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6 Characterization of iron in floating surface 7 films of some natural waters using EXAFS

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1 **Abstract**

2 Floating, iron bearing films have been observed in a wide range of environments,
3 including wetlands, seep waters in ground water discharge areas, small rivers and
4 lakes. To date, knowledge about their formation and composition is scarce. We have
5 investigated the form of iron in floating iron-rich films of different origin, including
6 a pond and a brook, as well as seep water pools of a groundwater discharge area.
7 Sampling sites were located in southern (pond, brook) and central (seep pools)
8 Sweden. Synchrotron-based X-ray absorption spectroscopy (EXAFS and XANES)
9 allowed identification of the iron precipitates present in the films, without any
10 pretreatment. The EXAFS data showed that the iron containing phase formed in the
11 floating films varied in composition between the sites investigated. In the films
12 from two ground water discharge areas, characterized by out-flowing iron(II) rich
13 ground water being high in pH and low in DOC, the iron phase was completely
14 dominated by ferrihydrite. In contrast, surface films sampled from a brook and a
15 pond, the iron speciation showed a mixture of iron(III)-organic complexes and iron
16 (hydr)oxide (most likely ferrihydrite). These waters were oxic and contained higher
17 concentration of DOC than the seep water pools in the ground water discharge
18 areas. The position of the pre-edge peak, which is sensitive to the oxidation state of
19 iron, did not indicate occurrence of iron(II) in any of the films. Elemental
20 composition of one film (seep water), suggested that films contained about one third
21 of organic matter. Ferrihydrite is probably present as small particles with humic
22 material sorbed onto surfaces or included in the particles, making the particles
23 sufficiently hydrophobic to not settle without physical disturbance. The films are
24 fragile and break easily down and become suspended upon disturbance. More

1 studies are warranted in order to understand the mechanism of the formation of
2 these fascinating films and their biogeochemical role.

3 *Key words:* surface film, natural water, wetlands, iron, ferrihydrite, EXAFS

5 **1. Introduction**

6 Iron is an abundant element in aquatic systems, being essential for almost all
7 living organisms (Crichton, 2001). The environmental chemistry of iron is very
8 complex, involving hydrolysis, complexation and redox reactions. The free hydrated
9 iron(III) ion, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, starts to hydrolyze at low pH values (<2) and the
10 formation of oxyhydroxide precipitates restricts the solubility of iron(III) in most
11 natural waters. However, due to the ability of natural organic matter (NOM) to form
12 strong complexes with iron(III), the overall solubility of iron(III) can increase
13 substantially (Perdue et al., 1976; Tipping et al., 2002). Colloidal and particulate
14 iron(III) oxyhydroxide precipitates have a profound effect on the biogeochemistry
15 of many other elements, including phosphorus, arsenic, alkaline earth elements and
16 trace metals, e.g. Pb, Cr, Cu and Zn (Stolpe et al., 2005). Furthermore, Howitt et al.
17 (2004) showed that amorphous iron(III) oxyhydroxide might enhance the
18 photodegradation of NOM by up to one order of magnitude, stressing the strong link
19 between the iron and carbon turnover in aquatic systems.

20 There are different ways by which iron(III) oxyhydroxide precipitates can be
21 formed in aquatic systems. In lakes that seasonally become anoxic, particulate
22 iron(III) oxyhydroxides can be formed in the oxic-anoxic boundary (Davison,
23 1993). Here, iron(II) released from the anoxic sediments is being oxidized to

1 iron(III), which subsequently hydrolyses and precipitates as iron(III)
2 oxyhydroxides, preferably ferrihydrite. Another mechanism seems to be initiated by
3 the photochemically mediated reduction of iron(III) complexed by NOM (cf. humic
4 substances). Miles and Brezonik (1981) demonstrated that the reduction of added
5 iron(III) by humic substances was enhanced by irradiation with tungsten filament
6 lamps. The reduced iron(II) formed was subsequently re-oxidized by dissolved
7 oxygen to iron(III), which might precipitate as iron(III) oxyhydroxide. One possible
8 mechanism for reduction of complexed iron(III) involves a photolysis of the
9 iron(III)-NOM carboxylate complexes via a ligand-to-metal charge transfer,
10 resulting in the formation of iron(II) and carboxylate radicals (Gao and Zepp, 1998).
11 Recent modeling and EXAFS works lend some support to the view that iron(III)
12 binds mainly to carboxylic groups on NOM (Weber et al., 2006; van Schaik et al.,
13 2008; Karlsson et al., 2008).

14 One additional source of particulate iron(III) formed in aquatic systems might
15 be suspending of floating iron-rich films. Iron-bearing films are frequently found
16 around the world, particularly in wetlands and iron-rich seeps, but they might also
17 be formed in small rivers and lakes during periods of stagnant waters and daylight.
18 The films are often mistaken for oil, because of their oily appearance. However,
19 they easily break and start to settle upon physical disturbances by e.g. rain and
20 wind. These floating iron-rich films are poorly described in the literature. In a recent
21 study Grathof et al. (2007) characterized iron films found on ephemeral pools where
22 iron(II) rich groundwater has been discharged on sand deposits along the Oregon
23 coast. Their results suggest that the films contained hydroxides of both iron(II) and

iron(III) in a ratio of 1:3 and that this precipitate was a precursor to 2-line ferrihydrite.

The objective of the present work was to characterize the iron component in floating surface films formed in a wider range of environments. We sampled floating iron-rich surface films from a pond and a brook; as well as from pools originating from the discharge of groundwater from an esker. We used synchrotron-based X-ray absorption spectroscopy (EXAFS and XANES) allowing us to identify the iron precipitates present in the films, without any pretreatment.

2. Materials and methods

2.1. Site description

Sampling was performed at four sites in south-central Sweden. Fornby and Frostbrunnsdalen are two ground water discharge areas, located 4 km southeast Borlänge (N 60° 27', E 15° 28'), in central Sweden. They both originate from a large esker, i.e. a long, narrow ridge of stratified glacial sand and gravel deposits, Badelundaåsen. We sampled surface films of small water pools formed on the ground, as well as fresh iron precipitates (bottom sediment and precipitate on a leaf that was collected from the creek bed). The other two sites, a pond and a brook, are both located in a forested region in southernmost Sweden. The pond (Lillsjödäl; N 56° 03', E 13° 40') is about 75 x 100 m in size and sampling was made in the south-eastern corner of pond where it is about 60 cm deep. The brook flows into lake Filesjön (N 56° 05', E 13° 41') that is about 500 x 1000 m in size. Surface film and

1 water samples were taken 30 m before the inflow to the lake. The depth of the brook
2 is about 50 cm. At both sites there is a mixed forest consisting of Norway spruce
3 (*Picea Abies* (L.) Karst), Pine (*Pinus Silvestris* (L.)), Oak (*Quercus robur* (L.)) and
4 European beech (*Fagus Sylvatica* (L.)). The major soil type is Haplic Podzol
5 developed on sandy loamy tills with low clay contents.

6 7 2.2. Field sampling

8 Sampling at Fornby and Frostbrunnsdalen was made on 4 May 2005. The
9 floating surface films (Figs. 1 and 2) were collected by gently draining the film into
10 a borosilicate bottle. The bottle was kept with its opening just below the surface
11 allowing the top-millimeter of the water and its film to be collected. As noted by
12 Grathoff et al (2007) the film easily breaks into small plates or “shards” when
13 physically disturbed. Upon arrival in the laboratory, the suspended film materials
14 were collected on a 0.2 µm membrane filter (Pall Corporation, Supor-450) through
15 vacuum filtration. We also sampled the slimy pile of iron precipitates at the Fornby
16 well (Fig. 2) and a leaf with iron precipitates at Frostbrunnsdalen well (Fig. 1).
17 Filter papers and samples were stored cold (+2 °C) and dark in polyethylene plastic
18 bags until EXAFS analysis (May 11, 2005). Water samples for a general chemical
19 characterization were sampled using polypropylene bottles.

20 Samplings of floating surface films at Lillsjödalen and Filesjön were made by
21 placing a cellulose based filter paper (Munktells OHK, Falun Sweden) on the water
22 surface; one collection per filter paper. The film was adhering to the filter paper.
23 The filter paper was sealed in a polyethylene plastic bag, which was kept dark and

1 cold until analysis. EXAFS analysis was made 6-8 hours after sampling on May 11,
2 2005. Water was sampled from both sites using polypropylene bottles. The content
3 of oxygen in the top 40 cm of the water columns was measured in the field using a
4 portable oxygen analyzer, OxyGuard, Handy Mk III.

6 2.3. *Standard chemical analyses*

7 Water samples were analyzed for pH, major cations and dissolved organic
8 carbon (DOC). pH was determined with a Radiometer glass electrode, GK2401C. A
9 portion of the samples was filtered (0.45 μm) and analyzed for Na, K, Mg, Ca, Fe
10 and Mn using ICP-AES, Perkin Elmer OPTIMA 3000 DV. The concentrations of
11 dissolved organic carbon were determined on a fully automated Shimadzu TOC-
12 VCPH analyzer. Carbon and nitrogen content of dried film and precipitates were
13 measured using a LECO CN-2000 analyzer. The iron, aluminum and manganese
14 concentrations in these materials were measured on an atomic absorption
15 spectrophotometer (Perkin Elmer AAnalyst 300), following dissolution in 7
16 $\text{mol}\cdot\text{dm}^{-3}$ nitric acid at 120 °C for 2.5 hrs.

17 The geochemical computer program Visual MINTEQ ver. 2.61 (Gustafsson,
18 2010) was used to evaluate possible mineral formation. Complexation by dissolved
19 organic ligands was accounted for by assuming 70% of DOC being fulvic acids,
20 having a carbon content of 50% (default assumption). The temperature was set to 10
21 °C. The saturation index (SI) was used to evaluate possible mineral equilibrium. SI
22 is defined as

$$23 \quad \text{SI} = \log IAP/K_{\text{so}}$$

1 where IAP denotes the ion activity product and K_{so} the solubility product. Positive
2 values of SI indicate supersaturation with respect to the mineral of interest, zero
3 values indicate equilibrium and negative values under-saturation.

4 5 2.4. EXAFS

6 2.4.1. Sample preparation

7 The filters, leafs and sediments were put in a sample holder without any
8 further preparation. Reference materials, 2-line ferrihydrite, goethite, lepidocrocite
9 and hematite, were prepared according to standard procedures (Schwertmann and
10 Cornell, 2000). We also measured a bog ore sample obtained from the bog ore
11 collection of the Porfyr- & Hagströmmuseet, Älvdalen, Sweden (www.alvdalen.se).
12 The synthesized iron(III) minerals and the bog ore samples were diluted with boron
13 nitride and pressed into 1-2 mm thick metal frames.

14 2.4.2. Data collection

15 The iron K-edge X-ray absorption spectra was recorded at the wiggler beam-
16 line I811 at MAX-lab, Lund University, Sweden. The beam-line was equipped with
17 a Si[111] double crystal monochromator, the storage ring operated at 1.5 GeV and a
18 maximum current of 200 mA was used. Higher-order harmonics were reduced by
19 detuning the second monochromator crystal to reflect 40% of maximum intensity at
20 the end of the scans. Internal calibration was performed by simultaneously
21 recording the XAS spectrum of an iron metal foil. The data collection was
22 performed in transmission mode for the reference samples synthetic ferrihydrite,
23 goethite, hematite and lepidocrocite and the bog ore sample, while fluorescence

mode using a Lytle detector with a manganese filter was applied for the other samples. All measurements were carried out at ambient room temperature.

2.4.3. Pre-edge Data Analysis

The pre-edge in the region 7109-7116 eV was subtracted from the background fitted with a sixth order polynomial from the energy ranges 7000-7109 and 7116-7120 eV.

2.5.4 EXAFS Data Analysis

The primary treatment (energy calibration and averaging) of the EXAFS data was performed with the EXAFSPAK program package (George and Pickering, 1993). The energy scale of each X-ray absorption spectrum was calibrated by assigning the first inflection point of the K edge of metallic iron foil as 7111.3 eV (Thompson et al., 2001). After primary data treatment, the EXAFSPAK (George and Pickering, 1993) and GNXAS (Filipponi et al., 1995; Filipponi and Di Cicco, 1995) program packages were used for further data treatment. The GNXAS code is based on calculation of the EXAFS signal and subsequent refinement of the structural parameters (Filipponi et al., 1995; Filipponi and Di Cicco, 1995). The GNXAS method accounts for multiple scattering (MS) paths by including the configurational average of all the MS signals to allow fitting of correlated distances and bond distance variances (Debye-Waller factors). A correct description of the distribution of the Fe-O distances in a coordination shell should in principle account for asymmetry (Hedin and Lundkvist, 1971; Filipponi, 1994).

In the refinement of the EXAFS data of ferrihydrite the Fe···Fe distances, the Debye-Waller factor coefficients and the number of Fe···Fe distances were allowed

1 to vary simultaneously in spite of the strong correlation between the latter. The
2 obtained the Debye-Waller factor coefficients were then used as fixed parameters in
3 the refinement of the natural samples, in order to evaluate the number of Fe...Fe
4 distances.

5 The standard deviations given for the refined parameters were obtained from
6 k^3 -weighted least squares refinements of the EXAFS function $\chi(k)$, and do not
7 include systematic errors of the measurements. These statistical error values provide
8 a measure of the precision of the results and allow reasonable comparisons of e.g.
9 the significance of relative shifts in the distances. However, the variations in the
10 refined parameters, including the shift in the E_0 value, for which $k = 0$, using
11 different models and data ranges, indicate that the absolute accuracy of the distances
12 given for the separate complexes is within ± 0.005 to $0.02 \text{ \AA}$ for well-defined
13 interactions. The 'standard deviation' values given in the text have therefore been
14 increased accordingly to include estimated additional effects of systematic errors.

16 **3. Results**

17 The seepage waters at Fornby and Frostbrunnsdalen were moderately hard
18 with pH values of 7.6 and 8.1, respectively (Table 1). The concentration of DOC
19 was about the same, 4.9 and 8.6 mg/l, whereas the iron concentration differed
20 markedly. In Fornby the iron concentration was only 0.08 mg/l compared to 1.2
21 mg/l in Frostbrunnsdalen. Unfortunately, we did not determine the individual
22 concentrations of iron(II) and iron(III), respectively, but thermodynamic
23 calculations suggest that solutions were near equilibrium (Fornby) or slightly

1 oversaturated (Frostbrunnsdalen) with respect to amorphous ferrihydrite ($\log K_{so} =$
2 3.20), even if we assume that only 1% of total concentration of iron was iron(III)
3 (Table 1). Accordingly, it is likely that ferrihydrite could be formed in these waters.
4 Among the two surface waters, Filesjön brook had the highest iron concentration
5 6.7 mg/l, compared to 0.3 mg/l in Lillsjödäl pond (Table 1). The DOC concentration
6 was also higher in Filesjön brook (33 mg/l) than in Lillsjödäl (13 mg/l), whereas pH
7 was lower. Field measurements of dissolved oxygen content showed that oxic
8 conditions (>50% saturation) occurred in waters at the Lillsjödäl and Filesjön sites
9 (Table 1).

10 In order to characterize the iron minerals present in the natural samples
11 studied, EXAFS data of goethite, lepidocrocite and hematite were collected and
12 refined (Table 2 and Fig. S1), and found to be in good agreement with reported
13 crystal structures (Table S1). The EXAFS data were also collected on 2-line
14 ferrihydrite, and the data analysis gave Fe-O and Fe $\cdots$ Fe distances in agreement
15 with previous studies (Mikutta et al. 2010; Mikutta, 2011; Cismasu et al., 2011).
16 Two Fe $\cdots$ Fe distances at 3.03 Å and 3.49 Å were identified (Table 2), representing
17 edge and double corner-sharing Fe atoms (Michel et al., 2007). The number of
18 Fe $\cdots$ Fe distances became larger in this study, 2.2 and 4.3, than reported by Mikutta
19 et al. (2010), 1.4 and 1.3, respectively. Our higher values seem more reasonable
20 assuming that the build-up of ferrihydrite as FeO₆ octahedra linked into the layer or
21 sheets (Eggletton and Fitzpatrick, 1988) is correct. However, we could not find any
22 evidence for tetrahedral iron sites as proposed to be present in ferrihydrite (Eggletton
23 and Fitzpatrick, 1988). In a recent study Mikutta (2011) found the number of Fe $\cdots$ Fe

distances at 3.03 Å and 3.47 Å to be higher, 3.4 and 1.7, respectively, illustrating the variability of the ferrihydrite structure at the nanoscale.

In the samples from the two ground water discharge areas, Fornby and Frostbrunnsdalen, as well as in the bog ore sample, it was not possible to detect any iron compounds beside the inorganic iron mineral, certainly strongly dominated by ferrihydrite. This was true for both the floating surface films and the precipitates. Normalized k^3 -weighted EXAFS spectra for iron in the natural samples, together with the reference materials are presented in Fig. 3, and the corresponding Fourier-transforms are presented in Fig. 4. The main difference between the natural samples and ferrihydrite is that the number of Fe···Fe distances was lower in the natural samples than in **synthetic** ferrihydrite (Table 2 and 3), indicating that the ferrihydrite formed in these environments had a slightly more distorted structure than synthesized 2-line ferrihydrite. Although ferrihydrite was doubtless the dominating iron phase in these samples, minor contents of other iron(III) oxide/hydroxide minerals cannot be excluded. Attempts to include a Fe···C distance and the corresponding 3-leg Fe-O-C back-scattering path in the model were not successful for the Fornby and Frostbrunnsdalen samples, and refinements resulted in unrealistic distances with very large Debye-Waller factor coefficients.

In the surface films from Lillsjödäl and Filesjön there was a significant contribution from a Fe···C distance and the corresponding Fe-O-C three leg back-scattering, besides a contribution from an iron(III) (hydr)oxide mineral. The fraction of iron(III) bound by NOM in the Filesjön and Lillsjödäl samples was estimated to be 60% and 70%, respectively (Figure S2), based on a linear combination fit using

1 the EXAFS spectra for ferrihydrite and iron(III) fulvic acid complex in Figure 3 as
2 end-members. Using these estimates of iron(III)-NOM and ferrihydrite contents, the
3 scattering path distances for Fe···C, Fe-O-C and Fe···Fe were refined and found to
4 be in reasonable agreement to those of pure systems (Table 3). The data quality of
5 these two film samples is fairly poor due to small amounts of materials collected,
6 and refinements were only possible out to $k = 9 \text{ \AA}^{-1}$, causing large uncertainties in
7 the structure parameters (Table 3). Only the shorter Fe···Fe distance could be
8 observed, and assessing the kind of iron(III) mineral becomes therefore uncertain,
9 but a likely candidate is ferrihydrite. The shorter Fe···Fe distance corresponds to the
10 distance of octahedral edge-sharing iron geometries present in ferrihydrite, as
11 mentioned above. A possible contribution from di- or trimeric polynuclear iron
12 complexes would give substantially longer Fe···Fe distances (Gustafsson et al.,
13 2007).

14 The position of the pre-edge in the X-ray absorption spectra can be used to
15 assess the oxidation state of iron in a sample (Petit et al., 2001). The pre-edge peak
16 for all the natural samples was almost identical with a maximum at 7113.2 eV (Fig.
17 5), which is close to that of hydrated iron(III) and ferrihydrite (7113.4 eV), and
18 significantly higher than that of hydrated iron(II) (7111.5 eV), confirming that the
19 iron in the studied precipitates has the oxidation state +III.

20 Elemental composition could only be determined on the film from Fornby
21 well, due to small amounts of film materials at the other sites. The analysis showed
22 that iron was the main constituent (19%), followed by carbon (14%) and aluminum
23 (0.3%) (Table 4). The low carbon-to-nitrogen molar ratio (17), suggest that the

1 major part of the carbon is organic. Thus, about 40% of the film constituted of
2 ferrihydrite, and about 30% of organic matter (assuming a carbon content of 50%).
3 A major fraction of the remaining mass could probably be attributed to strongly
4 bound water, and to some extent silicate precipitates. For example, Grathoff et al.
5 (2007) found a Fe:Si ratio of 3 to 1 in films of ephemeral pools sampled near the
6 Oregon coast, U.S.A. Bottom precipitates sampled at Fornby well had a very similar
7 elemental composition as the corresponding film material (Table 4). The elemental
8 composition of the bog ore sample resembled the Fornby samples closely.

9
10

1 **4. Discussion**

2 The EXAFS data show that the iron containing phase formed on the surfaces
3 of the natural waters varied in composition between the sites investigated. In the
4 two ground water discharge areas, Fornby and Frostbrunnalen, the films sampled
5 were completely dominated by ferrihydrite, whereas in the Filesjön brook and the
6 Lillsjödal pond, the films consisted of a mixture of iron complexes with NOM and
7 iron (hydr)oxide (likely ferrihydrite). At the Fornby and Frostbrunnalen sites the
8 films probably contained small particles of ferrihydrite, with humic material sorbed
9 onto surfaces or contained in the particles, making the particles sufficiently
10 hydrophobic to not settle without physical disturbance. An indicator of the
11 important role of NOM in film formation is the high organic carbon content of the
12 Fornby film (14%). At all four sites, the films were fragile, broke down easily and
13 became suspended in solutions upon disturbance, which is in accordance with the
14 findings of Grathoff et al. (2007).

15 Of the four iron (hydr)oxides investigated in this study, ferrihydrite is the
16 most soluble one, and thus least stable from a thermodynamic point of view
17 (Lindsay, 1991). Accordingly, its formation must be kinetically favorable compared
18 to the other mineral phases. Ferrihydrite has been found in many natural
19 environments, including hydromorphic and podzolic soils (Cornell and
20 Schwertmann, 2003; Prietzel et al., 2007), rivers (Konhauser and Ferris, 1997),
21 ground water discharge areas (Cornell and Schwertmann, 2003), and lake sediments
22 (Toevs et al., 2006). Dependent on environmental conditions, ferrihydrite is
23 transformed to goethite or hematite with time (Schwertmann and Fitzpatrick, 1992),

1 although this process can be hampered by sorption of NOM (Schwertmann, 1961;
2 Eusterhues et al., 2008). Thus, a relatively high organic matter content, as observed
3 in the Fornby film (Table 4), will contribute to stabilization of ferrihydrite relative
4 to the more crystalline iron (hydr)oxide phases. Furthermore, sorption of NOM
5 might affect the size of ferrihydrite particles by hampering the nucleation or
6 polymerization reactions, favoring the formation of small ferrihydrite nanoparticles
7 (Mikutta, 2011; Cismasu et al., 2011).

8 The chemical form of iron in floating surface films of natural waters is poorly
9 described in the literature. The most relevant study is the one by Grathoff et al.
10 (2007), who investigated iron in surface films of ephemeral pools near the Oregon
11 coast, U.S.A.. They proposed that the iron-bearing films contained a mixture of
12 iron(II) and iron(III), at a molar ratio of 1:3. Two-line ferrihydrite was identified in
13 their films by X-ray diffraction analysis (XRD), but acidic dissolution of films and
14 subsequent quantification of iron(II) and iron(III) suggested the presence of the
15 former oxidation state. The latter is in contrast to results in this study, where neither
16 the EXAFS spectra (Figs. 3 and 4) nor the pre-edge positions (Fig. 5) indicate any
17 occurrence of iron(II) in any of our samples. One possible reason for the
18 discrepancy in results regarding oxidation state of iron obtained with the acidic
19 dissolution method on one hand, and the XRD and EXAFS results on the other,
20 could be that former method was applied in the field whereas samples analyzed by
21 the latter two methods was handled in open atmosphere during the time between
22 sampling and analyses. Thus, possible iron(II) phases originally present in the
23 samples could have been oxidized to iron(III), even though this time was kept to a

1 minimum (e.g. 6-8 hours for the Fiesjö and Lillsjödal samples). However, also the
2 acidic dissolution method might have been subjected to artifacts. Grathoff et al.
3 (2007) dissolved films in $0.1 \text{ mol} \cdot \text{dm}^{-3}$ hydrochloric acid prior to analysis of iron(II)
4 and iron(III) in the laboratory, a technique which could have overestimated the
5 content of iron(II). It has been shown that natural organic matter can reduce iron(III)
6 to iron(II) in acidic solutions (Deiana et al., 1995; van Schaik et al., 2008), and it is
7 likely that some organic matter originating from the films was dissolved in the
8 hydrochloric acid. Furthermore, some of the iron(II) might have been bound by the
9 resident organic matter in films, electrostatically and/or as a complex, thus not being
10 a true component of the film structure itself.

11 During the last decades evidence has been presented to prove the existence of
12 a mixed-valent iron hydroxycarbonate green rust ($\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{CO}_3$) mineral in
13 in a range of natural environments in which redox conditions are being close to the
14 Fe(II)/Fe(III) transition zone; e.g. hydromorphic soils (Trolard et al., 1997) and
15 deep ground waters (Christiansen et al., 2009). However, this mineral is highly
16 reactive in oxic environments and will be transformed to oxidized iron mineral
17 forms within minutes (Christiansen et al., 2009; Ruby et al., 2010). Depending on
18 the solution composition and the rate of oxidation, goethite, magnetite or ferric
19 oxyhydroxycarbonate seem to be the main end-products formed (Benali et al., 2001;
20 Ruby et al., 2010). Since floating surface films are exposed directly to the
21 atmosphere it is unlikely that a mineral like iron^{II-III} hydroxycarbonate green rust
22 can be present in any significant amount in such films. Furthermore, at the Fiesjö
23 and Lillsjödal sites oxic conditions prevailed in the water bodies, making the

1 occurrence of iron^{II-III} hydroxycarbonate green rust even more unlikely at these
2 sites.

3 It is well established that ferrihydrite can be formed in natural systems by
4 oxidation of iron(II) to iron(III), which subsequently hydrolyzes and precipitates as
5 ferrihydrite. This reaction occurs for example when ground water reaches the
6 surface (Cornell and Schwertmann, 2003) or in the oxic-anoxic boundary in lakes
7 where iron(II) released from the anoxic sediments is being oxidized to iron(III)
8 (Davison, 1993). In the seep water pools at Fornby and Frostbrunnaldalen sites,
9 ferrihydrite in films was most likely formed by this mechanism. The rich occurrence
10 of ferrihydrite precipitates on the bottom of the pools, clearly visible in Fig. 2, is
11 indicative for out-flowing iron(II)-rich ground water. Following oxidation of
12 iron(II) and the formation of small ferrihydrite particles, sorption of dissolved
13 humic compounds might have increased the hydrophobicity and thereby the
14 tendency to “float”. The oxidation processes should be most intense near the water
15 surface where the dissolved oxygen concentration is highest.

16 The conditions in the Filesjön brook with high DOC concentration, 33 mg/L,
17 clearly oxic conditions, and relatively low pH, 6.5, but also in the Lillsjödal pond
18 with relatively high DOC, 13 mg/L, and oxygen saturation, the formation of
19 iron(III)-NOM complexes was favored and the formation of ferrihydrite thereby
20 suppressed. This is in line with the results of recent study of model systems
21 containing iron(III) and isolated, purified humic acids (Karlsson and Persson, 2010).
22 It was found that the humic acids strongly suppressed the formation of iron(III)
23 (hydr)oxides, but at high mass ratios of iron to humic acids and at pH > 5, iron was

found to be present as a mixture of mononuclear iron(III)-humic acid complexes and iron(III) (hydr)oxides. Also at these sites inflowing ground water could have been a source for iron(II). However, the water bodies are larger and oxic conditions occurred deeper through the water body (Table 1). In this case, light induced redox reactions occurring near the surface might also have played a role in the surface film formation. It has been shown that particulate iron(III) can form in a redox cycle involving photochemical reduction of organically bound iron(III) and a subsequent re-oxidation of iron(II) to iron(III) by O₂ (Stumm and Lee, 1961; Miles and Brezonic, 1981; Gao and Zepp, 1998). However, the chemical state of iron formed in this way is somewhat unclear and probably dependent on chemical and light conditions. According to results obtained by Gao and Zepp (1998), the conversion of dissolved to particulate forms of iron(III) might be substantial following irradiation (ca. 45%). A mechanism where sunlight driven photochemical processes play a role in film formation is logical in that respect that energy of irradiation is highest in the top millimeter and then decreases with depth in the water body.

5. Conclusions

The EXAFS data showed that the iron containing phase in the floating films varied in composition between the sites investigated. In the two ground water discharge areas, characterized by out-flowing iron(II) rich ground water being high in pH and low in DOC, ferrihydrite is the completely dominating iron phase. The films were surprisingly rich in organic carbon (ca. 15%), which probably largely affected the physico-chemical properties of the films. Sorption of NOM might

1 decrease the size of ferrihydrite particles and increasing their hydrophobicity. In
2 contrast, surface films sampled from the brook and the pond, consisted of a mixture
3 of iron(III)-NOM complexes and iron (hydr)oxide (most likely ferrihydrite). These
4 waters were oxic and contained higher concentration of DOC than the seep water
5 pools in the ground water discharge areas. Our data did not indicate occurrence of
6 iron(II) in any of the films. However, samples were handled in open atmosphere
7 prior to analysis and extremely redox labile iron(II) containing phases, such as
8 iron^{II-III} hydroxycarbonate green rust, would have been oxidized during the time
9 between sampling and analysis. On the other hand, the high reactivity of such a
10 phase in oxic environments makes it unlikely for them to exist in any significant
11 amount in floating surface films because they are directly exposed to the
12 atmosphere. Thus, we believe that the term “mixed-valent iron films”, as proposed
13 by Grathoff et al. (2007) for floating iron rich films, should be used with care.
14 However, more research is needed to explore the mechanisms of the formation of
15 and the environmental role of floating surface films in different kinds of natural
16 environments.

18 **Appendix A. Supplementary data**

20 Supplementary materials related to this article can be found online at
21 <http://dx.doi.org/10.1016/j.chemgeo.2012.06.012>.

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15

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3 **Fig. 1.** The sampling location at the Frostbrunnssdalen well. The surface film
4 corresponds to the sample “Frost film”.

5

6

7 **Fig. 2.** The sampling location at the Fornby well. The surface film corresponds to
8 the sample “Fornby film” and the slimy pile of iron precipitates to “Fornby pile”.

9

Fig. 3. Stacked, normalized k^3 -weighted EXAFS spectra for iron in natural films and precipitates. The spectra for synthetic 2-line ferrihydrite, goethite, lepidocrocite, and hematite are given for comparison. Black lines are measured data and thin red lines are model fits using the structural data given in Table 2 (reference materials) or Table 3 (natural samples). Also shown is the spectra of iron(III) complexed by a fulvic acid at pH 4.0 (van Schaik et al., 2008).

Fig. 4. Stacked Fourier transforms from the k^3 -weighted EXAFS spectra for iron in natural films and precipitates. The spectrum for synthetic 2-line ferrihydrite is given for comparison. Black lines are measured data and thin red lines are model fits using the structural data given in Table 2 (reference materials) or Table 3 (natural samples).

Fig. 5. Pre-edges for samples and ferrihydrite after subtraction of back-ground. The reference spectra for Fe^{2+} and Fe^{3+} were obtained by measurements on solutions containing 0.5 M $\text{Fe}(\text{ClO}_4)_2$ (pH 4) and 0.5 M $\text{Fe}(\text{ClO}_4)_3$ (pH 1), respectively.

1 **Table 1**

2 Chemical composition of water samples. Also given is the saturation index (SI) for
 3 amorphous ferrihydrite, assuming 100%, 10% or 1% of total iron concentrations
 4 being iron(III) (see text for calculations and assumptions). Positive values indicate
 5 super-saturation, zero equilibrium and negative under-saturation.

	Fornby well	Frostbrunnssdalen well	Lillsjödalen pond	Filesjön brook
O ₂ (mg/l)*	ND**	ND	10.2/10.1	6.8/5.0
O ₂ (% saturation)*	ND	ND	104/103	73/51
pH at 20 °C	7.6	8.1	8.0	6.5
DOC (mg/l)	4.9	8.6	13	33
IC (mg/l)	37	26	20	5.8
Na (mg/l)	7.2	5.1	7.0	7.4
K (mg/l)	4.9	3	3.3	0.9
Ca (mg/l)	56	41	37	16
Mg (mg/l)	6.7	3.6	3.8	2.8
Fe (mg/l)	0.03	1.2	0.3	6.7
Mn (mg/l)	<0.01	<0.01	0.2	1.0
SI, 100% Fe(III)	2.2	5.1	3.6	4.2
SI, 10% iron(III)	0.5	3.3	1.8	1.8
SI, 1% iron(III)	-0.8	1.6	0.3	0.0

6 *Measured in the field at 5 and 40 cm below the surface (5 cm/40 cm).

7 **Not determined

8

Table 2

Mean bond distances (d), Debye-Waller factor coefficients (σ^2), number of distances (N) and the amplitude reduction factor (S_o^2) for the reference minerals. The values are given with $\pm$ one standard deviation; parameters without a given error have been held fixed.

Sample	Interaction S_o^2	$d/\text{\AA}$	$\sigma^2/\text{\AA}^2$	N
<i>Ferrihydrite</i>	Fe-O	1.962 $\pm$ 0.002	0.0086 $\pm$ 0.0002	6
	0.88 $\pm$ 0.02			
	Fe $\cdots$ O	3.750 $\pm$ 0.007	0.010 $\pm$ 0.001	8.9 $\pm$ 0.8
	Fe $\cdots$ Fe	3.031 $\pm$ 0.003	0.0092 $\pm$ 0.0004	2.2 $\pm$ 0.1
	Fe $\cdots$ Fe	3.487 $\pm$ 0.008	0.0112 $\pm$ 0.0004	4.3 $\pm$ 0.3
	MS(FeO ₆)	3.93 $\pm$ 0.08	0.027 $\pm$ 0.002	3x6
<i>Goethite</i>	Fe-O	2.003 $\pm$ 0.004	0.0122 $\pm$ 0.0007	6
	0.88 $\pm$ 0.02			
	Fe $\cdots$ O	3.90 $\pm$ 0.03	0.031 $\pm$ 0.007	10
	Fe $\cdots$ Fe	3.020 $\pm$ 0.005	0.0022 $\pm$ 0.0005	2
	Fe $\cdots$ Fe	3.21 $\pm$ 0.02	0.006 $\pm$ 0.001	2
	Fe $\cdots$ Fe	3.430 $\pm$ 0.007	0.0070 $\pm$ 0.0007	4
	Fe $\cdots$ Fe	4.64 $\pm$ 0.02	0.008 $\pm$ 0.001	2
<i>Hematite</i>	Fe-O	1.953 $\pm$ 0.005	0.0102 $\pm$ 0.0009	6
	0.86 $\pm$ 0.02			
	Fe $\cdots$ O	3.76 $\pm$ 0.04	0.04 $\pm$ 0.02	9
	Fe $\cdots$ Fe	2.948 $\pm$ 0.004 ^a	0.0047 $\pm$ 0.0005 ^a	4
	Fe $\cdots$ Fe	3.332 $\pm$ 0.008	0.0052 $\pm$ 0.0009	3
	Fe $\cdots$ Fe	3.71 $\pm$ 0.03	0.006 $\pm$ 0.002	6
<i>Lepidocrocite</i>	Fe-O	1.989 $\pm$ 0.002	0.0074 $\pm$ 0.0005	6
	0.93 $\pm$ 0.02			
	Fe $\cdots$ O	3.61 $\pm$ 0.03	0.018 $\pm$ 0.004	6
	Fe $\cdots$ O	4.00 $\pm$ 0.02	0.010 $\pm$ 0.003	4
	Fe $\cdots$ Fe	3.071 $\pm$ 0.003	0.0055 $\pm$ 0.0002	6
	Fe $\cdots$ Fe	3.91 $\pm$ 0.02	0.010 $\pm$ 0.005	2
	Fe $\cdots$ Fe	4.845 $\pm$ 0.018	0.016 $\pm$ 0.002	6
	Fe $\cdots$ Fe	5.38 $\pm$ 0.02	0.018 $\pm$ 0.003	4

^a Average value for the two shortest Fe $\cdots$ Fe distance

Table 3

Summary of structural parameters for natural samples. Mean bond distances (d) for Fe-O and Fe...Fe interactions are given, together with the number of distances (N), the corresponding Debye-Waller factor coefficients (σ^2) and the amplitude reduction factor (S_o^2). The values are given with $\pm$ one standard deviation; parameters without a given error have been held fixed.

Sample/k range	Interaction	$d/\text{\AA}$	$\sigma^2/\text{\AA}^2$	N	S_o^2
<i>Filesjön brook, film</i> 2.0-9.0	Fe-O	1.997 $\pm$ 0.004	0.0108 $\pm$ 0.0010	6	0.92 $\pm$ 0.02
	Fe...C	2.80 $\pm$ 0.02	0.013 $\pm$ 0.003	2 $\pm$ 1	
	Fe-O-C	2.93 $\pm$ 0.03	0.011 $\pm$ 0.004	4 $\pm$ 2	
	Fe...Fe	3.01 $\pm$ 0.04	0.0093 $\pm$ 0.0004	1.4 $\pm$ 0.4	
	MS(FeO ₆)	3.94 $\pm$ 0.03	0.016 $\pm$ 0.005	3x6	
<i>Lillsjödäl pond, film</i> 2.0-9.0	Fe-O	1.983 $\pm$ 0.007	0.0164 $\pm$ 0.0009	6	0.93 $\pm$ 0.02
	Fe...C	2.78 $\pm$ 0.02	0.008 $\pm$ 0.003	1 $\pm$ 1	
	Fe-O-C	2.94 $\pm$ 0.03	0.011 $\pm$ 0.004	2 $\pm$ 1	
	Fe...Fe	3.04 $\pm$ 0.05	0.009 $\pm$ 0.001	1.8 $\pm$ 0.4	
	MS(FeO ₆)	3.94 $\pm$ 0.03	0.011 $\pm$ 0.007	3x6	
<i>Fornby, pile</i> 2.0-11.7	Fe-O	1.990 $\pm$ 0.002	0.0059 $\pm$ 0.0002	6	0.86 $\pm$ 0.02
	Fe...O	3.47 $\pm$ 0.03	0.0100	5.1 $\pm$ 0.6	
	Fe...Fe	3.095 $\pm$ 0.003	0.0092	1.7 $\pm$ 0.2	
	Fe...Fe	3.380 $\pm$ 0.007	0.0112	2.3 $\pm$ 0.7	
	MS(FeO ₆)	3.96 $\pm$ 0.03	0.028 $\pm$ 0.001	3x6	
<i>Fornby, film</i> 2.0-12.0	Fe-O	1.977 $\pm$ 0.002	0.0095 $\pm$ 0.0003	6	0.90 $\pm$ 0.02
	Fe...O	3.62 $\pm$ 0.02	0.0100	6.9 $\pm$ 0.8	
	Fe...Fe	3.038 $\pm$ 0.007	0.0092	1.3 $\pm$ 0.2	
	Fe...Fe	3.380 $\pm$ 0.007	0.0112	3.6 $\pm$ 0.3	
	MS(FeO ₆)	3.96 $\pm$ 0.03	0.035 $\pm$ 0.003	3x6	
<i>Frostbrunn., leaf</i> 2.0-13.0	Fe-O	1.982 $\pm$ 0.002	0.0091 $\pm$ 0.0003	6	0.92 $\pm$ 0.02
	Fe...O	3.63 $\pm$ 0.02	0.0100	4.2 $\pm$ 0.9	
	Fe...Fe	3.075 $\pm$ 0.004	0.0092	2.0 $\pm$ 0.2	
	Fe...Fe	3.447 $\pm$ 0.015	0.0112	1.4 $\pm$ 0.3	
	MS(FeO ₆)	3.99 $\pm$ 0.03	0.021 $\pm$ 0.002	3x6	
<i>Frostbrunn., film</i> 2.0-13.0	Fe-O	1.969 $\pm$ 0.002	0.0097 $\pm$ 0.0003	6	0.90 $\pm$ 0.02
	Fe...O	3.59 $\pm$ 0.02	0.0100	7.6 $\pm$ 0.9	
	Fe...Fe	3.042 $\pm$ 0.007	0.0092	0.8 $\pm$ 0.1	
	Fe...Fe	3.429 $\pm$ 0.012	0.0112	3.2 $\pm$ 0.3	
	MS(FeO ₆)	3.99 $\pm$ 0.03	0.021 $\pm$ 0.002	3x6	
<i>Bog ore</i> 2.0-13.0	Fe-O	1.970 $\pm$ 0.001	0.0095 $\pm$ 0.0002	6	0.86 $\pm$ 0.02
	Fe...O	3.586 $\pm$ 0.012	0.0100	7.4(7)	
	Fe...Fe	3.032 $\pm$ 0.004	0.0092	2.3(2)	

1	Fe...Fe	3.420±0.015	0.0112	1.4(3)
2	MS(FeO ₆)	3.94±0.03	0.053±0.002	3x6

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6

7 **Table 4**

8 Chemical composition of surface film and slimy pile at

9 Fornby well and bog ore. Metal content was determined

10 following dissolution in 7 mol·dm⁻³ nitric acid.

11

12		Fornby, film	Fornby, pile	Bog ore
13	Total C (mg/g)	143	121	114
14	Total N (mg/g)	9.7	7.2	ND ^a
15	Fe (mg/g)	188	234	335
16	Al (mg/g)	3.0	3.0	0.8
17	Mn (mg/g)	1.8	1.7	1.3

18 ^aNot determined

19

Characterization of iron in floating surface films of some natural waters using EXAFS

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Supporting Material

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Table S1

Reported crystal structures of hematite, goethite and lepidocrocite, and the shortest reported Fe···Fe distances, with the mean values given in bold.

Hematite

2.900, 2.971, 3.364, 3.705 Å	Blake, R. L.; Hessevick, R. E.; Zoltai, T.; Finger, L. W. <i>Am. Mineral.</i> 1966 , <i>51</i> , 123-129.
2.895, 2.969, 3.361, 3.701 Å	Antipin, M. Yu.; Tsirel'son, V. G.; Flugge, M. P.; Gerr, R. G.; Struchkov, Y. T.; Ozerov, R. P. <i>Dokl. Akad. Nauk SSSR</i> 1985 , <i>281</i> , 854-857.
2.887, 2.970, 3.368, 3.704 Å	Cox, D. E.; Takei, W. J.; Miller, C.; Shirane, G. <i>J. Phys. Chem. Solids</i> 1962 , <i>23</i> , 863-874.
2.895, 2.969, 3.362, 3.702 Å	Maslen, E. N.; Strel'tsov, V. A.; Strel'tsova, N. R.; Ishizawa, N. <i>Acta Crystallogr., Sect. B</i> 1994 , <i>50</i> , 435-441.
2.885, 2.969, 3.367, 3.702 Å	Wolska, E.; Schwertmann, U. <i>Z. Kristallogr.</i> 1989 , <i>189</i> , 223-237.
2.890, 2.965, 3.359, 3.697 Å	Tsirel'son, V. G.; Antipin, M. Yu.; Strel'tsov, R. P.; Ozerov, R. P.; Struchkov, Y. T. <i>Dokl. Akad. Nauk SSSR</i> 1988 , <i>298</i> , 1137-1141.
2.895, 2.969, 3.361, 3.701 Å	Shin, H.-S.; Kwon, S.-J. <i>Yoop Hakoechi (J. Korean Ceram. Soc.)</i> 1993 , <i>30</i> , 499-509.
2.892, 2.968, 3.363, 3.702 Å	Perkins, D. A.; Attfield, J. P. <i>J. Chem. Soc., Chem. Commun.</i> 1991 , <i>1991</i> , 229-231.
2.895, 2.969, 3.362, 3.702 Å	Maslen, E. N.; Strel'tsov, V. A.; Strel'tsova, N. R.; Ishizawa, N. <i>Acta Crystallogr., Sect. B</i> 1994 , <i>50</i> , 435-441.
2.911, 2.973, 3.358, 3.705 Å	Sadykov, V. A.; Isupova, L. A.; Tsybulya, S. V.; Cherepanova, S. V.; Litvak, G. S.; Burgina, E. B.; Kustova, G. N.; Kolomiichuk, V. N.; Ivanov, V. P.; Paukshtis, E. A.; Golovin, A. V.; Avvakumov, E. G. <i>J. Solid State Chem.</i> 1996 , <i>123</i> , 191-202.
2.895, 2.969, 3.362, 3.702 Å	Sawada, H. <i>Mater. Res. Bull.</i> 1996 , <i>31</i> , 141-146.
2.889, 2.961, 3.352, 3.692 Å	Yu, S.-C.; Lee, J.-S.; Tung, S.-F.; Lan, C.-L. <i>J. Geol. Soc. China (Taiwan)</i> 1999 , <i>42</i> , 349-358

2.898, 2.969, 3.362, 3.703 Å

2.894, 2.969, 3.362, 3.701 Å

2.887, 2.967, 3.366, 3.702 Å

2.896, 2.969, 3.360, 3.701 Å

2.893, 2.964, 3.356, 3.696 Å

2.894, 2.968, 3.361, 3.701 Å

Goethite

3.024, 3.283, 3.465 Å

3.020, 3.302, 3.447 Å

3.018, 3.311, 3.438 Å

3.016, 3.294, 3.444 Å

3.025, 3.315, 3.440 Å

3.021, 3.301, 3.447 Å

Lepidocrocite

3.055, 3.060, 3.870 Å

3.062, 3.072, 3.873 Å

2.887, 3.066, 3.878 Å

2.943, 3.070, 3.876 Å

2.987, 3.067, 3.874 Å

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Fig. S1. Stacked Fourier transforms from the k^3 -weighted EXAFS spectra for iron in synthetic 2-line ferrihydrite, goethite, lepidocrocite, and hematite. Black lines are measured data and thin red lines are model fits using the structural data given in Table 2. Also shown is the spectra of iron(III) complexed by a fulvic acid at pH 4.0 (van Schaik et al., 2008).

Fig. S2. Linear combination fit of the “Filesjön film” and “Lillsjödäl film” samples, where the black line is the raw EXAFS spectrum and the red line the combination of EXAFS spectra of FeFA pH=4 (model for Fe-NOM) and of ferrihydrite. Upper, for the “Filesjön film” the content is estimated to 70% Fe-NOM (green line offset 8) and 30 % ferrihydrite (blue line, offset 6) (rsme=0.83), and lower, for the “Lillsjödäl film” it is estimated to 60% Fe-NOM (green line offset 8) and 40 % ferrihydrite (blue line, offset 6) (rsme=83).