

POSSIBLE CONFUSION BETWEEN SO-CALLED FERRIHYDRITES AND HISINGERITES

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(Received 21 August 1991; revised 31 January 1992)

ABSTRACT: The term ferrihydrite, originally defined as a poorly ordered hydrous ferric oxide exhibiting five or more distinctive X-ray diffraction maxima, has come to be extended to include species that exhibit only 4, 3 or 2 of these maxima. It is pointed out here that hisingerites may exhibit a similar 2-line diffraction pattern. The laboratory synthesis of hisingerites show that they can form under soil conditions. Acid oxalate buffer of pH 3, a reagent considered a fairly specific solvent for ferrihydrite, extracts the iron content of these synthetic hisingerites quantitatively.

Ferrihydrite, as defined by the International Mineralogical Association (Fleischer *et al.*, 1975) is a hydrous ferric oxide with a characteristic X-ray diffraction (XRD) pattern of five broad diffraction maxima in the range 0.14 to 0.26 nm. Material of this type has been synthesized in the laboratory (Towe & Bradley, 1967), and identified in nature in weathering crusts on basic rocks (Jackson & Keller, 1970), as ore alteration products (Chukhrov *et al.*, 1973), as stream deposits (Carlson & Schwertmann, 1981) and in soils (Schwertmann *et al.*, 1982). Some better-ordered synthetic preparations show further resolution of two of the broad diffraction peaks to give six or seven diffraction maxima (Brown, 1980).

The term ferrihydrite, however, is widely used as a name for more poorly-ordered hydrous ferric oxides that exhibit only two to four of the characteristic diffraction maxima of ferrihydrite (e.g. Schwertmann & Taylor, 1989). Indeed, the originators of the name ferrihydrite probably meant it to apply to three-, four- and five-line species, as they proposed a different name, protoferrihydrite, for the two-line species (Chukhrov *et al.*, 1973). Only diffraction patterns with five or more maxima show a peak near 0.20 nm which is distinctive for ferrihydrite, but the use of the term ferrihydrite for species with four or less diffraction maxima may be justified because such materials often form under similar conditions to true ferrihydrites, and their diffraction envelopes are broadly similar to ferrihydrite. Thus, materials with from seven to two diffraction maxima can, possibly, be regarded as forming a sequence of decreasing degree of order in a single mineral species.

This use of the terms ferrihydrite or protoferrihydrite would be invalid if it were found that ferruginous materials with a chemical structure different from ferrihydrite gave similar diffraction patterns. In fact, Whelan & Goldich (1961) have listed a specimen of hisingerite which gave only a two-line diffraction pattern, with broad maxima at 0.25 and 0.15 nm, in the position of those of 2-line ferrihydrite. Hisingerites are poorly-ordered hydrous ferric silicates which are generally considered to incorporate nontronite-like layer-silicate structures. Their diffraction patterns range from examples which show weakly most of the *hk* diffraction features of nontronite, and even a weakly developed basal spacing around

1.6 nm (Kohyama & Sudo, 1975), to specimens showing only two or three diffraction maxima. A 3-line hisingerite is, however, distinct from a 3-line ferrihydrite, as the hisingerite exhibits an (02) *hk* diffraction feature at 0.45 nm (Whelan & Goldich, 1961), which is absent from 3-line ferrihydrite.

Parfitt & Childs (1988) have proposed that an acceptable estimate of the amounts of ferrihydrite in soils might be made from the amounts of Fe extracted by acid ammonium oxalate, pH 3, provided magnetite, maghemite and lepidocrocite, which are partially soluble in the reagent, are known to be absent. Here again confusion can arise between ferrihydrite and hisingerite, as the author has found that the Fe of synthetic hisingerites is soluble in the acid oxalate buffer. Farmer *et al.* (1991) prepared materials of this type by adjusting solutions containing 1.0 mM Fe(II) and 1.4 mM Si(OH)₄ to pH 8, and allowing them to oxidize slowly with restricted access to air. A precipitate digested at 89°C had an Si/Fe ratio of 0.80, and gave an infrared (IR) spectrum (Fig. 1) which showed an undoubted nontronite-like layer structure. Its XRD pattern (Fig. 2) showed a weak broad basal reflection at 1.60 nm, *hk* reflections at 0.460, 0.260, 0.173, 0.154 and 0.132 nm, and still broader features around 0.31 and 0.23 nm. Both its IR absorption and XRD patterns are close to those reported for an exceptionally well ordered hisingerite by Kohyama & Sudo (1975). A precipitate prepared at 23°C had an Si:Fe ratio of 0.72, and gave a similar but more featureless IR absorption pattern (Fig. 1), from which Farmer *et al.* (1991) concluded that layer-silicate formation had been initiated even at 23°C. A re-examination of its XRD pattern (Fig. 2) showed no basal reflections, a very broad band at 0.32 nm, and sharper *hk* reflections at 0.260 and 0.152 nm; the last two are close to those ascribed to 2-line ferrihydrite. Both these products were deferrated with 0.2 M oxalate buffer, pH 3, leaving colourless siliceous residues. The 23°C product was deferrated in only 10 min, whereas the 89°C product took 3 h for complete deferration, although much of the Fe was dissolved in 1 h. The recommended treatment time for ferrihydrite dissolution is 4 h (Parfitt, 1989).

The conditions of formation of the 23°C product could well be reproduced in intermittently water-logged calcareous soils. If present, the solubility of its Fe content in pH 3 oxalate, associated with the loss of XRD peaks at 0.26 and 0.15 nm, could well lead to the mistaken conclusion that a 2-line ferrihydrite is present. Its IR spectrum is close to that shown for a so-called synthetic ferrihydrite with a 0.75 Si/Fe molar ratio (Vampati & Loeppert, 1989) and is difficult to distinguish from those of natural ferric oxides incorporating polymerized silicate species which have been named as 2-line ferrihydrites (Henmi *et al.*, 1980).

Can a distinction be made between a 2-line ferrihydrite and 2-line hisingerite? Certainly natural hisingerites have higher Si contents than most natural materials classified as ferrihydrites. Fifteen of 16 analyses of hisingerites listed by Brigatti (1982) give molar ratios of Si/(Fe + Al + Mg) in the range 0.86–1.19 (mean 1.04; the exception gives a 1.41 ratio). This ratio for reported natural ferrihydrites does not exceed 0.46 (Childs *et al.*, 1982), although Henmi *et al.* (1980) described ochreous stream deposits which they regarded as intermediate ferrihydrite-hisingerite species with Si/(Fe + Al + Mg) ratios of 0.47 and 0.72. It might, therefore, be reasonable to limit the term hisingerite to species with molar ratios of Si/(Si + Al + Mg + Mn) greater than some value, possibly 0.5. This criterion could, however, only be applied to fairly pure hydrous ferric silicates. It could not be used to define the origin of oxalate-soluble Fe in soils and sediments, as the polymerized silicate sheets of hisingerites are not dissolved. Vampati & Loeppert (1989) named as ferrihydrites their range of synthetic ferric silicate precipitates with Si/Fe ratios up to 1.0, all of which

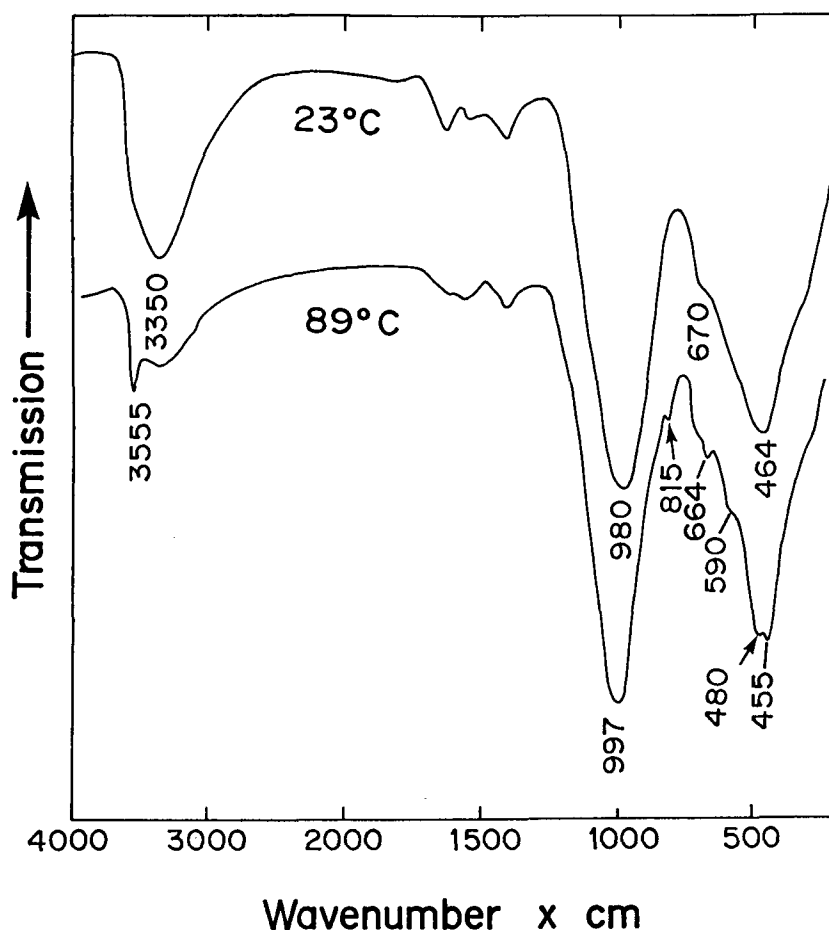


FIG. 1. IR spectra of ferric silicate precipitates from solutions originally containing 1 mM FeCl_2 and 1.4 mM $\text{Si}(\text{OH})_4$ incubated in the presence of CaCO_3 with restricted access to air for 8 weeks at 89°C and for 12 weeks at 23°C (systems 6040 of Farmer *et al.*, 1991). The residual uncombined $\text{Si}(\text{OH})_4$ in solution was 0.67 mM at 23°C, and 0.64 mM at 89°C. Calculated molar Si/Fe ratios in the precipitates were 0.72 (23°C) and 0.80 (89°C).

exhibited only two diffraction maxima at 0.297 and 0.150 nm for $\text{Si/Fe} > 0.1$. This nomenclature cannot be justified from the present evidence.

As yet, there are too few published XRD patterns for hisingerites to know if the patterns of 2-line hisingerites differ significantly from so-called 2-line ferrihydrites. The XRD traces in Fig. 2 certainly show a more pronounced feature at 0.31 nm than is present in published XRD traces of ferrihydrites (e.g. Carlson & Schwertmann, 1981). But this is not a pronounced feature in the 3-line diffraction trace shown for hisingerite by Eggleton (1988).

Infrared absorption patterns also do not allow a distinction to be made between hisingerites and some ferrihydrites. Naturally occurring ferric oxide precipitates named as ferrihydrites show a range of absorption maxima due to Si–O stretching from 930 to 1000 cm^{-1} (Carlson & Schwertmann, 1981; Childs *et al.*, 1982), where the lowest frequencies are probably due to isolated orthosilicate species. Hisingerites have been found

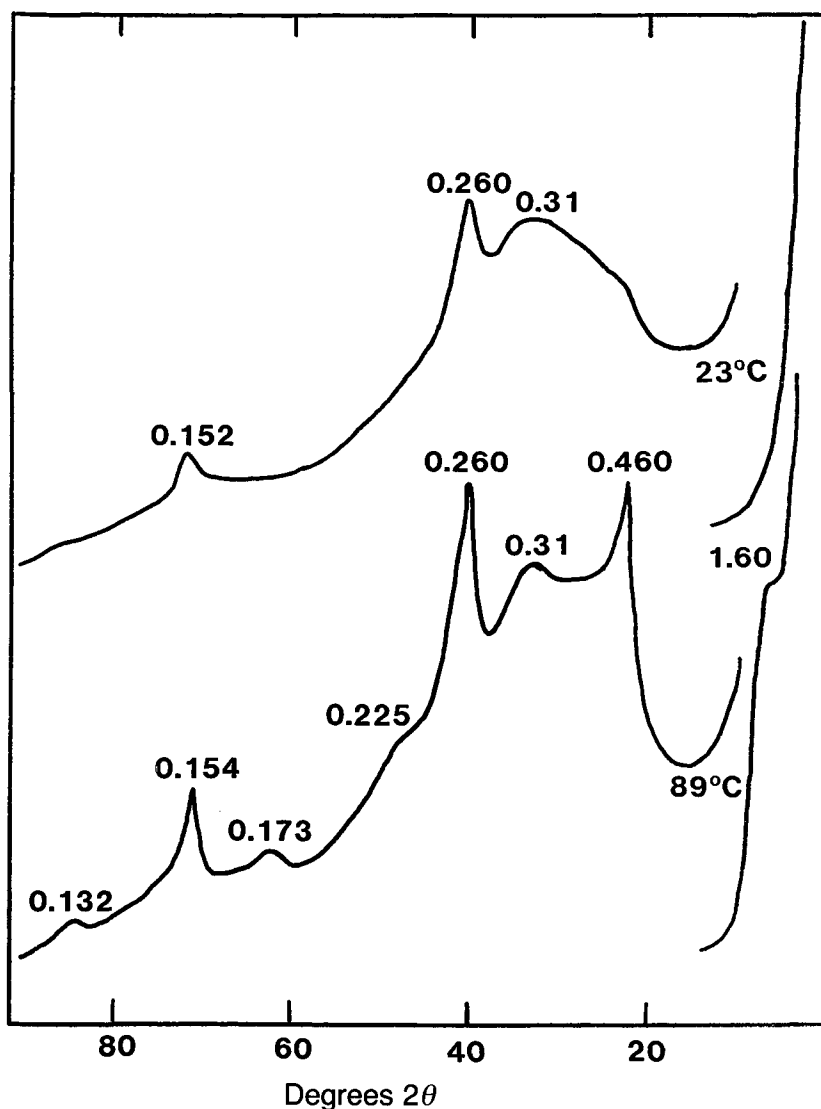


Fig. 2. XRD traces for the ferric silicate precipitates identified in Fig. 1. Samples were deposited from water dispersions on to glass slides, and examined with a Philips PW1130/90 2 kW X-ray diffractometer using Co- $K\alpha$ radiation. Peak spacings in nm.

to absorb around $1017\text{--}1029\text{ cm}^{-1}$ (Kohyama & Sudo, 1975; Shayan, 1984), but could show the whole range characteristic of nontronites ($1000\text{--}1020\text{ cm}^{-1}$, Goodman *et al.*, 1976), and apparently lower frequencies (980 cm^{-1}) for poorly-ordered species such as the 23°C product giving the spectrum in Fig. 1. Even authentic 5-line ferrihydrite specimens can exhibit Si-O stretching frequencies as high ($980\text{--}985\text{ cm}^{-1}$, Carlson & Schwertmann, 1981) as did the synthetic 23°C product. The IR spectra of hisingerites can, however, provide positive evidence for a nontronite-like layer structure. Probably particle morphology, as seen by high-resolution electron microscopy, can provide the clearest distinction between

hisingerites and ferrihydrites. Hisingerites show evidence of layer structures and fibres (Kohyama & Sudo, 1975; Shayan, 1984), whereas ferrihydrites consist of spheroidal particles, 3–7 nm in diameter with no platy or fibrous features (Schwertmann & Taylor, 1989). Even hisingerite as poorly-ordered as the synthetic 23°C preparation of Farmer *et al.* (1991) shows a crumpled sheet morphology (observation of F. Elsass, INRA, Versailles).

It will be seen from the above discussion that some features of poorly-ordered hisingerites can be taken as confirmation of their classification in this category: e.g. the presence of a fibrous or layer morphology and an IR spectrum similar to nontronite. On the other hand, there is as yet no structural evidence that justifies the naming of ferric oxides with a 2-line diffraction pattern as ferrihydrites, and it seems advisable that the term 2-line ferrihydrite be replaced by a less specific term such as “amorphous ferric oxide”. Use of the term “ferrihydrite” as a group name for poorly-ordered iron oxides as well as for a specific mineral as defined by Fleischer *et al.* (1975) is also inadvisable. The analogous use of the term “montmorillonite” as a group name is now almost universally replaced by the term “smectite”, to avoid the confusion of a group with a specific member of that group. The broader usage of the term ferrihydrite can lead, and indeed has led, to properties being ascribed to ferrihydrite which may not be true for ferrihydrite in the strict sense.

ACKNOWLEDGMENT

I am indebted to Mr. D. Duthie for the XRD traces, and to Drs. U. Schwertmann and C. W. Childs for helpful criticisms and comments on an earlier version.

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