

DIFFERENTIAL THERMAL ANALYSIS AND CELL DIMENSIONS OF SOME NATURAL MAGNETITES*

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ABSTRACT

The DTA curve of magnetite is characterized by two exothermic peaks.

X-ray examination of the products obtained by differential thermal analysis showed that both exothermic reactions are caused by oxidation of ferrous iron. The intensity of the first peak decreases with increasing particle size indicating that the intensity of the first peak is directly proportional to the total surface area of the particles.

The first reaction is caused by the oxidation of Fe^{2+} on the surface of the particles resulting in the formation of a protective film of Fe_2O_3 around the particles. The second reaction is caused by the oxidation of the remaining magnetite by diffusion of oxygen into the magnetite structure after the protective film of Fe_2O_3 had become porous by recrystallization of the Fe_2O_3 at higher temperatures. It appears that the transition from ferromagnetism to paramagnetism promotes the diffusion of oxygen into the lattice as the second exothermic peak follows the transition temperature, (Curie point) immediately.

Some new lattice measurements of magnetite are also presented and an attempt was made to correlate cell-edge dimensions with magnesium content. There seems to be a tendency for the cell-edge to decrease with an increase in magnesium content.

I. INTRODUCTION

In a general survey of the thermal behaviour of various minerals by means of differential thermal analysis it was found that magnetite gave a very distinctive curve showing two exothermic reactions.

In an attempt to interpret this interesting phenomenon, the effect of particle size on the differential thermal curve was determined. X-ray determinations were also made of the lattice parameters (a_0) of the unheated magnetites as well as after heating to a temperature where the first reaction had stopped but before the second one began. The resulting data provided a basis for a satisfactory explanation of the two reactions.

II. DESCRIPTION OF MAGNETITE SAMPLES

Five magnetite samples from the Transvaal were investigated as well as the classical material from Mineville, U.S.A. They may be described as follows:

- (a) *Sibasa, Zoutpansberg District.* Geological associations unknown.
- (b) *de Roodepoort 67, Ermelo District.* Material from this locality was described by Wagner (1) as bedded magnetic iron ore which is interstratified with sandstones and shales belonging to the Middle Ecca Series of the Karroo System (Carboniferous). These rocks are intruded by sills of dolerite which have metamorphosed the ore

* Published with the consent of the Department of Mines.

as well as the associated rocks. The ore consists of a finely granular aggregate of magnetite accompanied by secondary limonite. According to Wagner it is probable that the ore was originally a bedded sideritic ironstone.

- (c) *Barberton Chrysotile Mine, Barberton.* Magnetite veins which cut the chrysotile-bearing serpentine body. Hydrothermal origin.
- (d) *Witbank 59, Ermelo District.* Geological associations unknown. The sample was coarsely fibrous and is probably a pseudomorph of magnetite after an asbestiform mineral.
- (e) *Phalaborwa, Phalaborwa Complex.* At the present the general opinion is that the magnetite is of magmatic origin.
- (f) *Mineville, U.S.A.* U. S. Bureau of Standards, Sample No. 29a.

All the samples were carefully cleaned of impurities by hand picking, washing in water and by the use of a hand magnet. Microscopic examination showed that all the material used in this study was essentially free from all impurities. Tyler sieves were used for separating the various sizes.

III. DIFFERENTIAL THERMAL ANALYSIS

The *DTA* apparatus used in this investigation consisted of the following components:

- (1) A horizontal alundum tube furnace wound with Kanthal A wire, similar in construction to the one described by Gruver (2).
- (2) A Variac (General Radio Co. Type V20HM) continuously adjustable transformer used as the manual power control for the heating rate of the furnace.
- (3) A spotlight galvanometer (30 mm. per microampere sensitivity) for measurements of the e.m.f. from the differential thermocouple.
- (4) A nickel block sample holder, two inches long and one and a half inches in diameter, with two drilled cavities for holding the sample and inert material.
- (5) A temperature thermocouple and a differential thermocouple both made of Pt-Pt 13% Rh wire, 0.3 mm. in diameter.
- (6) An ordinary pyrometer for measuring the temperature of the inert material (Al_2O_3).

All samples were lightly tamped in the sample holder before the analyses. A cover was not used over the sample holder because the magnitude of the thermal reactions is suppressed considerably by its use. The heating rate used was 15° C. per minute and apart from the 50 ohms internal resistance of the galvanometer no additional external resistance was used in the circuit.

DTA curves of five magnetite samples from different localities are shown in Fig. 1. All the curves are characterized by a sharp exothermic peak at 360 to 375° C. which is followed by a broad exothermic peak beginning at 580° C. and having a varying maximum peak temperature. The intensity of the first peak varies in different samples of magnetite but the temperature of 580° C. where the second reaction begins is very characteristic for all samples examined. It was found that samples ground

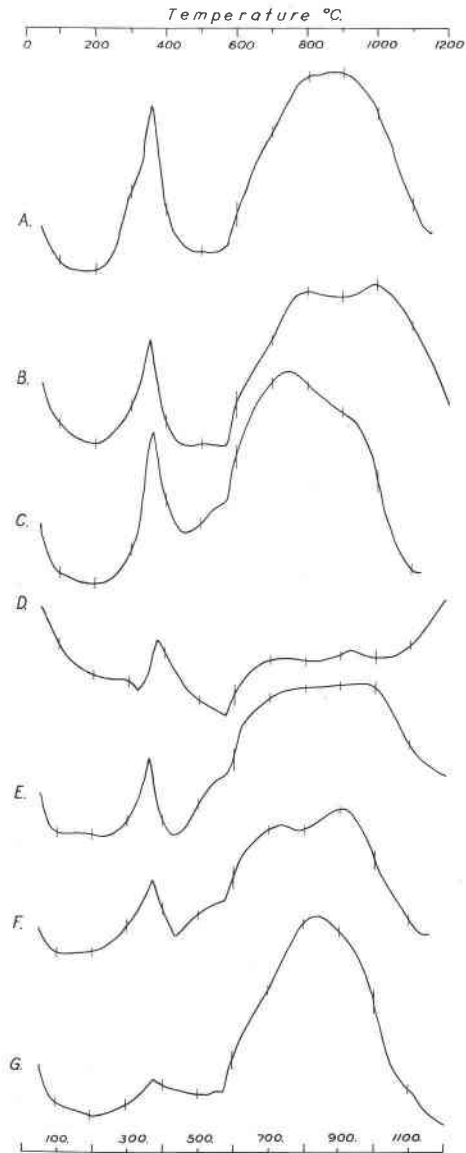


FIG. 1. DTA curves of magnetites from different localities. *A.* Sibasa. Grain size (-200) mesh. *B.* Sibasa, Grain size (-100) mesh. *C.* De Roodepoort. Grain size (-200) mesh. *D.* De Roodepoort. Grain size (-200) mesh, with cover on sample holder. *E.* Barberton. Grain size (-200) mesh. *F.* Witbank. Grain size (-200) mesh. *G.* Phalaborwa. Grain size (-200) mesh.

to -200 mesh gave better defined second peaks than those ground to -100 mesh. (cf. curves *A* and *B*, Fig. 1). In curve *B* there is a doubling of the second exothermic peak which is characteristic of samples of larger particle size. The phenomenon is also seen in Fig. 1 curve *F*. In this instance it is due to the fact that the sample was coarsely fibrous so that larger particles than -200 mesh were able to pass through the sieve.

In Fig. 1 curves *A* and *G* the curve is horizontal between the two exothermic reactions but in Fig. 1 curves *C*, *E* and *F* however, the second reaction starts immediately after the first one. In all the curves the second reaction is greatly accelerated at a temperature of 580° C.

The effect of using a cover over the sample holder can be seen by comparing curves *C* and *D* in Fig. 1. In curve *D* the second exothermic reaction is nearly completely suppressed and the height of the first peak is about half of that in the curve *C*.

In Fig. 2 the effect of particle size on the *DTA* curves are illustrated. A constant weight of 6.5 gms. were used for all the examples. The height of the first exothermic peak decreases with an increase in particle size, and that of the second peak increases with an increase in particle size. There is also a tendency for the second peak to split into two peaks in samples coarser than 325 mesh especially when the particle size range is kept in narrow limits. (cf. Fig. 1, *E* and Fig. 2, *C*). Curve *F*, Fig. 2 was obtained on a standard magnetite sample from Mineville, U.S.A., of the National Bureau of Standards of the U.S. Department of Commerce (Sample 29*a*). It was included in Fig. 2 to illustrate the effect of an extremely small particle size on the *DTA* curve. The intensity of the first peak is greater and that of the second peak smaller than in all the other curves in Fig. 2.

IV. THE OXIDATION OF NATURAL MAGNETITE

Both exothermic reactions as recorded by *DTA* analysis are due to the oxidation of ferrous iron in the magnetite structure. This was established as follows:

- (a) *X*-ray photographs of magnetite heated until just beyond the first peak ($\pm 510^{\circ}$ C.), revealed that it consisted of a mixture of magnetite and hematite. The relative intensities of the magnetite reflections remained the same, although the intensity of the pattern as a whole was slightly lower and the six strongest lines of hematite appeared. Lattice determinations of magnetites thus heated were identical to that of the original material.
- (b) Magnetite of $-115+150$ mesh size was heated up to 980° C. under normal conditions in the differential thermal analyzer. At this temperature nitrogen was introduced into the furnace and heating continued until 1200° C. The *DTA* curve indicated that oxidation was stopped immediately after the introduction of the nitrogen. The material so obtained, when ground to -325 mesh after cooling in a nitrogen atmosphere, consisted of a mixture of magnetite and hematite and when

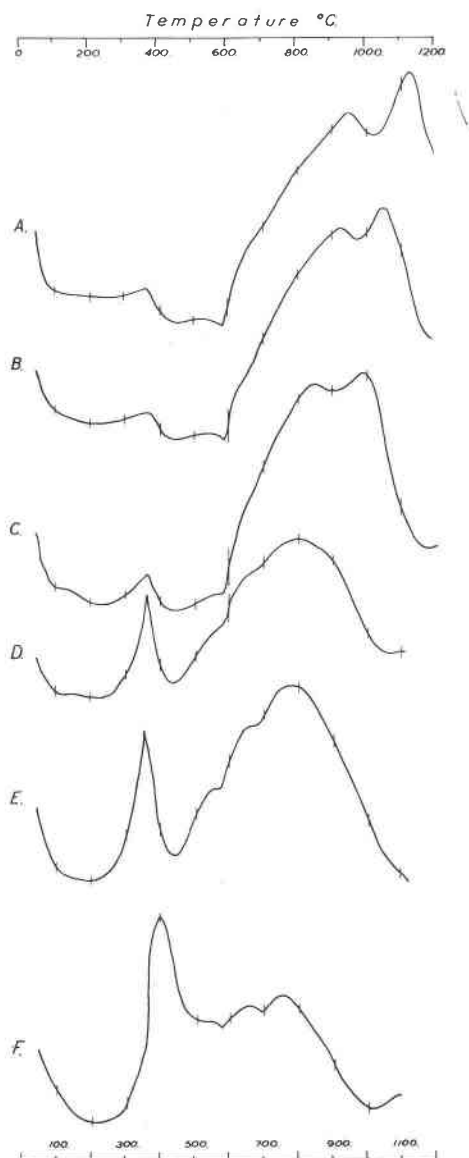


FIG. 2. DTA curves of magnetites showing the effect of grain size. *A.* Barberton. Grain size. (-115+150) mesh. *B.* Barberton. Grain size (-150+200) mesh. *C.* Barberton. Grain size (-200+325) mesh. *D.* Barberton. Grain size (-325) mesh. *E.* Barberton. The smallest grain size that could be obtained by hand grinding. *F.* Mineville. Extremely fine-grained; particles even smaller than *E.*

subjected to differential thermal analysis, again showed the two characteristic peaks for magnetite although these were less intense.

- (c) When magnetite was heated in an oxidizing atmosphere until the *DTA* curve showed that the second reaction was complete, no magnetite was detected in the oxidized material. In Fig. 2 curves *A* and *B* this reaction had not yet been completed at 1200° C. (due to the large particle size). In these two cases magnetite was again detected in the end products.
- (d) The formation of gamma Fe_2O_3 under the heating conditions used can be eliminated as this phase was never detected at any stage.

A. Interpretation of the first exothermic reaction

Gheith (3) recently ascribed the first sharp exothermic peak to the recrystallization of the extremely fine magnetite particles present in his samples. He mentions that such a recrystallization is due to the "high force of crystallization" of magnetite. Such an interpretation is not in accordance with the fact that *x*-ray examination of an extremely fine magnetite powder revealed a very high order of crystallization, the photographs showing no line broadening. Furthermore, the presence of hematite in material heated beyond the first peak is regarded as ample evidence that the first peak represents only an oxidation reaction.

When magnetite was heated to beyond the first peak (510° C) and then again rerun, the *DTA* curve showed only the second peak. On the other hand, when magnetite previously heated to beyond the first peak was ground and rerun the first peak was again recorded on the curve. This fact is significant because it indicates that the first reaction is arrested by the formation of a protective film of hematite around the magnetite particles. Furthermore, the observation that the intensity of the first peak increases with decreasing particle size is in accordance with the fact that in a constant weight of material the total surface area increases with decreasing particle size. The intensity of the first peak is therefore directly proportional to the total surface area of the particles. On the above mentioned evidence the authors have interpreted the first peak on the *DTA* curve as follows:

The *first* exothermic reaction is caused by the oxidation of Fe^{2+} on the surface of the particles resulting in the formation of a thin protective film of hematite around a core of unaltered magnetite.

B. Interpretation of the second exothermic reaction

The temperature of 580° C. where the second reaction begins, remains absolutely constant for all the samples examined and is preceded by a very small endothermic peak, the intensity of which is depressed by the second exothermic reaction. It is interesting to note that the so-called Curie point, where the ferromagnetism of magnetite changes to paramagnetism occurs at 590° C. (4).

In order to investigate whether the change from ferromagnetism to paramagnetism could be detected on the differential thermal analyzer, a sample of magnetite was examined in an atmosphere of nitrogen. The curve indicated that no oxidation took place; the two exothermic peaks were absent but a well defined endothermic peak at 585° C. was recorded. On cooling, this peak was again recorded at 585°C. (now exothermic) indicating that a reversible transition had taken place corresponding to a change from ferromagnetism to paramagnetism and vice versa. According to Mason (4) these changes are not accompanied by any structural alteration. It appears that the transition from ferromagnetism to paramagnetism promotes the diffusion of oxygen into the lattice as the second exothermic reaction follows the transition temperature immediately. The second peak on the *DTA* curve has therefore been interpreted as follows:

The *second* exothermic reaction is caused by the oxidation of the remaining magnetite at a temperature where the diffusion of oxygen into the magnetite structure becomes possible after the protective film of hematite had become porous by recrystallization at higher temperatures. However, the most important factor governing the second oxidation reaction is that the process of diffusion of oxygen into the lattice is promoted when a transition from ferromagnetism to paramagnetism takes place. By such a process it is understood that the oxygen diffuses into the lattice forming Fe_2O_3 immediately. Oxidation therefore, progresses from the surface of the grains towards the core. The intensity of the second peak increases with increasing particle size because the intensity of the first peak decreases with increasing particle size so that relatively more magnetite remains unoxidized after the first reaction is completed. The tendency for the second peak to split into two peaks in samples coarser than 325 mesh is difficult to explain and needs further investigation.

V. X-RAY EXAMINATION

X-ray powder diffraction patterns were obtained by using 57.3 mm. diameter cameras in which the film is mounted according to the Straumanis method. Unfiltered cobalt radiation was used. The method of mounting the samples in the camera and measuring the films is that usually employed in this Laboratory (5) and (6).

Values for the lattice parameter (a_0), calculated from the high angle lines were obtained by the graphical extrapolation method described by Henry, Lipson and Wooster (7). In this method the different values of the cell-edge (a) are plotted against the function

$$\frac{1}{2} \times \left(\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)$$

and the value for a_0 recorded where this function is equal to 0.
The results of lattice measurements are listed in Table 1.

TABLE 1. LATTICE MEASUREMENTS OF MAGNETITES

Locality	a_0 (Å)
Sibasa, Zoutpansberg district	8.394 (± 0.001)
de Roodepoort 67, Ermelo district	8.389 (± 0.003)
Barberton Chrysotile Mine, Barberton	8.398 (± 0.001)
Witbank 59, Ermelo district	8.386 (± 0.001)
Phalaborwa, Letaba district	8.387 (± 0.002)
Mineville, U.S.A.	8.392 (± 0.001)

In the literature measurements of the length of the cell-edge vary from 8.36 Å to 8.42 Å (4). The most recent values for artificial magnetite are probably those published by Tombs and Rooksby (8) and Abrahams and Calhoun (9). All these authors give a value of 8.394 Å.

The relatively large variation of the lattice parameters of the magnetites examined, suggested a variation of the cube-edge due to a variation in chemical composition. Qualitative spectrographic analyses showed that the only elements likely to affect the size of the unit-cell are aluminum, magnesium, and in the Witbank sample, also nickel.

Quantitative spectrographic analyses of magnesium and aluminum were carried out according to the Jaycox Method (10). The nickel content of the Witbank sample was determined chemically. FeO determinations varied between 25% and 28% indicating an excess of Fe_2O_3 of approximately the same order for all the samples examined. No definite relationship could be established between FeO content and unit-cell size.

In Table 2 spectrochemical and chemical data are given for the magnetites examined:

TABLE 2. SPECTROCHEMICAL AND CHEMICAL DATA OF MAGNETITES

Locality	MgO%	Al_2O_3 %	NiO%
Sibasa	1.48	0.38	—
de Roodepoort	1.73	0.45	—
Barberton	0.67	0.09	—
Witbank	1.05	0.07	1.76*
Phalaborwa	2.55	0.75	—
Mineville†	0.095	0.46	—

* Analyst: A. Kruger, Division of Chemical Services, Pretoria.

† U.S. Bureau of Standards Analysis (Sample 29a).

In Fig. 3 values for a_0 are plotted against the molecular proportion of MgO; for the Witbank sample the molecular proportion of (MgO+NiO) is used. The ionic radii of Mg^{2+} and Ni^{2+} are approximately the same and their influence on the size of the lattice parameter will therefore be of similar magnitude.

The replacement of Fe^{2+} (ionic radius 0.74 Å) by Mg^{2+} and/or Ni^{2+} (ionic radii 0.66 and 0.69 Å resp.) causes a contraction of the unit-cell of magnetite. Figure 3 indicates such a tendency, although it is obvious that much more results are needed to establish the exact magnitude of this shrinkage. No satisfactory explanation can be offered for the anomalous

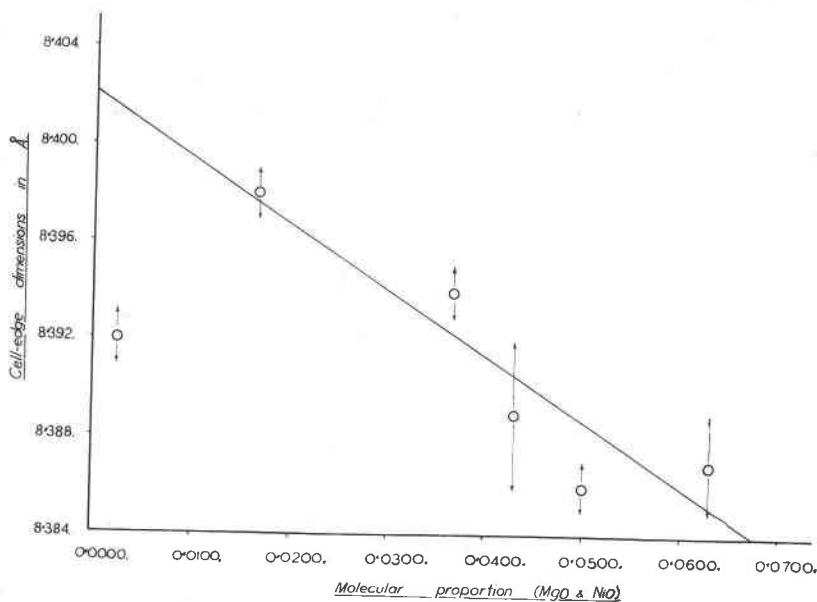


FIG. 3. Graphical representation of the variation of the cell-edge (a_0) with the molecular proportion of (MgO+NiO).

position of the Mineville sample on the curve.

In compiling the curve, the possible effects of an excess of Fe_2O_3 , or a replacement of Fe^{3+} by Al^{3+} on the unit-cell dimensions, were not considered because FeO-determinations on all samples indicated an excess of Fe_2O_3 of approximately the same order and a very low alumina content.

If the shrinkage of the unit-cell as indicated by the curve is correct then a magnesium-free magnetite should have a cube-edge of 8.402 Å (± 0.002). The corresponding calculated specific gravity of such a magnetite is 5.187.

VI. CONCLUSIONS

1. A differential thermal analysis and x -ray study of magnetite indicated that on heating, magnetite is oxidized in two distinct stages.
2. The first reaction is ascribed to the oxidation of Fe^{2+} on the surface of the magnetite particles.
3. The second reaction is ascribed to the oxidation of the magnetite particles by a process of diffusion of oxygen into the magnetite structure.
4. Some new precision lattice determinations of natural magnetites are given. There seems to be a tendency for the size of the unit-cell of magnetite to decrease with a replacement of Fe^{2+} by Mg^{2+} .

ACKNOWLEDGMENTS

The authors wish to thank Dr. R. Haul of the South African Council for Scientific and Industrial Research, Pretoria, for the interest shown in the work as well as for reviewing the manuscript. The National Chemical Laboratory of the C.S.I.R. is gratefully acknowledged for the FeO determinations and Mr. H. D. Russell of this Laboratory for the quantitative spectrographic analyses.

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Manuscript received May 7, 1954.