BONDING STATE OF SILICON IN NATURAL FERRIHYDRITES BY X-RAY PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

The bonding state and distribution of Si in five natural samples and one synthetic sample of "coprecipitated" siliceous ferrihydrite have been studied by X-ray photoelectron spectroscopy (XPS). For the natural samples, values of the Si 2s peak binding energy indicate that three-dimensional polymerisation of SiO₄ tetrahedra is, at most, only poorly developed. In contrast, the value for the synthetic "coprecipitated" sample suggests a significantly higher degree of three-dimensional SiO₄ polymerisation. For all of the natural samples the Fe/Si atomic ratio determined by XPS is comparable to, or slightly larger than, the average bulk ratio, indicating that the Si in these samples is well dispersed throughout or that the outer layers of the ferrihydrite aggregates are slightly depleted in Si. For the synthetic sample the Fe/Si XPS ratio is markedly smaller than the corresponding bulk ratio indicating surface precipitation of a Si-rich phase. Synthetic samples prepared by coprecipitation of Si and Fe may not be good models for natural siliceous ferrihydrites.

Key words: ferrihydrite, natural, synthetic, silicon, X-ray photoelectron spectroscopy, bonding state.

INTRODUCTION

Ferrihydrite, a poorly crystalline iron oxide mineral, is an important component of many surficial environments. Samples of ferrihydrite from soils and related environments commonly contain up to 9% Si but the location and function of Si have not been clearly defined (Childs, 1992 and refs. therein; Zhao et al., 1994; Manceau et al., 1995).

The primary particles of natural siliceous ferrihydrites are spheroidal with diameters ranging from 2 to 7 nm, and individual spherules are composed of 20–60 (Fe, O, OH, H₂O) structural domains (Childs, 1992; Parfitt et al., 1992). Electron micrographs show that spherules are associated into aggregates of up to several hundred microns in size (e.g. Childs et al., 1982, 1986, 1990; Schwertmann and Taylor, 1989).

Conventional and low-angle X-ray powder diffraction studies indicate that the Si in siliceous ferrihydrite is present as silicate that bonds to, and bridges, the surfaces of the structural domains within each primary particle (Parfitt et al., 1992). This model accounts
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for (i) the apparent chemical stability that silicate confers on the ferrihydrite structure even though it is not an essential structural component (Childs, 1992); (ii) the significant effect of Si content on the adsorption properties of ferrihydrites (Anderson and Benjamin, 1985); (iii) the ability of phosphate in solution to readily displace only a small fraction of the silicate from natural ferrihydrites although a slow reaction continues over time (Parfitt, 1989); and (iv) the inhibitory effect of Si on the thermal transition of natural ferrihydrites to hematite (Childs et al., 1993).

Here we have used X-ray photoelectron spectroscopy (XPS) to probe the nature of Si in five natural samples and one synthetic sample of ferrihydrite. Since the mean free path ("escape" depth) of electrons liberated in a sample by soft X-rays is a few nm (Defosse and Rouxhet, 1980; Paterson and Swaffield, 1994), XPS will "see" only the outer layers of ferrihydrite aggregates to a depth approximately equal to the size of a primary particle. Our results are compared with those of Vempati et al. (1990) who used samples synthesised in the laboratory by two alternative routes.

MATERIALS AND METHODS

Three previously characterised samples of natural siliceous ferrihydrite were investigated: PC863 from Kokowai Springs, New Zealand (Childs et al., 1986); PC991 from Tongariro National Park, New Zealand (Childs et al., 1982); and 1783 from Aso-Dani, Kumamoto, Japan (Childs et al., 1990). Two other natural samples, HF1 and HF2, were used. These were obtained from, respectively, Ferry Bank and Gibbons Creek, Hamilton, New Zealand, during a field tour associated with the 10th International Clay Conference (Lowe and Percival, 1993). A siliceous ferrihydrite, 9037, which exhibited seven lines in the X-ray diffraction pattern, was synthesised by stirring 200 ml 0.1 mol/l FeSO4 with 35 ml 0.1 mol/l Na2SiO3 at pH7 as described by Childs et al. (1993). All samples were lightly crushed to form powders for convenience of analysis.

X-ray photoelectron spectra were recorded on a Vacuum Generators ESCALAB 5 instrument using an AlKα X-ray source (12 kV, 5 mA) with an analyser pass energy of 50 eV. Sample powders were placed on double-sided adhesive tape fixed to a stainless steel sample holder. Electron energies were determined relative to the Au 4f7/2 binding energy (84.0 eV) of a gold film vacuum evaporated onto the sample. The uncertainty in the values of the electron binding energies is ±0.1 eV for both Si 2s and Fe 2p3/2. The Fe/Si ratio was calculated using atomic sensitivity factors of Fe 2p and Fe 3p lines relative to Si 2s, determined by experiment to be 10.2 and 0.99 respectively.

RESULTS AND DISCUSSION

Table 1 summarises XPS parameters for the samples studied and related minerals. The observed Fe 2p3/2 binding energies and Fe 2p line shapes (e.g. Fig. 1) are all similar to those for goethite and other FeOOH minerals, except for sample 1783 which has a relatively narrow Fe 2p3/2 line width (5.1 eV vs 5.6 eV) as well as a slightly different Fe 2p overall line shape. The reason for this exception is unknown.

All of the natural samples have a Si 2s peak binding energy of about 152.8 eV as
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TABLE 1. XPS data for ferrihydrites and related minerals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding energy/eV</th>
<th>Fe/Si atomic ratio</th>
<th>XPS</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe 2pₓ/₂</td>
<td>Si 2s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC863</td>
<td>711.4</td>
<td>152.8</td>
<td>7.7 ± 0.2</td>
<td>5.6ᵃ</td>
</tr>
<tr>
<td>PC991</td>
<td>711.3</td>
<td>152.7</td>
<td>7.5</td>
<td>4.4ᵇ</td>
</tr>
<tr>
<td>1783</td>
<td>711.4</td>
<td>152.8</td>
<td>4.7 ± 0.3</td>
<td>4.1ᶜ</td>
</tr>
<tr>
<td>HF1</td>
<td>711.3</td>
<td>153.1</td>
<td>2.1</td>
<td>2.3ᵈ</td>
</tr>
<tr>
<td>HF2</td>
<td>711.4</td>
<td>152.7</td>
<td>3.6</td>
<td>n.d.</td>
</tr>
<tr>
<td>9037</td>
<td>711.4</td>
<td>154.1</td>
<td>2.1</td>
<td>5.7ᵉ</td>
</tr>
<tr>
<td>olivine</td>
<td>n.a.</td>
<td>153.0ᵈ</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>quartz</td>
<td>–</td>
<td>154.4ᵈ</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FeO</td>
<td>709.5ᵍ</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>goethite</td>
<td>711.6ᵇ</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fe(II) silicates</td>
<td>710.4–710.8ᵃ</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fe(III) silicates</td>
<td>712.3–712.9ᵇ</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

n.a., not applicable to this work; n.d., not determined; ᵇ Childs et al. (1986); ᵇ Childs et al. (1982); ᵇ Childs et al. (1990); ᵇ Lowe and Percival (1993); ᵇ ratio used in synthesis, Childs et al. (1993); ᵇ Seyama and Soma (1985); ᵇ McIntyre and Zetaruk (1977); ᵇ Imai et al. (1991); ᵇ Seyama and Soma (1987), Soma et al. (1992).

shown in Fig. 2 for sample 1783. This value is close to that of olivine, a neosilicate with isolated SiO₄ tetrahedra, indicating the absence of a three-dimensional polymerised network of SiO₄ tetrahedra in natural ferrihydrites (Seyama and Soma, 1985). If such a component does exist in our samples, it can be, at most, poorly developed. This interpretation is supported by infrared spectroscopic data (Childs et al. 1982, 1986) which also provides evidence for a progressive increase in the proportion of Si-O-Si linkages with an increase in the sample Si/Fe ratio.

By comparison, the Si 2s peak binding energy for the synthetic sample (9037), at about 154.1 eV (Fig. 2), is significantly larger, and is close to that of quartz (Table 1). This sample apparently contains a component with a well developed three-dimensional SiO₄ network since, in general, the larger the Si 2s(2p) binding energy, the higher is the degree of three-dimensional SiO₄ polymerisation (Seyama and Soma, 1985).

For all of the natural samples the Fe/Si atomic ratio determined by XPS is comparable to, or (for PC863 and PC991) larger than, that of the bulk average (Table 1). We infer that the Si in natural ferrihydrites is well dispersed although the outer layers of the aggregates of PC863 and PC991 are somewhat depleted in Si. When a sub-sample of PC991 was thoroughly ground using a mortar and pestle the Fe/Si ratio determined by XPS decreased (from 7.5) to 5.4, approaching the bulk value of 4.4 (Table 1).

In line with the suggestions of Parfitt et al. (1992), based on X-ray diffraction data for samples PC863, PC991 and 1783 (see Introduction), we propose that silicate in natural siliceous ferrihydrites bonds to, and bridges between, surfaces of micro-crystalline domains within each primary particle. Silicate bridges may likewise form between the surfaces of
primary particles making up an aggregate as Naito et al. (1992) have postulated for zinc acetate dispersed in fine SiO$_2$ aggregates. Such bridges may have higher stability than silicate bound to only one surface and this could account for the apparent depletion of Si at the surface of aggregates of PC863 and PC991. Alternatively, the development of a relatively iron-rich phase on siliceous ferrihydrite could account for the depletion. Such a process seems unlikely here because the waters associated with the ferrihydrites at the time of sampling contained considerable amounts (35–75 g/m$^3$) of dissolved silica (Childs...
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Fig. 2. The Si 2s X-ray photoelectron spectra of ferrihydrites: (a) sample 1783 (natural) and (b) sample 9037 (synthetic).

et al., 1982, 1986, 1990). Kinetic factors, however, may be important in the deposition process.

In contrast to natural ferrihydrites, the Fe/Si XPS ratio for the synthetic sample (9037) is markedly smaller than the corresponding bulk value (Table 1). The surface enrichment of 9037 in Si may be ascribed to the development of silica-like layers on particle surfaces during preparation. This interpretation is supported by O 1s spectra. As shown in Fig. 3 the spectrum for 9037 has two peaks whereas that for sample 1783 has only one peak, although the asymmetric line shape for 1783 indicates the presence of more than a single O species. On the basis of binding energies in silicate minerals (Seyama and Soma, 1985), the peak with the higher binding energy can be assigned to O in a silica-like structure.

Earlier, Vempati et al. (1990) used XPS to characterise the bonding state of Si in Si-containing ferrihydrites synthesised by (i) adsorbing or precipitating silicate onto the surface of Si-free ferrihydrite, and (ii) coprecipitating silicate during the preparation of ferrihydrite. In order to compare our data with theirs, the Si 2p binding energy values, determined by Vempati et al., may be translated into the Si 2s equivalents by adding 51.0 eV, as verified in XPS measurements of silicate minerals. For their “coprecipitated” samples with Si/Fe atomic ratios ≥0.10 none of the Si 2s binding energies correspond to
our values for natural ferrihydrites (Table 1). Accordingly, the Si species with Si 2p
binding energy of 102.8 eV that Vempati et al. have likened to Si in layer silicates, is not
significantly present in the samples of natural ferrihydrites we have studied. Only one of
the three Si 2p binding energies (101.6 eV) that Vempati et al. reported for silicate
adsorbed onto ferrihydrite corresponds closely to the Si 2s binding energy of our natural
ferrihydrites. The full-width-at-half-maximum values that we observed for the Si 2s lines
of PC863, PC991 and 1783 were all 3.0 eV. This is only slightly larger than that for quartz
(2.8 eV), indicating that site variability is not a significant factor.
We conclude, firstly, that neither our synthetic sample 9037 nor the Si-containing
ferrihydrites synthesised by Vempati et al. (1990) are good models of the natural siliceous
ferrihydrites we have examined. Secondly, the Si in natural siliceous ferrihydrites is
present mainly as silicate bridging the surfaces of crystalline domains within primary
particles, and of primary particles within aggregates (Parfitt et al., 1992; Childs et al.,
1993; Zhao et al., 1994). The silicate does not form a three-dimensional network structure.
Rather, it exists, at most, as a poorly developed polymerised species.

REFERENCES
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