PROPERTIES OF IRON OXIDES IN TWO FINNISH LAKES IN RELATION TO THE ENVIRONMENT OF THEIR FORMATION

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Abstract—Fifteen iron oxide accumulations from the bottoms of two Finnish lakes ("lake ores") were found to contain as much as 50% Fe. Differential X-ray powder diffraction and selective dissolution by oxalate showed that the samples consisted of poorly crystallized goethite and ferrihydrite. The crust ores of one lake had higher ferrihydrite to goethite ratios than the nodular ores of the other lake. The higher ferrihydrite proportion was attributed to a higher rate of Fe^{2+} supply from the ground water and/or a higher rate of oxidation as a function of water depth and bottom-sediment permeability.

Values of Al-for-Fe substitution of the goethites determined from unit-cell dimensions agreed with those obtained from chemical extraction if the unit-cell volume rather than the c dimension was used. In very small goethite crystals a slight expansion of the a unit-cell dimension is probaby compensated by a corresponding contraction of the c dimension, so that a contraction of the c dimension need not necessarily be caused by Al substitution.

The goethites of the two lakes differed significantly in their Al-for-Fe substitutions and hence in their unit-cell sizes, OH-bending characteristics, dehydroxylation temperatures, dissolution kinetics, and Mössbauer parameters. The difference in Al substitution (0 vs. 7 mole %) is attributed to the Al-supplying power of the bottom sediments: the silty-clayey sediments in one lake appear to have supplied Al during goethite formation, whereas the gravelly-sandy sediments in the other lake did not. The compositions of the goethites thus reflect their environments of formation.

Key Words—Al-substitution, Ferrihydrite, Genesis, Goethite, Iron oxide, Lake environment.

INTRODUCTION

Iron oxide accumulations containing as much as 50% Fe (lake ores) are abundant in many lakes of Finland. Because of their economic importance in the past, lake ores and their areal distribution were studied a long time ago (Holmberg, 1858; Aschan, 1908; Aarnio, 1915). Although numerous chemical data exist (Vaasjoki, 1956), mineralogical information is sparse. Halbach (1972, 1976) identified goethite, birnessite, and small amounts of strengite in lake ores from four Finnish lakes. In the present paper iron oxides of lake ores from two selected lakes in Finland are described, and a correlation of their properties with the environments in which the ores formed is attempted. The insight that can be gained into the processes of iron oxide formation by a detailed description of the iron oxide minerals beyond simple identification is also demonstrated.

THE TWO LAKES

Lake Murto, about 1 km in diameter, is located in eastern Finland at lat. 62°27'N, long. 30°09'E, about 6 km from a pyrite-pyrrhotite-chalcopyrite mine. The main rock types are mica schists, black, sulfide-bearing schists, and quartzites. The Quaternary deposits are glaciofluvial sands and gravels. In August 1985, the pH of the lake water was determined as 6.7. The coarse lake-bottom sediments are covered with brownish gyttja. Iron-precipitating cold springs and iron and manganese precipitates are common in the sand and gravel deposits of this area; hence, the iron content of the ground water is high. Water flowing from a natural spring 5 km from the lake contains 4.2 mg/liter dissolved iron.

Lake Eno (1.5 × 3 km) is located in southern Finland at lat. 61°29'N, long. 25°54'E, in an area where no ore deposits are known. The main rock types are mica schists and migmatites, and the Quaternary deposits are till and lacustrine clay, which are covered by greenish gyttja on the lake bottom. In August 1985, the pH of the lake water was determined as 6.9. The concentration of dissolved iron in ground water is low (≤0.1 mg/liter). No iron precipitates are known in the natural springs of this area.

MATERIALS AND METHODS

Samples

The richest accumulations of ores in Lake Murto were found at water depths as much as 2 m in coarse-grained sediments (site 38) and also in the vicinity of an underwater spring (site 39). In Lake Eno, ores could only be found where the bottom sediment was more permeable than elsewhere in the lake, such as near small peninsulas (site 44) and islands (site 47).

Three morphological ore types were distinguished. *Crust ores* occur in more or less continuous plates as

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Table 1. Description of iron oxide samples from the Finnish lakes.

Sample	Bottom sediment	Depth (cm)	Ore type[1]	Color (Munsell) (dry powder)
Lake Murto				
37AI	Fe-rich gyttja over fine sand	5–15	cr	7.5YR 4/8
38B		40	cr	6.5YR 4/6
38C		60–70	cr	6.5YR 4/6
38D	Fe-rich gyttja over gravelly sand	110–120	cr	6.5YR 4/6
38E		150	cr	7.5YR 4/4
38F		170	cr	7.5YR 4/4
39B		10	cr	6.5YR 4/6
39C	Fe-rich gyttja over gravelly sand	40–50	cr	7.5YR 4/6
39D		100–130	cr, pen, pis	7.5YR 4/6
Lake Eno				
44	gyttja over clayey silt	60–100	pis	10YR 5/8
46A		50	pis, pen	10YR 4/4
46B	gyttja over clayey silt with boulders	60	pis, pen	10YR 4/4
46C		80	pis, pen, cr	10YR 3/4
47A	clayey silt with boulders	100	pis, pen	10YR 5/8
47B		140	pis, pen	10YR 5/8

[1] cr = crust; pen = penny; pis = pisolitic.

much as several centimeters thick; *penny ores* form disk-shaped nodules as large as a few centimeters; and *pisolitic ores* form spherical nodules usually <1 cm in size. Crust ores are usually found in the shallowest part of an ore field, penny ores at intermediate depths, and pisolitic ores in the lowest part (Halbach, 1976). In the present study, however, this distinction was made at only one sampling site (39). In Lake Murto crust ore prevails, the thickness of which decreases from 3 to 0.5 cm with depth. In Lake Eno mainly smooth, nodular ores occur (Table 1).

Methods

After removal of detrital rock fragments, the lake ores were powdered in an agate ball mill for 20 min (<50 μm). Total carbon was determined with a Wösthoff carmograph. Iron (Fe_d), Al (Al_d), and Mn (Mn_d) were extracted by dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960). Iron (Fe_o) and Mn (Mn_o) were also extracted by acid ammonium oxalate (Schwertmann, 1964). Fe was determined photometrically by sulfo-salicylic acid (Koutler-Anderson, 1953) and Mn and Al by atomic absorption spectroscopy (AAS). Si was extracted by treating 10 mg of sample with 10 ml of 1 M NaOH for 2 hr at 80°C and determined by the molybdenum blue method (Boltz and Mellon, 1947) after neutralization of the extract against phenolphthaleine. Dissolution kinetics were obtained using sets of separate 10-mg samples in 2 M HCl or in 0.2 M NH_4 oxalate, pH 3.0, in the dark at 25°C.

Iron oxide minerals were identified by X-ray powder diffraction (XRD) using CoKα radiation and a Philips PW 1050 vertical goniometer equipped with a graphite reflected-beam monochromator. The minerals re-

moved by oxalate were identified by differential X-ray powder diffraction (DXRD) (Schulze, 1981) in which a step-scanned XRD pattern (step size = 0.05°2θ; counting time = 10 s/step) of an oxalate-treated sample was subtracted from that of an untreated sample. Cell dimensions of goethite were determined from step-scanned XRD data (step size = 0.02°2θ; counting time = 10 s/step) after removing ferrihydrite by oxalate. Accurate line positions were measured relative to nearby lines of 25% corundum added as an internal standard using a curve-fitting procedure. Corrections were made for apparent line shift due to small crystal size as suggested by Schulze (1984). Al substitution of goethite was calculated both from a unit-cell volume vs. Al substitution relation (see below) and from the amounts of Al_d and Fe_d. Mean crystallite dimensions (MCD) were calculated from the linearly corrected widths at half height of the 110 (MCD_{110}) and 111 (MCD_{111}) goethite lines using the Scherrer formula (Klug and Alexander, 1974).

Differential thermal analysis (DTA) was carried out on a Linseis Model L 62 analyzer using 50-mg samples, a heating rate of 10°C/min, and hematite as inert substance. The sample chamber was flushed with dry N_2. Infrared spectra were recorded on a Beckman IR 4250 spectrometer using 1:300 KBr disks at a recording rate of 150 cm^{-1}/min. The exact positions of OH-bending modes of goethite were measured at a recording rate of 50 cm^{-1}/min using polystyrene as a standard. Mössbauer spectra of selected samples were taken in different velocity ranges at room temperature, at 77 K by cooling the absorber in a cold-finger cryostat, and at 4.2 K by immersing both the source and absorber in liquid helium. A 6-μm-thick metallic iron foil was used for velocity calibration.

Table 2.　Chemical and mineral compositions of the samples (air-dry basis).

Sample	C_t[1] (%)	Fe_d[2] (%)	Fe_o[3] (%)	Fe_o/Fe_d	Mn_d[2] (%)	Mn_o[3] (%)	Mn_o/Mn_d	Si_{NaOH} (%)	Minerals[4]
Lake Murto									
37AI	0.49	47.8	4.93	0.10	0.05	0.003	0.06	1.63	Gt, Fh
38B	0.47	45.3	14.87	0.33	0.44	0.41	0.94	2.97	Gt, Fh
38C	0.63	46.0	13.84	0.30	0.51	0.49	0.96	2.08	Gt, Fh
38D	0.67	45.8	17.53	0.38	0.29	0.25	0.86	2.27	Gt, Fh
38E	0.66	43.3	16.14	0.37	1.99	1.91	0.96	2.14	Gt, Fh, (Bn)
38F	0.64	39.6	13.72	0.35	4.53	4.41	0.97	3.03	Gt, Fh, Bn
39B	0.65	44.3	20.25	0.46	0.53	0.49	0.93	2.63	Gt, Fh
39C	0.48	42.4	10.82	0.25	1.87	1.81	0.97	2.03	Gt, Fh
39D	0.43	46.7	5.58	0.12	0.54	0.46	0.86	2.27	Gt, Fh
Lake Eno									
44	1.52	44.8	2.39	0.05	0.58	0.32	0.57	0.29	Gt, Fh
46A	0.98	39.4	6.38	0.16	3.85	3.56	0.92	0.96	Gt, Fh, Lp, (Bn)
46B	1.11	39.8	4.58	0.12	2.68	2.44	0.91	0.59	Gt, Fh, Lp
46C	1.21	31.1	7.03	0.23	6.84	6.47	0.95	0.58	Gt, Fh, Lp, (Bn)
47A	1.50	48.0	1.71	0.04	0.28	0.05	0.16	0.48	Gt, Fh
47B	1.60	48.7	1.92	0.04	0.43	0.16	0.37	0.30	Gt, Fh

[1] Total carbon.
[2] Dithionite-soluble Fe and Mn, respectively.
[3] Oxalate-soluble Fe and Mn, respectively.
[4] Gt = goethite; Fh = ferrihydrite; Lp = lepidocrocite; Bn = birnessite; ( ) = traces.

RESULTS AND DISCUSSION

Chemical composition (Table 2)

Most of the samples contained 40–48% Fe_d, indicating Fe oxides to be the major constituents. Mn_d varied between 0.3 and 6.8%. The oxalate solubility of the Fe oxides (Fe_o/Fe_d) varied widely between 0.04 and 0.46, and was generally lower for pisolitic and penny ores (i.e., nodular) than for crust ores. Consequently, in Lake Eno ores, where nodular ores predominate, the average Fe_o/Fe_d ratio (0.11 ± 0.08) was significantly lower than that of the Lake Murto ores (0.29 ± 0.12), which are of the crust ore type, except for the deepest sample of site 39 (39D) which is nodular and has a lower Fe_o/Fe_d than the upper ores of this site.

For most of the samples, the Mn_o/Mn_d ratio was >0.9. Most of the Mn must therefore have been present in the form of separate oxides rather than as Mn in goethite, although some may have been incorporated in ferrihydrite. The average value of the oxalate-insoluble Mn ($Mn_d - Mn_o$) is only $0.058 \pm 0.033\%$ in Lake Murto material, but $0.274 \pm 0.052\%$ in Lake Eno material.

The ores of Lake Eno contained more total carbon (avg. $= 1.26 \pm 0.24\%$) than those of Lake Murto ($0.56 \pm 0.10\%$ C_t), which may be due partly to the more favorable conditions for bioproduction in the clayey-silty sediments and soils of the Lake Eno area than in the sandy-gravelly sediments of the Lake Murto area. Finally, significantly more NaOH-soluble Si was found in the Lake Murto samples ($2.34 \pm 0.46\%$) than in the Lake Eno samples ($0.53 \pm 0.25\%$).

Iron oxide mineralogy

Goethite and ferrihydrite were found to be the dominating iron oxide minerals in all samples. At a similar total Fe oxide content, the concentration of ferrihydrite is higher in the crust ores of Lake Murto than in the nodular ones of Lake Eno, the latter being richer in goethite. These concentrations are in line with the difference in Fe_o/Fe_d, because oxalate essentially dissolves ferrihydrite but not goethite (Schwertmann *et al.*, 1982). The DXRD pattern in Figure 1 clearly shows the presence of a five-line ferrihydrite, whereas reasonably pure goethite was left after the oxalate treatment. The powdered samples having more ferrihydrite (Lake Murto) are redder (Munsell hues = 6.5–7.5YR) whereas those in which goethite prevails (Lake Eno) are yellower (10YR) (Table 1). Natural ferrihydrites are usually rich in adsorbed Si (Carlson and Schwertmann, 1981; Henmi *et al.*, 1980), explaining the higher NaOH-extractable Si in the Lake Murto samples.

Lepidocrocite was identified in three depths of one sampling site in Lake Eno. Birnessite was present in one sample from Lake Murto which contained 4.5% Mn_d.

Room-temperature Mössbauer spectra of oxalate-treated samples 38C and 47A consist mainly of a (super)-paramagnetic doublet, and a subordinate, strongly relaxed magnetically ordered component. At 77 K, Mössbauer spectra of sample 38C before and after two oxalate extractions were complex, comprising a sextet with asymmetrically broadened resonant lines and a strong and weak superparamagnetic Fe(III) doublet, respectively; after eight oxalate treatments the
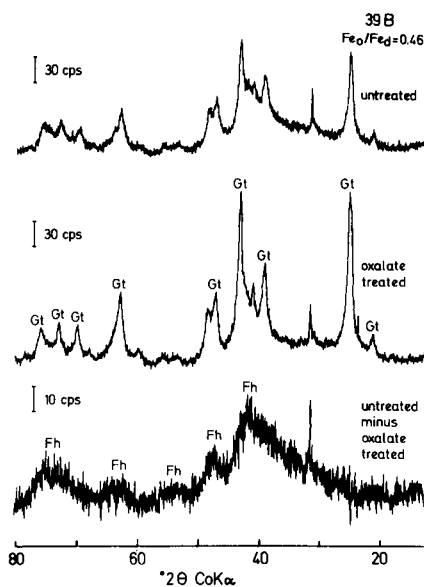
Figure 1. X-ray powder diffraction tracings of sample 39B prior to chemical treatment (top), after oxalate extraction (middle), and the difference between the two diagrams (bottom). Gt and Fh indicate goethite and ferrihydrite peaks, respectively.
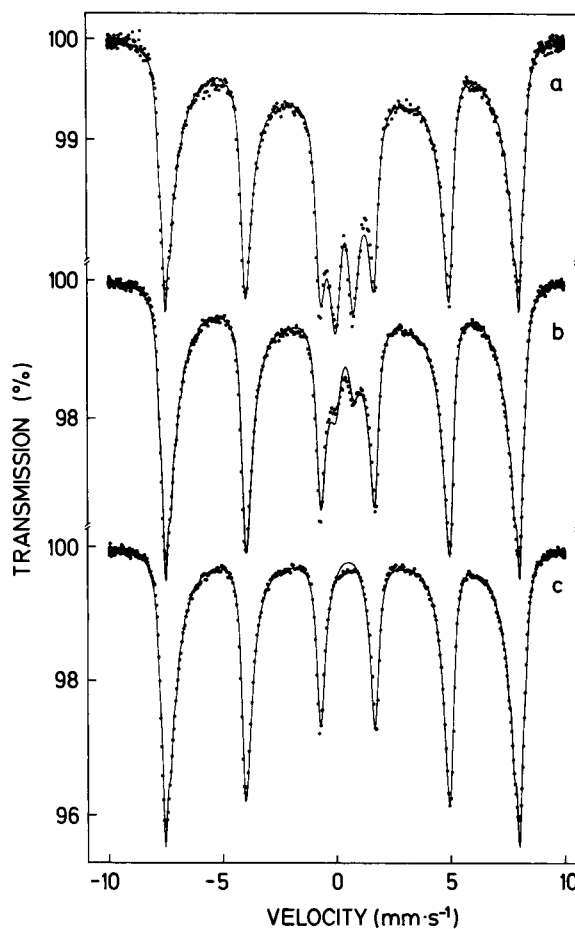

Figure 2. Mössbauer spectra at 78 K of sample 38C prior to chemical treatments (a), after two oxalate extraction (b), and after eight oxalate treatments (c).

doublet was no longer observed (Figure 2c). Because of the line asymmetry, the magnetically ordered components were fitted with distributions of hyperfine fields (Murad, 1982). Parameters characterizing the hyperfine field distributions (maxima of distributions at 48.4 ± 0.1 T, left half widths = 2.0 − 1.8, right half widths = 1.1 − 1.0 T) did not change as a result of the oxalate treatments, indicating that the treatments had little effect on the goethite content of this sample, whereas they removed ferrihydrite quite effectively. Ratios of areas of the paramagnetic to the magnetically ordered components at 77 K were 0.26 for the untreated sample and 0.11 for the oxalate-treated sample. For sample 47A, a single oxalate treatment was sufficient to remove ferrihydrite quantitatively; the maximum of the hyperfine field distribution of the remaining goethite was at 48.5 T, and left and right half widths were 1.6 and 1.0 T, respectively.

The existence of residual ferrihydrite in sample 38C after one oxalate treastment was confirmed by the average quadrupole splitting of the magnetically ordered sample of −0.17 mm/s at 4.2 K. This value is intermediate between the quadrupole splittings of magnetically ordered ferrihydrite (about −0.05 mm/s) and goethite (−0.24 mm/s), and thus typical for samples containing both of these minerals (Schwertmann *et al.,* 1982).

Properties of the goethites (Table 3)

The mean crystallite dimensions MCD_{110} and MCD_{111} were very small and on a narrow range of 11–

17 nm (neglecting possible strain effects on line broadening), indicating a rather poor ordering in these goethites compared with those from other weathering environments (Schwertmann, 1987a). Low temperatures and an environment relatively rich in soluble Si and humic substances could have been responsible for the poor crystallinity of the goethites.

The XRD intensity ratio I_{110}/I_{111} was nearly constant at 1.3, except for three samples, and agreed well with the ratio of 1.2 given by Brindley and Brown (1980) for a calculated pattern. It was, however, lower than those observed for many synthetic goethites, the higher values being due to preferred orientation of acicular crystals (Schultze and Schwertmann, 1984). This low I_{110}/I_{111} ratio suggests a non-acicular morphology for the goethite crystals (Schwertmann, 1987a).

Using the linear empirical relation between c and Al, given by Schulze (1984) for 81 synthetic goethites of different crystallinities as (mole % Al = 1730 − 572·c), to estimate Al substitution, all values for Al substitution are significantly *greater* than those ob-
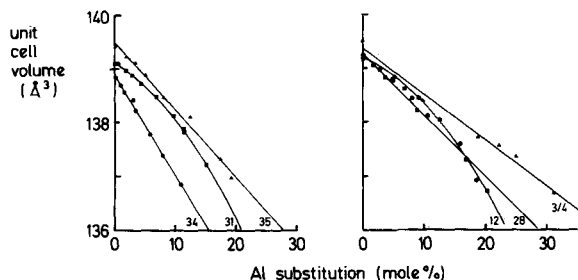
Figure 3. Relation between unit-cell volume and Al substitution for synthetic goethites. The goethites were prepared from ferrihydrites containing different amounts of Al in 0.3 M KOH at 70°C (series 28, 31, 34; Schulze, 1984); in 0.3 M KOH at 25°C (series 35; Schulze and Schwertmann, 1987) in 2 M KOH at 70°C (series 12; Schulze, 1984), and by oxidation of $FeCl_2$-$AlCl_3$ solutions at pH 6–7 and 25°C (series 3/4; Schulze, 1983).

tained chemically from Al_d. This deviation therefore cannot be explained by the extraction of Al from sources other than goethite. The goethites of Lake Murto, in particular, contain essentially no Al_d; yet their c values are significantly smaller than those of pure goethites. In these goethites the measured reduction in c therefore cannot be due to Al substitution, as is usual for goethites.

Because of this variability on one side and the rigid nature of the structure on the other side, a minute increase in a (or b) may be compensated by a corresponding decrease in c, which then in itself no longer indicates the degree of Al substitution. A negative correlation does indeed exist between a and c of the unsubstituted samples (Table 3). Thus, the cell volume seems to be a better indicator of the contracting effect of Al-for-Fe substitution than does the value of c.

Although the cell volume is strictly correlated with Al substitution for synthetic goethites, the relations for different synthesis series are statistically significantly different (Figure 3). Depending on the synthesis conditions, cell volumes at zero substitution varied between 138.7 and 139.3 Å³. An almost identical range of 138.8 to 139.5 Å³ was obtained for a series of non-substituted goethites of various crystallinities synthesized between 4° and 80°C (Schwertmann et al., 1985). At the same Al substitution, cell volumes are higher for goethites synthesized at 25° that at 70°C, though factors other than temperature may play a role too.

Among the different curves shown in Figure 3, the one that was selected for calibration was the curve for which the cell volume at zero Al substitution was closest to the cell volumes of natural goethites from which dithionite extracted no Al ($Al_d = 0$). This was the curve of series 35, which extrapolates to a cell volume of 139.3 Å³ at zero Al substitution (Figure 3), a value close to the cell volume of 139.2 Å³ for natural goethites containing <0.1% Al_d. The goethites of series 35 were formed at 25°C over a period of 4 yr, in contrast

Table 3. Properties of goethites after one oxalate treatment.

Sample	Fe [1] (%)	Dissol. rate [1] (hr⁻¹)	Unit-cell parameters				I_{110}/I_{111} [3]	MCD_{110} [2] (nm)	MCD_{111} [2] (nm)	Al-subst. (mole %)		DTA peak (°C)	IR		
			a_0 Å	b_0 Å	c_0 Å	Cell vol. Å³				XRD	Chem		δ_{OH} (cm⁻¹)	γ_{OH} (cm⁻¹)	$\delta_{OH} - \gamma_{OH}$ (cm⁻¹)
Lake Murto															
37AI	50.9	0.030	4.615(0)	9.979(8)	3.019(3)	139.0	1.29	12	14	1.3	0.12	252	880.2	788.7	91.5
38C	48.7	0.079	4.617(7)	9.991(6)	3.018(2)	139.2	1.30	11	14	0.5	0.08	235	882.1	788.7	93.4
38D	47.8	0.088	4.626(3)	9.980(2)	3.014(1)	139.2	1.51	13	17	0.3	0.09	248	885.3	789.5	95.8
39B	46.4	0.107	4.612(6)	9.997(5)	3.018(2)	139.0	1.35	13	16	1.0	0.03	234	n. m.[4]	n. m.[4]	n. m.[4]
39C	47.3	0.060	4.640(1)	9.961(1)	3.011(0)	139.2	1.31	12	15	0.4	0.09	278	883.1	790.4	92.7
39D	48.2	0.053	4.640(0)	9.966(0)	3.013(0)	139.3	1.37	11	12	-0.4	0	258	880.2	789.8	90.4
Lake Eno															
44	48.1	0.010	4.595(6)	9.950(6)	3.019(2)	138.0	1.31	12	13	6.5	8.6	257	896.7	798.4	98.3
46A	41.5	0.028	4.600(27)	9.958(23)	3.013(8)	138(0)	1.31	11	11	6.8	7.2	264	894.9	797.1	97.8
46B	39.5	0.022	4.594(28)	9.959(24)	3.013(8)	137.8	1.33	11	12	7.5	8.1	258	896.0	796.3	99.7
47A	49.9	0.011	4.598(8)	9.944(7)	3.015(2)	137.9	1.59	11	13	7.4	7.6	266	895.9	799.5	96.4
47B	48.2	0.011	4.606(6)	9.945(6)	3.017(2)	138.2	1.56	11	13	5.8	7.9	243	894.3	798.2	96.1

[1] Dithionite soluble Fe.
[2] Mean crystallite dimension perpendicular to (110) and (111) lines.
[3] X-ray intensity ratio of 110 and 111 lines.
[4] Not measurable.

Table 4. Goethite properties (average) of the two lakes.

Lake	Cell volume Å	Al subst. (mole %)	$\delta_{OH} - \gamma_{OH}$[1] (cm^{-1})	DTA peak (°C)	Dissolution rate (hr^{-1})	$Mn_d - Mn_o$[1] (%)
Murto	139.2(1)	0.04(4)	92.8(2.1)	251	0.070(29)	0.057(33)
Eno	138.0(2)	7.9(5)	97.7(1.5)	258	0.016(8)	0.277(52)

[1] Dithionite- and oxalate-soluble Mn, respectively.

to series 12, 28, 31, and 34, which were formed at higher temperatures within a few days or weeks, yielding goethites with smaller cell volumes (Schulze and Schwertmann, 1987). The second 25°C series (series 3/4) was less suitable, probably because the goethites also formed rather quickly by oxidation of $FeCl_2$-$AlCl_3$ mixed solutions at pH 7. This curve has a much flatter slope (0.12) than the others (0.17–0.19).

Table 3 shows that this approach led to a much better agreement between the chemically determined Al substitution and that calculated from XRD data.

The average unit-cell volumes are significantly different between the two lakes (139.2(1) vs. 138.0(2) Å³), as is the Al substitution, as derived from Al_d and Fe_d (0.07(4) vs. 7.9(5) mole %; see Table 4).

Inasamuch as both oxalate *and* dithionite completely dissolved the Mn oxides but only dithionite dissolved goethite, the difference $Mn_d - Mn_o$ could account for Mn in goethite. Because $Mn_d - Mn_o$ is significantly larger in the more goethite-rich samples of Lake Eno (0.274 ± 0.052%) than in the more ferrihydrite-rich samples of Lake Murto (0.058 ± 0.033%), some Mn-for-Fe substitution (too small to be detected by XRD line shift) may exist in the Lake Eno goethites.

A further difference between the goethites from the two lakes is the separation between the two OH-bending vibrations at ~800 and ~900 cm^{-1} ($\delta_{OH} - \gamma_{OH}$) in the IR spectra. The average values are 92.8 ± 2.1 and 97.7 ± 1.5 cm^{-1} for Lake Murto and Lake Eno, respectively. A similar separation (93 vs. 97 cm^{-1}) was observed for goethites formed at low (<40°C) and high (50°–80°C) temperatures (Schwertmann *et al.*, 1985). The separation, however, also increases with increasing Al substitution (Schulze and Schwertmann, 1984, 1987), so that these two effects cannot be separated in the present samples.

Small but significant differences were found in the dehydroxylation temperatures of the goethites from the two lakes (251 ± 6°C vs. 258 ± 4°C). The higher temperature can again be attributed to the Al substitution, in agreement with similar results on synthetic (Schulze and Schwertmann, 1984) and soil (Schwertmann and Latham, 1986) goethites.

The goethites were also characterized by dissolution kinetics. The rate of dissolution of goethite in strong acids has been found to depend on crystal morphology (Cornell *et al.*, 1974), particle size (Schwertmann *et al.*, 1985), and Al substitution (Schwertmann, 1984). The dissolution time curves could be fitted, rather than with a simple first-order reaction, with a modified first-order reaction as suggested by Kabai (1973):

$$1 - \frac{C}{C_0} = \exp^{-(kt)^\alpha}, \qquad (1)$$

the linear form of which is

$$\ln \ln 1/(1 - C/C_0) = \alpha \ln k + \alpha \ln t, \qquad (2)$$

where k is the reaction rate constant, α is believed to be a phase-specific constant, and C and C_0 are the amounts of Fe dissolved at time t and zero, respectively.

Nine of the ten curves obtained could be fitted by one (7) (Figure 4) or two (2) straight lines (r = .994 to 1); only one sample showed an S-shaped curve. The dissolution rate constants k for the nine samples ranged between 0.030 and 0.115 hr^{-1} for the Lake Murto samples and between 0.011 and 0.028 hr^{-1} for the Lake Eno samples. The statistically significant difference between the average values of the two lakes (Table 4) shows that the goethites of Lake Eno dissolve more slowly than those of Lake Murto, which, in agreement with results obtained on the synthetic Al-goethites (Schwertmann, 1984, 1987a), is attributed mainly to the difference in Al substitution. Moreover, a significant correlation was found between k and Fe_o/Fe_d (Fig-
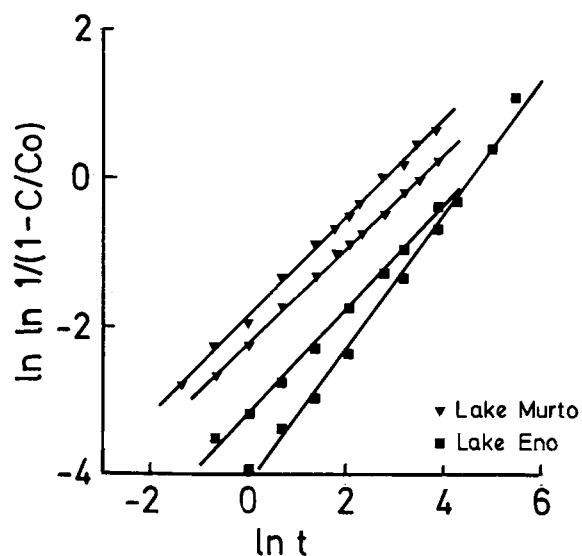

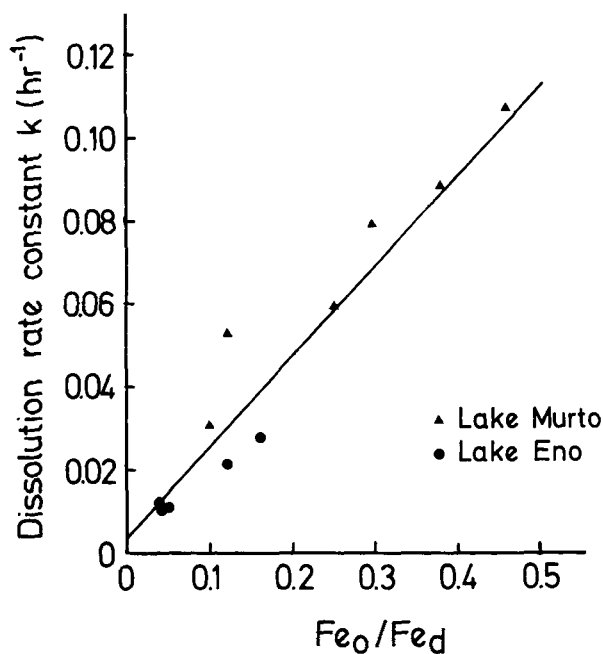Figure 4. Dissolution vs. time (in hr) curves of oxalate-treated samples in 2 M HCl at 25°C.

Figure 5. Relation between Fe_o/Fe_d and dissolution rate for oxalate-treated samples.

Table 5. Particle size distribution (%) of the bottom sediments.

Lake	Site	Clay	Silt	Sand	Gravel
Murto	37	1	9	84	6
	38	0	1	58	41
Eno	44	26	61	13	0
	47	28	63	9	0

ure 5), although k was measured on the oxalate-treated samples and Fe_o/Fe_d refers to the untreated sample. The relationship may therefore be due to an incomplete removal of ferrihydrite by a 2-hr oxalate treatment. The partial resistance of ferrihydrite to a 2-hr oxalate treatment was demonstrated by Mössbauer spectroscopy (see above) and dissolution kinetics in oxalate. Breaks in the plots of log dissolved Fe vs. log time for samples 38C and 39C (not shown) show that about 10% of the total Fe oxides dissolve more quickly than the rest.

GENERAL DISCUSSON

The different morphology of iron oxide accumulations in the two Finnish lakes and their ferrihydrite/goethite ratio (as ascertained from $Fe_{o/d}$ and XRD) may be explained by the different rates of Fe^{2+} supply, the rate of its oxidation, or both. The greater these values, i.e., the more rapidly the oxides formed, the more likely massive, irregular crusts formed as opposed to nodular forms, and the more ferrihydrite formed as opposed to goethite. The oxidation rate is mainly a function of water depth (Halbach, 1976) and explains the occurrence of more goethitic, nodular ores in the greatest sampling depth (100–130 cm) of Lake Murto (sample 39D). The Fe supply rate by ground water (entering the lake through its sediments or underwater springs) depends on the Fe^{2+} concentration of the ground water modified by the permeability of the sediments. The higher Fe^{2+}-input rate into and the coarse (Table 5), highly permeable sediments of Lake Murto therefore

led to crust ores abundant in ferrihydrite, whereas in Lake Eno a low Fe^{2+}-input rate and the clayey (Table 5), less permeable sediments resulted in nodular ores richer in goethite. The occurrence of lepidocrocite in Lake Eno but not in Lake Murto ores supports the concept of a lower oxidation rate in Lake Eno, because lepidocrocite typically forms by slow oxidation of Fe^{2+} in fine-grained sediments.

In addition to the mineralogical composition, the goethites themselves are different in the two lakes (Table 4). Most of these differences can be explained by a significant difference in Al substitution, which in turn appears to be a function of the clay content of the bottom sediments (much higher in Lake Eno than in Lake Murto, Table 5). The goethites therefore formed in two completely different environments, one very low in Al (predominance of quartz and coarse feldspars), and one rich in Al (predominance of illite, chloritevermiculite, and some smectite). Synthesis experiments have shown that clay minerals may supply Al during Fe oxide formation (Schwertmann, 1979, 1987c). The degree of Al subisution in the goethites of these lake ores thus appears to be an environmental indicator for these two lakes, reflecting the Al supply and thereby the mineralogy of their immediate environment. This environmental influence has been demonstrated earlier for goethites formed in different soils (Fitzpatrick and Schwertmann, 1982; Schwertmann, 1987b).

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