

Influence of montmorillonite on Fe(II) oxidation products

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ABSTRACT: Goethite and maghemite are the stable species of Fe oxyhydroxides-oxides formed in acidic and alkaline environments from the oxidation of Fe(II) perchlorate solutions. The influence of montmorillonite on the oxidation products of 0.02 M ferrous perchlorate at pHs of 6.0 and 8.0 was studied by X-ray diffraction, infrared and transmission electron microscopic analyses. Increased rate of OH consumption during the oxidation at constant pH indicated that the presence of montmorillonite accelerated the rate of Fe(II) oxidation. The presence of montmorillonite, with high surface reactivity, at an initial montmorillonite/Fe (w/w) ratios of 1.4 and 3.4 retarded the formation of goethite, lepidocrocite and maghemite, and maghemite and goethite, and promoted the formation of ferrihydrite and lepidocrocite at pHs of 6.0 and 8.0, respectively. Kaolinite, on the other hand, with relatively low surface reactivity had no influence on the nature of the Fe(II) oxidation products formed at either pH.

The nature of Fe oxide minerals in soils is of interest from the view points of both pedogenesis and soil behaviour. The effect of pedogenic environments on the formation and transformation of the crystalline iron oxides has been thoroughly reviewed (Schwertmann & Taylor, 1989). The presence of highly surface reactive Mn oxide minerals such as birnessite (δ -MnO₂) and cryptomelane (α -MnO₂) influenced the crystallization processes of Fe(II) oxidation resulting in the formation of poorly-ordered Fe oxides and/or akaganeite (Krishnamurti & Huang, 1987, 1988). The soil clay fraction consists of different forms of layer silicate minerals with high surface reactivity and, thus, is expected to influence the formation and transformation of Fe oxyhydroxides minerals. It was shown earlier (Schwertmann, 1979, 1988) that the presence of clay minerals retarded or even blocked the transformation of ferrihydrite to crystalline hematite and goethite. However, no attempt has so far been made to investigate the influence of the clay minerals on the crystallization processes of the precipitation products of Fe (II) oxidation. The present work reports the influence

of montmorillonite, an expandable 2:1 layer silicate mineral with high surface reactivity, on the precipitation products of Fe(II) oxidation.

MATERIALS AND METHODS

The montmorillonite (Swy-1, Na-montmorillonite, Wyoming) sample was ultrasonically dispersed and the <0.2 μ m size-fraction, separated by centrifugation (Jackson, 1979), was Na-saturated with NaCl solution. The excess chloride was removed by repeated centrifugation with demineralized distilled water at 10,000 g, followed by dialysis until a negative chloride test was obtained. The external and total surface area of montmorillonite, determined using N₂ adsorption isotherm on Autosorb-1, and the ethylene glycol monoethyl ether method of Eltantawy & Arnold (1973), were 22.5 and 810.5 m² g⁻¹, respectively.

To 100 ml of aqueous solution of 0.02 M ferrous perchlorate in a 250 ml beaker, different amounts of montmorillonite were added to obtain desired ratios (w/w) of montmorillonite/Fe(II) = 0 to 3.4. The suspensions were immediately titrated with freshly

prepared 0.1 M NaOH to pH 6.0 or 8.0 under ambient conditions and were maintained at the respective pH value for 4 h on a Metrohm titroprocessor using pH-stat mode. The NaOH consumption during oxidation at a constant pH was continuously recorded during the initial 2 h reaction period. The rate of Fe(II) oxidation was deduced from the rate of consumption of 0.1 M NaOH during the reaction period. The experiments were also conducted in the presence of kaolinite (KGa-1, Kaolin, Georgia), an aluminosilicate mineral of low surface reactivity. The external and total surface area of kaolinite (<2 μm), determined using N_2 adsorption isotherm on Autosorb-1, and the ethylene glycol monoethyl ether method of Eltantawy & Arnold (1973) were 2.8 and 32.6 $\text{m}^2 \text{g}^{-1}$, respectively.

All the samples were also aged in suspension at 25°C up to 100 d, and at 70°C for 30 d. During the ageing period, the pH of the suspensions was monitored and adjusted to the respective pH value once every week. The precipitation products formed after a reaction period of 4 h and after ageing the samples in suspension were separated by ultrafiltration (0.01 μm nitrocellulose filter) under vacuum. The filtrates were analysed for Si and Al using the molybdosilicic yellow method (Jackson, 1958) and the aluminon method (Krishnamurti *et al.*, 1974), respectively.

The freeze-dried precipitation products were examined by powder X-ray diffraction (XRD) using Fe- $K\alpha$ radiation on a Rigaku Rotaflex 2000 X-ray diffractometer equipped with graphite monochromator at a step-scan rate of $0.01^\circ 2\theta \text{ s}^{-1}$. Gently pressed self-supporting specimens were used. The infrared (IR) spectra of the samples were taken on a Perkin Elmer 983 IR spectrophotometer using the KBr pellet technique (1 mg of sample mixed with 300 mg of KBr). The transmission electron micrographs of the samples were obtained using a Philips EM 400 transmission electron microscope (TEM). For TEM examination, a drop of the sample suspension was deposited on C-coated Formvar film on a copper grid.

RESULTS AND DISCUSSION

pH 6.0

In the absence of montmorillonite, the precipitation product of Fe(II) oxidation formed at pH 6.0, under ambient conditions, was goethite ($\alpha\text{-FeOOH}$)

and lepidocrocite ($\gamma\text{-FeOOH}$) with traces of maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The XRD pattern had characteristic peaks of goethite at 4.18, 2.69, 2.46, 2.25, 2.19 and 1.56 Å and of lepidocrocite at 6.28, 3.29, 2.46, 1.93, 1.72 and 1.51 Å and that of maghemite at 2.95, 2.52, 2.09, 1.72, 1.61 and 1.48 Å (Fig. 1a). The Fourier transform infrared (FTIR) spectrum showed strong characteristic absorption bands of goethite at 880, 790 cm^{-1} and weak bands of lepidocrocite at 1026 and 350 cm^{-1} . The TEMs of the sample showed laths and needles characteristic of lepidocrocite and goethite, respectively (Fig. 3a). Ageing of the precipitation products in suspension for 100 d at 25°C or for 30 d at 70°C did not show any changes in the kind of Fe oxyhydroxides formed.

The presence of montmorillonite initially at an Mt/Fe ratio of 1.4 blocked the formation of goethite and maghemite, as indicated by the absence of their characteristic XRD peaks (Fig. 1b) and favoured the formation of ferrihydrite. Increasing amounts of montmorillonite modified the crystallization processes of the precipitation products blocking the formation of lepidocrocite and favouring the formation of ferrihydrite, a poorly-ordered Fe oxide (XRD peaks at 2.5, 1.9, 1.7 and 1.5 Å) at an Mt/Fe ratio of 3.4 (Fig. 1c). Synthetic ferrihydrite has characteristic XRD spacings at 2.50, 2.22, 1.96, 1.72, 1.51 and 1.48 Å (JCPDS 29-712). The precipitation product formed at a Mt/Fe ratio of 3.4 is characterized by a broad IR absorption band at 745 cm^{-1} , due to Fe–O stretching vibration. The TEM show aggregates of shapeless particles together with gel-like material of poorly-ordered Fe oxide, possibly ferrihydrite (Fig. 3b).

pH 8.0

In the absence of montmorillonite, the precipitation product of Fe(II) oxidation formed at pH 8.0, under ambient conditions, was maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$). The XRD peaks observed at 4.85, 2.96, 2.52, 2.09, 1.71, 1.61 and 1.48 Å (Fig. 3a) were assigned to maghemite. The cubic unit-cell $a = 8.372 \pm 0.014$ Å, calculated from the d -spacings, is too high for maghemite ($a = 8.350$ Å, JCPDS 24-81), but too low for magnetite (Fe_3O_4), which has a unit-cell of 8.396 Å (JCPDS 19-629). Because of the ease of oxidation of moist fine-grained magnetite (Fe_3O_4) (Feitknecht, 1959) and the tendency for an intermediate product to oxidize

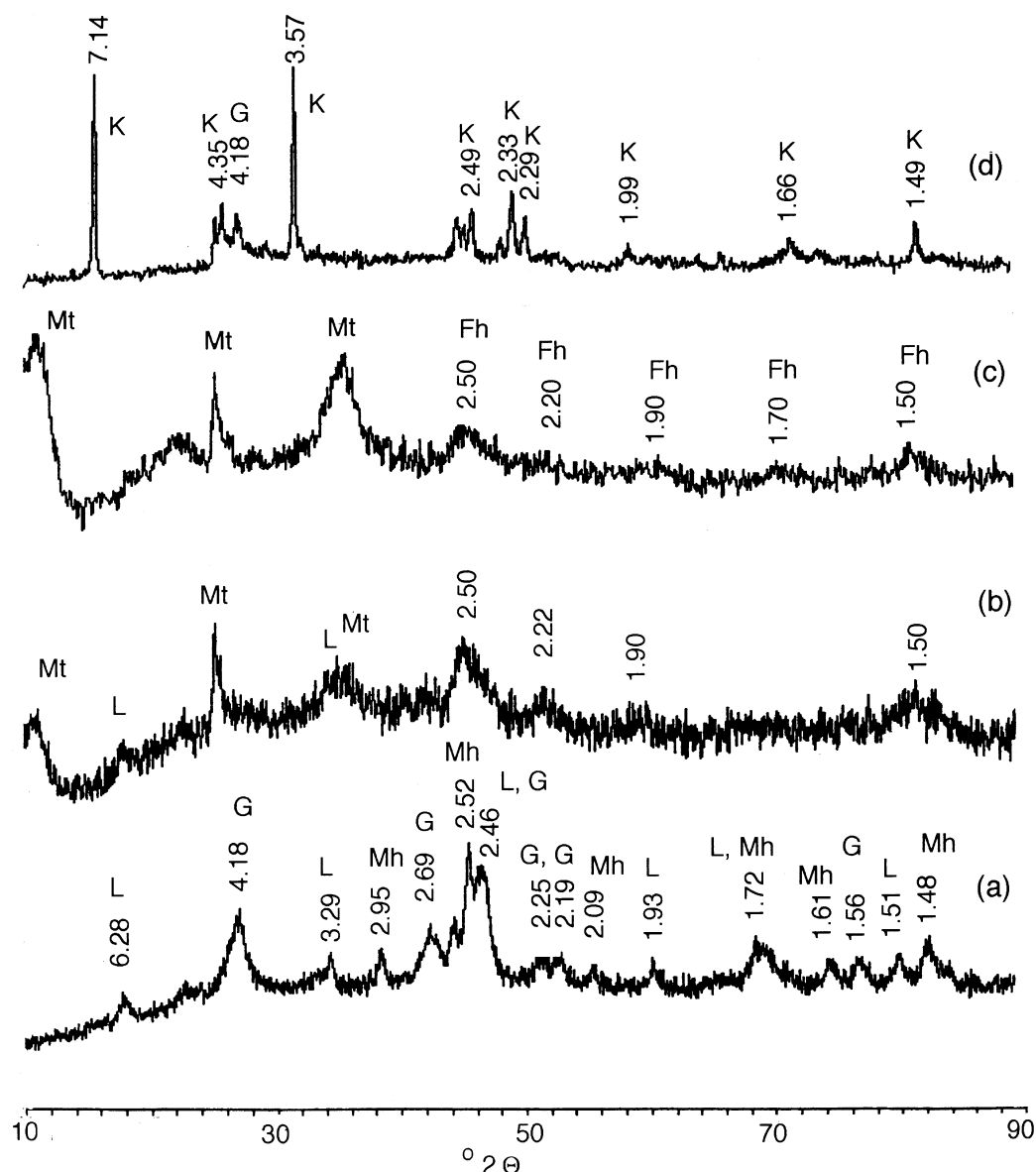


FIG. 1. X-ray diffractograms of precipitation products of Fe(II) oxidation formed at 25°C in 0.02 M $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ –NaOH system at pH 6.0 after reaction time of 4 h. In the absence of montmorillonite or kaolinite (a), in the presence of montmorillonite at an initial montmorillonite/Fe(II) ratio (w/w) of 1.4 (b) and 3.4 (c), and in the presence of kaolinite at an initial kaolinite/Fe(II) ratio (w/w) of 3.4 (d). The d -spacings are in Å. G = goethite, L = lepidocrocite, Mh = maghemite, Fh = ferrihydrite, Mt = montmorillonite, and K = kaolinite; Fe- $K\alpha$ radiation.

towards maghemite (Annersten & Hafner, 1973), most pedogenic magnetic oxides formed from oxidation of Fe(II) solution at pH >7.0 would fall

into the maghemite range. It is also possible that the product formed is magnetite surrounded by secondary maghemite, which produces overlapping

peaks and cell dimensions intermediate between both phases. The FTIR spectrum showed characteristic strong absorption bands of maghemite at 1088 cm^{-1} , due to -OH deformation vibration, and at 627 , 565 , and 393 cm^{-1} , due to -O-Fe-O deformation vibrations. The TEM photographs of the sample showed isometric particles characteristic of maghemite (Fig. 2c).

The presence of montmorillonite promoted the formation of highly crystalline lepidocrocite at an Mt/Fe ratio of 1.4 and 3.4 as indicated by the characteristic XRD peaks (Fig. 3b), and by the well-formed laths in TEM micrographs (Fig. 2d) of lepidocrocite.

The presence of kaolinite, even at a high Kl/Fe ratio of 3.4, however, did not exert any significant influence on the formation of Fe oxides at either pH (Figs. 1d and 3d).

GENERAL DISCUSSION

In the absence of complexing ligands, as Fe(II) is oxidized it passes through intermediate green solution complexes or green rusts. The green solution complexes are composed of both Fe(II) and Fe(III) held together by ol- and oxo-bridges formed during the consumption of OH^- . The configuration of green solution complexes and green rusts are the same and their composition may be represented as $[\text{Fe(II)}_2\text{Fe(III)}\text{O}_x(\text{OH})_y]^{(7-2x-y)+}$ and $[\text{Fe(II)}_2\text{Fe(III)}\text{O}_x(\text{OH})_y]^{(5-2x-y)+}$ (Feitknecht & Keller, 1950; Misawa *et al.*, 1974). Lepidocrocite ($\gamma\text{-FeOOH}$) or magnetite (Fe_3O_4) form by further oxidation of either green solution complexes or green rusts in acidic or mildly alkaline conditions, respectively (Misawa *et al.*, 1974). Lepidocrocite is less stable than its polymorph goethite ($\alpha\text{-FeOOH}$) and the transformation is through a solution phase rather than being topotactic (Schwertmann & Taylor, 1972). Magnetite that forms by oxidation of Fe(II) in slightly alkaline conditions slowly converts into maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (Taylor & Schwertmann, 1974a,b). Taylor & Schwertmann (1974b) were able to make synthetic maghemite under conditions similar to those expected in soils.

The precipitation products formed from the oxidation of Fe(II) solutions are influenced mainly by the rate of oxidation and the ionic environment in the system. It was shown earlier that the rate of Fe(II) oxidation decreases with increase in the stability constant of Fe(II)-ligand complex in the presence of ligands, and the nature of the

precipitation products formed varied significantly (Krishnamurti & Huang, 1990). Further, it was also shown that the presence of highly surface-reactive colloidal size Mn oxide minerals resulted in the formation of a wide range of different compounds such as maghemite, akaganeite ($\beta\text{-FeOOH}$), and poorly-ordered Fe-oxides (Krishnamurti & Huang, 1988).

The presence of montmorillonite in the system accelerated the oxidation of Fe(II) as reflected in the increased rate of OH consumption during the oxidation in the presence of increasing amounts of montmorillonite (Table 1). In the mildly acidic conditions, such as pH 6.0, the rapid oxidation in the presence of large amounts of montmorillonite (Mt/Fe = 3.4) might have blocked the crystallization of lepidocrocite and goethite and promoted the formation of relatively well-crystallized ferrihydrite. In the alkaline conditions, the presence of montmorillonite probably retarded the dehydration of the green rusts, and coupled with increased rate of oxidation might have inhibited the formation of maghemite. Initial dehydration and subsequent slow oxidation favour the transformation of green rusts to magnetite (Fe_3O_4) (Bernal *et al.*, 1959; Misawa *et al.*, 1974), which eventually converts to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) (Taylor & Schwertmann, 1974a,b). However, the presence of montmorillonite with high surface reactivity accelerated the oxidation rate of Fe(II) and the intermediate green solution complexes and green rusts, thereby inhibiting the formation of maghemite. Rapid oxidation of the intermediate green solution complexes favours the formation of lepidocrocite (Bernal *et al.*, 1959; Misawa *et al.*, 1974). The proportion of lepidocrocite relative to that of goethite increased with increase in the rate of Fe(II) oxidation (Carlson & Schwertmann, 1990), whereas slow oxidation favours the thermodynamically more stable goethite over lepidocrocite (Schwertmann, 1959). Lepidocrocite was observed to be the only species of Fe oxyhydroxides formed in alkaline conditions (at pH 8.0) in the presence of montmorillonite (Fig. 3b,c).

Another important factor which could have influenced the formation of Fe oxides during the oxidation of Fe(II) is the presence of an ionic environment. Aluminosilicate minerals present during the oxidation of Fe(II) solutions might release Al and Si to solution which could affect the nature of oxidation products formed in the system. It has already been shown that the presence

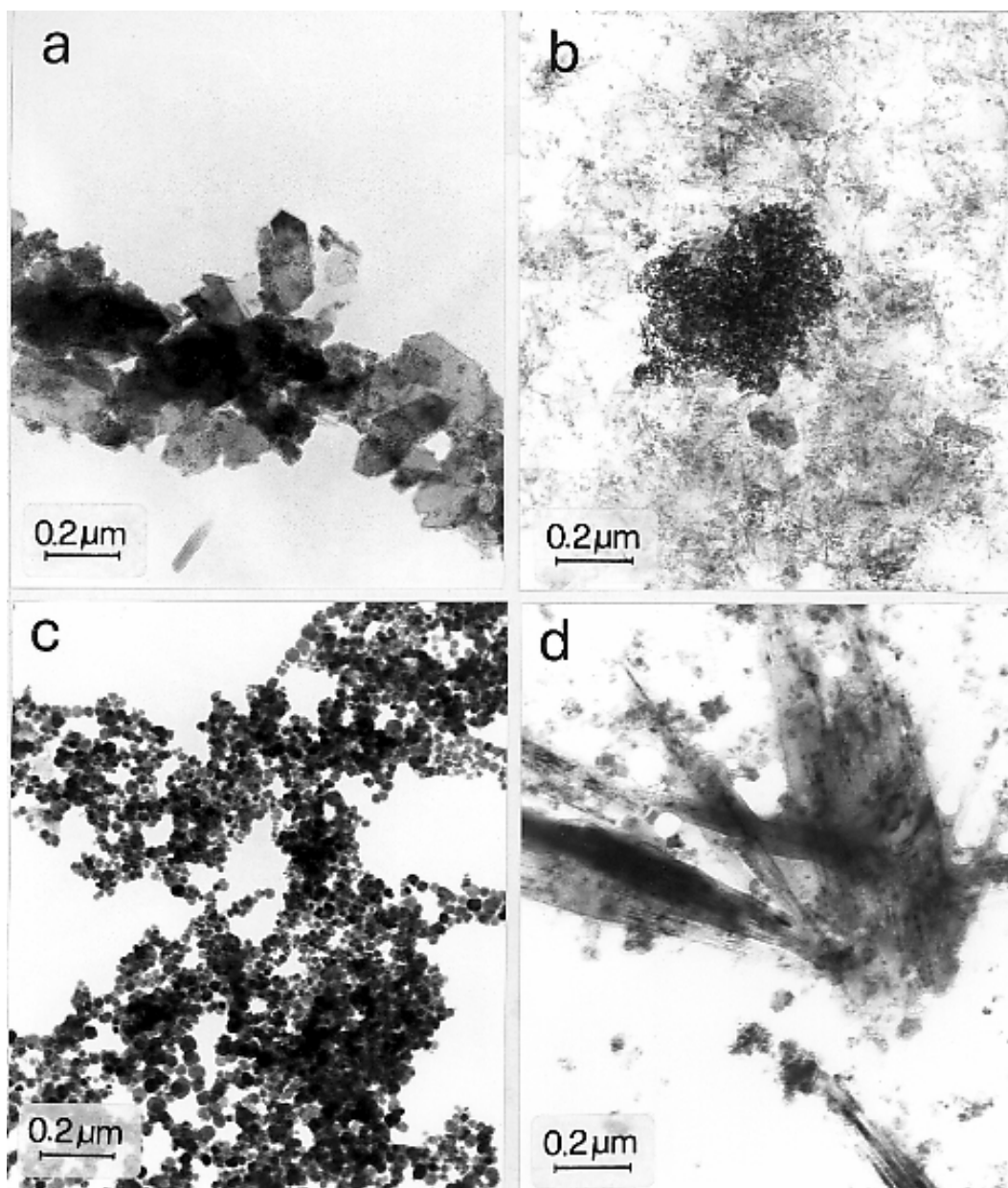


FIG. 2. Transmission electron micrographs of precipitation products of Fe(II) oxidation formed in 0.02 M $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ –NaOH system aged in suspension for 100 d at 25°C; at pH 6.0 (a) in the absence of montmorillonite, and (b) in the presence of montmorillonite at an initial montmorillonite/Fe(II) ratio (w/w) of 3.4; at pH 8.0 (c) in the absence of montmorillonite, and (d) in the presence of montmorillonite at an initial montmorillonite/Fe(II) ratio (w/w) of 3.4.

of Si exceeding an Si/Fe molar ratio of 0.05 (Schwertmann & Thalmann, 1976; Krishnamurti &

Huang, 1990), and the presence of Al exceeding the $\text{Al}/(\text{Al}+\text{Fe})$ molar ratio of 0.30 (Taylor &

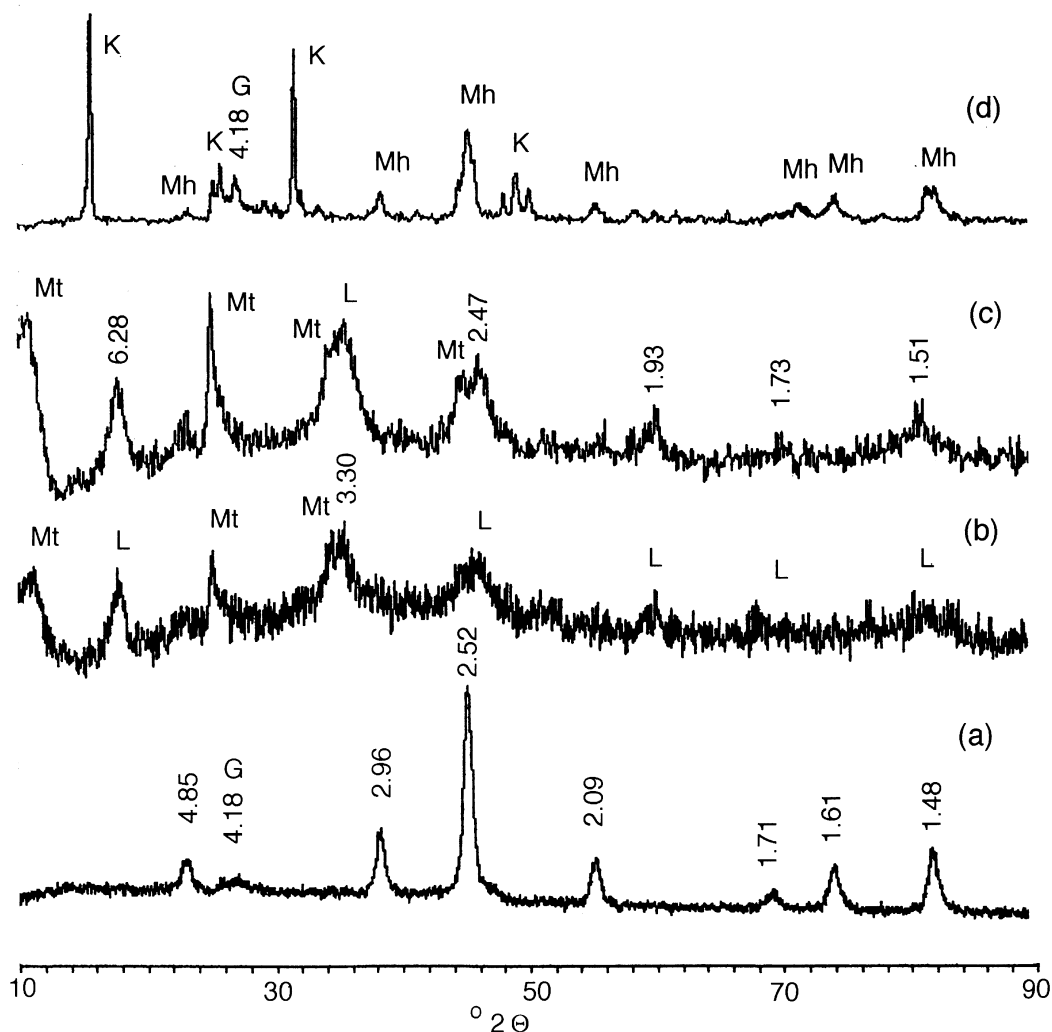


FIG. 3. X-ray diffractograms of precipitation products of Fe(II) oxidation formed at 25°C in 0.02 M $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ –NaOH system at pH 8.0 after reaction time of 4 h; in the absence of montmorillonite or kaolinite (a), in the presence of montmorillonite at an initial montmorillonite/Fe(II) ratio (w/w) of 1.4 (b) and 3.4 (c), and in the presence of kaolinite at an initial kaolinite/Fe(II) ratio (w/w) of 3.4 (d). The d -spacings are in Å. Mh = maghemite, L = lepidocrocite, G = goethite, Mt = montmorillonite, and K = kaolinite; Fe- $K\alpha$ radiation.

Schwertmann, 1978) retard the crystallization of Fe oxyhydroxides and promote the formation of ferrihydrite at pHs of 6.0 and 7.0. Appreciable amounts of Si were released from montmorillonite during the 4 h reaction period, with greater amounts released at pH 6.0 than at pH 8.0 (Table 1). Thus, the Si and Al released from montmorillonite during the oxidation of Fe(II) solutions might have

promoted the formation of poorly-ordered Fe oxides at the expense of Fe oxyhydroxides at pH 6.0 in the presence of montmorillonite.

The presence of increasing amounts of Si and Al was observed to decrease the rate of oxidation of Fe(II) and to promote the formation of poorly-ordered Fe oxides at pH 8 (authors' unpublished data). Thus, the promotion of the formation of

TABLE 1. Final composition, rate of consumption of NaOH, and the nature of iron oxides/oxyhydroxides formed in the system.

Initial component/Fe(II) ratio	Composition of the system at the end of 4 h reaction period		Rate of consumption of NaOH during the initial 2 h reaction	Mineralogy [†]
	Si	Al		
	mg l ⁻¹			
			μmoles min ⁻¹	
pH of the system: 6.0				
Control	0	0	7.8	G, L, Mh
Mt/Fe = 1.4	0.31	0.042	9.8	L, G (tr) ^{††}
Mt/Fe = 3.4	5.16	0.016	12.9	Fh
Kl/Fe = 3.4	1.65	0	9.8	G, L (tr)
pH of the system : 8.0				
Control	0	0	n.d.	Mh, G
Mt/Fe = 1.4	1.21	0.132	n.d.	L
Mt/Fe = 3.4	4.37	0.045	n.d.	L
Kl/Fe = 3.4	0.30	0	n.d.	Mh, G

[†] L - lepidocrocite, G - goethite, Mh- maghemite, Fh - ferrihydrite

^{††} tr - traces

n.d. - not determined

lepidocrocite at the expense of maghemite, the Fe oxide formed in the absence of montmorillonite, can only be attributed to the presence of montmorillonite, a colloidal aluminosilicate mineral with high surface reactivity. The increased intensity of the 020 XRD peak in the oriented sample of the precipitation products formed at pH 8.0 (data not shown) indicated the preferential development of the crystals of lepidocrocite along the *b*-axis. The pronounced growth of lepidocrocite along *b* is probably more an effect of growth velocity and/or surfactants, which might have retarded the development of other directions.

The influence of kaolinite, a highly crystalline 1:1 layer silicate mineral with low surface reactivity, on the precipitation products of Fe(II) oxidation was also studied at Kl/Fe ratios of 0 to 3.4, at the pHs of both 6.0 and 8.0. The rate of Fe(II) oxidation in the presence of kaolinite (Kl/Fe = 3.4) was observed to be the same as that observed in the presence of montmorillonite (Mt/Fe = 1.4) (Table 1), and appreciable amounts (0.3–1.65 mg l⁻¹) of Si were released to solution during the reaction (Table 1). However, the presence of kaolinite (even at Kl/Fe = 3.4) did not show any effect on the nature of Fe oxyhydroxides formed

(Figs. 1, 3); montmorillonite, on the other hand, with high surface reactivity, significantly influenced the crystallization processes resulting in the formation of poorly-ordered Fe oxides at pH 6.0 and of lepidocrocite at pH 8.0.

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