

A study of the thickness of ferrihydrite coatings on kaolinite

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Abstract

The form and thickness of the ferrihydrite coating on kaolinite basal surfaces was studied in mixes containing 1–10% ferrihydrite through a combination of TEM, shadowed replicas, selected area electron diffraction, and determinations of surface area and distribution of charge on the surfaces. At pH3 the ferrihydrite was found to attach initially as single particles to certain sites on the kaolinite. These particles grew laterally and vertically until with 4% ferrihydrite they were aggregates of from 8 to 25 layers of particles. With more ferrihydrite the aggregates coalesced. Despite the irregular cover on the kaolinite satisfactory electron diffraction patterns were obtained and as little as 2% ferrihydrite was detected in a mixture at pH3.

KEYWORDS: ferrihydrite, iron oxide, mineral coating, kaolinite, electron diffraction.

Introduction

IN following their interest in how the common inorganic components of soil interact, soil scientists have devoted a considerable amount of time to investigating the relationship of iron oxide particles to the surfaces of clay minerals (Oades, 1984; Follett, 1965; Greenland and Oades, 1968; Fordham, 1970; Chukhrov and Gorshkov, 1981). At pHs below about 5 colloidal iron oxides are positively charged and so may be attracted to the permanently negatively charged sites on clay mineral surfaces. The positive charge is inversely related to the size of the iron oxide particles and is especially important therefore with the most poorly crystalline iron oxide, namely ferrihydrite, which has been shown at pHs close to 3 to attach to the basal surfaces of kaolinite (Saleh and Jones, 1984). The increased surface area and reduced cation exchange capacity which result from a similar interaction between iron oxide polycations and other clay minerals have been explained as due to the piling up of the approximately spherical particles of iron oxide on the clay mineral surfaces (Oades, 1984). Electron micrographic studies have confirmed that ferrihydrite particles pile up on the surfaces where the negative charges are located. With increasing pH the charge on the ferrihydrite particles reverses and their presence on the kaolinite basal surfaces is reduced until at pH9 the ferrihydrite is

apparently completely separated from the kaolinite (Saleh and Jones, 1984).

The present paper reports on an attempt to examine the nature and thickness of the ferrihydrite coating on the kaolinite crystals by means of selected area electron diffraction in conjunction with other information.

Experimental details

Synthetic ferrihydrite was prepared as described previously (Saleh & Jones, 1984) and, after dialysing against distilled water, mixed with the < 2 micrometer diameter size fraction of either Pugu D or Supreme kaolinites using 1 g kaolinite and an amount of ferrihydrite equivalent to 1, 2, 4, 5, 8 and 10 wt. % in 30 ml water. The pH was adjusted with either HCl or NaOH and the mixture stirred mechanically for 24 hours. Pure minerals and mixtures were kept in suspension at room temperature.

Specific surface areas were determined on freeze-dried material by applying the BET equation to N₂ adsorption isotherms. Total negative and positive charges were as determined by Saleh and Jones (1984); the method used for the determinations on the kaolinites and on the kaolinite–5% ferrihydrite mixtures depended on the Cs⁺ and Cl⁻ retained from 0.02M CsCl solution at pH3 to 9, both Cs and Cl being detected by X-ray fluorescence spectroscopy (Greenland, 1974), and the determinations on

the ferrihydrite were made by potentiometric titration. All values are shown as $\text{meq } 100 \text{ g}^{-1}$.

Electron microscopy and selected area electron diffraction were accomplished using an Hitachi H800 instrument at 200 kV in both microscopic and diffraction modes. The selected area for diffraction was approximately 450 nm diameter, i.e. $0.16 \mu\text{m}^2$. Specimens were prepared and split for (i) transmission electron microscopy (TEM) by evaporating a 1–2% suspension on to grids coated with cellulose nitrate, and (ii) for carbon replicas prepared according to the method of Greenland and Wilkinson (1969) but using an angle of 30° for the carbon shadowing of the specimens. Thickness, T , of kaolinite crystals and the aggregates were determined from $T = (l \times a)/m$ where l is the length

of the shadow, m the magnification, and a is the tangent of the angle of shadowing and approximately = 0.5.

Negative films of selected area diffraction (SAD) patterns were examined by eye and with a microdensitometer and the number and smoothness of the diffraction rings of the ferrihydrite pattern noted from several areas on each grid.

Previous studies by TEM of the kaolinite–5% ferrihydrite mix showed that at pH3 the ferrihydrite appeared to attach to the basal surfaces of the kaolinite crystals, at pH6 this attachment was less and at pH9 the ferrihydrite and kaolinite were separated (Saleh and Jones, 1984). SAD patterns from a kaolinite–5% ferrihydrite mix at pH3 supported this conclusion by frequently showing a

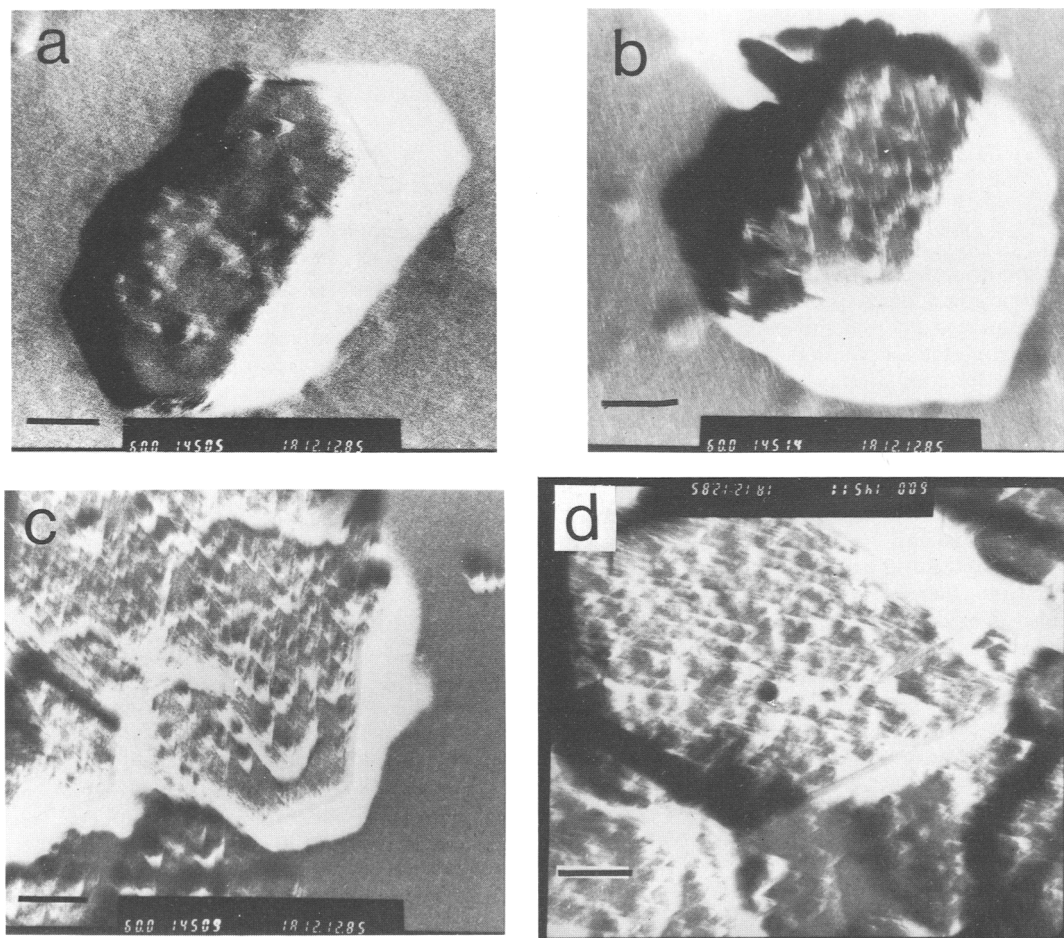


FIG. 1. Electron micrographs of carbon and platinum-shadowed replicas of Supreme kaolinite with (a) 1%, (b) 2%, (c) 4%, (d) 8% ferrihydrite (bar = $0.2 \mu\text{m}$).

diffraction pattern from ferrihydrite superimposed on a single crystal pattern from kaolinite; this feature showed only infrequently from the mix at pH6 and not at all from the mix at pH9 (Jones and Saleh, 1986). It was observed that the diffraction pattern from the mix at pH3 usually consisted of smooth rings while that from a mix at pH6 consisted, at best, of streaky rings. These effects seemed likely to result from a smaller volume of ferrihydrite on the kaolinite and in the selected area for electron diffraction; in order to check whether this was so, attempts have been made to estimate, directly or indirectly, the volume, or the thickness, of the ferrihydrite on the basal surface of the kaolinite as follows:

(i) the form and thickness of the ferrihydrite on the kaolinite in mixes containing various proportions of ferrihydrite were examined by TEM, and the thickness of the ferrihydrite on the basal surface of the kaolinite was measured on shadowed replicas;

(ii) the surface area and surface charges of the minerals and of the mixes were determined with the aim of determining the distribution of charge on the various surfaces.

Results

TEM and shadowed replicas of the mixes at pH3 showed that the distribution of ferrihydrite on the basal surfaces of the kaolinites was not uniform and this became particularly clear as the proportion of ferrihydrite in the mix was reduced. Thus with the 1 and 2 per cent mixes the ferrihydrite was scattered in small aggregates over the kaolinite surfaces (Fig. 1a, b). With increasing proportions of ferrihydrite these aggregates tended to coalesce until with the 8 per cent mix little of the kaolinite basal surface appeared to be clear of ferrihydrite (Fig. 1c, d). Repeated measurement of the approximate size of the kaolinite basal surfaces and of the approximate size and extent of the ferrihydrite revealed that the area covered by a ferrihydrite aggregate ranged from 20 nm² to 600 nm² (Table 1). The smallest ferrihydrite aggregates were commonly found in the 1 and 2 per cent mixes and the largest in the 4, 5 and 8 per cent mixes; in the 8 per cent mix it was difficult to determine the area covered by individual aggregates. Replicas of the 5 per cent kaolinite/ferrihydrite mixes after the pH of the suspension had been adjusted to pH9 showed that some aggregates of ferrihydrite remained on a few of the kaolinite basal surfaces; these aggregates were small and comparable in area to those found in the 1 and 2 per cent ferrihydrite mixes and measurements of their heights (Table 1) suggest that they have a higher, rounder shape than aggregates

at pH3. Shadowed replicas (Fig. 1a-d) also showed that even in the mixes at pH3 the unevenly distributed ferrihydrite aggregates formed separate mounds of from 5 to 100 nm height, i.e. the volume of aggregates at pH3 ranged from 0.1 to 60 × 10⁻⁵ μm³ (Table 1). In the mixes at pH6 these mounds were less frequent on the kaolinite surface but still comparable in size; in the mixes at pH9 they were infrequent and small. The approximate 'cover' by the ferrihydrite, as determined by the number of aggregates observed per 0.5 μm² surface of kaolinite and their total volume in the selected area of 0.16 μm² supported the visual evidence (Table 1).

TABLE 1. Size and volume of ferrihydrite aggregates on kaolinite crystals as measured from replicas.

	%	smallest			largest			approx. number ¹	approx. volume ²
		ab	h	v	ab	h	v		
pH3	1	20	5	0.1	80	20	1.6	31.5	1-16
	2	20	9	0.2	240	30	7.2	63	4-145
	4	180	20	3.6	240	30	7.2	56	65-129
	5	40	20	0.6	600	100	60	47	9-902
	*	180	30	9.0				50	144
pH9	5	70	60	4.2	200	50	10	-	-

ab=area, nm²; h=height, nm; v=volume, micrometer³ × 10⁻⁵

¹ number observed/0.5 micrometer² kaolinite surface

² volume calculated, micrometer³ × 10⁻⁵/0.16 micrometer²

* the commonest approximate size

The surface areas of the kaolinite-ferrihydrite mixes at pH3 were consistently greater than that of the kaolinite alone in proportion to the amount and surface area of ferrihydrite added (Table 2).

TABLE 2. Surface areas

Sample	Surface area, m ² g ⁻¹	
	Observed	Calculated
Ferrihydrite	249	
Pugu D kaolinite	26.3	-
+5%ferrihydrite	40.2	37.4
+10%ferrihydrite	44.2	48.6
Supreme kaolinite	14.3	-
+5%ferrihydrite	30.2	26.0
+10%ferrihydrite	38.3	37.8

The surface charges on the kaolinite, the ferrihydrite and the mixes (Table 3) are shown with the permanent charge on the kaolinite separate; the sign of other charges on both kaolinite and ferrihydrite depend on the pH. The charges for the mixes were calculated by setting all the positive charges on the ferrihydrite against the permanent negative charge on the kaolinite and thereafter putting all charges together. The results indicate that 5% ferrihydrite reduced the negative charge on Pugu kaolinite at pH3 by only 18 per cent although the positive charge from this amount of ferrihydrite at this pH would, in theory, counter 68 per cent of the permanently charged sites on the kaolinite. At the same time there was a slightly increased positive charge due, almost certainly, to free (unattached) ferrihydrite. At pH6 the reduction of negative charge was very small and there was still a small increase in positive charge, presumably again due to free ferrihydrite. At pH9 the charge on the mix was entirely negative.

TABLE 3. Charges (meq 100g⁻¹) on Pugu kaolinite-5%ferrihydrite mix.

pH	95%kaolinite	5%ferrihydrite	mix		% countering of permanent charge	
			calc.	obs.	calc.	obs.
3	-2.2*	+1.5	-0.7	-1.8	68	18
	+0.5		+0.5	+0.9		
6	-2.2*	+0.3	-1.9	-2.1	14	5
	-0.5		0.0	+0.3		
	+0.5					
9	-2.2*	-0.3	-4.7	-4.2	-	-
	-2.2					

* permanent charge on basal surface of kaolinite

SAD of the kaolinite-ferrihydrite mixes at pH3 varied somewhat, mainly because the ideal location for examining a diffraction pattern, i.e. a separate single crystal of kaolinite, was found relatively infrequently on any grid. Nevertheless, a pattern containing 4-10 distinct rings of the ferrihydrite diffraction pattern was often found from the mixes containing 4% or more ferrihydrite (Fig. 2c, d) while only the 2 or 3 most intense rings of the ferrihydrite pattern could be discerned from the mixes containing less ferrihydrite and from the 1% mix 2, incomplete rings could only just be discerned

(Fig. 2a, b). The cellulose nitrate supporting medium was chosen because it gave no detectable diffraction pattern.

Discussion

While previous electron microscopical studies of kaolinite-ferrihydrite mixes suggested that the ferrihydrite coating on the kaolinite basal surfaces was not uniform (Saleh and Jones, 1984) this has been more clearly established with mixes at pH3 where the proportion of ferrihydrite was less than 4%. On the basis that an individual ferrihydrite particle is roughly spherical with a diameter of 4 to 5 nm (Towe and Bradley, 1967; Saleh and Jones, 1984) the smallest aggregate in the 1% ferrihydrite-kaolinite mix at pH3 occupied 20 nm² × 5 nm so was virtually a single ferrihydrite particle. More often in the 1 to 4% ferrihydrite mixes there were several, and up to 100, particles piled up into as many as 5 layers. In the 4% mix the aggregates were made up of as many as 240 particles in 8 layers, and in the 5% mix as many as 3750 particles in 25 layers, although the commonest aggregates were about 360 particles in 8 layers. In mixes with 8% or more ferrihydrite it became impossible to discriminate between the coalesced aggregates. The increased surface area produced by 5 and 10% ferrihydrite is similar to that shown when iron polycations piled up on clay minerals (Oades, 1984). Further additions of polycations produced no further increase in surface area, an effect likely as a result of coalescence similar to that observed with greater concentrations of ferrihydrite particles.

The non-uniform distribution of the ferrihydrite aggregates over the kaolinite surface is borne out by the distribution of charge on that surface in a 5% ferrihydrite mix (Table 3). At pH3 the positively charged ferrihydrite particles did not attach at all the negatively charged sites but at only certain (perhaps 1 in 5) of these. Furthermore, despite there being negatively charged sites exposed on the kaolinite surfaces some of the ferrihydrite remained free and unattached. At pH6 much less ferrihydrite was attached at negative sites and at pH9 none.

While, in the best circumstances at pH3, the ferrihydrite aggregates coated and basal surfaces of kaolinite irregularly they were often large and frequent enough to ensure that there was enough ferrihydrite present in the selected area (450 nm diameter) to give a clear electron diffraction pattern. This pattern, or identifiable parts of it, could still be seen in SAD of the 2% ferrihydrite mixes when the volume of ferrihydrite contributing to the diffraction was possibly less than about 150 × 10⁻⁵ μm³; this is a smaller volume than expected to be required for successful diffraction (Beeston, 1972).

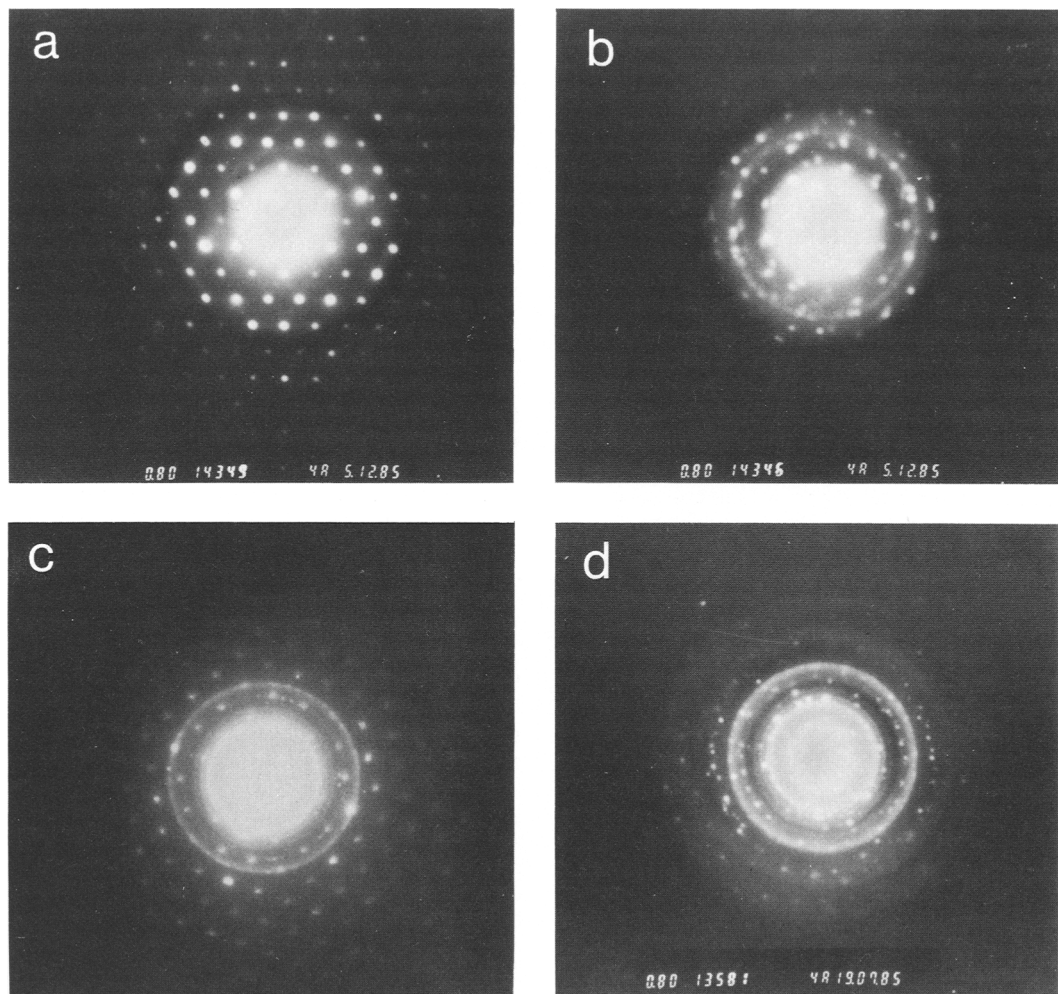


FIG. 2. Selected area electron diffraction patterns from crystals of kaolinites coated with (a) 1%, (b) 2%, (c) 5%, and (d) 8% ferrihydrite.

At pH6, or more especially at pH9, the likelihood of SAD encountering a similar or greater volume of ferrihydrite on the basal surface of a kaolinite crystal would be much reduced and so, as has been found earlier (Jones and Saleh, 1986), electron diffraction patterns of ferrihydrite from such mixes could be infrequent, poor in intensity and quality or even absent altogether.

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