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NOTES

BOTRYOIDAL GOETHITE: A TRANSMISSION ELECTRON MICROSCOPE STUDY

Key Words—Goethite, Lattice fringes, Morphology, Silica, Transmission electron microscopy.

INTRODUCTION

Natural botryoidal goethites (α-FeOOH) usually contain various impurities, the most abundant of which are generally Al, Mn, Si, and C (Posnjak and Merwin, 1919). Previous studies (Norrish and Taylor, 1961; Thiel, 1963) have shown that Al can replace Fe, and the existence of the isostructural groutite (α-MnOOH) suggests that Mn^{3+} also replaces Fe in goethite. It is also well known that goethite can adsorb cations (e.g., Balistrieri and Murray, 1982) and anions (e.g., Parfitt *et al.*, 1975), and Russell *et al.* (1975) showed that CO_2 is strongly sorbed by goethite as CO_3^{2-} (and HCO_3^-) ions. When Schwertmann and Taylor (1972) carried out experiments to determine the influence of silica on the transformation of lepidocrocite to goethite they found that the Si taken up during goethite formation is not in reversible adsorption equilibrium with the Si in solution. This finding prompted them to suggest that Si is structurally incorporated into goethite during crystal growth.

Most botryoidal goethites appear homogeneous in the optical microscope, and their X-ray powder diffraction (XRD) traces generally show broadened peaks which are indicative of small grain size. Some natural goethites were therefore examined using high-resolution, transmission electron microscopy (HRTEM) to see if widespread defect arrays or other structural irregularities were present which could accommodate silicon- or carbon-bearing impurities and also to characterize the TEM microstructure of goethite for future studies of goethite formation.

SPECIMENS

Goethite specimens from Minnesota, South Australia, Spain, and Cornwall, United Kingdom, were investigated.

Morphology

In hand specimen the Minnesotan and South Australian goethites exhibit typical botryoidal morphologies, the Spanish goethite is structureless and slightly porous, and the Cornish goethite is made up of approximately euhedral, equant goethite grains with diameters of ~3 mm, which are interspersed with irregular inclusions of quartz, amounting to ~10% of the total volume.

Blocks of each goethite were mounted in epoxy, polished, and examined in reflected light. The Spanish and South Australian specimens exhibit areas which appear to be cross sections of spheres of needles interspersed with featureless areas (see Figure 1a). Figure 1b is a typical optical micrograph of the Minnesotan goethite. The pock marks are not by-products of the polishing process, but may be regions where goethite needles point directly out of the surface. Reflected light microscopy of the Cornish goethite confirmed the presence of euhedral grains, and transmitted light microscopy of thin section revealed that the grains are optically homogenous.

Chemistry

Table 1 lists electron microprobe analyses of the goethites and bulk-sample water analyses of all but the Cornish goethite. The analyses are averages of data collected from ~10 points. Careful monitoring of the composition over extended regions of goethite (~1 mm) showed that the element distribution is uniform at the scale of the electron excited area (~5 μm across). The impurity elements P, Si, Al, Mn, and Mg must be present in very small particles (~1 μm) or substituted in the goethite structures. The Cornwall goethite shows no elements other than iron in amounts above the detection limit of the energy dispersion microprobe. K. Norrish (C.S.I.R.O. Division of Soils, Glen Osmond, South Australia, personal communication, 1982) reported similarly low levels of impurity from a separate specimen from Cornwall.

X-ray powder diffraction (XRD)

Unit-cell parameters for the goethites were determined by least squares fit or d-spacings measured by Guiner X-ray diffraction photography with a Si internal standard using the lines 130, 021, 111, 121, 221, 151, 002 (Minnesotan), also 040, 140, 061 (South Australian, Spanish) plus 101, 211, 240,

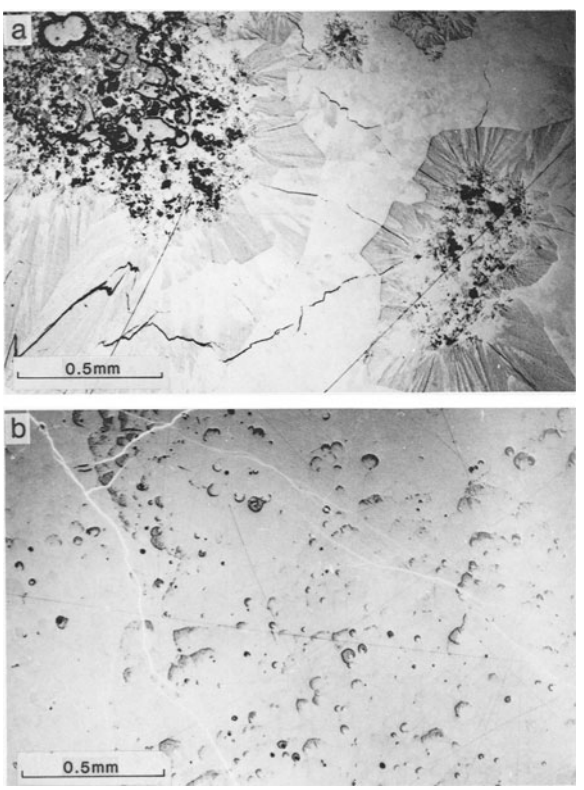

Figure 1. Reflected-light photomicrographs of polished blocks of goethite. (a) Area of the Spanish goethite (also typical of the South Australian goethite) showing cross-sections of spheres of needles separated by a featureless area. (b) Typical area of the Minnesotan goethite showing pock marks. The light veins are manganese rich.

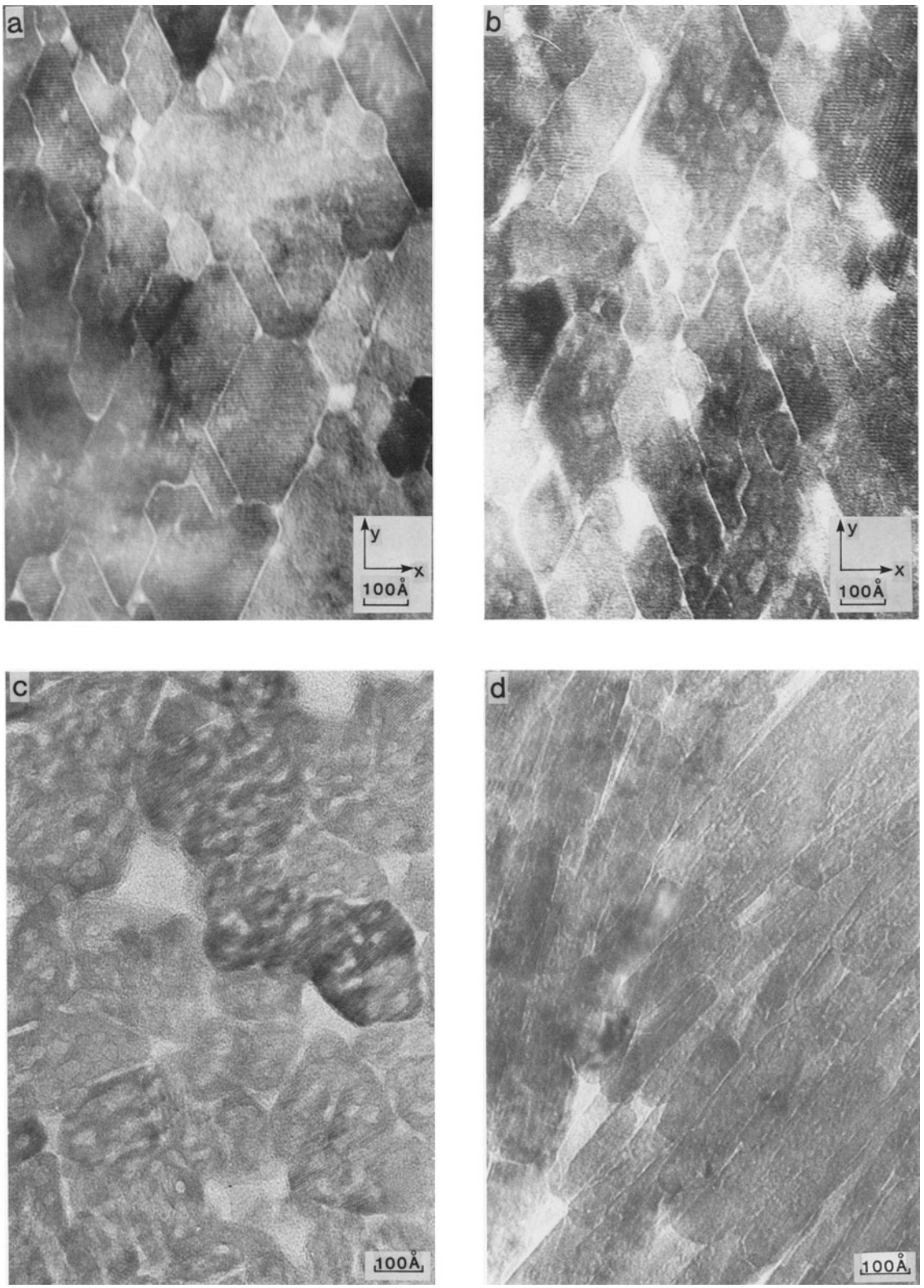

Figure 2. Transmission electron micrographs of typical areas of the (a) Spanish, (b) South Australian, and (c) Minnesotan goethites viewed parallel to z. (d) Micrograph of an area of the Minnesotan goethite viewed perpendicular to z.

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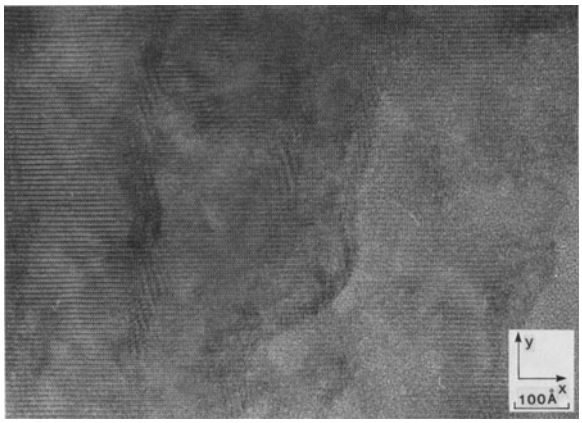

Figure 3. Transmission electron micrograph of a typical area of the Cornish goethite viewed parallel to *z*.

231, 112, 321 (Cornish). Crystallite size was estimated from the half-widths of the 130 and 140 reflections measured from diffractometer traces corrected for instrumental broadening by reference to Si metal. The corrected peak width at half-height (width of goethites minus width of Si) was converted to crystal dimensions using the Scherrer formula, following Schulz (1982) (Table 1).

HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY RESULTS AND DISCUSSION

Specimens for HRTEM were prepared from thin sections by ion-bombardment thinning and examined in a JEOL 100CX microscope operated 100 kV or a JEOL 200CX operated at 200 kV. The goethites from Spain, South Australia, and Minnesota viewed down *z* commonly show microstructures similar in shape and size to those shown in Figure 2a, 2b, and 2c respectively. Some of each of the goethites, however, consist of grains (discrete crystals) with cross-sectional areas 3 or 4 times those shown here. The average diameter of the small grains (as shown in Figure 2) is ~300 Å in all three goethites.

Individual grains in the Spanish and South Australian goethites are sharply euhedral, they are separated from neighboring grains by a gap, and they usually have the same orientations as adjacent needles. By contrast, grains in the Minnesotan goethite are almost anhedral; they commonly join directly to adjacent grains without a gap and are more randomly oriented around *z* with respect to their neighbors.

All of these fibrous goethites look similar when viewed perpendicular to *z*. Figure 2d shows a typical area of the Minnesotan goethite. The average width of the smallest grains is 300 Å. The grains in Figure 2d may be inclined to the plane of the foil; hence their maximum dimension may be truncated. Their length, however, is usually at least 5 times their width. Thus, it is reasonable that the goethites from Spain, South Australia, and Minnesota are composed of fine, needle-like grains with diameters as small as ~300 Å. The presence of such fine needles in these three goethites accounts for the observed XRD line broadening in diffractometer profiles.

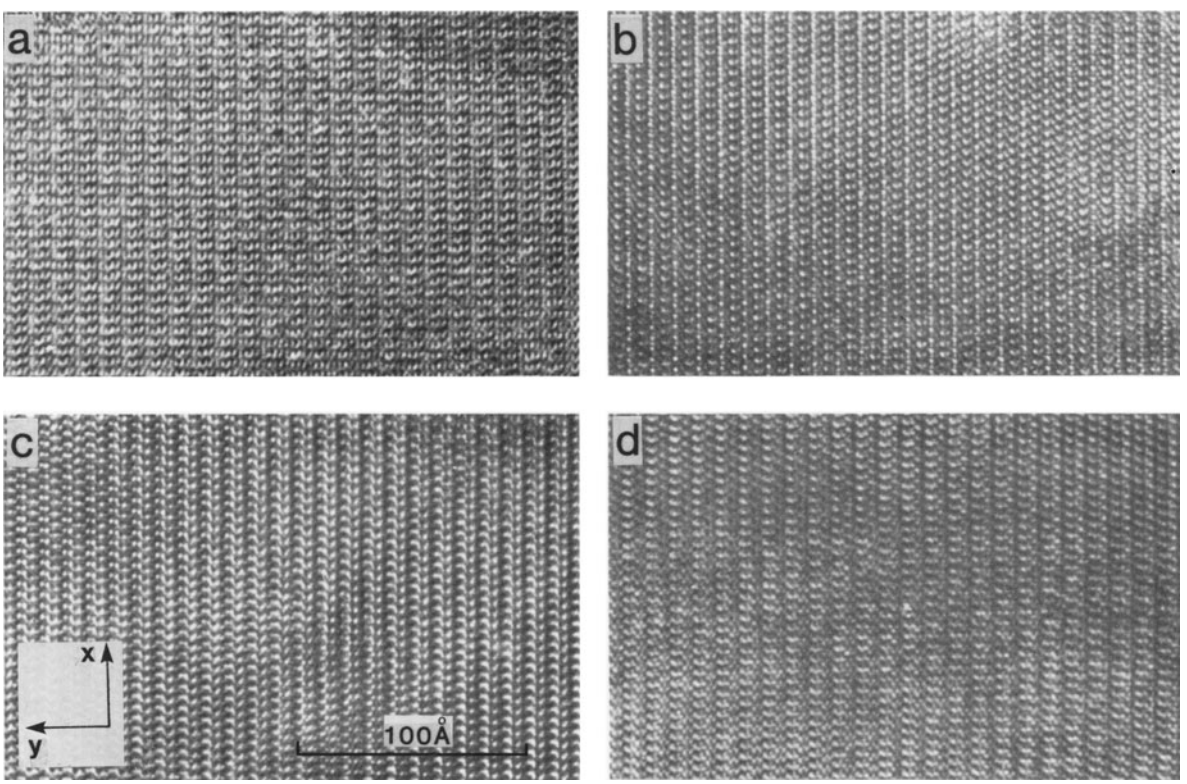

Figure 4. Transmission electron micrographs of the Cornish goethite. (a) and (c) show two areas of different thickness from the same specimen at the same focus. (b) and (d) are micrographs of the same area at two slightly different values of focus.

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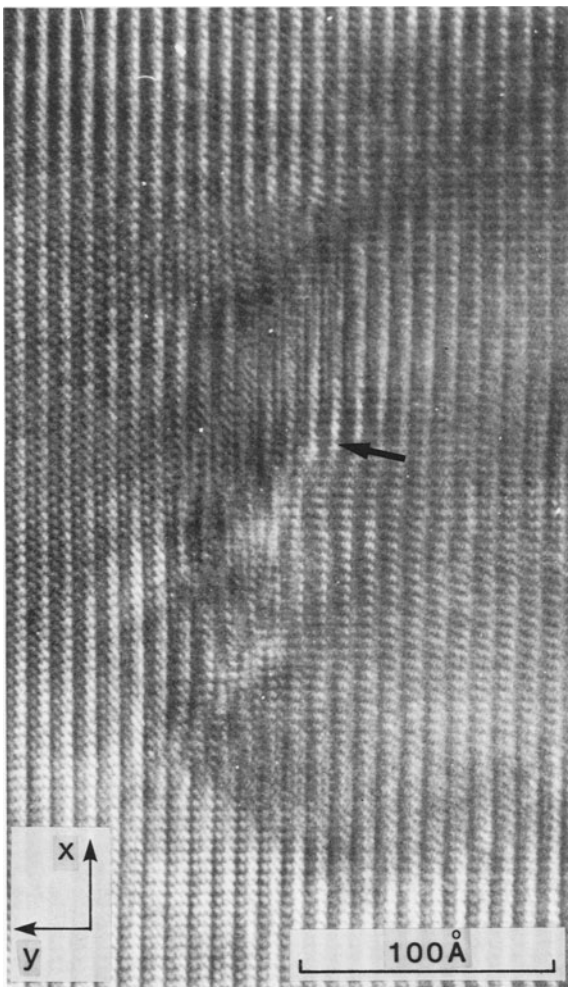

Figure 5. Transmission electron micrograph of a "dislocation" in the Cornish goethite. Arrow indicates terminating lattice fringe.

It is possible that the silica found in these three botryoidal goethite samples might be adsorbed to the surface of individual needle-like crystals. The surface : volume ratio shows good general agreement between the amount of silica observed (~2%) and the calculated amount predicted as a monolayer between the needles (~3%). Cornwall goethite does not have fibrous morphology and is free of silica.

In the electron microscope individual needles in the Spanish, South Australian, and Minnesotan goethites exhibit mottled contrast. This variation is not a product of the ion-beam thinning preparation process as it was also observed in manually ground powder specimens of the same goethites. Paler areas generally occur near the centers of the needles. Lattice fringes generally either continue across a pale area, or are discontinuous and aligned on opposite sides of a pale area.

Some insight into the nature of the mottling in the Spanish, South Australian, and Minnesotan goethites was attained by HRTEM investigation of single grains of the Cornish goethite. Microstructure typical of that in single grains of the Cornish goethite is shown in Figure 3. "Fingerprints" are common in specimens in all orientations, generally in bands parallel to the edge of the specimen. Electron images of goethite vary immensely with thickness and focus (see Figure 4). Calculation of electron images of goethite (made using the SHRLI programs) showed that at some thickness, small changes in thickness could produce large changes in the image and that the differences in images seen on either side of a fingerprint band could result from thickness variation. Thus, fingerprint bands likely delineate areas of slightly different thickness where small changes in thickness cause large changes in image.

In some areas of the Cornish goethite, contrast variations occur where there is no change in image. These variations could not be caused by composition changes as the impurity level of the Cornwall goethite is extremely low (see Table 1). The mottled contrast in the Cornish, Spanish, South Australian, and Minnesotan goethites could be the result of thickness variation; however, if this is the case, there is no obvious reason why the paler (presumably thinner) areas of the three latter goethites should generally occur in the centers of needles.

Figure 5 shows what is thought to be an edge dislocation in the Cornwall goethite. It is possible that the mottled contrast in the Spanish, South Australian, and Minnesotan goethites arises from strain initiated by dislocations and/or thickness variation due to preferential loss of material in the high strain areas around dislocations.

Table 1. Specimen properties.

	Spain	Beltana, South Australia	Biwabik, Minnesota	Cornwall, United Kingdom
a (Å)	4.6134 (18)	4.6110 (49)	4.6119 (09)	4.5977 (16)
b (Å)	9.9619 (16)	9.9535 (22)	9.9608 (14)	9.9561 (34)
c (Å)	3.0190 (05)	3.0196 (06)	3.0213 (02)	3.0211 (11)
Crystallite size[1] (Å)	590	650	380	large
P_2O_5	0.46	0.24	1.27	0.00
SiO_2	2.68	1.57	1.34	0.00
Al_2O_3	0.23	0.28	0.00	0.00
Fe_2O_3	86.08	85.28	85.64	88.76
Mn_2O_3	0.18	0.73	0.30	0.00
MgO	0.00	0.31	0.18	0.00
Total	89.63	88.41	88.73	88.76
Water[2]	10.70	11.10	10.79	
Adjusted total	100.33	99.51	99.52	

[1] Average diameter in *x*-*y* plane from XRD half-width.
[2] Measured on bulk samples.

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It is well known that goethite dehydrates to hematite (Fe_2O_3) when it is heated (e.g., Smith and Kidd, 1949), and akagaenite (α-FeOOH) has been shown to undergo structural changes during HRTEM exmination. Thus, it was thought that goethite would suffer radiation damage in the electron microscope; but no appreciable damage was detected when the goethites were exposed to the electron beam for long periods (~20 min).

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