

## New method for separation of magnetite from rock samples for oxygen isotope analysis

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**Abstract:** A new procedure is described to separate magnetite from milligram sized samples of crushed rock for oxygen isotope analysis. This method is based on magnetic separation of magnetite after heating the mixture to a temperature that exceeds the Curie point for other magnetic minerals in a sample. The relatively low temperature of this procedure (350 °C) does not induce any reaction between magnetic mineral nor does it alter the isotope composition of magnetite. This procedure was tested on samples containing known percentages of magnetite and pyrrhotite. The percentage of magnetite in a sample was increased by 10–20 % through successive enrichment cycles until a pure magnetite separate was achieved. The separation should be performed before measuring the oxygen isotope composition of the magnetic fraction of a rock sample by laser fluorination, because the presence of contaminating phases such as pyrrhotite may cause unwanted isotope partitioning of the oxygen released during fluorination.

Our data show that contamination of a magnetite sample, even with a non O-bearing phase, can lead to systematically misleading O isotope data in a standard total laser fluorination system. Enrichment of the apparent magnetite value is indicated, possibly as a result of the formation of an O-S-bearing phase.

**Key-words:** magnetite, pyrrhotite, oxygen isotope, mineral separation.

### 1. Introduction

Comparing the oxygen isotope composition of magnetite (Fe<sub>3</sub>O<sub>4</sub>) with that of a carbonate or silicate mineral provides a sensitive isotope geothermometer because of the relatively large difference in oxygen isotopic composition between these phases (*e.g.* Clayton & Kieffer, 1991; Zhao & Zheng, 2003). This is particularly advantageous because it requires no knowledge of the isotope composition of the fluid from which these minerals precipitated. Furthermore, the determination of the oxygen isotope composition of magnetite is useful in other applications. For instance, magnetite-water isotope fractionation can be used to determine fluid sources and origins of secondary magnetite in natural settings (Cole *et al.*, 2004). Also, the oxygen isotope signature of magnetite has been proposed as a marker to detect biological activity on Earth and elsewhere (Faivre & Zuddas, 2006).

High quality stable isotope analyses are best obtained through the separation of pure mineral phases. Being strongly magnetic, magnetite can be separated easily from non-magnetic minerals by using a magnet on fine grained

samples. However, this technique does not permit the separation of magnetic minerals of similar magnetic susceptibility such as pyrrhotite (Fe<sub>1-x</sub>S). This is important because magnetite and pyrrhotite are two minerals that are found associated in many geological environments, including: 1) sediments (Kao *et al.*, 2004; Horng & Roberts, 2006; Raposo *et al.*, 2006; Wakabayashi *et al.*, 2006), 2) metallic ore deposits (Faure & Brathwaite, 2006), 3) hydrothermally altered igneous rocks (Alt *et al.*, 1989), 4) carbonaceous chondrites (Hsu *et al.*, 2006), and even 5) Martian crust (Dunlop & Arkani-Hamed, 2005) and Martian meteorites (McKay *et al.* 1996; Rochette *et al.*, 2001). They are also disseminated in metamorphic and magmatic rocks, where they may constitute a continuous record of Earth's magnetic field variations which can be used for paleomagnetic studies (Wehland *et al.*, 2004). The coexistence of magnetite and pyrrhotite in Martian meteorite ALH84001 is of particular importance, since some ALH64001 magnetites have been attributed to a biological origin (Thomas-Keptra *et al.* 2000), although this issue is controversial. Faivre & Zuddas (2006) proposed a combination of oxygen isotope fractionation for the system magnetite-water

and crystal size distribution as a reliable indicator of biogenicity. Therefore, highly valuable information could be extracted from the oxygen isotope composition of magnetites in ALH84001 if this phase could be unambiguously measured as a mineral separate. Currently, there are several available techniques for oxygen isotope analysis of oxide minerals based on standard fluorination (Clayton & Mayeda, 1963; Borthwick & Harmon, 1982), laser fluorination (Sharp, 1990) and ion probe methods (Ripperdan *et al.*, 1998).

The oxygen isotope composition of magnetite is determined using a fluorination process to release the oxygen as  $O_2$ . Thereafter it can be isotopically analysed as  $O_2$ , or quantitatively converted to  $CO_2$  and subsequently analysed. This is accomplished in several ways depending on the amount of sample available. The common laser fluorination technique (not *in situ*) is especially useful for analyzing small amount of sample (as small as 0.5 mg) (Sharp, 1990; Matthey & MacPherson, 1993). The laser is used to heat the sample in the presence of a fluorinating agent such as  $BrF_5$ ,  $ClF_3$  or  $F_2$ . Unfortunately, if there are any other minerals present, they may potentially react to form O-bearing phases or cause incomplete fluorination. It is possible that this procedure could cause oxygen isotope partitioning during fluorination. Therefore, as with all high quality stable isotope analyses, a pure separate must be sought prior to oxygen isotope analyses.

Techniques are traditionally available to separate magnetic minerals from relatively large samples (grams; Parfenoff *et al.* 1970). However, these techniques are less useful when the amount of sample is limited (micrograms), and there is no procedure described in the literature, to date, to separate milligram sized mixtures of magnetic minerals.

The goals of this study are (i) to develop a procedure to separate magnetite from milligram sized mixtures of magnetic minerals for oxygen isotope analysis, and (ii) to demonstrate that failure to obtain pure separates of fine-grained samples, even if the contaminating phase is not O-bearing, can result in misleading magnetite O isotope data. The separation technique developed makes use of the Curie temperatures of these minerals. The Curie point is the temperature above which a ferromagnetic minerals loses their permanent magnetism. The technique is demonstrated for mechanical mixtures of fine grained magnetite and pyrrhotite, which commonly co-occur in rock samples. While the Curie point for pyrrhotite is  $\sim 320^\circ C$  (Wakabayashi *et al.*, 2006), that for magnetite is  $\sim 587^\circ C$  (Liu *et al.*, 2003). The procedure involves heating the mixture *in vacuo* in excess of the Curie point for pyrrhotite followed by the magnetic separation of magnetite.

## 2. Material and methods

### 2.1. Experimental procedure

Magnetite,  $Fe_3O_4$ , and pyrrhotite,  $Fe_{11}S_{12}$  were obtained from Ward's Natural Scientific Establishment Inc. Magnetite was a lodestone collected at Ceder City, Utah and pyrrhotite was collected from Galax, Virginia.

About 10 g of magnetite and pyrrhotite were ground separately in a cryomill (Certiprep 6750; SPEX) to a final particle size of 50  $\mu m$ . The powder was stored under anaerobic conditions to avoid oxidation of the samples prior to separation and analysis.

Eleven mixtures of magnetite and pyrrhotite were prepared as indicated in Table 1. Samples were weighted with a Mettler AJ 100 scale with an error of  $\pm 0.1$  mg. Three series of mixtures were prepared independently as replicates.

A 25 mg sample of each mixture was introduced to a Pyrex glass tube of 16 cm  $\times$  6 mm O.D. (1.5 mm wall), having one end welded closed. Each tube was bent at a  $45^\circ$  angle in the middle of the tubing. Once the sample was loaded, the tube was connected to a vacuum line using a Swagelok Cajon stainless steel Ultra-Torr vacuum fitting union. After evacuating the tube, it was sealed using a gas flame.

Once sealed, the tube was heated in a furnace at  $350^\circ C$  for 3 h. After this time, the tube was removed and the magnetic fraction of the sample was immediately separated by transferring it to the opposite empty end of the tubing using a magnet. This separation was completed ( $< 4$  s) before samples cooled below the Curie point of pyrrhotite ( $320^\circ C$ ).

Once the fractions are separated, the tube was sealed at the bend using a gas flame. The magnetic and the non-magnetic fractions may be kept under vacuum in this state until they are analyzed. This procedure prevents oxidation of the separated fractions.

### 2.2. Analyses

#### 2.2.1. X-ray diffraction

X-ray diffraction analyses were performed on the original mixtures and on the magnetic fraction after each separation using a single-crystal X-ray diffractometer equipped with an area detector (Bruker D8 SMART APEX, Germany). For every sample, a frame (or 2D diffraction pattern) was collected using the following experimental conditions: Mo  $K\alpha$ , 50 kV, 30 mA, 0.5 mm collimator diameter and 30 s exposure time. Sample powders were analysed in transmission mode. XRD2DScan software (Rodriguez-Navarro, 2006) was used to convert 2D diffraction patterns into regular  $2\theta$  linear scans. This software was also used for background subtraction and integration of peaks in the  $2\theta$  scans. To determine the percentage of magnetite in a mixture, the integrated intensity of the strongest magnetite reflection (*e.g.*, 311 at 2.53  $\text{\AA}$ ) was measured. Because each recovered mixture contained a distinct mass of solid, it was necessary to standardize the integrated peak area of each measurement. Therefore, the intensity of the (311) magnetite peak ( $I_{mag}$ ) was normalized to the total peak intensity ( $TPI$ ) calculated as the sum of the intensity of all the peaks displayed in the XRD pattern. The resulting peak intensity ratio ( $I_{mag}/TPI$ ) was determined to generate a calibration curve allowing the estimation of the percentage of magnetite (%mag) in the original mixture and the fractionated separate of each run (Fig. 1).

Table 1. Relative percentage and amount of magnetite and pyrrhotite in the original mixture.

Sample	% Magnetite	% Pyrrhotite	Magnetite (mg)	Pyrrhotite (mg)
Mt100	100	0	25	0
Mt90	90	10	22.5	2.5
Mt80	80	20	20	5
Mt70	70	30	17.5	7.5
Mt60	60	40	15	10
Mt50	50	50	12.5	12.5
Mt40	40	60	10	15
Mt30	30	70	7.5	17.5
Mt20	20	80	5	20
Mt10	10	90	2.5	22.5
Po100	0	100	0	25

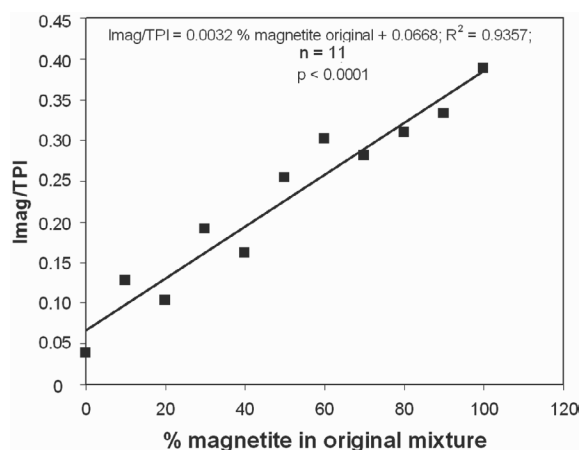


Fig. 1. XRD calibration curve showing the relationship between the intensity of the (311) magnetite reflection normalized to the total intensity of peaks and the percentage of magnetite in the magnetite-pyrrhotite mixtures.

For comparison, the same standard mixtures were also analyzed using a standard powder diffractometer (Scintag, USA) and  $\text{CuK}\alpha$  radiation. The XRD patterns collected this way were relatively imprecise and had high background, resulting in very poor calibration curves. This problem is caused by the X-ray fluorescence of Fe-bearing minerals when a  $\text{CuK}\alpha$  source is used. Additional advantages of the single crystal diffractometer are the small X-ray beam (0.5 mm) and area detector which allow the efficient analysis of small samples (< 1 mg) (Bhuvanesh & Reibenspies, 2003).

### 2.2.2. Differential scanning calorimetry

The thermal stability of the magnetite-pyrrhotite mixtures was assessed by analyzing 10 mg of a mixture by differential scanning calorimetry (DSC; DSC-50Q, Shimadzu, Japan). These analyses were performed under flowing  $\text{N}_2$  to prevent oxidation of the samples. Samples were heated to a final temperature of 400 °C, by increasing the temperature 10 °C per min.

### 2.2.3. Oxygen isotope composition of magnetite

About 1–4 mg of the magnetic fraction of each standard mixture (containing 1–2 mg of magnetite) was analysed by laser fluorination, where the sample is heated in excess of 1500 °C (Sharp, 1990) in the presence of  $\text{ClF}_3$  using a  $\text{CO}_2$  laser. The reaction liberated 100 % release of  $\text{O}_2$  from magnetite, which was converted to  $\text{CO}_2$  by reaction with hot graphite. The  $\text{CO}_2$  was then analysed by a VG SIRA-10 mass spectrometer. Reproducibility was better than  $\pm 0.5$  ‰ ( $1\sigma$ ), determined by replicate analyses of an internal laboratory quartz standard. Results are reported in standard delta notation ( $\delta^{18}\text{O}$ ) as per mill (‰) units calibrated to the Vienna Standard Mean Ocean Water (V-SMOW) international standard.

## 3. Results and discussion

### 3.1. Thermal stability of mineral mixtures

One of the main requirements of the separation method is that the thermal treatment does not induce chemical reactions or promote oxygen isotope exchange among the mineral phases in a mixture. Pure magnetite, pure pyrrhotite and a mixture of both phases were analyzed using differential scanning calorimetry (DSC) to test for chemical reactions during heating. Figure 2 displays the DSC pattern of the pure phases and 1:1 mixture over the temperature range of the separation experiment. Note that the DSC spectrum of the mixture is intermediate in form to the spectra for the pure minerals suggesting there is no reaction among these phases over the temperature range of the experiments. Therefore, the temperature chosen for heating mixtures during the separation procedure (350 °C) is low enough to: a) preclude decomposition of either the two mineral phases, and b) high enough to exceed the Curie point for pyrrhotite. Unfortunately, DSC analyses cannot detect oxygen isotope exchange reactions among the phases. Therefore additional experiments are required to test for this potential effect.

### 3.2. Efficiency of the separation methodology

Once the magnetic fractions were separated, the mineral composition of each fraction was analyzed by XRD and

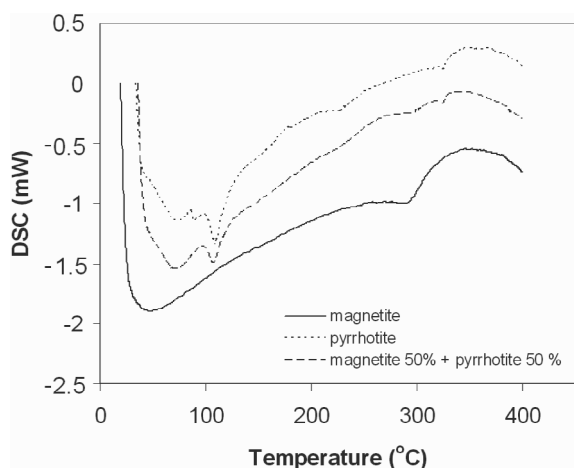


Fig. 2. Differential Scanning calorimetry analyses for pure magnetite, pure pyrrhotite and 1:1 mixture of magnetite and pyrrhotite.

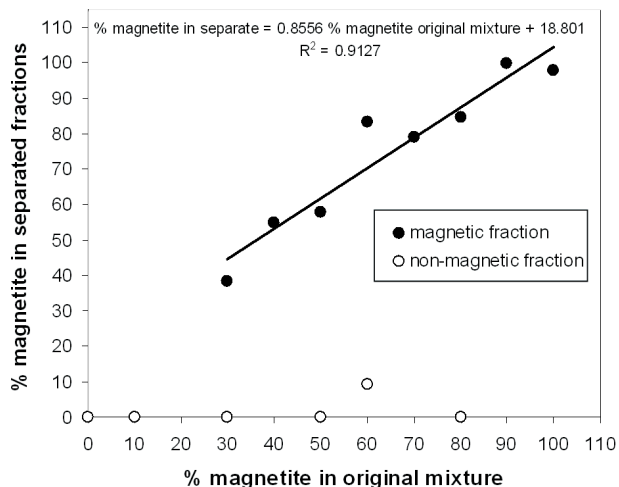


Fig. 3. Composition of the magnetic (●) and the non-magnetic (○) fractions separated from mixtures with different starting compositions.

the percentage of magnetite was calculated using the correlation equation developed in Fig. 1.

The mineralogical composition of the magnetic and non-magnetic fractions separated from mixtures is shown in Fig. 3. The non-magnetic fraction did not contain magnetite over the entire range of mixture compositions measured by XRD. The magnetic fraction, however, contained a considerable proportion of pyrrhotite though its composition was enriched in magnetite as compared to the original mixture. The separated magnetic fraction contained ~ 10–20 % more magnetite than the original mixture. Only when the original mixture was  $\geq 90$  % magnetite, was the magnetic separate composed of pure magnetite.

Therefore, to completely separate these minerals, the separation procedure must be repeated several times, with the number of times depending on the starting composition of the mixture. For instance, considering the curve shown in Fig. 3, for a starting composition of 50 % magnetite,

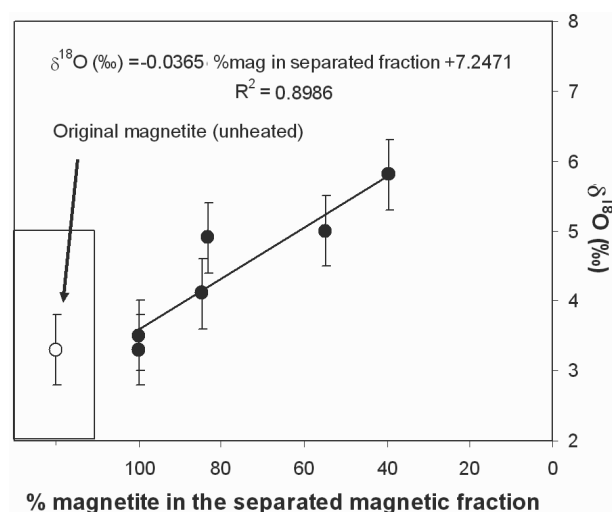


Fig. 4. Oxygen isotope composition of the separated magnetic fractions (●) corresponding to different percentages of magnetite in the separated magnetic fractions and  $\delta^{18}\text{O}$  of raw (unheated) 100 % magnetite (○).

the separation procedure should be performed five times to yield a fraction with 94 % magnetite.

This technique may also be used to separate other magnetic minerals that exist in rock, sediment and soil samples such as ilmenite, hematite, titanohematite and titanomagnetite (e.g. Anderson & Morrison, 2005; Zwing *et al.*, 2005; Alva-Valdivia *et al.*, 2003; Ryabchikov & Kogarko 2006), greigite (e.g. Kao *et al.*, 2004), maghemite (e.g. Guerrak, 1988), franklinite (e.g. Stalder & Rozendaal, 2005) or feroxyhyte (Costantini *et al.*, 2006) as long as the minerals in the mixture have different Curie points (feroxyhyte: 180 °C, ilmenite: 233 °C, greigite: 333 °C, hematite: 675 °C, maghemite: 300 °C; Cullity, 1972).

### 3.2.1. Oxygen isotope composition of heated magnetite

The  $\delta^{18}\text{O}$  value for the original unheated magnetite was 3.3 ‰ while  $\delta^{18}\text{O}$  values for the heated 100 % magnetite were 3.3 ‰ and 3.5 ‰, being identical to the original (unheated) magnetite within the analytical error ( $1\sigma$ ) (Table 2). Therefore, heating the original pure magnetite during separation did not alter the  $\delta^{18}\text{O}$  value.

Separated magnetic fractions of mixtures displayed  $\delta^{18}\text{O}$  values ranging between 3.3 and 5.8 ‰ (reproducibility was excellent even in the mixture containing around 40 % magnetite which gave 5.8 ‰). An increase in  $\delta^{18}\text{O}$  value was detected as the percentage of pyrrhotite in the separated magnetic fraction increased (Fig. 4). Such an increase in  $\delta^{18}\text{O}$  value with an increase of the relative amount of pyrrhotite can be fitted to the following linear equation:

$$\delta^{18}\text{O}(\text{‰}) = (0.037 \pm 0.006) \% \text{pyrrhotite} + (3.6 \pm 0.2);$$

$$n = 7; \quad R^2 = 0.89860.$$

The intercept of  $3.6 \pm 0.2$  is identical to the measured values of 100 % magnetite. Based on these data, the heating pro-

Table 2. Oxygen isotope composition ( $\delta^{18}\text{O}$ ) of the original (unheated) magnetite and the separated magnetic fractions in differing magnetite/pyrrhotite mixtures. AH = after heating.

Sample name	% magnetite in the original mixture	% magnetite in the separated magnetic fraction	$\delta^{18}\text{O}(\text{‰})$
AH Mt20	20	39.7	5.8
AH Mt40	40	54.9	5.0
AH Mt60	60	83.2	4.9
AH Mt80	80	84.6	4.1
AH Mt100a	100	100.0	3.3
AH Mt100b	100	100.0	3.5
Raw (unheated) magnetite	100	–	3.3

cedure during separation does not alter the isotope composition of magnetite. However, when pyrrhotite exists in the mixture (> 10 % in the sample), there is a shift in oxygen isotope value of the mixture. Whatever the process causing fractionation of the O isotopes from the original magnetite value, it is clear that contamination of a magnetite sample, even with a non O-bearing phase, can lead to misleading O isotope data in a standard total laser fluorination system. We speculate that this may result from the formation of O-S-bearing gas phase that does not react with  $\text{ClF}_3$  once it is formed. This is plausible because laser directs energy only at the solid phase and the temperature outside may be too low to facilitate some reaction of O-bearing gases with the fluorination agent. The trend in the data suggests this process is controlled by a kinetic fractionation in which a O-S-bearing phase preferentially incorporates  $^{16}\text{O}$ , leaving the remaining  $\text{O}_2$  enriched in the heavier isotope ( $^{18}\text{O}$ ). Additional analyses need to be performed with larger aliquots of samples in conventional Ni bombs to test this hypothesis. In this case, the temperature of the gas phase is raised sufficiently for reaction with  $\text{ClF}_3$  to preclude the formation of O-bearing gases other than  $\text{O}_2$ .

#### 4. Conclusions

A new procedure to quantitatively separate small amounts of magnetic minerals making use of their differential Curie points is presented in this paper. The methodology demonstrated that magnetite-pyrrhotite mixtures can be efficiently separated. Samples with a low initial percentage of magnetite can be purified by applying this procedure a number of times. Our results show that the thermal treatment necessary to surpass the Curie point of pyrrhotite (and render this phase non-magnetic) did not alter the composition of the mineral phases or affect the oxygen isotopic composition of magnetite. The separation procedure described in this study may be especially useful in cases when there is a very limited amount of samples and/or the samples are valuable (*e.g.*, meteorites). Also, in real samples there could be other magnetic mineral mixtures besides pyrrhotite and magnetite. For instance, meteorites contain metallic Fe, Ni which are also highly magnetic and would be separated along with magnetite. Although presence of these metals does not alter the O-isotopic composition, it may require

larger amounts of sample and of fluorination reagent to release enough O for the analyses. In future studies, we will apply this methodology to more complex magnetic mineral mixtures.

In addition, our data show that contamination of a magnetite sample, even with a non O-bearing phase, can lead to misleading O isotope data in a standard total laser fluorination system. An increment in the apparent  $\delta^{18}\text{O}$  magnetite value is indicated, possibly as a result of the formation of an O-S-bearing phase which escapes the influence of the fluorinated agent. While further work is required to establish this process, it is nonetheless clear that the tenet that a pure sample gives the best results is reinforced by this study, even when the contaminant does not bear the element under consideration.

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