

TRANSFORMATION OF TRACE ELEMENT-SUBSTITUTED MAGHEMITE TO HEMATITE

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Abstract—X-ray powder diffraction (XRD), transmission electron microscopy, infrared spectroscopy, differential thermal analysis, and surface area (BET) measurements were employed to investigate the transformation of microcrystalline maghemite to hematite. At 500°C pure maghemite was completely altered to hematite in 3 hr, whereas maghemites containing small amounts ($\leq 1\%$) of Co, Ni, Zn, Cu, Mn, Al, V, and Cr required much longer heating times. The maghemite-to-hematite transformation temperature varied from 540° to 650°C. XRD line widths suggest that each particle of maghemite and hematite may have been a mosaic of many independent, coherently diffracting crystals. The transformation of maghemite to hematite at 650°C was accompanied by a reduction in surface area due to sintering of particles.

Key Words—Hematite, Iron, Maghemite, Magnetite, Particle size, Sintering, Trace elements.

INTRODUCTION

The oxidation of magnetite (Fe_3O_4) to hematite ($\alpha\text{-Fe}_2\text{O}_3$) proceeds either directly or via maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The direct oxidation of magnetite to hematite has been extensively investigated (Davis *et al.*, 1968), and, although considerable work has also been carried out on the oxidation of magnetite to hematite (Colombo *et al.*, 1968; Gallagher *et al.*, 1968) and the formation of maghemite in soils (Taylor and Schwertmann, 1974), the transformation or inversion of maghemite to hematite has received relatively little attention (Schwertmann and Taylor, 1977).

Several divalent and trivalent ions may replace iron in natural magnetite, and this mineral is believed to be an important source of trace elements in soils and rocks (Elsdon, 1975; Mathison, 1975). Sidhu *et al.* (1977) showed that the presence of trace elements reduced the rate of oxidation of magnetite to maghemite. The present paper describes the effect of these trace elements on the transformation of maghemite to hematite.

MATERIALS AND METHODS

Preparation of samples

Maghemites were prepared by oxidation of precipitated magnetites. Magnetite samples were synthesized according to the technique described by Sidhu *et al.* (1978) and contained various amounts of Co, Ni, Zn, Cu, Mn, Al, V, and Cr. The magnetites were heated in air at 220°C for 3 hr to form maghemite. X-ray powder diffraction (XRD) and transmission electron microscopic (TEM) observations showed that no other phases were present. The release pattern of Fe and trace elements during the dissolution of these maghemites

in HCl indicated that the trace elements substituted for Fe in the crystal structure of maghemite (Sidhu *et al.*, 1980).

Transformation of maghemite to hematite

Maghemite samples (~ 100 mg) were heated in silica crucibles in a muffle furnace for different periods at 250°, 300°, 320°, 400°, 450°, 500°, and 650°C and rapidly cooled by placing the crucibles in ice. Quantitative XRD using a Philips vertical diffractometer and a curved-crystal monochromator was employed to determine the concentrations of maghemite and hematite in these samples. The peak areas of the 220 and 113 reflections of maghemite and hematite, respectively, were used for analysis by reference to calibration curves obtained from mixtures of maghemite and hematite. The standards of maghemite and hematite were obtained by heating precipitated magnetite at 220° and 700°C for 3 hr, respectively (Sidhu *et al.*, 1980).

Changes in the shape of particles which accompanied the transformation of maghemite to hematite were studied by TEM using a Hitachi HU11 instrument and the procedure described by Sidhu *et al.* (1977). Infrared (IR) spectra were recorded on a Perkin Elmer Model 337 Grating Spectrophotometer using KBr as the matrix. Differential thermal analyses (DTA) were carried out in air on 100-mg samples at a heating rate of 10°C/min using a Stanton Redcroft 67 thermal analysis system. Crystal size was calculated from the corrected widths at half-maximum intensity of maghemite (220) and hematite (113) XRD reflections neglecting line broadening from structural defects. Quartz powder was used for the determination of instrumental broadening (Klug and Alexander, 1974). The specific surface area measurements were made using the BET nitrogen adsorption technique.

Table 1. Concentration and average crystal size (calculated from X-ray powder diffraction line broadening) of maghemite and hematite during the alteration of pure maghemite to hematite at 500°C.

Heating time (min)	Concentration (%)		Crystal size (Å)	
	Maghemite	Hematite	Maghemite	Hematite
0	100	0	550 (1260) ¹	0
1	97	2	480	210
2	95	5	560	320
4	88	11	530	440
8	72	27	490	430
13	56	42	530	420
20	49	52	540	450
60	14	85	500	400
180	1	98	330	460
360	1	98	180	450
1200	0	100	0	450 (1310) ¹

¹ Values of crystal size in parentheses are calculated from the BET surface areas, assuming cubic particles.

RESULTS AND DISCUSSION

Kinetics of the maghemite-to-hematite transformation

Maghemite samples heated in air at temperatures ranging from 250° to 300°C for periods as long as 5 days showed no changes in mineralogy. Heating the maghemites at >320°C produced hematite, but the transformation rate was very slow at <450°C (about 10% reaction completed in one week). The kinetics of transformation determined at 500°C are shown in Figure 1. At 500°C, transformation rates were rapid during the initial stages of reaction. About 70 to 90% of the transformation was completed during the first 60 min. Complete alteration to hematite occurred after 3 hr heating for pure maghemite, whereas complete alteration of substituted maghemites required much longer periods of heating. At all stages, the sum of maghemite and hematite concentrations in the samples was about 100% (Table 1), indicating that little or no intermediate product had formed. No shifts in the XRD spacings of maghemite or hematite were observed. Substituted maghemites altered at a slower rate than pure maghemites, and all substituted maghemites altered at a similar rate, irrespective of the nature and extent of substitution ($\leq 1\%$). The substituting elements may have stabilized the cubic spinel structure of maghemite against its transformation to the hexagonal phase (hematite) with which some of these elements are incompatible. Sidhu *et al.* (1980) showed that during the transformation of maghemite to hematite as much as about 60% of the Co, Ni, Zn, and Cu present in the crystal structure of maghemite is ejected from the crystals, whereas the Mn, Cr, and Al present in maghemite are redistributed in hematite particles. It is likely that some additional activation energy over that required for the alteration of pure maghemite is required to eject

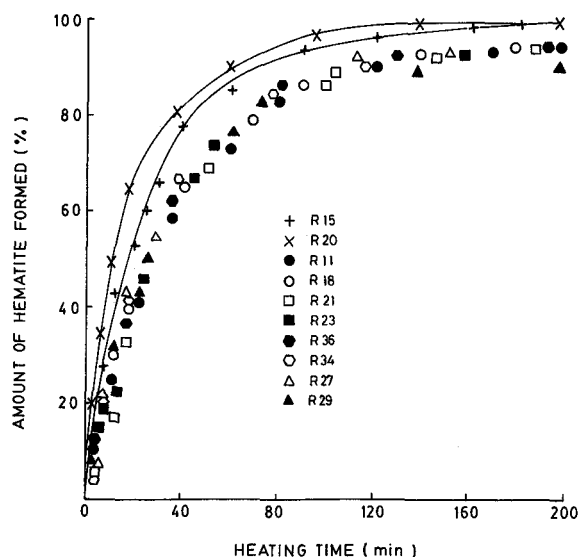


Figure 1. Kinetics of transformation of various maghemites to hematite at 500°C.

or redistribute these elements. This requirement of additional energy might therefore reduce the transformation rate. Of the two pure maghemites, the more rapid alteration of sample R20, having a greater specific surface area (12.9 m²/g) than sample R15 (9.5 m²/g) is consistent with Farrell's (1972) conclusion that the rate of transformation is inversely related to particle size.

Colombo *et al.* (1968) reported that the presence of small amounts of hematite as impurities in natural magnetite and as nuclei in synthetic magnetite was necessary for the direct oxidation of magnetite to hematite at low temperatures (~200°C). The hematite apparently acted as nuclei for the autocatalytic growth of hematite in preference to maghemite. To test whether the formation of hematite nuclei in crystals of maghemite enhanced the rate of transformation, a sample of maghemite was heated at 500°C for 1 min to produce about 2% hematite. Subsequent heating of this sample at temperatures as high as 300°C for 2 days did not increase the hematite content. At temperatures >320°C, this sample transformed to hematite at rates similar to the original hematite-free maghemite, showing that hematite nuclei did not promote the low-temperature alteration to hematite.

XRD patterns of hematites prepared by heating maghemites for 3 hr at 650°C showed that d-values and intensities of reflections were unaffected by the low levels of Co, Ni, Zn, Cu, Mn, V, Al, and Cr substitution.

Changes in line widths during maghemite-to-hematite transformation

During the initial stages of transformation, hematite reflections were broad and weak. Heating pure mag-

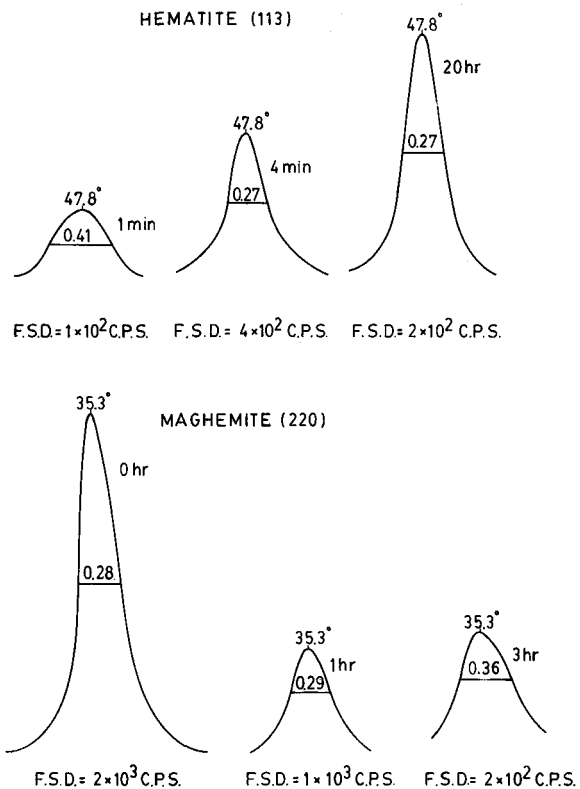


Figure 2. The 113 X-ray powder diffraction reflections of hematite and 220 reflections of maghemite for transformed maghemite after different periods of heating at 500°C. Peak widths at half-maximum intensity are in $^{\circ}2\theta$. Full-scale deflection (F.S.D.) is in counts per second (C.P.S.). $\text{CoK}\alpha$ radiation.

hemite at 500°C for 4 min (11% completion of the reaction) increased the intensity and decreased the width of hematite reflections. No further changes in hematite peak widths were observed (Figure 2) on prolonged heating (~20 hr). The widths of the maghemite reflections were constant up to 95% completion of the reaction and increased only during the final stages of the transformation.

The increase in XRD line broadening may be due to reduction in the size of coherently diffracting ordered domains within particles and/or dislocations and distortions within the crystal (Klug and Alexander, 1974). The average crystal sizes of maghemite and hematite calculated from the broadening of XRD line profiles, neglecting line broadening from structural defects, are given in Table 1. These data indicate that the hematite crystals grew during the initial stages of transformation without a reduction in the average size of maghemite crystals. A reduction in the average size of maghemite crystals was detected only after about 95% of the maghemite had changed to hematite.

The sizes of maghemite and hematite crystals measured by XRD line broadening were about one-third

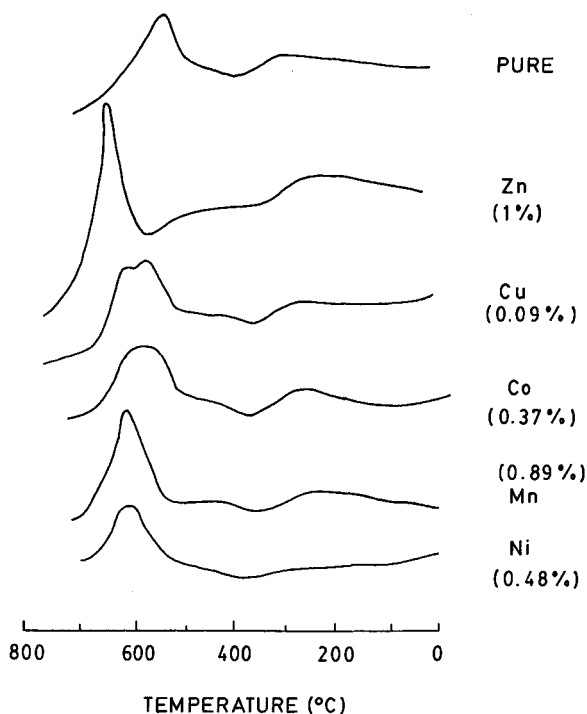


Figure 3. Differential thermal analysis curves for selected maghemites.

of the particle sizes calculated from surface area and electron microscopy. The individual particles of maghemite and hematite may have been composed of coherently diffracting domains rather than each being a single coherently diffracting crystal. The volume of a crystal calculated from XRD line broadening was about 5% of the volume of a particle calculated from the surface area measurements assuming cubic shape of particles. These observations suggest that each particle of maghemite or hematite may be a mosaic of many

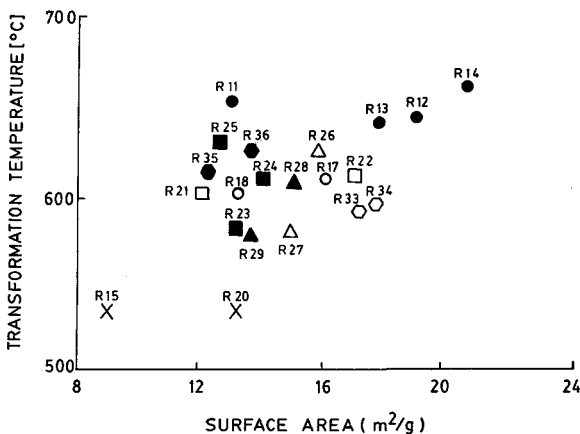


Figure 4. Effect of surface area and trace element substitution on maghemite-to-hematite transformation temperature determined from differential thermal analysis curves.

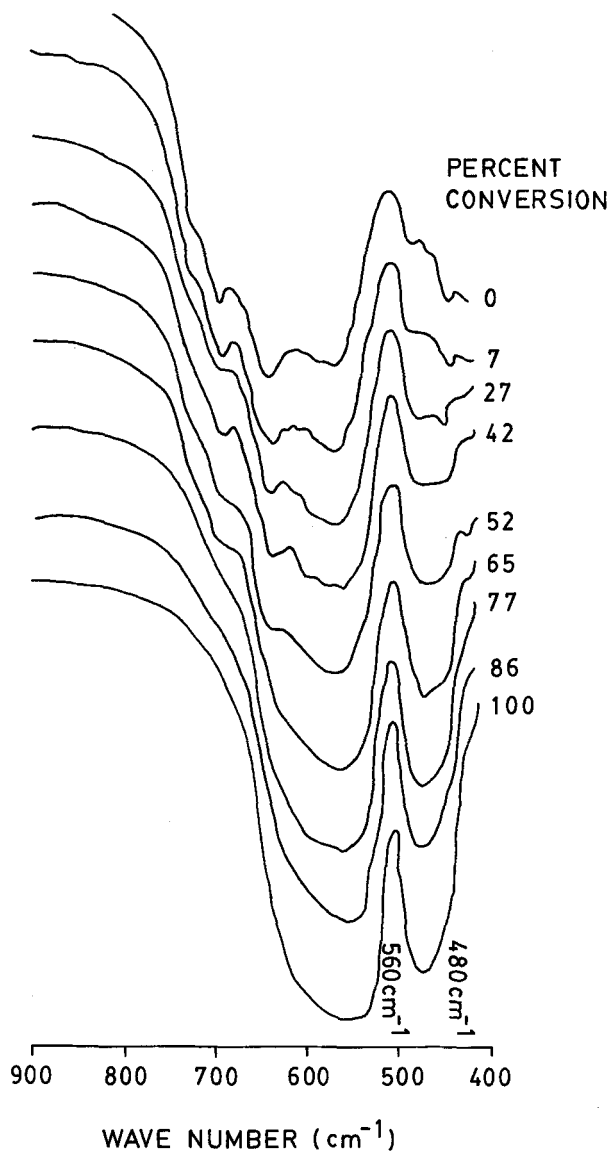


Figure 5. Infrared absorption spectra of pure maghemite exhibiting various degrees of transformation to hematite. Percent value refers to the content of hematite in sample as determined by X-ray powder diffraction analysis.

independent, coherently diffracting crystals. Thus, the constant crystal size observed throughout most of the alteration may simply reflect the size of the domain and not that of the particles. Each particle at intermediate stages of alteration may have consisted of a mixture of maghemite and hematite crystallites. Attempts to demonstrate the polycrystalline nature of individual particles by electron diffraction were unsuccessful due to the small size of particles.

Differential thermal analysis

The DTA curves (Figure 3) of maghemites were characterized by an intense exothermic peak at about

Table 2. Concentration of substituted elements and surface area of maghemites and hematites.¹

Sample	Trace element content of maghemite (%)	Surface area (m ² /g)	
		Maghemite	Hematite
R15	0	9.5	4.7
R20	0	12.9	6.0
R37	0	8.5	4.3
R12	0.05 (Zn)	18.9	7.1
R11	0.08 (Zn)	13.0	6.6
R13	2.22 (Zn)	17.8	7.3
R16	5.20 (Zn)	20.5	9.0
R14	1.00 (Zn)	20.8	9.5
R17	0.09 (Cu)	15.9	6.6
R18	0.24 (Cu)	13.1	4.8
R21	0.10 (Co)	11.9	6.7
R22	0.37 (Co)	17.1	7.2
R23	0.20 (Mn)	13.1	8.3
R24	0.46 (Mn)	13.8	5.6
R25	0.89 (Mn)	12.5	4.3
R26	0.21 (Ni)	15.9	7.3
R27	0.48 (Ni)	14.7	5.2
R28	0.49 (Cr)	15.1	6.9
R29	0.96 (Cr)	13.6	5.0
R33	0.19 (Al)	17.1	6.5
R34	0.50 (Al)	17.6	6.9
R35	0.48 (V)	12.1	4.5
R36	0.97 (V)	13.5	4.1

¹ The hematites were formed by heating the maghemites at 650°C for 3 hr.

600°C and a weak endothermic peak at about 350°C. XRD analysis of specimens heated to these temperatures indicated that the exothermic peak represented the transformation of maghemite to hematite.

The shape of the maghemite-to-hematite transformation exotherm was variable. Some samples gave a very sharp exotherm, whereas others gave broadened or split exotherms. No quantitative relationship between exotherm breadth and surface area or trace element content was observed. Schmidt and Vermaas (1955) described splitting of magnetite-to-hematite exotherms for natural magnetites coarser than 50 μm.

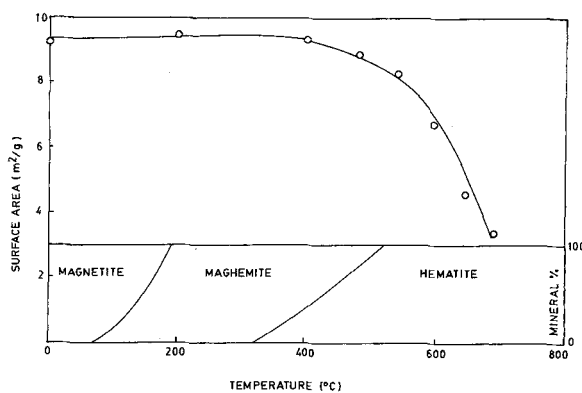


Figure 6. Effect of heating on surface area and mineralogy of iron oxides. Samples were prepared from pure magnetite heated at a particular temperature for 3 hr.

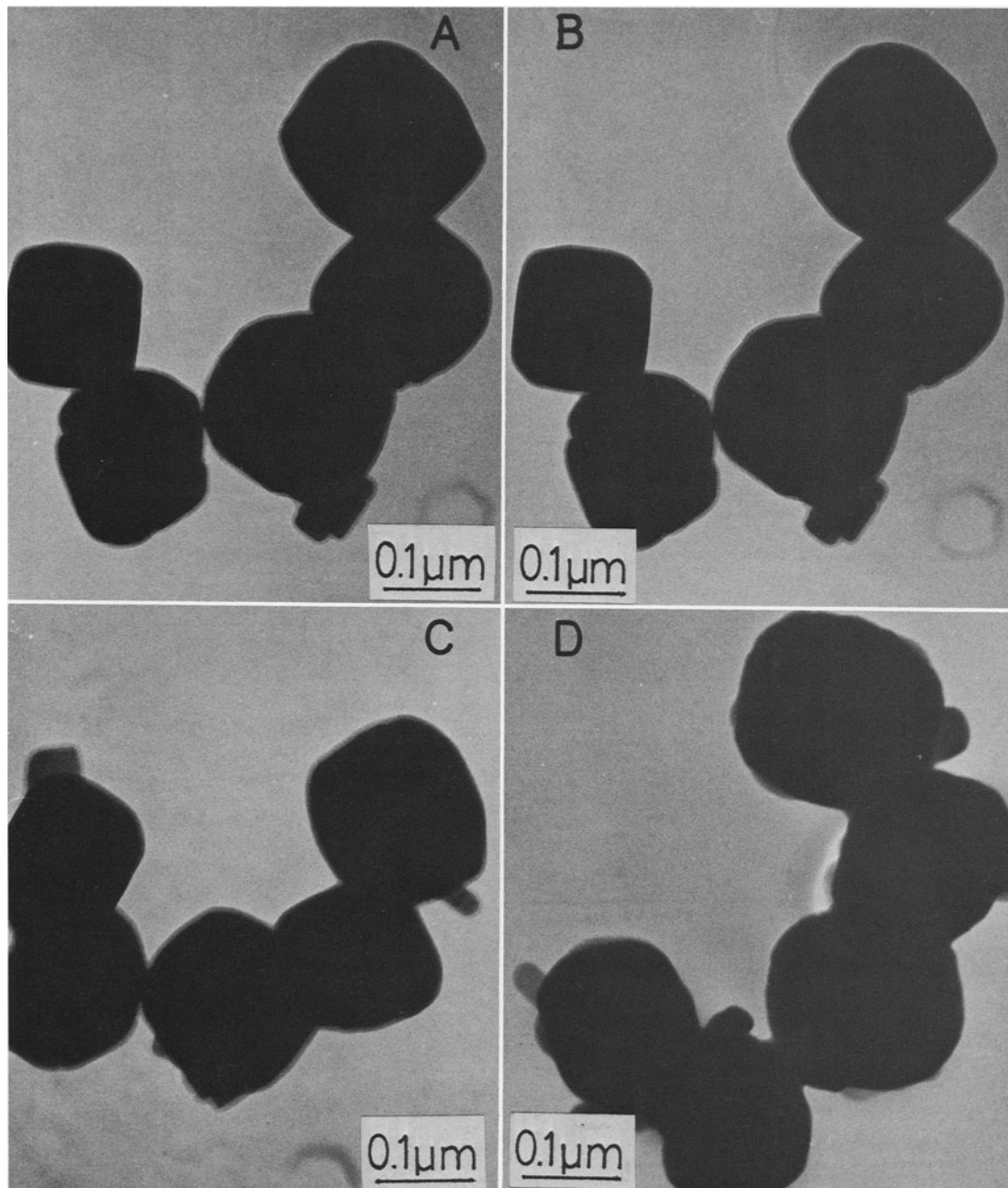


Figure 7. Transmission electron micrographs of particles heated to various temperatures. (A) Maghemite heated to 220°C, showing the same morphology as the parent magnetite; (B) maghemite heated to 500°C, showing no change in morphology; (C) maghemite heated to 550°C, showing protuberances; (D) maghemite heated to 650°C, showing sintering of particles.

The particle sizes of the present maghemites, however, were much smaller, and the splitting of the exotherm was not systematically related to the particle size of the specimens. The maghemite-to-hematite exotherm occurred between 540° and 650°C (Figure 4). For some samples the exact inversion temperature was difficult to determine due to the broad or split nature of the exothermic peaks. No systematic trend of inversion

temperature with increasing surface area or level of substitution was noted for any series of substituted maghemites, contrary to the observation of Farrell (1972), who reported a decrease in inversion temperature with increasing surface area. Despite the larger surface area of most substituted maghemites relative to pure maghemite, the presence of substituted elements increased the inversion temperature, consistent

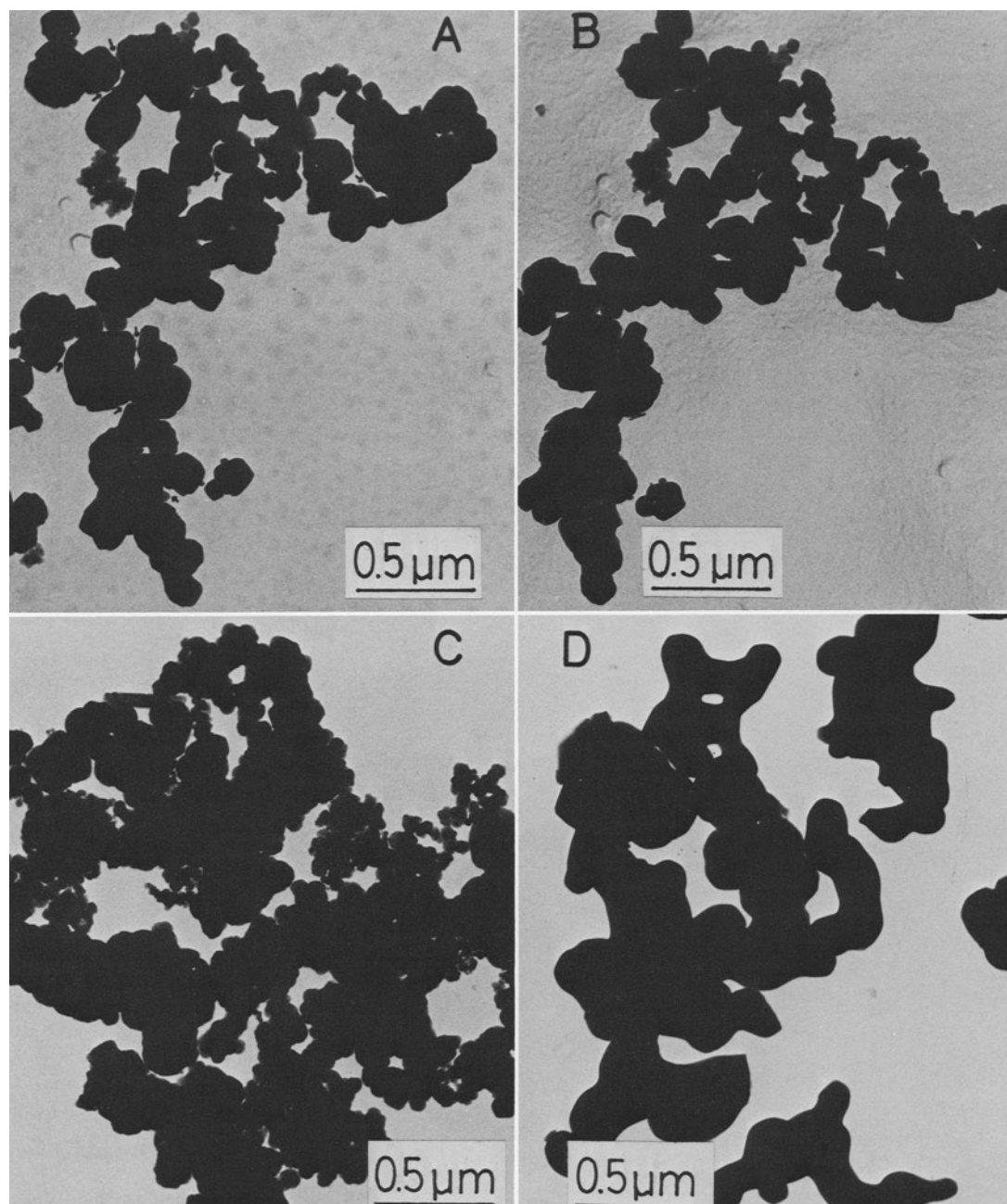


Figure 8. Transmission electron micrographs of maghemite and hematite. (A) Small arrows indicate pores enclosed between maghemite crystals; (B) hematite produced from the maghemite crystals shown in (A) by heating at 550°C for 3 hr. Note absence of pores that are shown in (A); (C) maghemite showing a range of particle size and shape; (D) hematite obtained by heating maghemite at 650°C for 3 hr, showing entirely different morphology than parent maghemite in (C).

with the slower transformation rates of substituted maghemites at 500°C.

All maghemites invariably showed a weak, diffuse endothermic peak at about 350°C (Figure 3). This peak is in the temperature range in which various oxyhydroxides (i.e., lepidocrocite, goethite, akaganeite) lose their structural water (Mackenzie, 1970). TEM and

XRD observations did not indicate the presence of such minerals in the samples examined in this study. Braun (1952) and David and Welch (1956) reported that small amounts of water are always present in synthetic maghemites. The presence of this combined water may be due to protons replacing Fe^{3+} in the structure leading to the formation of OH^- (David and Welch,

1956). The diffuse endothermic peak at about 350°C may represent the loss of this combined water. Thermogravimetric analysis of the present maghemites indicated the presence of about 1% water, which corresponds to about one proton per 12 Fe³⁺ ions in the maghemite structure.

Infrared spectra

The IR spectra of unsubstituted maghemite after varying degrees of alteration to hematite are shown in Figure 5. The IR spectra of maghemite and problems involved in assigning absorption bands to particular vibrations were discussed by Farrell (1972), who empirically assigned various bands to Fe–O stretching and deformation vibrations. The IR spectra of hematites were characterized by a sharp band at 480 cm⁻¹ and a broad asymmetric band at about 560 cm⁻¹, which are probably due to Fe–O stretching vibrations. Farrell also observed adsorption bands at 480 and 570 cm⁻¹ in hematites that he obtained by heating magnetites and maghemites.

The intensity of a particular maghemite or hematite absorption band could not be used for quantitative mineralogical analysis in this study due to overlapping of the bands. Qualitatively, the IR spectra of samples at intermediate stages of transformation resembled those of physical mixtures of maghemite and hematite. The substituted elements did not produce a shift in the position or intensity of various maghemite and hematite absorption bands.

Surface area

As shown by the data in Table 2, the surface area of maghemites was not systematically dependent on the nature or level of substitution. Transformation of maghemite to hematite at 650°C for 3 hr was accompanied by a decrease in surface area, i.e., an increase in the size of particles. Alteration to hematite at <500°C reduced the surface area only slightly (Figure 6). At temperatures >550°C, major reductions in surface area were noted. These observations are consistent with several reports concerning the effect of heat treatments on the particle size of iron oxides (Pritchard and Ormerod, 1976) and appear to be due to sintering of particles.

Transmission electron microscopy

TEMs of individual particles or aggregates taken at successive stages during the transformation of maghemite to hematite showed major changes in morphology (Figure 7). No changes in particle morphology were observed for heating temperatures <500°C, whereas particles heated at 550°C and 650°C showed an irregular growth of protuberances around crystal boundaries. Particles in contact with each other retained sharp boundaries after heating to 500°C, how-

ever, at higher temperatures (550° and 650°C) individual particles coalesced as a result of an increased area of contact between the particles. Pores between the particles diminished in size, and some of the pores completely disappeared as the region of contact between the particles enclosing a pore grew on heating (Figure 8). The overall effect of heating maghemite at 650°C for 3 hr was to produce larger hematite particles having an entirely different morphology of well-rounded, sub-spherical components joined into irregular aggregates.

The larger size of hematite particles relative to the initial maghemite crystals is consistent with a 60% decrease in surface area. This increase in particle size was due to sintering of particles. Sintering may be due to migration of vacancies in the structure (Kuczynski, 1972) away from the contact area (volume diffusion) or to surface migration of defects and ions (surface diffusion). Volume diffusion is operative above the Tamman temperature at ~650°C, whereas surface diffusion is operative at ~350°C. Sintering of hematite particles at 500°–650°C, as observed in the present study, therefore, appears to be due to surface diffusion rather than volume diffusion.

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