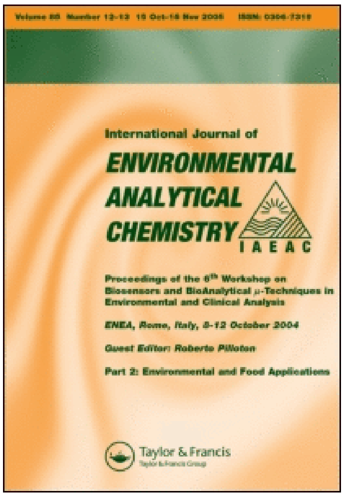

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Speciation of Heavy Metals in Finnish Lake Ores; Selective Extraction Analysis†

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The speciation of Fe, Mn, Co, Cu, Ni, and Zn are studied in Finnish lake ores from areas where weathering of black schists and mica schists, containing abundant sulphide minerals, causes natural pollution by heavy metals.

The lake ores were investigated by means of a sequential selective extraction procedure to differentiate between loosely bound elements, and those bound by MnO_2, by poorly ordered Fe oxyhydroxides, and by well ordered Fe oxides. The Fe and Mn oxide minerals were identified using XRD and electron diffraction.

In areas where the Fe and Mn contents are high in ground water and where the rate of lake–ore production is rapid, poorly ordered goethite and ferrihydrite will form. Fe, Co, Cu, Ni, and Zn are predominantly bound by these Fe oxides. The contents of loosely bound Fe, and Zn are also relatively high. Both Co and Ni are bound by Mn oxides vernadite and birnessite in this environment.

However, in areas characterized by a low rate of lake–ore production, well ordered goethite and minor amounts of ferrihydrite are formed. Ni, and to a lesser extent Zn, is bound by these well ordered oxides. The Cu content of these lake ores is also higher than the Cu content of rapidly-formed lake ores.

KEY WORDS: Lake ores, Fe and Mn oxides, natural pollution, selective extraction analysis.

INTRODUCTION

The prevailing climatological conditions in Finland (mainly the low average temperature, moderate precipitation, and relatively low

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evaporation) have been responsible for the development of acid podzol soils and bogs, where decomposition of organic detrital matter is relatively slow. Sometimes, annual cycles cause in soils varying degrees of local gleization, which is accompanied by biogeochemical cycles. As a consequence, the Eh decreases and the CO_2 content in superficial deposits increases, leading to dissolution of hydrous Fe (and Mn) oxides and associated elements and to their transport by surface waters to be later reprecipitated.[1] The dissolved elements may be transported into ground water, where the microbially catalyzed decomposition of organic matter also causes a decrease in pH, an increase in contents of CO_2, DOC, etc., and dissolution of elements present. Consequently, conditions exist in which dissolved elements predominate. The differences in the contents of readily weatherable material in bedrock and in glaciogenic sediments lead to differences in the contents of Fe, Mn and other heavy metals present in ground water at different localities. The main source of heavy metals (e.g., Fe, Cu, Ni, Co, and Zn) seems to be the easily weatherable sulphide minerals (mainly from black schists and mica schists), which cause natural environmental pollution.

The element supply and the natural processes also affect lake ore formation in Finland. Lake ores are a mixture of detrital silicate minerals and hydrous Fe (and Mn) oxides in the form of concretions. Lake ores form in shallow parts of lakes, where higher Eh and O_2 content exist. The availability of Fe (and Mn) and suitable geological and limnological conditions are the main requirement for lake–ore formation. The ores may be classified, according to their environmentally controlled formation conditions and to their size and form, into pisolitic, penny, and crust ores.[2]

The most widely used method of total chemical analysis is not sufficient to distinguish between the different environmental-bound lake–ore types, and to determine their manner of formation. Therefore, a selective extraction procedure is applied in this study. In addition, differential X-ray diffraction method[3] and electron diffraction have been used.

MATERIALS AND METHODS

Lake ores were sampled from two lakes: Lake Enovesi in southern

Finland (61°29′ N Lat.; 25°54′ E Long.) and Lake Murtojärvi in eastern Finland (62°27′ N Lat.; 30°10′ E Long.). The bedrock in the Lake Enovesi area consists of mica gneiss[4] and in the Lake Murtojärvi area of phyllite and mica schist.[5] Areas of quartz diorite and granodiorite occur north and south of Lake Enovesi and black schists and meta-arkose occur west of Lake Murtojärvi. The superficial deposits in both areas are glaciogenic Quaternary sediments which contain erratics of sulphide–mineral bearing schists. In the Lake Murtojärvi area there are many eskers and other sorted glaciofluvial deposits, whereas in the Lake Enovesi area, till and clay deposits predominate.

Ore types, bottom sediments and sampling depths are given in Table I.

The selective extraction procedures are given in Table II. Separate extractions for ordered hydrous Fe oxides and for non-silicate bound element contents were made using 0.7 M HCl, 0.1 M HXl, and 0.4 M HAc (3 h at 60°C) and HCl, HNO_3, and $HClO_4$ (maximum temperature 160°C).

RESULTS AND DISCUSSION

Lake ores are fresh-water equivalents of deep-sea Fe and Mn nodules. However, their growth rate is more rapid (for lake ores 0.1–4 mm/year and for nodules 10–52 mm/10^6 years[6,2,7]), which in addition to differences in formation mechanism, is undoubtedly responsible for the relatively low Co, Cu, Ni, and Zn contents in lake ores. Moreover, the exceptionally low Cu content in lake ores is thought to be caused by the common tendency of Cu to be organically bound in natural waters[8] and its migration into reducing sediments rich in organic matter, followed by precipitation as a sulphide.

Among the loosely bound elements only Mn, Zn, and Ni are to some degree extractable using NH_4Ac (Fig. 1). Only Fe and Mn appeared in the most strongly bound, hot-acid extractable forms (Fig. 1, Table III). The distribution of Ni, Co, Cu, and Zn between co-existing Fe and Mn oxide phases resembles the distribution of Ni, Co, Cu, and Zn in deep-sea sediments and nodules.[9,10] Co is more strongly bound by Mn oxides, and Cu and Zn are more strongly

TABLE I

Bottom sediments, sampling depth, ore types, Munsell colours of dry powdered ore, and oxide minerals identified. Gt, goethite; Gt, well ordered goethite; Fh, ferrihydrite; Vr, vernadite; Br, birnessite.

Sample No.	Locality	Bottom sediment	Depth cm	Ore type	Munsell colour	Oxide minerals
	Lake Murtojärvi					
38B	N	sand, stones covered by Fe-rich gyttja	40	thick crust ore	6.5 YR 4/6	Gt, Fh
38C	N		60–70	thick crust ore	6.5 YR 4/6	Gt, Fh
38D	N		110–120	thinner crust ore	6.5 YR 4/6	Gt, Fh
38E	N		150	thin crust ore	7.5 YR 4/4	Gt, Fh, Vr, (Br)
38F	N		170	thin crust ore	7.5 YR 4/4	Gt, Fh, Vr, Br
39B	NE	sand, stones covered by Fe-rich gyttja	10	thick crust ore	6.5 YR 4/6	Gt, Fh
39C	NE		40–50	thinner crust ore	7.5 YR 4/6	Gt, Fh, Vr, Br
39D	NE		100–130	thin crust ore, penny, and pistolitic ore	7.5 YR 4/6	Gt, Fh
	Lake Enovesi					
44	N	fine sand, gyttja	60–100	pisolitic ore	10 YR 5/8	Gt, Fh
45	SW	clay, gyttja	30–60	pisolitic ore		
46A	SW	clay, gyttja, boulders	50	pisolitic and penny ore	10 YR 4/4	Gt, Fh, Lp
46B	SW		60	pisolitic and penny ore	10 YR 4/4	Gt, Fh, Lp
46C	SW		80	pisolitic, penny, and crust ore	10 YR 3/4	Gt, Fh, Lp
47A	W	till (boulders, gravel, sand)	100	pisolitic and penny ore	10 YR 5/8	Gt, Fh
47B	W		140	pisolitic and penny ore	10 YR 5/8	Gt, Fh

TABLE II

Sequential extraction procedure.

Step		Fraction extracted	Procedure for about 300 mg sample
I	NH_4Ac	Loosely bound, sorbed	1 M ammonium acetate solution, pH 4.8 adjusted by HAc, 5 ml, 8 h, occasional shaking
II	HXI	Oxidized forms of Mn	1 M hydroxylammonium chloride solution (pH ca. 3), 5 ml, rapid dissolution using ultrasonic agitation
III	HXI-HAc	Poorly ordered hydrous Fe oxides	1 M hydroxylammonium chloride plus 4 M acetic acid solution (pH ca. 1.8), 10 ml, 6 h at 60°C, occasional shaking

TABLE III

Total (acid digested) element contents in lake ores.

	Sample No.	Fe %	Mn %	Co mg/kg	Cu mg/kg	Ni mg/kg	Zn mg/kg
Lake Murtojärvi	38B	50.8	0.530	45	5.2	195	150
	38C	49.7	0.611	50	9.5	245	230
	38D	50.0	0.353	50	4.0	165	195
	38E	46.1	2.400	120	8.5	315	285
	38F	43.2	4.660	200	7.3	430	310
	39B	48.3	0.618	60	8.0	255	225
	39C	46.8	2.000	60	5.3	415	310
	39D	50.8	0.608	50	4.0	220	180
Lake Enovesi	44	47.2	0.650	90	35.5	70	330
	46A	41.9	3.700	155	24.0	65	275
	46B	40.3	2.870	145	24.0	65	320
	46C	32.6	6.720	210	22.0	90	350
	47A	47.6	0.320	75	25.0	75	290
	47B	48.5	0.480	85	20.0	70	290

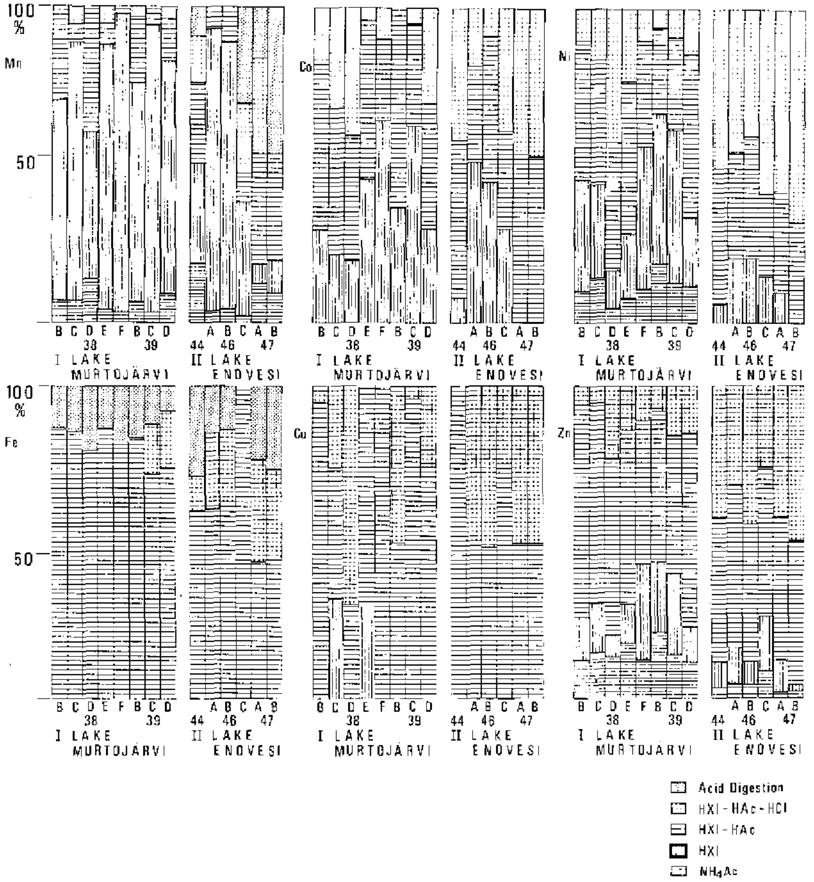

FIGURE 1 Contents of Fe, Mn, Co, Cu, Ni, and Zn in sequential extractions counted as per cent of total element contents in lake ores.

bound by Fe oxides. Ni shows binding by both oxides. However, the loosely bound metal forms are more pronounced in Lake Murtojärvi ores than in Lake Enovesi ores. This is obviously caused by environmental factors. In the Lake Murtojärvi area, precipitation of hydrous Fe (and Mn) oxides in springs and in superficial sediments is a common feature.[11] The dissolution by ground water of Fe (and Mn) from bedrock and from superficial deposits and the subsequent reprecipitation–dissolution cycles seem to be the main feature controlling the geochemistry of iron in the Lake Murtojärvi area. In this environment, the rate of lake–ore production is evidently rapid, and poorly ordered ferrihydrite and poorly ordered goethite are formed. In general, ferrihydrite is formed as a consequence of oxidation of ground–water Fe when in contact with atmospheric oxygen. The formation of ferrihydrite is obviously caused by the rather high Si content in Finnish ground waters (7–12 mg Si/l), since Si interacts chemically with precipitating hydrous Fe oxides and inhibits the formation of lepidocrocite, which is formed during rapid oxidation of Fe^{2+} from Si-free solutions.[12]

Fe, Co, Cu, Ni, and Zn are predominantly bound by the ferrihydrite-containing lake ores. The amounts of loosely bound Mn, Ni, and Zn are also relatively high. Co, and Ni are bound by Mn oxides (birnessite and vernadite, Table I) in these lake ores.

In contrast to Lake Murtojärvi ores, Lake Enovesi ores seem to be characterized by a low rate of production, since well ordered goethite is formed along with minor amounts of ferrihydrite. Ni, and to a lesser extent Zn, is bound by these well ordered oxides. The Cu content of Lake Enovesi ores is higher than the Cu content of Lake Murtojärvi ores.

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