

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

Running title: New method for separation of magnetite from rock samples

Plan of the article:

1. Introduction
 2. Material and methods
 - 2.1 Experimental procedure
 - 2.2 Analyses
 - 2.2.1 X-Ray Diffraction
 - 2.2.2 Differential Scanning Calorimetry
 - 2.2.3 Oxygen isotope composition of magnetite
 3. Results and Discussion
 - 3.1 Thermal stability of mineral mixtures
 - 3.2 Efficiency of the separation methodology
 - 3.3 Oxygen isotope composition of heated magnetite
 4. Conclusions
- Acknowledgements
- References

Corresponding author: Christopher S. Romanek.

Postal address: Savannah River Ecology Laboratory, University of Georgia,
Savannah River Site, Building 737-A, Aiken, SC 29808, USA

E-mail: romanek@srel.edu

Tlf: 803 725 2472

Fax: 803 725 3309

Type of Computer: Compatible PC

Operating system: Windows XP

Word-processor: Microsoft Word 2003

Number of characters: 27584

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

CONCEPCIÓN JIMÉNEZ-LÓPEZ¹, ALEJANDRO RODRÍGUEZ-NAVARRO², TERESA
PÉREZ-GONZÁLEZ¹, JAVIER CARRILLO-ROSÚA³, ADRIAN J. BOYCE³ and
CHRISTOPHER S. ROMANEK^{4*}

⁽¹⁾ Departamento de Microbiología, Universidad de Granada. Avda. Fuentenueva s/n, 18002 Granada,
Spain

⁽²⁾ Departamento de Mineralogía y Petrología, Universidad de Granada, Avda. Fuentenueva s/n, 18002
Granada, Spain

⁽³⁾ Scottish Universities Environmental Research Centre, East Kilbride, Glasgow G75 0QF, Scotland,
U.K.

⁽⁴⁾ Savannah River Ecology Laboratory and Department of Geology, University of Georgia, Savannah
River Site, Building 737-A, Aiken, SC 29808, USA.

* Corresponding author: romanek@srel.edu

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 ablation, 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 which escapes the influence of the plasma created by the laser.

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

1. Introduction

Comparing the oxygen isotope composition of magnetite (Fe_3O_4) 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 & Keiffer, 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 (Fe_3O_4) 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_{1-x}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.

The oxygen isotope composition of magnetite is determined using a fluorination process to release the oxygen as O₂. Thereafter it can be directly analysed isotopically as O₂, or quantitatively converted to CO₂ and subsequently analysed. This is accomplished in several ways depending on the amount of sample available. The common total laser fluorination technique (not *in situ*) is especially useful for analyzing small amount of sample (even few µg) (Sharp, 1990; Matthey & MacPherson, 1993). The laser is used to heat the sample in the presence of a fluorinating agent such as BrF₅ or ClF₃. Unfortunately, if there are any other minerals present, they may potentially react to form O-bearing phases, cause incomplete fluorination or they may be O-bearing. It is possible that this procedure could cause isotope partitioning of the oxygen during fluorination, if contamination is present, as our results will show. 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, those 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 is (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 material loses its permanent magnetism. The technique is demonstrated for mechanical mixtures of fine grained magnetite and pyrrhotite, which commonly occur in rock samples. While the Curie point for pyrrhotite is ~320 °C (Wakabayashi *et al.*, 2006), that for magnetite is ~587 °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, Fe₃O₄, and pyrrhotite, Fe₁₁S₁₂ 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 µm. 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 ± 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 x 6 mm O.D. (1.5 mm wall), having one end welded closed. Each tube was bent at a 45° 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° C for 3 hours. 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 sec) before samples cooled below the Curie point of pyrrhotite (320° 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 α , 50 kV, 30 mA, 0.5 mm collimator diameter and 30

seconds exposure time. Sample powders were analysed in transmission mode. XRD2DScan software (Rodríguez-Navarro, 2006) was used to convert 2D diffraction patterns into regular 2θ linear scans. This software was also used for background subtraction and integration of peaks in the 2θ scans. To determine the percentage of magnetite in a mixture, the integrated intensity of the strongest magnetite reflection (e.g., 311 at 2.53 Å) 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).

For comparison, the same standard mixtures were also analyzed using a standard powder diffractometer (Scintag, USA) and $CuK\alpha$ 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 Cu $K\alpha$ 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 N₂ to prevent oxidation of the samples. Samples were heated to a final temperature of 400 °C, by increasing the temperature 10°C per minute.

2.2.3 Oxygen isotope composition of magnetite

About 1-2 mg of the magnetic fraction of each standard mixture was analysed by laser fluorination, where the sample is heated in excess of 1500° C (Sharp, 1990) in the presence of ClF₃ using a CO₂ laser. The reaction liberated 100% release of O₂ from magnetite, which was converted to CO₂ by reaction with hot graphite. The CO₂ was then analysed by a VG SIRA-10 mass spectrometer. Reproducibility was better than ±0.5‰ (1σ), determined by replication of internal lab quartz standard. Results are reported in standard delta notation (δ¹⁸O) 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 the percentage of magnetite was calculated using the correlation equation developed in Figure 1.

The mineralogical composition of the magnetic and non-magnetic fractions separated from mixtures is shown in Figure 3. The non-magnetic fraction did not contain magnetite over the entire range of mixture compositions measured by XRD. Alternatively, the magnetic fraction contained a considerable proportion of pyrrhotite although in each mixture the percentage of magnetite in the separated fraction was always greater than in the original mixture (the separated magnetic fraction contained ~10 - 20 % more magnetite than the original mixture). Only when the original mixture was ≥ 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, the separation procedure should be performed five times to yield a fraction with 94 % magnetite.

Additionally, this technique may 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 ferrosityte (Costantini *et al.*, 2006) as long the minerals in the mixture have different Curie points (ferrosityte:180°C, ilmenite: 233 °C, greigite: 333 °C, hematite: 675 °C, maghemite: 300°C; Cullity, 1972).

3.3 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 (1σ) (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 magnetite in the separated magnetic fraction decreased (Figure 4), and the percentage of pyrrhotite increased. 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:

$$\delta^{18}\text{O}(\text{‰}) = (0.037 \pm 0.006) \% \text{pyrrhotite} + (3.6 \pm 0.2); \quad n = 7; \quad R^2 = 0.8986$$

The intercept of 3.6 ± 0.2 is identical to the measured values of 100% magnetite. Based on these data, the heating procedure 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 ClF₃ once it is formed. This is plausible because laser ablation directs energy only at the solid phase outside the plasma region and the temperature is 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 ¹⁶O, leaving the remaining O₂ enriched in the heavier isotope (¹⁸O). 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 ClF₃ to preclude the formation of O-bearing gases other than O₂.

4. Conclusions

A new procedure is presented in this paper to quantitatively separate small amount of magnetic minerals making use of their differential Curie points. 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).

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. Enrichment of the apparent magnetite value is indicated, possibly as a result of the formation of an O-S-bearing phase which escapes the influence of the plasma created by the laser. 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.

Acknowledgements

This research was supported by research projects CGL2004-03910, RNM2003-07375 from the MEC (Spain) and by the U.S. Department of Energy through Financial Assistance Award No. DE-FC09-96-SR18546 to the University of Georgia Research Foundation. CJL wishes to thank the Fulbright/MEC Program. SUERC is supported by NERC and the Scottish Universities consortium. AJB is funded by NERC Scientific Services' support of the Isotope Community Support Facility at SUERC.

References

- Alt, J.C., Anderson, T.F., Bonnell, L., Muehlenbachs, K. (1989): Mineralogy, chemistry, and stable isotopic compositions of hydrothermally altered sheeted dikes: ODP Hole 504B, Leg 111. *Proc. Scientific Results, ODP, Leg 111, Costa Rica Rift*, 27-40.
- Alva-Valdivia, L.M., Rivas, M.L., Goguitchaichvili, A., Urrutia-Fucugauchi, J., Gonzales, J.A., Morales, J., Gómez, S., Henríquez, F., Nyström, J.O., Naslund, R.H. (2003): Rock-magnetic and oxide microscopic studies of the El Laco iron Ore deposits, Chilean Andes, and implications for magnetic anomaly modelling. *International Geology Review*, **45**, 533-547.
- Anderson, J.L. & Morrison, J. (2005): Ilmenite, magnetite and peraluminous Mesoproterozoic anorogenic granites of Laurentia and Baltica. *Lithos*, **80**, 45-60.
- Bhuvanesh, N.S.P. & Reibenspies, J.H. (2003): A novel approach to micro-sample X-ray powder diffraction using nylon loops. *J. Appl. Crystallogr.*, **36**, 1480-1481.
- Clayton, R.N. & Keiffer, S.W. (1991): Oxygen isotopic thermometer calibrations. in “Stable Isotope Geochemistry: A tribute to Samuel Epstein”, Taylor, H.P. *et al.*, eds. *Geochem. Soc., Special Publication*, **3**, 3-10.
- Cole, D., Horita, J., Polyakov, V.B., Valley, J.W., Spicuzza, M.J., Coffey, D.W. (2004): An experimental and theoretical determination of oxygen isotope fractionation in the system magnetite-H₂O from 300 to 800°C. *Geochim. Cosmochim. Acta*, **68**, 3569-3585.

- Costantini, E.A.C., Lessovaia, S., Vodyanitskii, Y. (2006): Using the analysis of iron and iron oxides in paleosols (TEM, geochemistry and iron forms) for the assessment of present and past pedogenesis. *Quat. Inter.*, **156-157**, 200-211.
- Cullity, B.D. (1972): Introduction to Magnetic Minerals. Addison-Wesley, Reading Massachusetts, 666 p.
- Dunlop, D.J. & Arkani-Hamed, J. (2005): Magnetic minerals in the Martian crust. *J. Geophys. Res.*, **110**, 1-11.
- Faivre, D. & Zuddas, P. (2006): An integrated approach for determining the origin of magnetite nanoparticles. *Earth Planet. Sci. Lett.*, **243**, 53–60.
- Faure, K. & Brathwaite, R.L. (2006): Mineralogical and stable isotope studies of gold–arsenic mineralization in the Sams Creek peralkaline porphyritic granite, South Island, New Zealand. *Mineral. Deposita*, **40**, 802–827.
- Guerrak, S. (1988): Geology of the Early Devonian oolitic iron ore of the Gara Djebilet Field, Saharan Platform, Algeria. *Ore Geo. Rev.*, **3**, 333-358.
- Horng, C.S. & Roberts, A.P. (2006): Authigenic or detrital origin of pyrrhotite in sediments?: Resolving a paleomagnetic conundrum. *Earth Planet. Sci. Lett.*, **241**, 750–762.
- Hsu, W., Guan, Y., Hua, X., Wang, Y, Leshin, L.A., Sharp, T.G. (2006): Aqueous alteration of opaque assemblages in the Ningqiang carbonaceous chondrite: Evidence from oxygen isotopes. *Earth Planet. Sci. Lett.* **243**, 107–114.
- Kao, S.J., Horng, C.S., Roberts, A.P., Liu K.K. (2004): Carbon–sulfur–iron relationships in sedimentary rocks from southwestern Taiwan: influence of geochemical environment on greigite and pyrrhotite formation. *Chem. Geol.*, **203**, 153–168.

- Liu, H., Jiang, E.Y., Bai, H.L., Zheng, R.K., Wei, H.L., Zhang, X.X. (2003): Separation and magnetoresistance in $\text{Nd}_{0.52}\text{Sr}_{0.48}\text{MnO}_3$. *Appl. Phys. Lett.*, **83**, 3531-3533.
- Mattey, D. & Macpherson, C. (1993): High-precision oxygen isotope microanalysis of ferromagnesian minerals by laser-fluorination. *Chem. Geol.*, **105**, 305-318.
- McKay, D.S., Gibson, E.K. Jr., Thomas-Keprta, K.L., Vali H., Romanek, C.S., Clemett, S.J., Chilier, X.D.F., Maechling, C.R., Zare, R.N. (1996): Search for past life on Mars: possible relic biogenic in Martian meteorite ALH84001. *Science*, **273**, 924–930.
- Parfenoff, A., Pomerol, C., Tourenq, J. (1970): Les minéraux en grains: methods d'étude et détermination. Masson et Cie, Paris, 578 p.
- Raposo, M.I.B., McReath, I., D'Agrella-Filho, M.S. (2006): Magnetic fabrics, rock magnetism, cathodoluminescence and petrography of apparently undeformed Bambuí carbonates from São Francisco Basin (Minas Gerais State, SE Brazil): An integrated study. *Tectonophysics*, **418**, 111–130.
- Rochette, P., Lorand, J.P., Fillion, G., Sautter, V. (2001): Pyrrhotite and the remanent magnetization of SNC meteorites: A changing perspective on Martian magnetism. *Earth Planet. Sci. Lett.*, **190**, 1-12.
- Rodriguez-Navarro, A.B. (2006): XRD2DScan: new software for polycrystalline materials characterization using two-dimensional X-ray diffraction. *J. Appl. Crystallogr.*, **39**, 905-909.
- Ryabchikov, I.D. & Kogarko, L.N. (2006): Magnetite compositions and oxygen fugacities of the Khibina magmatic system. *Lithos*, **91**, 35-45.

- Sharp, Z.D. (1990): A laser-based microanalytical method for the in situ determination of oxygen isotope ratios in silicates and oxides. *Geochimica et Cosmochimica Acta*, **54**, 1353-1357.
- Stalder, M. & Rozendaal, A. (2005): Calderite-rich garnet and franklinite-rich spinel in amphibolite-facies hydrothermal sediments, Gamsberg Zn-Pb deposit, Namaqua Province, South Africa. *Can. Mineral.*, **43**, 585-599.
- Thomas-Keprta, K.L., Bazlinski, D.A., Kirschvink, J.L., Clemett, S.J., McKay, D.S., Wentworth, S.J., Vali, H., Gibson, E.K Jr., Romanek, C.S. (2000): Elongated prismatic crystals in ALH84001 carbonate globules: potential Martian magnetofossils. *Geochim. Cosmochim. Acta*, **64**, 4049–4081.
- Wakabayashi, K., Tsunakawa, H., Mochizuki, N., Yamamoto, Y., Takigami, Y. (2006): Paleomagnetism of the middle Cretaceous Iritono granite in the Abukuma region, northeast Japan. *Tectonophysics*, **421**, 161–171.
- Wehland, F., Alt-Epping, U., Braun, S. Appel, E. (2005): Quality of pTRM acquisition in pyrrhotite bearing contact-metamorphic limestones: possibility of a continuous record of earth magnetic field variations. *Phys. Earth Planet. Inter.*, **148**, 157-173.
- Zhao, Z.F. & Zheng, Y.F. (2003): Calculation of oxygen isotope fractionation in magmatic rocks, *Chem. Geol.*, **193**, 59-80.
- Zwing, A., Matzka, J., Bachtadse, V., Soffel, H.C. (2005): Rock magnetic properties of remagnetized Palaeozoic clastic and carbonate rocks from the NE Rhenish massif, Germany. *Geophys. J. Int.*, **160**, 477-486.

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

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	$\delta^{18}\text{O}(\text{‰})$
AHMt20	20	39.7	5.8
AHMt20	20	39.7	5.8
AHMt40	40	54.9	5.0
AHMt60	60	83.2	4.9
AHMt80	80	84.6	4.1
AHMt100	100	100.0	3.3
AHMt100	100	100.0	3.5
Raw (unheated) magnetite	100	-	3.3

Figure 1. XRD calibration curve showing the relationship between the normalized intensity of the (311) magnetite peak at 2.52 Å and the percentage of magnetite in the magnetite-pyrrhorite mixtures.

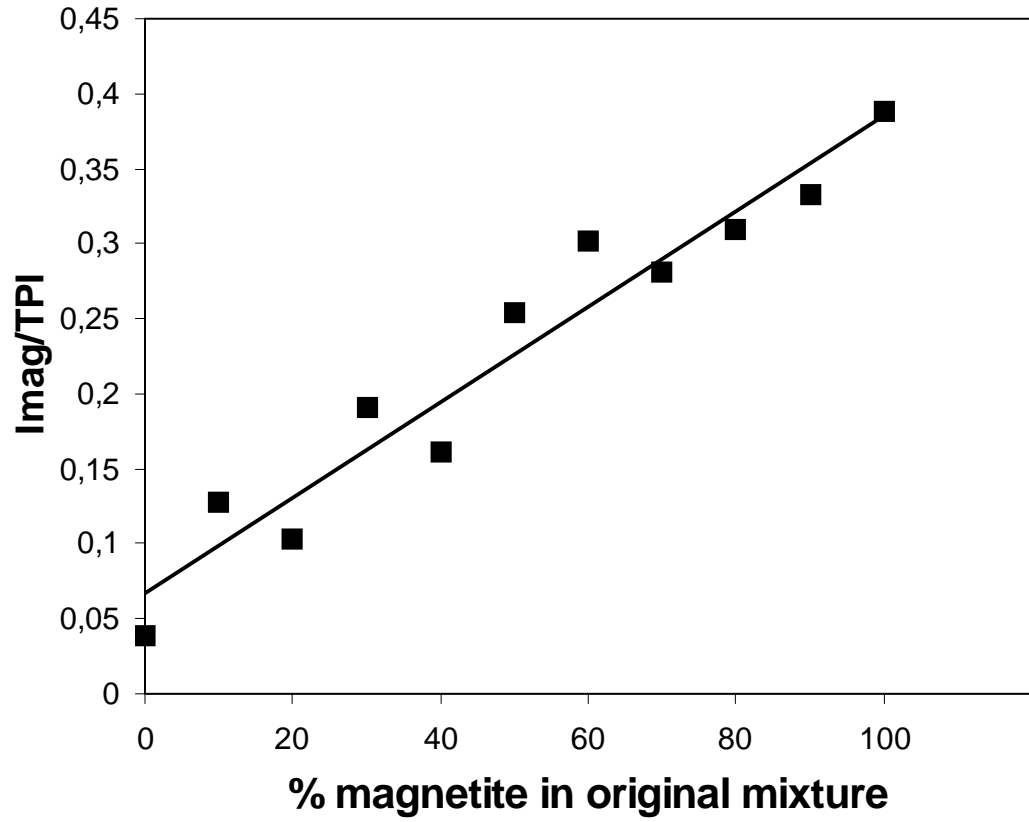


Figure 2.- Differential Scanning calorimetry analyses for pure magnetite, pure pyrrhotite and 1:1 mixture of magnetite and pyrrhotite.

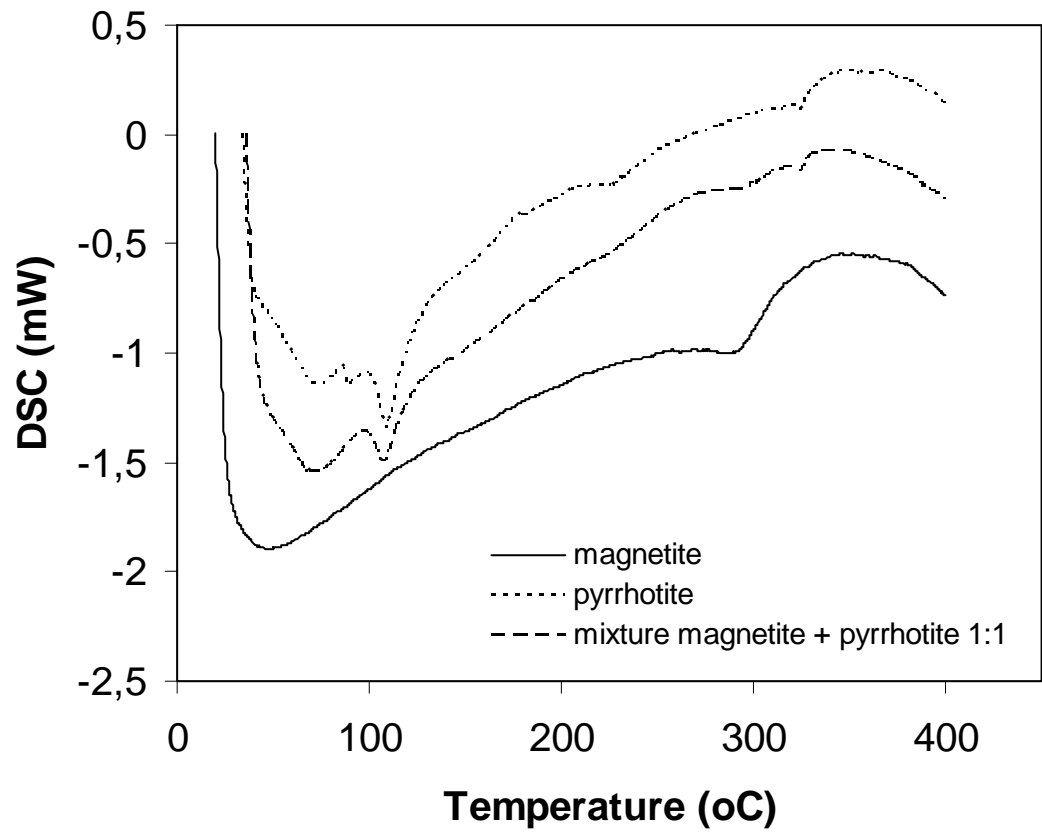


Figure 3.- Composition of the magnetic (open-squared) and the non-magnetic (solid-squared) fractions separated from mixtures with different starting compositions.

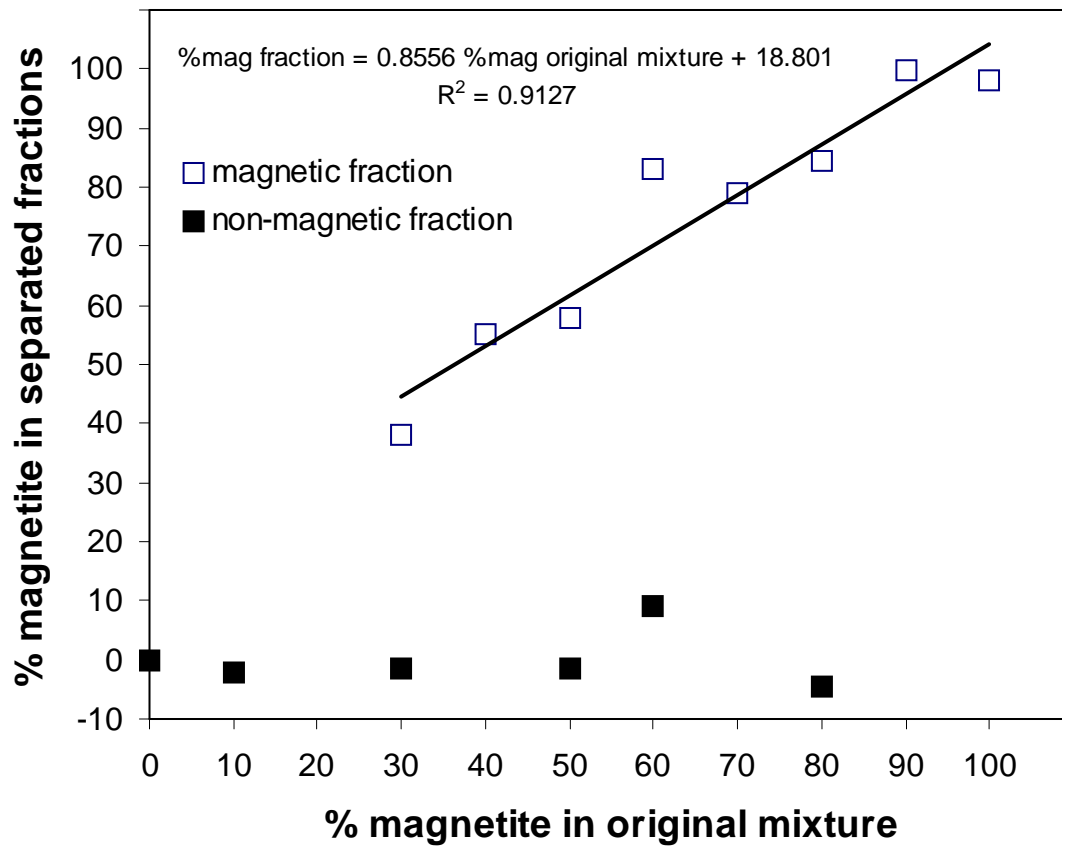


Figure 4.- Oxygen isotope composition of the separated magnetic fractions (solid circles) corresponding to different percentages of magnetite in the separated magnetic fractions and $\delta^{18}\text{O}$ of raw (unheated) 100 % magnetite (open circle).

