

Estuarine Sediments from the Boreal Region – an Indication of Weathering

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Öre estuary (Northern Sweden) was chosen as a model for other anthropogenically unpolluted estuaries in the boreal region. Sediments were studied in detail in order to characterize the weathering products of silicate rocks. Primary rocks are mostly composed of granite and gneiss. Chemical analysis of total sediments was performed by the XRF method. SiO₂ predominated (71.1–59.2 %) in all samples, decreasing seaward. Al₂O₃ (11.58–12.89 %) and Fe₂O₃ (3.71–6.92 %) were the other main chemical components and they increased seaward. Fourteen elements within the fine silt and clay fraction ($f < 32 \mu\text{m}$) were analyzed by the ICP-AES method. The most abundant microelement was Ti, followed by Mn, Zn, Ba, Cr, Sr, V, while Cu, Co and Ni were the least abundant. Organic matter was characterized as total carbon, hydrogen and nitrogen. Mineralogical composition was studied by the XRD method. The minerals found were quartz, different minerals from the feldspar group (albite, microcline, plagioclase, sanidine), biotite, chlorite and hornblende. Some weathering products, such as montmorillonite-15Å and Al(OH)₃, were detected in the fine silt and clay fraction ($f < 32 \mu\text{m}$). Amorphous iron hydroxide could not be detected by the XRD method. Most of the trace elements determined by ICP-AES (Co, Mg, Cr, Ni, Cu, Mn, Zn) were in very good correlation with iron. ⁵⁷Fe Mössbauer spectroscopy was used for further characterization. Measured at room temperature, Mössbauer spectra did not display magnetic ordering. In only one sample, closest to the river mouth, a better fit was obtained by adding one sextet pattern, but it was of minor significance. Relative amounts of Fe(II) and of Fe(III) were determined in each sample and the Fe(III)/Fe(II) ratio was calculated. It was observed that the amount of Fe(III) increased with the distance from the river mouth and it was either retained at the silicate sites or precipitated as amorphous iron oxide. Mössbauer spectroscopy indicates that the sediments sampled are mostly formed from metamorphic rocks due to the presence of altered biotite and chlorite. The results of this work demonstrate that sediments can be used to study weathering. Some of the reactions, according to the literature, are connected with the consumption of CO₂. Examples of such reactions include the weathering of K-feldspar, albite and hornblende.

Key words

silicate weathering
estuarine sediments
boreal region
X-ray diffraction
X-ray fluorescence
Mössbauer spectroscopy

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INTRODUCTION

There is still significant disagreement over the influence of chemical weathering of rocks on the regulation of the »greenhouse effect« and global climate.¹ Numerical models in the literature and interpretation of geological records show that chemical weathering of rocks had a significant role in regulating climatic stability during different geological periods. In the context of quantifying the global influence of carbonate and silicate weathering on atmospheric CO₂ consumption, weathering rates were examined² under temperate climatic conditions. Chemical weathering of silicate rocks and CO₂ consumption are important in the boreal region.^{3–5} The determined stability sequence with respect to weathering is: apatite < biotite < titanite < hornblende < garnet < epidote < muscovite < zircon.⁶

The aim of this work was to use complementary methods (mineralogical and chemical characterization and Mössbauer spectroscopy) to investigate estuarine sediments as possible records of the types of weathering products of silicates in the boreal regions. The work performed here on a selected pristine estuary suggests that due to the absence of carbonates in this region, it can serve as a »natural laboratory« to study products of silicate weathering. The obtained results can be of global interest.

STUDY AREA

The Öre Estuary is situated in the northern part of the Bothnian Sea in Sweden (Figure 1). It is a semi-enclosed water-body, partly isolated from the outer sea by a dense archipelago. The salinity, which was measured in practical salinity units, varies between 1 and 7, depending on the discharge of the Öre River. The mean annual salinity is 5.00 ± 1.2 and the mean annual pH is 7.7 ± 0.2 . The total area of the estuary is 50 km², the water volume is about 10⁹ m³ and the maximum and mean depths are 35 and 15 m, respectively. The River Öre catchment has an area of 2940 km². Precambrian granites and gneiss are the main rock types. Approximately 65 % of the superficial quaternary deposits in the drainage basin consist of glacial till. A permanent snow cover accumulates from November until March. The rapid snow melt in April and May causes a pronounced single high-flow event. The summer is characterized by low single high-flow events caused by rainstorms. More details about this »natural laboratory« in the boreal region can be found in a series of papers^{7–12} and about ongoing sedimentation monitoring at the web-address: <http://www2.ecology.su.se/dbbm/var/Sedumf.htm>

Erosion processes in the Öre river valley were studied within degree projects. Forsgren (unpublished) reported that erosion rate was the strongest during intensive snow melting and during rainy autumn periods.

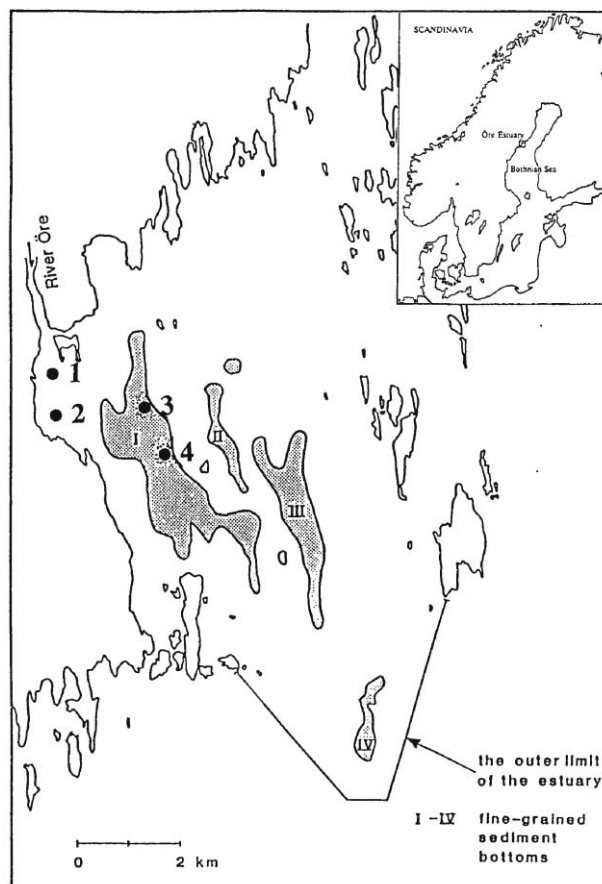


Figure 1. Öre estuary with sampling stations and water depth:

- 1 (63°30'893 N, 19°44'189 E, 2 m);
- 2 (63°30'624 N, 19°44'257 E, 6 m);
- 3 (63°30'672 N, 19°45'931 E, 19 m);
- 4 (63°30'218 N, 19°46'168 E, 21 m).

EXPERIMENTAL

Sampling and Sample Preparation

Sediment samples were taken on 29th September 1999 at 4 stations (Figure 1). Sampling was performed by the boat »Lotty«, using a coring device GEMINI (OY KART AB, Finland) of 80 mm in diameter and a length of 790 mm. From each core, samples were taken from the surface layer (0–5 cm) and from the deeper layer (30–35 cm). This were labeled as samples a and b, respectively. Sample 2 contained only surface sediment, since the corer could not get any deeper at this location.

Samples were dried at room temperature without applying liofilization. This seems to be justified because it was shown that organic carbon in the estuary was very poorly removed from estuarine sediments by aggregation and sedimentation processes.⁸

Laboratory Analysis

The mineralogical composition of the estuarine sediments was determined by the XRD method using a Philips PW 1050 X-ray diffractometer with a proportional counter and

TABLE I. Results of XRF analysis of sediments from the Öre estuary, Northern Sweden (in w/% of corresponding oxides)

	1 ^a	1 ^b	2	3 ^a	3 ^b	4 ^a	4 ^b
SiO ₂	71.1	72.0	68.9	63.0	61.0	59.5	59.2
TiO ₂	0.64	0.68	0.76	0.74	0.75	0.73	0.72
Al ₂ O ₃	11.68	11.58	12.30	12.70	12.54	12.89	12.72
Fe ₂ O ₃	3.71	3.73	4.73	6.05	6.92	6.83	6.79
MnO	0.06	0.06	0.07	0.12	0.11	0.11	0.13
MgO	1.20	1.19	1.52	1.78	1.81	1.97	1.99
CaO	2.17	2.33	2.38	2.07	2.06	1.90	1.91
Na ₂ O	2.17	2.10	2.31	2.25	2.36	2.24	2.54
K ₂ O	2.73	2.73	2.83	2.87	2.84	2.93	2.90
P ₂ O ₅	0.14	0.15	0.17	0.26	0.25	0.27	0.24
L.O.I.*	4.29	3.58	3.97	8.18	9.76	10.69	10.88
Σ oxides	99.89	100.13	99.94	100.02	100.40	100.06	100.02

*L.O.I. = loss upon ignition at 900 °C (1^b, 2, 3^a, 4^a, 4^b) or 1025 °C (1^a, 3^b).

Cu-K α radiation. Crystalline phases were identified using the Powder Diffraction File (1997).¹³ Analysis of macrocomponents was performed by the XRF method, using the wave dispersive (WDS) instrument ARL 8410. Analysis of microcomponents was performed by the ICP-AES method in the fraction < 32 μ m, which was obtained by wet sieving. Samples were previously dissolved in aqua regia. Quantitative

organic microanalysis was performed in the Central analytical laboratory of »Ruder Bošković« Institute to obtain total organic carbon, hydrogen and nitrogen. The fraction of fine silt + clay ($f < 32 \mu\text{m}$) was chosen for analysis instead of the total silt + clay one ($f < 63 \mu\text{m}$) in order to remove a greater part of quartz contained in coarse silt. Samples of total sediments were used as thin absorbers for Mössbauer analyses at

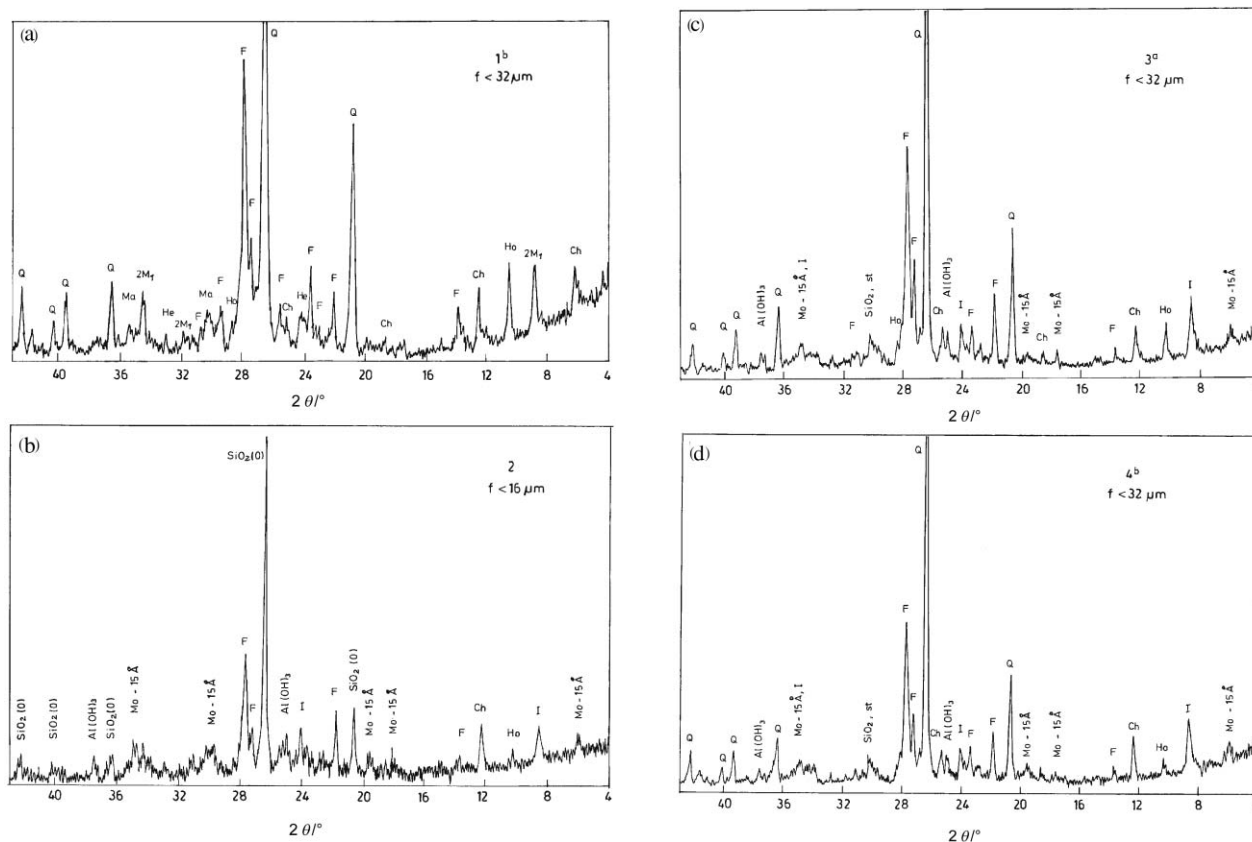


Figure 2. XRD patterns of fine silt + clay fractions separated from selected Öre estuarine sediments: (a) 1^b, $f < 32 \mu\text{m}$; (b) 2, $f < 16 \mu\text{m}$; (c) 3^a, $f < 32 \mu\text{m}$; (d) 4^b, $f < 32 \mu\text{m}$. Characteristic peaks are marked as: Q – quartz; SiO₂(0) and SiO₂, st – stishovite?; 2M₁ – muscovite; F – feldspar group; Ho – hornblende; Ch – chlorite group; Mo – Montmorillonite-15Å; I – illite; Al(OH)₃.

TABLE II. Results of microanalysis of organic matter of sediments from the Öre estuary

Elem. (w/%)	Total sediment						f < 32 µm		
	1 ^a	1 ^b	2	3 ^a	3 ^b	4 ^a	4 ^b	4 ^a	4 ^b
C	1.05	1.01	1.04	2.27	2.11	2.93	2.61	3.01	2.64
H	0.52	0.45	0.84	0.85	2.00	0.68	0.86	0.33	0.69
N	0.09	0.09	0.10	0.55	0.54	0.36	0.23	0.36	0.29

TABLE III. Results of ICP-AES analysis of the Öre river estuarine sediments of fraction < 32 µm*

Element	Sample (fraction < 32 µm)						
	1 ^a	1 ^b	2	3 ^a	3 ^b	4 ^a	4 ^b
Zn	68	89	77	118	152	122	164
Co	7	6	9	12	14	13	17
Ni	19	15	19	25	28	29	35
Ba	36	35	42	75	100	71	68
Mn	200	211	295	372	387	384	457
Fe	18410	16133	22310	31728	37252	34530	43433
Cr	26	27	32	39	48	44	54
Mg	4897	4275	5821	8384	9375	9865	11489
Al	9848	10168	12142	17867	23074	22243	27047
V	24	24	31	42	53	30	50
Ca	5707	7681	9843	9001	10316	9988	11304
Cu	14	14	14	22	24	22	28
Ti	1029	1591	1934	1107	2262	1168	1520
Sr	19	30	34	35	49	45	53

* µg of elements per 1g of sample.

TABLE IV. Weathering indices A and B calculated according to Kronberg and Nesbitt¹⁴ from the XRF analysis of macrocomponents (Table I).

Sample	Index A	Index B
1 ^a	0.8700	0.3770
1 ^b	0.8931	0.3821
2	0.8614	0.3793
3 ^a	0.8468	0.3614
3 ^b	0.8448	0.3667
4 ^a	0.8377	0.3540
4 ^b	0.8395	0.3662

300 K. One sample was measured at 4.5 K. One sample was measured also as f < 32 µm. We used a ⁵⁷Co source with an activity of ~10 mCi in a Rh matrix for all experiments. The velocity scale was calibrated by metallic Fe, which was also used as reference for the isomer shift parameters. The speciations were computer fitted by assuming Lorentzian or Voigt shapes for the resonance lines.

RESULTS AND DISCUSSION

Elemental Analysis

XRF analyses of macrocomponents in estuarine sediments, expressed in w of oxides, are given in Table I. SiO₂ prevailed in all samples (71.1–59.2 %). Percentage

of SiO₂ decreases seaward. Percentages of the other two oxides, Al₂O₃ and Fe₂O₃, and the loss on ignition (L.O.I.) increase seaward. Organic matter was determined directly, as w of total carbon, hydrogen and nitrogen. Results are presented in Table II.

It was confirmed by XRD, as shown in Figure 2 a–d for selected samples, that sediments did not contain inorganic carbon. It was found that the percentages of organic carbon and nitrogen were lower at locations 1 and 2 than at 3 and 4. XRF results of total sediments (Table I) also indicate that there are two sets of samples, 1 and 2 on the one hand, and sites 3 and 4, on the other hand. There is a clear difference in the chemical composition between these two groups, indicating a distinct difference in the parent material. It can be assumed that the two parent materials are gneiss and till, respectively.

Fourteen elements in the fine silt and clay fraction (f < 32 µm) were analysed by the ICP-AES method. Their results are presented in Table III. Of these elements Fe, Al, Mg and Ca are macrocomponents. The concentrations of the microcomponents decrease in the order Ti > Mn > Zn > Ba > Cr > Sr > V. The lowest concentrations were those of Ni, Cu and Co. Concentrations of all of these elements increased in the seaward direction. All trace elements in f < 32 µm, except Ti, show a good positive correlation with iron. The following values of r² were determined for each trace element, using the statistical program »Sigma Plot«: Co (r² = 0.9945), Mg (r² = 0.9831), Cr (r² = 0.9819),

Ni ($r^2 = 0.9627$), Cu ($r^2 = 0.9625$), Mn ($r^2 = 0.9568$) and Zn ($r^2 = 0.8915$). Based on the good correlation, it can be assumed that iron minerals incorporate these elements into a crystal lattice and transport them in a seaward direction.

Determination of the Degree of Weathering

Chemical analysis of total sediments was found to be useful in the studies of weathering phenomena. The amount of SiO₂ (59–72 %) points to the conclusion that the weathering of acid igneous rocks, of glacial till and of metamorphic rocks (gneiss) formed these sediments. The degree of weathering was determined using the results from Table I and the method of weathering indices:¹⁴

$$\text{Index A} = (\text{SiO}_2 + \text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O}) / (\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O})$$

$$\text{Index B} = (\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O}) / (\text{Al}_2\text{O}_3 + \text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O})$$

These indices reflect the degree of silicate hydrolysis and accumulation of Al- and Si-oxides with a simultaneous release of alkaline and earth-alkaline cations. The processes include transformation of easily weathered primary minerals, formation of new products, release of ions and accumulation of residual oxides during the course of weathering. Calculated weathering indices for the Öre estuarine sediments are presented in Table IV. Both indices decrease and the values are between those for gneiss

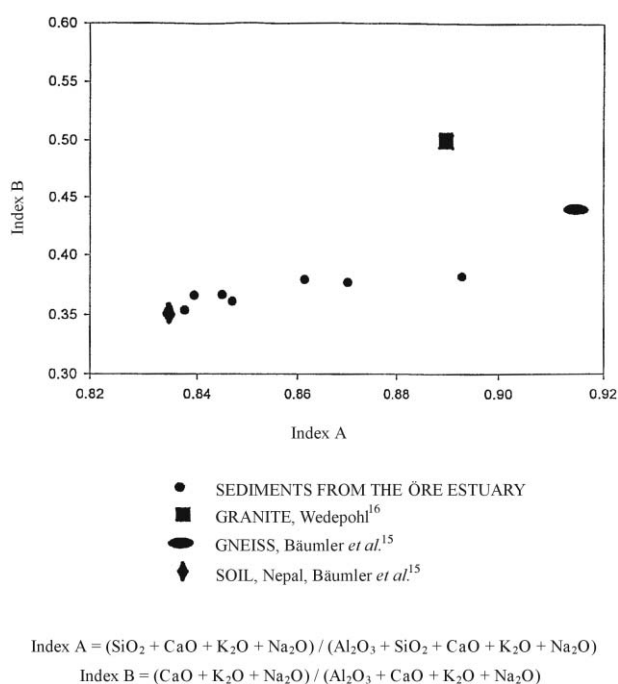
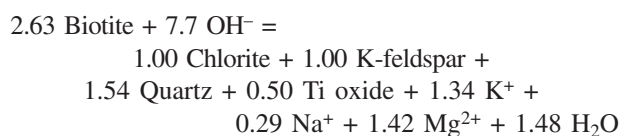


Figure 3. Weathering indices A and B from Table IV were calculated according to Kronberg and Nesbitt,¹⁴ from the XRF analysis of macrocomponents given in Table I.

and soil,¹⁵ while the values for granite¹⁶ are different (Figure 3). From these results it can be concluded that chemical weathering occurs also in the boreal region.

Mineralogical analysis also supports the above conclusion. Mineralogical composition of sediments reflects cumulative effects of composition of parent rocks, chemical weathering, hydraulic sorting, erosion and abrasion.¹⁷ Because of the flat relief we assume that erosion cannot be important. Also, because the estuary is partly isolated from the outer sea by a dense archipelago (see Figure 1), abrasion is negligible. In the Öre estuary, SiO₂ predominates in all sediment samples, even in the clay fraction as quartz (Q), distorted quartz [SiO₂ (0)], or less certainly traces of stishovite (SiO₂-st). In northern Sweden, quartz silt is primarily formed by the »cold weathering mechanism«. In the present work, it is suggested that quartz is a product of physical weathering. Other minerals identified in total sediments are biotite, feldspar group (albite, microcline, anortite, plagioclase, sanidine) and some mafic minerals (chlorite, hornblende, diopside). To better identify the weathering products, XRD patterns of the fine silt and clay fraction were taken and selected results are presented in Figure 2 a–d. Minor minerals found are from the chlorite group (Ch) [clinochlore (JCPDF # 46–1323), chamosite (JCPDF # 46–1324)], montmorillonite-15Å (JCPDF # 13–135), illite (I) (JCPDF # 43–685), and Al(OH)₃ (JCPDF # 26–25). Some weathering reactions described in the literature are worth presenting, because we think they are related to our findings. Traces of muscovite (2M1), hematite (He) and magnetite (Ma) are possible from the XRD pattern presented in Figure 2a, but were not proved with certainty.

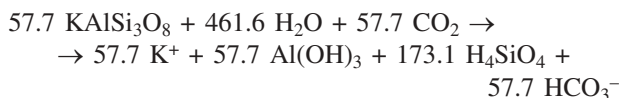
The weathering of biotite can be described according to Morad (see Eq. 4, Table II):¹⁹



According to the same author,¹⁹ chlorite is not necessarily the only weathering product of biotite. Other possible products are kaolinite and siderite, or illite and dolomite, but such products were not found in the Öre estuary sediments. Malmström and Banwart²⁰ performed an experiment of biotite dissolution at 25 °C, which indicated that biotite is transformed to vermiculite. Blum and Erel²¹ described formation of hydrobiotite and vermiculite from the rapid weathering of biotite. These minerals were not found in sediments from the Öre estuary, either.

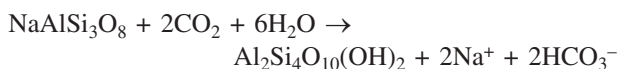
We concluded that chlorite was not subjected to any further weathering, because neither kaolinite and vermiculite²² nor 1 : 1 semi-regular chlorite – vermiculite²³ had been detected.

Weathering of K-feldspar, which is a possible weathering product of biotite,¹⁹ produces Al hydroxide:²⁴



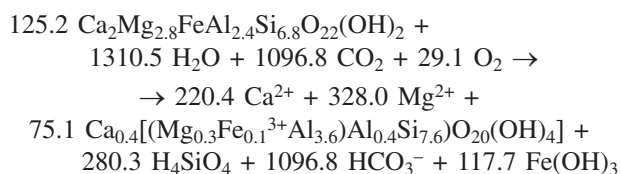
We have identified microcline, KAlSi_3O_8 (JCPDF # 19–932) in total sediment 3^b, and Al hydroxide (JCPDF # 26–25) in fine silt and clay fractions (see Figure 2 b–d).

Montmorillonite can be a weathering product of albite:²⁵



Albite (JCPDF # 41–1480) was identified in all the total sediments studied.

Weathering of hornblende (JCPDF # 28–81) can also produce montmorillonite²⁴ and amorphous iron hydroxide:



Montmorillonite-15 Å (JCPDF # 13–135) was identified (see Figure 2 b–d).

From the above reactions one can conclude that during the weathering of K-feldspar, albite and hornblende, CO_2 (g) is consumed. At this stage of research we are unable to quantify the influence of silicate weathering on the atmospheric CO_2 consumption in the boreal region. The Öre estuary offers the possibility of examining the weathering rates in a flat sedimentary environment under cold climatic conditions, similarly as those described for the Seine river in temperate climatic conditions.²

Mössbauer Spectroscopy

Chemical analysis obtained by the XRF method (Table I) gives the total concentration of iron, which is in most sediments distributed among several mineral phases. Iron occurs in oxidation states Fe (II) and Fe (III). Some iron compounds are either poorly crystalline or amorphous. Mössbauer spectroscopy is a suitable comparative method for studying individual iron compounds and also a mixture of iron minerals in sediments.^{26,27} The ability of Mössbauer spectroscopy to discriminate between Fe(III) and Fe(II) in various minerals is of great importance to geochemists.²⁸ The reason why the method is not widely used in environmental sciences is that the required spectral interpretation and analysis are complicated. As reported,²⁹ at room temperature, in the Mössbauer spectra of most paramagnetic silicate and oxide minerals that contain both Fe(III) and

Fe(II), the low energy lines of the Fe^{3+} doublets overlap with the low energy lines of the Fe^{2+} doublets, whereas their high energy lines are usually resolved. Being aware of these difficulties, the conclusions on the relative population of the iron species presented in this work (see Table V) can be considered approximate.

The measured Mössbauer spectra are presented in Figure 4. The spectrum for sample 1^a was fitted with four doublets and one sextet, two for iron (II) sites and two for iron (III) sites. The spectrum for sample 1^b was fitted with five doublets, one for iron (III) and four for iron (II) sites. The spectrum for 1^b, $f < 32 \mu\text{m}$ was fitted with six doublets, two for iron (III) sites and four for iron (II) sites. The spectrum for sample 2 was fitted with three doublets, one for iron (II) sites and two for iron (III) sites. The spectra for samples 3^a, 3^b and 4^b were fitted with four doublets, two for iron (II) sites and two for iron (III) sites. The spectra for sample 4^a taken at room temperature and at 72 K were fitted with three doublets, two for iron (III) sites and one for iron (II) sites. Assuming equal recoilless fractions for each subspectrum, relative amounts of Fe (III) / Fe (II) were determined and are presented in Table V.

It was not possible to determine the spectral contributions of chlorite and muscovite, as the Mössbauer parameters for chlorite and muscovite are too close to those of biotite. It was observed that Fe (III) increased with the distance from the river mouth. This Fe (III) is either retained in the silicate sites or precipitated as finely divided iron oxides.³⁰ Two minerals from the chlorite group: chamosite (JCPDF # 46–1324) and clinocllore (JCPDF # 46–1323), which contain Fe are very probable in sediments, as identified by XRD (see Figure 2 a–d). Iron oxides could not be detected by XRD, due to poor crystallinity.

CONCLUSIONS

The Öre estuary was chosen as an example of an anthropologically unpolluted microtidal estuary of the boreal region. It was possible to use estuarine sediments to study the silicate weathering products.

From the XRF analysis of macrocomponents, it was concluded that weathering of acid igneous rocks, of gneiss and of glacial till had formed these sediments, as the calculated weathering indices are between those for gneiss and soil.

Quartz is present in all fractions, which is an indication of physical weathering. Chemical weathering was confirmed in $f < 32 \mu\text{m}$ by the presence of montmorillonite-15Å and aluminium hydroxide, while amorphous iron hydroxide could not be identified by XRD.

From the ICP-AES analysis, it was found that there was a good correlation between the microconstituents and the total concentration of iron. This indicates that iron compounds net as a trap for trace elements.

TABLE V. Hyperfine parameters of the Mössbauer spectra of sediments from the Öre estuary obtained at room temperature

Sample	sub-spectra	IS/mm s ⁻¹	QS/mm s ⁻¹	H _{eff} /kOe	Site	A / %	Fe (III)/Fe(II)
1 ^a	du1	1.145(10)	2.650(16)	0	Fe (II)	33.3(59)	0.82
	du2	0.932(42)	2.502(44)	0	Fe (II)	18.2(68)	
	du3	0.3557(96)	0.753(18)	0	Fe (III)	31.7(20)	
	du4	0.776(25)	1.165(55)	0	Fe (III)	10.6(23)	
	se1	1.225(25)	-0.011(26)	113.0(13)	?	6.1(13)	
1 ^b	du1	0.240(21)	1.001(41)	0	Fe (III)	32.6(28)	0.48
	du2	0.598(23)	1.600(48)	0	Fe (II)	6.0(18)	
	du3	1.187(11)	2.427(20)	0	Fe (II)	58.7(34)	
	du4	1.81(13)	2.53(26)	0	Fe (II)	1.0(17)	
	du5	0.624(59)	2.48(12)	0	Fe (II)	1.8(19)	
1 ^b f < 32 μm	du1	0.23(13)	0.77(28)	0	Fe (III)	11.0(18)	0.56
	du2	0.31(12)	0.97(18)	0	Fe (III)	25.0(21)	
	du3	1.262(12)	2.364(18)	0	Fe (II)	41.7(34)	
	du4	1.401(69)	3.31(14)	0	Fe (II)	2.9(10)	
	du5	0.510(44)	1.733(78)	0	Fe (II)	13.1(31)	
	du6	0.711(43)	2.728(59)	0	Fe (II)	6.0(32)	
2	du1	0.399(10)	0.681(19)	0	Fe (III)	38.3(18)	0.84
	du2	1.1074(95)	2.610(19)	0	Fe (II)	54.4(18)	
	du3	0.619(35)	1.537(67)	0	Fe (III)	7.3(17)	
3 ^a	du1	0.401(13)	0.695(24)	0	Fe (III)	47.1(21)	1.04
	du2	1.145(13)	2.619(18)	0	Fe (II)	32.7(84)	
	du3	0.951(61)	2.527(47)	0	Fe (II)	16.4(92)	
	du4	0.712(41)	1.307(79)	0	Fe (III)	3.8(16)	
3 ^b	du1	0.3969(93)	0.690(17)	0	Fe (III)	48.7(17)	1.12
	du2	1.145(12)	2.643(21)	0	Fe (II)	27.0(98)	
	du3	0.994(69)	2.527(51)	0	Fe (II)	20.0(11)	
	du4	0.676(52)	1.352(95)	0	Fe (III)	4.0(15)	
4 ^a	du1	0.77(23)	1.19(37)	0	Fe (III)	13.0(11)	1.15
	du2	1.111(17)	2.610(31)	0	Fe (II)	46.5(53)	
	du3	0.379(22)	0.704(56)	0	Fe (III)	40.3(70)	
4 ^a (72K)	du1	0.225(32)	1.001(22)	0	Fe (III)	28.0(10)	1
	du2	1.268(22)	2.625(44)	0	Fe (II)	50.1(17)	
	du3	0.590(58)	0.825(38)	0	Fe (III)	22.0(10)	
4 ^b	du1	0.3879(41)	0.672(11)	0	Fe (III)	43.4(19)	1.22
	du2	0.611(54)	1.070(68)	0	Fe (III)	11.6(25)	
	du3	1.1431(38)	2.6161(79)	0	Fe (II)	33.5(24)	
	du4	0.964(18)	2.483(20)	0	Fe (II)	11.6(28)	

IS/mm s⁻¹, isomer shift relative to metallic iron; QS/mm s⁻¹, electric quadrupole splitting; A/%, relative resonance area in percent of total iron

Mössbauer spectroscopy was used to study poorly crystalline iron compounds. This technique, which can provide information about the relative population of the iron species together with specific properties of individual iron sites as the oxidation state, is of great importance to geochemists. Increase of Fe (III) / Fe (II) ratio at locations more distant from the river mouth was observed.

It can be concluded that the weathering results can be obtained from sediments and that some of the reactions involve the consumption of CO₂ either from the atmosphere or from some other source. The weathering of K-feldspar, albite and of hornblende are examples of such weathering reactions and they can influence the global cycling of CO₂ in the boreal region. In addition,

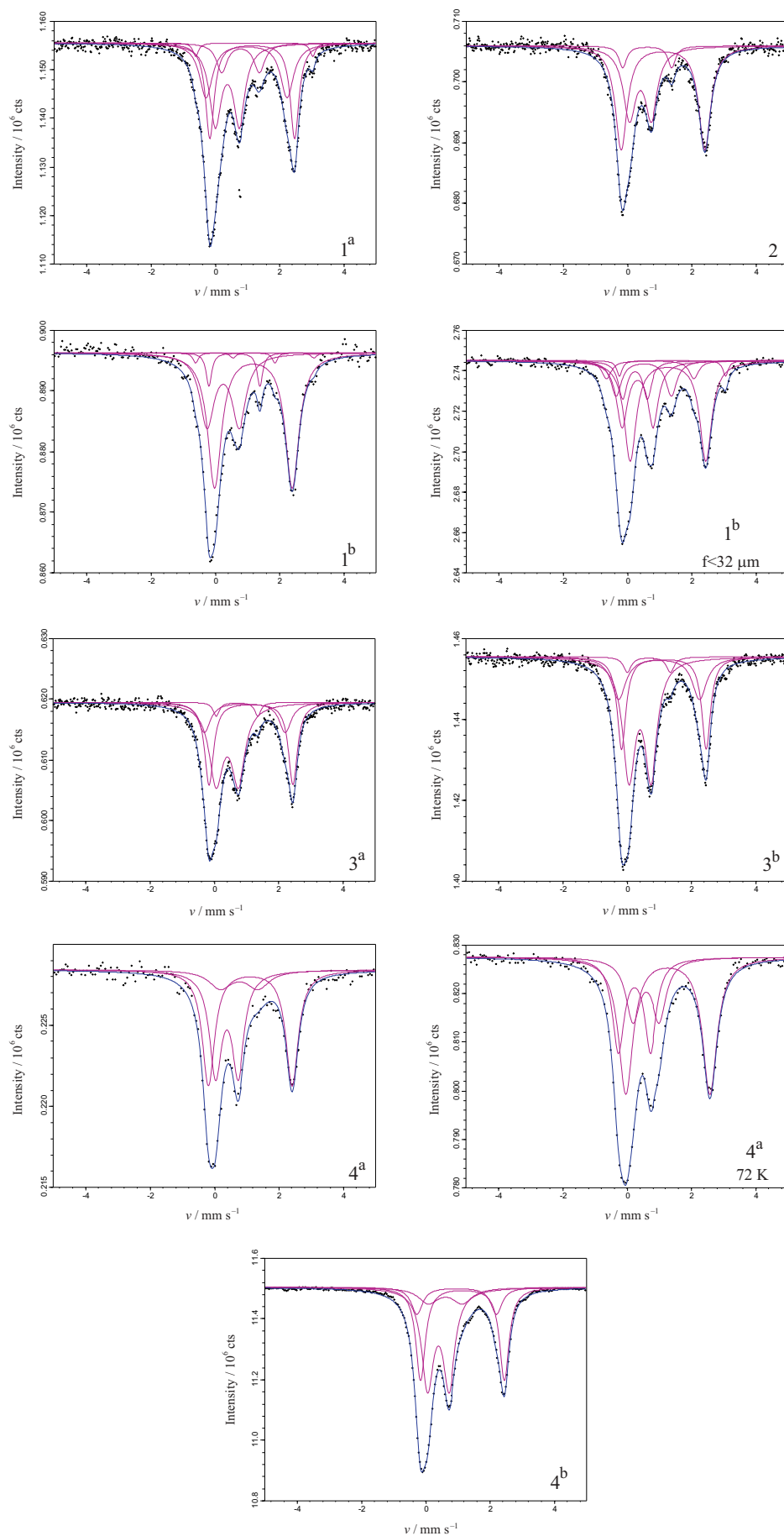


Figure 4. Mössbauer spectra of ^{57}Fe taken at room temperature with a source of ^{57}Co in a Rh matrix: of total sediments 1^a, 2, 1^b, 3^a, 3^b, 4^a, 4^b and of a sediment fraction $f < 32 \mu\text{m}$ of 1^b; Mössbauer spectrum taken at 72 K of total sediment 4^a.

one should be aware, as shown in the recent literature,³⁰ that in the interpretation of Mössbauer spectra taken at room temperature certain overlaps of doublets are possible, which complicates the spectral analysis.

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REFERENCES

1. L. R. Kump, S. L. Brantley, and M. A. Arthur, *Annu. Rev. Earth. Planet. Sci.* **28** (2000) 611–667.
2. S. Roy, J. Gaillardet, and C. J. Allègre, *Geochim. Cosmochim. Acta* **63** (1999) 1277–1292.
3. J. Gaillardet, B. Dupré, P. Louvat, and C. J. Allègre, *Chem. Geol.* **159** (1999) 3–30.
4. J. Gaillardet, B. Dupré, and C. J. Allègre, *Geochim. Cosmochim. Acta* **23/24** (1999) 4037–4051.
5. S. Anderson, *Geology* **25** (1997) 399–402.
6. L.-O. Lång and R. L. Stevens, *GFF* **121/2** (1999) 145–153.
7. G. Forsgren, *Geographical Reports, Umeå University* **13** (1994).
8. G. Forsgren and M. Jansson, *Hydrobiologia* **235/236** (1992) 585–596.
9. G. Forsgren and M. Jansson, *Hydrobiologia* **253** (1993) 233–248.
10. G. Forsgren, M. Jansson, and P. Nilsson, *Estuar. Coast. Shelf Sci.* **43** (1996) 259–268.
11. L. Malmgrön and M. Jansson, *Aquat. Sci.* **57** (1995) 144–160.
12. Ž. Kwokal, S. Frančičković-Bilinski, H. Bilinski, and M. Branica, *Mar. Pollut. Bull.* **44** (2002) 1152–1157.
13. *Powder Diffraction File*, International Centre for Diffraction Data, Newton Square, Pennsylvania, 1997.
14. B. I. Kronberg and H. W. Nesbitt, *J. Soil Sci.* **32** (1981) 453–459.
15. R. Bäumler, W. Zech, H. Heuberger, and K. Weber-Diefenbach, *Geoderma* **48** (1991) 223–243.
16. K. H. Wedepohl, *Handbook of Geochemistry*, Part I, Springer-Verlag, Berlin, 1969, pp. 422.
17. H. W. Nesbitt, C. M. Fedo, and G. M. Young, *J. Geol.* **105** (1997) 173–191.
18. J. S. Wright, *Geomorphology* **36** (2001) 231–256.
19. S. Morad, *Clays Clay Miner.* **38** (1990) 584–590.
20. M. Malmström and S. Banwart, *Geochim. Cosmochim. Acta* **61** (1997) 2779–2799.
21. J. D. Blum and Y. Erel, *Geochim. Cosmochim. Acta* **61** (1997) 3193–3204.
22. T. Murakami, H. Isobe, T. Sato, and T. Ohnuki, *Clays Clay Miner.* **44** (1996) 244–256.
23. J. F. Banfield and T. Murakami, *Am. Mineral.* **83** (1998) 348–357.
24. M. Land, J. Ingri, and B. Öhlander, *Appl. Geochem.* **14** (1999) 761–774.
25. W. Stumm and J. Morgan, *Aquatic Chemistry*, Wiley Interscience, third edition, New York, 1996.
26. E. Murad and U. Schwertman, *Am. Mineral.* **73** (1988) 1395–1400.
27. H. Bilinski, R. Giovanoli, A. Usui, and D. Hanžel, *Am. Mineral.* **87** (2002) 580–591.
28. M. Drodts, A. Lougear, A. X. Trautwein, I. König, E. Suess, and C. B. Koch, *Hyperfine Interact.* **117** (1998) 383–403.
29. D. G. Rancourt, *Hyperfine Interact.* **117** (1998) 3–38.
30. U. Schwertmann and R. M. Cornell, in: *Iron Oxides in the Laboratory*, VCH Ed., Weinheim, 1991, pp.14–18.

SAŽETAK

Estuarijski sedimenti borealnoga područja – indikacija trošenja

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Estuarij Öre (sjeverna Švedska) je odabran kao model za druge nezagađene estuarije borealnoga područja. Sedimenti su detaljno proučavani, da bismo do u pojedinosti karakterizirali produkte trošenja silikatnih stijena. Primarne su stijene sastavljene uglavnom od granita i gnajsa. Kemijska analiza ukupnih sedimenata izvedena je XRF metodom. U svim uzorcima prevladava SiO₂ (71,1–59,2 %), a smanjuje se prema moru. Al₂O₃ (11,58–12,89 %) i Fe₂O₃ (3,71–6,92 %) povećavaju se prema moru. Četrnaest elemenata u frakciji sitnoga silta i gline (f < 32 μm) analizirani su ICP-AES metodom. Od mikroelemenata, najzastupljeniji je Ti, zatim Mn, Zn, Ba, Cr, V, dok su Cu, Co i Ni najmanje zastupljeni. Organska tvar je karakterizirana kao ukupni ugljik, vodik i kisik.

Mineralni sastav je određen XRD metodom. Prisutni minerali su kvarc, različiti minerali iz grupe feldspata (albit, mikroklin, plagioklas, sanidin), biotit, klorit i hornblenda. U frakciji < 32 μm detektirani su neki pro-

dukti trošenja, kao montmorilonit-15Å i Al(OH)₃. Amorfni željezni hidroksid nije bilo moguće detektirati XRD metodom. Većina je elemenata u tragovima, određena metodom ICP-AES (Co, Mg, Cr, Ni, Cu, Mn, Zn), u vrlo dobroj korelaciji sa željezom. ⁵⁷Fe Mössbauerova spektroskopija je upotrebljena za daljnju karakterizaciju željeza. Mössbauerovi spektri na sobnoj temperaturi ne pokazuju magnetsko uređenje. Samo u jednemu uzorku, najbližemu ušću, bolje slaganje je dobiveno dodavanjem jednog seksteta, koji je od manjega značaja. Određene su relativne količine Fe(II) i Fe(III) u svakom uzorku te je izračunan omjer Fe(III)/Fe(II). Opaženo je da količina Fe(III) raste s udaljenošću od ušća rijeke, a može biti u silikatima, ili u amorfnome željeznome oksidu. Mössbauerova spektroskopija ukazuje da su proučavani sedimenti većinom nastali iz metamorfnih stijena, zbog prisustva promijenjenoga biotita i klorita. Rezultati ovoga rada dokazuju da se trošenje može proučavati u sedimentima i da su neke reakcije povezane s uvlačenjem CO₂ iz atmosfere. Primjeri takvih reakcija su trošenje K-feldspata, albita i hornblende.