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A STRUCTURAL MODEL FOR NATURAL SILICEOUS FERRIHYDRITE

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Abstract—X-ray diffraction of four natural samples of ferrihydrite indicates the presence of crystalline domains within the primary particles. The average diameter of the primary particles (determined from low-angle powder patterns) decreases from 4.1 nm to 2.5 nm as the domain size in the xy-plane (determined by applying the Scherrer equation to the broad [110] XRD peak at 0.26–0.27 nm) decreases from 1.0 nm to 0.77 nm. The Si content (measured by acid-oxalate extraction) increases from 4.1% to 6.1% as both the domain and particle sizes decrease; other factors, however, are likely to be important in influencing particle size. For one sample of ferrihydrite, the smallest possible domain (i.e., c = 0.94 nm in the z-direction) contains 36 O atoms and three Si atoms. A model for ferrihydrite is suggested in which silicate bonds to, and bridges, the surfaces of the domains. The model can account for several aspects of the behavior of siliceous ferrihydrites.

Key Words—Domain size, Ferrihydrite, Low-angle X-ray diffraction (LAXRD), Particle size, Silicate, Structure, X-ray diffraction (XRD).

INTRODUCTION

Ferrihydrite is a hydrous Fe oxide which, because of short-range structural order, gives broad X-ray diffraction (XRD) peaks (e.g., Schwertmann, 1988). Up to five peaks are usually observed for natural ferrihydrites though seven have been recorded for synthetic samples. These can be indexed to a hexagonal unit cell with a = 0.508 nm and c = 0.94 nm. There appears to be a range of naturally occurring ferrihydrites from those that show at least five peaks and may be considered "well ordered," down to those which show only two and which have sometimes been tentatively called "protoferrihydrite" or "two-line ferrihydrite" (Childs, 1992).

Various formulae have been proposed for ferrihydrite. These include $5Fe_2O_3 \cdot 9H_2O$ (Fleischer *et al.*, 1975), $Fe_5HO_8 \cdot 4H_2O$ (Towe and Bradley, 1967) and $Fe_2O_3 \cdot 2FeOOH \cdot 2 \cdot 6H_2O$ (Russell, 1979).

The structure of ferrihydrite is not as well understood as those of other Fe oxide minerals (Childs, 1992). The IMA (Fleischer *et al.*, 1975) adopted a structural model of hexagonal-close-packed layers of O^{2-}, OH^-, and H_2O with Fe^{III} occupying octahedral positions. Relative to the distribution of Fe atoms in hematite, some of those in ferrihydrite are vacant and, therefore, the repeat period is four planes of O atoms rather than six as in hematite (Towe and Bradley, 1967).

Recently, a different structural model for synthetic ferrihydrite based on a trigonal cell with ⅔ octahedral and about ⅓ tetrahedral Fe was proposed by Eggleton and Fitzpatrick (1988), though Manceau *et al.* (1990), in response, claimed that the evidence from X-ray absorption spectroscopy pointed to the absence of tetrahedral Fe.

Naturally occurring ferrihydrites from soil-related environments contain Si, typically of the order of 5% (w/w), although this varies considerably from sample to sample (Childs, 1992). Evidence of Si–O–Fe bonds is observed in infrared spectroscopy (Carlson and Schwertmann, 1981; Childs *et al.*, 1986). Whether silicate is "in the structure" or "adsorbed on the surface" of ferrihydrite is still a subject of debate and research (e.g., Vempati and Loeppert, 1989). The presence of Si may be responsible for the slow rate of transformation of natural ferrihydrite to more crystalline Fe oxides.

In this paper we use low-angle X-ray powder diffraction (LAXRD) analyses to measure the average diameter of the primary particles of four naturally occurring ferrihydrite samples, and the Scherrer equation (Brindley, 1980) is applied to the (110) broad peak observed in conventional XRD patterns to help estimate the size of the crystalline domains, i.e., portions of the structure that diffract X-rays coherently.

SAMPLES AND METHODS

Samples of four natural deposits arising from the oxidation of groundwaters derived from the weathering of volcanic ejecta were selected for study. The occurrence of these samples has been described elsewhere: PC538/6 and PC863 (Henmi *et al.*, 1980; Childs *et al.*, 1986) from a streambed on Mount Egmont, New Zealand; PC991 (sample A_1, Childs *et al.*, 1982) from a streambed on Mount Ruapehu, New Zealand; and 1783 (Childs *et al.*, 1990) from a paddy race, Aso-Dani, within the caldera of Mount Aso, Japan. Element concentrations (except C) have been redetermined by X-ray fluorescence (XRF) as described in Childs *et al.* (1986),

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Table 1. Chemical composition of samples (weight % of element in 110°C-dry material).

	Sample				
	PC538/6	PC863	PC991	1783	±[1]
Fe	52.2	53.7	50.0	49.3	5
Si	5.2	4.9	5.8	6.2	4
Na	0.1	0.1	0.1	0.1	1
K	0.03	0.03	0.04	0.04	1
Ca	1.07	0.28	0.92	0.66	2
Mg	0.08	0.04	0.06	0.04	3
Al	<0.03	<0.03	<0.03	<0.03	–
Mn	0.09	0.05	0.08	0.04	1
Ti	0.01	0.01	0.01	0.01	1
P	0.32	0.25	0.73	1.09	2
C	n.d.[2]	0.5	0.6	0.8	1
$H_2O(+)$	9.0	8.5	9.8	10.6	1
$H_2O(-)$	24.0	22.0	21.7	20.8	2

[1] ± values are estimated uncertainties in last significant figures.

[2] n.d., not determined.

analysing the four samples within one batch (Table 1). The results correspond closely, apart from minor differences in $H_2O(+)$ and $H_2O(-)$ values, with those given in the referenced publications. The Munsell colors of the lightly crushed air-dried samples were: PC538/6, 7.5YR5/8 (strong brown); PC863, 7.5YR6/8 (reddish yellow); PC991, 7.5YR5/8 (strong brown); 1783, 10YR7/6 (bright yellowish brown).

The amounts of Fe, Al, and Si (Fe_0, Al_0, Si_0) extracted by acid-oxalate reagent (0.2 mol l^{-1}, pH3) were obtained using sample : solution ratios of 1:500 with shaking for 4 hr in the dark. Acid-oxalate reagent is a fairly specific extractant of ferrihydrite (Parfitt and Childs, 1988) and the Fe_0 and Si_0 values were used to estimate the ferrihydrite concentrations (Table 2).

Infrared spectra were obtained using KBr discs and a Digilab FTS-7R spectrometer.

Thin, flat specimens were prepared for LAXRD by suctioning suspensions of samples in distilled water onto polished porous ceramic plates. The specimens were then dried at room temperature. For conventional XRD, dry material was pressed in a 1 mm deep depression in a metal support. XRD was carried out with a wide-angle goniometer (Philips, PW1050/25). CoKα radiation (40 kV, 40 mA) from a long fine-focus tube, a graphite monochromator in the diffracted beam, and a vacuum/helium device to minimize the absorption of radiation by air (Van der Gaast and Vaars, 1981) were also used. The instrument was equipped with a variable divergence slit designed to keep the irradiated specimen area constant as the incident beam angle changed (Van der Gaast, Vaars, and Jansen, in preparation). For LAXRD, the following settings were used: irradiated specimen length, 20 mm; receiving slit, 0.1 mm; antiscatter slit, 0.5°; counting time, 4 s/0.02° 2θ. For conventional XRD, the following were used: irradiated specimen length, 12 mm; receiving slit, 0.2 mm; antiscatter slit, 1.0°; counting time, 40 s/0.05° 2θ. The specimen chamber was flushed with dry He gas during scanning to prevent the absorption of water, which causes weak broad bands at 0.31 nm and 0.22 nm (Compton and Allison, 1960).

Table 2. Acid-oxalate extraction data for ferrihydrite samples (weight % of element in 110°C-dry material).

Sample	Fe_0 (%)	Si_0 (%)	Al_0 (%)	Ferrihydrite (%)	Goethite (%)[1]
PC538/6	36.4	4.1	0.02	70	25
PC863	44.6	4.2	0.02	85	15
PC991	47.5	5.5	0.02	92	4
1783	49.6	6.1	0.0	97	0

[1] Upper limits; see text.

XRD patterns were stored on floppy discs and were corrected for the Lorentz polarization factor (McEwan *et al.*, 1961) and for the irradiated specimen volume. LAXRD patterns were plotted with a linear diffraction spacing scale on the x-axis to improve the accuracy of determining peak positions. All patterns were smoothed (5 points, equal weight). Peak positions and widths were determined graphically.

The average diameters of the primary particles of the ferrihydrites were obtained by multiplying the LAXRD peak positions by the factor 1.225 based on the assumption that the particles are hexagonally close-packed.

The average diameters of the crystalline domains were determined from the conventional XRD patterns by applying the Scherrer equation

$$L = K\lambda/\beta \cos\theta \qquad (1)$$

to the (110) broad peak, where L is the average diameter of the domain, K is the factor 0.91 (Brindley, 1980), λ is the wavelength of the applied X-rays, β is the full width (in radians) at half maximum (FWHM) of the peak, and θ is the angle of the position of the peak.

RESULTS

Ferrihydrite concentrations were estimated as ($1.7Fe_0 + 2.1Si_0$), which corresponds to ($Fe_2O_3 \cdot 2FeOOH \cdot 2 \cdot 6H_2O + SiO_2$). Si_0 was assumed to represent Si associated in some way with the ferrihydrite particles. High proportions of the total Fe (Fe_t) and Si (Si_t) were extracted by acid oxalate (Tables 1 and 2). There is very little Al in the samples (Tables 1 and 2).

Estimates of goethite concentrations (Table 2) were obtained as $1.6(Fe_t - Fe_0)$ by assuming that all Fe remaining after the acid-oxalate extractions was present as goethite (α-FeOOH). This assumption was made because of XRD evidence (see below) of the presence of goethite in three of the samples. The values should be regarded as "upper limits" because of the possibility that a small proportion of the ferrihydrite is not ex-

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tracted by acid oxalate (Parfitt and Childs, 1988), and the likelihood of a few small grains of Fe silicates, insufficient to show up in XRD, within the samples. A six-line magnetic hyperfine component was not evident in the Mössbauer spectrum of PC863 at 77 K (Childs *et al.*, 1986), indicating that the concentration of goethite in this sample is less than about 10% (i.e., considerably less than that indicated in Table 2), or the goethite particles are too small to be magnetically ordered.

Small concentrations of alkali metal and alkaline earth elements in the samples (Table 1) are attributable, at least in part, to traces of feldspars and other primary minerals. The P is likely to be present as adsorbed phosphate (Childs *et al.*, 1982). Some of the C may be present as carbonate because the spring waters commonly release CO_2 on venting.

The LAXRD patterns (Figure 1) show distinct maxima between 2.06 nm and 3.37 nm. The peaks tail towards low angles (higher spacings) because of the axial divergence aberration of the instrument. This aberration is inherent to the Bragg-Brentano para-focussing geometry used in the technique (Wilson, 1963). The peak maxima (Figure 1), which relate to the average primary particle diameters, are probably not shifted by this effect. Comparable reflections were found for allophane and imogolite (Van der Gaast *et al.*, 1985) and for curved smectite (Van der Gaast *et al.*, 1986). The primary particles of ferrihydrite were assumed to be spherical. Values obtained for the average diameters lie in the range 2.5–4.1 nm (Table 3) and are similar to those estimated previously from transmission electron microscopy for PC538/6 and PC863 (Henmi *et al.*, 1980).

The conventional XRD patterns (Figure 2) all show broad peaks at 0.15 nm and at about 0.26 nm, attributable to ferrihydrite (300) and (110) reflections, respectively. For sample 1783, however, the (110) maximum occurs at 0.273 nm, consistent with the pattern previously reported for this sample (Childs *et al.*, 1990). The inclining baselines, toward lower angles, in Figure 2 are caused by strong low-angle reflections.

Sample 1783 shows only two broad peaks attributable to ferrihydrite plus two relatively weak and very broad peaks at 0.22 nm and 0.31 nm, which are probably due to residual adsorbed water (Figure 2). Samples PC991 and PC863 have additional small broad peaks at 0.257 nm, 0.224 nm, 0.20 nm, and 0.17 nm, which are attributable to ferrihydrite. They also have a small peak at 0.42 nm attributable to goethite. Although other goethite peaks cannot be distinguished, small proportions of the areas of all five broad "ferrihydrite" peaks are likely to be due to goethite. For sample PC538/6 several peaks attributable at least in part to goethite can be distinguished (G, Figure 2).

Calculations based on the ferrihydrite unit cell suggest that reflections could also occur in the region of 0.30–0.50 nm and some small broad peaks have been observed previously in this region (Eggleton and Fitzpatrick, 1988; Childs, 1992). Such reflections may make a small contribution to the shoulders indicated in Figure 2.

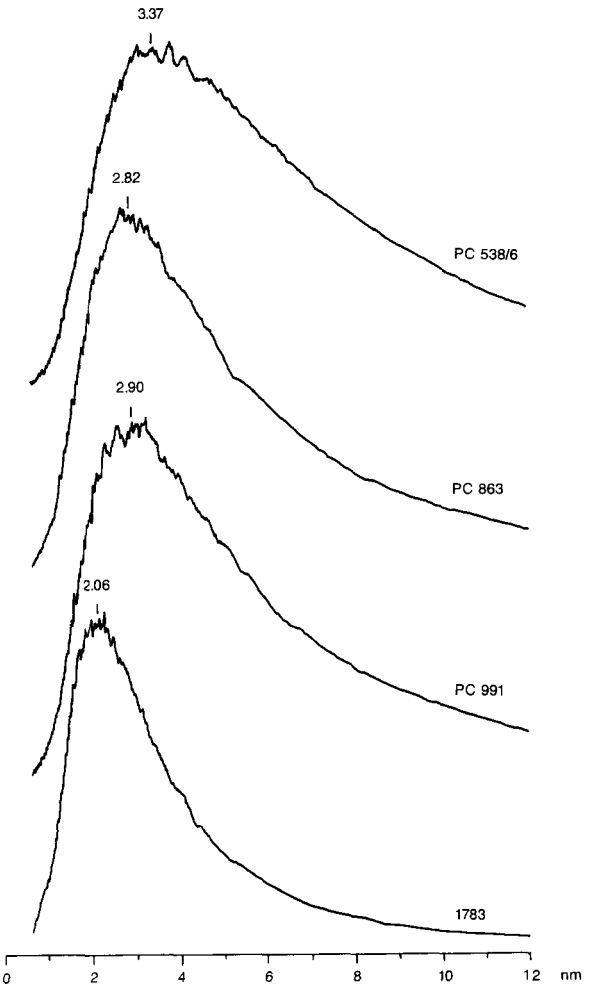


Figure 1. Low-angle X-ray powder diffraction (LAXRD) patterns of ferrihydrite samples.

The average dimensions of domains in the xy-plane, which were determined from the FWHM values of the (110) peaks, lie in the range 0.77–1.00 nm (Table 3). Broadening of XRD peaks is generally caused by small crystallite size and structural distortions (Klug and Alexander, 1974). Eggleton and Fitzpatrick (1988), however, concluded from high resolution electron micrographs of synthetic ferrihydrites that, although many structural defects in the particles could be seen, broadening of the (110) line could be attributed essentially to small crystal sizes rather than to distorted structures or noncrystalline material. This conclusion is the underlying assumption we make in estimating domain sizes in the xy-plane (Table 3). If each of the primary

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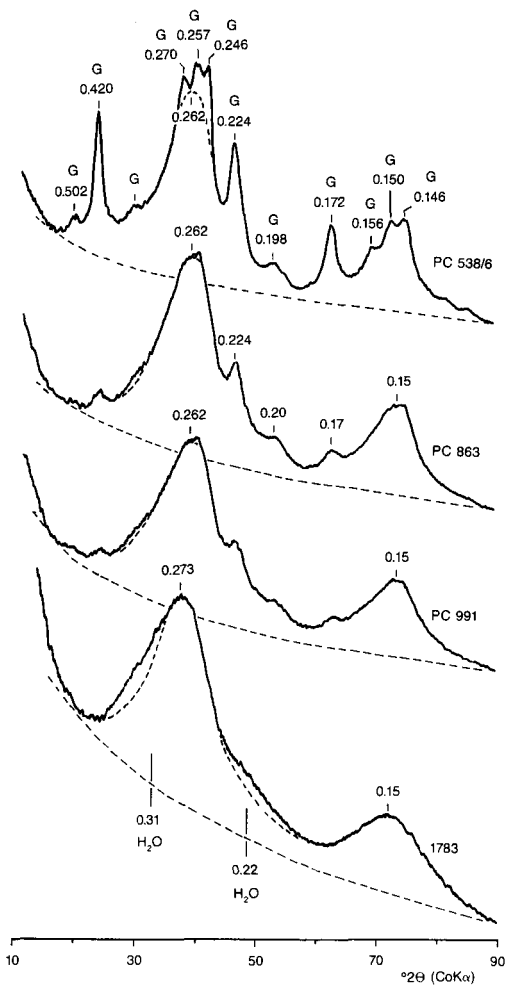


Figure 2. Conventional X-ray powder diffraction patterns of ferrihydrite samples. d-Spacings are in nm; G, goethite.

particles consisted of only one crystal, the FWHM values of the (110) peak would be expected to lie in the range 2.40–3.91° 2θ according to Eggleton and Fitzpatrick (1988). They are, however, about four times larger (Table 3).

The domain size for goethite in PC538/6, based on the FWHM of the 0.42 nm (110) peak corrected for instrumental broadening, is 6.7 nm.

Infrared spectra (Figure 3) of the samples show silicate mainly in a partially polymerized form (977–1011

Table 3. Average diameter of primary particles and domains of ferrihydrites.

Sample	LAXRD spacing (nm)	Particle diameter (nm)	Domain diameter (xy-plane) (nm)
PC538/6	3.37	4.1	1.00
PC863	2.82	3.5	0.92
PC991	2.90	3.6	0.81
1783	2.06	2.5	0.77

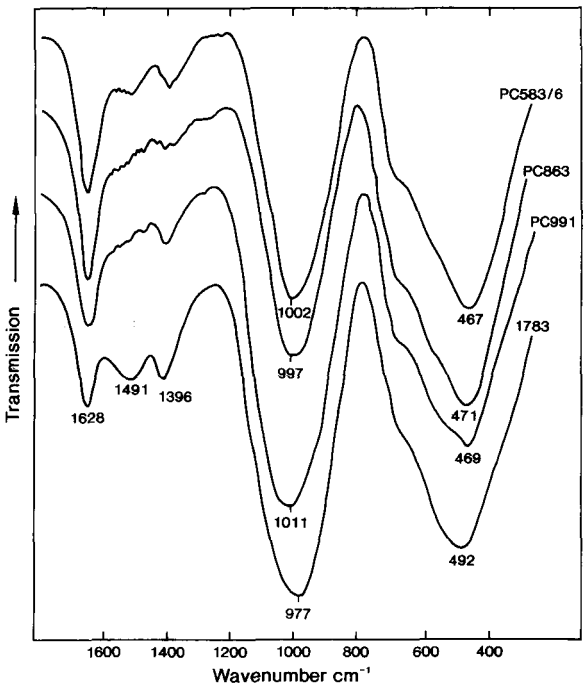


Figure 3. Infrared spectra of ferrihydrite samples.

cm^{-1}), but orthosilicate (930 cm^{-1} shoulder) is also present. Carlson and Schwertmann (1981) concluded that both Fe–O–Si and Si–O–Si bonds occur in natural ferrihydrites, and the infrared spectra (Figure 3) are consistent with this conclusion. A shoulder near 3150 cm^{-1} (not shown) indicates goethite in sample PC538/6 though the concentration may be less than 25%.

DISCUSSION

All four ferrihydrite samples were formed by the oxidation of Fe^{II} to Fe^{III} as groundwaters associated with volcanoes emerge through spring-vents to the open atmosphere. Each of the samples contains several percent of Si coprecipitated with Fe from the oxidizing groundwaters (Table 1). Groundwaters may contain polymerized silicate in addition to monomeric silicate (Alvarez and Sparks, 1985). The primary particle sizes and the domain sizes of our samples both tend to decrease as the Si_0 content increases (Tables 2 and 3); however, since we have examined only four samples and the range of Si_0 values is not large, this observation may not have general significance. Samples PC991 and 1783 contain close to 1% P in addition to Si. The mole ratios, Si/Fe and (Si + P)/Fe, for our samples are 0.19–0.24 and 0.20–0.28, respectively.

Both silicate and phosphate are known to exchange readily with exposed OH groups on the surfaces of Fe oxides, though phosphate binds more strongly than, and can displace, silicate (Parfitt, 1978). When phosphate is added to natural ferrihydrite, however, only a

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Table 4. Make-up of smallest domain for sample 1783.

Element	Content (%)	No. of atoms	Atomic charge per domain
Fe	49.6	12	36+
Si	6.1	3	12+
O	42.0[1]	36	72−
H	1.8[1]	24	24+

[1] Estimated by difference.

small fraction (about 1–2%) of the total Si is desorbed (Parfitt, 1989). We conclude that most of the silicate is held on relatively inaccessible sites, probably within the primary particles.

Silicate forms inner sphere complexes with the surfaces of Fe oxides over a wide pH range (Sigg and Stumm, 1980; Barrow and Bowden, 1987). It is considered to restrict the crystal growth of Fe oxides by adsorbing on growth sites (Karim, 1984; Quin *et al.*, 1988). Thus it is possible to envisage silicate complexing with the surfaces of incipient ferrihydrite particles (domains). The concentration of silicate in solution is likely to be a factor in determining the size of the domains (Table 3), though other factors, such as pH, speciation, and rate of precipitation, are probably also important. Similar surface coatings have been suggested for some goethite crystallites (Smith and Eggleton, 1983). As each primary particle of ferrihydrite is composed of many domains, only a relatively small proportion of the silicate present would lie on the surface of the primary particles and be readily exposed to exchange by other anions such as phosphate. Silicate may also act as a "glue" holding domains together by cross-linking between domain surfaces. In some cases, O atoms may be shared by Fe octahedra and Si tetrahedra. Any phosphate present in oxidizing groundwaters would, presumably, also adsorb on the domain surfaces.

The average diameter of domains in sample 1783 is estimated to be 0.77 nm in the xy-plane (Table 3). As a layer of hexagonally close-packed O atoms is 0.26 nm thick, the xy-plane can be envisaged as three rows each of three O atoms. For ferrihydrite c = 0.94 nm, i.e., four planes of O atoms. We suggest that each domain may be some small multiple of c in the z-direction, and the smallest possible domain (i.e., 0.94 nm in the z-direction) would therefore contain 36 O atoms. The total atoms in this domain can be calculated from the data in Table 2 and from balancing the charges on the atoms (Table 4), giving 12 Fe, 24 OH, 12 O and 3 Si atoms and a molecular weight of about 1300.

The average diameter of the ferrihydrite primary particles in sample 1783 is 2.5 nm. Hence, each particle contains a maximum of about 27 of the smallest possible domains (three in each of the three dimensions of space). A simplistic illustrative model for ferrihydrite consistent with these data is shown in Figure 4.

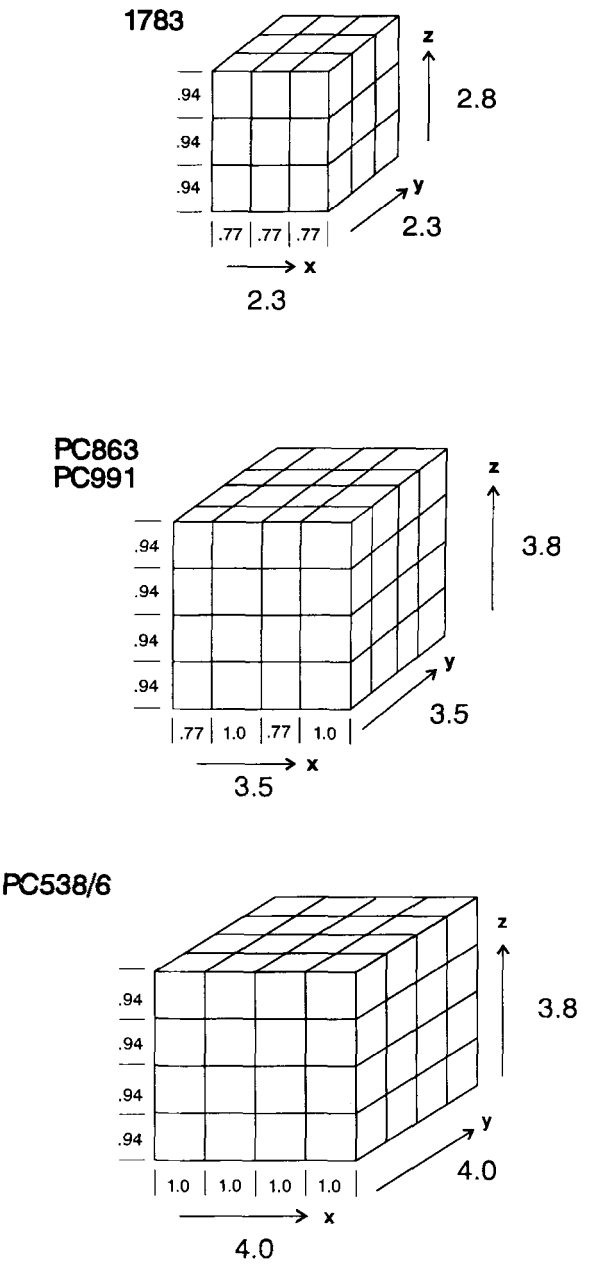


Figure 4. Models of ferrihydrite particles showing domains. Dimensions in nm.

The dimensions are 2.8 nm in the z-direction and 2.3 nm in the xy-plane, and these are close to the 2.5 nm obtained from LAXRD. Note that the omission of the corner domains would produce a primary particle tending toward a spherical shape and containing 19 domains.

A similar model of a primary particle for sample PC538/6 contains 64 domains (each being 1.0 × 1.0 × 0.94 nm) (Figure 4). The total would be 56 if the corners were omitted. In each of these larger domains,

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there may be four rows of four O atoms, rather than three, in the xy-plane. The particle dimensions are close to the 4.1 nm obtained from LAXRD (Table 3).

Samples PC863 and PC991 appear to be intermediate between 1783 and PC538/6 (Figure 2 and Table 3) and a similar model for them might, therefore, contain four domains in each of the three dimensions of space with the domain sizes being a mixture of those suggested for 1783 and PC538/6 (Figure 4). This model contains 64 domains—or 56 domains if the corner ones are omitted. The particle dimensions are 3.8 nm (z) and approximately 3.5 nm (x, y), which are close to the 3.5–3.6 nm obtained from LAXRD assuming spherical shape (Table 3).

We believe that this model goes some way towards accounting for:

1) the presence of up to about 9% Si as silicate in natural ferrihydrites (Childs, 1992);
2) the apparent stability that silicate confers on the ferrihydrite structure even though it is not an essential structural component (Childs, 1992);
3) the marked effect of Si content on the surface properties of ferrihydrites (Anderson and Benjamin, 1985);
4) the ability of phosphate in solution to readily displace only a small fraction of the silicate from natural ferrihydrite, although a slow reaction continues over time (Parfitt, 1989); and
5) the inhibitory effect of Si on the thermal transition of natural ferrihydrites to hematite (e.g., Childs *et al.*, 1986).

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