THE INFLUENCE OF OXIDIZING AND REDUCING CONDITIONS UPON THE DISTRIBUTION OF SOME ELEMENTS IN LAKE SEDIMENTS¹

Eville Gorham

Department of Botany, University of Minnesota, Minneapolis

and

Dalway J. Swaine

C.S.I.R.O. Division of Coal Research, Chatswood, N. S. W., Australia

ABSTRACT

Analyses for Fe, Mn, Pb, Zn, Co, P, Mo, Ba, Sr, Ti, Li, Rb, Na, K, Be, Cr, V, Y, Ag, Cu, C, S, Sn, Ni, Ga, Zr, and La have been carried out on some oxidate crusts, oxidized surface muds, reduced subsurface muds, and glacial clays collected in Windermere and Esthwaite Water in the English Lake District. The relatively organic lake muds exhibit the highest concentrations of C, S, Cu, Sn, and Ni. Many of the oxidate crusts exhibit strong enrichment in Mn, Fe, Ba, Sr, Pb, and Zn. Ti, Li, Rb, Co, P, and Mo are also enriched in some crusts. S, Sn, and Ni reach their highest levels in the reducing subsurface muds, but Mn, and to a lesser extent Fe and Mo, are higher in the oxidized than in the reduced muds.

Relations between the elements in the various sediments are examined, and the English oxidate crusts are compared with lake and stream ores in Sweden and Finland, and with marine manganese nodules. These marine nodules are frequently enriched in Cu, Ni, Co, Mo, V, Ag, and Sn to a far higher degree than the freshwater ferromanganese concretions. Some freshwater crusts exhibit enrichments in Pb, Zn, and Ba of the same order as those observed in marine manganese nodules.

INTRODUCTION

One of the most important factors affecting the exchange of dissolved substances between mud and water in lakes is the redox potential gradient in the system (Mortimer 1941-1942; Hutchinson 1957; Gorham 1958). Little is known, however, of the effects of redox potential upon the total chemical composition of lake sediments, and the present study was undertaken to investigate this question.

The main object was to compare the elemental composition of oxidizing and reducing muds from the uppermost layers of sediment in Esthwaite Water and Win-

dermere in the English Lake District. In the course of the study several ferromanganese "oxidate crusts" were discovered in Windermere and Ullswater, and these too were examined, together with three samples of glacial clay found under a thin layer of mud at the site of the first "crust" discovery.² Information regarding Windermere and Esthwaite Water is given in Table I.

METHODS

Sampling

Samples of undisturbed surface mud were collected in October and November of 1954 using a Jenkin surface mud sampler (Mortimer 1941-1942, Fig. 22). Subsamples were taken with a stainless steel spoon from the surface, 5, and 10 cm depths of the mud in these cores and placed in polyethylene bottles (cleaned with dilute chromic-sulfuric acid and immediately

¹ This work was done while the first author was at the Freshwater Biological Association, Ambleside, England, and the second was at the Macaulay Institute for Soil Research, Aberdeen, Scotland. They are grateful to Mr. F. J. H. Mackereth, Mr. J. Heron, and the laboratory staff of the Freshwater Biological Association for advice and assistance, and to Dr. R. L. Mitchell of the Macaulay Institute for Soil Research for allowing the spectrographic analyses to be made in his laboratory and for reading the manuscript. Contribution No. 20, Limnological Research Center, University of Minnesota.

² These crusts were first found in Windermere some years ago by Professor H. P. Moon, and are known by the staff of the FBA Laboratory there as "Moon Crust."

TABLE 1. *Some characteristics of Windermere North Basin and Esthwaite Water**

	Windermere, North Basin	Esthwaite Water
Area (km ²)	8.2	1.0
Mean depth (m)	26	6.8
Maximum depth (m)	67	16.1
Rocks of drainage basin	Hard volcanics and some Silurian sedimentaries	Mainly Silurian sedimen- taries (slates, grits, flags)
Phytoplankton productivity	Moderate	Relatively high
Aeration of bottom water and mud surface	Continuously oxygenated	Anoxic in late summer
Oxygen absorption by mud in summer (gm m ⁻² day ⁻¹)	0.52	0.65
Winter thickness of oxidized surface mud layer (cm)	1.1	0.7
Winter redox potential (E _r) at 5 cm depth (volts)	-0.05	-0.07
Calcium	0.27	0.41
Magnesium	0.07	0.12
Sodium	0.16	0.20
Potassium	0.01	0.02
Bicarbonate	0.17	0.31
Sulfate	0.14	0.20
Chloride	0.17	0.20

* Data from Mortimer (1941-1942) and Gorham (1960).

rinsed in five changes of tap and 10 of distilled water). The crust from the Wray Castle location (Boathouse Bay) was collected during the same period, together with samples of the thin surface mud layer and the glacial clay underlying it. The other crusts were collected at various times.

Analysis

The samples were dried and ground in an agate mortar. All analyses were made on material dried at 100-110C.

Carbon, mostly organic, was determined gravimetrically by dry combustion, free carbonate being negligible. Sulfur was estimated by a technique devised by F. J. H. Mackereth (unpublished). Phosphorus, iron, and manganese were estimated spectrophotometrically as phosphomolybdate, ferric chloride, and permanganate, respectively, after digesting the sediments with hydrofluoric and perchloric acids. A Unicam SP 500 spectrophotometer was used. Sodium and potassium were determined by EEL flame photometer on diluted subsamples of the same digests.

The remaining elements were estimated semi-quantitatively by the cathode layer

arc method (Mitchell 1948). A mixture of equal weights of the finely ground sample and carbon powder was filled into a carbon electrode which was used as the cathode in a 9 amp d-c arc. Two 1-min exposures were taken with a Hilger Large Quartz spectrograph (E492) on each of two plates covering the ranges 2,470-3,550 Å and 3,180-8,000 Å. The precision may be about $\pm 30\%$, but it is usually better than this, especially at low concentrations.

The following elements were not detected, the limits of detection (when known) being given in parentheses as ppm: As (3,000); Au, Bi (30); Cd (200); Hg (1,000); In (10); Ir, Pt, Sb (300); and Tl (10). Ge was possibly present (10? ppm) in three of the Windermere muds (107,773-107,775), and Sc (10 ppm) was detected in two of the oxidate crusts (107,782 and 107,784) (numbers are those of the Macaulay Institute, where the spectrographic analyses were carried out; the prefix 107 will be omitted).

DESCRIPTION OF SAMPLES

Samples 761-3 were collected 7 October 1954, in shallow water (approx 4 m), from

mud at the mouth of the Congo Beck, a small stream entering the northwest end of Windermere. The first sample taken from the surface of the core was rusty in color; the second sample, from 5 cm, was brown, and the third, from 10 cm, was blackish brown.

Samples 764–8 and 779 were taken 7 October 1954 from shallow water (approx 3–4 m) in the Wray Castle Boathouse Bay of Windermere. The first of these was from a layer of dark brown mud a few centimeters thick; the second was a number of small pieces of oxidate crust apparently embedded in this mud at its boundary with the clay beneath. The next was a rusty colored clay immediately beneath the mud; a number of soft friable pieces of incipient (or degraded) crust were removed from this sample. The fourth was a whitish clay showing no evidence of iron migration into it. The fifth was greenish clay having the mottled or *gleyed* appearance characteristic of reducing conditions, although small bits of crust were embedded in it (these were removed). The final sample (779) was composed of large pieces of oxidate crust dredged from this site, probably from the surface mud.

Samples 773–5 were taken from the deepest point (approx 60 m) of Windermere 29 November 1954. The first was reddish brown surface mud, the second blackish brown mud from about 5 cm depth, and the third blackish mud from 10 cm.

Samples 770–2 were taken from the deepest part (approx 16 m) of Esthwaite Water on 11 October 1954. The first was surface rusty mud, the second blackish brown mud from 5 cm, and the third more blackened mud from 10 cm depth.

Samples 776–8 were also from Esthwaite Water, 16 m, but were collected on 29 November 1954. The surface of the first was brown rather than rusty colored, while the second and third, from 5 and 10 cm, were black.

The color of the samples was a guide to their redox potential. The surface samples all exhibited varying degrees of rusty colored ferric hydroxide deposition and were oxidizing. The deeper samples, with

varying amounts of black ferrous sulfide precipitates, were all reducing. The autumn and winter redox potentials given for these two lakes by Mortimer (1941–1942), and later measured occasionally by us, support the view that the surface muds are oxidizing and that the subsurface muds are strongly reducing. Mortimer points out that the mud surface in the deep Windermere is permanently oxidizing, while that of Esthwaite becomes reducing each summer owing to de-oxygenation of the bottom waters of this shallow and fertile lake. Thus, sample 770 must have been reducing shortly before collection.

Samples 780–5 were all oxidate crusts. The first was probably collected from Ash Landing on Windermere, and the second was caught in a perch net off Ferry House, Windermere, 14 October 1954. The third was taken in a perch net 100 m north of Thompson Holm on Windermere, 1 November 1954. Sample 783 was an irregularly shaped crust including many tiny stone fragments, collected from approx 4–5 m depth in Ullswater in October 1954. Sample 785 was collected near the shore of Ullswater at the same time, but was one of a series of more regular and rather saucer-shaped crusts with raised edges and without stony inclusions. Sample 784 was a clayey crust formed over laminated clay on the Chicken Rocks, Windermere, collected 29 November 1954.

The color of these crusts was generally patchy or layered, pale or reddish brown to purplish brown, but when the samples were finely ground, the colors ranged from pale fawn in the clayey crust from Chicken Rocks (784) to dark chocolate brown in the large pieces of crust from near Wray Castle (779). The depth of brown color (estimated visually on a six-point scale) showed a positive correlation with the manganese content. Sample 765 had a distinctly reddish tint when ground and was exceptionally rich in iron.

From the scant information available about the collection sites, it appears that oxidate crusts are formed where the relatively organic lake mud deposits are thin or absent above the basal glacial deposits,

that is, where muds accumulate slowly if at all. In such a situation, divalent iron and manganese can be supplied continually to an unchanging surface at which they are oxidized and precipitated. Rock faces at many depths in Windermere sometimes have a thin coat of material resembling oxidate crusts. This phenomenon and the occurrence of such crusts on stones in brooks (Ljunggren 1953) and in lakes (Kindle 1935, 1936) suggests that the iron and manganese which form these crusts may come at least partly from the water and not wholly from the sediment (although the sediment may be the major source when present). Both elements may be combined with or adsorbed on particulate or soluble organic compounds, and if these were metabolized by surface bacteria, the iron and manganese would become available for crust formation in sites where silting or organic deposition is too slow to bury or again reduce the oxides as they are deposited (Hutchinson 1957, p. 711; Graham 1959; Graham and Cooper 1959).

Another hypothesis of oxidate crust formation on stony or gravelly substrata near the water surface involves photosynthesis by algae (Kindle 1932, 1935) or aquatic bryophytes (Ljunggren 1953), which may precipitate iron and manganese by raising the pH and oxygen concentration near the surface of the organisms, although this mechanism could not operate in the dark. Zapffe (1931) indicates that after bacteria begin the oxidation of iron and manganese, the aggregates formed catalyze their own accretion. It is also possible that the mechanism is wholly chemical, at least in some sites (Ljunggren 1953; Goldberg and Arrhenius 1958).

Kindle (1936) has reported that in Nova Scotian lakes, manganese crusts usually form on stony or gravelly shores where wave action is strong, and not on the soft and organic bottom muds (*see* Aarnio, cited by Ljunggren 1953, for Fennoscandian lakes; Moore 1910 for Ontario lakes; and Zumberge 1952 for Rabbit Lake in Minnesota). It appears that manganese nodules and crusts in the sea are located in areas of slow sedimentation, such as on sea mounts

or other elevated features of the ocean floor (Goldberg 1954), with the crusts often forming on exposed rocks (Dietz 1955). Freshwater oxidates must accumulate much more rapidly than marine ones, since Goldberg and Arrhenius (1958) quote a rate of 1 mm/1,000 years or more in the ocean, while Kindle (1935) indicates that visible coatings may develop on rocks in dammed Nova Scotian lakes within 25 years. Ljunggren (1953, quoting Naumann) states that ore-scraping for economic use could take place about once every 50 years in the ore lakes of southern Sweden.

RESULTS

The mud, clay and oxidate crust analyses are presented in Table 2. The average lithosphere values have been selected from Goldschmidt (1954), Fleischer (1953), Vinogradov (1956), Green (1959), and from recent surveys dealing with specific elements, namely silver (Hamaguchi and Kuroda 1959), chromium (Fröhlich 1960), cobalt (Carr and Turekian 1961), gallium (Burton, Culkin, and Riley 1959), and tin (Onishi and Sandell 1957). Mean values for Scottish soils (Swaine 1951, 1955) are also given.

Comparison of different types of sediment

In comparing the concentrations of different elements in the oxidized and reduced phases of the uppermost lake muds, it appears that generally there is no great enrichment or depletion of either phase. The most marked difference is that shown by Mn, which is 6.5 times as great in the oxidized surface layers as in the reduced muds a few centimeters beneath. Molybdenum is about twice as plentiful in the oxidized phase, which also contains over a third more Fe than does the reduced phase. Other enrichments appear to be minor, being less than 10% in all cases except for P and Ba, where the average enrichment reaches about 20% but is highly variable in the four sets of samples.

The oxidized muds are poorer in some elements than the reduced subsurface sediments, but the differences are small in most cases. Among the elements showing the

TABLE 2. *Elemental composition of lake sediments**

Number	%										ppm																	
	C	Fe	K	Na	S	Ti	P	Mn	Zn	Ba	Pb	Zr	V	Y	Ni	Rb	Cr	La	Cu	Co	Li	Sn	Ga	Sr	Be	Mo	Ag	
Oxide crusts																												
107,779 Large crusts	1.1	22.1	1.00	0.42	0.43	~1.0	4.1	132	0.4	0.8	80 (10)	60	2	15	10	(1)	4	20	<5	20	<1	<5	(1)	25	5	10	<1	
780	1.3	16.2	1.28	0.39	0.48	2.0	2.3	132	1.5	~5.0	6,000	60	60	40	25	60	30	20	8	40	30	<5	5	100	(5)	10	<1	
781	0.8	11.5	1.83	0.65	0.30	4.0	4.2	100	(0.3)	1.5	30	60	80	40	20	100	40	30	5	40	25	<5	20	30	5	<1	<1	
785	0.5	11.1	1.60	0.68	0.15	3.0	1.8	80	2.0	~8.0	6,000	60	40	30	40	60	30	20	60	80	<5	10	100	5	10	<1		
765 Small lumps	0.8	38.6	0.50	0.18	0.30	1.0	6.2	70	1.0	1.5	200 (10)	80	20	(10)	15	(1)	5	30	<5	25	3	<5	(1)	40	8	10	<1	
783 Stony	0.4	5.9	2.12	0.85	0.10	5.0	1.0	29	3.0	3.0	8,000	100	80	40	40	100	60	30	15	30	60	<5	25	60	<5	<1	<1	
782	0.9	8.5	1.73	1.03	0.28	6.0	1.5	23	0.4	1.5	50	150	80	60	40	100	40	40	15	25	30	<5	20	60	<5	<1	<1	
784 Clayey	0.3	7.2	2.91	0.96	0.05	3.0	1.1	14	(0.3)	2.0	50	100	100	40	20	150	60	30	10	30	40	<5	25	60	(5)	<1	<1	
Windermere muds																												
107,764 Surface	8.3	5.3	1.76	0.62	2.60	2.0	2.0	4.0	1.0	0.8	600	100	80	60	40	60	40	40	30	20	30	25	20	25	8	3	2	
761 Surface	14.7	6.0	1.40	0.52	3.90	2.0	2.5	7.1	0.6	1.0	200	100	80	60	40	40	40	25	25	25	15	10	30	5	6	2		
762 5 cm	12.4	3.6	1.52	0.55	4.60	2.0	2.0	0.6	0.6	0.6	400	100	80	60	60	60	40	60	40	25	25	20	20	25	5	4	(1)	
763 10 cm	12.2	3.9	1.75	0.62	4.70	2.0	1.6	0.8	0.8	0.8	400	100	80	60	60	60	40	60	25	30	25	20	20	25	5	3	1	
773 Surface	8.7	7.1	1.80	0.89	2.30	2.5	3.0	23.0	0.6	0.8	600	60	80	60	25	40	40	40	25	20	20	10	10	20	8	6	1	
774 5 cm	8.9	5.4	1.80	0.68	3.10	2.5	2.9	3.6	0.8	0.6	600	80	100	80	40	40	40	40	30	25	25	15	15	20	10	1	2	
775 10 cm	8.1	5.4	1.82	0.65	2.90	2.5	3.0	3.6	0.8	0.8	800	80	80	60	30	40	40	40	25	20	25	40	15	20	8	2	3	
Esthwaite muds																												
107,770 Surface	11.5	8.3	1.61	0.59	3.30	2.5	3.1	13.8	1.0	0.8	300	60	80	40	40	40	40	30	30	20	20	10	15	20	5	4	<1	
771 5 cm	10.5	4.8	1.76	0.75	5.10	2.5	1.9	0.8	1.0	0.8	400	200	80	40	60	60	40	40	25	20	20	15	20	20	5	<1	1	
772 10 cm	8.4	5.3	1.88	0.70	4.10	2.5	1.6	1.9	0.6	0.8	600	80	80	40	60	60	40	40	25	20	25	15	20	25	5	<1	1	
776 Surface	11.6	5.1	1.83	0.59	4.40	2.5	3.1	0.6	0.6	0.8	600	80	80	60	40	60	40	40	20	20	25	15	15	25	(5)	1	(1)	
777 5 cm	11.2	4.4	2.00	0.68	6.80	2.5	3.0	0.3	1.0	0.8	400	150	80	80	60	60	80	40	25	20	20	15	20	20	(5)	<1	(1)	
778 10 cm	9.9	4.4	1.96	0.55	4.70	2.5	2.5	0.6	0.6	0.6	400	150	100	80	60	60	40	60	40	25	20	20	25	20	5	<1	(1)	
Glacial clays																												
107,766 Rusty	0.18	7.8	1.61	0.62	0.50	5.0	1.5	3.6	<0.3	0.8	40	80	80	40	20	40	30	30	<5	20	30	<5	15	30	5	1	2	
768 Greenish	0.13	9.9	1.45	0.50	0.40	2.0	3.9	4.4	<0.3	0.8	30	40	60	40	20	30	30	40	<5	15	20	<5	15	20	8	1	1	
767 White	0.09	3.2	1.52	0.50	0.30	2.5	0.5	0.4	(0.3)	0.8	80	150	80	60	25	40	40	80	15	15	25	<5	20	20	5	<1	<1	
Average values																												
Reduced muds	10.2	4.65	1.81	0.66	4.50	2.4	2.3	1.5	0.8	0.7	500	120	85	65	55	55	50	45	30	25	25	20	20	20	6	2	1	
Oxidized muds	11.0	6.36	1.68	0.64	3.30	2.3	2.8	9.7	0.8	0.9	450	80	80	55	35	45	45	40	30	20	25	15	15	25	6	4	1	
Oxidate crusts	0.75	15.1	1.62	0.65	0.26	3.1	2.8	72.5	1.1	2.9	2,600	70	60	35	25	70	35	30	10	35	35	<5	15	60	5	5	<1	
Lithosphere	0.03	4.7	2.59	2.83	0.52	4.4	1.0	1.0	0.1	0.6	16	220	150	28	100	280	90	18	70	27	50	2	17	350	5	2	0.1	
Scottish soils	—	—	—	—	—	10.0	1.0	2.0	<0.3	1.0	30	700	180	60	100	280	240	45	45	35	80	—	40	400	6	2	<1	

* Data are given on dry weight basis, in order of abundance in the reduced muds. Parentheses indicate samples in which the concentration appears just at the detectable limit and is somewhat doubtful. When samples contained less than the minimum detectable concentration, the average was computed as if those samples contained half the detectable amount.

greatest depletion are Zr, Ni, S, Ga, and Sn, which range from 33 to 25% lower in the oxidized than in the reduced phase.

The sediments, oxidate crusts, and the glacial clay are compared in Fig. 1, which gives a value of 100 to the highest average concentration and proportional values for the average concentrations of the other sediments (one sample only of white clay is included, since the other two were undoubtedly altered by element migration along redox gradients). To illustrate the method, the oxidate crusts have the highest Sr concentration, averaging 60 ppm. The other values are given as percentages of 60. Elements showing similar distributions among the four kinds of sediment are assembled in the figure. Fe, Mn, Zn, Co, Pb, P, and Mo are lowest in the white glacial clay and highest in the oxidate crusts. Sr and Ba are much higher in the oxidate crusts than in the other sediments, whereas V and Y are distinctly lower. C, Cu, S, Ni, and Sn reach maximum levels in the organic muds. Ga, Zr, and La are highest in the white glacial clay, and lowest in the oxidate crusts.

Variation among oxidate crusts

In general, the oxidate crusts vary in composition much more than the muds, where only Mn and Mo show marked variability. Among the most variable crust elements are Pb, Rb, Li, V, and Ga, for which the *maximum : minimum* ratios of concentration in the crusts are 270, 150, > 80, 50, and 25, respectively. Among the least variable elements are La, Co, Ni, Sr, and C, with ratios of 2, 3, 4, 4, and 4, respectively. The ratios for Fe and Mn are 7 and 9, respectively.

In some of the crusts there is less Fe or Mn than in some of the oxidized surface muds. For instance, the three crusts lowest in Fe range from 5.9 to 8.5%, while the five oxidized muds range from 5.1 to 8.3%. Likewise, the two crusts lowest in Mn, with 2.3 and 1.4%, contain almost the same concentrations as the two richest oxidized muds. The crusts are poorer in organic matter than the muds, so that even when their Fe and Mn contents are similar, the

crusts are cemented into recognizable aggregates, while the muds are loose and unconsolidated.

Fe and Mn are positively correlated in the large crusts, but the small crust pieces from Wray Castle Boathouse Bay (sample 765) deviate from this relationship, being by far the richest in Fe but intermediate in their Mn content. Their Fe : Mn ratio is the highest in the eight samples of crust, at 5.5; and also closest to the average ratio of the oxidized muds, 6.6. In general, the samples rich in Fe and Mn have low Fe : Mn ratios, between 1 and 2; while the samples poorest in these elements have Fe : Mn ratios above 2. It appears that crust development involves a greater enrichment of Mn than of Fe. According to Naumann (1922) and Ljunggren (1953), manganese crusts develop on primary iron concretions, and Goldberg and Arrhenius (1958) suggest that iron accumulations pave the way for the formation of marine manganese nodules. The Wray Castle Boathouse samples seem to conform to this hypothesis, with the small pieces yielding a high and the large crust a low Fe : Mn ratio. In Scandinavia, the same lake may contain some oxidates dominated by Fe and others dominated by Mn (Ljunggren 1953).

Only four elements show a distinctly positive correlation with Fe and Mn in the crusts: C, S, P, and Mo. These are biophile elements, which suggest some influence of organisms upon crust accumulation. The ratio of Mn to C increases as these elements increase in concentration, while the ratio of Fe to C exhibits only a slight tendency in this direction, owing to a high value for the small crust pieces richest in Fe.

The relationship between P and Fe, which is much closer than that between P and Mn, is presumably due to precipitation of ferric phosphate or to adsorption of phosphate by ferric hydroxide incorporated in the crusts. The Fe : P ratio varies generally between 54 and 70, except for a single anomalous value of 27 for the Ferry House sample (781). The ratios in the muds average in the low twenties, probably owing to the presence of a good deal of organic phosphorus.

FIG. 1. Distribution of elements in (1) the white clay, (2) reducing mud, (3) oxidizing mud, and (4) oxidate crust. The sediment type exhibiting the highest concentration is rated at 100, the concentrations in the others are shown as percentages of the highest. Downward pointing arrows indicate the percentage is not calculable, but is less than the indicated value.

The Mo content of the crusts varies widely, with the three samples richest in Fe and Mn containing about 10 ppm, and the three poorest < 1 ppm. In comparison, the oxidized surface muds range from 1 to 6 ppm. How Mo accumulates in the oxidized sediments is not entirely clear, but the fact that both Mo and Mn are considerably more abundant in Windermere than in Esthwaite muds, while Fe is much the same in both, suggests that Mo follows Mn preferentially according to general geochemical expectation (Goldschmidt 1954).

Most of the elements analyzed in the crusts yield negative correlations with the amounts of Fe and Mn accumulated in them. Among the elements exhibiting the most marked declines are Rb, Li, V, Ga, and Zr, some of the elements that are also most variable in concentration. These reach exceptionally low levels in the iron-rich crusts from the Wray Castle Boathouse Bay. Lesser decreases occur in Cr, Ti, Y, Cu, Ni, Na, and K.

Among the elements not showing definite correlations with Fe and Mn accumulations are Pb, Zn, Ba, Sr, Co, and Be. The first three of these are abundant in the Ullswater crusts and in the sample believed to be from Ash Landing in Windermere, while the next two show a less marked tendency in the same direction. Accessory minerals rich in Pb, Zn, and Ba occur rather locally in the Lake District, and any oxidate crusts formed in the vicinity of such mineral occurrences may be expected to scavenge these elements by sorption processes (Smith 1960). It is noteworthy that Pb, Zn, and to a lesser degree Ba are present in much greater abundance in the Lake District crusts and muds than in Scottish soils or the lithosphere (Table 2). Among elements which have lower concentrations in the crusts and muds than in Scottish soils or the lithosphere are Sr, Rb, Cr, V, Cu, Ni, and Zr.

The relatively high contents of Ba in the oxidate crusts cannot be due entirely to barite formation, since the corresponding sulfur concentrations are too low. However, it is probable that any sulfate released

during oxidation of organic matter in the vicinity of the crusts would form barite.

DISCUSSION

Comparison of Esthwaite and Windermere sediments

In spite of the fact that Windermere drains mostly hard volcanic rocks while Esthwaite receives most of its drainage off softer sedimentary slates and grits, there is slight difference between the muds of Windermere and Esthwaite Water in their concentrations of most elements. Esthwaite muds are notably poorer in Mn and Mo, probably because of summer reduction of the profundal mud surface, where both elements tend to accumulate. This reduction no doubt allows Mo as well as Mn to escape from the surface of the mud into the bottom waters, and eventually to the outflow following autumnal breakdown of thermal stratification (Mackereth 1959). The profundal Esthwaite muds sampled in October were richer in Mn, Mo, and Fe than those sampled in November. The former, collected shortly after the restoration of isothermal circulation, appeared more oxidized, judging by their color. Iron, although released to the bottom waters of Esthwaite during summer, is not so easily kept in solution (Mortimer 1941-1942; Hutchinson 1957), and does not appear to be lost from the lake to the same extent as are Mn and Mo.

Silver is apparently more concentrated in Windermere than in Esthwaite mud. However, the above escape mechanism seems unlikely to operate for Ag, because this element is not enriched at the surface as are Mn and Mo.

The element most enriched in Esthwaite mud as compared with Windermere is sulfur. Carbon is similar in the mud samples from both lakes (although collections at other times suggest that Esthwaite muds are on the average richer in this element), and so the C : S ratio is much lower (22) in Esthwaite than in the Windermere muds (30). The low Esthwaite ratio undoubtedly reflects a greater degree of reduction in the mud as a whole (Mortimer 1941-1942),

which both inhibits the oxidative breakdown of organic sulfur compounds and strengthens the fixation of inorganic sulfur as ferrous sulfide.

It thus appears that while there are appreciable differences between the muds of the two lakes in four elements, the remaining 23 are much the same in both.

Factors influencing accumulation of elements

While enrichment of a given element in any sediment may be affected by a variety of environmental factors, it is possible to distinguish certain general tendencies in the data of Table 2 and Fig. 1.

A few elements are more concentrated in the organic muds than in the inorganic clays and crusts, the major ones being C and S. The metals Cu, Sn, and Ni are also in this group, and organic complexing of metals may be involved. For example, porphyrins, well known in lake sediments (Vallentyne 1960), complex readily with Ni and Cu under certain conditions, but not with Co; and Cu and Ni are higher in the muds than in the oxidate crusts, in contrast to Co (Table 2). Sn and Ni resemble S in being slightly more abundant in the reduced than in the oxidized muds. Precipitation of these metals as sulfides in the reduced phase may be responsible for this difference. Sn is much higher in the lake muds than in the lithosphere.

The effects of oxidation are manifested by Fe and more particularly by Mn, both elements being strongly enriched in the oxidized sediments. The greater mobility of Mn is probably responsible for its enrichment relative to Fe in aquatic plants from Windermere, which are usually rich in both elements (Fe averaging 1,500 ppm and Mn 1,420 ppm dry weight, Mayer and Gorham 1951). The Fe:Mn ratio for the plants is only 1.1, in contrast to ratios of 5.4 and 21 for the oxidized and reduced Windermere muds, respectively. The ratio for the white glacial clay is highest of all—80.

The accumulation of a number of other elements in the oxidate crusts is probably due to the marked sorptive properties of

the ferromanganese minerals, which allow them to scavenge various elements such as Ba, Sr, Mo, P, Pb, Zn, and Co where these are plentiful in the environment. Krauskopf (1956) has shown that hydrated oxides of both Fe and Mn can adsorb positive as well as negative ions. The last five elements mentioned above also appear to be distinctly more concentrated in the organic deposits than in the white glacial clay.

The accumulative properties of a reducing environment are best shown by sulfur, which reaches its highest levels in the sub-surface organic muds. Ni and Sn appear to follow S in these aquatic sediments. Although some Fe is trapped as FeS in the reduced muds, the amount of S available is insufficient to tie up a large amount of Fe in this way, and in any case some S may be present in organic and elemental forms.

Comparison of oxidate crusts from various environments

The oxidate crusts from Windermere and Ullswater resemble the Swedish lake and stream ores whose chemistry has been investigated by Ljunggren (1953, 1955a and b), and the Finnish "bog" ores (apparently of freshwater origin) examined by Lander-gren (1948). They are also similar to the manganese nodules collected from the ocean bottom, which have been studied by Goldberg (1954), Dietz (1955), Riley and Sinhaseni (1958), Mero (1960) and Willis and Ahrens (1962). Manheim (1961) has studied similar nodules from the Baltic Sea. Table 3 presents the ranges of concentration for a number of elements analyzed in more than one of these oxidate deposits. (Fe and Mn ranges for Swedish samples represent only those samples analyzed for trace elements, the lake ores so analyzed being well below average in Mn.)

A comparison of Swedish and English oxidates reveals that the Swedish lake ores are highest in Fe, and the English ones lowest. The Swedish stream ores are highest in Mn, and the Swedish lakes ores lowest (although samples not analyzed for trace elements range up to 37%). Both types of Swedish ore are richer in Sr than the English oxidate crusts, while the man-

TABLE 3. *Elemental composition of ferromanganese concretions from different environments**

Element	English lakes		Finnish fresh waters		Swedish lakes		Swedish rivers		Baltic Sea		Oceans	
	min	max	min	max	min	max	min	max	min	max	min	max
Fe %	5.9	39.0	12.0	50.0	41.0	56.0	13.0	43.0			0.4	24.0
Mn "	1.4	13.0	0.2	23.0	0.6	3.2	6.0	35.0			11.0	50.0
K ‰	5.0	29.0	<0.4	0.7	0.5	1.0	0.5	5.0			12.0	13.0
Na "	1.8	10.0									18.0	22.0
Ba "	0.8	8.0			0.1	2.0	0.5	5.0			2.6	3.6
P "	1.0	6.2							1.0	10.0	1.2	20.0
Ti "	1.0	6.0	<0.1	10.0							0.3	14.0
Zn "	0.3	3.0							0.1	0.3	3.0	3.8
Pb ppm	30	8,000			<30		<30	80	100	300	25	3,500
S "	50	480									5,500 (1 sample)	
Zr "	10	150									18	220
Rb "	1	150	<10	10	<100		<100	500				
Sr "	25	100			<100	800	<100	1,000			430	1,100
V "	2	100	<10		50	100	30	100	3	10	270	850
Li "	<1	80	<5	40								
Co "	20	60	60	300	≤10	50	30	600	20	60	70	20,000
Y "	10	60									10	20
Cr "	4	60	<10		<20		<20	30	<5		<5	
La "	20	40									60	170
Ni "	10	40	<10	100	≤10	50	≤10	100	30	100	290	16,000
Ga "	1	25							<5		4	15
Cu "	<5	20							30	100	160	18,000
Mo "	<1	10	<50	60	<30		<30	30	<5		190	2,000
Be "	<5	8	<10	10	50		<10	50	1	3		
Sn "	<5								1	3	160	230
Ag "	<1										10	
B "			20	40			10	20	100	300	70	500

* Elements are given in order of maximum abundance in the English samples.

ganiferous stream ores are also richer in Co. Ni, Sr, and Ba tend, like Co, to be more concentrated in the manganiferous stream ores, but these correlations with Mn are not evident in the English crusts. The Swedish ores are much lower in K than the English crusts, and do not show the striking enrichment of Pb exhibited by three English samples. There is a marked positive correlation between radioactivity and Mn content in the Swedish ores (Ljunggren 1955a).

The freshwater Finnish ores are also notably richer in Fe than the English crusts, and have a much wider range of Mn content. They are poorer in V, Cr, and the alkalis, but are relatively rich in Co. As in the English crusts, but in contrast to the Swedish ores, there is no correlation between Co or Ni and Mn.

It is of special interest to compare freshwater ferromanganese concretions with those of the sea. In Fig. 2, where a distinctly inverse relationship is evident between Fe and Mn, it is clear that Fe predominates in the freshwater crusts and Mn in the marine nodules. The median values for the Fennoscandian freshwater

oxidates are 31% Fe and 13% Mn, while for the marine oxidates the medians are 13% Fe and 22% Mn. This difference presumably reflects the general tendency of Fe to precipitate more readily than Mn from weathering solutions under oxidizing conditions (Krauskopf 1957), so that earlier deposits tend to be enriched in Fe and later deposits in Mn. Three of the crusts from the English lakes are anomalous in being comparatively low in both Mn and Fe. Two of these (783 and 784) clearly show much clastic mineral sediment cemented into them.

A number of elements are strikingly more abundant in the deep-sea oxidates than in those of freshwater origin, namely Mo, V, Ag, Cu, Sn, Ni, and B. Co is also very high in many of the marine oxidates. Such enrichments probably reflect the strong sorptive properties of the hydrated oxides of Fe and Mn, coupled with a very slow rate of formation that has allowed a high degree of sorptive incorporation of trace elements. Manheim (1961) has remarked that manganese nodules from the Baltic Sea have much lower trace element concentrations, prob-

FIG. 2. Manganese and iron in oxide concretions. Solid circles—Fennoscandian freshwaters, crosses—English lakes, open circles—sea.

ably because they have formed more rapidly than the deep-sea nodules. The freshwater oxidate crusts have likewise grown much more rapidly than the marine nodules. However, the degree of enrichment of Pb and Zn in certain crusts from the English lakes is comparable to that of marine manganese nodules, presumably because of the exceptional local abundance of these elements in an area where ore bodies are not uncommon.

Goldberg (1954) has claimed that, in marine manganese nodules, Ni and Cu correlate positively with Mn; and Co, Ti, and Zr with Fe. However, the Cu-Mn and Zr-Fe correlations are insecurely founded (Riley and Sinhaseni 1958). The Ni-Mn correlation is shown to some degree by the Swedish freshwater ores, but not by the Finnish or English oxidates. The Co-Fe correlation is, if anything, negative, rather than positive as in the marine nodules; and the same may be said of the Ti-Fe relationship. The Lake District crusts were the only freshwater samples analyzed for Zr and Cu; the former shows a negative rather than a positive correlation with Fe, and the

latter tends, if anything, to be negatively correlated with Mn.

Willis and Ahrens (1962) have reported a distinct correlation between Ni and Cu in Pacific manganese nodules, and it is also evident in the English lake crusts. However, in the freshwater samples both elements tend to be less abundant in the crusts richer in Fe and Mn, contrary to the case in the ocean.

In conclusion, it appears that no geochemical regularities can be established over the whole range of ferromanganese oxidate deposits, for even the general inverse relationship between Fe and Mn is reversed in the series of English freshwater samples. Probably the most rewarding field for future investigation would be the detailed analysis of elemental abundance in water, sediments, and associated ferromanganese concretions within small areas. Analysis of crusts forming directly on rocks, and of the ambient waters, might be of especial interest.

REFERENCES

- BURTON, J. D., F. CULKIN, AND J. P. RILEY. 1959. The abundances of gallium and germanium in terrestrial materials. *Geochim. Cosmochim. Acta*, **16**: 151-180.
- CARR, M. H., AND K. K. TUREKIAN. 1961. The geochemistry of cobalt. *Geochim. Cosmochim. Acta*, **23**: 9-60.
- DIETZ, R. S. 1955. Manganese deposits on the northeast Pacific sea floor. *Calif. J. Mines Geol.*, **51**: 209-220.
- FLEISCHER, M. 1953. Recent estimates of the abundances of the elements in the earth's crust. *U.S. Geol. Surv., Circ.* 285. 7 p.
- FRÖHLICH, F. 1960. Beitrag zur Geochemie des Chrms. *Geochim. Cosmochim. Acta*, **20**: 215-240.
- GOLDBERG, E. D. 1954. Marine geochemistry. 1. Chemical scavengers of the sea. *J. Geol.*, **62**: 249-265.
- , AND G. O. S. ARRHENIUS. 1958. Chemistry of Pacific pelagic sediments. *Geochim. Cosmochim. Acta*, **13**: 153-212.
- GOLDSCHMIDT, V. M. 1954. *Geochemistry*. Clarendon Press, Oxford. 730 p.
- GORHAM, E. 1958. Observations on the formation and breakdown of the oxidized microzone at the mud surface in lakes. *Limnol. Oceanogr.*, **3**: 291-298.
- . 1960. Chlorophyll derivatives in surface muds from the English lakes. *Limnol. Oceanogr.*, **5**: 29-33.