

Thermomagnetic behaviour of greigite which was used in the mixture with pyrite shows minimum magnetisation at 400°C, maximum remagnetisation at ~460°C and demagnetisation to 0 at ~580°C (Fig. 4a). Samples with a mixture of greigite and pyrite show, in all cases, minimum magnetisation during heating at 400°C, and its subsequent immediate increase (Fig. 4b-d). The maximum of the newly built magnetisation occurs above 500°C in the sample dominated by pyrite and in the sample with equal parts of pyrite and greigite (Fig. 4b-c), and presents a flattening between 460°C and 520°C in the sample dominated by greigite (Fig. 4d). This increase of magnetisation is much bigger in the sample dominated by pyrite (representing about 50% of the initial magnetisation) than in the sample dominated by greigite (representing about 20% of the initial magnetisation). On cooling, magnetisation decreases with increasing amount of greigite in these samples and presents 100% in the sample dominated by pyrite, 35% in sample with ½ pyrite and 0% in the sample dominated by greigite (Fig. 4b-d).

3. DISCUSSION

In the studied pyrite, thermomagnetic behaviour is coherent with the DTA curve with the change due to the oxidation of pyrite observed at about 540°C (Fig. 1). Nevertheless, our data show that the change is not to hematite, but always to magnetite. This magnetite starts to appear above 400°C, and depending on experimental conditions (time of heating) and/or the alteration degree of pyrite in the sample, appears progressively or by steps at different temperatures, as shown by DTA high resolution data. This magnetite persists or can change afterwards to more oxidised iron oxide such as hematite, as observed during cooling in our samples. The oxidation of magnetite depends once more on experimental conditions (time of heating) and/or the degree of alteration of pyrite.

The thermomagnetic behaviour of pyrite allows its identification in sediment; nevertheless, other paramagnetic minerals can change into magnetite at temperatures close to 550°C and mask its identification. For instance, siderite is characterized in DTA analysis by an endothermic effect at about 585°C (see, Webb and Kruger, 1970) due to the decomposition of carbonate to iron oxide. Therefore, we performed Curie balance experiment of a sample of pure siderite (F. Mélières collection). During cooling, at the Curie temperature of magnetite, magnetisation starts to increase (Fig. 3g). In this case, the difference with pyrite is evident. But the change of siderite to magnetite, which can afterwards continue to hematite, can start before 585°C. Therefore, we will observe an increase in magnetisation during heating below this temperature, as is the case in natural samples containing siderite and identified by XRD, from sediment of Lake Ferto (Neusiedlersee) region, Austria-Hungary (Fig. 3h,
Fig. 3. Thermomagnetic curves (heating and cooling are indicated by arrows) of pure pyrite from the Department of Earth Sciences in Orsay collection (a-e): (a) heated 25 minutes; (b) heated 1 hour; (c) heated 2 hours; (d)-(e) two samples pulverised and stored for several months before analysis (called “altered samples”) heated 1 hour; (f) bulk sediment sample from Lake Aibi, NW China, with fromboidal pyrite, slightly altered on the surface; *continuation on the next page.*
Fig. 3 cont. (g) pure siderite (F. Mélières collection); (h) bulk sediment sample from Lake Ferto (Neusiedlersee) with siderite. Curves (f), (g), and (h) heated 25 minutes. Experiments were done in magnetic field of 0.375 T in atmosphere. Relative magnetisation means ratio: magnetization/initial magnetisation ($M/M_0$). High values are due to small initial magnetisation, negative values correspond to diamagnetic signal of the sample holder being larger than any signal of the sample.
and Jelinowska et al., 2000). The thermomagnetic behaviour of such a siderite is quite similar to that of pyrite (for siderite see also: Ellwood et al., 1986; Hus, 1990). After
Bollin (1970), DTA for pyrrhotite and chalcopyrite (CuFeS$_2$) show changes to iron oxides around the same range of temperatures just below 600°C. This complicates an easy identification of pyrite by its magnetic monitoring during heating, but can suggest its presence in studied samples. Indeed, the thermomagnetic experiments on bulk sediment samples allowed identification of pyrite in many sediments as from Black Sea (André 1999; Strechie et al., 2002), from Lake Aibi, north-western China (Fig. 2g), from mangroves (unpublished data). In the Black Sea sediments and mangroves, pyrite was confirmed by XRD, and after heating disappeared from the spectra. In Lake Aibi, pyrite (fromboidal, slightly altered on the surface particles) was identified using scanning electron microprobe fitted with an energy-dispersive spectrometer (SEM/EDS) (Jelinowska, 1995). The increase of magnetisation or susceptibility around 550°C in samples from sedimentary rocks was observed also by other authors (Geiss and Banerjee, 1997; Stockhausen and Zolitschka, 1999), but they made different identification of minerals. Geiss and Banerjee (1997) suggested the presence of iron sulphide-bearing minerals, while Stockhausen and Zolitschka (1999) explained it as due to pyrite, metastable pyrrhotite or olivine.

In pyrite-greigite mixtures, for a higher content of pyrite, the relative increase of magnetisation near 500°C during heating is higher. This occurs somewhat above 500°C for samples dominated by pyrite, and somewhat below for samples dominated by greigite. Also during cooling, the increase of magnetisation is much higher in samples dominated by pyrite. This is conformed with the behaviour of pure pyrite and greigite used in this study. Therefore, our experiments show the possible identification of pyrite in the mixture with greigite and allow the discrimination of its dominant component; high content of pyrite increases the relative rise of magnetisation both during heating above 400°C and during cooling. This relative quantification is possible in the case described in this study, where the heating time is short and the pyrite is finally changed to magnetite and not to hematite.

Nevertheless, the shape of the thermomagnetic curve of greigite is not always exactly the same as observed in this study. Indeed, as the decrease of magnetisation during heating occurs always about 400°C, the maximum increase of magnetisation can be above or below 500°C (e.g., Roberts and Turner, 1993, Reynolds et al., 1994). This is due to the change of pyrite, marcasite and pyrrhotite, effecting the first step of alteration of greigite into magnetite (Krs et al., 1992). As the change of the pyrite to magnetite can occur at temperatures above and below 500°C, the maximum increase of magnetisation can take place below or above 500°C. It is certainly the same for pyrrhotite and marcasite. However, there are examples of greigite when the increase of magnetisation above 400°C is almost negligible, as in some samples from the Black Sea sediments (Strechie et al., 2002).

The cooling curves of greigite depend clearly on the final product of oxidation. The magnetite shows significant rise of magnetisation, but if the oxidation process continues towards hematite the remagnetisation is very low.
Curie balance experiments, in neutral argon atmosphere, on magnetic extracts of sediment samples from the Lake Manas, the same region as Lake Aibi in north-western China (Jelinowska et al., 1995) show a behaviour suggesting the presence of greigite, which was identified by XRD. Nevertheless, the remagnetisation observed during cooling could be due to products of heating of the pyrite. In this sample, we used for analyses the magnetic extract, but the pyrite was always associated with greigite, as shown by XRD. On the other side, in Lake Bledowo (Jelinowska et al., 1997), the cooling curves do not show the remagnetisation, and XRD shows clearly only greigite. It is possible that in other studies the remagnetisation during cooling could be due to products of the heating of the pyrite.

4. CONCLUSIONS
This study provides following conclusions:

1. The magnetic monitoring of the alteration of pyrite with temperature shows that at about 500°C there always appears magnetite which can change afterwards to hematite depending on the experimental conditions and state of the mineral before heating. The appearance of magnetite results in an increase of magnetisation on heating.

2. Therefore, such an increase of magnetisation at about 500°C suggests the presence of pyrite in the studied samples, but this must be verified by other analyses (e.g., XRD), as it is in the case for identification of greigite.

3. In order to preserve magnetite as an effect of transformation of pyrite, the samples have to be fresh and heated quickly (0.5 hour).

4. This behaviour of pyrite can allow its identification in a greigite/pyrite mixture: increase of magnetisation near 500°C and possibly during cooling will be higher than in pure greigite due to relative change of specific magnetisation as pyrite is altered to magnetite. The relative increase of magnetisation at 500°C and during cooling reflects the quantity of pyrite comparing to greigite in the mixture.

5. Remagnetisation at 500°C of the sample of greigite can not be significative of its quantity if the presence of pyrite (or other minerals, which transform to magnetite near 500°C: pyrrhotite, siderite…) is not ruled out.

6. Magnetisation of rocks containing greigite and submitted to temperature will change with time, with alteration of greigite towards pyrite, and magnetite into hematite.
References


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