SYNTHESIS OF FERRIHYDRITE AND FEROXYHYTE

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ABSTRACT

Ferrihydrite and feroxyhyte were synthesized at room temperature from 0.1M FeSO₄. Ferrihydrite, with 6 to 7 diffraction lines, formed at pHs 5–11 in the presence of Si (Fe:Si = 10:1). The use of Ge, in place of Si, resulted in the same, with the same d-spacings of the diffraction peaks. This indicates that the Si or Ge is not in the structure of ferrihydrite, but forms Fe-O-Si (or Ge) at the periphery of “domain” of ferrihydrite. The presence of Si or Ge was a requisite for the formation of ferrihydrite, because their absence led, at the pHs investigated, to the formation of goethite or lepidocrocite. Synthetic products at pH 7 from Fe(NO₃)₃ and Fe(ClO₄)₃ were 2-line ferrihydrites irrespective of the presence of Si, and those from FeCl₂ were lepidocrocite in the presence and magnetite in the absence of Si.

The products from FeSO₄ at pH 12 yielded 4 diffraction lines for feroxyhyte. Either Si or Ge seemed to effect the formation of the mineral, because, in the absence of these cations at the same pH, the oxidation of Fe(II) never proceeded from the stage of green rust. Electron microscopic examination showed that ferrihydrite appears as shapeless assemblies of granular texture, and feroxyhyte consists of numerous “rod-like” particles about 4 nm wide and 70 nm long.

Key words: Ferrihydrite, feroxyhyte, Fe(II)-sulfate, particle morphology, synthesis.

INTRODUCTION

Ferrihydrite is a ferric hydroxide mineral represented by a chemical formula 5Fe₂O₃·9H₂O (Schwertmann and Taylor 1989). Its occurrence has been reported in a variety of environments (Childs 1992; Childs et al. 1990, 1991; Parfitt et al. 1988; Schwertmann and Taylor 1989), and its synthesis has successfully been attempted from ferric and ferrous systems (Schwertmann and Taylor 1989; Vempati et al. 1990). Feroxyhyte is a mineral name designated by Chukhrov et al. (1976) (see Fleischer 1977) to δ'-FeOOH which is a nonmagnetic, disordered member of δ-FeOOH. It has been reported to occur naturally in Fe-Mn marine nodules and in certain gleized soils (Chukhrov et al. 1976; see Fleischer 1977), in an ochreous band in sand from Finland (Carlson and Schwertmann 1980), and in a podsized coastal dune sand from Australia (Fitzpatrick 1988). Its presence has also been suggested on the surface of Mars (Burns 1980). So far as the authors ascertained, synthesis of feroxyhyte has been attempted by two groups of investigators: Chukhrov et al. (1976) (see Fleischer 1977), by oxidizing slowly the iron in Fe(OH)₂ in solutions at pH > 8 by simple contact with atmospheric air, and Carlson and Schwertmann (1980), by oxidizing dilute FeCl₂ solutions with concentrated H₂O₂ at pH
between 5 and 8.

In this paper, we report the synthesis of ferrihydrite and feroxyhyte in which a solution of FeSO₄ was used as the starting material, in the presence and absence of silicon (Si) or germanium (Ge). The purposes of the study were to know the roles of these cations in the formation and to differentiate the synthetic conditions of formation of these two minerals. Products synthesized at pH 7 from Fe(NO₃)₃ and Fe(ClO₃)₃ and those at pH 7 and 12 from FeCl₂ were also described.

METHODS

A 200 cm³ of 0.1 M FeSO₄ (5.6g of FeSO₄·7H₂O dissolved in 200 cm³ of water) was mixed with 20 cm³ of 0.1 M Si (30g of Na₂SiO₃·9H₂O dissolved in 1 L water) or with 40 cm³ of 0.05 M Ge (in 0.25 M NaOH), which was prepared by dissolving a mixture of 4g GeO₂ and 8g NaOH pellets in a small amount of water and then diluting with water to 800 cm³. The mixed solutions, and unmixed ones as well, were placed on a pH-stat (Commite-7 type Hiranuma Co. Ltd.) and maintained at pH 5 (4.95–5), 6 (5.95–6), 7 (6.95–7), 8 (7.95–8), 9 (8.95–9), 10 (9.95–10), 11 (10.95–11), and 12 (11.95–12) while stirring, with the addition of 0.1 M NaOH automatically, until the oxidation of Fe(II) to Fe(III) was complete. The precipitates formed were centrifuge-washed with water, ethanol, acetone, and air-dried, and subjected to analysis by X-ray diffraction (XRD) after ground to pass through 150 mesh sieve.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the products synthesized from FeSO₄ at pHs between 5 and 11. The patterns make essentially no difference and indicate ferrihydrite as the main product, with 6 to 7 diffraction peaks at 0.255, 0.245, 0.224, 0.197, 0.173, 0.151, and 0.147 nm (Brindley and Brown 1980, Schwertmann and Taylor 1989), of which the 111 peak (0.245 nm) is well-resolved only in the product at pH 7. The product at pH 5 showed some strong lines of goethite (0.414, 0.268, 0.250, and 0.158 nm), in addition to those for ferrihydrite. At further low pH (4), the product was almost totally goethite (pattern, not shown). Figure 2 is the XRD patterns of the products synthesized using Ge, in place of Si, at pHs between 6 and 9. The products showed the patterns similar to those of the Si members (Fig. 1), indicating ferrihydrite as the main product. The “crystallinity” of the product at pH 7 seems to be higher than the Si member formed at the same pH (Fig. 1), as judged from the relative intensity of each peak and the separation between the 110 (0.254 nm) and 111 (0.245 nm) peaks. The results may provide an evidence that Si (or Ge) is not in the structure of ferrihydrite, because, if it is, then the d-spacings of Si and Ge members should be different according to the ionic radii of the cations: the ionic radii are 0.26 and 0.400 nm for Si and 0.390 and 0.530 nm for Ge for four- and six-fold coordination, respectively (Liebau 1985). This is contrary to the hypotheses that Si may be incorporated into the structure of ferrihydrite (Eggleton and Fitzpatrick 1988; Vempati and Loeppert 1989; Vempati et al. 1990). Most probably, we can conclude that Si (or Ge) is not in the structure but forms Fe-O-Si (or Ge) at the periphery of the “domain” of.
FIG. 1. XRD patterns of ferrihydrites synthesized at pH 5–11 from FeSO₄ in the presence of Si (Fe:Si = 10:1). Spacings are shown in nm. The peaks at 0.14, 0.268, 0.250, and 0.158 nm are for goethite.
The presence of Si or Ge was a requisite for the formation of ferrihydrite, because the absence of these cations led, at the pHs investigated, to the formation of goethite or lepidocrocite without any trace of ferrihydrite (not shown).

In the present study, the procedure of Towe and Bradley (1967) for synthesis of 6-line ferrihydrite was followed in success (Fig. 3), and the result was nearly the same even with the addition of Si (12 cm$^3$ of 0.1 M Na$_2$SiO$_3$ mixed with 200 cm$^3$ of 0.1 M Fe(NO$_3$)$_3$)

ferrihydrite (Carlson and Schwertmann 1981; Parfitt et al. 1992).

Fig. 2. XRD patterns of ferrihydrites synthesized at pH 6–9 from FeSO$_4$ in the presence of Ge (Fe:Ge = 10:1). Spacings are shown in nm.
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FIG. 3. XRD patterns of ferrihydrites synthesized at pH 1.3 from Fe(NO₃)₃ in the absence of (Towe and Bradley 1967) and presence of Si (Fe:Ge = 10:1). Spacings are shown in nm. The diffraction effect at 0.328 nm is probably from lepidocrocite, and those at 0.421 and 0.269 nm are from goethite.

(Fig. 3). The final pH of the suspensions (mother solutions) was nearly the same, about 1.3, for both with and without Si added, in contrast to those with above pH 6 in which ferrous sulfate solution, with Si added, was used as source material (Fig. 1). This indicates that the formation of well-crystallized (6-line) ferrihydrite does not necessarily require the presence of Si (or Ge) depending on the kind of source materials, though the reason why ferric iron (nitrate) does not necessarily and ferrous iron (sulfate) does need the presence of Si (or Ge) for the formation of well-crystallized (6- or 7-line) ferrihydrite is not fully clear.

It is of interest in this respect that the underground waters from Aso, Kyushu and Tongariro, New Zealand, from which two-line siliceous ferrihydrites were deposited, contained 540–560 mg L⁻¹ of SO₄ in contrast to 76–105 mg L⁻¹ of Cl (Childs et al. 1990). The underground waters from Finland showed the similar pattern of anion composition, being dominated by SO₄ (Carlson and Schwertmann 1987). Also, all these underground waters were characterized by the presence of a large amount of ferrous iron (Childs et al. 1990; Carlson and Schwertmann 1987). It may be assumed thus that “direct” formation of ferrihydrite from ferric iron (Fe(NO₃)₃) does not necessarily need, while “indirect”
formation from ferrous iron (through oxidation of $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$) does need, the presence of Si (or Ge). However, the reason why the product from the former is well-crystallized (6-line), while that from the latter is poorly-crystalline (2- or 3-line), is still unclear, though there is a possibility that the presence of Si might have interfered with the development of crystallinity (Carlson and Schwertmann 1981) when ferrihydrite is formed from ferrous iron through its oxidation. Lower pH of formation (about 1.3) in the ferric solution might have been a reason of the formation of well-crystallized ferrihydrite (see next paragraph).

Synthetic work was also performed, at pH 7, from Fe(NO$_3$)$_3$, FeCl$_2$, and Fe(ClO$_4$)$_3$, in the same manner as that from FeSO$_4$ (Fig. 1). The precipitates formed from Fe(NO$_3$)$_3$ in the presence and absence of Si were 2-line ferrihydrite with haloes centered at 0.26 and 0.16 nm, being quite different from the product formed at about pH 1.3 (Fig. 3). The product from FeCl$_2$ in the presence of Si was mainly lepidocrocite with a small amount of

![XRD patterns](image)

**Fig. 4.** XRD patterns of ferrihydrite synthesized at pH 12 from FeSO$_4$ in the presence of Si(a) and Ge(b).

Spacings are shown in nm. The diffraction effects at 0.414 and 0.151 nm are probably from goethite.
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Fig. 5. Electron micrographs of ferrihydrite and feroxyhyte synthesized at pH 7 in the presence of Si and Ge (see Figs. 1 and 2 for XRD patterns).

Scale line: each print is approximately 50 nm.
goethite, and that in the absence of Si was almost pure magnetite (not shown), in contrast to ferrihydrite. The product from Fe(ClO₄)₃ was 2-line ferrihydrite with diffraction haloes at 0.26 and 0.16 nm, regardless of the presence of Si (not shown). Thus, at pH 7, none of the three salts used produced well-crystallized ferrihydrite (5-, 6-, or 7-line), and it seems that the kind of anions present may have exerted some effect on the type of the products.

The products from FeSO₄ at pH 12 yielded 4 diffraction lines at 0.254, 0.223, 0.170, and 0.147 nm, with or without weak ones at 0.416, 0.330, 0.270, 0.156 and 0.151 nm which may have come from goethite (Fig. 4). The lack of 0.45 and 0.31 nm, which are diffraction lines of δ-FeOOH, together with very faint diffraction at 0.198 nm may establish feroxyhyte as the product of synthesis (Chukhrov et al. 1976 (see Fleischer 1977); Eggleton 1988). Either Si or Ge seems to have effected the formation of the mineral, because, in the absence of these cations at the same pH, oxidation of Fe(II) never proceeded from the stage of green rust, indicating that the formation of feroxyhyte requires at least the presence of these cations though appropriate range of their concentration was not explored. Synthesis of feroxyhyte was attempted using FeCl₃ at pH 12 with and without Si added (Fe/Si = 10/1). The products were both green rust irrespective of the presence of Si. The results, together with those obtained at pH 7, were quite different from those of Carlson and Schwertmann (1980), even though the synthetic procedures were different. The reason for this is not known.

Formation of feroxyhyte also needed an alkalinity as high as above around pH 12. This may pose a problem for the formation of this mineral in soils. Its occurrences reported so far in soils are rather limited to peculiar environments, such as those in which Fe(II)-containing underground water is quickly oxidized (Chukhrov et al. 1976 (see Fleischer 1976); Carlson and Schwertmann 1980). Such a condition is not the case for most of soils occurring on the usual landscapes. Furthermore, soil reaction as high as pH 12 or higher is uncommon. It is concluded, therefore, that formation or occurrence of feroxyhyte is doubted in usual soils in light of the present experimental results.

Figure 5 shows the electron micrographs of the products at pH 7 (ferrihydrite) and pH 12 (feroxyhyte). It is seen that the particle morphology of ferrihydrite (prints a and b) and feroxyhyte (c and d) is very different from each other. The former appeared generally as shapeless mass consisted of spherules apparently 4–7 nm diameter, and there was no essential difference of morphology between Si- and Ge-members. The shapeless mass has been reported by Eggleton (1988) for ferrihydrite from Australia. On the other hand, feroxyhyte appeared as “rods” about 4 nm wide or thinner and about 70 nm long or shorter (Ge-feroxyhyte), or as a mixture of the “rods” and shapeless mass (Si-feroxyhyte). Such a “rod-like” particle has been reported for feroxyhyte from Finland (Carlson and Schwertmann 1980).

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