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NOTES

GOETHITE MORPHOLOGIES INVESTIGATED VIA X-RAY DIFFRACTION OF ORIENTED SAMPLES

ROBERT G. FORD,† PAUL M. BERTSCH AND JOHN C. SEAMAN

University of Georgia, Advanced Analytical Center for Environmental Sciences, Savannah River Ecology Laboratory, Aiken, South Carolina 29802

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INTRODUCTION

Synthetic and natural goethites display a variety of particle morphologies that are dependent on solution conditions during formation (Schwertmann 1990). Factors influencing goethite morphology include pH and the presence or absence of specifically adsorbing ions in solution. Particle morphology can affect goethite dissolution behavior and will govern the distribution of coordination sites available on the particle surface (Cornell et al. 1974; Colombo et al. 1994). Morphological information can be obtained via electron microscopic imaging (Schulze and Schwertmann 1984) or profile analysis of X-ray diffraction (XRD) patterns (Koch et al. 1986). These methods are essential for determination of absolute particle dimensions, but they may require a significant time commitment or advanced level of analysis. In order to facilitate rapid preliminary comparison of synthetic goethite samples, we have investigated the use of powder XRD to derive similar qualitative information via the influence of preferred orientation during sample preparation.

Samples for XRD analysis were prepared according to the procedure outlined by Drever (1973) with some modifications. This and similar methods are commonly used to prepare clay powder samples displaying enhanced relative intensities in basal reflections (Brown and Brindley 1980). Filtering clay minerals from suspension leads to the formation of films of particles preferentially oriented with their basal planes parallel to the plane of the support. This preparation results in a sample with a biased distribution of crystallographic planes (in this case $00l$) coincident with the diffracting plane of the XRD instrument. This is manifested in the diffraction pattern as enhanced and suppressed intensities for basal and nonbasal reflections, respectively. In principle, the tendency towards preferred orientation could be used for preliminary comparison of any suite of minerals displaying systematic morphological differences due to the conditions of formation.

Several authors have noted the effects of preferred orientation on XRD intensities in patterns of goethites synthesized under various conditions even after attempts to achieve a random distribution (Landa and Gast 1973; Cornell et al. 1974; Brown 1980; Schulze and Schwertmann 1984; Schwertmann et al. 1985). The effect most often observed is a change in the relative intensity of the (110) and (111) Bragg reflections compared to that predicted for a random sample (Schulze and Schwertmann 1984; Schwertmann et al. 1985). In addition, preferred orientation in some natural goethites is expected based on published electron micrographic images (Rozenson et al. 1982; Schwertmann 1990). In an attempt to derive the maximum amount of information from limited sample quantities, we have employed a method for powder XRD analysis which takes advantage of the preferred orientation phenomenon.

MATERIALS AND METHODS

Prior to filtering onto a 25-mm, 0.2-μm membrane filter (Gelman Suprapore 200, polysulfone), 5–10 mL of a goethite slurry was dispersed in a sonication bath for 1 min at 43 kHz. The slurry concentration was adjusted prior to filtering to yield about 3–5 mg of goethite on the filter (0.15–0.25 mg cm^{-2}). Corundum (25% w/w) from Baikowski International in Charlotte, North Carolina, and glass wool (2 mg) prepared by the procedure of Rich (1975) were included in the slurry as an internal peak position standard and a film binder, respectively. Corundum and processed glass wool

† Present Address: University of Deleware, Department of Plant and Soil Sciences, Newark, Delaware 19717.

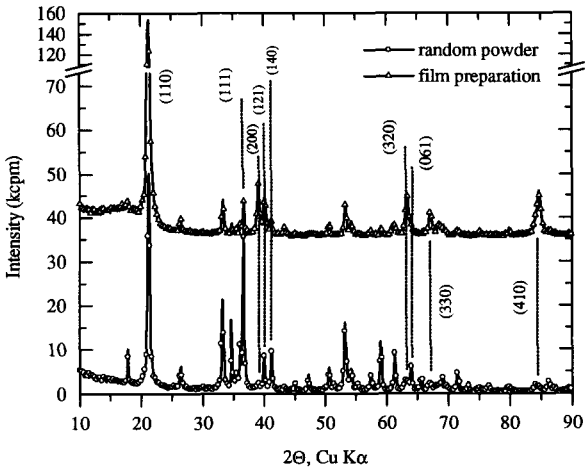

Figure 1. Whole XRD pattern comparison for a synthetic goethite prepared to give a random particle orientation and a preferentially oriented film using the filter method. Select Bragg reflections are indicated with *(hkl)* indices.

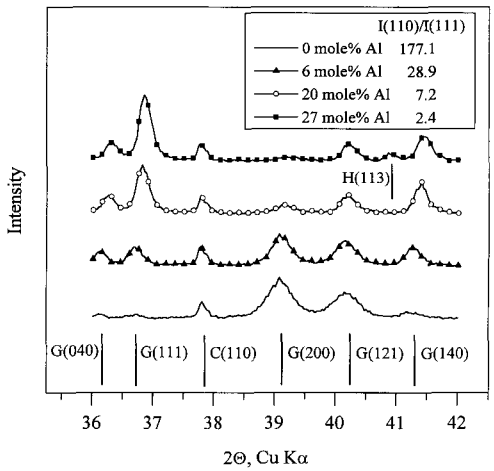

Figure 2. Partial diffraction patterns for goethites synthesized in the presence of increasing amounts of aluminum. Bragg reflections for the minerals present are indicated with *(hkl)* indices; G = goethite, C = corundum and H = hematite. The legend includes intensity ratios calculated for the (110) and (111) goethite reflections.

were added from 0.6 g L^{-1} and 1.25 g L^{-1} stock suspensions. Volumetric additions were calibrated by weight after drying at 110 °C. The addition of glass wool was necessary to ensure film integrity after room temperature drying. Films were left attached to the membrane support for further analysis. The films were then characterized by XRD on a Scintag XDS 2000 diffractometer equipped with a vertical theta-theta goniometer employing Cu*K*α radiation and a solid state intrinsic germanium detector. Membrane-supported films were attached to circular glass cover slips by gluing along the outer edge. The rigid sample was then supported over petroleum jelly in a 25-mm circular cavity sample support provided by Scintag. Most samples were scanned over 10–70 °2θ at a rate of 0.5 °2θ min^{-1} and a 0.03 degree step size (3.6 s/step).

RESULTS AND DISCUSSION

We first examined a synthetic goethite prepared from an Fe(III) system which resulted in acicular crystals elongated along (00*l*) (Schwertmann and Cornell 1991). Large differences in diffraction intensities between samples prepared either as a nearly-random or as an oriented mount were discernible (Figure 1). Most notable are the enhanced intensities for (*hk*0) reflections in the oriented sample. For the random mount, the ratio of integrated intensities (mixed Gaussian–Lorentzian profile) for (110) and (111) is 1.9 while for the oriented mount this ratio is 24. Both values differ from that predicted for a pattern produced by a theoretical random particle distribution (1.25, Brown 1980), and suggest that even careful loading procedures are insufficient to achieve a truly random distribution of particle orientations. However, duplicate preparations of a sample using our method resulted in a mean and standard error of 11.8 ± 2.8 in measured *I*(110)/*I*(111), and we feel that additional refinement of the procedure could decrease this variability.

Schwertmann and Cornell (1991) and Cornell et al. (1989) have observed that the presence of specifically adsorbing ions during the synthesis and aging of goethite can significantly alter its growth morphology. Knowledge of the influence on growth morphology is important for interpreting the environmental conditions under which goethites have formed in engineered and natural systems. One important example is shown for goethites synthesized in the presence of various levels of coprecipitated Al (Figure 2). Partial diffraction patterns are shown for samples prepared using the oriented film method along with a list of the "oriented" intensity ratios for the (110) and (111) Bragg reflections (inset, Figure 2).

Several observations point to systematic differences in the ability to achieve strongly oriented samples for this series of goethites. First, there is a systematic variation in the intensities of the (200), (121) and (140) Bragg reflections as a function of Al loading. The relative intensities of these reflections for the 27 mol% Al goethite is more typical of a population of randomly oriented particles (compare to Figure 1). Secondly, the *I*(110)/*I*(111) ratios for these samples (inset, Figure 2) are consistent with the transition from a strongly (0 mol% Al) to a weakly (27 mol% Al) orienting goethite. Finally, near extinction of the (111) Bragg reflection for the strongly oriented 0 mol% Al goethite is due to misorientation of this crystallographic plane with respect to the instrumental plane of diffraction. These results are consistent with morphological differences observed for these samples via scanning electron microscopy (SEM) in Figure 3. Goethite particles

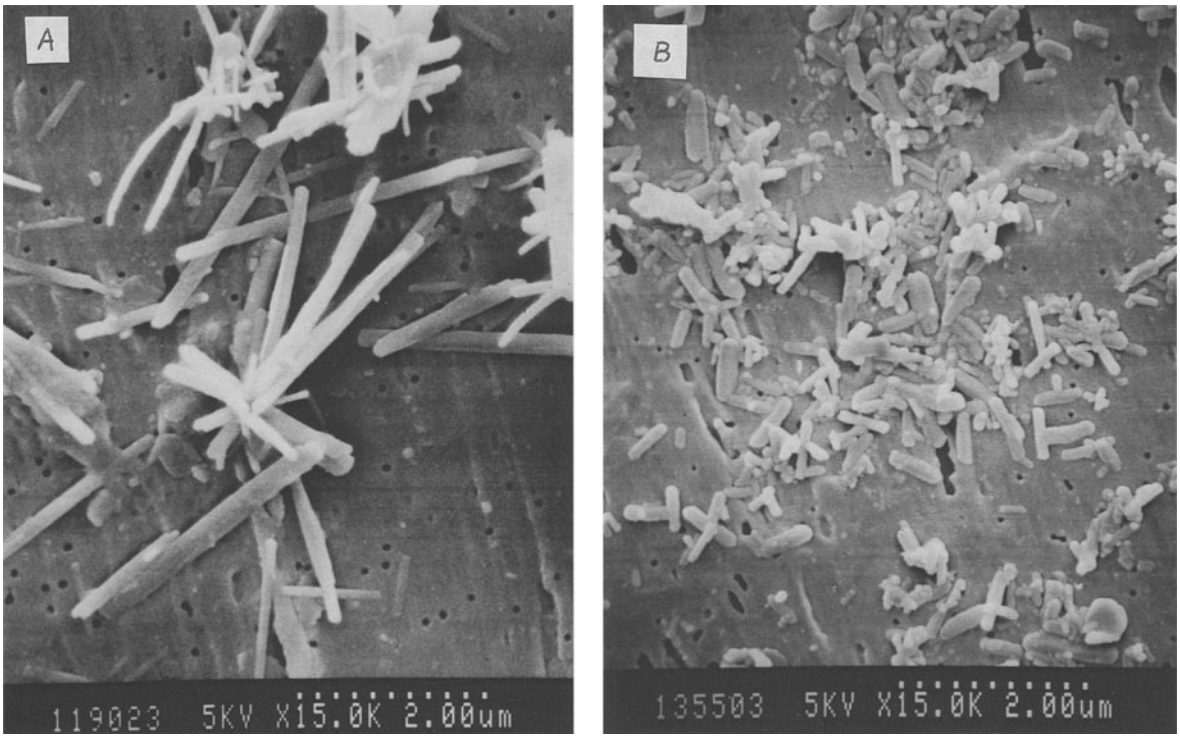

Figure 3. SEM photomicrographs of the A) 0 and B) 27 mol% Al goethites deposited on a 0.1 μm pore size polycarbonate filter (<0.5 μg cm $^{-2}$) displaying the difference in particle morphology induced by Al adsorption during particle growth.

produced in the presence of high Al concentrations are more unidimensional and do not orient well using this procedure.

Similar to other work (Sugimoto et al. 1993), this method of sample preparation is quite simple and does not require specialized equipment. It clearly demonstrated morphological changes induced by variable synthesis conditions for synthetic goethites. Systematic changes in integrated intensity distributions were primarily related to particle orientation relative to the instrumental diffracting plane, thus the need to distinguish particle size- and disorder-induced broadening for morphological determinations via profile analysis is averted (Delhez et al. 1988). While the method appears suitable for preliminary characterization of synthetic mineral preparations, it may prove unreliable for natural samples where physical isolation of the mineral of interest may be required to achieve strong orientation effects.

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REFERENCES

Brown G. 1980. Associated minerals. In: Brindley GW, Brown G, editors. Crystal structures of clay minerals and their X-ray identification. London: Mineral Soc. p 361–408.

Brown G, Brindley GW. 1980. X-ray diffraction procedures for clay mineral identification. In: Brindley GW, Brown G, editors. Crystal structures of clay minerals and their X-ray identification. London: Mineral Soc. p 305–359.

Colombo C, Barron V, Torrent J. 1994. Phosphate adsorption and desorption in relation to morphology and crystal properties of synthetic hematites. Geochim Cosmochim Acta 58:1261–1269.

Cornell RM, Giovanoli R, Schneider W. 1989. Review of the hydrolysis of iron(III) and the crystallization of amorphous iron(III) hydroxide hydrate. J Chem Tech Biotechnol 46:115–134.

Cornell RM, Posner RM, Quirk JP. 1974. Crystal morphology and the dissolution of goethite. J Inorg Nucl Chem 36: 1937–1946.

Delhez R, de Keijser TH, Mittemeijer EJ, Langford JI. 1988. Size and strain parameters from peak profiles: Sense and nonsense. Aust J Phys 41:213–227.

Drever JI. 1973. The preparation of oriented clay mineral specimens for X-ray diffraction analysis by a filter–membrane peel technique. Am Mineral 58:553–554.

Koch CJW, Madsen MB, Morup S, Christiansen G, Gerward L, Villadsen J. 1986. Effect of heating on microcrystalline synthetic goethite. Clays Clay Miner 34:17–24.

Landa ER, Gast RG. 1973. Evaluation of crystallinity in hydrated ferric oxides. Clays Clay Miner 21:121–130.

Rich CI. 1975. Curling inhibition of clays mounted on slides for X-ray diffraction analysis. Soil Sci Soc Am Proc 33: 155–156.

Rozenson I, Spiro B, Zak I. 1982. Transformation of iron-bearing kaolinite to iron-free kaolinite, goethite, and hematite. Clays Clay Miner 30:207–214.

Schulze DG, Schwertmann U. 1984. The influence of aluminum on iron oxides: X. Properties of Al-substituted goethites. Clay Miner 19:521–539.

Schwertmann U. 1990. Some properties of soil and synthetic iron oxides. In: de Boot MF, Hayes MHB, Herbillon A, editors. Soil colloids and their associations in aggregates. New York: Plenum Pr. p 57–103.

Schwertmann U, Cambier P, Murad E. 1985. Properties of goethites of varying crystallinity. Clays Clay Miner 33: 369–378.

Schwertmann U, Cornell RM. 1991. Iron oxides in the laboratory: Preparation and characterization. New York: VCH. 137 p.

Sugimoto T, Muramatsu A, Sakata K, Shindo D. 1993. Characterization of hematite particles of different shapes. J Colloid Interface Sci 158:420–428.

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