Geochemistry of ferromanganese concretions and associated sediments in the Gulf of Bothnia

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Introduction

In 1976 Professor Kurt Boström initiated a geochemical research program in order to investigate how an estuarine area like the Baltic Sea affects the flux of river-introduced elements to the open ocean. The research program consisted of five major sections: the composition and weathering characteristics of till, the composition of river-introduced material, the fate of river-introduced matter at the sediment-water interface, the composition of suspended and dissolved matter in the water column, and the role of biological matter for the estuarine sedimentation. Throughout this system the behaviour of Mn, especially, was stressed, as near-shore processes could be part of the explanation of the excess of Mn found in deep-sea sediments.

This study has concentrated on the element interactions occurring at the sediment-water interface in the Gulf of Bothnia. The purpose of the present work was to find an answer to two important questions raised, when this thesis was initiated. How does the formation of secondary Fe-Mn oxyhydroxides affect the flux of elements through the Baltic basin? Are ferromanganese concretions in the Gulf of Bothnia a significant "ore reserve" for Mn or other metals?

The following pages discuss the results obtained during the investigation and this doctoral thesis constitutes a summary of the papers listed below:
Paper 1
Distribution, composition and origin of ferromanganese concretions in the Gulf of Bothnia.
J. Ingri.

Paper 2
Fe and Mn layering in Recent Sediments in the Gulf of Bothnia.
J. Ingri and C. Pontér.
Submitted to Chemical Geology.

Paper 3
Scavenging properties of Fe-Mn nodules in the Gulf of Bothnia.
J. Ingri and C. Pontér.
Accepted in the Proceedings from the "ICES symposium on contaminant fluxes through the coastal zone", Nantes, France, 14-16 May 1984.

Paper 4
REE patterns in ferromanganese concretions and sediments from the Gulf of Bothnia and the Barents Sea.
J. Ingri and C. Pontér.
Submitted to Geochimica et Cosmochemica Acta.

Paper 5
The geochemical stratification of waters and particulates in the Landsort Deep, NW Baltic Sea.
J. Ingri, C. Pontér and K. Boström.
Paper 6
Geochemistry and origin of ferromanganese concretions in the Gulf of Bothnia.
K. Boström, L. Wiborg and J. Ingri.

Paper 7
Selective removal of trace elements from the Baltic by suspended matter.
K. Boström, J-O. Burman and J. Ingri.

Paper 8
A geochemical massbalance for the Baltic.
K. Boström, J-O. Burman and J. Ingri.

Paper 9
Geochemistry of ferromanganese concretions in the Barents Sea.
J. Ingri.
Accepted in Marine Geology.
Acknowledgements

I wish to thank Professor Kurt Boström for introducing me into the fascinating field of geochemistry. I also wish to thank the whole research group K. Boström, C. Pontér, J-O. Burman, S. Brandløf, M. Sandström and B. Boström for their help during sampling and laboratory work, and for suggesting improvements of the manuscripts. A special thanks is given to the crew onboard R.V. Strombus for their skilful help and very good company at sea. I also thank I. Lundmark and B. Keskiniva for their typing and retyping of the manuscripts throughout this work, and M. Vnuk for his excellent drawings. The library did a great work searching for obscure references and P-O. Ehlin translated the texts in Russian, a much appreciated support. I thank P. McMillen for improving the English of the manuscripts. Major financial support was provided by the Swedish Board for Technical Developments (STU), the Swedish Natural Science Research Council (NFR) and the Department of Economic Geology, Luleå University, this is gratefully acknowledged.
Summary

Ever since the detailed studies of Fe-Mn-rich nodules in the deep-sea by the Challenger expedition 1872-1876, their mode of formation and the origin of the elements have been vehemently discussed. Submarine vulcanism, continental run-off, extra-terrestrial sources, submarine weathering, organisms and diagenetic reactions have all been claimed to contribute to Fe-Mn nodule formation (see review articles in Glasby 1977, and Cronan 1980).

In the Baltic Sea area it is still a matter of dispute whether Fe-Mn-rich nodules are formed owing to a diagenetic redistribution of river-introduced elements in the sediments (Manheim 1965, Winterhalter 1966, Boström et al. 1982), or whether they are formed directly from laterally supplied river-introduced matter (Varentsov 1973). It is, however, generally agreed upon that only continental run-off can be a primary source for the Mn and Fe found accumulated in concretions in the Baltic Sea.

A series of enrichment processes contribute to the formation of the ferromanganese concretions found in the Gulf of Bothnia. One main factor governing the accumulation process is changing redox levels, induced by the break-down of organic matter. The ultimate source of Fe, Mn and some associated trace elements, found enriched in concretions, is the vast till areas surrounding the Gulf of Bothnia. Accumulation processes concentrate Fe and Mn in the concretions by one and two orders of magnitude respectively.
above their average values in north Swedish till deposits (Table 1).

Mobilization of elements from a lattice position in various "till minerals" may occur in several ways. One fundamental factor is the activity of organic matter. Rootlets penetrating the permeable, freshly exposed glacial debris are acid-producing (Bowling 1976), and primary minerals are leached. This acid attack and the lowered pH produced by the formation of humus out of abundant needle and leaf litter, together with the humid climate typical of the coniferous/deciduous forest belt of the northern Hemisphere, results in the podzol soil profile (Brady 1974). A pronounced weathering of Fe and Mn occurs in these profiles, and a huge pool of mobilized Fe and Mn is created.

In the case of Mn a significant quantity could also be mobilized simply by plant accumulation and decay. Much of the Mn held within plant tissue may be returned to the soil in an immediately water-soluble form. Levanidov (1957) has found that birch leaves on the southern Ural Steppes annually deposit about 2 kg Mn per acre (4047 m²), some 50% of this being water-soluble. Analyses of coniferous needles from northern Sweden have shown a pronounced accumulation of Mn (pine-needle 4.4% ash weight, spruce-needle 2.8% ash weight, Table 2). Enrichment of Mn and other trace elements in living matter is illustrated by the podzol profile from northern Sweden shown in Table 1. A striking feature is the strong enrichment of Mn, Zn, Cu, Ba and Sr, the latter two elements being enriched also in spruce-needs (Ba 830 ppm
Table 1  Composition of a podzolprofile from Svartberget, Västerbotten, northern Sweden.

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<th>Fe₂O₃</th>
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<th>MgO</th>
<th>CaO</th>
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<th>K₂O</th>
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<th>Ni ppm</th>
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<th>V ppm</th>
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So = living green plants, F, H = humified layers, A₂ = leached zone, 
B₁,2,3 = layers of Fe-enrichment, C₁,2 = "unweathered till".

Note that this profile is atypical compared to the average SiO₂ (62.5 %), 
Fe₂O₃ (6.3 %), MgO (2.2 %), CaO (3.8 %), Na₂O (3.6 %), K₂O (2.4 %) and 
V (120 ppm) values found in till samples (C-horizon, 1 m depth) from the 
county of Norrbotten, northern Sweden.
Table 2  Ashweight composition of needles from northern Sweden.

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<th>SiO₂</th>
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<td>ppm</td>
<td>ppm</td>
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<tr>
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<td>6.2</td>
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<td>605</td>
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and Sr 605 ppm, Table 2). Additionally some elements migrate from vegetation either by transpiration of exudates or by leaching of needles and leaves by rain and snow (Curtin et al. 1974, Horler et al. 1980, Boström et al. 1985). Birch exudates sampled outside Luleå (northern Sweden) are selectively enriched in Ba, Sr, Mn, Zn and Cu—compared to average crust (Burman 1982).

Eventually, most weathered elements reach the major rivers draining into the Gulf of Bothnia. Burman (1982) has shown that northern Swedish rivers transport larger amounts of Mn, Fe, Ca, Na, Mg, Ba, Sr, Zn, Cu, Ni, Cr and V than can be found in permanently depositing (below the redox cline) grey reduced sediment in the Gulf of Bothnia. Most of the river-introduced Fe and Mn are transported as a non-detrital suspended phase. Mean composition of 17 rivers draining into the Gulf of Bothnia, sampled during the spring-flood in May, exhibits approximately 0.3% Mn and 10% Fe in a suspended phase (Burman 1982).

The unregulated Kalix river, which debouches into the Bothnian Bay, was investigated during 4 years. Results show that suspended Mn increases drastically at the end of July with a peak value in the middle of August; the ratio, non-detrital Mn to detrital Mn then being around 33. Ninety-seven percent of suspended matter in July and August is present in a non-detrital fraction contributing 30% of the annual load of Mn in the Kalix river (Burman 1982). To account for the strong enrichment of Mn (around 2% Mn as a suspended peak value, registered both in the Kalix and Torne rivers) and
the changing Fe/Mn ratio in river-suspended matter from May to September (Fig. 1), an efficient enrichment process for Mn must be operative.

It has been propounded that the Mn-peak observed in August is related to changing redox levels in lakes draining into the Kalix river (Pontér et al., to be published). Summer stratification of lakes together with a high organic production results in an oxygen deficiency in the lake sediments and a lowered redox level in the bottom-waters. The break-down of organic matter within the sedimentary column reduces Fe-Mn oxyhydroxides, which results in a subsequent migration of Fe and Mn into bottom-waters. This brings about a significant flux of Mn, whereas much Fe is trapped in more oxidized parts of the lake (Davison et al. 1982, Lidén 1983). This separation of Fe and Mn, together with groundwater seepage, explains the Fe-rich concretions found in lakes all over Scandinavia. Most Mn, however, reaches the major rivers, causing a change in the Fe/Mn ratio of suspended matter, as observed in the Kalix river (Fig. 1). Several other elements also exhibit strong seasonal changes which are related to the annual, spring and autumn turn-over, and summer and winter stratification occurring in lakes. Several trace element correlations observed in concretions in the Gulf of Bothnia are established already in the lake-river-borne suspended matter, emphasizing their genetic relationship (Pontér et al., to be published).
Figure 1. Changing Fe/Mn ratio in the suspended phase in the Kalix river (data from Pontér et al., to be published).
Pathways of river-introduced Fe-Mn in the Gulf of Bothnia

The fate of the lake-river-borne Mn-rich suspended phase upon burial in the sedimentary column, is quite different in the three major regions of the Gulf of Bothnia; the archipelago region, the open Bothnian Bay and the open Bothnian Sea.

In the archipelago region of northern Bothnian Bay very high interstitial water contents of Fe and Mn have been recorded in the sediments. Values between 30 and 50 mg/l Mn are frequently found; figures that are 20 to 100 times higher than those registered in the open Gulf of Bothnia (Table 3). During biological decomposition of organic matter in the absence of oxygen, bacterial reduction of sulphate results in the formation of bicarbonate ions (Berner 1971). High interstitial bicarbonate, therefore, may bring about the precipitation of dissolved Ca$^{2+}$ as CaCO$_3$, or, when much Mn$^{2+}$ is present, as a mixed Ca-Mn-carbonate (Calvert and Price 1972, Robbins and Callender 1975). HCl-leaching of cores from the archipelago region suggests the presence of a carbonate, as leachable Ca abruptly increases at some 15 to 25 cm downwards in analysed profiles. Generally, sediment samples taken in the archipelago region of the northern Bothnian Bay contain on the average 10 times more Mn in the reduced permanently depositing sediment compared to the open
<table>
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<td>7750</td>
<td>754</td>
<td>1160</td>
<td>59</td>
<td>132</td>
</tr>
<tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
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<tr>
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<td></td>
</tr>
<tr>
<td>0-2 cm</td>
<td>12.00</td>
<td>3.08</td>
<td>7.80</td>
<td>-</td>
<td>303</td>
<td>629</td>
<td>2040</td>
<td>121</td>
<td>221</td>
</tr>
<tr>
<td>3-5.5 cm</td>
<td>21.82</td>
<td>0.52</td>
<td>8.20</td>
<td>-</td>
<td>51</td>
<td>1760</td>
<td>2050</td>
<td>124</td>
<td>219</td>
</tr>
<tr>
<td>5.5-7.5 cm</td>
<td>8.79</td>
<td>0.09</td>
<td>8.07</td>
<td>-</td>
<td>177</td>
<td>1690</td>
<td>2080</td>
<td>115</td>
<td>203</td>
</tr>
<tr>
<td>7.5-9.5 cm</td>
<td>9.00</td>
<td>0.10</td>
<td>8.09</td>
<td>-</td>
<td>1330</td>
<td>2480</td>
<td>2090</td>
<td>118</td>
<td>208</td>
</tr>
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</table>
Gulf of Bothnia. Formation of an authigenically mixed Mn-Ca carbonate is the most likely explanation of this enrichment. Mn-carbonates have previously been reported from highly reduced sediments in the Baltic proper (Manheim 1961, Suess 1979). Evidently, some Fe is also trapped in a reduced state, as archipelago sediments usually are totally black and turn grey when exposed to air, indicative of Fe-monosulphides (Berner 1971). However, the strong concentration gradient observed (Table 3) suggests a significant flux of Fe and Mn out of the sediment. Only small deposits of Fe-Mn concretions can be found within the archipelago regions, and hardly any Fe and Mn are trapped in the very thin (few mm) oxidized zone of the muddy sediments encountered in this area. Hence, many near-shore sediments probably act as sources of Mn-enriched suspended matter. "Pumping" of Mn in the coastal zone very likely follows seasonal cycles in a manner similar to the ones discussed above for lakes.

Fe-Mn-stratified surface sediments

Sedimentation of lake-river-(archipelago?)-born Fe-Mn-enriched suspended matter in the open Bothnian Bay results in enhanced interstitial levels of dissolved Mn and Fe, and, hence, a migration upwards (Table 3). But, in contrast to the archipelago region, a thick oxidized surface sediment layer is present at all loca-
tions in the open Bothnian Bay. Boxcore data reveal that the thickness of the oxidized surface sediment increases from a few mm in the archipelago regions to 15 cm at locations off the coast. Owing to the strong oxygen tension prevailing all over the open Bothnian Bay, much ascending interstitial Fe and Mn are fixed within the sedimentary column. This results in a stratification of the oxidized zone. The layering is essentially visible owing to a separation of black Mn-rich sediment from yellow-orange-brown Fe-rich sediment (Fig. 3). In a well developed oxidized surface sequence overlying grey reduced sediment, up to five layers can be recognized: a yellow-grey transition zone (~ 5-10% Fe$_2$O$_3$) - an orange-brown Fe-rich layer (~ 10-25% Fe$_2$O$_3$) - a brown, hard Fe-crust (25-45% Fe$_2$O$_3$) - a black Mn-rich layer (~ 2-10% MnO) - a brown water-rich top layer often with Mn-rich spherical nodules. Some elements display a clear preference for the authigenically Mn-enriched layer, others a preference for the authigenically Fe-enriched layers. Mo, Ba, Ni, Cu and Zn are related to Mn, whereas P, Ca, Sr and As are correlated to Fe (Paper 1, 2 and 4, this volume).

A strong redox gradient has been measured in the porewaters within these oxidized sediments, whereas pH varies only to a small extent (Table 3). The formation of these layers is linked to the developed redox gradient, and, as Fe precipitates prior to Mn, going from reducing to oxidizing conditions at a constant pH (Krauskopf 1957), the Fe-rich layers always occur below the Mn-enriched strata.
Figure 3. Large picture to the right shows a diagenetically altered sediment profile from the Bothnian Bay. In the ~ 4 cm thick water-rich brown surface layer small spherical nodules are seen. This zone is followed by a ~ 2 cm thick black Mn-rich sediment layer resting on a few mm thick lithified orange-brown Fe-rich crust. Subsequently below, a yellow coloured Fe-rich zone grades into grey reduced sediment. The whole sediment profile represents the latest part of Holocene (Scale 1:1).

(Upper, left). Tilted sediment profile (surface sediment, brown water-rich, in the upper left corner) from the Bothnian Bay (N64°06, E21°48, water-depth 102 m), showing a buried (below ~ 2 cm of reduced sediment) Mn-Fe enriched sequence. This Mn-Fe oxyhydroxide sequence does not show any signs of dissolution. Note how the black Mn-rich layer consists of small micronodules coalesced into a crust (lower left).

(Middle, left). Top view of a sediment with a brown water-rich surface sediment. Subsequently followed by a few mm thick black Mn-rich layer and a 3 mm thick lithified brown Fe-rich crust, formed above a grey reduced sediment. Sample from the Bothnian Bay (N64°56, E21°50, water depth 80 m).

(Lower, left). A boxcore profile from the Bothnian Bay, showing the oscillating redoxcline within the water-rich brown surface sediment. Upper part of section exhibits black Mn-precipitation onto nodules whereas lower portion displays brown Fe-precipitation above a grey reduced sediment. Note the partly black, partly brown nodule situated at the sharp redoxcline, dividing Mn- from Fe-precipitation. This movement of the redoxcline explains the concentric Fe- and Mn-layering seen in spheroidal nodules. Scale 1:1.
Stratified oxidized surface sediments are frequently encountered on muddy bottoms all over the Gulf of Bothnia (Paper 2, this volume). From the 140 boxcore samples taken, the surface sediment can be classified into five main types of profiles (Figure 4). Top sediments with a pronounced Mn-rich layer are common in the Bothnian Bay, whereas they are sparsely occurring in the Bothnian Sea. Fe-rich strata are, however, frequently seen in the Bothnian Sea, often present as a "continuous" Fe-pavement at the sediment-seawater interface. This difference has been interpreted as being due to a generally lower redox level in the Bothnian Sea (Paper 2, this volume).

In the Baltic proper large areas are covered by totally reduced surface sediments with $H_2S$ appearing in bottom waters in the deeper parts. Layered oxidized surface sediments are very rare in this basin and nodule occurrence is sparse compared to the Gulf of Bothnia. Stratification of Fe and Mn of the type seen in sediments in the Gulf of Bothnia has been observed in the water column above the Landsort Deep in the Baltic proper (Paper 5, this volume). The chain of reactions occurring in the water column above the Landsort Deep (Table 4) illustrates how the Fe-Mn-stratified surface sediments seen in the Gulf of Bothnia might form. If we assume that the reduced section of post-glacial sediments is represented by depths below 150 m in the Landsort profile, that depths between 40-150 m represent the oxidized surface sediment and that depths above 40 m represent overlying seawater, the following reactions can be predicted to occur in a modelled sediment profile.

It has been suggested that average Baltic suspended matter consists of a mixture of 3 parts biogenic matter and 1 part grey re-
Figure 4. The different types of profiles developed in the oxidized top section of Recent soft bottom sediments in the Gulf of Bothnia.
Table 4  
Formation of a Mn-Fe stratified water column above the Landsort Deep, Baltic proper.

| Dept | Temp. (°C) | Salinity (o/oo) | Oxygen (ml/l) | % | H₂S (µmol/l) | pH | Alk. (mmol/l) | PO₄³⁻ (µmol/l) | NO₃⁻ (µmol/l) | NH₄⁺ (µmol/l) | SiO₂ (µg/l) | Mn (µg/l) | Fe (µg/l) | Ca (mg/l) | Suspended* (Mn %) | Suspended* (Fe %) |
|------|------------|----------------|--------------|---|--------------|----|-------------|----------------|--------------|--------------|-------------|------------|----------|---------|----------|----------------|----------------|
| 0    | 7.24       | 7.350          | 7.85         | 98| 7.93         | 1.493 | 0.35       | 0.70           | 0.77         | 11.1         |             |           |          |          | 0.56     | 3.13     |
| 2    | 7.24       | 7.351          | 7.86         | 98| 8.03         | 1.498 | 0.34       | 0.76           | 0.42         | 13.6         |             |           |          |          |          |          |          |
| 5    | 7.24       | 7.350          | 7.84         | 97| 8.05         | 1.491 | 0.34       | 0.70           | 0.38         | 10.8         | 6          | 14       | 168      |          | 0.56     | 3.13     |
| 10   | 7.25       | 7.352          | 7.87         | 98| 8.06         | 1.535 | 0.30       | 0.74           | 0.32         | 11.6         |             |           |          |          |          |          |          |
| 15   | 7.22       | 7.354          | 7.85         | 98| 8.07         | 1.549 | 0.32       | 0.75           | 0.40         | 11.0         |             |           |          |          |          |          |          |
| 20   | 7.08       | 7.371          | 7.79         | 97| 8.04         | 1.518 | 0.35       | 0.83           | 0.38         | 12.0         |             |           |          |          |          |          |          |
| 30   | 6.71       | 7.443          | 7.72         | 95| 8.04         | 1.539 | 0.42       | 1.11           | 0.31         | 13.1         |             |           |          |          |          |          |          |
| 40   | 5.77       | 7.562          | 7.54         | 91| 7.92         | 1.588 | 0.54       | 1.57           | 0.34         | 14.1         |             |           |          |          |          |          |          |
| 50   | 3.67       | 7.928          | 6.65         | 76| 7.71         | 1.598 | 0.91       | 3.49           | 0.36         | 21.1         | 6          | 18       | 182      |          | 0.56     | 3.59     |
| 60   | 3.85       | 9.205          | 2.75         | 32| 7.33         | 1.608 | 2.25       | 4.82           | 0.17         | 47.0         |             |           |          |          |          |          |          |
| 70   | 4.01       | 9.704          | 1.55         | 18| 7.25         | 1.615 | 2.68       | 4.53           | 0.44         | 56.6         |             |           |          |          |          |          |          |
| 80   | 4.07       | 9.823          | 0.95         | 11| 7.24         | 1.649 | 2.80       | 3.98           | 0.11         | 60.0         |             |           |          |          |          |          |          |
| 90   | 4.20       | 9.998          | 0.87         | 10| 7.20         | 1.639 | 3.01       | 3.42           | 0.24         | 62.4         |             |           |          |          |          |          |          |
| 100  | 4.22       | 9.984          | 0.62         | 7 | 7.25         | 1.673 | 2.97       | 3.39           | 0.32         | 62.6         | 15         | 13       | 239      | 7.62     | 5.23     |
| 125  | 4.29       | 10.111         | 0.32         | 4 | 7.21         | 1.664 | 3.09       | 2.73           | 0.48         | 66.1         |             |           |          |          |          |          |          |
| 150  | 4.41       | 10.325         | 0.00         | 0 | 7.30         | 1.664 | 3.22       | 1.90           | 0.88         | 68.6         | 112        | 16       | 259      | 2.83     | 7.43     |
| 200  | 4.51       | 10.623         | 3.4          |   | 7.29        | 1.695 | 3.51       | <0.10          | 1.71         | 72.5         | 493        | 30       | 255      | 0.34     | 4.46     |
| 250  |            |                |             |   |             |       |           |                |             |             | 362       | 29       | 260      | 0.29     | 6.21     |
| 300  | 4.64       | 10.861         | 10.0        |   | 7.30        | 1.715 | 3.77      | <0.10          | 2.98         | 75.5         | 689       | 36       | 260      | 0.25     | 4.56     |
| 400  | 4.67       | 10.886         | 11.2        |   | 7.30        | 1.739 | 3.77      | <0.10          | 3.36         | 76.0         | 554       | 32       | 264      | 0.35     | 5.22     |
| 425  | 4.65       | 10.893         | 11.3        |   | 7.30        | 1.746 | 3.79      | <0.10          | 3.43         | 77.2         |           |          |          |          |          |          |
| 440  | 4.71       | 10.901         | 12.2        |   | 7.30        | 1.754 | 3.82      | <0.10          | 3.42         | 78.5         |           |          |          |          |          |          |

*Al-normalized
Figure 5. A model suspendate for the Baltic Sea, assumed to consist of one part Mn-poor sediment and three parts biological matter (BM). The excess of Na and Mg is probably due to admixed sea-salt.
duced sediment (Paper 7, this volume). To account for the Mn content a Mn-rich phase must also be added to the modelled suspended matter (Fig. 5). When a suspended particle of this type reaches the sediment surface, a pronounced increase in the dissolution of biogenic fraction occurs owing to the high amount of bacteria present at the sediment-water interface (Zobell and Anderson 1936). In the presence of molecular oxygen, organic decomposition is dominated by organisms using oxygen as an electron acceptor (Goldhaber and Kaplan 1974). This can be represented by the equation

\[
(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138 \, O_2 + 106 \, CO_2 + 122 \, H_2O + 16 \, NO_3^- + \, P_4O_{12}^- + 19 \, H^+ \quad (1) \quad \text{(C:N:P ratio living plankton Flemming 1940)}
\]

This is illustrated in Table 4 (50-60 m) by a decrease in pH, a significant decrease in dissolved oxygen, a large increase in dissolved P, N and Si, together with a small increase of dissolved Mn and Fe. Both the decrease in pH and redox (\(\sim O_2\) content), and the enhanced values of Mn and Fe have been measured in the interstitial waters sampled (Table 3). If the hard parts of the plankton mass (Si+Ca) are also added in equation 1 the constant increase of dissolved Si measured in the interstitial waters can be explained analogously to the Landsort profile. There is no pronounced increase in dissolved Ca in Table 4, and no significantly enhanced Ca values can be seen in the porewaters sampled. Interstitial Ca figures measured within the surface sediments only reflect salinity variations in the bottom-waters (Table 3).

Coupled with the slightly reduced redox level (illustrated by the lowered oxygen content in Table 4) in the uppermost oxidized
surface sediment, a desorption of Cu, Ni, Zn, Co, Y and the REE (possibly with an exception for Ce) from Mn-oxyhydroxides is possible. These elements show a strong surface dependency in nodules from the Gulf of Bothnia, as well as a redox level-governed accumulation (Papers 1 and 3, this volume). The slightly lowered redox level encountered in the oxidized surface sediment may, therefore, strip off loosely held elements like Cu, Ni, Zn, Co, Y and the REE from a sedimenting Mn-rich suspended particle. This process probably is part of the explanation to the decreasing content of these elements in nodules with depth of burial within the oxidized surface sediment (Paper 3, this volume). In the deep-sea environment this has been referred to as oxic diagenesis (Dymond et al. 1984).

When molecular oxygen has been used up, organic matter decomposition continues, now mediated by organisms which use progressively less efficient electron acceptors. Sulphate reduction may be represented with the following equation:

\[
(CH_2O)_{106}(NH_3)_{16}(H_3P0_4) + 53 S0_4^{2-} + 119 H^+ + 106 CO_2 + 53 H_2S + 16 NH_4^+ + P0_4^{3-} + 106 H_20
\]

Sulphate reduction produces H2S, and nitrate is further reduced to ammonia. Closely related to the deficiency in oxygen (at 150 m depth in the Landsort profile) a pronounced dissolution of Mn occurs, whereas dissolved Fe reached its highest values a bit further down. Together with the rapidly increasing dissolution of Mn and Fe at the oxygen boundary, a small increase in pH is predicted by equation 2, which is seen both in the Landsort pro-
file and in the pore-waters sampled (Table 3). With the total conversion of Mn from the (IV) to the (II) valence (and Fe from (III) to (II) (referred to as suboxic diagenesis, Dymond et al. 1984), it is suggested that Ba and Mo are released into interstitial waters together with P from the Fe-rich phase. These elements are correlated only to total Mn and Fe-content respectively in concretions, and no association to Mn-Fe surface characteristics is seen (Paper 1, this volume).

Both Mn and Fe reach a maximum in their dissolved phase at 300 m depth in the Landsort profile, and the values appear to fall off beneath this depth. This illustrates the formation of Fe-monosulphides and the precipitation of a reduced Mn-phase within the modelled sedimentary column. However, much of the dissolved Fe and Mn diffuses back to the oxidized zone. Fe precipitates instantly when molecular oxygen reappears in the profile, whereas Mn migrates some distance in the presence of oxygen, finally precipitating at a somewhat higher oxygen tension compared to Fe (Table 4). The oxidation of dissolved Fe$^{2+}$ and Mn$^{2+}$ is $H^+$-producing, and this could be an additional explanation to the lowered pH observed in the pore-waters close to the sediment-water interface.

Formation and composition of Fe-Mn concretions

Intimately associated with the high interstitial Fe and Mn contents, and the subsequent migration upwards forming stratified oxidized surface sediments, is the development of concretions.
Three major groups of concretions can be recognized: spheroidal concretions, discoidal concretions and flat crusts and slabs. Concretions found in the Gulf of Bothnia are similar in composition to other shallow-marine Fe-Mn deposits and fall into a group between fresh-water concretions and deep-sea nodules (Paper 1). Typically, concretions in the Gulf of Bothnia are much lower in Cu, Ni and Co compared to the deep-sea ones, whereas their P content is 5 to 10 times higher.

Spherical nodules are formed within the water-rich, uppermost sediment layer at well oxidized sites. Nodules most likely derive their spherical form from a supply of elements from all sides. They are concentrically built with alternating Fe-rich and Mn-rich layers, indicative of changes in the redox level within the surface sediment. Nodules are found in vast amounts in the Bothnian Bay, in contrast to their much less frequent occurrence in the Bothnian Sea. Spherical concretions are rich in Mn (Paper 1), and closely associated with the Mn-phase are Mo, Ba, Ni, Cu, Co and Zn. Mo and Ba are strictly correlated only to the Mn content, whereas the accumulations of Ni, Cu, Co and Zn are dependent on the surface characteristica of the Mn-phase. A strong correlation between size of nodules and their Ni, Cu, Co, Zn, Y and REE contents is observed. With decreasing size of nodules the contents of these trace elements increase in inverse proportion to the radius. This has been interpreted as due to an increase of specific surface area, because data points closely cluster around a theoretical 1/r function (surface
area to volume of a sphere). Depth of burial of spherical nodules within the oxidized surface sediment also has a profound impact on nodule composition. Ni, Cu, Zn, Y and REE accumulate to a higher extent in nodules found close to the sea-water - sediment interface, whereas a constant decrease (in nodules of equal size) can be observed down-wards towards the reduced-oxidized interface. Hence, it is suggested that the redox status of the Mn-surface governs the scavenging of these trace elements (Paper 3, this volume). The light REE are preferentially enriched in nodules, and Mn-rich nodule samples all exhibit a small but significant Ce anomaly (Paper 4, this volume).

Discoidal concretions, the less abundant of the three major groups of concretions, have a composition similar to spheroidal nodules. These concretions, however, show a negative Ce anomaly, in spite of a high Mn content. This is probably due to the fact that girdle-shaped concretions are formed at the reduced-oxidized interface in contrast to spherical nodules, which form at a more oxidized level. Hence, the Ce behaviour in concretions in the Gulf of Bothnia is consistent with the assumption suggesting that the Ce anomaly is a measure of the redox level (Paper 4, this volume).

Flat slabs and crusts, the dominating concretionary type in the Bothnian Sea, are Fe-rich and low in Mn. P is correlated to Fe, together with Si, Ca, Sr and As. Some Fe-crusts, very rich in P,
in the Bothnian Sea are also enriched in Na and Ba. The accumu-
lation of the REE is small, but a clear negative Ce anomaly is
observed (Papers 1 and 4, this volume).

In the Bothnian Bay Fe-rich strata, lithified into hard flat
crusts, are frequently found within the sedimentary column, som-
times 30 to 40 cm below the oxidized surface zone. The vast amounts
of P trapped together with Fe might be one explanation of the
deficiency of phosphate compared to nitrate observed in the water-
column in this basin (Paper 2, this volume). Many of the irregu-
larly distributed thin Fe-crusts, found at shallow depths (20-30 m)
on sandy bottoms within the Bothnian Bay, most likely represent
erosional remains of former buried Fe-layers formed within an
oxidized muddy sediment.

Economic aspects

Only spherical nodules contain significant amounts of Mn to be con-
sidered as a potential ore in the Gulf of Bothnia. The accumula-
tion of trace elements (e.g. Cu, Ni, Co) is small, and probably
only the Mn content has any commercial interest.

In comparison with the Bothnian Bay, nodule recovery in the
Bothnian Sea is sparse. This difference is illustrated by Fig. 6,
where maximum size of spheroidal nodules has been plotted at each
sampling spot. The maximum size is a rough estimate of the amounts
of nodules found. Any commercial dredging for nodules should, there-
Figure 6. Maximum size of spheroidal nodules found at each sampling site. The largest dots represent a diameter of 25 to 30 mm and the smallest 0.5 to 4 mm. The amount of nodules at each sampling site is roughly proportional to the size of nodules; indicating the vast occurrence of rich nodule sites in the Bothnian Bay compared to the relatively sparse occurrence in the Bothnian Sea. Data from Winterhalter (1966) and this study.
fore, be concentrated on the Bothnian Bay. Although spheroidal concretions have been found at all depths in the Bothnian Bay most abundant recovery is done in the depth range 60 to 80 m. However, depth per se is not a very useful prospecting tool. In an area around N 64° 25, E 22° 18, at water-depths between 90 to 100 m, the richest deposits of nodules discovered so far in the Gulf of Bothnia have been sampled.

Generally, formation and survival of Fe-Mn concretions demand oxidizing conditions. They do not withstand high sedimentation rates. In order to understand and predict the distribution of nodules, a detailed knowledge of the sedimentation patterns must be gained. Mean post-glacial sedimentation rate in the Bothnian Bay has been estimated to 0.15 mm/year. A figure similar to estimated mean growth rate of spherical nodules (Paper 1, this volume, Winterhalter and Siivola 1967). With this value areas of erosion, transportation and sedimentation can be outlined (Table 5). Boxcore data have shown that samples taken from areas with 2 to 4 m of post-glacial cover mostly contain only small sized nodules, and bottoms with more than 4 m of Recent sediments usually are barren of nodules. Large nodules are abundantly found on bottoms with a post-glacial cover less than 2 m. Hence, a conventional echo-sounder together with Table 5 is a good first approximation when prospecting for nodules in the Bothnian Bay. However, owing to the patchy appearance of nodules even within "nodule fields", a detailed mapping must be based on camera or TV views of the bottom. This surface view of the bottom has to be combined with a measure-
Table 5  Apparent postglacial sedimentation rates in the Bothnian Bay.

<table>
<thead>
<tr>
<th>postglacial sediment cover (m)</th>
<th>apparent sedimentation rate* (mm/year)</th>
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<tbody>
<tr>
<td>0-0.5</td>
<td>0.03 erosion</td>
</tr>
<tr>
<td>0.5-1</td>
<td>0.09 erosion</td>
</tr>
<tr>
<td>1-2</td>
<td>0.19 transportation</td>
</tr>
<tr>
<td>2-4</td>
<td>0.38 sedimentation</td>
</tr>
<tr>
<td>4-6</td>
<td>0.63 &quot;</td>
</tr>
<tr>
<td>6-8</td>
<td>0.88 &quot;</td>
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<tr>
<td>8-10</td>
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</tr>
<tr>
<td>10-12</td>
<td>1.38 &quot;</td>
</tr>
<tr>
<td>12-14</td>
<td>1.63 &quot;</td>
</tr>
</tbody>
</table>

* 8000 years of sedimentation is assumed.
Figure 7. Relict bottoms in the Bothnian Bay (postglacial cover 0-0.5 m). In these areas can large amounts of Fe-Mn concretions be found, if erosion is not to severe. Map redrawn from K. Wannäs et al. 1979 (unpublished).
Figure 8  The shaded areas cover 45% of the Bothnian Bay and within this zone can spheroidal nodules be found in large numbers. In the densely shaded areas (10% of the bottom) nodules are very abundant and within the most densely shaded zones (1% of the bottom) approximately 15 kg nodules/m² (wet weight) are found.
men of the thickness of the nodule-bearing strata, as this can vary by up to 10 cm, strongly affecting the recovery of nodules.

From the investigations made it can be deduced that approximately 45% of the bottom of the Bothnian Bay is covered with spheroidal nodules. Thirty percent is estimated to have a nodule frequency of 0.5 to 2 kg/m², whereas four smaller areas (the remaining 5%) are rich (5 kg/m²) to very rich (15 kg/m²) in nodules. The dense shaded area A in Fig. 8, with nodule closeness between 10 to 40 kg nodules/m², is approximately 200 km². With an assumed mean nodule frequency of 15 kg/m², 3 million metric tons, or at a dry weight basis 0.2 million tons of Mn (45% water content, 13% Mn content), are estimated to be found in this area. Any future commercial dredging of nodules should first be focused on this region.

The total amount of spheroidal nodules in the Bothnian Bay can roughly be calculated to be around 10.6 million metric tons on a dry weight basis. With a mean content of 13% Mn, 1.4 million tons of Mn are estimated to be trapped in nodules in the Bothnian Bay (Paper 1, this volume).

Only small manganese ore deposits are found on land in Sweden (Magnusson 1973, Grip and Frietsch 1973). Profitable ore resources on land have been estimated to contain 220 000 metric tons of Mn (calculated at a price of 510 kr/metric ton). Some Swedish Fe-ores contain Mn, but the useful amounts present are limited compared to the total Mn consumption (SOU 1979). Today no Mn is mined in Sweden. Primarily, Mn is imported in Fe-alloys (73%) and as Mn-ore (19%).
Only a small amount (7%) is imported as the pure metal (Figures from 1975, SOU 1979). Mn is a very important metal in the steel industry as it is regarded as irreplaceable. A question of the utmost importance can, therefore, be raised: how can the need for Mn be satisfied in the case of the total isolation of Sweden from world trade (Molinder 1982)?

The yearly consumption of Mn is to more than 90% dependent upon the market for steel-products, but approximately 75 000 metric tons of Mn are used annually (mean figure 1973-1975). The use of Mn has been estimated to remain fairly constant at this level for the coming 20 years (SOU 1979). In other words, the richest nodule-field (area A, Fig. 8) in the Bothnian Bay could theoretically supply Mn to the Swedish steel-industry during approximately 15 years.

From the discussion above it may be deduced that the Mn nodules present in the Bothnian Bay are Sweden’s primary Mn reserve. However, it is still unknown whether it is at all possible to use Mn nodules in the manufacture of steel. The metallurgical properties of Mn nodules in steel production must be investigated in order to assess the status of nodules as the primary national resource of Mn.

Conclusions

Porewaters in the Gulf of Bothnia sediments are enriched in Fe, Mn, Si, Ba and Zn (and other elements not analysed in this study)
suggesting a pronounced migrating upwards. Much of the Fe is, however, trapped at the reduced-oxidized interface, as Fe-rich strata are extensively occurring, either buried some cm in the sediment (Bothnian Bay), or as Fe-rich crusts at the sediment-water interface (Bothnian Sea). Ascending P is to a large extent co-precipitated with Fe, resulting in a loss of P from the water-column. In particular, the oxidized sediments in the Bothnian Bay act as a major sink for P. Within a dissolving buried nodule layer vivianite has been found, indicating the possibility for the fixation of P also in a reduced Fe-phase in the sediment. Interstitial Si is trapped in Fe-rich concretions only in small amounts and is to a large extent lost from the sediment (Fig. 9).

On a regional scale Mn is lost from the sediment. Probably also Mo and Ba, which are closely related to Mn in concretions (Fig. 5 and 9). It is possible that Ni, Cu, Zn, Co, Y and the REE are lost even to a greater extent. These trace elements have been shown to significantly accumulate together with Mn in nodules, only if strongly oxidizing conditions prevail.

Mn and related elements are probably transported in a looping process along the bottoms, being buried, released, transported and buried again. Depressions, or areas with a high input of organic matter act as sources, while elevated areas or bottoms with a low sedimentation rate act as sinks. The water-rich brown surface sediment usually enclosing spherical nodules is very easily stirred up. This sediment has been observed on bottom-photographs as a sus-
Figure 9. Relative element abundances (in logarithmic units), reduction loss fraction and mean Baltic nodules, after normalization such that Fe (in nodule) = Fe (in loss fraction). As Mn-rich sediments are reduced to Mn-poor sediments a fraction of the sediment is lost, assuming Al to be the permanent component. Note that much Mn, Si, Ba and Ni are not incorporated in nodules after their release from the oxidized sediment.
pended cloud above sandy bottoms, indicating its nepheloid character. This nepheloid layer is probably important for the transportation of Fe-Mn-enriched suspended matter along the bottom in the Gulf of Bothnia.

Fe-Mn-enriched suspended matter settles preferentially in deeper areas in the Gulf of Bothnia (Figs. 10, 11). In the well oxidizing shallow Bothnian Bay, Mn-rich sediments and nodules are frequently found, whereas in the Bothnian Sea there are mainly Fe-rich concretions and sediments which are found, close to the sediment-water interface (Fig. 6, 12). This difference has been interpreted as being due to a generally lowered redox level in the Bothnian Sea. In the Baltic proper the redox conditions are even more reduced, with totally reduced surface sediments in deeper parts. Stratification of Fe and Mn, of the type observed in surface sediments in the Gulf of Bothnia, have been observed in the water-column above the Landsort Deep in the Baltic proper. Mn is more susceptible to a decrease in the redox level compared to Fe and, hence, has a higher mobility. This sedimentation pattern is illustrated on a large scale by the Mn content in surface sediments in the major subbasins of the Baltic Sea (Fig. 13, 14). The lowered redox level, together with and assumed lower river-input of Fe-Mn (Paper 2, this volume) in the Baltic proper, explains the relatively sparse occurrence of ferromanganese concretions in this basin. Within the Baltic proper concretions are confined to the oxidized low sedimentation areas surrounding larger (often \( \text{H}_2\text{S} \) producing) basins (Fig. 15).
Figure 10. Distribution of MnO in the surface sediment in the Gulf of Bothnia. Sediments from deeper areas are richer in Mn than shallow water deposits. Additionally, surface sediments in the Bothnian Bay are distinctly richer in Mn compared to the Bothnian Sea. Note that the pattern pertains only to the upper 2-10 cm in the sediments below this oxidized layer the sediments are commonly poor in Mn, containing about 0.05-0.20 \% MnO. Data from Boström and Ingri (1985).
Figure 11. Distribution of Fe$_2$O$_3$ in the surface sediment (mostly 2-5 cm thick) in the Gulf of Bothnia. Note the drastic increase in Fe-content in deep water deposits. Data from Boström and Ingri (1985).
Figure 12. The Mn/Fe ratio in surface sediments in the Gulf of Bothnia, indicating the more oxidized deep-water sediments in the Bothnian Bay. Data from Boström and Ingri (1985).
Figure 13. Distribution of excess Mn as a function of latitude in sediments in the Baltic Sea (samples from deep water deposits). The map (right) shows the locations of the cores on the same vertical as the data in the graph (left). Filled symbols - surface sediments, open symbols - deeper layers (below ~ 10 cm). Dashed line represent excess MnO = 0, defined as $E^* = E_m - f \times Al_2O_3$ where $E_m$ = measured value, $f = 0.0075$ (ratio of MnO to Al2O3 in mean crust). In NW Baltic only 25% of samples exceed the 0-line; in the Bothnian Sea some 50% and in the Bothnian Bay 75% of all samples exceed the 0-line. Note that also the deep-layer values tend to be higher in the north. All samples near the coast, in very shallow areas or in bays in the archipelagoes are deleted to avoid additional scatter. Yet, even coastal sediments in the north show higher MnO-contents than those in the south. Data from Boström and Ingri (1985).
<table>
<thead>
<tr>
<th>Location</th>
<th>Max Depth</th>
<th>Redox Conditions</th>
<th>Primary Production</th>
<th>Mn and Fe Pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kalix river</td>
<td>30 m</td>
<td>Thin oxidized surface sediments</td>
<td>15 g C/m²/year</td>
<td>Decreasing redox level</td>
</tr>
<tr>
<td>Archipelago region</td>
<td></td>
<td>Very weak halocline</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bothnian Bay</td>
<td>147 m</td>
<td>Max depth 294 m</td>
<td>100 g C/m²/year</td>
<td></td>
</tr>
<tr>
<td>Bothnian Sea</td>
<td>294 m</td>
<td>Max depth 459 m</td>
<td>200 g C/m²/year</td>
<td></td>
</tr>
<tr>
<td>Baltic proper</td>
<td></td>
<td>Well developed halocline</td>
<td></td>
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</tr>
</tbody>
</table>

Figure 14. Mn and Fe pathways in the Baltic Sea.
Figure 15. Distribution of ferromanganese concretions in the Baltic Sea. Map redrawn and modified from Boström 1982. Data based on Winterhalter (1966), Varentsov and Blashchishin (1976), Kulesza-Owsikowska (1981), Manheim (1965) and this study. Sporadic to common occurrence of Fe-Mn concretions can be found also in the Kiel Bight (Djafari, 1976) and in the archipelago regions in the Baltic proper. In the rich areas in the Gulf of Bothnia, the Gulf of Finland and the Gulf of Riga usually Mn-rich spheroidal concretions are encountered. Fe-rich flat concretions are abundantly occurring in the Bothnian Sea. In the Baltic proper, Mn-rich concretions frequently are of the girdle type. In the non-dashed areas in the Gulfs of the Baltic sporadic occurrence of concretions can be found, whereas deeper areas in the Baltic proper are barren of nodules.
Active nodule formation in the Gulf of Bothnia is fast. During optimal conditions a growth rate of 0.15 mm/year has been estimated (Paper 1, this volume, Winterhalter 1966). This growth rate refers to conditions within the oxidized surface sediment with much interstitial Fe and Mn present. When nodules are exposed to bottom waters and found at erosive sites a much lower growth rate is obtained. Maximum age of concretions in the Gulf of Bothnia is estimated to ~ 3000 years, owing to a proposed "dissolution event" in the early Litorina Sea (Paper 1, this volume).
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Distribution, composition and origin of ferromanganese concretions in the Gulf of Bothnia

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Abstract

Two hundred ferromanganese concretions from the Gulf of Bothnia have been analysed for 24 elements. These deposits are similar in composition to other shallow-marine concretions, but are much lower in Cu, Ni, Zn and Co contents, in particular, compared to their deep-sea equivalents.

Three major types of concretions are found in the Gulf of Bothnia, Mn-rich spheroidal and discoidal concretions, together with Fe-rich flat crust-formed concretions. The accumulations of Cu, Ni, Zn, Co, Y, Yb and La are strongly dependent upon the surface characteristics of the Mn-rich phase. Both the specific surface area and the redox potential affect the attachment of these elements onto the Mn surface. Mo and Ba are probably present in a lattice position within a Mn-phase, as these elements are strictly correlated to the Mn content. P, Si, As and Zr are associated with the Fe-rich phase. A diagenetic source for the formation of spheroidal and discoidal concretions, and for flat crusts formed on muddy post-glacial sediments is suggested. The enriched elements ("enriched", compared to the underlying sediment) found in the concretions mostly have an interstitial source.

Distribution maps for the three groups of concretions are presented. Mn-rich spheroidal nodules dominate in the Bothnian Bay, whereas only flat Fe-rich concretions are abundantly occurring in the Bothnian Sea. This has been interpreted as being due to a
slightly lower redox level in the Bothnian Sea. The amounts of Mn trapped in spheroidal concretions is estimated to 1.4 million metric tons in the Bothnian Bay.

Concretions are mostly found on elevated parts of the bottom and on other erosive current-swept sites. The distribution of the concretions is closely associated with the sedimentation rate. A mean post-glacial sedimentation rate of 0.15 mm/year is calculated for the Bothnian Bay, a rate proposed also for optimal active nodule formation. On bottoms with a post-glacial cover of 0.5 to 2 m concretions are frequently occurring, whereas a sedimentation rate exceeding ~ 0.4 mm/year usually inhibits the formation of nodules in the Bothnian Bay. Concretions found at erosive sites represent relict deposits, growing slowly or not at all today. The active formation of spheroidal nodules is rapid and probably occurs within a few hundred years. The maximum age of the concretions found in the Gulf of Bothnia can probably be set to around 3000 years, owing to a supposed dissolution event in the early Litorina Sea.
INTRODUCTION

The Baltic Sea is one of the best studied environments of near-shore ferromanganese oxide deposition. Reports of Fe-Mn concretions in the Baltic proper appeared at the end of the 19th century (Manheim 1965). Russian scientists have closely studied these deposits together with the concretions found in the Klaipeda-Gdansk area and the Gulf of Riga (Samoilov and Titov 1922, Gorshkova 1961, Varentsov and Blashchishin 1976). Early work in the Gulf of Bothnia and the Gulf of Finland was done by Hessle (1924), Gripenberg (1934) and Winterhalter (1966). Recently, Fe-Mn concretionary deposits in the western Baltic Sea have been investigated by Djafari (1976) and Kulesza - Owsikowska (1981) and, in the Gulf of Bothnia, by Boström et al. (1978, 1982).

In spite of the comparably large amount of information available about Fe-Mn concretions in the Baltic Sea, several important questions remain to be answered. Deposits of Fe-Mn concretions, especially in the spherical form, accumulate significantly only in the Gulfs of Baltic. Areas regarded as "rich" in the Baltic proper are in comparison with the Gulfs, particularly the Bothnian Bay, very poor in Fe-Mn concretions. Whether this deficiency is due to a removal of Fe and Mn from the Baltic proper, an incorporation into reduced sediments, or a small input of Fe and Mn into this area, is not fully understood. It is still a matter of dispute whether Mn-rich nodules are formed owing to a diagenetic redistribution of river-introduced elements in the
sediments (Manheim 1965, Winterhalter 1966, Boström et al. 1982), or whether they are formed directly from laterally supplied, river-introduced matter (Varentsov 1973). Furthermore, the significance of Fe-Mn concretions in regulating the cycling of trace elements through the subbasins in the Baltic Sea has been very little investigated.

**METHODOLOGY**

Field methods

Concretions were recovered using two types of bottom samplers: a dredge, consisting of a steel box with a 70x40 cm opening, and a boxcore sampler described by Jonasson et al. 1966. Almost undisturbed 30x30x50 cm cores can be obtained using the box sampler. This type of "large sample coring" is absolutely necessary in the study of the often thin nodule-bearing oxidized surface sediment.

Samples for pore water analysis were recovered from the boxsampler by inserting a plexiglass tube (diameter 100 mm) into the center of the core. The pre-sliced tube allowed sampling of thin sediment layers. Pore water was immediately extruded in an argon-flushed glove box using four modified Reeburgh sampler (Reeburgh 1967). Interstitial water was recovered by squeezing through a 0.45 mm Millipore filter with increasing N₂ pressure. One to four atm. pressure gave the desired pore water volume (~20 ml) within a few hours. Measurements of pH and redox were made in the inert atmosphere within the glove box. The pore water was acidified to pH = 1 with HNO₃, stored at 8°C and analysed with ICP (see below).
Analytical technique

Most of the elements analysed were determined by optical emission spectroscopy (OES) using an Inductively Coupled Plasma (ICP) as excitation source. The spectrometer system consists of a monochromator, ARL 35000 and a polychromator, ARL 33000, which are both mounted on the same optical axis around a joint ICP-light source (Burman 1979, 1981 and Burman et al. 1979, 1981). Yb, La, Sc, P, Mo and Co were analysed with the ARL 35000 scanning unit and the other elements with the 33000 instrument. K was measured by Atomic Absorption.

The sediments were analysed by ICP-OES using two digestion procedures; thus, major elements, Cr, Zr, Ba and Sr were dissolved with a metaborate digestion procedure, and trace element contents were measured on sediment samples dissolved by HF-HCl$_4$ (Burman et al. 1978).

Nodules were dissolved with a HCl leaching method (discussed in this paper), and the soluble fraction was measured directly with ICP-OES. The non-HCl-soluble residue obtained was fused with the metaborate procedure prior to analysis.

MORPHOLOGY AND DISTRIBUTION

The iron-manganese concretions found in the Gulf of Bothnia can be divided into three major groups:
1) Spheroidal concretions

2) Discoidal concretions

3) Flat slabs, crusts and sheets

These groups are also readily observed in other parts of the Baltic (Winterhalter 1966, Varentsov and Blashchishin 1976), in other shallow-marine areas (Calvert and Price 1977) and in freshwater deposits (Callender and Bowser 1976). Usually, the words concretion and nodule are used synonymously, but in this paper the word nodule is restricted to the spheroidal type of concretions, whereas the word concretion is used as a general term.

Form and distribution of concretions found in the Gulf of Bothnia are closely related to the character of the sedimentation at the nodule site. Generally, formation and survival of iron-manganese concretions demand oxidizing conditions. They do not withstand high sedimentation rates, or a significant input of organic matter. Fe-Mn concretions are, therefore, preferentially found at elevated areas in deeper basins, on morain ridges and other current-swept areas. In all 333 dredge and boxcore samples were taken during the investigation (Fig. 1). Of these samples 63% contained concretions, and there was a similar recovery in the two subbasins (65% Bothnian Bay, 60% Bothnian Sea). Although concretions were found at all water depths above 170 m most abundant recovery was done in the depth range 40 to 80 m (Fig. 2).
Figure 1. Distribution of dredge (▲▲) and boxcore (■■) samples taken during this study. Filled symbols denote samples with concretions and unfilled symbols, no concretions. Note that sampling has been concentrated to the Swedish side of the Gulf of Bothnia.
Figure 2. Depth-distribution of boxcore and dredge samples. Filled symbols denote samples with spheroidal concretions (•) and discoidal and/or flat concretions (△). Unfilled symbols (○) represent no concretions. Samples with both spheroidal and flat and/or discoidal concretions are marked (x). *Two samples deeper than 170 m with no concretions.
Discoidal and flat concretions are preferentially found at more shallow depths compared to spherical nodules (Fig. 2). The recovery of spheroidal concretions (compared to samples containing nodules) constantly increases with depth in both of the subbasins of the Gulf. Only 9 dredge samples (Fig. 2) (no boxcore samples) contained nodules together with flat crusts or girdle concretions. This clearly indicates their different growth conditions. This distribution pattern refers to the surface of the sediment. In many boxcores, especially in the Bothnian Bay, flat crusts have been found some cm below spheroidal nodules.

The spheroidal nodule is the dominant form of concretions in the Bothnian Bay, in contrast to the Bothnian Sea, where flat crusts and sheets are plentiful (Fig. 3, 5). This difference between the two subbasins is even more pronounced if the maximum size of spheroidal nodules from each sampling-station is plotted (Fig. 4). The discoidal concretion, usually in the form of an equatorial rim on a pebble or a boulder (girdle shaped), is the less abundant growth form (Fig. 6). This is partly due to the fact that pebbles and boulders are difficult to dredge. Areas rich in gravel are mostly sites of erosion, and boxcoring, therefore, is also a poor sampling method for girdle concretions.

Flat concretions

This group, consisting of slabs and crusts of concretionary material, covers a wide range of subtypes. However, two main types are easily recognized: flat crusts found on or within muddy (mud by
Figure 3. Distribution of spheroidal ferromanganese nodules in the Gulf of Bothnia. Data from Winterhalter (1966) and this study.
Figure 4. Maximum size of spheroidal nodules found at each sampling site. The largest dots represent a diameter of 25 to 30 mm and the smallest 0.5 to 4 mm. The amount of nodules at each sampling site is roughly proportional to the size of nodules; indicating the vast occurrence of rich nodule sites in the Bothnian Bay compared to the relatively sparse occurrence in the Bothnian Sea.
Data from Winterhalter (1966) and this study.
Figure 5. Distribution of flat ferromanganese concretions in the Gulf of Bothnia. Data from Winterhalter (1966) and this study.
Figure 6. Distribution of discoidal ferromanganese concretions in the Gulf of Bothnia. Data from Winterhalter (1966) and this study.
definition, a wet mixture of silt and clay) post-glacial sediments and concretions formed as encrustations of till fragments and glacial clay. Stained boulders and pebbles are frequently seen in the Gulf of Bothnia, but these have not been regarded as concretions in the present work, and their occurrence has not been mapped in fig. 5.

In many locations, especially in the Bothnian Sea, varved, stiff glacial clay is exposed to submarine erosion (Winterhalter 1972). The varves are easily separated and often become encrusted mostly with a few millimeters of Fe oxy-hydroxide. These Fe-rich erosional remains, often quite large, form a peculiar "mosaic structure" on the bottom, as shown with photographs by Winterhalter (1980). A special type of flat concretions, known as the Korsö-type (Winterhalter 1966), show bizarre forms of Fe-impregnated glacial clay (Fig. 7d). Flat crusts formed on silty post-glacial sediments represent a growth form different from the more or less Fe-impregnated relict sediment discussed above. Echo-sounding in the Bothnian Sea often shows a "hard surface reply" on an otherwise soft bottom; in many cases this is due to a "continuous" Fe-crust at the sediment-seawater interface (Fig. 7a, b). These crusts are usually found at 80 to 120 m depth in the Bothnian Sea. In the Bothnian Bay, buried Fe-rich crusts are frequently found within the oxidized surface sediment, often as thin crusts below a layer of spheroidal nodules. Buried (10 to 15 cm below the oxidized zone) flat Fe-rich crusts are common in the Bothnian Bay (Fig. 8), indicating that dissolution of flat concretions within a reduced grey sediment sometimes is remarkably slow.
Discoidal concretions

The formation of a rim or girdle around some nucleus, often a pebble or a boulder, on fragments of concretionary material, or on relict sediment, is the most frequently occurring, type of discoidal concretion in the Gulf of Bothnia (Fig. 9). This type of concretion is abundantly encountered in the shallow-marine and fresh-water environments and is referred to as girdle concretions (Calvert and Price 1977). They grow laterally, showing concentric layering of Fe- and Mn-rich bands. The layers generally seem to be thicker than corresponding ones in spheroidal nodules (see also Winterhalter and Siivola 1967). This may indicate that the supply of Mn-rich and Fe-rich material changes less frequently in the depositional environment of girdle concretions. Occasionally, no visible nucleus is present, and an almost perfect discoidal concretion is formed.

The upper sea-water facing side of girdles is usually covered with a black, knobby, (gritty) surface, and the side resting on underlying sediment is yellow-brown in colour with a smooth surface (compare Fig. 15). Although the girdle is formed at the sediment-water interface bottom photographs reveal that the girdle is mostly wrapped in a nepheloid layer.

At sampling sites close to the coast between Skellefteå and Luleå very thin (2-3 mm) and flat discoidal concretions were found in almost clean sand (Fig. 11). Concretions of this type are known as "penny ore" and are frequently occurring in sandy sediments in
Figure 7a. Boxcore sample from the Bothnian Sea (N 64°42' E 18°37', depth 88 m) showing flat concretions, on a silty sediment, at the sediment-water interface. Scale, 3 cm.

Figure 7b. "Continuous" crust at the sediment-water interface sample, from the Bothnian Sea (N 61°49' E 17°46', depth 62 m).
Figure 7c. Flat concretion found as an erosive residue on a sandy substrate in the Bothnian Bay (N64°08 E21°15, depth 65 m).

Figure 7d. Sediments more or less impregnated by Fe-oxyhydroxides, referred to as the Korsö type of flat concretions.
Figure 8a. Boxcore sample with a 3-4 mm thick Fe-rich crust buried ~ 3 cm below the oxidized (~ 2 cm) brown surface sediment (with spherical small nodules).

Figure 8b. Thin (~ 1 mm) Fe-rich crusts buried within a grey reduced sediment, with a ~ 2 cm thick brown oxidized surface layer (N64°05 E21°36, depth 99 m).
Figure 9. Discoidal concretions of the girdle type from the Bothnian Bay (N64°32 E21°38, depth 37 m). Scale, 1 cm.
Figure 11. Thin (2-3 mm) discoidal concretions known as "penny ore" found on a sandy sediment at 50 m depth, N64°51 E 21°40.
lakes of Scandinavia (Naumann 1922, Aarnio 1918, Vogt 1915).

Spheroidal nodules

These concretions develop within the muddy water-rich oxidized surface sediment layer (Fig. 12). They are almost perfectly spherical, sometimes black, sometimes yellow-brown in colour. The black nodules exhibit a knobby (gritty) porous surface, whereas the yellow-brown have a more firm, smooth surface. Sectionized concretions show concentric growth layers of Mn-rich horizons, alternating from dark brown to black, and Fe-rich horizons, alternating from yellow to reddish brown. No visible sign of foreign nuclei (e.g. a larger mineral grain or its equivalent) can be found in the spherical nodules.

In some oxidized sections the uppermost nodules are black, whereas the lowermost are yellow-brown, and in-between half black and half brown nodules are found (Fig. 13). The presence of partly black and partly yellow-brown concretions seen in several boxcore profiles strongly supports the opinion of Winterhalter and Siivola (1967) that the Fe- and Mn-layering in the spherical nodules are primary features. They based their statement on the fact that ionic diffusion within the concretions, separating Fe and Mn, cannot keep pace with the high accumulation rate (0.01-0.2 mm/year) calculated for Baltic Sea concretions (Manheim 1965, Winterhalter and Siivola 1967).

With increasing nodules size the ideal spherical shape becomes distorted (Fig. 14). Lateral outgrowth, often as an equatorial rim,
is frequently seen on spheroidal nodules when these are partly exposed to bottom waters. These rims may grow together into continuous crusts of spherical nodules (Fig. 15). The lateral outgrowth occurs at the sediment-water interface and, therefore, more deeply buried nodules can grow their rims more like "hats" into a "mushroom" shape. If the bottom water energy is low, a brown nefeloid layer usually covers the nodules (Winterhalter 1966, this study). In this case the sea-water side of the concentrations exhibits a black knobby surface (Fig. 15), and, if the oxidized zone is rather thin (less than a few cm), the lower sediment side shows a yellow-brown smooth surface (Fig. 15). When spheroidal nodules are found on very sandy sediments, or other strongly eroded bottoms, they often exhibit a hard, smooth, brown surface (Fig. 16). This type of nodule is frequently found on the sand areas around Nordströms Grund (N 65° 07, E 22° 20) and on moraine ridges with sand deposits in the central Bothnian Bay. The fragile, porous, black nodule surface is easily weathered by mechanical erosion, but the hard surface shown by brown concretions obviously withstand higher mechanical action. The more black, fragile layers are Mn-rich, the brown, hard layers are Fe-rich. Photographs of grinded and polished Mn-rich and Fe-rich concentric layers within spheroidal nodules clearly show the difference in hardness; Fe layers have a "dense", smooth surface, whereas Mn layers are gritty even on polished sections.

Spheroidal concretions have been found in the depth range 5 to 170 m, but abundant recovery is usually done in a much narrower
Figure 12. Bottom photograph of a rich nodule area with most nodules buried in the, easily stirred up, brown surface sediment (size of nodules ~ 2 cm in diameter). Boxcore profile (to the right) with spheroidal nodules in a 3 cm thick water-rich surface sediment.
Figure 13. Partly black, partly yellow-brown spheroidal concretions from a brown surface sediment in the Bothnian Bay (N64°44 E22°57, depth 83 m). Scale 1 cm.
Figure 14. Large spheroidal nodules from the Bothnian Bay, N64°42' E22°24', depth 92 m. Scale 1 cm.
Figure 15. Aggregate of spheroidal nodules. Upper photograph show the sea-water facing side with a Mn-rich black surface. Lower photograph exhibit the sediment facing portion, with a hard smooth yellow-brown Fe-rich surface. Scale 1 cm.
Figure 16. Smooth "hard" nodules with a Fe-rich surface found at erosive sites. Lower photograph shows nodules with a knobby Mn-rich black surface, found within a surface sediment. Scale 1 cm.
range at intermediate depths. Generally, below 90 m depth nodules are usually small in size, and above 30 m wave erosion disperses the "nodule fields". However, depth per se is not a very useful prospecting tool, especially not in the Bothnian Bay. In an area around N 64° 25, E 22° 18, at water depths of 90 to 100 m, where nodules "should be" sparsely occurring, the richest deposits of spheroidal nodules discovered so far in the Gulf of Bothnia have been sampled (Fig. 17). In order to understand and predict the distribution of nodules, a detailed knowledge of the sedimentation pattern must be gained.

SEDIMENTATION RATE IN RELATION TO NODULE GROWTH

Thickness of post-glacial sediments in the Bothnian Bay

The thickness of the post-glacial sediment cover in the central parts of the Bothnian Bay has been investigated by the Department of Marine Geology at the University of Stockholm (K. Wannäs et al. 1979, unpublished). Their map (Fig. 18) has been used to calculate the post-glacial sedimentation rate in the Bothnian Bay. The area shown in Fig. 18 was divided into 36 profiles, each 150 km long (east-west direction), starting with profile 17500 and ending with 24700; The profile separation was 5 km. For each profile the area of the post-glacial sediment cover in the vertical direction was calculated and subsequently multiplied with the distant to next line, 5 km, giving the volume of post-glacial sediment cover. The total length (east-west direction) of each sedi-
Figure 17. Bold squares represent boxcore samples. Values within the squares show the amounts of spheroidal nodules in kg/m² (wet weight). Other figures represent amounts of nodules in kg (net weight) recovered with dredging. Dredge figures are minimum values as most nodules were disregarded at sea but they give a rough indication of rich nodule sites. DS denote dredge sample with few spheroidal nodules.
Figure 18. Thickness of the postglacial sediment cover in the central Bothnian Bay (isocontours in meters). Map redrawn and simplified from Wannäs et al. 1979, unpublished.
mentation depth class (0-0.5 m, 0.5-1 m etc) was also multiplied with 5 km, and thus the total horizontal area for each class was obtained profile by profile. All profiles were added with the results shown in Table 1. In the areas not covered by measurements, although included in the calculations (north of profile 23500 and in the nearshore areas in the western parts), a mean post-glacial cover of 0-0.5 m was assumed (land areas within the area of calculation have been excluded, and figures shown in Table 1 are based on sea-area). This assumption is not true for the area north of profile 23500, not for the archipelago regions along the Swedish coast, but to compensate for the vast eroded areas east of longitude 24°E not included in the calculations, the assumption seems reasonable. South of profile 17500 it is believed that mean post-glacial cover is similar to that measured, a belief based on the echo-soundings made by the Institute of Marine Research, Helsinki (Tulkki 1977). It is, therefore, assumed that the calculated mean post-glacial sedimentation thickness, 1.19 m is valid for the whole of the Bothnian Bay, although this is based only on the calculations made from Fig. 18.

If total volume of post-glacial sediments in the Bothnian Bay is compared with river-introduced inorganic matter during 8000 years, only approximately 20% is explained by river debouching (Table 2). The missing 80% can be explained by submarine erosion, a significant source for the accumulation of post-glacial sediments also in the Bothnian Sea and the Baltic proper (Winterhalter 1972, Boström et al. 1978, Ignatius et al. 1981). The fast land uplift in the
Table 1  Calculation of the postglacial sedimentation rate in the Bothnian Bay (all values based on the measured area in Fig. 18).

<table>
<thead>
<tr>
<th>postglacial sediment cover</th>
<th>assumed mean depth</th>
<th>volume $\times 10^6 m^3$</th>
<th>percent of total volume</th>
<th>area $\times 10^6 m^2$</th>
<th>percent of measured area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.5</td>
<td>0.25</td>
<td>2988</td>
<td>11.4</td>
<td>11952</td>
<td>54.7</td>
</tr>
<tr>
<td>0.5-1</td>
<td>0.75</td>
<td>2217</td>
<td>8.5</td>
<td>2957</td>
<td>13.5</td>
</tr>
<tr>
<td>1-2</td>
<td>1.5</td>
<td>4661</td>
<td>17.9</td>
<td>3108</td>
<td>14.2</td>
</tr>
<tr>
<td>2-4</td>
<td>3</td>
<td>6563</td>
<td>25.1</td>
<td>2188</td>
<td>10.0</td>
</tr>
<tr>
<td>4-6</td>
<td>5</td>
<td>5772</td>
<td>22.1</td>
<td>1132</td>
<td>5.2</td>
</tr>
<tr>
<td>6-8</td>
<td>7</td>
<td>2478</td>
<td>9.5</td>
<td>354</td>
<td>1.6</td>
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<tr>
<td>8-10</td>
<td>9</td>
<td>1179</td>
<td>4.5</td>
<td>131</td>
<td>0.6</td>
</tr>
<tr>
<td>10-12</td>
<td>11</td>
<td>187</td>
<td>0.7</td>
<td>17</td>
<td>0.08</td>
</tr>
<tr>
<td>12-14</td>
<td>13</td>
<td>52</td>
<td>0.2</td>
<td>4</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Sum: 26097  Sum: 21842

mean sedimentation

\[
\frac{26097}{21842} = 1.19 m
\]

mean sedimentation rate

\[
\frac{1.19}{8000} = 0.15 \text{ mm/year}
\]

total postglacial sediment volume in the Bothnian Bay

\[
36800 \times 1.19 = 43792 \text{ km}^3
\]
Table 2

Comparison between total river inflow of inorganic matter and total deposited postglacial sediments in the Bothnian Bay.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg/l</td>
<td>x 10^6 Kg/year</td>
<td>x 10^{12} Kg</td>
</tr>
<tr>
<td>6.9 (1)</td>
<td>690</td>
<td>5.52</td>
</tr>
<tr>
<td>9.1 (2)</td>
<td>910</td>
<td>7.28</td>
</tr>
<tr>
<td>15.0 (3)</td>
<td>1500</td>
<td>12.00</td>
</tr>
</tbody>
</table>

**D**
g/cm³  | E       | F       |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x 10^6 Kg/m³</td>
<td>x 10^{12} Kg</td>
</tr>
<tr>
<td>0.5</td>
<td>43 792</td>
<td>21.9</td>
</tr>
<tr>
<td>1.0</td>
<td>43 792</td>
<td>43.8</td>
</tr>
<tr>
<td>1.5</td>
<td>43 792</td>
<td>65.7</td>
</tr>
</tbody>
</table>

amounts of postglacial sediments explained by river introduced inorganic matter

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.52</td>
<td>7.28</td>
<td>12.00</td>
</tr>
</tbody>
</table>

A: mean concentration of river introduced inorganic suspended matter (1)

average of Torne 8.8, Kalix 4.4, Råne 8.9, Lule 2.6, Pite 14.4, Skellefte
2.0 mg/l rivers (2) regulated rivers Lule and Skellefte river excluded

(3) assumed "high value" data from SMHI Norrköping, Sweden. Brandt (1981)

B: annual river discharge of inorganic matter.

C: total weight of river introduced inorganic matter during 8000 years.

D: dry weight density of postglacial sediments.

E: total volume of postglacial sediments, based on Table 1.

F: total weight of postglacial sediments

* assumed best value.
Bothnian Bay region and, hence, the significant rate of submarine erosion is of major importance for nodule growth in the area.

Role of post-glacial sediment thickness for nodule recovery

After the regression of the Weichselian ice-sheet sediment deposition became feasible, and, if this time limit is set to 8000 years B.P., a mean post-glacial sedimentation rate of 0.15 mm/year is obtained (Table 1). This figure is not altered much if 7000 years (0.17 mm/year), or 9000 years (0.13 mm/year) is assumed. In other words, areas with post-glacial sediment covers between 0-1 m are sites of erosion, whereas a cover of more than 2 m has experienced a net sedimentation. Bottoms in-between are transient in nature, that is, they are areas where erosion keeps pace with sedimentation. The classification seen in Table 3 is, of course, generalized, and so-called sedimentation areas might be erosional areas at present and vice versa, but in the life span of nodule formation (100 to 1000 years) the concept outlined in Table 3 is useful. Spheroidal nodule recovery within the Bothnian Bay clearly shows that bottom samples with large nodules are found at erosive sites (often with a skew size distribution) and on bottoms with less than 2 m post-glacial sediments. Whenever samples taken from areas with 2 to 4 m thick post-glacial cover contain nodules, they mostly contain only small sized nodules, (Fig. 19). Bottoms with more than 4 m post-glacial sediments usually are barren with regard to nodules. Size distribution in Fig. 19 indicates that rich, active nodule production in the Bothnian Bay today is present on bottoms with
Table 3  Apparent postglacial sedimentation rates in the Bothnian Bay.

<table>
<thead>
<tr>
<th>postglacial sediment cover (m)</th>
<th>apparent sedimentation rate* (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.5</td>
<td>0.03 erosion</td>
</tr>
<tr>
<td>0.5-1</td>
<td>0.09 erosion</td>
</tr>
<tr>
<td>1-2</td>
<td>0.19 transportation</td>
</tr>
<tr>
<td>2-4</td>
<td>0.38 sedimentation</td>
</tr>
<tr>
<td>4-6</td>
<td>0.63</td>
</tr>
<tr>
<td>6-8</td>
<td>0.88</td>
</tr>
<tr>
<td>8-10</td>
<td>1.13</td>
</tr>
<tr>
<td>10-12</td>
<td>1.38</td>
</tr>
<tr>
<td>12-14</td>
<td>1.63</td>
</tr>
</tbody>
</table>

* 8000 years of sedimentation is assumed.
Figure 19. Size distributions of spheroidal concretions found at different types of bottoms. a/ and b/ are distributions from active nodule producing sites with a 1-2 m thick post-glacial cover. c/ and d/ are seen in "young" nodule areas resting on a rather thick post-glacial cover 2-4 m. e/ and f/ are typical size distributions on eroded, less than 0.5 m of post-glacial cover, "old" nodule sites where nodule formation more or less has ceased.
1 to 2 m post-glacial cover, whereas areas having a 2 to 4 m thick recent sediment layer nodule production has just started. Nodules found at erosive sites, with a post-glacial thickness of less than 1 m, are old deposits not significantly growing today. Much of the regions with high sedimentation rates (more than 4 m post-glacial sediments) probably act as local manganese sources within the Bothnian Bay. Locally, however, a given site might change from an erosive stage back into an active sedimentation regime. Evidence for this is changing nodule growth conditions indicated by bimodal nodule size populations within a single boxcore sample (30x30 cm) (Fig. 20).

The areas with a mean post-glacial cover of 0 to 0.5 m in the central Bothnian Bay, have been closely investigated by box coring and dredging. Concretions have been found in almost 100% of the samples taken in these areas. If erosion is not too severe, spheroidal nodules can be found in large numbers, and all rich spheroidal nodule deposits within this area are confined to these low sedimentation bottoms. Some of the very rich nodule samples taken overlaid a micro-layered, greenish sediment, where each layer is easily separated. Sediment cores from various parts of the Baltic Sea indicate that the transition from the Ancylus Lake stage to the beginning of the Litorina Sea stage, 7500 years B.P. (Ignatius et al. 1981) is marked by a sharp lithostratigraphic boundary (Jerbo 1961, Ignatius et al. 1981). A change from the depositions of homogeneous grey clay to the deposition of a micro-layered, soft greenish mud, rich in organic
Figure 20. Bimodal nodule size distributions, indicative of changing nodule growth conditions within the area of the boxcore sample (30x30 cm).
matter, makes this boundary easy to recognize in sediment cores. This boundary was found in three boxcoring profiles in the Bothnian Bay and on one occasion in the Bothnian Sea. All three profiles from the Bothnian Bay contained spherical nodules. At station N 64° 47, E 21° 55 a 6 cm thick nodule layer (23 kg/m², wet weight) overlaid a 2 cm stiff yellow-grey clay, with a 8 cm thick, layered, greenish early Litorina sediment resting on a homogeneous grey clay. A 5 cm thick nodule layer (15.7 kg/m², wet weight) at station N 64° 51.5, E 22° 48 (90 m depth) was found resting directly on a layered early Litorina sediment. The presence of nodules on a sediment laid down more than 3000 years B.P. indicates a very low sedimentation rate, or possibly an erosive event prior to nodule formation, this is surprising for such a great depth and are a good illustration of the complicated sediment pattern in the Bothnian Bay.

At station N 64° 48, E 22° 24 (depth 90 m) a nodule layer (9.4 kg/m²) rested on the same type of layered early Litorina sediment as above. However, this layer was buried beneath 35 cm of grey sediment with a stratified oxidized surface layer (2 cm brown surface layer with a 2 mm Mn-rich layer and 1 mm Fe-rich orange layer). This buried nodule layer had exactly the same appearance as the one found at N 64° 51.5, E 22° 48 and did not show any sign of dissolution. If a sedimentation rate of 0.38 mm/year is assumed, or a very high rate of 1 mm/year, the nodule layer must be between 300 to 900 years old. This indicates that nodule dissolution in the reduced zone sometimes is remarkably slow or possibly not operative at all.
The transient sedimentation pattern at bottoms with a post-glacial cover corresponding to the mean sedimentation rate of 0.15 mm/year, coupled with the abundant nodule recovery in these areas, is consistent with the assumption that Fe-Mn nodule growth is favoured by a non-deposition, non-erosion environment (transportation bottom). In other words, the above-mentioned data support the accumulation rate of 0.15-0.20 mm/year obtained by Winterhalter and Siivola (1967) for spheroidal nodules in the Gulf of Bothnia.

Manganese ore estimate for the Bothnian Bay

Only spheroidal nodules accumulate significant amounts of Mn to be considered as a profitable resource. An ore estimate should, furthermore, be focused on the occurrence of nodules in the Bothnian Bay, as the deposits in the Bothnian Sea are small (Fig. 4).

First, it must be emphasized that nodule occurrence in the Bothnian Bay is patchy. Continuous "nodule fields" do exist, but generally the thickness of the nodule layer varies within broad limits. Owing to the irregular distribution of nodules, dredging of the bottom is not sufficient to make an ore estimate. Bottom photographs must be used to calculate the surface covering, and, as the mineralized strata varies between 1 cm and 10 cm (strongly affecting the recovery of nodules), surface cover has to be combined with a thickness measurement of the nodule-layer. It is therefore very difficult to make a "correct" estimate of the
Figure 21. The shaded areas cover 45% of the Bothnian Bay and within this zone can spheroidal nodules be found in large numbers. In the densely shaded areas (10% of the bottom) nodules are very abundant and within the most densely shaded zones (1% of the bottom) approximately 15 kg nodules/m² (wet weight) are found.

Table 4  Estimated total amounts of spheroidal nodules in the Bothnian Bay

<table>
<thead>
<tr>
<th>Occurrence of spheroidal concretions</th>
<th>Amounts of nodules covered (wet weight) kg/m²</th>
<th>Amounts of nodules (wet weight) x 10⁹ kg</th>
<th>Amounts of nodules (dry weight) x 10⁹ kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;fairly rich&quot;</td>
<td>0.5-2</td>
<td>5.5-21.9</td>
<td>3.0-12.0</td>
</tr>
<tr>
<td>&quot;rich&quot;</td>
<td>5</td>
<td>7.3</td>
<td>4.0</td>
</tr>
<tr>
<td>&quot;very rich&quot;</td>
<td>15</td>
<td>5.5</td>
<td>3.0</td>
</tr>
<tr>
<td>&quot;best estimate&quot;</td>
<td>1.5</td>
<td>19.2</td>
<td>10.6</td>
</tr>
</tbody>
</table>
total amount of nodules. The patchy appearance should always be kept in mind when the distribution maps and the calculations below (Table 4) are examined.

Approximately 45% of the bottom of the Bothnian Bay is covered with spheroidal nodules. Of this 30% is estimated to have a nodule abundance of 0.5 to 2 kg/m², whereas four smaller areas (remaining 5%) are rich (5 kg/m²) to very rich (15 kg/m²) in nodules (Fig. 21). The densely shaded area A in Fig. 21 is approximately 200 km² and has 10 to 40 kg nodules/m². With the assumption of a mean nodule frequency of 15 kg/m², 3 million metric tons is calculated to be found in this area. On a dry weight basis this corresponds to 0.2 million tons of Mn (water-content 45%, Mn-content 13%). Any future commercial dredging of nodules should first be focused on this region. The total amount of spheroidal nodules in the Bothnian Bay can roughly be estimated to around 10.6 million metric tons on a dry weight basis (Table 4). With a mean content of 13% Mn, 1.4 million metric tons of Mn is calculated to be trapped in spheroidal nodules in the Bothnian Bay.

COMPOSITION

To check the analytical technique two standard nodules, A-1 and P-1, provided by the U.S. Geological Survey (Flanagan and Gottfried 1980) were measured together with the nodule samples during routine analyses (Table 5). The agreement between certified values and those obtained in this investigation is good for all elements but As. With the
Table 5  ICP-OES measurements of two standard nodules, P-1 and A-1, compared to "certified" values.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>USGS-NOD-P1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl soluble</td>
<td>0.47</td>
<td>0.25</td>
<td>1.48</td>
<td>6.20</td>
<td>30.40</td>
<td>1.91</td>
<td>2.16</td>
<td>1.55</td>
<td>0.18</td>
</tr>
<tr>
<td>Stand.dev.</td>
<td>0.05</td>
<td>0.01</td>
<td>0.09</td>
<td>0.38</td>
<td>1.10</td>
<td>0.10</td>
<td>0.11</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Max.</td>
<td>0.55</td>
<td>0.26</td>
<td>1.65</td>
<td>6.61</td>
<td>31.80</td>
<td>2.06</td>
<td>2.36</td>
<td>1.67</td>
<td>0.19</td>
</tr>
<tr>
<td>Min.</td>
<td>0.39</td>
<td>0.24</td>
<td>1.36</td>
<td>5.59</td>
<td>28.50</td>
<td>1.74</td>
<td>1.94</td>
<td>1.44</td>
<td>0.18</td>
</tr>
<tr>
<td>Residue</td>
<td>5.84</td>
<td>0.05</td>
<td>0.98</td>
<td>0.08</td>
<td>0.00</td>
<td>0.04</td>
<td>0.12</td>
<td>0.21</td>
<td>-</td>
</tr>
<tr>
<td>Stand.dev.</td>
<td>0.27</td>
<td>0.00</td>
<td>0.05</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>This study</td>
<td>6.31</td>
<td>0.30</td>
<td>2.46</td>
<td>6.28</td>
<td>30.40</td>
<td>1.95</td>
<td>2.28</td>
<td>1.76</td>
<td>0.18</td>
</tr>
<tr>
<td>Recommended</td>
<td>6.51</td>
<td>0.30</td>
<td>2.55</td>
<td>5.78</td>
<td>29.14</td>
<td>1.99</td>
<td>2.19</td>
<td>1.64</td>
<td>0.20</td>
</tr>
</tbody>
</table>

| USGS-NOD-A1 |    |    |    |     |     |     |     |     |    |
| HCl soluble | 0.57 | 0.28 | 1.73 | 11.84 | 19.32 | 2.65 | 11.61 | 0.83 | 0.51 |
| Stand.dev. | 0.03 | 0.01 | 0.05 | 0.73 | 0.83 | 0.10 | 0.52 | 0.03 | 0.04 |
| Max.      | 0.62 | 0.29 | 1.84 | 12.80 | 20.50 | 2.75 | 12.10 | 0.89 | 0.58 |
| Min.      | 0.52 | 0.27 | 1.66 | 10.30 | 17.40 | 2.42 | 10.50 | 0.78 | 0.43 |
| Residue   | 0.80 | 0.02 | 0.25 | 0.03 | 0.00 | 0.01 | 0.00 | 0.04 | -   |
| Stand.dev. | -   | -   | -   | -   | -   | -   | -   | -   | -   |
| This study | 1.37 | 0.30 | 1.98 | 11.87 | 19.32 | 2.66 | 11.61 | 0.87 | 0.51 |
| Recommended | 1.78 | 0.32 | 2.05 | 10.93 | 18.54 | 2.87 | 11.03 | 0.78 | 0.60 |

NOD-P1, HCl-soluble values are mean of 10 samples, except for P (n=6), Co (n=3), La (n=9), Mo (n=3) and Yb (n=9). Residual values are means of 6 determinations.

NOD-A1, HCl-soluble figures are mean of 10 samples, except for Cu (n=9), Co (n=9), Mo (n=6), Ni (n=9). Residue figures represent means of a composite sample consisting of 6 residual fractions. Recommended values from Flanagan and Gottfried 1980.
<table>
<thead>
<tr>
<th>As ppm</th>
<th>Ba ppm</th>
<th>Cr ppm</th>
<th>Cu %</th>
<th>Co ppm</th>
<th>La ppm</th>
<th>Mo ppm</th>
<th>Ni ppm</th>
<th>Sc ppm</th>
<th>Sr ppm</th>
<th>V ppm</th>
<th>Y ppm</th>
<th>Yb ppm</th>
<th>Zn ppm</th>
<th>Zr ppm</th>
</tr>
</thead>
<tbody>
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<td>20</td>
<td>1.18</td>
<td>0.22</td>
<td>95</td>
<td>601</td>
<td>1.40</td>
<td>-</td>
<td>624</td>
<td>504</td>
<td>85</td>
<td>14</td>
<td>1690</td>
<td>239</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>4</td>
<td>0.04</td>
<td>0.02</td>
<td>3</td>
<td>91</td>
<td>0.03</td>
<td>-</td>
<td>22</td>
<td>44</td>
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<td>2610</td>
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<td>0.24</td>
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<td>687</td>
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<td>-</td>
<td>659</td>
<td>590</td>
<td>89</td>
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<td>253</td>
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<tr>
<td>2320</td>
<td>16</td>
<td>1.11</td>
<td>0.20</td>
<td>90</td>
<td>475</td>
<td>1.35</td>
<td>-</td>
<td>577</td>
<td>410</td>
<td>78</td>
<td>12</td>
<td>1560</td>
<td>219</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>27</td>
<td>-</td>
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<td>40</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>2560</td>
<td>28</td>
<td>1.18</td>
<td>0.22</td>
<td>95</td>
<td>601</td>
<td>1.40</td>
<td>-</td>
<td>651</td>
<td>504</td>
<td>85</td>
<td>14</td>
<td>1690</td>
<td>279</td>
<td></td>
</tr>
<tr>
<td>3350</td>
<td>[18]</td>
<td>1.15</td>
<td>0.22</td>
<td>[120]</td>
<td>762</td>
<td>1.34</td>
<td>-</td>
<td>680</td>
<td>570</td>
<td>[89]</td>
<td>[14]</td>
<td>1595</td>
<td>[280]</td>
<td></td>
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<td>551</td>
<td>1413</td>
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<td>0.11</td>
<td>0.29</td>
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<td>0.65</td>
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<td>0.36</td>
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<td>735</td>
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<td>458</td>
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<td>0.29</td>
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<td>358</td>
<td>0.65</td>
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<td>1512</td>
<td>640</td>
<td>114</td>
<td>14</td>
<td>634</td>
<td>296</td>
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</table>
instrumental set-up used it was not possible to measure As values below 150 ppm. However, most concretions contained more than 150 ppm As, and corrections could be made. Although 551 ppm was obtained for the A-1 standard nodule instead of 298 (this represents a result from only one laboratory and, hence, is not a certified value), it is assumed that the results obtained for the Gulf of Bothnia concretions are valid. As values in sediments from the Bothnian Bay measured by N. Holm (pers. comm. 1984) vary between 250-500 ppm in the brown surface layers and corroborate our high values in nodules.

The HCl leaching method

Fe-Mn concretions in the Gulf of Bothnia consist of three major components: a Fe-rich phase, a Mn-rich phase and a detrital fraction. The detrital fraction is mechanically admixed sediment. This fraction is uninteresting when trying to understand the composition and genesis of the authigenically formed Fe and Mn phases and merely acts as a dilutant, obscuring authigenic composition. A convenient way to circumvent the detrital fraction is to use leaching methods, dissolving only the authigenic phases. A HCl leaching method, therefore, has been used in this work to evaluate nodule geochemistry.

Half a gram of dried and grinded nodule sample was leached with 12% HCl at 60-70°C during two to three hours. A "knife-edge" of a reducing agent (hydroxylammoniumhydrochloride) was added to improve the dissolution of the Fe-Mn phases, which otherwise is
sluggish. A grey residue, composed of quartz, feldspars and minor amounts of insoluble silicates, such as amphiboles and zirconium, is left after the treatment.

However, leaching methods often produce ambiguous results owing to the dissolution of constituents regarded as "non soluble", and great care must be taken when interpreting leaching results. In the present case it is very important to know how the detrital fraction is affected by the HCl-leaching method, as significant leaching of detrital elements can totally obscure relations in the authigenic phases owing to the large amount of admixed sediment in the concretions from the Gulf of Bothnia. To evaluate this effect, grey reduced sediment samples were leached with the same method as was used for nodules (Table 6). Three types of sediment were chosen; a sample from the Bothnian Bay archipelago region, one sample from an intermediate depth in the Bothnian Bay and one from a great depth in the Bothnian Sea. With these three samples a good average composition of grey sediment is achieved. The values obtained in Table 6 are in accordance with results gained from the leaching of till samples. Some till samples from northern Sweden were x-ray-investigated prior to and after treatment in warm HCl. The sheet-silicates, biotite and chlorite, present in the samples were totally destroyed after eight hours in warm, 60° to 70°C, 4% HCl, as indicated by the disappearance of their x-ray patterns (Fig. 22). The peaks of quartz, plagioclase group minerals, microcline and hornblende, on the other hand, remained unaffected by the treatment (Fig. 22). With this
### Table 6 The HCl-leachable fraction of grey reduced sediment in the Gulf of Bothnia

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>P$_2$O$_5$</th>
<th>residue</th>
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<tr>
<td><strong>Bothnian Bay</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>6-7 cm</td>
<td>0.73/64.3</td>
<td>0.23/0.63</td>
<td>2.84/13.3</td>
<td>3.93/5.03</td>
<td>0.03/0.07</td>
<td>1.35/2.03</td>
<td>0.69/2.32</td>
<td>0.31/3.18</td>
<td>0.16/0.29</td>
<td>0.160/0.50</td>
</tr>
<tr>
<td>leachable %</td>
<td>1.1</td>
<td>36.5</td>
<td>21.3</td>
<td>78.1</td>
<td>42.9</td>
<td>66.5</td>
<td>29.7</td>
<td>9.7</td>
<td>53.7</td>
<td>32.0</td>
</tr>
<tr>
<td>11.5-12.5 cm</td>
<td>0.62/63.4</td>
<td>0.25/0.57</td>
<td>2.82/13.2</td>
<td>4.87/5.89</td>
<td>0.04/0.07</td>
<td>1.32/1.85</td>
<td>0.74/2.28</td>
<td>0.32/3.24</td>
<td>0.13/0.23</td>
<td>0.151/0.50</td>
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<tr>
<td>leachable %</td>
<td>1.0</td>
<td>43.9</td>
<td>21.3</td>
<td>82.7</td>
<td>57.1</td>
<td>71.4</td>
<td>32.5</td>
<td>9.9</td>
<td>56.5</td>
<td>30.2</td>
</tr>
<tr>
<td><strong>Bothnian Sea</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.5-7.5 cm</td>
<td>0.83/54.6</td>
<td>0.50/0.70</td>
<td>6.70/18.4</td>
<td>8.17/8.79</td>
<td>0.08/0.09</td>
<td>2.72/3.36</td>
<td>0.88/1.52</td>
<td>0.54/2.75</td>
<td>0.16/0.21</td>
<td>0.168/0.50</td>
</tr>
<tr>
<td>leachable %</td>
<td>1.5</td>
<td>71.4</td>
<td>36.4</td>
<td>92.9</td>
<td>88.9</td>
<td>81.0</td>
<td>57.9</td>
<td>19.6</td>
<td>76.2</td>
<td>33.6</td>
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<tr>
<td>7.5-9.5 cm</td>
<td>0.93/54.7</td>
<td>0.54/0.85</td>
<td>6.61/18.2</td>
<td>8.60/9.00</td>
<td>0.09/0.10</td>
<td>2.84/3.73</td>
<td>0.93/1.64</td>
<td>0.53/2.73</td>
<td>0.13/0.22</td>
<td>0.167/0.50</td>
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<tr>
<td>leachable %</td>
<td>1.7</td>
<td>65.9</td>
<td>36.3</td>
<td>95.6</td>
<td>90.0</td>
<td>76.1</td>
<td>56.7</td>
<td>19.4</td>
<td>59.1</td>
<td>33.4</td>
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<tr>
<td><strong>archipelago region</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-3 cm</td>
<td>0.71/56.5</td>
<td>0.18/0.58</td>
<td>2.14/10.8</td>
<td>7.27/8.06</td>
<td>0.84/0.79</td>
<td>1.08/1.60</td>
<td>0.77/2.28</td>
<td>0.53/2.92</td>
<td>0.34/0.37</td>
<td>0.158/0.50</td>
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<tr>
<td>leachable %</td>
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<td>31.0</td>
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<td>90.2</td>
<td>100</td>
<td>67.5</td>
<td>33.8</td>
<td>18.2</td>
<td>92.0</td>
<td>31.6</td>
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<tr>
<td>12-14 cm</td>
<td>0.69/56.0</td>
<td>0.22/0.57</td>
<td>2.48/12.2</td>
<td>6.97/8.24</td>
<td>1.08/1.06</td>
<td>1.22/1.79</td>
<td>1.95/2.86</td>
<td>0.44/3.10</td>
<td>0.27/0.34</td>
<td>0.167/0.50</td>
</tr>
<tr>
<td>leachable %</td>
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<td>38.6</td>
<td>20.3</td>
<td>84.6</td>
<td>100</td>
<td>68.2</td>
<td>68.2</td>
<td>14.2</td>
<td>79.4</td>
<td>33.4</td>
</tr>
<tr>
<td>leachable average</td>
<td>1%</td>
<td>48%</td>
<td>26%</td>
<td>87%</td>
<td>70%</td>
<td>72%</td>
<td>42%</td>
<td>15%</td>
<td>70%</td>
<td>32%</td>
</tr>
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</table>

The Bothnian Bay sample from N64°09, E21°26 depth 78 m, Bothnian Sea N61°02, E19°21 depth 116 m, archipelago region (northwestern Bothnian Bay) N65°29, E22°14 depth 30 m. Figures denoted with cm are sampling depths in cores and ratios represent leached fraction/total analysis. **these values have been excluded as they probably represent authigenic formed Mn-carbonate.
Table 6 cont.

<table>
<thead>
<tr>
<th>Ba</th>
<th>Cr</th>
<th>Cu</th>
<th>La</th>
<th>Ni</th>
<th>Sc</th>
<th>Sr</th>
<th>V</th>
<th>Y</th>
<th>Yb</th>
<th>Zn</th>
<th>Zr</th>
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<td>114/618</td>
<td>28/55</td>
<td>31/31</td>
<td>29/36</td>
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<td>5.8/8.8</td>
<td>32/228</td>
<td>54/88</td>
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<td>1.5/3.1</td>
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<td>3/252</td>
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<td>18.4</td>
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<td>31/31</td>
<td>30/37</td>
<td>6.5/7.2</td>
<td>35/221</td>
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<td>23/24</td>
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<td>100</td>
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<td>81.1</td>
<td>90.2</td>
<td>15.8</td>
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<td>95.7</td>
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<td>70/64</td>
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<td>100</td>
<td>100</td>
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<td>26/30</td>
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<td>76.2</td>
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<td>20.2</td>
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<td>33/94</td>
<td>41/44</td>
<td>33/42</td>
<td>6.1/6.8</td>
<td>53/234</td>
<td>59/85</td>
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<td>1.8/2.3</td>
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<td>25.9</td>
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<td>78.6</td>
<td>89.7</td>
<td>22.6</td>
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<td>93.1</td>
<td>64.3</td>
<td>86.5</td>
<td>2.5</td>
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<tr>
<td>25%</td>
<td>59%</td>
<td>100%</td>
<td>94%</td>
<td>84%</td>
<td>86%</td>
<td>21%</td>
<td>67%</td>
<td>94%</td>
<td>66%</td>
<td>88%</td>
<td>14%</td>
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</tbody>
</table>
Figure 22. Reduction of X-ray diffraction intensities for the biotite and the chlorite groups of minerals, in a till sample, by leaching with warm HCl. Identical instrument parameters were used in both measurements (Cu Kα radiation, primary slit 1°, detector slit 1°, time constant 1 s, goniometer speed 1/2° 20/min).
knowledge in mind the results obtained by leaching grey sediment are readily explained. The Si content is almost unaffected by the HCl treatment since it is present mostly in quartz and feldspars. Much of the Al, Na, Ca, Ba and Sr is trapped in unleachable feldspars, and Zr is probably trapped in the resistant mineral, zirconium, as little Zr is leached. Some Al, Ca, Ba and Sr are leached, however, together with Ti and Cr, much of the P, Mg, V, Co and Yb content and almost all Cu, Ni, Zn, Y, La and Sc. It is also seen from Table 6 that Al, Ti, Mg and most trace elements are enriched in the fine grained sediment, as is exemplified by the sample from the central Bothnian Sea, whereas the "placer elements", including Si, Zr, Ca, Na and Sr, are depleted. However, leachability of Ca, Na and Zr increases in the fine grained sample, although the total amounts have decreased.

Variation in concretion composition due to admixed sediment

Using the data in Table 6 and Table 10 the amount of leachable and non-leachable detrital fraction can be estimated in the different nodule types. On the average approximately 32 % of grey sediment is leachable (Table 6) and using this figure the acid-soluble fraction of occluded sediment has been calculated as 24.8/0.68 minus 24.8 for spheroidal nodules, 18.2/0.68-18.2 for discoidal and 37.7/0.68-37.7 for flat concretions (Fig. 23)
Figure 23. Average amounts of occluded sediment in the concretions from the Gulf of Bothnia.
These residual figures have been used to predict element variations in the HCl leachable fraction due to admixed HCl-soluble detrital particles (Table 7). Most of the Al, Sc, Ti and Cr present in the HCl-soluble fraction of Fe-Mn concretions from the Gulf of Bothnia are derived from occluded detrital sediment (Table 7). Practically no Mn, P, Ba, Sr, Ni or Zn (the same most certainly applies also for Co, As and Mo) are present in the leachable fraction of spherical and discoidal concretions owing to occluded sediment. In flat concretions approximately 30% of Zn and Ni are leached, whereas only little of the Mn, P, Ba and Sr content have a detrital source. V, La Y and Zr form a separate group with a significant sediment input of 20 to 30% in spheroidal and girdle concretions, and up to 60% in flat concretions. Yb and Cu also have a comparably large detrital origin, although not as marked as for the V, La, Y, Zr group. Mg and Na, both have 30 to 60% contribution from occluded sediment, whereas comparably little Si and Ca (~20%) have a detrital source.

Treatment of data

Since comparison between different analyses must be based on the same amount of sample, in all leaching procedures values are recalculated to 100% leachable fraction to compensate for the different amounts of admixed residual phase. However, in correlation statistics this recalculation can obscure some element relations. Elements exclusively related to the authigenic phase or to the admixed sediment usually stand out more clearly in a correlation
Table 7  Element variations explained by occluded detrital fraction in the concretions

<table>
<thead>
<tr>
<th>Type</th>
<th>Si %</th>
<th>Al %</th>
<th>Fe %</th>
<th>Mn %</th>
<th>Mg %</th>
<th>Ca %</th>
<th>Na %</th>
<th>P %</th>
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<tr>
<td>Spheroidal measured</td>
<td>0.73</td>
<td>0.68</td>
<td>18.4</td>
<td>13.1</td>
<td>0.86</td>
<td>0.92</td>
<td>0.37</td>
<td>0.99</td>
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<tr>
<td>predicted (0.37)</td>
<td>0.10</td>
<td>0.73</td>
<td>1.72</td>
<td>0.02</td>
<td>0.39</td>
<td>0.21</td>
<td>0.12</td>
<td>0.03</td>
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<tr>
<td>leached from detrital fraction</td>
<td>14%</td>
<td>107%</td>
<td>9%</td>
<td>0%</td>
<td>45%</td>
<td>23%</td>
<td>32%</td>
<td>3%</td>
</tr>
<tr>
<td>Discoidal measured</td>
<td>0.65</td>
<td>0.58</td>
<td>21.8</td>
<td>12.0</td>
<td>0.88</td>
<td>1.06</td>
<td>0.39</td>
<td>1.33</td>
</tr>
<tr>
<td>predicted (0.27)</td>
<td>0.07</td>
<td>0.53</td>
<td>1.25</td>
<td>0.01</td>
<td>0.29</td>
<td>0.15</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>leached from detrital fraction</td>
<td>11%</td>
<td>92%</td>
<td>6%</td>
<td>0%</td>
<td>33%</td>
<td>14%</td>
<td>23%</td>
<td>1%</td>
</tr>
<tr>
<td>Flat measured</td>
<td>0.52</td>
<td>1.51</td>
<td>21.3</td>
<td>2.00</td>
<td>1.02</td>
<td>0.89</td>
<td>0.32</td>
<td>1.37</td>
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<tr>
<td>predicted (0.56)</td>
<td>0.15</td>
<td>1.11</td>
<td>2.60</td>
<td>0.03</td>
<td>0.59</td>
<td>0.32</td>
<td>0.19</td>
<td>0.05</td>
</tr>
<tr>
<td>leached from detrital fraction</td>
<td>29%</td>
<td>74%</td>
<td>12%</td>
<td>2%</td>
<td>58%</td>
<td>36%</td>
<td>59%</td>
<td>4%</td>
</tr>
</tbody>
</table>

Measured values from Table 10, recalculated (with residue values) to dry-sample basis. Predicted values, calculated as, e.g. Si (spheroidal), 27.23 ("mean" Si content of grey reduced sediment from Table 6) x 0.01 (leachable average from Table 6) x 0.37 (total amount of admixed sediment, from Fig. 23) = 0.10.
<table>
<thead>
<tr>
<th></th>
<th>Ba ppm</th>
<th>Cr ppm</th>
<th>Cu ppm</th>
<th>La ppm</th>
<th>Ni ppm</th>
<th>Sc ppm</th>
<th>Sr ppm</th>
<th>Ti ppm</th>
<th>V ppm</th>
<th>Y ppm</th>
<th>Yb ppm</th>
<th>Zn ppm</th>
<th>Zr ppm</th>
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<tr>
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<td>31%</td>
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<td>4%</td>
<td>86%</td>
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<td>58%</td>
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<td>70%</td>
<td>19%</td>
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<td>15%</td>
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<td>32%</td>
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<td>41%</td>
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</tbody>
</table>
Table 8  Correlation figures obtained in the HCl-soluble fraction of flat concretions.

Correlation matrix based on original data

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
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<td>-0.072</td>
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<td>Mg</td>
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<tr>
<td>Ca</td>
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<td>0.526</td>
<td>0.114</td>
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<tr>
<td>Na</td>
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<td>0.324</td>
<td>0.360</td>
<td>0.033</td>
<td>0.517</td>
<td>0.702</td>
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<tr>
<td>P</td>
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<td>-0.123</td>
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<td>0.584</td>
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Correlation matrix based on 100 % soluble fraction

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
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</tr>
<tr>
<td>Mn</td>
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<td>-0.232</td>
<td>-0.524</td>
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<tr>
<td>Mg</td>
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<td>-0.288</td>
<td>-0.091</td>
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<tr>
<td>Ca</td>
<td>-0.135</td>
<td>0.596</td>
<td>-0.028</td>
<td>-0.060</td>
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<tr>
<td>Na</td>
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<td>0.518</td>
<td>0.003</td>
<td>-0.093</td>
<td>0.528</td>
<td>0.607</td>
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</tr>
<tr>
<td>P</td>
<td>-0.099</td>
<td>-0.339</td>
<td>0.565</td>
<td>-0.341</td>
<td>-0.330</td>
<td>0.096</td>
<td>0.307</td>
</tr>
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</table>

Values larger than $|\pm 0.25|$ resp. $|\pm 0.19|$ are significant at the 0.01 resp. 0.05 level. Number of samples = 102.
matrix based on 100% leachable fraction, compared to original data based on dried sample. However, for elements present to a significant degree in both the residual (leachable part) and the authigenic phase, correlations are concealed by the normalization procedure. This is illustrated in the matrix obtained for flat concretions shown in Table 8. In the 100% soluble fraction correlation matrix Ca and Si are both strongly associated with the insoluble fraction, and no correlation to Fe can be seen. In original data, their correlations to Fe are significant.

It is easy to imagine what happens to the correlations in these cases. For example, Ca is present in fairly large amounts in the leachable fraction, even when the detrital phase is small. When the residue becomes larger, increased leaching is able to keep pace with the declining content from the authigenic part. The sample with a large detrital fraction is subsequently raised by the normalisation, and the relation to the authigenic phase is obscured. All correlation figures seen in the text are, therefore, based on dried sample and not on 100% soluble fraction.

Composition of concretions from the Gulf of Bothnia in comparison with other Fe-Mn nodule deposits

Ferromanganese concretions found in the Gulf of Bothnia are similar in composition to concretions found in other shallow-marine areas (Table 9). They fall into an intermediate group between fresh-water concretions and deep-sea nodules. The contents of Cu, Ni and Co are generally several orders of magnitude higher in the deep-sea
Table 9 Composition of concretions in the Gulf of Bothnia and their fresh-water, shallow-marine and deep-sea counterparts

<table>
<thead>
<tr>
<th></th>
<th>Gulf of Bothnia</th>
<th>Shallow-marine concretions</th>
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</thead>
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<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>13.2</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>4.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>26.7</td>
<td>31.3</td>
</tr>
<tr>
<td>MnO</td>
<td>16.9</td>
<td>15.5</td>
</tr>
<tr>
<td>MgO</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>CaO</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.4</td>
<td>1.1</td>
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<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
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<td>2.3</td>
<td>3.0</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>-</td>
</tr>
<tr>
<td>As</td>
<td>317</td>
<td>301</td>
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<tr>
<td>Ba</td>
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<tr>
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<td>V</td>
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<td>105</td>
</tr>
<tr>
<td>Y</td>
<td>30</td>
<td>28</td>
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<tr>
<td>Yb</td>
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<tr>
<td>Zn</td>
<td>464</td>
<td>338</td>
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<tr>
<td>Zr</td>
<td>87</td>
<td>69</td>
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1: Spheroidal concretions  7: Gulf of Finland
2: Discoidal concretions  8: Gulf of Riga
3: Flat concretions  9: Black Sea
4: Baltic proper, composite analysis  10: Jervis Inlet, British Columbia
5: Baltic proper, clayey crust  11: Loch Fyne, Scotland
6: Barents Sea, discoidal concretions
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<th>Deep-sea nodules</th>
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<td>18 20.5 24.4</td>
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<td>6.7 16.8 14.7 - - - 10.5 17.8 -</td>
<td>SiO₂</td>
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<td>TiO₂</td>
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<tr>
<td>2.2 2.5 2.1 - - - 2.2 5.8 -</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>35.6 50.9 54.5 21.6 28.5 29.7 33.4 17.1 29.7 -</td>
<td>Fe₂O₃</td>
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<tr>
<td>28.4 6.1 3.7 9.4 11.3 11.8 28.3 25.5 20.4 19.5</td>
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<tr>
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<td>MgO</td>
</tr>
<tr>
<td>2.0 1.7 0.5 - - - 1.6 1.4 2.7 4.1</td>
<td>CaO</td>
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</tr>
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</tr>
<tr>
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<td>20 - - 29 51 - - 160 - -</td>
<td>La</td>
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<td>60 30 50 10 - 36 - 440 490 290</td>
<td>Mo</td>
</tr>
<tr>
<td>150 40 40 26 - 239 12 6340 3280 4640</td>
<td>Ni</td>
</tr>
<tr>
<td>0.2 - - - - - 10 - -</td>
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<td>Sr</td>
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<tr>
<td>48 10 10 58 1 - 6 530 530 440</td>
<td>V</td>
</tr>
<tr>
<td>13 - - 34 - - 310 - -</td>
<td>Y</td>
</tr>
<tr>
<td>3 - - - - - 31</td>
<td>Yb</td>
</tr>
<tr>
<td>2130 50 - 1112 205 324 181 680 840 690</td>
<td>Zn</td>
</tr>
<tr>
<td>33 - - 69 - - 520 - -</td>
<td>Zr</td>
</tr>
</tbody>
</table>

12: Tiankijokken, Northern Sweden  
13: Swedish lakes  
14: Karelian-Finnish lakes  
15: Windermere and Ullswater lakes  
16: Green Bay, Lake Michigan  
17: Green Bay, Lake Michigan  
18: Eningi-Lampi Lake, Central Karelia  
19: Pacific Ocean  
20: Atlantic Ocean  
21: Indian Ocean
Full references to Table 9

1: Spheroidal concretions, SiO₂ to K₂O figures including Ba, Cr, Sr and Zr represent total analyses of 48 samples (except from K₂O, 3 samples). Other figures are HCl leachable values of 81 samples (based on dried weight). Data from Tables 10 and 11.

2: Discoidal concretions, SiO₂ to K₂O figures including Ba, Cr, Sr and Zr represent total analyses of 20 samples (except for K₂O, 1 sample). Other figures are HCl leachable values of 35 samples (based on dried weight). Data from Tables 10 and 11.

3: Flat concretions, SiO₂ to K₂O figures including Ba, Cr, Sr and Zr represent total analyses of 39 samples (except for K₂O, 15 samples). Other figures are HCl leachable values of 102 samples (based on dried weight). Data from Tables 10 and 11.

4: Baltic proper, composite analysis from the circum-Gotland region (Manheim, 1965).

5: Baltic proper, clayey crust from the circum-Gotland region (Manheim, 1965).

6: Barents Sea, mean of 4 discoidal concretions (Ingri, 1985).

7: Gulf of Finland, mean of 9 analyses (Varentsov, 1973).

8: Gulf of Riga, mean of 19 analyses (Varentsov, 1973).

9: Black Sea, mean of 15 analyses for Fe, Ti, Mn, P, Ni, Co, Cu, Mo, V and Cr, 8 analyses for Si, Al, Ca, Mg, C and CO₂ and 4 analyses for Zr (Sevastyanov and Volkov, 1967a, b; Sevastyanov, 1967).

10: Jervis Inlet, British Columbia, mean of 2 analyses calculated on total sample basis, except for Co, Cu, Ni, V and Zn, which are for HCl-soluble fractions (Grill et al., 1968a).
11: Loch Fyne, Scotland, mean of 2 analyses of composite nodule samples (Calvert and Price, 1970). Values for SiO$_2$ to CO$_2$ in percent, others in ppm.

12: Tiankijokken, a small stream in Northern Sweden, 2 mm thick crust scraped off from a boulder, figures from SiO$_2$ to P$_2$O$_5$ including Ba, Sr, Zr and Cr represent total analyses and other HCl-leached values (based on dried sample) (Ingri this study).


15: Windermere and Ullswater lakes, mean of 8 crusts, except for Cu (6) and Mo (4) (Gorham and Swaine, 1965).

16: Green Bay, Lake Michigan, mean of 6 analyses (Edgington and Callender, 1970).

17: Green Bay, Lake Michigan, mean of 52 analyses of HCl-H$_2$O$_2$ extracts. (Rossman, 1973).


19: Pacific Ocean (Cronan, 1980).

20: Atlantic Ocean (Cronan, 1980).

21: Indian Ocean (Cronan, 1980).

Columns 7 to 18, except 12, taken from the compilation made by Calvert and Price, 1977.
nodules compared to their shallow-marine and fresh-water counterparts. No pronounced difference in the contents of these three elements can be seen between the shallow-marine and lacustrine concretions (Table 9). The concentrations of Zn are generally higher in deep-sea nodules, but fresh-water concretions can occasionally show a remarkable enrichment of Zn (Table 9). The very high Zn value, 2130 ppm, found in the remote, unpolluted small stream Tiankijokken in northern Sweden (column 12, Table 9) indicates that high Zn values are not necessarily pollution effects in the lacustrine environment. Na, Mg, Ca, V, Sr and Mo tend to increase their amounts in the concretions, going from the lacustrine to the deep-sea environment. Ba usually exhibits the strongest enrichment in fresh-water concretions, and P definitely reaches highest abundance in shallow-marine concretions. It is suggestive to correlate the Ba content in nodules to fresh-water input. One major difference between Barents Sea and Gulf of Bothnia concretions is the low Ba contents and the very low river input in the Barents Sea, although other parameters are similar (Mn content, nodule morphology etc., column 2 and 6, Table 9). Barite formation, due to the higher salinity in the Barents Sea, does not seem to be a significant explanation to the difference, as Ba contents in the Atlantic nodules are much higher than for corresponding nodules in the oceans with similar salinity but smaller river input, e.g. the Pacific, Southern and Indian Ocean.
Composition of spheroidal nodules

The most abundant Mn deposits in the Gulf of Bothnia are found in spheroidal nodules. Fe-Mn ratios in these concretions have a median value of 1.3, similar to girdle-formed concretions, but in contrast to flat Fe-rich concretions with a median ratio of 19.4 (Table 10). Average total composition of spheroidal nodules is seen in Table 9, column 1; HCl leachable fraction in Table 10 and the residual fraction in Table 11.

The contents of Cu, Ni, Zn, Co, Mo and Ba are much higher in spheroidal nodules compared to flat concretions, indicating their association with Mn. The correlations between Mo and Mn, and Ba and Mn are very strong (Table 12), whereas the Cu to Mn, Ni to Mn and Zn to Mn relations are less distinct. Co does not show a statistically significant correlation to Mn (Table 12). Ca, Na, Mg and Sr are significantly associated with the Mn-rich phase (Table 12). Only a few K analyses have been made, but they show the presence of K in the authigenically formed phase, although K is mainly present in the detrital fraction. According to the analyses made, K is correlated to Mn in spheroidal nodules. This is also indicated in a microprobe investigation (Fig. 24). The correlation obtained between Mn and Al in Table 12 is probably an artifact produced by the association between Ca, Mg and Na with Al. Table 7 indicates that practically no Al is present in the oxy-hydroxide fraction. P, As, Si and Zr are positively correlated to Fe (Table 12). Six samples of spheroidal nodules have been analysed for Ag and Au, and the re-
Table 10  Composition of the HCl-leachable fraction* in concretions from the Gulf of Bothnia.

<table>
<thead>
<tr>
<th></th>
<th>Si %</th>
<th>Ti %</th>
<th>Al %</th>
<th>Fe %</th>
<th>Mn %</th>
<th>Mg %</th>
<th>Ca %</th>
<th>Na %</th>
<th>K %</th>
<th>P %</th>
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*Values recalculated to 100% leachable fraction. Original data based on 0.5 g dried sample can be obtained using the residue figures. **below detection limit.
Table 10 cont.

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<th>Ni ppm</th>
<th>Sc ppm</th>
<th>Sr ppm</th>
<th>V ppm</th>
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Table 11  Composition of the HCl-insoluble residue in the Gulf of Bothnia concretions

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<td>11.7 (8.1)</td>
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Figures in percent except for Ba, Cr, Sr and Zr which are in ppm. Values within brackets are standard deviations. All values recalculated to original dried sample weight (0.5 g). * number of samples, n = 3, ** number of samples, n = 1.
Table 12  Element correlations in the HCl-leachable fraction of spheroidal concretions from the Gulf of Bothnia.

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<th>Mg</th>
<th>Si</th>
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<td>0.568</td>
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<td>0.598</td>
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<td>0.109</td>
<td>-0.383</td>
</tr>
<tr>
<td>Yb</td>
<td>0.145</td>
<td>-0.383</td>
<td>0.115</td>
<td>0.138</td>
<td>0.220</td>
<td>0.180</td>
<td>0.479</td>
<td>-0.278</td>
<td>-0.239</td>
</tr>
<tr>
<td>Sc</td>
<td>-0.356</td>
<td>0.275</td>
<td>-0.392</td>
<td>0.206</td>
<td>0.473</td>
<td>-0.326</td>
<td>0.604</td>
<td>0.213</td>
<td>0.085</td>
</tr>
<tr>
<td>Mo</td>
<td>-0.584</td>
<td>0.845</td>
<td>-0.467</td>
<td>0.454</td>
<td>0.628</td>
<td>-0.421</td>
<td>0.343</td>
<td>0.523</td>
<td>0.547</td>
</tr>
<tr>
<td>Co</td>
<td>-0.089</td>
<td>0.034</td>
<td>-0.228</td>
<td>0.185</td>
<td>0.625</td>
<td>-0.002</td>
<td>0.536</td>
<td>-0.138</td>
<td>0.058</td>
</tr>
<tr>
<td>residue</td>
<td>-0.442</td>
<td>-0.101</td>
<td>-0.535</td>
<td>-0.261</td>
<td>0.020</td>
<td>-0.229</td>
<td>0.357</td>
<td>-0.282</td>
<td>-0.147</td>
</tr>
<tr>
<td>depth</td>
<td>-0.348</td>
<td>0.433</td>
<td>-0.214</td>
<td>0.371</td>
<td>0.477</td>
<td>-0.237</td>
<td>0.591</td>
<td>0.577</td>
<td>0.266</td>
</tr>
<tr>
<td>latitude</td>
<td>0.185</td>
<td>0.041</td>
<td>-0.194</td>
<td>-0.305</td>
<td>0.412</td>
<td>-0.054</td>
<td>-0.685</td>
<td>0.165</td>
<td>-0.136</td>
</tr>
<tr>
<td>size</td>
<td>0.450</td>
<td>-0.210</td>
<td>0.598</td>
<td>-0.150</td>
<td>0.427</td>
<td>-0.049</td>
<td>0.667</td>
<td>-0.102</td>
<td>0.166</td>
</tr>
</tbody>
</table>

| Ti     | 0.180 |
| As     | 0.189 |
| Zn     | 0.595 |
| Ni     | 0.578 |
| Sr     | 0.067 |
| V      | 0.418 |
| La     | 0.444 |
| Cu     | 0.621 |
| Y      | 0.086 |
| Zr     | 0.384 |
| Cr     | 0.457 |
| Yb     | 0.513 |
| Sc     | 0.273 |
| Mo     | 0.541 |
| Co     | 0.325 |
| residue| 0.423 |
| depth  | 0.554 |
| latitude| 0.490|
| size   | 0.635 |
| Cr     | 0.571 |
| Yb     | 0.032 |
| Sc     | -0.273 |
| Mo     | 0.405 |
| Co     | -0.190 |
| residue| 0.076 |
| depth  | -0.260 |
| latitude| -0.089|
| size   | 0.050 |

Figures larger than $|t| > 0.29$ are significant at the 0.01 level and larger than $|t| > 0.23$ at the 0.05 level (number of samples, n = 81). Correlations larger than $|t| > 0.35$ (0.01 level) and $|t| > 0.27$ (0.05 level) are significant values for La, Yb, Mo and Cu (n = 52). Depth is defined positive with increasing depth and latitude positive northwards. Figures have not been recalculated to 100% leachable fraction.
Figure 24. Point analysis with the microprobe on a Mn-rich resp. Fe-rich layer in a spheroidal nodule from the Bothnian Bay.
results were below the detection limits 5 ppm for Ag and under 0.1 ppm for Au.

Nodule size-dependent element variations

The correlation matrix in Table 12 exhibits a strong negative correlation between size of nodules and their Zn, Ni, Cu, Co, La, Y and Yb contents. No correlations to nodule size are seen for the elements, Ba, Mo, As, Zr, Na, Si, Ca and Mn. P, Fe and Sr (at the 0.05 level) are the only elements showing a positive correlation to increasing nodule size. Al, Ti, Mg, V, Cr and Sc are also negatively correlated to size, but this is coupled with the significant correlation between residual fraction and size (Table 12). During sampling large amounts of sediment are present during the sieving of small nodules, and, inevitably, much sediment is mechanically admixed in the samples. It is obvious that the high values obtained for Cu, Ni, Zn and Co in small sized nodules (Fig. 25) are not derived from the leaching of the detrital fraction. Also the elements Yb, La and Y are present in amounts far above the values that would be reached if nodules were sediment altogether. However, the contents of Sc, Cr, Ti, Al, V and Mg can be explained by the leaching of an admixed detrital fraction. It is, therefore, assumed that these latter elements are nodule size independent. The curve plotted in Fig. 25 is a theoretical graph showing the ratio of nodule area to nodule volume (assuming a perfect sphere). This relationship is a \(1/r\) function, where \(r\) is the nodule radius. Data-points closely cluster around this curve, suggesting that the accumulations of Zn,
Figure 25. Compositional variation due to size of spherical nodules. Figures within circles represent number of samples at each point. The vertical rows represent nodule analysis from the size classes 0.5-2 mm, 2-4 mm, 4-5.6 mm, 5.6-8 mm, 9.5-12.5 mm, 12.5-14 mm, 14-16 mm, 16-19 mm, 19-22 mm and 22-25 mm. Vertical axis in ppm recalculated to 100% HCl leachable fraction. Theoretical graph shows relation between surface area $4\pi r^2$ to volume $4\pi r^3/3$ of a sphere.
Table 13  Regression models for Zn, Ni and Cu in spheriodal nodules.

<table>
<thead>
<tr>
<th>Model with</th>
<th>Variation explained by the model*</th>
</tr>
</thead>
<tbody>
<tr>
<td>one variable</td>
<td></td>
</tr>
<tr>
<td>Zn = 16.4 Mn + 229</td>
<td>28%</td>
</tr>
<tr>
<td>Ni = 25.8 Mn + 107</td>
<td>40%</td>
</tr>
<tr>
<td>Cu = 4.8 Mn + 23</td>
<td>56%</td>
</tr>
<tr>
<td>two variables</td>
<td></td>
</tr>
<tr>
<td>Zn = 9.3 Mn - 28.0 size + 590</td>
<td>68%</td>
</tr>
<tr>
<td>Ni = 18.3 Mn - 29.5 size + 487</td>
<td>68%</td>
</tr>
<tr>
<td>Cu = 4.0 Mn - 3.3 size + 66</td>
<td>72%</td>
</tr>
</tbody>
</table>

* these values are adjusted for the increased "degree of explanation" always obtained when a new variable is added.
Table 14  Element variations in spheroidal nodules of equal size due to depth of burial

<table>
<thead>
<tr>
<th></th>
<th>Fe %</th>
<th>Mn %</th>
<th>P %</th>
<th>Ca %</th>
<th>Mg %</th>
<th>Si %</th>
<th>Al %</th>
<th>Na %</th>
<th>Mn+Fe %</th>
<th>Mn/Fe</th>
<th>Residue %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spheroidal nodules</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-1 cm</td>
<td>16.0</td>
<td>26.6</td>
<td>0.50</td>
<td>1.37</td>
<td>1.46</td>
<td>0.57</td>
<td>1.15</td>
<td>0.43</td>
<td>42.6</td>
<td>1.66</td>
<td>31.7</td>
</tr>
<tr>
<td>2-3 cm</td>
<td>18.1</td>
<td>23.6</td>
<td>0.61</td>
<td>1.17</td>
<td>1.33</td>
<td>0.60</td>
<td>0.96</td>
<td>0.43</td>
<td>41.7</td>
<td>1.30</td>
<td>34.6</td>
</tr>
<tr>
<td>3-4 cm</td>
<td>17.1</td>
<td>24.0</td>
<td>0.59</td>
<td>1.11</td>
<td>1.32</td>
<td>0.77</td>
<td>0.89</td>
<td>0.42</td>
<td>41.1</td>
<td>1.40</td>
<td>30.9</td>
</tr>
<tr>
<td>4-5 cm</td>
<td>16.2</td>
<td>20.7</td>
<td>0.60</td>
<td>1.08</td>
<td>1.21</td>
<td>0.65</td>
<td>0.85</td>
<td>0.39</td>
<td>36.9</td>
<td>1.28</td>
<td>23.6</td>
</tr>
<tr>
<td>5-6 cm</td>
<td>14.7</td>
<td>20.1</td>
<td>0.61</td>
<td>1.09</td>
<td>1.15</td>
<td>0.61</td>
<td>0.88</td>
<td>0.35</td>
<td>34.8</td>
<td>1.37</td>
<td>28.7</td>
</tr>
<tr>
<td>crust 6 cm</td>
<td>20.7</td>
<td>16.5</td>
<td>1.55</td>
<td>1.49</td>
<td>1.12</td>
<td>0.95</td>
<td>1.03</td>
<td>0.65</td>
<td>37.2</td>
<td>0.80</td>
<td>60.9</td>
</tr>
<tr>
<td><strong>Spheroidal nodules</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-1 cm</td>
<td>15.0</td>
<td>25.0</td>
<td>0.47</td>
<td>1.29</td>
<td>1.37</td>
<td>0.53</td>
<td>1.08</td>
<td>0.40</td>
<td>40.0</td>
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</tr>
<tr>
<td>2-3 cm</td>
<td>17.4</td>
<td>22.6</td>
<td>0.58</td>
<td>1.12</td>
<td>1.28</td>
<td>0.58</td>
<td>0.92</td>
<td>0.41</td>
<td>40.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-4 cm</td>
<td>16.6</td>
<td>23.4</td>
<td>0.57</td>
<td>1.08</td>
<td>1.28</td>
<td>0.75</td>
<td>0.87</td>
<td>0.41</td>
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</tr>
<tr>
<td>4-5 cm</td>
<td>17.6</td>
<td>22.4</td>
<td>0.65</td>
<td>1.17</td>
<td>1.31</td>
<td>0.70</td>
<td>0.92</td>
<td>0.42</td>
<td>40.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-6 cm</td>
<td>16.9</td>
<td>23.1</td>
<td>0.70</td>
<td>1.25</td>
<td>1.32</td>
<td>0.70</td>
<td>1.01</td>
<td>0.40</td>
<td>40.0</td>
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</tr>
<tr>
<td>crust 6 cm</td>
<td>22.3</td>
<td>17.7</td>
<td>1.67</td>
<td>1.60</td>
<td>1.20</td>
<td>1.02</td>
<td>1.11</td>
<td>0.70</td>
<td>40.0</td>
<td></td>
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</tr>
</tbody>
</table>

Upper part of the Table shows HCl-leachable values recalculated to 100 % leachable fraction and figures in the lower part represent values normalized to a Fe+Mn sum = 40 %. Data from Ingri and Pontér 1985, except for As and V (this study). Figures based on dried sample can be obtained using the residue values.
Table 14 cont.

<table>
<thead>
<tr>
<th></th>
<th>Ba ppm</th>
<th>Ti ppm</th>
<th>As ppm</th>
<th>Zn ppm</th>
<th>Ni ppm</th>
<th>Sr ppm</th>
<th>Mo ppm</th>
<th>Co ppm</th>
<th>V ppm</th>
<th>La ppm</th>
<th>Cu ppm</th>
<th>Y ppm</th>
<th>Zr ppm</th>
<th>Cr ppm</th>
<th>Yb ppm</th>
<th>Sc ppm</th>
</tr>
</thead>
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<td>463</td>
<td>505</td>
<td>272</td>
<td>135</td>
<td>110</td>
<td>179</td>
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<tr>
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<td>487</td>
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<td>125</td>
<td>92</td>
<td>147</td>
<td>44</td>
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<td>88</td>
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<td>79</td>
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<td>28</td>
<td>22</td>
<td>4.4</td>
<td>10.2</td>
<td></td>
</tr>
</tbody>
</table>
Ni, Cu, Co, La, Y and Yb are due to a surface area change. More strictly speaking, data fit a $\frac{1}{c^2} + c$ function, where \( c \) is the content derived from the admixed detrital fraction (\( c = \) the uplift from zero seen on the ppm axis, Fig. 25).

With this new information regression models with two variables, Mn content and nodule size, can explain much of the variations for Zn, Ni and Cu (Table 13). However, there is still an annoying gap in the "degree of explanation" for these elements. Approximately 85% of the variation around the regression line is explained for Ba and Mo, whereas "only" 70% is explained by the two-variable-model for Zn, Ni and Cu.

Element variations in spheroidal nodules due to depth of burial

In Table 14 a profile with a 6 cm thick oxidized zone studded with spherical nodules was divided into five sediment layers each 1 cm thick, and the nodule fraction from each layer was analysed, together with a Fe-Mn-rich crust formed at the interface between the brown surface layer and the grey sediment. As seen in Table 14 the contents of Zn, Cu, Ni, Yb, Y, La and As decrease with the depth of burial, whereas Si and P increase downwards. Fe, P, Si, Ca, Na, Sr and Ba are significantly enriched in the crust formed at the reduced-oxidized sediment interface. Nodules of similar size were analyzed from each horizon, and, hence, the relations seen in the profile may explain the large variation in element content.
for nodules of equal size in Fig. 25. The "vertical scatter" in each nodule size class is readily explained if nodules with low contents of Ni, Cu, Zn, Y, Yb and La represent samples taken close to the reduced-oxidized interface whereas high contents represent nodules formed at a strongly oxidized site. Ba and Mo (together with Zr, Cr, Ti, Sc, Sr, Al, Ca, Mg and Na) are constant in the nodule fraction throughout the profile. This relation for Ba and Mo and their mutual independence of nodule size may explain why these elements are so strongly correlated only to the Mn content in spheroidal nodules.

Composition of discoidal concretions

Discoidal concretions, developed as a girdle around a visible nucleus, have absolute element contents similar to spheroidal nodules (Table 9 10). Mg, Na, Ba, Ni and Cu are statistically correlated to Mn, and P, Si, As, Zr, Sr, V and Yb are correlated to Fe (Table 15). The latter three elements did not show any preference to Fe in spheroidal nodules (Table 12). Ca shows a correlation both to Mn and Fe in discoidal concretions (Table 15).

There is a difference in element contents in the upper and lower sides of girdle concretions compared with their bulk composition. Fe and related elements are enriched on the lower side of girdles facing the sediment, whereas samples scraped off the sea-water side are enriched in Mn and related elements (Table 16). The correlation matrix in Table 15 indicates a preference of the heavy REE, repre-
Table 15: Element correlations in the HCl-leachable fraction of discoidal concretions from the Gulf of Bothnia.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>P</th>
<th>Ca</th>
<th>Mg</th>
<th>Si</th>
<th>Al</th>
<th>Na</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>-0.419</td>
<td>-0.423</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.789</td>
<td>0.388</td>
<td>-0.341</td>
<td>0.49</td>
<td>0.491</td>
<td>-0.292</td>
<td>0.092</td>
<td>-0.229</td>
</tr>
<tr>
<td>P</td>
<td>0.388</td>
<td>0.352</td>
<td>-0.346</td>
<td>0.403</td>
<td>-0.082</td>
<td>-0.648</td>
<td>-0.491</td>
<td>-0.430</td>
</tr>
<tr>
<td>Ca</td>
<td>-0.341</td>
<td>0.174</td>
<td>0.174</td>
<td>-0.082</td>
<td>-0.647</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Mg</td>
<td>0.49</td>
<td>0.142</td>
<td>-0.063</td>
<td>-0.607</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Si</td>
<td>-0.292</td>
<td>-0.085</td>
<td>-0.229</td>
<td>0.401</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Al</td>
<td>0.092</td>
<td>-0.085</td>
<td>-0.607</td>
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Figures larger than |± 0.44| are significant at the 0.01 level and larger than |± 0.34| at the 0.05 level (number of samples, n = 35). Correlations larger than |± 0.57| (0.01 level) and |± 0.46| (0.05 level) are significant values for La, Yb, Mo and Co (n = 19). Depth is defined positive with increasing depth and latitude positive northwards. Correlations are based on dried samples of discoidal concretions of the girdle type.
Table 16  The different composition of "upper" and "lower" sides of a girdle concretion

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<tr>
<th></th>
<th>Si (g)</th>
<th>Al (g)</th>
<th>Fe (g)</th>
<th>Mn (g)</th>
<th>Mg (g)</th>
<th>Ca (g)</th>
<th>Na (g)</th>
<th>P (g)</th>
<th>Residue (g)</th>
<th>Mn/Fe</th>
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<td>Sea-water side</td>
<td>0.57</td>
<td>0.78</td>
<td>14.3</td>
<td>25.7</td>
<td>1.36</td>
<td>1.44</td>
<td>0.58</td>
<td>0.63</td>
<td>11.6</td>
<td>1.80</td>
</tr>
<tr>
<td>Sediment side</td>
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<td>0.51</td>
<td>23.8</td>
<td>17.1</td>
<td>0.97</td>
<td>1.16</td>
<td>0.56</td>
<td>1.64</td>
<td>11.0</td>
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<table>
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<tr>
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<th>Ba (ppm)</th>
<th>Cr (ppm)</th>
<th>Cu (ppm)</th>
<th>Co (ppm)</th>
<th>La (ppm)</th>
<th>Mo (ppm)</th>
<th>Ni (ppm)</th>
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<tbody>
<tr>
<td>Sea-water side</td>
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<td>3303</td>
<td>25</td>
<td>204</td>
<td>133</td>
<td>75</td>
<td>691</td>
<td>1538</td>
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<tr>
<td>Sediment side</td>
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<td>2493</td>
<td>22</td>
<td>79</td>
<td>145</td>
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<th>Sr (ppm)</th>
<th>Ti (ppm)</th>
<th>V (ppm)</th>
<th>Y (ppm)</th>
<th>Yb (ppm)</th>
<th>Zn (ppm)</th>
<th>Zr (ppm)</th>
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<td>834</td>
<td>157</td>
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<td>120</td>
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Values represent 100% HCl-leachable fraction. Sample from N 64°56 E 23°06.5, depth 104 m.
Table 17 Composition of "penny ore" in the Bothnian Bay

<table>
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<tr>
<th></th>
<th>Si</th>
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<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>P</th>
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<tr>
<td>%</td>
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<td>0.92</td>
<td>42.2</td>
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<td>1.22</td>
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<th>Cu</th>
<th>La</th>
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<th>Ni</th>
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<td>806</td>
<td>40</td>
<td>45</td>
<td>31</td>
<td>50</td>
<td>87</td>
<td>98</td>
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<table>
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<tbody>
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<td>31</td>
<td>5.5</td>
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Sample from a boxcore with a 2 cm sandy surface layer overlying a yellow-grey silty sediment (N 64°51 E 21°40, depth 50 m). Figures based on 100% leachable fraction. Original data can be obtained using the residue figure given.
presented by Yb for Fe, although from Table 16 is clear that all three elements accumulate on the more oxidized Mn-rich upper surface of girdles. This is possibly a reflection of the surface-dependent nature of the REE accumulation (preferentially for the light REE, e.g. La) previously shown in spherical nodules. The sea-water side of the girdles usually has a knobby surface and, hence a larger surface area compared to the smooth underside. Upper surface is more oxidized compared to the sediment-facing portion, and a "depth of burial" phenomenon analogous to spheroidal nodules is also likely.

The special type of discoidal concretions known as "penny ore", described earlier, is dissimilar in composition to ordinary girdle concretions. "Penny ore" concretions are Fe-rich with hardly any Mn present and are, hence, depleted in Mo, Ba, Zn, Cu, Ni and Co (Table 17).

Composition of flat concretions

These deposits have a high Fe/Mn ratio and are depleted in the Mn-related trace elements (Table 10). The high values of Al, Mg, Ti, Zr, Cr and Sc are a reflection of the large amount of admixed sediment in the concretions (non soluble 37.3%, total ~ 53%). In flat concretions P, Si, As, Zr, Sr, V, Y, Yb, Na and Ca are statistically associated with the Fe-rich phase, whereas Ba, Zn, Ni, Cu, La, Sr, Mo and Co (the latter two usually under the detection limit, but in Mn-rich samples their presence are seen) are related to Mn (Table 18).
Table 18  Element correlations in the HCl-leachable fraction of flat concretions from the Gulf of Bothnia.

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<tr>
<td>Sr</td>
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<td>0.384</td>
<td>0.584</td>
<td>0.065</td>
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<tr>
<td>V</td>
<td>0.223</td>
<td>0.326</td>
<td>0.473</td>
<td>0.343</td>
<td>0.064</td>
<td>0.405</td>
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<tr>
<td>La</td>
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<td>0.306</td>
<td>0.703</td>
<td>0.709</td>
<td>0.283</td>
<td>0.474</td>
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</tr>
<tr>
<td>Cu</td>
<td>0.268</td>
<td>0.393</td>
<td>0.656</td>
<td>0.259</td>
<td>0.225</td>
<td>0.815</td>
<td>0.666</td>
<td>0.605</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>0.191</td>
<td>0.322</td>
<td>0.265</td>
<td>-0.154</td>
<td>0.161</td>
<td>0.689</td>
<td>0.355</td>
<td>0.266</td>
<td>0.490</td>
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<td>Zr</td>
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<td>0.210</td>
<td>0.175</td>
<td>-0.247</td>
<td>-0.208</td>
<td>0.530</td>
<td>0.268</td>
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<td>0.482</td>
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<tr>
<td>Cr</td>
<td>0.662</td>
<td>0.725</td>
<td>0.614</td>
<td>0.159</td>
<td>0.450</td>
<td>0.794</td>
<td>0.661</td>
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<td>0.824</td>
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<tr>
<td>Yb</td>
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<td>-0.006</td>
<td>-0.259</td>
<td>-0.443</td>
<td>0.267</td>
<td>0.146</td>
<td>0.090</td>
<td>0.325</td>
</tr>
<tr>
<td>Sc</td>
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<td>-0.668</td>
<td>-0.398</td>
<td>-0.277</td>
<td>-0.777</td>
<td>-0.295</td>
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<td>0.093</td>
<td>0.076</td>
<td>0.182</td>
<td>0.093</td>
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<td>-0.296</td>
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<td>-0.606</td>
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<tr>
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<tr>
<td>Yb</td>
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<td>0.449</td>
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</tr>
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<tr>
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<td>0.191</td>
<td>-0.503</td>
<td>0.499</td>
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<tr>
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<td>latitude</td>
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<td>-0.406</td>
<td>-0.393</td>
<td>0.112</td>
<td>-0.348</td>
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</table>

Figures larger than \(| \geq 0.25|\) are significant at the 0.01 level and larger than \(| \geq 0.19|\) at the 0.05 level (number of samples, \(n = 102\)) correlations larger than \(| \geq 0.40|\) (0.01 level) and \(| \geq 0.32|\) (0.05 level) are significant values for La and Yb (\(n = 44\)). Correlations are based on dried sample.
contrast to spheroidal and girdle nodules, are Ca and Na exclusively associated to the Fe content. Sr is correlated to both Mn and Fe.

P-rich Fe crusts forming on soft bottoms in the Bothnian Sea show a clear enrichment of Ba, Ca, Na and Sr (Table 19). It seems as if these elements (note the very high Ba values in these Mn-poor concretions) have accumulated into the crusts because of a P-rich phase. No significant increase of other Fe-related elements, i.e. Zr, Si, As, V, Yb and Y can be seen in these P-rich crusts.

In many locations, especially in the Bothnian Bay, flat concretions show an enrichment of Mn, as extensive botryoidal growth form, on the sea-water side of the concretion. This phenomenon is analogous to the one previously discussed for girdle concretions, and exhibits the same type of compositional difference between upper and lower side. A flat concretion sampled in the archipelago region north-east of Luleå illustrates the difference (Table 20).

Comparison between the concretionary types

The data mentioned above have shown the mutual increases of Mg, Ni, Cu, (Co), Mo and Ba with Mn content, and the increase of Si, P, As, Zr and possibly also V with Fe content. Al, Sc, Ti and, most likely, Cr are almost to 100% tied up to the detrital fraction together with much of the Mg, Ca and Na. These relations are seen in all concretionary types. The status of Ca, Na, Sr and
Table 19  Enrichment of Ca, Na, Ba and Sr in P-rich Fe crusts from the Bothnian Sea.

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Ca</th>
<th>Na</th>
<th>P</th>
<th>Ba</th>
<th>Sr</th>
<th>residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>ppm</td>
<td>ppm</td>
<td>ppm</td>
<td>%</td>
</tr>
<tr>
<td>38.7</td>
<td>1.21</td>
<td>1.77</td>
<td>0.75</td>
<td>4.03</td>
<td>685</td>
<td>833</td>
<td>25.6</td>
</tr>
<tr>
<td>35.3</td>
<td>0.29</td>
<td>1.71</td>
<td>0.74</td>
<td>4.47</td>
<td>1339</td>
<td>880</td>
<td>30.9</td>
</tr>
<tr>
<td>36.5</td>
<td>1.14</td>
<td>1.17</td>
<td>0.55</td>
<td>3.21</td>
<td>939</td>
<td>450</td>
<td>21.2</td>
</tr>
<tr>
<td>39.7</td>
<td>2.34</td>
<td>1.31</td>
<td>0.59</td>
<td>3.44</td>
<td>867</td>
<td>538</td>
<td>27.4</td>
</tr>
<tr>
<td>39.2</td>
<td>1.76</td>
<td>1.47</td>
<td>0.58</td>
<td>3.27</td>
<td>928</td>
<td>636</td>
<td>26.0</td>
</tr>
<tr>
<td>35.4</td>
<td>0.97</td>
<td>1.77</td>
<td>0.81</td>
<td>3.66</td>
<td>648</td>
<td>725</td>
<td>37.9</td>
</tr>
<tr>
<td>35.3</td>
<td>1.13</td>
<td>1.59</td>
<td>0.64</td>
<td>3.38</td>
<td>762</td>
<td>588</td>
<td>37.9</td>
</tr>
</tbody>
</table>

35.4 | 1.15 | 1.46 | 0.58 | 2.16 | 615 | 447 average n=33
4.4  | 0.54 | 0.25 | 0.09 | 0.53 | 181 | 79 Stand. dev.

Values below the line shows the "composition" of 33 flat concretions from the Bothnian Sea with P content < 3.20% and Mn < 2.40%. All figures based on 100% leachable fraction.
Table 20 Composition of "upper" and "lower" sides of a flat concretion from the archipelago region in the North-western Bothnian Bay.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>P</th>
<th>residue</th>
<th>Mn/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea-water side</td>
<td>0.74</td>
<td>0.76</td>
<td>19.8</td>
<td>22.4</td>
<td>1.17</td>
<td>1.32</td>
<td>0.25</td>
<td>0.44</td>
<td>27.3</td>
<td>1.13</td>
</tr>
<tr>
<td>Sediment side</td>
<td>0.87</td>
<td>0.25</td>
<td>44.0</td>
<td>2.4</td>
<td>0.67</td>
<td>1.16</td>
<td>0.17</td>
<td>2.13</td>
<td>8.4</td>
<td>0.05</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Ba</th>
<th>Cr</th>
<th>Cu</th>
<th>Co</th>
<th>La</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea-water side</td>
<td>495</td>
<td>3508</td>
<td>44</td>
<td>132</td>
<td>118</td>
<td>67</td>
<td>316</td>
<td>702</td>
</tr>
<tr>
<td>Sediment side</td>
<td>535</td>
<td>775</td>
<td>33</td>
<td>19</td>
<td>&lt;32</td>
<td>24</td>
<td>59</td>
<td>109</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Sr</th>
<th>Ti</th>
<th>V</th>
<th>Y</th>
<th>Yb</th>
<th>Zn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea-water side</td>
<td>1.4</td>
<td>440</td>
<td>1073</td>
<td>133</td>
<td>58</td>
<td>5.4</td>
<td>605</td>
<td>45</td>
</tr>
<tr>
<td>Sediment side</td>
<td>0.9</td>
<td>469</td>
<td>415</td>
<td>109</td>
<td>23</td>
<td>4.4</td>
<td>306</td>
<td>44</td>
</tr>
</tbody>
</table>

Analysis of a flat concretion with black botryoidal growth forms on the upper side and a smooth hard lower side facing the sediment. Concretion taken at 10 m depth, N65°38 E22°23. Figures based on 100% leachable fraction. Original data can be obtained using the residue values given.
REE, including Y, is not fully clear, and this applies to some extent also for Ba.

A close investigation of the relations between Ca, P, Na, Sr and Ba reveals the different behaviour of these elements in the concretionary types. No correlation of Na with Fe is seen in girdle and spheroidal nodules, but in flat concretions a strong association is obvious. Ca is correlated to Mn in spheroidal concretions, associated to both Mn and Fe in discoidal concretions and correlated to Fe in flat concretions (Tables 12, 15, 18). Furthermore, there is no statistical correlation between P and Ca in spheroidal nodules, although this is seen in girdle and flat concretions. There is a close relation between Sr and Ca throughout the material and the phase changes of Ca is seen also for Sr. Ba is strongly anticorrelated to P in girdle and spheroidal concretions, but shows an enrichment in P-rich flat concretions (Table 19). The REE and Y are closely related to the surface characteristics of the oxyhydroxide phase, and seem to prefer highly oxidized Mn-rich surfaces. However, heavy REE (e.g. Yb) and Y appear to have a correlation also to Fe in girdle and flat concretions (Tables 15, 18).

Variation in composition with latitude and depth

Most elements show a strong latitudinal correlation and also a depth correlation (Tables 12, 15, 18). To interpret these correlations a division of samples between the two subbasins of the Gulf
of Bothnia must be done (Table 21). The negative correlation between latitude and Al, Mg, Ti, V, Zr, Cr and Sc contents is most likely due to the more fine grained, more leachable admixed sediment in the Bothnian Sea samples (compare Table 6), as there is no significant difference in the amount of HCl-insoluble detrital fraction in the two subbasins. Average depth of collected samples in the Bothnian Sea is larger compared to the Bothnian Bay and this promotes the incorporation of more fine grained sediment. The strong latitudinal correlations for Zn, Ni, Cu, Co, As, La, Yb and Y, but not for Ba and Mo in spheroidal nodules are related to the average nodule size sampled (see above). In the Bothnian Sea average spheroidal nodules are significantly smaller compared to the Bothnian Bay (Table 21). If spheroidal nodules of the same size are compared, the difference disappears for all these elements except for As, Y and Co (Table 22). In other words the contents of As, Y and Co are, at the 0.05 level, significantly higher in the Bothnian Sea spheroidal nodules, when equally sized nodules are compared. There is no difference in the Fe content of spheroidal and flat concretions in the two subbasins. Also the Mn content is equal in spheroidal nodules, but flat concretions found in the Bothnian Bay are richer in Mn. Within the Bothnian Sea the Mn, Na, Ba, Zn, Ni and Cu contents in flat concretions are all correlated to increasing depth, but this is not seen in the Bothnian Bay. Mn increases significantly with depth in spheroidal nodules within both basins and there is a negative correlation between Fe and depth (Table 12). The Si content is higher in flat (and girdle) concretions found in the Bothnian Bay, but this is not seen in spheroidal nodules (Table 21).
Table 21  Composition of spheroidal and flat concretions in the Bothnian Bay compared to the Bothnian Sea.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>P</th>
<th>residue</th>
<th>depth</th>
<th>size</th>
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<td></td>
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<td></td>
</tr>
<tr>
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<td>n=64</td>
<td>n=64</td>
<td>n=64</td>
<td>n=64</td>
<td>n=64</td>
<td>n=64</td>
<td>n=64</td>
<td>n=64</td>
<td>n=64</td>
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<tr>
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<td>1.19</td>
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<td>1.39</td>
<td>24.4</td>
<td>72.8</td>
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<td>6.5</td>
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<td>0.28</td>
<td>0.16</td>
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- indicates data not available.
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<th>Ni</th>
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<th>Sr</th>
<th>Ti</th>
<th>V</th>
<th>Yb</th>
<th>Zn</th>
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Significant difference at the 0.05 level: no no no yes yes yes no no

Values based on 100% HCl-leachable fraction.
Geochemistry of Fe-related elements

Goethite is the most frequently reported Fe phase in ferromanganese nodules (Burns and Burns 1981), but in most cases the Fe-rich phases appear amorphous to conventional x-ray diffraction techniques, and the Fe mineralogy has remained obscure. In the Baltic Sea concretions both goethite and feroxyhyte have been reported (Winterhalter 1966, Varentsov 1973, Chuckhrov et al. 1976). Feroxyhyte (non-magnetic δ'-FeOOH) is formed where dissolved Fe$^{2+}$ is rapidly oxidized and has been claimed to be the precursor of goethite formation in concretions found in the Baltic Sea (Chuckhrov et al. 1980). Analyses of Fe-rich crusts formed at the reduced-oxidized interface, sampled in this study, failed to show any goethite, using conventional x-ray diffraction technique on bulk samples.

The close association between Fe and P has been shown to exist in concretions not only from the Baltic Sea, but also from a number of shallow-marine environments in the Barents Sea (Ingri 1985), Black Sea (Sevastyanov and Volkov 1967), Loch Fyne (Calvert and Price 1970) and the Australian shelf (Cook and Marshall 1981). This close relationship has been explained by the adsorption of P by hydrous ferric oxides (Winterhalter and Siivola 1967), or by the formation of a ferric phosphate in the Fe-rich phase of the concretions (Sevastyanov and Volkov 1967). The formation of a pure Fe (III)-phosphate seems unlikely, however, as such a phosphate precipitates only in acid solutions. With increasing pH, an Fe
(III)-hydroxophosphate with increasing $\text{OH}^-/\text{PO}_4^{3-}$ ratio is formed (Stumm and Morgan 1970).

In a more or less dissolved buried nodule layer, 30 cm below the sediment surface, small sand-sized white aggregates were found. These white spots turned blue-green during storage, indicative of the mineral vivianite (Palache et al. 1951, Dell 1973). The x-ray diffraction pattern produced by the blue-green aggregates was also positively identified as vivianite (Table 23), although the blue-green colour is probably due to an oxidized phase called kertschenite (Palache et al. 1951). However, vivianite is not likely to be encountered in the Fe-rich crusts formed at the oxidized-reduced interface; instead a number of ferrosoferric hydroxyphosphates are thermodynamically possible (Nriagu and Dell 1974).

There are some indications suggesting the formation of a "phosphatic phase" within the Fe-rich part of flat and girdle-formed concretions. With the microprobe, Winterhalter and Siivola (1967) revealed a correlation between Ca and P in a discoidal concretion from the Baltic, and in the Barents Sea a close association between Ca and P in girdle concretions is seen (Ingri 1985). The accumulation of Na, Sr and Ba together with P and Ca in flat Fe-rich concretions seen above could be associated with the formation of a "phosphatic phase". From the sediment profile displayed in Table 14 it is seen that most P is trapped in the Fe-rich crust formed at the boundary between the reduced grey sediment and the oxidized surface sediment. Upwards in the profile P exhibits decreasing
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<td>VS</td>
<td>2.22</td>
<td>VW</td>
<td>1.68</td>
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</table>

Vivianite crystals found in a buried nodule layer 30 cm below the sediment-water interface, sample from N64°29 E22°02, depth 104 m. Reflections are very similar to syn. Vivianite, Fe₃(PO₄)₂ • 8H₂O, 3-70 JCPDS index. The overall intensities of the peaks were low and the notations VS = very strong, S = strong, W = weak, VW = very weak refer to relative intensities. Scan speed used 1/2°/min, time constant 1 s, Cu_Kα radiation (with monochromator), d values were calculated using the wavelength Cu_Kα(=\frac{1}{3}(Kα₂+2Kα₁)) = 1.5418.
values, indicative of a subsurface source. However, the correlation between large "old" Fe-rich nodules and P (Table 12) could be interpreted as a late enrichment of P (and Fe), directly from sea-water, onto already existing spheroidal nodules.

The accumulation of Si in the Mn-Fe crust seen in Table 14 and the high silica values obtained at the lower sides of girdle-formed concretions (Table 16) suggest a pronounced accumulation of Si at the interface between the grey reduced sediment and the oxidized surface sediment. Furthermore, Si is statistically correlated only to the Fe content in concretions, which indicates an enrichment of Si in the Fe-phase, especially at reduced-oxidized interfaces. Very high dissolved Si and Fe contents in the pore-waters from the Gulf of Bothnia (see below) support this conclusion. Ferrihydrite (bulk composition $5 \text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) is formed where Fe(III) is supplied at a very high rate, such as during the rapid oxidation of dissolved Fe(II) from interstitial waters in sediments (Chuckrov et al. 1976). Ferrihydrite is known to accumulate considerable amounts of Si (Carlsson and Schwertmann 1981). A phase of this type might explain the enrichment of Si in flat and discoidal concretions from the Gulf of Bothnia.

As and Zr are also closely related to Fe in concretions from the Gulf of Bothnia, and the same is seen in Loch Fyne Fe-Mn concretions (Calvert and Price 1970). Accumulation of As in Black Sea nodules is also related to Fe (Sevastyanov 1967). Kanamori (1965) in a study of As geochemistry in lakes suggested that Fe-oxyhydroxides regulate the As content by coprecipitation and dissolution in
the same manner as suggested for P by Mortimer (1942). Table 24 indicates that redistribution of As within the sedimentary column is a working process, and much of the As present in concretions from Gulf of Bothnia may have been diagenetically mobilized. Depth of burial affects the accumulation of As into spheroidal nodules (Table 14) and, hence, the redox status of the nodule surface seems to be important, as well as the Fe content.

Geochemistry of Mn-related elements

There is still great confusion about the crystal structure and terminology of Mn minerals found in ferromanganese nodules (Burns and Burns 1977). Usually, however, x-ray diffraction data exhibit strong reflections at ~7Å and/or ~10Å both in near-shore and deep-sea nodules. The 7Å phase with additional reflections at ~3.6, 2.4 and 1.4Å is usually referred to as birnessite (Manheim 1965), owing to the similarity of x-ray diffractogram with the terrestrial mineral birnessite found first in a fluvio-glacial deposit near Birness, Scotland (\((\text{Na, Ca}) \text{Mn}_4\text{O}_{14} \cdot 2.8 \text{H}_2\text{O}\), Jones and Milne 1956). The name todorokite for the 10Å phase (with additional reflections at 4.8, 3.2, 2.4 and 1.4Å) found in deep-sea nodules was suggested by Straczek et al. (1960), because of the similarity in x-ray patterns between nodules and the terrestrial mineral, todorokite (Yoshimura 1934).

If only diffuse reflections at 2.4 and 1.4Å are present, the term \(\delta\)-MnO\(_2\) or vernadite (Chukhrov et al. 1978) has been used to
Table 24  The composition of the HCl-soluble fraction of diagenetically formed layers in a sediment-profile from the Bothnian Bay.

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Boxcore profile with a 5 cm brown surface sediment with inbedded small (maximum 6 mm in diameter) knobby black nodules, overlying a brown-orange coloured hard crust with an yellow-orange coloured sediment below. The oxidized zone being 7 cm thick altogether. Sample from N 64°35' E 21°57.5', depth 105 m. All figures recalculated to 100% HCl-soluble fraction. Original data can be obtained using residue values.
distinguish this phase as a separate mineral (Burns and Burns 1977). The weak and diffuse x-ray diffraction reflections produced by this phase are probably due to small and extremely thin crystallites.

Giovanoli et al. (1971) synthesized a 10A manganate which has cation exchange properties. This phyllomanganate, which they called buserite, readily dehydrates into birnessite, if not kept under water. It has been suggested that "expandable" phases of buserite type are common in nodules, and the widespread occurrence of birnessite might be an artifact produced by the dehydration and oxidation of buserite type phases (Burns and Brown 1972, Halbach et al. 1981, Dymond et al. 1984). However, in situ oxidation of 10A manganate, forming a 7A reflection, might occur, since changing redox potential most likely influences the mineralogy of nodules (Cronan and Tooms 1967). Incorporation of cations like Cu, Ni and Zn in the 10A phase probably stabilizes the structure and prevents the collapse of the lattice upon dehydration and oxidation (Halbach 1981).

Ferromanganese concretions from the shallow-marine environment appear to contain 10A manganate (Calvert and Price, 1977). Manheim (1965) reported x-ray diffraction data from the Baltic proper, where both the 10A and the 7A reflections were seen. From the Gulf of Bothnia Winterhalter (1966) reported a 7A peak in a spheroidal nodule.
Air-dried samples of spheroidal nodules studied in this investigation frequently showed x-ray diffraction peaks at 7.1-7.2Å, 2.45Å, 2.34Å and 1.43Å. Unfortunately, no precaution was undertaken to prevent dehydration and oxidation during sampling and the observed 7Å peak could be an artifact, caused by the collapse of a former 10Å phase. A complete dehydration, induced by the drying at 80°C and for 24 hours of the air-dried nodule samples showed an enhancement of the 7Å peak. It has been suggested that the size of the 7Å peak might be used as a measure of the amount of unstable 10Å manganate in a sample, in a manner analogous to ethylene glycol expansion of smectite in clay mineral analyses (Dymond et al. 1984). This concept was used in order to detect any change of the 7Å peak with depth of burial of spheroidal nodules. Oven-dried nodule samples from the profile shown in Table 14 were x-ray-investigated, but no change in the intensity of the 7Å peak between the 5 layers of nodules could be observed.

The accumulation of Cu, Ni and Zn is believed to be due to a substitution of these metals for Mn$^{2+}$ into a 10Å phase (Burns and Burns 1978). However, several authors have shown that 10Å-rich nodules from the shallow-marine environment mostly have rather low Cu, Ni and Zn contents, and the mineralogy appears not to be the only determining factor (Cronan 1980).

In the Gulf of Bothnia Zn, Ni and Cu are all surface-related and it is probable that only small amounts of these elements are present in a lattice position. Shallow-marine and lacustrine concre-
tions grow much faster than their abyssal counterparts (Manheim 1965), and this could be one part of the explanation of the low Cu, Ni and Zn values encountered in the shallow-marine concretions (Cronan 1980). Additionally, Ingri and Pontér (1985c) suggested that the general lower redox level in the Gulf of Bothnia, compared to the "red clay-related" deep-sea nodules, promotes a high activity of Mn$^{2+}$, which inhibits a significant substitution of Mn$^{2+}$ by Zn$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$.

In contrast to Cu, Zn, Ni and Co, Mo and Ba are enriched in the Gulf of Bothnia nodules in amounts which approach deep-sea averages (Table 9). Ba and Mo are perfectly linearly correlated only to the Mn content in spheroidal nodules, and do not show any changes with size of nodules or with depth of burial. Very high Ba values (10,000 ppm) found in Lake Michigan concretions have been explained by the presence of psilomelane (Rossman 1973), but in the shallow-marine environment no psilomelane has so far been reported. However, large ions like Ba$^{2+}$, K$^+$ and Pb$^{2+}$ are probably present in the large cavities formed in Mn-phases with a framework structure, like hollandite and psilomelane (Burns and Burns 1977).

Most of the elements associated with Mn are present as mono and divalent cations in sea-water in contrast to Mo, present as an oxyanion (Riley and Chester 1971). It has been suggested (see Murray and Brewer 1977 for references) that Fe-oxyhydroxides are positively charged, whereas Mn phases are negatively charged in the
marine environment, and hence, anions should preferentially be correlated to Fe by simple electrostatic coupling. However, not only Mo, but also Sb have been shown to correlate to Mn in nodules (Glasby 1974). A few analyses made by the author indicate the presence of W in the Mn-rich phase in the Gulf of Bothnia, and both Sb and W exist as anions in sea-water (Riley and Chester 1971). While further verification is needed, it is plausible that Mo exists as a Mn compound in concretions from the Gulf of Bothnia.

The rare earth elements (REE), including Y, are definitely present in the concretions from the Gulf of Bothnia in amounts too high to be explained by occluded aluminium-silicate debris. Much of the variation in REE content is regulated by the surface characteristics of the nodules. Both the surface area to volume ratio of spheroidal concretions and depth of burial strongly affect the REE accumulation (Tables 12, 14). There is no statistically verified correlation of La, Y and Yb to total Mn content, nor to total Fe content in spheroidal concretions. However, increased amounts of the REE are detected in Mn-rich nodules compared to flat Fe-rich concretions, suggesting a relationship between the surface of Mn-phases, especially, and the REE (Ingri and Pontér 1985a). The light REE (e.g. La) appear to have stronger affinity for the Mn-enriched surface compared to the heavy REE (Yb; including Y). Statistically significant correlations between Yb and Fe, and Y and Fe are seen both in discoidal and flat concretions.
Ce shows properties dissimilar to the other REE in the Gulf of Bothnia. Ce appears to be strictly correlated to the Mn content and is probably a measure of the redox level (Ingri and Pontèr 1985a). Ce may occur as a tetravalent cation and could substitute Mn\(^{4+}\) in framework structures (Burns and Burns 1977), thus being a measure of the Mn\(^{4+}\)/Mn\(^{2+}\) ratio or the degree of oxidation of the Mn-rich phase.

ORIGIN

Interstitial water compositions

Porewater compositions within the Gulf of Bothnia are summarized in Table 25. Salinity variations are immediately reflected in the interstitial waters sampled. The almost freshwater character of the archipelago region of the northern Bothnian Bay and the increasing salinity going from the Bothnian Bay to the Bothnian Sea are clearly seen in the increasing amounts of interstitial Na, Mg and Ca going south. Na, Mg and Ca show similar values in the porewaters as seen in overlying sea-water. The Si, Fe, Mn, Ba and Zn values, on the other hand, are much higher in the interstitial waters compared to sea-water. There is a major difference in the interstitial water composition between the archipelago region (close to river mouths) and the open parts of the Gulf of Bothnia. Porewaters taken in the archipelago region are significantly higher in Mn, Fe and Si; for Mn the difference is several orders of magnitude (Table 25).
Table 25  Composition of interstitial waters in Fe-Mn stratified sediments in the Gulf of Bothnia

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<td>south-eastern</td>
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<tr>
<td>0-1.5 cm</td>
<td>7.06</td>
<td>0.39</td>
<td>6.90</td>
<td>zero level</td>
<td>b.d.</td>
<td>239</td>
<td>1170</td>
<td>61</td>
<td>134</td>
<td>1920</td>
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<tr>
<td>1.5-3 cm</td>
<td>6.68</td>
<td>0.34</td>
<td>6.90</td>
<td>+1</td>
<td>56</td>
<td>128</td>
<td>1220</td>
<td>63</td>
<td>138</td>
<td>4020</td>
</tr>
<tr>
<td>3-4 cm</td>
<td>7.28</td>
<td>1.10</td>
<td>7.01</td>
<td>+16</td>
<td>31</td>
<td>541</td>
<td>1220</td>
<td>64</td>
<td>136</td>
<td>5110</td>
</tr>
<tr>
<td>4-5 cm</td>
<td>15.62</td>
<td>6.38</td>
<td>7.12</td>
<td>+26</td>
<td>282</td>
<td>150</td>
<td>1270</td>
<td>65</td>
<td>136</td>
<td>6330</td>
</tr>
<tr>
<td>5-6 cm</td>
<td>14.34</td>
<td>0.25</td>
<td>7.00</td>
<td>-236</td>
<td>1210</td>
<td>161</td>
<td>1160</td>
<td>59</td>
<td>126</td>
<td>6580</td>
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<tr>
<td>6-7 cm</td>
<td>5.03</td>
<td>0.07</td>
<td>7.12</td>
<td>-305</td>
<td>2740</td>
<td>362</td>
<td>1200</td>
<td>60</td>
<td>129</td>
<td>7310</td>
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<td>7-8 cm</td>
<td>5.50</td>
<td>0.07</td>
<td>7.20</td>
<td>-392</td>
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<td>496</td>
<td>1140</td>
<td>58</td>
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<tr>
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<td>0.07</td>
<td>7.25</td>
<td>-405</td>
<td>7750</td>
<td>754</td>
<td>1160</td>
<td>59</td>
<td>132</td>
<td>8560</td>
</tr>
<tr>
<td>Bothnian Sea</td>
<td></td>
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<tr>
<td>0-2 cm</td>
<td>12.00</td>
<td>3.08</td>
<td>7.80</td>
<td>-</td>
<td>303</td>
<td>629</td>
<td>2040</td>
<td>121</td>
<td>221</td>
<td>5630</td>
</tr>
<tr>
<td>3-5.5 cm</td>
<td>21.82</td>
<td>0.52</td>
<td>8.20</td>
<td>-</td>
<td>51</td>
<td>1760</td>
<td>2050</td>
<td>124</td>
<td>219</td>
<td>7590</td>
</tr>
<tr>
<td>5.5-7.5 cm</td>
<td>8.79</td>
<td>0.09</td>
<td>8.07</td>
<td>-</td>
<td>177</td>
<td>1690</td>
<td>2080</td>
<td>115</td>
<td>203</td>
<td>7020</td>
</tr>
<tr>
<td>7.5-9.5 cm</td>
<td>9.00</td>
<td>0.10</td>
<td>8.09</td>
<td>-</td>
<td>1330</td>
<td>2480</td>
<td>2090</td>
<td>118</td>
<td>208</td>
<td>7590</td>
</tr>
</tbody>
</table>
Si values probably reflect the intimate association between Si and diatom production. Siever et al. (1965) proposed that the dominant control on dissolved Si in interstitial waters is the abundance and rate of dissolution of diatoms in the sediments. Si values found in the samples from the archipelago region are twice as high as those from the open Bothnian Bay and Bothnian Sea (Table 25), possibly a reflection of the high diatom production in the near-shore region.

Ba is enriched by approximately 5 times the bottom water values in the porewaters from the archipelago region and in the Bothnian Sea (Table 25). Barite is probably formed authigenetically in deep-sea sediments and hence regulates the maximum dissolved Ba content in the porewaters (Church and Wolgemuth 1972). However, Ba is strongly enriched in the porewaters of terrigeneous deposits, owing mainly to the depletion of sulphate (Manheim 1976). In the analysed profiles (Table 25) Ba is high when dissolved Mn is high, and Ba is very likely brought into solution by the dissolution of Mn oxyhydroxides. As dissolved $\text{SO}_4^{2-}$ rapidly decreases with depth, owing to bacterial reduction of sulphate, precipitation of barite should be less feasible. High Ba values in interstitial waters have also been explained by organic complexing agents preventing the formation of barite (Michard et al. 1974).

The behaviour of Zn in the interstitial profiles is more difficult to interpret. No correlation of dissolved Zn with Mn or Fe can be seen, and there is no obvious difference between the sub-areas in the Gulf of Bothnia.
Formation of stratified surface sediments

The high interstitial values observed suggest a pronounced migration upwards within the uppermost surface sediment. Closely related to this flux is the formation of Fe-Mn-stratified top sediments and concretions (Table 26) (Ingri and Pontér 1985b). These stratified sediments, with up to 45% Fe$_2$O$_3$ and 10% MnO in rich horizons, must have formed owing to diagenetic redistribution within the sedimentary column. Hence, the calculations made by Varentsov (1973) showing that diagenetic reactions in Baltic sediments can only produce a 1.3% Mn layer and a 0.2% Fe layer, are not valid in the Gulf of Bothnia. Several trace elements are associated with the Fe-and Mn-enriched sediment strata, indicating an interstitial source also for these elements (Ingri and Pontér 1985a, b). The boxcores, especially from the Bothnian Bay, display how both spherical Mn-rich and flat Fe-rich concretions are formed within the sedimentary column. Most of the flat Fe-rich crusts, found at the sediment-water interface on mud bottoms in the Bothnian Sea, have probably formed from a subsurface source, as indicated by elevated values of suboxic derived elements, e.g. P, Ba, Ca and Sr (see below). Some of the Fe-impregnated glacial sediment known as the Korsö type of concretions have been suggested to form directly from sea-water (Winterhalter 1966). Mn coatings formed on exposed relict sediments, found on current-swept moraine ridges, probably also have a direct sea-water origin, especially when such ridges are found close to an area with a rather high sedimentation rate, which promotes the flux of Mn$^{2+}$ into the water column.
Table 26  Composition of a diagenetically altered sediment profile from the Bothnian Bay.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
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<td>%</td>
<td>%</td>
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</tr>
<tr>
<td>brown water-</td>
<td>52.0</td>
<td>0.64</td>
<td>12.1</td>
<td>8.76</td>
<td>0.55</td>
<td>2.28</td>
<td>2.18</td>
<td>3.16</td>
<td>2.41</td>
</tr>
<tr>
<td>rich surface</td>
<td>(1.0)</td>
<td>(1.0)</td>
<td>(-)</td>
<td>(1.6)</td>
<td>(5.2)</td>
<td>(1.0)</td>
<td>(1.1)</td>
<td>(1.1)</td>
<td>(1.0)</td>
</tr>
<tr>
<td>black layer</td>
<td>49.0</td>
<td>0.62</td>
<td>11.6</td>
<td>8.28</td>
<td>5.40</td>
<td>2.26</td>
<td>2.12</td>
<td>2.92</td>
<td>2.36</td>
</tr>
<tr>
<td>(1.0)</td>
<td>(1.0)</td>
<td>(-)</td>
<td>(1.6)</td>
<td>(52.8)</td>
<td>(1.1)</td>
<td>(1.1)</td>
<td>(1.1)</td>
<td>(1.1)</td>
<td>(1.0)</td>
</tr>
<tr>
<td>orange-</td>
<td>25.3</td>
<td>0.32</td>
<td>5.56</td>
<td>36.8</td>
<td>0.57</td>
<td>1.46</td>
<td>2.05</td>
<td>1.46</td>
<td>1.23</td>
</tr>
<tr>
<td>brown crust</td>
<td>(1.1)</td>
<td>(1.0)</td>
<td>(-)</td>
<td>(14.4)</td>
<td>(11.6)</td>
<td>(1.4)</td>
<td>(2.2)</td>
<td>(1.1)</td>
<td>(1.1)</td>
</tr>
<tr>
<td>orange-</td>
<td>49.9</td>
<td>0.62</td>
<td>11.6</td>
<td>12.7</td>
<td>0.28</td>
<td>2.26</td>
<td>2.30</td>
<td>3.16</td>
<td>2.41</td>
</tr>
<tr>
<td>brown layer</td>
<td>(1.0)</td>
<td>(1.0)</td>
<td>(-)</td>
<td>(2.4)</td>
<td>(2.7)</td>
<td>(1.1)</td>
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<tr>
<td>grey sediment</td>
<td>56.4</td>
<td>0.72</td>
<td>12.6</td>
<td>6.26</td>
<td>0.12</td>
<td>2.48</td>
<td>2.30</td>
<td>3.24</td>
<td>2.70</td>
</tr>
<tr>
<td>(1.0)</td>
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<td>(-)</td>
<td>(1.0)</td>
<td>(1.0)</td>
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<td>(1.0)</td>
<td>(1.0)</td>
<td>(1.0)</td>
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</tr>
<tr>
<td>grey sediment</td>
<td>54.0</td>
<td>0.68</td>
<td>12.9</td>
<td>7.98</td>
<td>0.24</td>
<td>2.52</td>
<td>2.18</td>
<td>3.12</td>
<td>2.53</td>
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<tr>
<td>with black Fe-</td>
<td>(1.0)</td>
<td>(1.0)</td>
<td>(-)</td>
<td>(1.4)</td>
<td>(2.1)</td>
<td>(1.1)</td>
<td>(1.0)</td>
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<td>(1.0)</td>
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<tr>
<td>monosulphide</td>
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</table>

Boxcore profile from N 64°56'E 21°50' (depth 80 m) with a 2 cm brown water-rich surface layer and a 3 mm thick Mn-rich layer below. A 5 mm hard crust had formed above a 2 cm thick orange coloured Fe-rich zone. Note the formation of a reduced Mn-phase in the Fe-monosulphide layer. Values within brackets are Al-normalized enrichment figures, compared to grey sediment. Calculated as, e.g. MnO in black layer, 5.40/11.6/0.12/13.6 = 52.8.
Oxic and suboxic diagenesis

Two types of diagenesis have been suggested to contribute to nodule formation in the deep-sea. Oxic diagenesis involves the reactions that occur within the oxidized surface sediment, whereas suboxic diagenesis refers to a total reduction and dissolution of Mn from the (IV) to the (II) valence state (Dymond et al. 1984). These concepts can be used to interpret the composition of Fe-Mn concretions also in the Gulf of Bothnia.

From the previous discussion (Table 12, 14) it is clear that the accumulation of Ni, Cu, Zn, Co, Y, Yb and La is closely related to the surface of the Mn-rich phase. Their surface dependency suggests that they are loosely held onto the Fe-Mn particles. When a descending Fe-Mn-enriched particle reaches an oxidized surface sediment, from the water column above, it is subjected to a change in pH and Eh. There is a small decrease in pH (approximately 0.5 pH units), going from the bottom waters into the oxidized surface sediment, together with a lowered redox potential. This change may bring about a desorption of loosely held elements like Ni, Cu, Zn, Co, Y, Yb and La. Part of the "depth of burial effect" shown above (Table 14) could be explained by this mechanism (Ingri and Pontér 1985c). The lack of correlation between interstitial Zn and Mn-Fe (Table 25) could be caused by the desorption of Zn from a solid Mn-Fe-enriched phase.

Ba and Mo, on the other hand, are strictly correlated to the Mn content in concretions and do not show any surface dependency
(Table 12, 14). Only a total dissolution of the Mn-oxyhydroxide phase can unfix a major portion of these elements. The joint increase of Ba and Mn values in the pore-waters supports their close relationship. Enrichment of Ba in Fe-crusts formed at the reduced-oxidized interface also corroborates a suboxic source for Ba. Fe-related elements like P, Si, Na, Ca and Sr also indicate a suboxic origin in flat concretions (Table 14), and P shows a clear decreasing trend in nodules, going upwards, in the profile displayed in Table 14.

The oscillating redoxcline

The Fe-Mn layering seen in nodules from the Gulf of Bothnia is a primary feature (Winterhalter and Siivola 1967, Fig. 13, this study). This implies that the redoxcline, dividing Fe-precipitation from Mn-precipitation, is oscillating within the sediment. Winterhalter and Siivola (1967) suggested that this might occur on a yearly basis. One Fe-rich and one Mn-rich band (~0.1 mm each) might represent one year, under optimal conditions.

The largest spheroidal nodules found in this study are 3 cm in diameter, and Winterhalter (1966) has not reported any nodules above this limit. This implies that active nodule formation takes place within a few hundred years, with a mean nodule growth rate of 0.15 mm/year. Furthermore, this indicates a mean upward (steady state) movement of the reduced-oxidized interface, or the redoxcline, in the order of 0.2 - 1 mm/year (assuming a nodule growth rate of 0.15 mm/year and a 2 - 10 cm thick oxidized zone).
The only parameter that could significantly change the redox level, annually, in the Bothnian Bay surface sediment, is the supply of organic matter (changes in bacterial activity due to the seasonal changes in bottom-water temperature are, however, a parameter that could possibly be of significance, see Ingri and Pontér 1985b). Organic matter, debouched into the Bothnian Bay in large amounts during the spring flood, probably settles in late autumn in the central Bothnian Bay, together with remnants of the primary production formed during the summer period. The bacterial break-down of this material induces a somewhat lowered oxygen content in the surface sediment, and the redoxcline (dividing Fe- from Mn-precipitation) might rise into the bottom-waters in late winter. Mn-precipitation onto nodules, within the sedimentary column, should be most pronounced in late summer and in the autumn, whereas Fe-rich layers form preferentially during winter and spring in the central parts of the Bothnian Bay.

Age of nodules in the Gulf of Bothnia

An active nodule growth rate of 0.15 mm/year is a very high rate in comparison to the estimated rates based on radiometric methods. Ku and Glasby (1972), using $^{230}$Th and $^{231}$Pa, calculated the growth rates of nodules from Loch Fyne and Jarvis Inlet to 0.3 mm/1000 years. Krishnaswami and Moore (1973), using the decay of unsupported $^{226}$Ra, showed accretion rates of 2 mm/1000 years in fresh-water concretions. Both in the Loch Fyne (Calvert and Price 1977) and in the Gulf of Bothnia these radiometric mean growth rates give an accre-
tion 100 to 1000 times slower than mean sedimentation in these areas. The same paradox as that seen in the deep-sea (Cronan 1980), is present also in the shallow-marine environment. However, this does not imply that all concretions in the Gulf of Bothnia are younger than a few hundred years. A growth rate of 0.15 mm/year refers to active nodule formation within the sedimentary column, with an access to much interstitial Mn$^{2+}$ and Fe$^{2+}$. Several rich nodule deposits seen today are, however, found on erosive sites, and growth rates are probably very much reduced when nodules become exposed to the bottom-waters. The Weichselian ice-sheet puts a maximum age of approximately 9000 years to the concretions in the Gulf of Bothnia, but a closer study of the history of the Baltic suggests that concretions found in the Gulf of Bothnia are not older than approximately 3000 years.

Although the post-glacial development of the Baltic basin is complicated, four main stages can be recognized (Munthe 1940, Ignatius et al. 1980):

1) The Baltic Ice Lake, prior to 10000 years B.P.
2) The Yoldia Sea, $\sim$ 10000 - 9300 years B.P.
3) The Ancylus Lake, $\sim$ 9300 - 7500 years B.P.
4) The Litorina Sea, $\sim$ 7500 - 3000 years B.P.

grading into the present, less saline Limnaen Sea.

Approximately 9000 years B.P. the Bothnian Bay was probably free from ice (Ignatius et al. 1981), implying that Yoldia Sea sediments should be sparsely occurring in the Gulf of Bothnia.
In the beginning of the Ancylus Lake stage the summer temperature was similar to today's, and during this stage the air temperature rose and reached a maximum in the Litorian period. This temperature rise promoted the spreading of birch, pine and lower vegetation to the northern part of Sweden (Liljequist 1970), and an extensive chemical weathering of the freshly exposed till, of the type seen today, could be initiated. Hence, the formation of ferromanganese nodules in the Gulf of Bothnia probably became feasible during the Ancylus Lake. Little is known about the redox status of the waters and sediments during this stage. The water level in the Bothnian Bay stood approximately 200 m above the present sea-level, but no halocline should have formed in this fresh-water basin. Ancylus clays are blue-grey, homogeneous (Ignatius et al. 1981), and the samples of Ancylus sediment found in this investigation are low in organic matter. The bottom-waters in the Gulf of Bothnia during this stage were probably strongly oxidizing. This would have favoured the formation of Fe-Mn concretions.

The differential land uplift, greater in the north than in the south, promoted a transgressing in the south, finally establishing a new contact with the raising ocean through the Danish Sounds. In-flowing saline waters initiated a new stage, the Litorina Sea. Because the Gulf of Bothnia was the deepest part of the Baltic, at that time (Mörner 1979, displayed in Georgala 1980), the halocline should have been well developed. Owing to the presence of a distinct halocline during the early Litorina stage, deep basin water exchange was slow, dissolved oxygen was consumed, and anoxic condi-
tions were established. In support for this scenario is the exceptionally sharp lithostratigraphic boundary dividing the Ancylus Lake stage and the early Litorina Sea. Early Litorina sediments consist of micro-layered mud with a high organic content (Jerbo 1961, Ignatius et al. 1968). This rapid change in the oxygen content of the bottom-waters in the Gulf of Bothnia probably induced a dissolution of the "supposed" Fe-Mn concretions formed during the Ancylus stage. It seems likely that this occurred on a regional scale, all over the Gulf of Bothnia. Only concretions formed at elevated bottom areas at intermediate depths should have survived the change in bottom-water chemistry.

As the land uplift continued the Kvarken threshold and the Aland threshold restricted the flow of saline water into the Gulf of Bothnia. With the increased influence of fresh-water input and decreasing depth the halocline weakened and Fe-Mn nodule formation once more became feasible, owing to the increased oxygen content in the bottom-water, in the Gulf of Bothnia. The majority of the concretions found in the present Gulf of Bothnia are probably younger than the dissolution event in the early Litorina Lake, i.e. not older than approximately 3000 years.

Today, no distinct halocline is seen in the Bothnian Bay and Mn-rich nodules are formed at all depths. As no halocline restricts the penetration of oxygen into the surface sediment, the sedimentation rate and associated organic input are the primary regulating factors for nodule growth in the Bothnian Bay. Areas with a sedimenta-
tion rate exceeding ~ 0.4 mm/year in the Bothnian Bay (Table 3), usually are barren of nodules at present. However, the land uplift rapidly changes sedimentation areas into young active Fe-Mn nodule producing bottoms, and former productive sites change into erosive areas with no pronounced nodule growth (Fig. 19). The presence of irregularly distributed flat Fe-rich crusts and large nodules on sandy sediments, at intermediate depths, in the zone between the archipelago region and the mud bottoms in the central Bothnian Bay, most likely represents relict deposits growing slowly or not at all today.

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Paper 2
Fe and Mn layering in Recent sediments in the Gulf of Bothnia

by

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Abstract

The oxidized surface layer of Recent soft sediments in the Gulf of Bothnia has been investigated. Distinct stratification of Fe and Mn is observed with up to five different oxidized horizons in well developed profiles. These layered top sediments, although not previously investigated, are extensively occurring in the Gulf of Bothnia, especially in the Bothnian Bay. A close association between Mn and Ni, Ba, Zn and Cu is present, whereas P, Ca and Sr accumulate together with Fe. High dissolved Fe and Mn contents coupled to a strong redox gradient are recorded in the interstitial waters.

Formation of the layers is linked to varying redox conditions. Fe and Mn tend to be solubilized under reducing conditions, to migrate upwards and to precipitate as oxy-hydroxides along favourable redox horizons. Reaching oxidizing conditions Fe precipitates prior to Mn and is always found below the Mn-rich strata. The character of the oxidized zone is quite different in the two subbasins of the Gulf of Bothnia. Mn-rich horizons together with spherical Mn-rich nodules are frequently found in the Bothnian Bay, but in the Bothnian Sea mostly Fe-rich layers are present together with abundant Fe-rich flat concretions. This difference is interpreted as being due to a general lower redox level in the Bothnian Sea. The vast occurrence of buried Fe-rich layers with much associated P found in the Bothnian Bay might be one explanation of the noticed deficiency in phosphate compared to nitrate observed in the water column in this area.
Introduction

The postglacial sediments in the Gulf of Bothnia are mainly formed by submarine erosion of till and other glacial sediments (Winterhalter 1972, Tulkki 1977, Boström et al. 1978, Boström et al. 1982). In shallow waters panning of till has created a sandy sediment almost granitic in composition, whereas in deeper areas (>40 m) much of the fines have been deposited and postglacial sediments with an element distribution close to average shale have formed in many locations (Boström et al. 1978). These deep water deposits show a 1 to 15 cm thick, well oxidized Fe-Mn-rich top layer above a pale-grey to almost black reduced Mn-poor sediment. The grey to black sediment represents permanently depositing postglacial sediment in the Gulf of Bothnia whereas the oxidized top section is much influenced by exchanges between sediment and bottom waters. Commonly, in the Bothnian Bay these top centimeters of oxidized deposits are studied with spherical knobby nodules, whereas in the Bothnian Sea flat Fe-rich concretions are more abundant (Winterhalter 1966, Boström et al. 1978, 1982). Very often these top layers also show a distinct Fe-Mn layering indicating large redox variations (this paper).

Well defined Mn and Fe layers in an oxidized top zone have been reported from Recent sediments in the Great Lake district and from Karelian lakes in the U.S.S.R. (Mothersill and Shegelski 1973, Sly and Thomas, 1974, Profilev and Gabe 1965). From the shallow-marine environment Turner (1971) described Fe and Mn horizons of the type found in the Gulf of Bothnia from cores taken in the Kara Sea.
In laboratory experiments Butkevich (1928) showed the development of layers in brown water-rich top sediments from the Petschora and White Seas, by placing sediment in sealed and stored bottles. The brown sediment turned brown-grey in the lowermost part of the bottles, while the surface of the sediment which was in contact with the water-phase in the uppermost part of the bottle, remained brown. When opening the bottles a third brown-red horizon developed in between the brown top layer and the grey sediment below. These layers were sampled and Fe-related micro-organisms were identified. Butkevich stressed the importance of these organisms for the formation of the layers but he also noted the significance of the oxygen and CO₂ gradients that must develop. He proposed a diagenetic model to explain the formation of Mn-Fe-rich top sediments and nodules in the Petschora and White Seas. Support for this diagenetic migration theory was furnished by Manheim (1965) and Winterhalter (1966) and today this mechanism may explain many near-shore nodule occurrences (Calvert and Price 1977), although lateral transport of diagenetically mobilized material and Mn-Fe-rich river-borne suspended matter also have significance (Manheim 1965, Winterhalter 1966, Varentsov 1973 and Boström et al 1982).

The Baltic Sea receives much river-introduced Mn-Fe-enriched suspended matter (Burman 1983) and the fate of this material within the two major subbasins of the Baltic, the Bothnian Bay and the Bothnian Sea is discussed in this paper. The major role of the redox level explaining the composition of the surface sediment is emphasized.
Shipboard operations

The character of the uppermost zone of Recent sediments in the Gulf of Bothnia was investigated using a boxcorer (grab type sampler) described by Jonasson et al (1966). Almost undisturbed 30x30x50 cm cores can be obtained with the sampler; such large samples are necessary in order to get a detailed picture of the layering in the sediments. Samples for porewater analyses were taken by the lowering of a plexiglass tube into the core sample. Top and bottom were subsequently sealed and the tube was inserted into a Argon flushed glove box. The sediment was sampled by inserting a thin plate into prefabricated slits in the sampling tube and squeezed through a 0.45 μm Millipore filter using four modified Reeburgh samplers (Reeburgh 1967). Interstitial water was recovered with increasing N₂ pressure from 1 to 4 atm which gave 10 to 30 ml porewater within a few hours. The inert atmosphere in the glove box prevented the oxidization of Fe²⁺ and Mn²⁺ at the filter. Redox and pH measurements were made in the porewaters within the glove box using a Metrohm E 604 pH meter. The samples were acidified with 5 μl HNO₃ per ml sample and stored at 6°C.

Analytical methods

The elements analysed were determined by optical emission spectroscopy (OES) using an Inductively Coupled Plasma (ICP) as excitation source. Sc and P were analysed with an ARL 35000 scanning unit and
the other elements with an ARL 33000 instrument (Burman 1979, 1981 and Burman et al 1979, 1981). K was measured with Atomic Absorption. The sediments were analysed by ICP-OES using two digestion procedures. Thus, major elements, Cr, Zr, Ba and Sr were dissolved and determined with a metaborate digestion procedure and trace element contents were measured on sediment samples dissolved by HF-HClO₄ (Burman et al 1978). A HCl leaching method was used for the nodules and the soluble fraction was measured directly with ICP-OES, whereas the residue was fused with the metaborate procedure prior to analysis (Boström et al 1982). Interstitial waters were introduced directly into the plasma and analysed without preconcentration.

Description of the oxidized top section

Five main types of oxidized top sections in Recent soft sediments from the Gulf of Bothnia can be recognized from the 140 boxcores mapped in Fig. 1.

Type one (Fig. 2), represents a sediment with a reduced grey layer overlaid by a water-rich brown horizon. The light to medium bluish grey (all colours refer to wet samples) layer presumably represents permanently deposited reduced postglacial sediment and often contains irregularly shaped and distributed black bands and sometimes is totally black. This black colour is due to iron monosulphides which rapidly change to shades of grey in oxidized
Figure 1. Distribution of boxcore stations in the Bothnian Bay (upper part) and the Bothnian Sea (lower part). Thickness of the oxidized surface layer and type of layers developed (see Fig. 2) with nodule types and depth is shown.
Figure 2. The different types of profiles developed in the oxidized top section of Recent soft bottom sediments in the Gulf of Bothnia.
environments. Commonly in the Bothnian Bay the moderate to dark yellowish brown water-rich upper layer is 2-5 cm thick, with extreme values from 1 mm occurring within the archipelago region (north-western part of the Bothnian Bay) and up to 15 cm at some locations off the coast.

Type two (Fig. 2), has a brown water-rich top and a grey reduced zone as in type 1 but between these layers is a yellow-grey transition zone. This zone is usually a few cm thick but can on some occasions be up to 10 cm and often shows increasing tints of yellow going upwards. The boundary towards the grey layer is often diffuse.

In type three, a very distinct orange-brown to orange coloured layer is developed. The limits of this zone are very sharp, both to overlying strata and to the underlying zone.

Type four shows the development of a thin, hard limonite coloured hard crust forming the boundary between overlying sediment and the brown-orange zone beneath. In most studied profiles, however, this boundary was only seen as a gradual change in colour from orange to dark reddish brown with a "felt-like" appearance of the sediment close to the overlying layer.

Type five represents the most developed profile with formation of a black layer above the brown hard crust and underlying the water-rich brown top sediment. Usually this layer is thin, only a
few mm, and can be hard to detect. However, at some investigated sites this layer was up to 2 cm thick. At two locations a black crust was developed within this zone. A close investigation of the black horizon reveals the presence of porous knobby micro nodules ranging from those invisible to the naked eye, to concretions with a diameter of some millimeters.

In all profile types (Fig. 2) nodules can be present in the water-rich brown surface layer. About half of the boxes taken, contained visible nodules. Although spherical nodules are found in the Bothnian Sea, well developed profiles of type 5 are rare. This is in contrast to the Bothnian Bay where 40% of all boxes had a well defined, black oxidized layer present. Silty mud bottoms in the Bothnian Bay all exhibit well defined oxidized top sections, although extremely thin in the archipelago regions (Fig. 1).

The recovered and analysed sediment (Fig. 1) was 30x30x40 cm and showed a grey zone with some black Fe monosulphide horizons at the bottom of the core. The grey layer was sampled at 20 cm depth where no interfering black zones were present. The yellow-grey transition zone, extending to 8 cm depth, formed above the grey sediment is not included in this study because it merely represents a grey layer with small amounts of oxidized Fe. The 4 cm thick yellowish-brown water-rich layer at the top of the profile contains knobby porous spherical nodules, with a maximum diameter of 1 cm. Cut nodules from the profile exhibit concentric layering of alternating black-brown and light-brown bands.
Chemical composition

In the five authigenically formed layers overlying the grey reduced sediment a distinct separation of many elements is seen (Table 1). The element enrichments indicate the importance of the oxidized zone as a trap for diagenetically mobilized elements. The spherical nodules, especially, are important scavengers for both Mn- and Fe-related elements. The composition of the water-rich top layer represents sieved sediment with nodules larger than 0.25 mm separated from the enclosing sediment. This sieved brown top layer has a composition very similar to the grey layer with most of the trace elements concentrated in the nodule fraction (Table 1). Assuming that the concretions present in the brown layer, put together, occupy approximately 1 cm of the 4 cm thick layer, then a composition very close to the black horizon is achieved, when 1/4 of the nodule layer mixes with 3/4 of the brown layer (Fig. 3). This illustrates their genetic relationship.

Already in original data it is obvious that many trace elements are enriched in the Fe-Mn-rich sediment layers and in the concretions if compared to the reduced permanently depositing grey sediment. But, both in nodules and in the diagenetically formed layers there is incorporation of a detrital aluminium-silicate phase, poor in trace elements. This fraction tends to obscure or dilute the element contents of the oxy-hydroxide authigenically formed phases. To get the enrichment factors of the elements, normalization to Al has been used, since this element does not appear to take
part in the diagenetic reactions caused by early burial (Calvert and Price 1977, Boström et al. 1982). Normalization to 14.6% Al₂O₃, the content in the grey layer, provides a multiplication factor for each horizon. Multiplication of all elements with their related factor and division by corresponding element values in the grey layer gives the enrichment figures shown in Table 2.

Si, Ti, K, Na, Mg, V, Zr and Cr show ratios close to one in the profile and do not accumulate to a significant degree within the formed Mn-Fe-rich sediment layers (Table 2). However, V, Mg, Na and K significantly accumulate in the nodule fraction. In other analysed profiles Si and Na have shown a small but significant accumulation in Fe-rich crusts. HCl-leached, Fe-rich flat concretions from the Bothnian Sea definitely indicate an enrichment of Si and Na (Ingri 1985a). The enrichments of Cr and Sc in the hard Fe-crust in Table 2 probably are insignificant. P, Ca and Sr show a clear association to Fe in the sediment layers. The accumulation of Ca and Sr in the nodule fraction is also affected by the Mn content, as these elements have been shown to correlate to Mn in spheroidal concretions from the Gulf of Bothnia (Ingri 1985a). This is also illustrated by the high ratios for Ca and Sr compared to Fe and P in the nodules in Table 2. The association between Ca-P and Fe close to the reduced interface has also been demonstrated under the microprobe by Winterhalter et al. 1967, on a girdle formed concretion from the Gulf of Bothnia. Similarly, a girdle concretion from the Barents Sea proved a strong correlation between Fe and Ca and P (Ingri 1985b). This type of concretions always develops at
Table 1  Element distribution in the oxidized top section of a Recent sediment from the Bothnian Bay.

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
<th>%</th>
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Nodules

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Sediment

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<th>%</th>
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<th>%</th>
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<td>2.08</td>
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<td>8.09</td>
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<td>2.08</td>
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<td>2.04</td>
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Thickness and general appearance of the profile are shown in Fig. 1 and are also discussed in the text. Some of the trace elements in the nodule residual fraction have not been determined (n.d.). This contribution is however negligible and leached values have been used as total figures.
Table 1 cont.

<table>
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<th></th>
<th>Ba ppm</th>
<th>Cr ppm</th>
<th>Cu ppm</th>
<th>Ni ppm</th>
<th>Sc ppm</th>
<th>Sr ppm</th>
<th>V ppm</th>
<th>Zn ppm</th>
<th>Zr ppm</th>
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<td>16</td>
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<td>310</td>
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<td>78</td>
<td>105</td>
<td>164</td>
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Table 2  
Element enrichments in the oxidized top section of a Recent sediment from the Bothnian Bay.

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<th></th>
<th>Si</th>
<th>Ti</th>
<th>K</th>
<th>Na</th>
<th>Mg</th>
<th>V</th>
<th>Zr</th>
<th>Cr</th>
<th>Sc</th>
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<tr>
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<tr>
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<td>1.5</td>
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<td>0.9</td>
<td>1.3</td>
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<td>0.4</td>
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<tr>
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<td>1.1</td>
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<table>
<thead>
<tr>
<th></th>
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<table>
<thead>
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<th>Ba</th>
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<td>0.9</td>
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</table>

All figures based on data from Table 1. The enrichment values are Al normalized and compared to the grey layer (see text).
Figure 3. Comparison between the Mn-rich sediment layer and a mixture of overlying horizon with nodules (1/4 nodules + 3/4 brown water-rich sediment layer). All data from Table 1.
the reduced-oxidized sediment interface (Winterhalter 1966, Calvert and Price 1977, Ingri 1985a). Ni, Ba, Zn and Cu are accumulating in the oxidized zone and are associated to Mn. A close correlation between these elements and Mn in nodules from the Gulf of Bothnia is also seen (Winterhalter 1966, Boström et al. 1982, Ingri 1985a).

Interstitial Mn and Fe in two diagenetically altered surface sediments demonstrate a strong concretion gradient for both elements (Table 3). Measurements of pH in the porewaters demonstrate a smooth increase downwards (Table 3). A jump in pH is observed only at the sediment-water interface with a slightly more acid pH in the oxidized surface sediment compared to the more basic bottom waters. The sharp redox shift seen in Table 3 with a change of approximately 200 mV is recorded in the interface between grey reduced sediment and the orange coloured Fe-rich zone. Redox measurements by Bågander and Niemistö (1978) in Baltic Sea sediments fell into three distinct Eh ranges and according to their results the redox shift observed probably is related to the redox couple Fe$^{2+}$ to Fe$^{3+}$. This assumption is also reinforced by the increase of dissolved Fe at this level (Table 3).

Discussion

The stratification of the oxidized sediment layers appears to be predominantly the result of a solution-precipitation mechanism. Fe and Mn oxy-hydroxides tend to be solubilized under reducing conditions, thus creating the concentration gradient observed in the
Table 3 The interstitial contents of Fe and Mn in diagenetically altered sediments from the Gulf of Bothnia.

<table>
<thead>
<tr>
<th>Depth in profile (mm)</th>
<th>Bothnian Bay Sediment</th>
<th>Porewater</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe₂O₃ (%)</td>
<td>MnO (%)</td>
</tr>
<tr>
<td>0-15</td>
<td>7.06</td>
<td>0.39</td>
</tr>
<tr>
<td>15-30</td>
<td>6.68</td>
<td>0.34</td>
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<tr>
<td>30-40</td>
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<td>15.6</td>
<td>0.38</td>
</tr>
<tr>
<td>50-60</td>
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<td>60-70</td>
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<td>0.07</td>
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<tr>
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</tr>
<tr>
<td>115-125</td>
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<td>0.07</td>
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</table>

<table>
<thead>
<tr>
<th>Depth in profile (mm)</th>
<th>Bothnian Sea</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>0-20</td>
<td>12.0</td>
</tr>
<tr>
<td>30-55</td>
<td>21.8</td>
</tr>
<tr>
<td>55-75</td>
<td>8.79</td>
</tr>
<tr>
<td>75-95</td>
<td>9.00</td>
</tr>
</tbody>
</table>

Depth 0 to 40 mm in the profile from the Bothnian Bay represents a water-rich brown surface sediment with a thin (few mm) black Mn layer at 40 mm. A moderate reddish-brown Fe-rich layer is present between 40 to 50 mm and this horizon is mixed with grey sediment between 50 to 60 mm. The samples 60 to 70 and 70 to 80 mm represent grey sediment with increasing amounts of black iron-monosulphides downwards. Section 0-20 mm in the profile from the Bothnian Sea represents a brown water rich sediment with small spherical nodules partly black, partly brown in colour. The sample at 30 to 55 mm is an orange-brown layer and the two subsequent horizons are grey sediment. *Measured values have been subtracted with the surface value and the variation in Eh is shown.
porewaters, to migrate upwards and precipitate as oxy-hydroxides along favourable oxidized horizons. A strong redox gradient develops and as Fe precipitates at a lower redox value than Mn (with constant pH) (Krauskopf 1957) the Fe-rich layers always occur below the Mn strata. Changes of pH seem to be of minor importance whereas the redox gradient is of major significance and governs the composition of the oxidized zone in the sediments from the Gulf of Bothnia. The element enrichment patterns suggest that most elements accumulating in nodules are dissolved together with the Mn-Fe oxyhydroxides when buried and that they are scavenged with Fe and Mn preferentially at strongly oxidizing conditions in the nodule layer. A redox-dependent accumulation of Zn, Cu and Ni in nodules from the Bothnian Bay has been discussed by Ingri et al. 1985. Most of the P, on the other hand, precipitates together with Fe close to the reduced interface. This also applies for Si and Na which have been shown to be enriched in Fe crusts close to the reduced substrate (Ingri 1985a, Ingri et al. 1985).

The alternating Mn-rich and Fe-rich concentric layers seen in the spherical nodules indicate changes in the redox level within the uppermost water-rich sediment layer. At several coring sites nodules with colours from black to yellow-brown, some being partly black, partly yellow-brown have been found (Fig. 4). The black knobby porous surfaces are facing seawater (although interbedded in the brown water-rich sediment) and the rather smooth yellow-brown surfaces are orientated towards the sediment (underlying Fe-rich
Figure 4. Spherical nodules, partly knobby black (Mn-rich) and partly smooth yellow-brown (Fe-rich), from a water-rich brown surface sediment in the Bothnian Bay. Note the sharp redox boundary between Mn-precipitation (upper part) and Fe-precipitation (lower part).
strata). This strongly supports the assumption (Winterhalter 1967) that Fe-Mn layering in spherical nodules from the Gulf of Bothnia are primary features. If the redox cline "moves up and down", with Mn precipitation, sometimes in the water column, sometimes within the sediment, the layering in nodules becomes logical. The calculations displayed in Fig. 3 support an oscillating redoxcline within the Mn-rich uppermost zone. These calculations show that the Mn-rich sediment layer and the uppermost nodule bearing surface sediment, essentially, is one Mn-rich layer. The enrichment of elements in the nodule fraction readily explains the "contradictory" occurrence of 17% Fe (in nodules) formed above a 8% Fe-layer (the Mn-rich layer).

Winterhalter and Siivola (1967) suggested that the rhythmic banding observed in spheroidal nodules might reflect seasonally changes in the redox level. They proposed that one Fe-rich (~0.1 mm thick) and one Mn-rich (~0.1 mm thick) band represents one year during optimal conditions. We believe that transient supply of organic matter might induce the upward movement of the Fe-Mn redoxcline. This transient supply most likely originates from the sinking of dead plankton in the autumn, together with settling of the huge amounts of continentally derived organic matter debouched during the spring flood each year. Furthermore, formation of ice all over the Bothnian Bay might contribute to a lowered redox level during the winter. This implies that precipitation of interstitial Mn (within the sedimentary column in the Central Bothnian Bay) dominates in the summer whereas Fe precipitation at nodule surfaces predominates in the winter.
Development of redox gradients in near-shore sediments together with the subsequent interstitial enrichment of Mn, Fe and trace elements has been extensively discussed in the literature and purely inorganic precipitation appears to be a sufficient explanation of Mn-Fe stratified sediments. However, Perfilev et al. (1965) have suggested kinetic barriers overcome by the catalysing effect of bacteria both in the reduction-dissolution and oxidization-precipitation of Mn-Fe oxy-hydroxides in sediments. Karelian lake sediments exhibit a layering of the oxidized surface zone identical to the stratification observed in this study. In numerous experiments with Fe-Mn-rich muds from these lakes Perfilev et al. (1965) have obtained the same type of stratification as seen in the field. This layering was intimately coupled to a distinct suite of Mn-Fe oxidizing and reducing bacteria with Siderococcus especially found in the orange Fe-rich layer and Metallogenium in the black Mn-rich layer. In mud samples sterilized by heat no layers developed (Gabe et al. 1965). An interesting notation by Klaveness (1977) is that Metallogenium in Norwegian lakes follows seasonal cycles.

Some observations in the present study are in favour of the view of Perfilev et al explaining the origin of the stratification. In the Bothnian Bay Fe layers are frequently seen buried in grey sediment, sometimes as much as 30-40 cm below the oxidized zone. This indicates that the dissolution of the Fe layers sometimes is remarkably slow. Also at three boxcoring sites buried nodule layers were found and these nodules did not show any clear dissolution marks. If these layers were covered due to a "transient supply" of sediment
and were rapidly buried, this instant burial would strongly affect any micro-organisms that thrive at a very distinct redox level (Perfiliev et al. 1965) and could prevent the dissolution usually catalysed by a special group of bacteria.

Winterhalter (1966) found round structures resembling iron bacteria in a concretion from the Bothnian Bay and Ghiorse (1980) showed the presence of Mn-related bacteria on the surfaces of nodules from the southern Baltic. However, the more presence of microorganisms is poor evidence and does not imply that they have formed the Mn-Fe-rich layer they are found in, but the role of microorganisms as electron transferrer overcoming kinetic barriers in the Bothnian Bay sediments ought to be further investigated.

From the boxcores mapped in Fig. 1 it is obvious that the character of the oxidized zone is quite different in the two subbasins of the Gulf of Bothnia. In the Bothnian Bay Mn-rich sediment layers were found in 40% of the cores, whereas none of the obtained cores in the Bothnian Sea showed a visible black Mn-rich sediment layer. Spherical Mn-rich nodules are extensively occurring in the Bothnian Bay in contrast to the Bothnian Sea where iron-rich flat concretions are totally dominating nodule type. (The samples from the Bothnian Sea in Fig. 1 have deliberately been taken where spherical nodules are known to occur and that is why as much as 11 of the 26 "nodule boxes" contained spherical nodules). Analysis of flat iron-rich nodules from the Bothnian Sea also shows the relative depletion of Mn-related elements in these deposits (Winterhalter
This difference in the Mn content of the oxidized zone demonstrated by the coring could be explained if the conditions in the Bothnian Sea were somewhat less oxidizing. With a larger mean depth, larger organic production and a more developed halocline, the redox value in the bottom waters of the Bothnian Sea should be somewhat lower than in the Bothnian Bay. Measurements made by the Institute of Hydrographic Research (National Board of Fisheries, Sweden) twice a year in the Gulf of Bothnia also indicate a small difference in oxygen content in the bottom waters of the two subbasins. In 1982 the oxygen saturation was 87% (st. dev. 2.6 n = 12) in the Bothnian Bay and 70% (st.dev. 11.6 n = 16) in the Bothnian Sea, at stations deeper than 80 m (hydrographical data no. 27, 28 1983). This difference, together with the boxcore results and the comparably high Mn content in the porewaters close to the sediment-water interface (Table 3), suggests that the sediments in the Bothnian Sea are less oxidized compared to the Bothnian Bay; a conclusion also drawn by Boström et al. 1978 from Mn0/Fe2O3 ratios in surface sediments. As implied by a redox model, this may inhibit the precipitation of Mn relative to Fe and hence manganese and related elements would easily leave the sediment and migrate into the bottom waters. This might explain the Fe-rich crusts frequently found almost at the sediment-water interface on soft bottoms in the Bothnian Sea. In the Baltic proper the general redox level is even more reduced and several depressions are completely stagnant, with H2S appearing in the water column. Fe-Mn-rich concretions are found mostly on current swept relict sediments and in comparison with the Gulfs of the Baltic Sea their abundances are sparse (Winterhalter 1966, Varentsov 1973, Boström et al. 1982).
Together with the redox dependence the difference in river input can explain the decreasing amounts of Fe-Mn-rich concretions found in the three largest subbasins of the Baltic. Per square meter the annual river inflow to the Bothnian Bay is 2717 l, the Bothnian Sea 1048 l and the Baltic proper 531 l (river data Mikulski 1970, 1972, basin dimensions Winterhalter et al. 1980). With an assumed similar Mn content in all river-introduced water the Bothnian Bay receives twice the amount reaching the Bothnian Sea and five times the amount transported to the Baltic proper.

The vast occurrences of Fe-P-rich sediment strata revealed by the boxcoring disclose the enormous amounts of P trapped in the sediments from the Gulf of Bothnia and particularly in the Bothnian Bay. The effective fixation of P with Fe in the oxidized section could possibly be one of the explanations of the deficit of phosphate (compared to nitrate) found in the Gulf of Bothnia, especially in the northern basin (Voipio 1976, Pietikäinen et al. 1978, Alasaarela 1979).

Environmental aspects

The strong "redox-dependent" character of the top sediments in the Gulf of Bothnia makes the sedimentary column very sensitive to changes in the oxygen tension. For example, input of large quantities of nutrients or other oxygen-consuming substances would immediately affect the quality of the water mass due to a release of heavy metals from nodules and sediment. The accumulation of a typical
suite of trace elements together with Mn and another suite of elements with Fe makes it possible, using the proposed redox model, to predict the elements which most easily leave the sediment. Firstly Mn-related elements and Mn would enter the water column and soon the eutrophication would be "self-generating" because of the huge amounts of P that would be released together with dissolving Fe-rich sediment layers.

Another important consequence of diagenetic recycling is the enrichments of many heavy metals in the top layers. This seriously affects interpretation of pollution effects (Price et al. 1978, Suess 1978). The element enrichments seen in the analysed profile indicate the importance of the oxidized zone as a trap for diagenetically mobilized elements. Spherical nodules are important scavengers for both Mn- and Fe-related elements. As seen from Table 2 the water-rich brown surface layer is strongly impoverished with regard to heavy metals by the nodules and shows a composition close to the grey layer. The conditions in the Bothnian Bay are, in particular extremely unfavourable for interpretation of "pollution data". As seen from Fig. 1 large areas are covered by highly diagenetically altered sediments and, together with abundant nodule occurrences, complicated sediment patterns (partly due to glacial morphology and fast land uplift) and a large supply of river-borne, natural heavy metal content (Burman 1983), trace element patterns are hard to predict. All the above factors must be carefully considered when evaluating pollution investigations in the Gulf of Bothnia.
Acknowledgements

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In: A. Voipio (Editor), The Baltic Sea. Elsevier, Amsterdam, pp. 1-121.

Paper 3
Scavenging properties of Fe-Mn nodules in the Gulf of Bothnia

by

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Abstract

The scavenging capacity of spherical Fe-Mn nodules from the Gulf of Bothnia and their use as pollution indicators have been investigated. Their role in regulating trace metal contents in the oxidized surface sediment and the flux of heavy metals through the northern Baltic Sea is stressed.

Depth of burial has a profound impact on nodule composition. Likewise nodules with a diameter less than 2 mm accumulate Cu, Zn, Ni, Y, Yb and La in inverse proportion to the radius. It is suggested that specific surface area and the redox conditions govern the scavenging Fe-Mn surface and the enrichment of these elements. The enrichment patterns for Y, Yb and La are similar to those of Cu, Ni and Zn, suggesting a natural accumulation process of heavy metals at Fe-Mn oxy-hydroxide surfaces. This seriously affects the interpretation of anthropogenic input in the diagenetically altered sediments found in the Gulf of Bothnia.
Introduction

Almost all toxic elements are found enriched, sometimes several orders of magnitude, in ferromanganese nodules, crusts and coatings. The scavenging effect (Goldberg 1954) of Fe-Mn oxy-hydroxides is an important factor regulating water quality in many natural waters (Krauskopf 1956, Jenne 1968); both metals and nutrients like P (Mortimer 1941, 1942) are affected due to sorption of such oxy-hydroxides. The surface of Fe-Mn precipitates therefore monitor the flux of heavy metals at a sampling site; this monitoring has been used in ore prospecting with good results (Carpenter et al. 1978). As the Fe-Mn concretion continuously grows a "record" on the water quality will form and any change in the input of heavy metals should be detected. A comparison between metal content in surface and interior layers of Fe-Mn nodules hence could be a measure of, for example, anthropogenic input. Suess and Djafari 1977 have used this approach on a discoidal nodule from the South Baltic and have calculated the pollution effect of Zn. This interpretation assumes, however, that no selective desorption takes place in older parts of the nodule due to diagenesis, recrystallization etc.

The Baltic Sea receives much river-introduced Fe-Mn-enriched suspended matter. Most of the Mn and Fe is present as a non detrital suspended phase. Investigations during 4 years of the unregulated Kalix river debouching into the Bothnian Bay show that suspended
Mn increases drastically at the end of July, with a peak value in the middle of August; the ratio of non detrital Mn to detrital Mn then being around 33. Ninety-seven percent of suspended matter in July and August is present in a non detrital fraction contributing 30% of the annual load of Mn in the Kalix river (Burman 1982). The seasonal changes in Mn (and several other elements) have been interpreted as being due to redox changes in lakes draining into the Kalix river (Pontér et al., to be published). The fate of this Fe-Mn-enriched suspended matter is quite different during sedimentation in the three major subbasins of the Baltic Sea; the Bothnian Bay, the Bothnian Sea and the Baltic proper.

Some of the river-introduced Fe-Mn-rich suspended matter settles close to the river mouth. In the archipelago region of the northern Bothnian Bay very high interstitial water contents of Fe and Mn have been recorded in the sediments. Values between 30 to 50 mg/l Mn are frequently found; figures that are 20 to 100 times higher than those registered in the open Gulf of Bothnia (Ingri 1985). Much of this interstitial Mn leaves the archipelago region probably as suspended matter, as very Mn-Fe-rich concretions are found within these areas. Fine grained Fe-Mn-rich suspended matter settling in the open Bothnian Bay tends to dissolve within the sedimentary column and migrate upwards, but owing to the strongly oxidizing conditions in the open Bothnian Bay most interstitial Fe and Mn are precipitated along favourable redox horizons. Boxcore data show that the thickness of the oxidized surface sediment increases from a few mm in the
archipelago regions up to 15 cm at locations off the coast. Soft bottoms in the Gulf of Bothnia are highly altered by this diagenetic recycling of Mn and Fe. The oxidized surface sediment is clearly stratified, showing five distinct layers in well developed profiles (Ingri and Pontér 1985). Usually a water-rich brown layer with spherical nodules is found at the water-sediment interface, subsequently followed by a Mn-rich layer, a Fe-rich zone and a grey reduced sediment down-wards. Trace metal enrichments in these profiles indicate the importance of the oxidized zone as a trap for diagenetically mobilized elements. The water-rich brown surface layer is strongly impoverished with regard to metals by the nodule fraction, which emphasizes their importance as scavengers (Ingri and Pontér 1985). This affects the flux of elements through the Baltic Sea and the composition of the surface sediment. Generally, the top sediment in the shallow, low productive and well oxygenated Bothnian Bay acts as a sink (although not 100% effective) for both Fe and Mn. Surface sediments in the Bothnian Sea on the other hand are lower in Mn, instead Fe is found enriched, often as a Fe-rich hard crust, close to the sediment-water interface. This difference has been interpreted as being due to a somewhat lower redox level in this basin (Ingri and Pontér 1985). The redox level is even more reduced in the Baltic proper. This basin has large areas covered with totally reduced sediments with H₂S appearing in bottom waters in the deeper parts. Stratification of Fe and Mn of the type seen in sediments from the Gulf of Bothnia has been observed in the water column above the Landsort depth in the Baltic proper. At 100 m depth
a Mn-rich suspended phase (6.4% Mn) was found with a Fe-rich suspended phase 50 m below (5.6% Fe) forming above the $H_2S$ zone (Ingri et al., to be published). It has been suggested (Ingri 1985) that sedimentation of Mn, in particular, occurs in a looping process along the bottom of the Baltic Sea. In areas with high sedimentation rates (that is, high organic input, implying a low redox level) Fe-Mn-enriched suspended matter is rapidly redistributed within the sedimentary column, and a local source of Fe and Mn is created. With lowered sedimentation rates and organic input (higher redox level) Fe and Mn is trapped within the surface sediment. At highly oxidized sites much Mn and associated trace elements (e.g. Cu, Zn, Ni, Ba and Mo) are fixed. With a slightly reduced redox level mainly Fe and correlated elements (e.g. P) are significantly trapped within the sediment.

The significance of the redox level in explaining the composition of the surface sediments on a regional scale in the Baltic Sea (Boström et al. 1978, Ingri 1985) can be traced back to the scavenging properties of individual Fe-Mn-accumulates. In this paper we will discuss the mechanisms causing enrichment of some trace elements onto Fe-Mn nodules in the Bothnian Bay. We belive that these data have a bearing not only upon the composition of shallow-marine ferromanganese nodules, but also point out how trace elements might be transported and fixed in estuarine environments in the presence of Fe-Mn oxy-hydroxides (Ingri 1985). The role of Fe-Mn micronodules in the transportation and sedimentation of some heavy metals was
also emphasized by several authors at the workshop held after the "Symposium on contaminant fluxes through the near-shore zone" (Nantes 1984). Furthermore, the existence of Fe-Mn micro-particles affects the interpretation of pollution effects (Price et al. 1978, Suess 1978).

Field relations and sampling

The spherical nodules analysed in this paper have been sampled by boxcoring (Jonasson and Olausson 1966) in the Bothnian Bay (Fig. 1). The general appearance of Fe-Mn concretions in the Bothnian Bay have been discussed by Winterhalter 1966, Boström et al. 1982 and Ingri 1985.

At station 82-54 a 30x30x20 cm boxcore was recovered from a depth of 48 m. Six centimeters of light brown oxidized water-rich sediment studded with black spherical Fe-Mn nodules overlaid a grey reduced sediment with some irregular black iron-sulphide horizons. At the boundary between the brown surface-layer and the grey sediment a 3 mm thick crust had developed. This crust was black and knobby at the upper side and yellowish-brown, and rather smooth at the lower side facing the grey layer. The brown top layer was divided into 5 layers approximately 1x30x30 cm and the spherical nodules from each layer were sieved into 9 size classes. The size distribution at each level was surprisingly uniform and all nodules larger than 0.5 mm from each horizon were grinded in an agate mortar (Table 3, the 9 size classes have been joined into 3 classes).
Figure 1. Sampling sites in the Bothnian Bay. Filled squares represent boxcore samples and the triangle a dredge sample.
From station 82-44 twenty-five spherical nodules, all some 22 mm in diameter, were cut into segments. The segments, surface to 18 mm, 18 to 14 mm, 14 to 10 mm, 10 to 6 mm and 6 to 0 mm (core were sampled from each nodule and joined together into five samples (Table 4).

At station 82-43 a 30x30x20 cm boxcore was taken from 94 m depth. The core showed a 10 cm thick oxidized layer with spherical nodules overlaying a grey sediment. All nodules were sieved, and a sample from each fraction were grinded and analysed (Table 1). A dredge sample from station 79-22 containing spherical black knobby nodules was also sieved and 10 size classes were analysed (Table 1).

Analysis and treatment of data

Nodule samples (0.5 dried weight) were leached in 80°C 12% HCl with some reducing agent (hydroxylammoniumchloride) during 2-3 hours. This treatment brought the Fe-Mn-rich oxy-hydroxide fraction into solution and a grey insoluble residue was left. The HCl leachable fraction was analysed using inductively coupled plasma emission technique with an ARL 33000 instrument and an ARL 35000 sequential reading unit (Burman 1979, Burman et al. 1978, 1979, 1981).

The grey residue left by the HCl leaching procedure consists of insoluble silicates. Spherical nodules usually have 10-30% residual fractions in the Gulf of Bothnia. However, the very small nodule classes can not fully be separated from the enclosing sediment by
sieving, and the residual fraction can therefore rise to 60\% due to admixed sediment. Because of the different amount of oxy-hydroxide phase present, all values have been recalculated to 100\% HCl leachable fraction in order to be comparable. The relation $f_1 = \frac{100}{100 - \text{insoluble fraction in } \%}$ has been used to recalculate original data.

Fe-Mn nodules are basically a 3-component system with an Fe-rich phase, an Mn-rich phase and a detrital phase. Variations in the amount of the relatively trace-element-poor detrital phase produce therefore, false variations in the composition of the HCl leachable fraction (Calvert and Price 1970, Boström et al. 1982, Glasby and Thijssen 1982). This variation is removed using the $f_1$ factor and usually in the Baltic Sea the $f_1$ normalized Fe+Mn value approaches 40\% in the leachable fraction. However, there is a remaining scatter around the Fe + Mn = 40\% sum. This scatter also produces false anomalies and a factor, $f_2$, defined as $f_2 = \frac{40}{\text{Fe+Mn in } \%}$, has been used to normalize all values to constant sum of Fe + Mn. All tables show the $f_2$ normalized values but original data is easily obtained by reverse calculations.

Results and discussion

It has previously been shown that Ba, Mo, Zn, Ni and Cu are closely associated to a Mn phase in nodules from the Gulf of Bothnia, whereas P and As are enriched in an Fe phase. Si, Al, Na, Mg, Ca
and K together with Zr and Cr are mainly detrital in origin and belong to the occluded sediment fraction (Winterhalter 1966, Boström et al. 1982). Usually a linear correlation between Fe-Mn and related trace elements is assumed. However, data in Table 1, 2, 3 and 4 suggest that other factors also govern the trace metal accumulation in spherical nodules from the Bothnian Bay.

Nodule size dependent element variations

Table 1 shows that some of the trace element abundances are correlated with the size of nodules. The contents of Zn, Ni, Cu, Co, Y, La and Yb are highest in small nodules whereas the contents of Ba, Zr and Mo are independent of nodule size. The changing Fe/Mn ratio reflects the concentric Fe-Mn layering in spheroidal nodules. These data are in agreement with a study of 81 spheroidal nodules from the Gulf of Bothnia, Table 2, Fig. 2. P, Fe and Sr (at 0.05 level) are the only elements showing a positive correlation to increasing nodule size. However, also the contents of Al, Ti, Mg, V, Cr and Sc are negatively associated to size but this is coupled to the significant correlation between residual fraction and size (Table 2). In the sieving operations of small ("sand sized") nodules inevitably much sediment is mechanically admixed. It is obvious that the high values obtained for Cu, Ni, Zn and Co in small sized nodules are not derived from leaching of the detrital fraction. Also the elements Yb, La and Y are present in amounts
far above the values that would be reached if nodules were sediment altogether. The contents of Sc, Cr, Ti, Al and Mg can, however, almost exclusively be explained by the leaching of an admixed detrital fraction (Ingri 1985).

Approximately 2 mm diameter appears to be the "critical size": smaller nodules show a drastic change whereas the element contents in larger nodules are almost constant or fall off only slowly with increasing radius (Table 1). The enriched elements have one to three times higher values in the size classes around 0.2 mm compared to nodules around 20 mm. The curve plotted in Fig. 2 is a theoretical graph showing the ratio nodule area to nodule volume (assuming a perfect sphere). This relationship is a 1/r function where r is the nodule radius. Data points closely cluster around a \(\frac{1}{r} + c\) function suggesting that the accumulations of Zn, Ni, Co, La, Y and Yb with decreasing nodule size are due to a surface area increase. The uplift in element contents from the zero level, C, is due to the leaching of the detrital fraction, admixed into nodules.

Element variations due to depth of burial

The composition of spherical nodules is also affected by the degree of burial in the uppermost oxidized surface sediment layer. At station 82-54 there is a trend with increasing Zn, Cu, Ni, La, Yb and Y values in the nodules approaching the sediment-water interface (Table 3). The P and Si values tend to increase downwards in the
Table 1. Size dependent element variations in spherical nodules from the Bothnian Bay.

<table>
<thead>
<tr>
<th>Station 82-43</th>
<th>Spherical nodules</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>Ca</th>
<th>P</th>
<th>Ti</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter in mm</td>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
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<tr>
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<td>26.1</td>
<td>1.11</td>
<td>1.92</td>
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<td>25.5</td>
<td>0.72</td>
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<td>1.50</td>
<td>1.27</td>
<td>0.74</td>
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<td>0.20</td>
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<td>16.8</td>
<td>0.96</td>
<td>0.90</td>
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<td>1.23</td>
<td>1.38</td>
<td>0.10</td>
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<td>15.9</td>
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<td>1.34</td>
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<tr>
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<td>1.04</td>
<td>1.27</td>
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<td>1.08</td>
<td>1.02</td>
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<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>Ca</th>
<th>P</th>
<th>Ti</th>
<th>Ba</th>
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<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
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<td>0.85</td>
<td>0.18</td>
<td>0.23</td>
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<td>1.30</td>
<td>0.99</td>
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<td>0.76</td>
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<td>8.00 - 9.50</td>
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<td>0.86</td>
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<td>1.19</td>
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<td>11.00 - 12.50</td>
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<td>0.85</td>
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<td>1.18</td>
<td>1.13</td>
<td>0.12</td>
<td>0.24</td>
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<tr>
<td>14.00 - 16.00</td>
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<td>0.68</td>
<td>1.20</td>
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</table>

All values represent normalized HCl-leachable fraction (see text). Residue values have not been recalculated with \( f_1 \) and \( f_2 \) and the original portion not leachable is shown.
<table>
<thead>
<tr>
<th>Sr ppm</th>
<th>Zr ppm</th>
<th>Sc ppm</th>
<th>Mo ppm</th>
<th>Zn ppm</th>
<th>Cu ppm</th>
<th>Ni ppm</th>
<th>Co ppm</th>
<th>Y ppm</th>
<th>La ppm</th>
<th>Yb ppm</th>
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<tbody>
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<td>11.2</td>
<td>478</td>
<td>923</td>
<td>245</td>
<td>926</td>
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<tr>
<td>377</td>
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<td>6.8</td>
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<td>885</td>
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<td>31</td>
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<td>360</td>
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<td>395</td>
<td>237</td>
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<td>426</td>
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<td>356</td>
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<td>447</td>
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<td>422</td>
<td>336</td>
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<td>353</td>
<td>214</td>
<td>23</td>
<td>39</td>
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<table>
<thead>
<tr>
<th>Cu ppm</th>
<th>Ni ppm</th>
<th>Co ppm</th>
<th>Y ppm</th>
<th>La ppm</th>
<th>Yb ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>245</td>
<td>926</td>
<td>374</td>
<td>38</td>
<td>82</td>
<td>3.8</td>
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<td>204</td>
<td>1084</td>
<td>1102</td>
<td>241</td>
<td>84</td>
<td>153</td>
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<tr>
<td>1390</td>
<td>204</td>
<td>1082</td>
<td>1043</td>
<td>50</td>
<td>101</td>
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<td>816</td>
<td>138</td>
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<td>93</td>
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<tr>
<td>438</td>
<td>73</td>
<td>444</td>
<td>73</td>
<td>29</td>
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<tr>
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<td>498</td>
<td>87</td>
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<tr>
<td>492</td>
<td>90</td>
<td>436</td>
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<td>465</td>
<td>91</td>
<td>365</td>
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<td>47</td>
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<td>241</td>
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<td>502</td>
<td>29</td>
<td>507</td>
<td>55</td>
<td>22</td>
<td>31</td>
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<td>484</td>
<td>25</td>
<td>421</td>
<td>56</td>
<td>21</td>
<td>28</td>
</tr>
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</table>
Figure 2. Compositional variation due to size of spherical nodules. Figures within circles represent number of samples at each point. The vertical rows represent nodule analysis from the size classes 0.5-2 mm, 2-4 mm, 4-5.6 mm, 5.6-8 mm, 9.5-12.5 mm, 12.5-14 mm, 14-16 mm, 16-19 mm, 19-22 mm and 22-25 mm. Vertical axis in ppm recalculated to 100% HCl leachable fraction. Theoretical graph shows relation between surface area $4\pi r^2$ to volume $4\pi r^3/3$ of a sphere. All samples from the Gulf of Bothnia. Data from Ingri 1985.
Table 2. Correlation coefficients between element content and size of spheroidal nodules in the Gulf of Bothnia.

<table>
<thead>
<tr>
<th>Elements with no significant* correlation to nodule size</th>
<th>Elements correlated to nodule size due to leaching of admixed sediment</th>
<th>Elements significantly correlated to nodule size (small nodules)</th>
<th>Elements significantly correlated to nodule size (large nodules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn ( r = -0.21 )</td>
<td>Al ( r = -0.67 )</td>
<td>Zn ( r = -0.67 )</td>
<td>Fe ( r = 0.45 )</td>
</tr>
<tr>
<td>Ca ( r = -0.15 )</td>
<td>Mg ( r = -0.43 )</td>
<td>Ni ( r = -0.63 )</td>
<td>P ( r = 0.60 )</td>
</tr>
<tr>
<td>Si ( r = -0.05 )</td>
<td>Ti ( r = -0.49 )</td>
<td>Cu ( r = -0.57 )</td>
<td>Sr ( r = 0.27 )</td>
</tr>
<tr>
<td>Na ( r = -0.10 )</td>
<td>V ( r = -0.32 )</td>
<td>La** ( r = -0.56 )</td>
<td></td>
</tr>
<tr>
<td>Ba ( r = -0.17 )</td>
<td>Sc ( r = -0.48 )</td>
<td>Y ( r = -0.53 )</td>
<td></td>
</tr>
<tr>
<td>As ( r = -0.14 )</td>
<td>Cr ( r = -0.29 )</td>
<td>Yb** ( r = -0.51 )</td>
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<tr>
<td>Mo** ( r = -0.11 )</td>
<td>(residue ( r = -0.35 ))</td>
<td>Co** ( r = -0.38 )</td>
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<tr>
<td>Zr ( r = -0.09 )</td>
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<td></td>
<td></td>
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</table>

Correlations larger than \(|±0.29|\) significant at the 0.01 level (\(|±0.23|\) at 0.05 level); number of samples 81. **\( n=52 \) and hence \(|±0.35|\) significant at the 0.01 level (\(|±0.27|\) at 0.05 level). All correlations based on unnormalized HCl-leachable fraction. Data from Ingri (1985).
Table 3. Element variations in Fe-Mn spherical nodules due to depth of burial.

| Depth of burial (mm) | Size distribution | f1 | f2 | Fe | Mn | Si | Al | Mg | Ca | Na | P | Ti | Ba |
|----------------------|-------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|
|                      | weight %          | %  | %  | %  | %  | %  | %  | %  | %  | %  | %  | %  | %  | %  |
| 0.5 - 2.0 - 5.6 - 16.0(mm) |                |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Surface - 10         |                  | 26 | 21 | 53 | 1.464 | 0.939 | 15.0 | 25.0 | 0.53 | 1.08 | 1.37 | 1.29 | 0.40 | 0.47 | 0.12 | 0.34 |
| 10 - 20              |                  | 21 | 14 | 65 | 1.530 | 0.959 | 17.4 | 22.6 | 0.58 | 0.92 | 1.28 | 1.12 | 0.41 | 0.58 | 0.09 | 0.31 |
| 20 - 30              |                  | 23 | 17 | 59 | 1.447 | 0.973 | 16.6 | 23.4 | 0.75 | 0.87 | 1.28 | 1.08 | 0.41 | 0.58 | 0.08 | 0.31 |
| 30 - 40              |                  | 29 | 15 | 55 | 1.310 | 1.084 | 17.6 | 22.4 | 0.70 | 0.92 | 1.31 | 1.17 | 0.42 | 0.65 | 0.12 | 0.31 |
| 40 - 50              |                  | 33 | 28 | 49 | 1.403 | 1.149 | 16.9 | 23.1 | 0.70 | 1.01 | 1.32 | 1.25 | 0.40 | 0.70 | 0.15 | 0.33 |
| 60 crust             |                  | 25 | 21 | 53 | 2.560 | 1.075 | 22.3 | 17.7 | 1.02 | 1.11 | 1.20 | 1.60 | 0.70 | 1.67 | 0.18 | 0.42 |

Sr ppm 435 420 425 437 421 586
Zr ppm 24 25 24 24 25 28
Sc ppm 5.6 5.6 5.4 6.0 6.9 10.2
Mo ppm 474 467 442 468 449 256
Zn ppm 1553 950 638 555 513 259
Cu ppm 168 141 123 115 131 44
Ni ppm 1277 986 839 749 648 272
Co ppm 255 234 230 219 229 247
Y ppm 50 42 38 37 37 35
La ppm 103 88 79 77 77 58
Yb ppm 6.6 5.8 5.0 5.1 5.5 4.4

All values represent normalized HCl-leachable fraction (see text).
Table 4. Element composition of concentric layers within a bulk sample of spheroidal nodules from the Bothnian Bay

<table>
<thead>
<tr>
<th>Depth in nodule (mm)</th>
<th>f₁</th>
<th>f₂</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>Ca</th>
<th>Na</th>
<th>P</th>
<th>Ti</th>
<th>Ba</th>
</tr>
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<tbody>
<tr>
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<td>0.879</td>
<td>27.3</td>
<td>12.7</td>
<td>0.93</td>
<td>0.54</td>
<td>0.83</td>
<td>1.02</td>
<td>0.43</td>
<td>1.72</td>
<td>0.07</td>
<td>0.19</td>
</tr>
<tr>
<td>4 - 8</td>
<td>1.312</td>
<td>0.879</td>
<td>24.5</td>
<td>15.5</td>
<td>0.79</td>
<td>0.58</td>
<td>0.91</td>
<td>1.00</td>
<td>0.41</td>
<td>1.67</td>
<td>0.08</td>
<td>0.22</td>
</tr>
<tr>
<td>8 - 12</td>
<td>1.340</td>
<td>0.885</td>
<td>19.8</td>
<td>20.2</td>
<td>0.79</td>
<td>0.63</td>
<td>1.07</td>
<td>0.97</td>
<td>0.42</td>
<td>1.40</td>
<td>0.08</td>
<td>0.26</td>
</tr>
<tr>
<td>12 - 16</td>
<td>1.408</td>
<td>0.885</td>
<td>16.2</td>
<td>23.8</td>
<td>0.75</td>
<td>0.80</td>
<td>1.25</td>
<td>1.03</td>
<td>0.44</td>
<td>1.04</td>
<td>0.12</td>
<td>0.29</td>
</tr>
<tr>
<td>16 - 22</td>
<td>1.395</td>
<td>0.939</td>
<td>17.1</td>
<td>22.9</td>
<td>0.86</td>
<td>0.90</td>
<td>1.28</td>
<td>1.04</td>
<td>0.47</td>
<td>1.22</td>
<td>0.12</td>
<td>0.30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sr (ppm)</th>
<th>Zr (ppm)</th>
<th>Sc (ppm)</th>
<th>Mo (ppm)</th>
<th>Zn (ppm)</th>
<th>Cu (ppm)</th>
<th>Ni (ppm)</th>
<th>Co (ppm)</th>
<th>Y (ppm)</th>
<th>La (ppm)</th>
<th>Yb (ppm)</th>
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<td>250</td>
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</tr>
<tr>
<td>548</td>
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<td>2.4</td>
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<td>127</td>
<td>218</td>
<td>26</td>
<td>40</td>
<td>3.8</td>
</tr>
</tbody>
</table>

All values represent normalized HCl-leachable fraction (see text). Figures represent bulk samples of 25 spheroidal nodules.
profile, and P, Si, Na, Ca, Ba and Sr are clearly enriched in the Fe-rich crust found at the interface between the oxidized surface sediment and the reduced grey sediment.

Nodules of similar size were analyzed from each horizon, and hence the relations seen in the profile may explain the large variation in element content for nodules of similar size in Fig. 2. The "vertical scatter" in each nodule size-class is readily explained if nodules with low contents of Ni, Cu, Zn, Y, Yb and La represent samples taken close to the reduced-oxidized interface whereas high contents represent samples formed at a strongly oxidized site.

Enrichment of elements in nodule surface layers

A surface enrichment of some trace elements is also seen for individual nodules (Table 4). The outermost 4 mm thick layer of nodules from station 82-44 is enriched in Ni, Zn, Co and possibly also Y, La and Yb whereas the trace elements Cu, Sr, Sc, Zr and Mo do not show any surface preference. Nickel, Zn and Co all being Mn related elements are enriched in spite of an Fe-rich surface layer.

The increase of trace elements in the surface layers of the nodules presented could be interpreted as a pollution effect. However, we find such an interpretation unsatisfactory. Antrophogenic input of Zn, Cu and Ni at the sampling sites should mostly be affected by the smelter at Rönnskär (Fig. 1). The proportions between
Zn/Ni and Cu/Ni introduced directly into the water column from the smelter are approximately 40 to 1 and 50 to 1 respectively (Lithner 1974). In the nodules on the other hand, the enrichment of Ni is equal to Zn and higher than Cu, in spite of a supposed similar speciation of the ions Ni\(^{2+}\) and Zn\(^{2+}\) in eustarine waters (Dyrssen and Wedborg 1980). No enrichment of Cu is seen at the nodule surface at station 82-44, whereas a pronounced accumulation of Ni and Zn can be seen. Additionally Y, Yb and La, with no documented significant anthropogenic input show similar enrichment patterns to those seen for Ni, Cu and Zn. These data suggest that nodules are poor indicators of pollution effects in the Bothnian Bay because of the probable existence of natural enrichment processes. We believe that local redox changes and surface area changes may explain the accumulation patterns observed (see below). Any pollution effect, however, most certainly reinforces the enrichment process but it appears to us rather difficult to distinguish between natural and man made contributions of Zn, Ni and Cu in concretions from the Baltic Sea.

Data in Table 1 suggest a pronounced surface area dependence for the enrichment of Zn and Ni, whereas trace elements like Mo, and Ba show no accumulation with decreasing nodule size. Any increase in surface exchange sites should mostly affect small or highly charged ions. Larger ions like Ba\(^{2+}\), or elements present as anions (e.g. Mo) should be less affected. The patterns of enrichment in Table 1 could therefore be explained simply by a surface area change. However, several trace elements show increased accumulation
tendencies going upwards in the profile seen in Table 3; and this is in spite of a normalized constant sum of Fe and Mn and a constant nodule size distribution in each layer. A change in nodule surface area only does not explain the total surface enrichment mechanism.

Measured pH values in porewaters from a sediment profile similar to the analysed showed nearly a constant pH in the oxidized sediment layer. Only a small increase from 7.0 close to the sediment-water interface up to 7.5 in the uppermost part of the grey sediment was registrated. Redox measurements in the same profile showed a change in Δ Eh of 400 m V from the surface layer, down to the uppermost reduced grey layer (Ingri and Pontér 1985); i.e. the redox potential shows a significant change in the profile (Table 3). At low redox values Mn-Fe-rich oxy-hydroxides start to dissolve, and in the grey sediment layer no oxidized Mn-Fe species are thermodynamically stable; this results in high concentrations of dissolved Mn and Fe. It is likely then that nodule surfaces in each of the analysed layers have formed at different concentrations of Mn$^{2+}$. The high activity of Mn$^{2+}$ in the more reduced levels outranges all other trace elements in the porewaters, and Mn$^{2+}$ probably occupies most of the available surface sites. Besides, the sorption capacity of the hydrous MnO$_2$ for the Mn$^{2+}$ ion is considerably greater on a mole-ratio basis than for any other divalent ion (Posselt et al. 1968). It is only when Mn$^{2+}$ activity is lowered due to oxidization that other trace elements can successfully compete for the possible sites. We therefore believe that the smooth accumulation of especially Zn, Ni, Cu, Yb, Y and La
towards the sediment-water interface partly reflects the less competitive activity of Mn\textsuperscript{2+} for the available surface sites.

Together with this effect we believe that oxic diagenesis (Dymond et al 1984) also may contribute to the observed pattern in Table 3. The surface dependency of Ni, Cu, Zn, Y, Yb and La observed in Fig. 2 imply that much of these elements are loosely held at the Mn-oxy-hydroxide surface. When such a Mn-particle descends from the water column into the oxidized surface sediment much of the surface attached contents of Ni, Cu, Zn, Y, Yb and La could be desorbed due to the slightly lowered redox level and pH in the surface zone. Ba and Mo on the other hand are closely associated to Mn and are probably significantly released from the Mn-phase only during suboxic diagenesis (Ingri 1985). Suboxic diagenesis refers to the process where Mn-oxy-hydroxides are totally reduced and dissolve (Dymond et al 1984).

Additionally, a change in Mn-mineralogy could also affect the adsorptive capacity. The crystallinity of the major Mn-phases increases in the order, vernadite (also called 5-MnO\textsubscript{2}) - 7 Å phases (referred to as birnessite) - 10 Å phases (usually called todorokite), with a decrease of surface area in the same order (Glover 1977). Buser and Grütter (1956) reported higher surface areas for 7 Å manganese samples compared to 10 Å Mn-bearing nodules in the Pacific Ocean, and similar values were obtained by Weisz (1968), Johnson and Glasby (1968) and Brooke and Prosser (1969). Rapid precipitation of Mn, during high oxygen tension, tends to form amorphous or poorly
crystalline phases (high surface area). Usually the oxidization of $\text{Mn}^{2+}$ is a slow process but it may be catalysed by old Mn-Fe surfaces (Stumm and Morgan 1970), disproportionation reactions (Hem 1978) and by bacteria (Chukhrov et al. 1978). With increasing oxygen tension and lowered interstitial $\text{Mn}^{2+}$, going upwards in the analysed profile (Table 3), it seems likely that vernadite or the "amorphous" phase (very small crystallites, not seen by conventional x-ray technique) increases in the nodules. This would promote a higher surface area and an increased accumulation of, e.g., Zn, Cu, Ni, Y, Yb and La.

The crystallites of the Fe-rich phase may change their surface area in Fe-Mn nodules with time. Mössbauer spectra of Pacific nodules showed higher quadropole splittings for outer portions than for inner portions of nodules and this was related to differences in average size of particles (Hryniewicz et al. 1972). These results suggest either that older (central) parts were formed during conditions different from those of outer parts or that recrystallization to coarser grained crystallites occurs inside the nodules in the course of time. Van der Giessen (1966) measured surface areas of 265-270 m$^2$/g for young Fe (III) oxide hydrated gel whereas one year old specimens already yielded coarser grained crystallites with surface areas of 215-220 m$^2$/g. Chukhrov et al. have revealed the presence of $\delta'$-FeOOH or feroxhyte coexisting with goethite in Fe-Mn nodules from the Baltic. Feroxhyte is a poorly ordered (large surface area) Fe-phase formed in oxidized environments with comparably high supply of $\text{Fe}^{2+}$, and it is assumed that the more ordered geothit is a product
of feroxyte (Chukhrov et al. 1980). Freshly precipitated Fe-Mn phases might be one explanation of the enrichment of trace metals in the outermost layers of individual nodules (Table 2).

Conclusions

It seems as if the precipitation mechanism, set by the redox conditions and catalysing effects, and time govern the scavenging surface. At highly oxidized nodule surfaces forming in the Baltic Sea freshly precipitated Fe and Mn probably form poorly crystalline phases, which have very large surface, areas, and hence the possibility arises for small or highly charged ions like Zn, Cu, Ni, Co, Yb, La and Y to adsorb. The aging of Mn-Fe oxy-hydroxides and the possibility of higher activity of Mn$^{2+}$ at a reduced redox level favours, therefore, the enrichment of especially uncomplexed and highly charged cations in surface layers; so that a continuously high surface concentration of Zn, Cu, Ni, Co, Yb, La and Y forms. Larger ions like Sr$^{2+}$ and Ba$^{2+}$ and elements forming anions (Mo, P, V and As) are less affected by surface area changes and do not show any significant surface dependence in the analysed nodules (Tables 2-3).

Natural enrichment processes, largely governed by the redox level, might explain high concentrations of Zn, Cu and Ni at Fe-Mn nodule surfaces. This makes ferromanganese concretions a poor sampling object in pollution investigations. Furthermore, the presence
of Fe-Mn micronodules in surface sediments obscures the interpretation of heavy metal pollution. Usually a linear relation between Fe-Mn-normalized ratios in surface sediments are used as pollution indicators. However, the drastic increase of heavy metals (e.g. Cu, Ni, Zn) in hardly visible micronodules (less than ~2 mm) must be taken into account in pollution studies in the Baltic Sea. Interpretations are more seriously hampered by the "depth of burial" effect presented. This effect makes comparison between two oxidized surface sediments very difficult. Even if they are sampled at the same depth in the core, and the size distribution of Fe-Mn micronodules is known, there is still no measure telling you at what in situ redox level the sample was taken. Possibly, non anthropogenic elements like La, Y and Yb might be used as normalization elements as they appear to show enrichment patterns similar to Zn, Ni and Cu.

Acknowledgements

We wish to thank Professor K. Boström for valuable comments on the text. We also thank the crew onboard R/V Strombus for assistance at sea and P. McMillen for his improvements of the English text. This study was financed by grants from NFR and STU given to K. Boström, a support gratefully acknowledged.
References


Abstract

Fe-Mn concretions from the Svalbard shelf in the Barents Sea show a convex shale-normalized REE pattern and concretions from the Gulf of Bothnia exhibit a LREE enrichment. This difference is explained by a different supply of the REE to the sediment. It is suggested that dissolving biogenic debris contribute to the convex pattern obtained in the Barents Sea whereas weathering of till via river input explains the LREE in the Gulf of Bothnia.

An exponential increase of the REE content with decreasing nodule size is observed, suggesting an adsorptive enrichment mechanism. Furthermore, the accumulation of the REE increase with increasing redox level. Small nodules are 3 to 5 times enriched in REE compared to "average shale", whereas Mn-poor Fe crusts are low in REE. One Fe-Ca-P-rich concretion from the upwelling area in the south western Barents Sea exceeds most deep-sea nodules in REE content with a maximum for Eu, 30 times the "average shale" value.

The strong Ce anomaly observed in deep-sea nodules is only weakly developed in the analysed concretions but a redox level dependence is clearly seen.
Introduction

Several papers have been published concerning the geochemistry of the Rare Earth Elements (REE) in deep-sea ferromanganese nodules and crusts (Goldberg et al 1963, Ehrlich 1968, Piper 1974a, Glasby 1973, Addy 1979, Elderfield et al 1981a,b,c). The most striking feature of the enrichment pattern is the strong positive Ce anomaly (although negative Ce anomalies have also been reported, Elderfield et al 1981c) and the overall accumulation of REE compared to average shale (Piper 1974b). Goldberg (1961) suggested that the different behaviour of Ce from that of the other REE in Fe-Mn nodules is attributed to the oxidation of Ce\(^{3+}\) to Ce\(^{4+}\). This enrichment of Ce in nodules with the complementary depletion found in seawater (Högdahl et al 1968) has been considered as a positive evidence in support of the precipitative behaviour of Ce and probably the incorporation of all REE directly from seawater (Glasby 1973, Piper 1974). Elderfield et al 1981a,b concluded that for the trivalent REE (Ce not included), diagenetic remobilization reactions also influence the REE patterns found in Pacific nodules.

From the shallow-marine, continental margin and epicontinental seas there are few data concerning REE distribution in Fe-Mn concentrations (Fomina et al 1969, Ehrlich 1968, Glasby 1973). Typically, these deposits show much lower absolute concentrations of REE compared to the deep-sea nodules and the Ce anomaly generally seems to be much weaker or absent. The very low total REE sum obtained
by Fomina et al (1969) in the Black Sea and by Glasby (1973) in Loch Fyne precludes any preferential uptake of any REE by the Fe-Mn-rich authigenic fraction and occluded detrital debris appear to be the only REE carrier. However, data by Boström et al 1982, Ingri 1985a and this study definitely indicate that the Fe-Mn-rich authigenic fraction scavenges REE both in the Gulf of Bothnia and in the Barents Sea.

Together with the REE, contents of Zn, Cu, Ni and Co are also displayed. This points out their similar patterns of accumulation in nodules from the Gulf of Bothnia. The mechanism causing this similarity will be discussed in this paper.

Analytical methods

Grinded and dried samples were dissolved using HF-HClO₄ and filtered; residual fraction was fused with LiBO₂. The dissolved residue was added to the HF-HClO₄ solution and REE together with Y and Sc were separated from the matrix using an ion exchange procedure described by Walsh et al 1981. The REE solution was analysed using ICP spectrometry with a modified sequential reading unit, ARL 35 000 (Burman 1981). Major and trace element composition of the sediments and the nodules were also determined with ICP-OES; the sediments were brought into solution by a procedure described in Burman et al 1978 and the nodules were HCl-leached according to Boström et al 1982.
To check the procedure for the REE determinations four samples of a certified granite were analysed at different occasions. The precision of the determinations are better than 10% for all elements except for Ce (20%) and absolute values are close to results obtained by instrumental neutron activation analyses (Kramar et al 1982) (Table 1). Two standard nodules P-1 and A-1 (Flanagan et al 1980) were analysed to detect any matrix effects due to large amounts of Mn and Fe in the ion exchange procedure. No certified values are available for the nodules but obtained REE figures are in agreement with the single analyses available, although Ce deviates from the rest, being 20% higher than "suggested" (Table 1).

Treatment of data

To circumvent the confusing zig-zag pattern exhibited by the REE (Oddo-Harkin's rule) normalization to a standard is usually performed (Coryell et al 1963). In studies of ferromanganese nodules, average shale has been used as the standard (Piper 1974b); thereby allowing small differences in the fractionation of one REE from another to be identified graphically. The scatter in the average shale values reported is small (Haskin et al 1979) and does not affect normalized patterns for deep-sea nodules. In the shallow-marine environment, however, the enrichment of the REE in Fe-Mn concretions is much lower compared to the deep-sea and the choice of average shale becomes more critical.
Table 1
REE determinations obtained with ion-exchange ICP-OES compared to instrumental neutron activation analysis (INAA).

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Ce</th>
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<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Yb</th>
<th>Lu</th>
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<tbody>
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<td>granite GA&lt;sup&gt;1)&lt;/sup&gt;</td>
<td>38.5</td>
<td>92.5</td>
<td>29.9</td>
<td>5.10</td>
<td>1.10</td>
<td>3.95</td>
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<td>1.95</td>
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<td>7.5</td>
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<td>5.7</td>
<td>7.4</td>
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<td>4.7</td>
<td>8.9</td>
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<td>10</td>
<td>7.6</td>
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<td>41.7</td>
<td>72.0</td>
<td>26.0</td>
<td>5.0</td>
<td>1.0</td>
<td>2.7</td>
<td>3.9</td>
<td>0.7</td>
<td>-</td>
<td>2.0</td>
<td>0.35</td>
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<td>nodule standard</td>
<td></td>
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<td>P1&lt;sup&gt;3)&lt;/sup&gt;</td>
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<td>370</td>
<td>143</td>
<td>35.3</td>
<td>9.04</td>
<td>32.5</td>
<td>27.0</td>
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<td>85.3</td>
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<td>26.5</td>
<td>-</td>
<td>-</td>
<td>16.3</td>
<td>1.92</td>
<td></td>
</tr>
</tbody>
</table>

1) Four aliquots of the standard were analysed at four different occasions.
2) Data from Kramar et al. 1982.
3) Data from Flanagan et al. 1986, value from one laboratory. All figures in ppm.
It has been suggested that grey reduced sediment found below the oxidized surface layer in the Gulf of Bothnia represents "permanently depositing" sediment, with a major and trace-element composition similar to average shale in many locations (Boström et al 1978). REE analysis of such a grey sediment shows values that are very similar to average shale (Table 2) confirming the results by Boström et al 1978. In this paper REE content in grey sediment from the Gulf of Bothnia is used for normalization instead of the average shale values found in Piper 1974.

Sc and Y values shown in Table 3, 5 and 6 have been analysed using the ion exchange procedure and are displayed together with the REE.

Sample description

Sediments in the Gulf of Bothnia are highly altered by diagenetic recycling of Fe and Mn. The oxidized surface zone is well stratified, showing five distinct layers in well developed profiles (Ingri et al 1985a). Such a laminated sediment with a 2 cm water-rich brown surface layer subsequently followed by a 2 mm black Mn-rich layer, a 4 mm orange-brown coloured Fe-rich zone, a yellow-grey transition zone and grey reduced sediment were sampled and analysed for their REE distribution (Table 3). The boxcore with the profile was taken from 88 m depth in the Bothnian Bay at N64°10, E21°32.
Table 2

Comparison between REE content in "average shale" and grey reduced sediment from the Bothnian Bay.

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Ce</th>
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<th>Sm</th>
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<th>Ho</th>
<th>Er</th>
<th>Yb</th>
<th>Lu</th>
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<tr>
<td>Composite of North American shales (Haskin 1968)</td>
<td>32</td>
<td>73</td>
<td>33</td>
<td>5.7</td>
<td>1.24</td>
<td>5.2</td>
<td>5.8</td>
<td>1.04</td>
<td>3.4</td>
<td>3.1</td>
<td>0.48</td>
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<tr>
<td>Average shale (Piper 1974)</td>
<td>41</td>
<td>83</td>
<td>38</td>
<td>7.5</td>
<td>1.61</td>
<td>6.35</td>
<td>5.5</td>
<td>1.34</td>
<td>3.75</td>
<td>3.53</td>
<td>0.61</td>
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<tr>
<td>Grey sediment Bothnian Bay (this study)</td>
<td>41.0</td>
<td>109</td>
<td>41.2</td>
<td>7.48</td>
<td>1.45</td>
<td>6.46</td>
<td>5.95</td>
<td>1.21</td>
<td>3.43</td>
<td>3.07</td>
<td>0.49</td>
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Grey sediment values from Table 3. All figures in ppm.
Table 3 Composition of a diagenetic altered sediment from the Bothnian Bay.

<table>
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<tr>
<th>depth in sediment (mm)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>P₂O₅</th>
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<tr>
<td>0-20</td>
<td>56.9(1.0)</td>
<td>10.9(-)</td>
<td>0.55(1.0)</td>
<td>6.0(1.5)</td>
<td>0.35(64)</td>
<td>1.27(1.0)</td>
<td>1.96(1.0)</td>
<td>2.63(1.0)</td>
<td>0.25(1.0)</td>
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<tr>
<td>20-22</td>
<td>49.9(0.9)</td>
<td>10.0(-)</td>
<td>0.52(1.0)</td>
<td>5.7(1.5)</td>
<td>5.45(99)</td>
<td>1.45(1.2)</td>
<td>1.90(1.1)</td>
<td>2.38(1.0)</td>
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<tr>
<td>22-26</td>
<td>44.2(0.9)</td>
<td>8.7(-)</td>
<td>0.45(1.0)</td>
<td>20.8(6.4)</td>
<td>0.48(10)</td>
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<td>26-32</td>
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<td>10.7(-)</td>
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<td>7.4(1.8)</td>
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<td>1.00(4.1)</td>
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<tr>
<td>32-</td>
<td>59.4(1.0)</td>
<td>10.9(-)</td>
<td>0.56(1.0)</td>
<td>4.1(1.0)</td>
<td>0.06(1.0)</td>
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<table>
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<tr>
<td>537(0.9)</td>
<td>45(1.6)</td>
<td>28(1.1)</td>
<td>47(1.0)</td>
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<td>183(1.0)</td>
<td>87(1.0)</td>
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<td>75(3.3)</td>
<td>83(1.9)</td>
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<td>94(1.1)</td>
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<td>531(1.1)</td>
<td>24(1.0)</td>
<td>20(1.0)</td>
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<td>28(1.1)</td>
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<td>29(1.0)</td>
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<td>91(1.0)</td>
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<tr>
<td>42.8(1.1)</td>
<td>132(1.2)</td>
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<td>1.56(1.1)</td>
<td>6.99(1.1)</td>
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<td>3.78(1.1)</td>
<td>3.14(1.0)</td>
<td>0.51(1.0)</td>
</tr>
<tr>
<td>38.1(1.0)</td>
<td>127(1.3)</td>
<td>37.7(1.0)</td>
<td>7.05(1.0)</td>
<td>1.39(1.1)</td>
<td>6.50(1.1)</td>
<td>5.75(1.1)</td>
<td>0.94(0.9)</td>
<td>3.11(1.0)</td>
<td>2.72(1.0)</td>
<td>0.41(0.9)</td>
</tr>
<tr>
<td>34.2(1.1)</td>
<td>102(1.2)</td>
<td>33.9(1.0)</td>
<td>6.10(1.0)</td>
<td>1.18(1.0)</td>
<td>5.43(1.1)</td>
<td>4.43(0.9)</td>
<td>0.82(0.9)</td>
<td>2.66(1.0)</td>
<td>2.37(1.0)</td>
<td>0.39(1.0)</td>
</tr>
<tr>
<td>39.7(1.0)</td>
<td>109(1.0)</td>
<td>39.7(1.0)</td>
<td>6.90(0.9)</td>
<td>1.38(1.0)</td>
<td>6.57(1.0)</td>
<td>5.47(0.9)</td>
<td>1.11(0.9)</td>
<td>3.16(0.9)</td>
<td>2.86(1.0)</td>
<td>0.46(1.0)</td>
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<tr>
<td>41.0(1.0)</td>
<td>109(1.0)</td>
<td>41.2(1.0)</td>
<td>7.48(1.0)</td>
<td>1.45(1.0)</td>
<td>6.46(1.0)</td>
<td>5.95(1.0)</td>
<td>1.21(1.0)</td>
<td>3.43(1.0)</td>
<td>3.07(1.0)</td>
<td>0.49(1.0)</td>
</tr>
</tbody>
</table>

Description of boxcore sample in the text. Values represent total analyses with major elements in % others in ppm. Figures within brackets are Al-normalized enrichment values compared to grey reduced sediment. For example, Mn enrichment in layer 20-22 mm 5.45/10.0/0.06/10.9 = 99.
Fe-rich flat crusts are frequently found below the Mn-rich sediment layer within the oxidized zone in the Bothnian Bay, whereas in the Bothnian Sea iron crusts are usually formed at the sediment-seawater interface; probably due to a lowered redox level in this basin (Ingri et al 1985a). Some of these flat concretions have been determined for their REE content, (Table 5, sample 9, 10, 11 and 12).

In many locations in the Gulf of Bothnia the water-rich brown top sediment is studded with spherical nodules (Winterhalter 1966, Boström et al 1982, Ingri 1985a). To investigate REE fractionation in this most oxidized surface zone a 6 cm thick brown water-rich layer with nodules was sampled. The core was sliced in centimeter thick layers and nodules from each horizon were separated and analysed. At the interface between reduced-grey-sediment and the oxidized surface-layer a 3 mm thick Mn-Fe crust was recovered. Major and trace element geochemistry of this profile has been discussed by Ingri et al (1985b) (Table 4). Three of these layers have been REE determined in this study (Table 5, sample 2, 3 and 9).

In the Gulf of Bothnia discoidal concretions, in the form of a developed rim or girdle on a pebble or other fragments, have been shown to be enriched in Mn, Cu, Ni, Zn, Ba and Mo on the upper seawater-facing side whereas the sediment side is enriched in Fe and P (Ingri 1985a). REE enrichment in such a concretion is shown in Table 5 (sample 7, 8).
Table 4

Accumulation of trace elements in equal sized Fe-Mn nodules in an oxidized surface sediment from the Bothnian Bay.

<table>
<thead>
<tr>
<th>Sample depth (mm)</th>
<th>Fe</th>
<th>Mn</th>
<th>P</th>
<th>Zn</th>
<th>Ni</th>
<th>Cu</th>
<th>Co</th>
<th>La</th>
<th>Y</th>
<th>Yb</th>
<th>Sc</th>
<th>residue</th>
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<tbody>
<tr>
<td>0-10</td>
<td>16.0</td>
<td>26.6</td>
<td>0.50</td>
<td>1654</td>
<td>1360</td>
<td>179</td>
<td>272</td>
<td>110</td>
<td>53</td>
<td>7.0</td>
<td>6.0</td>
<td>31.7</td>
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<tr>
<td>10-20</td>
<td>18.1</td>
<td>23.6</td>
<td>0.61</td>
<td>990</td>
<td>1028</td>
<td>147</td>
<td>244</td>
<td>92</td>
<td>44</td>
<td>6.0</td>
<td>5.8</td>
<td>34.6</td>
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<tr>
<td>20-30</td>
<td>17.1</td>
<td>24.0</td>
<td>0.59</td>
<td>656</td>
<td>862</td>
<td>126</td>
<td>236</td>
<td>81</td>
<td>39</td>
<td>5.1</td>
<td>5.5</td>
<td>30.9</td>
</tr>
<tr>
<td>30-40</td>
<td>16.2</td>
<td>20.7</td>
<td>0.60</td>
<td>512</td>
<td>689</td>
<td>106</td>
<td>202</td>
<td>71</td>
<td>34</td>
<td>4.7</td>
<td>5.5</td>
<td>23.6</td>
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<tr>
<td>40-50</td>
<td>14.7</td>
<td>20.1</td>
<td>0.61</td>
<td>446</td>
<td>595</td>
<td>114</td>
<td>199</td>
<td>67</td>
<td>32</td>
<td>4.8</td>
<td>6.0</td>
<td>28.7</td>
</tr>
<tr>
<td>crust</td>
<td>20.7</td>
<td>16.5</td>
<td>1.55</td>
<td>241</td>
<td>253</td>
<td>41</td>
<td>230</td>
<td>54</td>
<td>33</td>
<td>4.1</td>
<td>9.5</td>
<td>60.9</td>
</tr>
</tbody>
</table>

Values represent 100% HCl-leachable fraction. Figures based on dried sample can be obtained using the residual values. Fe, Mn, P and residue in % others in ppm. Data from Ingri and Pontén (1985 b).
The concretions from the Barents Sea were collected from R.V. Norvarg during the Ymer expedition 1980. The morphology and geochemistry of these Svalbard shelf-related deposits have been discussed by Ingri (1985b). Two cobbles with a developed rim or girdle at the sediment-water interface (sample 13 and 14), a flat Fe-rich concretion (sample 15), a thin continuous Fe crust formed at the sediment-water interface (sample 16), together with a thick Fe-rich crust (sample 17), were analysed for their REE content, (Table 6). Samples 13 and 15 were recovered from the same station together with underlying grey reduced sediment (sample 18).

Results

The REE content in concretions seen in this study is similar to a composite sample analysis obtained from the Baltic proper (Ehrlich 1968) but 3 to 10 times higher compared to the absolute REE values reported from the Black Sea (Fomina et al 1969) and Loch Fyne (Glasby 1973). Five measurements of Pr in concretions in this study (Table 5) do not show the peak in Pr observed in the Black Sea and Loch Fyne.

Analysed concretions contain HCl-insoluble residues between 7.8 and 52.8 % (Table 5) but all samples do show a "grey sediment-normalized" ratio above 0.5 (Figs. 1 and 2). Hence, Fe-rich crusts from both the Gulf of Bothnia and the Barents Sea with absolute REE values similar to or below average shale (Table 5 and 6) also
Table 5  REE contents in Fe-Mn concretions from the Gulf of Bothnia.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Dy</th>
<th>Ho</th>
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<tbody>
<tr>
<td>Spherical nodules</td>
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<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>1. 1-2 mm diam.</td>
<td>125</td>
<td>600</td>
<td>n.a.</td>
<td>116</td>
<td>23.2</td>
<td>3.53</td>
<td>14.9</td>
<td>15.3</td>
<td>2.75</td>
</tr>
<tr>
<td>N61° 28, E 17° 53, 64 m</td>
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</tr>
<tr>
<td>2. 0.5-16 mm diam.</td>
<td>75.3</td>
<td>260</td>
<td>19.2</td>
<td>60.8</td>
<td>11.3</td>
<td>1.55</td>
<td>9.09</td>
<td>8.65</td>
<td>1.49</td>
</tr>
<tr>
<td>0-1 cm depth in sediment</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N64° 56, E 21° 34, 48 m</td>
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</tr>
<tr>
<td>3. 0.5-16 mm diam.</td>
<td>62.8</td>
<td>215</td>
<td>n.a.</td>
<td>49.0</td>
<td>8.68</td>
<td>1.44</td>
<td>6.40</td>
<td>5.88</td>
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<td>2-3 cm depth in sediment</td>
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<td>N64° 56, E 21° 34, 48 m</td>
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<td></td>
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</tr>
<tr>
<td>4. 5.6-8.0 mm diam.</td>
<td>39.6</td>
<td>102</td>
<td>n.a.</td>
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<td>7.02</td>
<td>1.07</td>
<td>5.33</td>
<td>5.64</td>
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<td>Discoidal concretions</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>5. Bulk rim</td>
<td>40.7</td>
<td>67.9</td>
<td>9.16</td>
<td>32.9</td>
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<td>0.93</td>
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<td>5.16</td>
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<td>6. Bulk rim</td>
<td>41.7</td>
<td>81.6</td>
<td>10.9</td>
<td>31.8</td>
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<td>4.98</td>
<td>0.86</td>
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<tr>
<td>N65° 11, E 23° 17, 70 m</td>
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<tr>
<td>7. Upper surface, rim</td>
<td>65.3</td>
<td>100</td>
<td>n.a.</td>
<td>51.5</td>
<td>9.53</td>
<td>1.60</td>
<td>7.42</td>
<td>7.40</td>
<td>1.33</td>
</tr>
<tr>
<td>N64° 56, E 23° 07, 104 m</td>
<td></td>
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</tr>
<tr>
<td>8. Lower surface, rim</td>
<td>33.3</td>
<td>55.0</td>
<td>n.a.</td>
<td>27.5</td>
<td>4.23</td>
<td>0.79</td>
<td>4.03</td>
<td>3.43</td>
<td>0.63</td>
</tr>
<tr>
<td>N64° 56, E 23° 07, 104 m</td>
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<td>Flat concretions</td>
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<tr>
<td>9. Thin crust (see 2, 3 and text)</td>
<td>29.5</td>
<td>83.0</td>
<td>7.23</td>
<td>25.7</td>
<td>4.79</td>
<td>0.83</td>
<td>4.77</td>
<td>3.83</td>
<td>0.82</td>
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<tr>
<td>10. Thin crust, below a 23 mm thick oxidized surface zone</td>
<td>27.5</td>
<td>54.7</td>
<td>n.a.</td>
<td>22.7</td>
<td>4.04</td>
<td>0.77</td>
<td>4.08</td>
<td>2.69</td>
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<tr>
<td>11. Thin crust at sediment-water interface</td>
<td>47.2</td>
<td>102</td>
<td>11.0</td>
<td>42.1</td>
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<td>5.16</td>
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<tr>
<td>12. Thin crust fragments from a sandy sediment</td>
<td>48.2</td>
<td>97.7</td>
<td>n.a.</td>
<td>40.2</td>
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</tbody>
</table>

REE values including Sc and Y are based on total analysis. *Values represent 100% HCl-leachable fraction. **Figures represent total analysis. Fe, Mn, P and residue in % others in ppm. n.a. = not analysed.
Table 5 cont.

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<thead>
<tr>
<th>Er</th>
<th>Yb</th>
<th>Lu</th>
<th>Y</th>
<th>Sc</th>
<th>Fe*</th>
<th>Mn*</th>
<th>P*</th>
<th>Co*</th>
<th>Ni*</th>
<th>Cu*</th>
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<td>3.75</td>
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<td>184</td>
<td>79</td>
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<tr>
<td>2.32</td>
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<td>0.22</td>
<td>16.3</td>
<td>5.85</td>
<td>25.7**</td>
<td>0.4**</td>
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<td>n.a.</td>
<td>40**</td>
<td>20**</td>
<td>110**</td>
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<td>46</td>
<td>90</td>
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Table 6  REE contents in Fe-Mn concretions from the Barents Sea.

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<th>Ce</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Dy</th>
<th>Ho</th>
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<tbody>
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<td>Discoidal concretions</td>
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</tr>
<tr>
<td>13. N79°58.5, E30°15.9 depth 187 m</td>
<td>25.4</td>
<td>61.0</td>
<td>25.9</td>
<td>5.90</td>
<td>1.27</td>
<td>5.13</td>
<td>4.73</td>
<td>0.84</td>
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</tr>
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REE values including Sc and Y are based on total analysis. *Values represent 100% HCl-leachable fraction. Fe, Mn, P, Ca and residue in % others in ppm. b.d. = below detection limit.
Table 6 cont.

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Figure 1. Normalized REE patterns in Fe-Mn concretions from the Gulf of Bothnia, values from Table 5. *grey sediment identical to "average shale", see Table 2.
Figure 2. Normalized REE patterns in Fe-Mn concretions from the Barents Sea, values from Table 6. *grey sediment identical to "average shale", see Table 2.
Figure 3. Compositional variation due to size of spherical nodules. Figures within circles represent number of samples at each point. The vertical rows represent nodule analyses from the size classes 0.5-2, 2-4, 4-5.6, 5.6-8, 9.5-12.5, 12.5-14, 14-16, 16-19, 19-22 and 22-25 mm. Vertical axis in ppm recalculated to 100% HCl-leachable fraction. Theoretical graph shows the relation between surface area to volume of a sphere. All samples from the Gulf of Bothnia. Data from Ingri (1985 a).
exhibit a small REE enrichment and observed values can not be explained simply by an occluded REE bearing detrital fraction. A pronounced accumulation is seen in Mn-rich spheriodal nodules from the Gulf of Bothnia. Small nodules show the highest figures with La mostly enriched, two to three times the average shale value.

The elevated REE values seen in micronodules (sample 1) are in agreement with the results obtained by Ingri 1985a. In a study of spherical nodules from the Gulf of Bothnia a strong correlation between size of nodules and the accumulation of some trace elements is seen. Together with Cu, Ni, Zn and Co, La, Y and Yb are also shown to increase exponentially in micronodules having a diameter less than approximately 2 mm (Fig. 3).

The strong Ce anomaly typical of deep-sea nodules is only weakly developed in Mn-rich spherical nodules from the Gulf of Bothnia, except for the micronodule sample, whereas iron-rich crusts and discoidal concretions are depleted in Ce from both sampling areas (Figs. 1 and 2). In the analysed rim-developed concretion (samples 7 and 8), the upper, more oxidized and Mn-rich side is enriched in REE whereas the sediment-facing Fe-rich lower part has a smaller accumulation. The Ce anomaly, on the other hand, is negative on both sides of the rim.

Depth of burial has a pronounced effect on nodule geochemistry in the Gulf of Bothnia and the Zn, Ni and Cu content especially
have been shown to increase towards the sediment-water interface (Ingri et al. 1985b). Also La, Yb and Y increase their content in equally sized spherical nodules going upwards in an oxidized surface layer (Table 4). Data in Table 5 (samples 2, 3 and 9) confirm the similar behaviour for all of the REE. Additionally, the Ce anomaly (Ce norm $\frac{2}{3}$ La norm $+\frac{1}{3}$ Nd norm) decreases from 1.72 in the surface layer, 1.39 at 2 to 3 cm depth down to 1.11 in the Fe-Mn crust developed at the oxidized-reduced interface. However, in the diagenetically altered sediment profile, without larger nodules present in the uppermost surface layer, no pronounced enrichment of the REE can be noted (Table 3). Ce, though, appears to accumulate in the Mn-rich sediment layer.

Concretions from the Gulf of Bothnia exhibit a LREE enrichment compared to HREE, although not as pronounced in flat Fe-rich samples (Figs. 1 and 2). Concretions from the Barents Sea all show a positive Eu anomaly in contrast to the Gulf of Bothnia where most concretions have a negative Eu peak (Figs. 1 and 2). The shale-normalized patterns in the Barents Sea area are clearly convex compared to the LREE enrichment in the Gulf of Bothnia. The Ca-P-rich Fe crust sampled from 155 m depth at the Svalbard shelf exhibits a convex shale-normalized curve similar to the REE pattern observed for deep water (> 3500 m) nodules (Piper 1974a). This crust, 30 times higher in Eu than average shale, has a total REE sum of 1749 (Ce and Y excluded); a tremendous accumulation far above reported values in Fe-Mn nodules from the deep sea (Piper 1974a, Addy 1979, Elderfield 1982a,b,c).
Sc does not behave like a lanthanide in the concretions; clearly dissimilar to the behaviour of Y. A close relation between the detrital fraction and Sc is obvious and a strong correlation to Al has been shown both in the Gulf of Bothnia and the Barents Sea (Boström et al 1982, Ingri 1985a). However, Sc is markedly enriched in the Ca-P-rich Fe crust from the Barents Sea (Table 6), once more stressing the anomalous behaviour of this sample.

Discussion

Accumulation of REE in spherical nodules from the Gulf of Bothnia shows a pronounced surface dependency. The observed enrichment of La, Yb and Y with decreasing nodule radius displayed in Fig. 3 exhibits a curve similar to a $1/r$ function ($r = $ nodule radius). Specific surface area of a sphere (surface area to volume) increases with decreasing radius according to this function and it is plausible to interpret the accumulation of REE in small nodules as simply due to a surface area change. Additionally, the redox status of the surface appears to have a major impact on the enrichment of both REE and trace elements like Zn, Ni, Cu and Co. The smooth accumulation of REE in equally sized nodules towards the sediment-water interface (Table 4) can readily explain the large scatter in each nodule size class observed in Fig. 3.

The accumulation of trace elements like Ba, Mo, Ni, Zn and Cu in the Mn-rich sediment layer and P, and Sr in the Fe-rich zone
(Table 3) is strong evidence for a digenetic enrichment of these elements. The lack of enrichment observed for the REE (except Ce) does, however, not necessarily imply that these elements are enriched in nodules directly from sea-water. As seen in Table 4 the REE accumulate together with Mn and Fe only if strongly oxidizing conditions prevail. Most likely the redox level is not high enough to trap the REE within the sedimentary column analysed in Table 3. Cu is a good illustration of this phenomenon. In other profiles (Ingri et al 1985a), Cu has been shown to accumulate only in nodules found in the uppermost water-rich brown surface sediment. This is also indicated in Table 3.

It has been suggested that the magnitude of the Ce anomaly of nodules might reflect the redox level of the environment of deposition (Glasby 1973, Piper 1974). Ce data from the Gulf of Bothnia corroborate this assumption. A negative Ce anomaly is observed in Fe-rich crusts and rim-developed concretions, whereas spherical nodules have a positive Ce anomaly. The Fe-rich crusts and girdle concretions are formed close to the reduced-oxidized interface in the Gulf of Bothnia in contrast to spherical nodules which often are found several centimeters from the reduced interface (Ingri 1985a). Samples from the 6 cm thick surface layer analysed in Table 5 illustrate the increasing Ce anomaly going from the less oxidized subsurface sample (No. 9) to the surface layers (Nos. 3 and 2). The anomaly is probably not regulated by total Mn content, as one spherical nodule with 25% Mn does not show any Ce enrichment and
Mn-rich rim formed concretions all have a negative anomaly (Fig. 1). Total REE content and the Ce anomaly have been shown to be smaller on the lower surface compared to upper surface in discoidal nodules from the Pacific Ocean (Elderfield et al. 1981), similar to the rim-formed concretion analysed in Table 5. However, in contrast to conditions in the Gulf of Bothnia Mn and related elements are enriched on the lower surface in Pacific nodules whereas Fe and P are present in higher amounts on the sea-water-facing side (Raab 1972). This relationship together with other data led Elderfield et al. (1981a,b) to conclude that REE were correlated to Fe and P in deep-sea nodules.

Statistical treatment of La, Y and Yb values in 81 spherical, 35 discoidal and 102 flat concretions from the Gulf of Bothnia (Ingri 1985a) demonstrated a correlation to Fe in the latter two concretionary types. In spherical concretions only a strong correlation to nodule size was noted. However, Mn-rich concretions are more enriched in REE compared to Mn-deficient Fe crusts. This is probably a reflection of a larger surface area of the Mn phases compared to the Fe phases and a high redox level when much Mn is present.

Dissimilar to the adsorptive behaviour of the REE and the comparably weak accumulation seen in most of the analysed concretions, is the strong enrichment of the lanthanide elements observed in the Ca-P-rich iron crust sampled from the Svalbard Shelf (sample 17). X-ray diffraction data show the typical reflections
of carbonate fluoro-apatite in this crust; the mineral present in most marine phosphorites (Kolodny 1981). A pronounced introduction of REE into the apatite structure is possible and the presence of this phase is the most likely explanation of the strong accumulation of REE detected in this sample.

There is a clear difference between the REE patterns from the Barents Sea and those from the Gulf of Bothnia. Convex patterns with a maximum for Eu are evident from the Barents Sea, whereas concretions from the Gulf of Bothnia exhibit a LREE enrichment. In comparison to the conditions in deep-sea nodules the samples from the Barents Sea resemble patterns observed in nodules found deeper than 3500 m (Piper 1974a). Piper (1974b) showed a similarity between the shale-normalized pattern for trivalent REE in deep water nodules and the pattern for foraminefera and suggested a biologically related mechanism for the transportation of REE to these nodules. Elderfield et al (1982) proposed that diatom opal is a sufficient carrier of the REE; being able to explain all of the enrichment observed in ocean deep waters.

Several indications suggest that biogenic material might be the primary conveyor of REE to sediments and concretions found on the Svalbard shelf. River input into the Barents Sea is limited. Only a few larger rivers drain into the basin and eolian transport of REE probably is small, as large areas surrounding the Barents Sea are permafrost areas and woodlands. This is in contrast to
the significant eolian input noted by Elderfield et al 1982 in Atlantic surface waters east of the Sahara desert. In other words, only organic matter is present in sufficient amounts to be a possible scavenger. The enormous primary production present along the Svalbard shelf, due to upwelling of nutrient rich polar water, manifests itself by the abundant amounts of cod and capeline caught in these waters (The Mitchell Bently Atlas of the Oceans 1977); this furthermore stresses the importance of organic matter in the Svalbard shelf area. It is suggestive to interpret the dissolved REE content of surface water in the Barents Sea (Högdahl 1968, displayed in Piper 1974b) as a mirror image of the concretionary patterns.

Dissimilar to the eastern Barents Sea primary production in the Gulf of Bothnia is abnormally low and the large outflow of rivers into this basin most likely outranges organic matter as the primary conveyor of REE to sediments and concretions. Analysis of podzol profiles in the till areas of northern Sweden indicates a significant weathering of LREE in the leached A horizon compared to underlying less affected till (1 m depth). HREE are leached to a smaller extent and there is a pronounced peak in Eu suggesting a lower degree of weathering for this element (Fig. 4). This is furthermore illustrated if grey reduced sediment from the Bothnian Bay, "unweathered till" (1 m depth) and the leached zone is normalized to chondritic meteorites (Fig. 5). From this figure it is evident that weathered REE leave the A zone and are transported into the Gulf of Bothnia.
Figure 4. Ratio between the leached A horizon and the C horizon (at 1 m depth) of a podzol profile from northern Sweden (data from Pontér et al., to be published).
Figure 5. I, represent grey sediment from the Bothnian Bay (Table 3). II, represent unweathered till and III highly weathered A horizon from the same podzol profile sampled in northern Sweden (data from Pontér et al., to be published). *Chondrite values from Boynton (1984).
Analysis of the Fe-rich B horizon in the podzol profile confirms a significant outflow of REE, as no enrichment can be detected in this zone. Some of the introduced REE are trapped together with Mn-rich concretions and the LREE enrichment observed is readily understood considering Fig. 4. However, weathered REE are probably also trapped in grey sediment as absolute values are higher in the sediment compared to "unweathered till" (1 m depth). This enrichment is probably due to adsorption of the REE onto the clay (mica group) fraction. Roaldset (1973), using EDTA leaching of Quaternary clays from Norway, concluded that most of the REE content was loosely held, suggesting an adsorptive mechanism for the accumulation in these clays. The depletion of Eu in grey sediment from the Bothnian Bay (Fig. 5) is likely a reflection of the less efficient weathering of this element from podzol profiles surrounding the Gulf of Bothnia.

Conclusions

Shale-normalized REE patterns in concretions from the Svalbard shelf are convex, whereas Gulf of Bothnia concretions exhibit a LREE enrichment. The reason for this discrepancy is explained by a difference in the supply of the REE to the sediment. In the highly productive Svalbard shelf area organic matter dominates the suspended fraction and it is proposed that the plankton mass scavenge preferentially intermediate REE, sink to the bottom, dissolve in bottom waters and in the sediment, thus creating a convex pattern
in concretions. In the low, productive Gulf of Bothnia river-introduced matter plays a key role for the supply of the REE to the sediment. The LREE accumulation in concretions from the Gulf of Bothnia is a reflection of the pronounced weathering of LREE from surrounding podzolic till areas. Nodules from the Bothnian Bay show an exponential increase in the REE content with decreasing nodule radius, suggesting that suspended Fe-Mn-rich matter could be an efficient scavenger and conveyor of REE to the sediment in this basin.

There is a striking similarity in the behavior of the REE, including Y and elements like Cu, Zn, Ni and Co, in the samples from the Gulf of Bothnia. All show a strong surface dependency and accumulate primarily in Mn-rich samples formed at a high redox level. Ce deviates somewhat from the behaviour of the other REE; whether this is due to an oxidation of Ce$^{3+}$ to Ce$^{4+}$, or a difference in acceptance of Ce$^{3+}$, remains to be shown. Present data do, however, suggest that cerium is a measure of the redox level, although the mechanism for this is obscure.
Acknowledgements

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Paper 5
The geochemical stratification of waters in the Landsort Deep, NW Baltic Sea.

by

J. Ingri*, C. Pontér*, and K. Boström**

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Abstract

The Landsort Deep, NW Baltic Sea, shows a strong tendency to be a stagnant basin with anoxic conditions at depth. At such events the waters show a pronounced compositional stratification both with regard to particulates as to dissolved components. Particulates near the redoxcline are enriched in Mn, Ba and Fe, whereas these elements show their highest dissolved loads below the redoxcline.

The elements enriched in these suspended matters are the same that occur in well oxidized toplayer sediments in shallower areas of the Baltic Sea. Reduction of such sediments easily explains the origin of the Mn-Ba-Fe rich particulates at the redoxcline and the enrichment of these elements in anoxic waters. It is probable that some of the selective loss of Mn and Ba from the Baltic Sea takes place when such particulates are occasionally swept out through the Baltic straits.
Introduction

Anoxic basins are wellknown for their chemical stratifications; thus beside oxygen and hydrogen sulfide also many other chemical species show marked variations as a function of the redox potential etc.

These major parameters have a pronounced controlling action on several metal distributions, as is shown by Brewer and Spencer (1974) for the Black Sea or in the Framvaren fjord by Skei (1983). However, to date little has been done to illuminate the metal distributing processes in stagnant parts of the Baltic Sea, but in view of the abundance of poorly oxidized or reducing bottoms in that sea (Grasshoff and Voipio, 1981) such processes could be of great significance. One reason for this suspicion is the need to find a mechanism that enriches Mn, Ba etc in suspended and dissolved loads to be exported out from the Baltic Sea - otherwise the selective loss of these elements from this basin is hard to explain (Boström et al. 1981, 1983).

We therefore decided to study these problems further by sampling the Landsort Deep (58°30'N, 18°10'E), NW Baltic Sea for dissolved and particulate loads at different depths.
Field work, methods

The field work was done in late August 1982 onboard the R/V Strombus of University of Stockholm. Water samples were obtained at depths of 5, 50, 100, 150, 200, 250, 300 and 400 m, using 60 l GO-FL0 bottles coated with teflon on the inside. After landing on deck the water samples were transferred to plastic bottles (25 l) for temporary storage before filtering in a teflon-coated pressure tank; filtering took place as soon as was practically possible and always on station. The filtering was done letting water pass through 0.45 μm millipore filters. In total some 26 to 57 l of sample were used for this procedure. Filtered waters were partly saved in a 1 l plastic bottle after acidification and were used for major element analysis (Si, Ba, Na, Mg, Ca), whereas another fraction (1.5 l) was treated with MgSO₄ and thereupon with NaOH. This procedure precipitates dissolved matter (Fe, Mn, and some other traces) by the so called Koroleff-method (Koroleff, 1980).

In the laboratory the suspended matters were prepared, digested and analysed as described in Boström et al. 1981. The Koroleff precipitates (essentially Mg(OH)₂ with co-precipitated metals) were centrifuged (if they had not settled on their own, which was usually the case), excess liquid siphoned off and remaining hydroxide phase was then dissolved in a small amount of warm HNO₃. The produced solutions were analysed in an ARL sequential reading emission spectrograph (model 33000) with and inductively coupled argon plasma as source. The results are partly given in Table 1, 2 and Fig. 1.
Discussion

The data show a distinct stratification in the waters, especially for Mn, Fe, Ba and Sr in the suspended phase (Table 1). Mn exhibits a pronounced variation also in the dissolved phase (< 0.45 μm) whereas Fe is around 15 ppb above the redoxcline and increases to around 30 ppb below this boundary (Table 2, Fig. 1). Ba is slightly enriched in deeper waters (Fig. 1) in contrast to dissolved Cu and Zn values (not shown) which are highest above the redoxcline (Cu and Zn values ~ 1 ppb and ~ 5 ppb above 50 m depth resp. ~ 0.5 ppb and 3 ppb below this depth).

The Fishery Board cruise report (1982) showed that marked traces of hydrogen sulfide were detected at 150 m in the fall of 1982 and that at 100 m the levels of oxygen were low but measurable (Table 2). Although our samples were collected in late August and their data are from November (15), the results are comparable. Only a slight raise of the H₂S level can be suspected to have occurred from our sampling event. The result of this distribution seems to be that Mn migrates out of the sulfide rich deeper water up into the oxidized top layer. As Mn encounters oxygen it deposits as Mn-oxyhydroxides on particles in the water - this is quite clear whether original data or Al-normalized data (see Fig. 1) are studied. This explanation is similar to that suggested by Brewer and Spencer (1974) and corroborates their reasoning. Our pattern for dissolved Mn, though, differs from that reported by Brewer and Spencer (1974). They report a maximum for dissolved Mn of
Table 1  Chemical composition of suspended matters from the Landsort Deep, NW Baltic Sea

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A. Original data for the depths at 5-400 m.
B. Normalized data, all recalculated to a constant Al-basis.
Figure 1. Distribution of elements in particulate matter and in solution (Fe, Mn, Ba). Original data, see top part of figure. Al-normalized data, see lower part of figure.
Table 2. Formation of a Fe-Mn stratified water-column above the Landsort Deep, Baltic proper.

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<th>Dept (m)</th>
<th>Temp (°C)</th>
<th>Salinity (o/oo)</th>
<th>Oxygen (ml/l)</th>
<th>H$_2$S (μmol/l)</th>
<th>pH</th>
<th>Alk. (mmol/l)</th>
<th>Suspended* Mn (%)</th>
<th>Fe (%)</th>
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Data from Fishery Board Hydrographic Cruise Report, 1982.
Mn and Fe values this study.
*Al-normalized, Table 1.
450 ppb only some 50 m below the redoxcline, but in our data dissolved Mn keeps increasing with depth and reaches some 700 ppb 150-200 m below the redoxcline.

The original data suggest a co-variation between Al, Si and Fe, i.e. much of these elements should be tied up in a silicate phase. Furthermore, Al, Si and Fe are negatively correlated with Mn, which instead is associated with Sr and Ba. The enrichment of Si, Al, Fe and Mn at the halocline (50 m water-depth, Table 1 and 2), probably, partly, is an artifact produced by the variation in admixed sea-salt. Na values scatter around ~ 15% in the profile but at 50 m only 9% is encountered, the low Na value most likely enhanced the Si, Al, Fe, Mn, Sr and Ba values at this level, due to the smaller dilution of sea-salt. If all values are normalized to 15% Na fairly constant Al values, throughout the profile, are obtained. However, the "false" variation for Si, Fe, Mn, Sr and Ba is removed (this does not include Na, Ca and Mg) if Al-normalization is performed (Table 1, Fig. 1). The parallelism between Ba and Mn is obvious whereas Sr is slightly more enriched in the Fe-rich layer 50 m below the Mn particulate peak. This correlation between Sr and Fe is also seen in flat Fe-rich concretions forming at the reduced-oxidized sediment interface in the Gulf of Bothnia (Ingri 1985).

The layer of suspended particles at 100-150 m is especially interesting, in view of the mobility of this zone. Since Mn for instance cannot sink without dissolving and by migration upward once again
precipitates as oxide it appears that its main migration direction would be laterally. One possibility is that the iron-manganese oxides deposit, as concretions, where this layer hits upsticking areas of the bottom; another possibility is that the suspension layer occasionally e.g. during storms is mixed into upper layers and drifts out of the Baltic Sea. In view of the high loads of fine detritus in the waters this appears likely (Krey, 1974). The Baltic Sea has a significant net outflow of water (Ehlin, 1981). Most likely both loss processes occur. Such processes would explain the selective loss for Mn and Ba observed for the Baltic (Boström et al., 1981, 1983), although, a fraction of the Mn does deposit as a Mn-carbonate and as a Mn-sulphide in very reducing areas (Manheim, 1982, Suess, 1979).

The composition of the enriched layer at 100-150 m depths in the profile is similar to the composition obtained if element contents in the oxidized surface sediment in the Gulf of Bothnia is subtracted from the contents in lower reduced layers, i.e. the elements that are lost from the sediment due to reduction (Boström and Ingri, 1985). This does not necessarily prove that reduction processes in the Gulf of Bothnia alone account for the total metal content in this layer at 100-150 m. Although most probably some Fe, Mn etc have their origins further north, it appears very likely that much material also is derived locally, i.e. sinking matter is reduced and loses Mn etc already during the descent to the sea floor.
Conclusions

The anoxic conditions in deeper areas of the Baltic Sea cause extensive reduction and mobilization of many elements, either in dissolved form or in particulates. Such mobilizations probably explain both the genesis of some Fe-Mn concretions as well as some selective element losses from the Baltic Sea.

Acknowledgements

We want to thank skipper K. Wannäs and crew of R/V Strombus for much help on station. We also thank Dr. Jan-Ola Burman, Solweigh Brandlöf and Birgitta Boström for help in the laboratory and discussions of results. This work was supported by grants from NFR (Swedish Natural Sciences Board) and from STU (Swedish Board of Technical Development) to Dr. Kurt Boström.
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Boström, K. and Ingri, J. 1985. The geochemistry and origin of sediments in Gulf of Bothnia and NW Baltic Sea (MS in prep.)


Paper 6
GEOCHEMISTRY AND ORIGIN OF FERROMANGANESE CONCRETIONS IN THE GULF OF BOTHNIA

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ABSTRACT


Ferromanganese concretions cover large areas of the Gulf of Bothnia. They are flat to well-rounded, the rounded ones being richer in oxyhydroxides of iron and manganese. Rounded and ellipsoidal nodules, particularly those in the northern Gulf of Bothnia, are richest in Mn, Ni, Ba and Cu, which probably coexist in a Mn oxyhydroxide phase. Flat nodules are enriched in Fe, P, rare earths and As, probably associated with an Fe oxyhydroxide component. Aluminum, V, Cr and Ti occur in still another phase.

The sediments of the gulf generally consist of a 10—50 mm-thick layer of oxidized surface sediment, enriched in Mn, Ba, P and Ni lying on top of reduced sediments which are diagenetically depleted in these elements. The remobilized elements have redeposited in the nodules, but this process cannot explain the origin of all the nodular material. Some released Mn, Ba and Ni furthermore enter into suspended phases, which eventually leave the Baltic Sea. The economic value of the nodules in the Gulf of Bothnia is probably limited at present.

INTRODUCTION

During the last decade several hundred studies of deep-sea nodules have been published, see for instance Glasby (1977) and Meylan et al. (1981). Considerably less research effort has been spent on nodules from shallow marine environments, although some important studies have been published (e.g. Manheim, 1965; Winterhalter, 1966; Sevast’yanov and Volkov, 1967; Grill et al., 1968; Calvert and Price, 1970; Varentsov, 1973; Varentsov and Blashchishin, 1976). Additional references are listed by Calvert and Price (1977).

The reason for this difference in attention is probably that shallow marine nodules in general have been considered to be less interesting from both geochemical and economical standpoints. Geochemical processes in shallow marine environments, such as in estuaries and epicontinental seas, however,
proceed much faster than in the deep-sea, due to a large extent to biological processes that strongly affect the migration of many major and trace elements. Some biological products and suspended matters formed in this environment subsequently migrate to the deep ocean, where they are an important source for the deep-sea sediments (Boström et al., 1981). The distribution, composition and genesis of nodules in shallow seas hence yield much information about such geochemical processes.

Gripenberg (1934) and Veltheim (1962) described nodules from the Gulf of Bothnia, but the first extensive study was done by Winterhalter (1966) who showed that nodules are abundant there (Fig.1). He also treated geological, mineralogical and genetical aspects and the major-element geochemistry of the nodules and 10 trace-element analyses were given. These observations were confirmed by Boström et al. (1978), who reported 25 additional analyses for acid-insoluble matter, Fe, Mn, Ni and Cu in nodules.

Fig.1. Distribution of nodule finds in the Gulf of Bothnia.
and presented geochemical and mineralogical maps of the associated sediments. In this work we will discuss the distribution, geochemistry, geological setting and origin of 97 additional nodules from the Gulf of Bothnia.

**PHYSIOGRAPHY AND GENERAL GEOLOGY**

The sill at the North Kvark divides the Gulf of Bothnia into two major basins, the Bothnian Sea and the Bothnian Bay (Fig. 2). Waterdepths exceeding 100 m cover only minor areas of the Bothnian Bay and Sea, and depths exceeding 200 m occur only near the Swedish coast at about 63° N 19° E.

The topography of the floor is characterized by numerous ridges, hills and depressions, see Winterhalter (1972) and Tulkki (1977). Most of the floor is covered by Quaternary deposits such as tills, eskers and glacial clays. Post-glacial clays are depositing even today and are furnished by river-transported

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![Fig. 2. Distribution of analyzed nodules. Dashed line represents the 50-m depth interval, dash-dot line the 100-m depth. Small square shows position of the area in Fig. 3.](image-url)
material from land and by abrasion of old sediments by ice, waves and currents. The erosion is promoted by the postglacial uplifting of Scandinavia, at present some 9 mm yr\(^{-1}\) near the N. Kvark. Therefore, shallow areas (about 0–20 m) of exposed coastal regions are characterized by intense abrasion of coarse sediments (sand and pebbles), and at depths of 20–50 m transport and erosion of fine sediments (silt) still occurs. In the 50–70-m depth interval, transport of clayey matter is still extensive, but below this level clay-sized matter is settling permanently. These depth intervals are approximative; local variations exist due to bottom currents and the protective action of islands and shallow sills in the archipelagos.

FIELD METHODS

Our research group has collected nodules each summer in the period 1976–1979 during in total 10 weeks, primarily in the Gulf of Bothnia; only two weeks were spent in the Baltic proper. The nodules were collected with pipe and box dredges with 50–100-liter volumes; the dredging took 4–8 min at slow speed at each site.

After surfacing, the dredge content was dumped on deck or in a large plastic vat for inspection and sampling. Large oxide-stained rocks and nodules were collected by hand, rinsed and curated. After this, the sediment was washed in a plastic sieve; this method retrieved nodules as small as 2 mm in size. Unwashed sediments were also sampled for future studies of the sediment–nodule relations. Many nodule areas also proved to be rich in benthic organisms, particularly Mesidothea entomon. Navigation was checked using the Decca system and depths were continuously monitored with a 30-kHz echosounder; proper tuning made it possible to differentiate areas with postglacial clays from regions with transport of sediments, etc.

Distribution of nodules

About 200 dredge stations were occupied during 1976–1979 in the Gulf of Bothnia; 92 of these yielded nodules (Fig.1). Most of the failed attempts took place N and E of about 65°10'N and 23°30'E in the Bothnian Bay, where vast sand bottoms occur, and in the SE and S central Bothnian Sea and just off the Swedish coast between 62°30' and 63°30'N, where coarse sand and boulders are abundant.

The local distribution is hard to predict, even in areas where nodules are abundant. At Sta 1976-19 (Fig.3), for example, one dredge attempt failed, yielding only sand whereas the next attempt on the same station yielded a very large harvest of various nodules, suggesting a patchy distribution. In other areas, the nodules seem to cover the floor evenly, e.g. at Sta 40B (Fig.2). Some 40 l of nodules were recovered there in one single attempt; renewed samplings close to this station in 1979 also yielded large catches. The distribution shown in Fig.2 is therefore probably representative of where the nodules are most frequently encountered, but more quantitative studies
Fig. 3. Samples (=filled circles) from W. Bothnian Bay, provided by the Swedish Environmental Protection Board; the position of the area is indicated in Fig. 2.

with grab samplers and bottom cameras must be done before a reliable distribution map can be produced.

Most successful dredge attempts were made on hilltops and hillslopes above the depth zone of permanent clay deposition but below the zone of intense abrasion, whereas dredging in clay and mud basins invariably fail to yield nodules. Furthermore, none of our very large catches has been made near the coast; obviously the transport of coarse sediments and the annual reworking of the bottom by ice is too intense to permit nodule growth in such areas. On the other hand, isolated hills in the depth range of 40–80 m (Bothnian Bay) and 50–100 m (Bothnian Sea) frequently are covered by very extensive nodule occurrences, e.g. at Sta 1977-40B and its vicinity. These observations agree with those by Winterhalter (1966).

Description and distribution of analyzed material

The distribution of the analyzed nodules is shown in Figs. 2 and 3; the latter were obtained from SNV (=the Swedish Environmental Protection Board, see Fig. 3).

The nodules belong to three morphological types, namely: (1) flat crusts and thin discs; frequently these nodules contain a large stone nucleus; (2) thicker ellipsoidal discs with the ratios of the maximum to minimum radii between 1.10 and 2.75; stone nuclei are absent; and (3) spheroidal nodules, in which the maximum and minimum radii differ by less than 10% from each other; coarse detrital matter such as sand is absent in these nodules. In the following they are referred to as the: (1) flat; (2) ellipsoidal; and (3) spheroidal types. This grouping of the nodules largely coincides with that of Winterhalter (1966) and was selected to make our data comparable with his results; for further morphological descriptions see Winterhalter (1966).
Table I shows the geographical distribution of the analyzed nodules which are further divided into those occurring (a) near the coast; and (b) in the open sea. Table I is misleading, however, insofar that it gives the impression that 63% of all open-sea nodules would be flat whereas only 44% of the coastal nodules are. Thus, whereas flat nodules do occur in the open sea, they are rather infrequent there in contrast to the abundant spheroidal nodules; flat and ellipsoidal nodules are abundant near the coast where the spheroidal nodules are rare.

In this study we have not included the brown stains and thin coatings that are locally abundant on stones even in shallow waters; for our purposes, to be classified as a nodule the hydroxide phase must exceed 3 mm in thickness. It is furthermore well known that most iron, manganese and associated metals occur in a mixture of oxides and hydroxides in the nodules, but for simplicity this assemblage is referred to as the hydroxide phase below.

Analytical methods

All samples were crushed to small pieces with a Plattner mortar or by hand. Stone-nuclei (if present) were removed and after this the remaining, seemingly homogenous hydroxide phase was ground in an agate mortar. It should be noted that all nodule analyses refer to this stone-nucleus-free fraction. Spheroidal and ellipsoidal nodules which never contain large stone or sand nuclei were ground without prior processing. All ground materials were dried at 100°C.

500 mg of the dried materials were placed in glass beakers and 25 ml acid (1 part HCl, 2 parts H2O) and a few mg of reducing agent (hydroxylamine hydrochloride) was added. Heating at 50 to 75°C for 1—3 hours dissolved all hydroxide material, forming a yellow to brown solution.

The acid-insoluble residue is of siltsize or finer and has a pale greyish to almost white color. X-ray diffraction studies reveal the presence of much quartz, minor quantities of feldspar and illite and some amphibole, particularly in nodules from Bothnian Bay (Boström et al., 1978). The acid leach treatment destroys some sheet-silicates but it is unlikely that significant quantities of trace elements derive from leaching of the detrital terrigenous matter as is demonstrated below. Some of the Si, Al, Na and Ca, in the leached fraction may derive from this detrital fraction.

The acid-soluble fractions were analyzed by emission spectroscopy, using an inductively coupled plasma (ICP) as source. Most elements were measured in an ARL 33000 sequential reading unit, but Yb, La, Sc and P were determined in an ARL 35000 scanning quantometer. (Burman et al., 1978; Burman and Boström, 1978, 1979, 1980; Burman, 1979, 1981).

The lack of standard nodules with recommended values is a problem. However, matrix effect studies (Burman, 1981) show that most element determinations are little affected by the high iron concentrations except for Ti and As, but these element determinations could be corrected and yielded good values in the concentration ranges found in the nodules; almost all
**TABLE I**

Distribution of analyzed nodules and their shapes (see Figs. 2 and 3)

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Total 48 34 15

1Less than 20 nautical miles (36 km) from mainland.
2More than 20 nautical miles (36 km) from mainland.

Sta No. = Station number; SNV = Samples obtained from Swedish Board of Environmental protection.
samples contain more than 300 ppm Ti and 150 ppm As which are the approximate detection limits under our experimental conditions. Tests on steel standards with low recommended Ti-contents yielded excellent results.

RESULTS

Treatment of data

The analyses are given in weight units, see Table II and in Figs.4—9. Most analyzed fractions contain much acid-insoluble matter, some samples 76% of the total dry weight. Since this fraction essentially represents an admixed trace element poor, silicate-rich diluent, it will tend to obscure the element interrelations in the acid-soluble fraction. All original analyses were therefore recalculated to an acid-insoluble free fraction.

The recalculated analyses showed that the sum of Fe + Mn clustered near 40% (see also Boström et al., 1978). However, the sum is not constant; this cannot fully be explained as due to admixed phases such as barite and phosphate since they are not present in sufficient quantities. However, nodules rich in insoluble detritus also contain much Al, Ti, Ca, Mg and Na in the dissolved fraction, probably deriving from leached silicates. Furthermore, the degrees of oxidation and hydration of the Fe—Mn phases can vary considerably (Calvert and Price, 1977; Burns and Burns, 1977). We therefore assume that most of the scatter in the (Fe + Mn) sum is due to variations in hydration, oxidation and admixture of dissolved silicates and other non-hydroxide phases. To remove this scatter we therefore multiplied all analyses with a factor \( f = 40/(\text{Fe} + \text{Mn}) \), i.e. we normalized all acid-leached fractions to a constant sum of \((\text{Fe} + \text{Mn}) = 40\%\); in most cases this factor deviates little from that used to obtain the acid-insoluble free fraction. These normalized values are referred to as the HF fraction below. A major advantage is that this presentation makes the relations between Fe, Mn and other metals fairly easy to interpret.

Most of the Figs.7—14 are based on such HF-values as are also elemental abundances in various nodules and grouped means (Table II).

Sedimentary petrologists are usually reluctant to use various types of processed data, contrary to igneous petrologists, who freely use various Niggli-, CIPW- and standard cell normalizations (Barth, 1950); such procedures make it easier to detect variations that otherwise are hidden in the figures. Normalization of data versus for instance \((\text{Al} + \text{Fe} + \text{Mn})\) or functions such as \(\text{SiO}_2/\text{Al}_2\text{O}_3\) and \(\text{Fe}/\text{Ti}\) reveals important aspects of some sediments (Boström and Petersson, 1969; Boström, 1970; Boström et al., 1972).

To understand the element relations, some correlation coefficients and partial correlations have been calculated. Statistical studies of closed-sets of data often yield misleading conclusions, however (Chayes, 1967), and therefore the obtained information must be tested, e.g. by genetic models.
Synoptical trends in composition

The primary (uncorrected) values for Mn in flat nodules (Fig.4), in spheroidal and ellipsoidal nodules (Fig.5) and acid-insoluble residue (Fig.6) show distinct regional trends. The nodules in the Bothnian Bay are richer in Mn than are those in the Bothnian Sea, where for instance 67% of the flat nodules contain less than 2% Mn. Corresponding contents in spheroidal and ellipsoidal nodules likewise reach higher values in nodules in the Bothnian Bay. Furthermore, 72% of all nodules in the Bothnian Bay contain less than 30% detritus whereas only 26% of the nodules in Bothnian Sea contain that little detritus (Table III).

The Mn(HF)-values hence show remarkable latitudinal trends, see Fig.7. The hydroxide fractions of the Bothnian Sea nodules are remarkably poor in manganese; only 16% of all nodules there contain 10% Mn or more, whereas 50% of all nodules in the Bothnian Bay contain more than 10% Mn; some even exceeding 20% Mn.

The P (HF) content varies much less drastically than does Mn (HF); and P and Fe tend to covary, see Fig.8. In the Bothnian Sea 63% of all nodules contain more than 2% P (HF) whereas only 24% of the nodules in the Bothnian Bay exceed this value. These results also indicate that P (HF) is negatively correlated with Mn (HF).

Additional synoptical maps could reveal more interelement relations, but the interelement relations are more easily detected in scatter plots and by correlation calculations.

Interelement relations

Data in Figs.6 and 7 show a negative correlation between Mn (HF) and the acid insoluble fraction. This means that the content of Mn in the hydroxide fraction is not constant but increases as the total amount of the hydroxide phase increases, see also Fig.9; particularly the spheroidal and ellipsoidal nodules have very Mn-rich hydroxide fractions.

Iron and manganese form a closed set, i.e. show a negative correlation which is implicit by the definition of the HF-phase (see Table IVa). Hence, in all plots below the iron content is defined as Fe = 40-Mn, i.e. a positive correlation for a given element with Mn implies a corresponding negative correlation with Fe.

The correlations Al—Fe and Al—Mn are less than 0.70, i.e. less than 50% of the covariations are explained by Al when the influence from insoluble fraction (=IF), Si or P is removed (Fig.10). The correlation of uncorrected Al contents with acid-insoluble residue is the best of all tested correlations and indicates that some Al is dissolved from micas, etc., during the leaching. This interpretation is supported by the Al—Ti relation, which is very constant and is close to 10 (Fig.11, Tables IVa and b). Other elements that form refractic compounds are Sc, V and Cr, all being well correlated with Al, but not with IF.
### TABLE II

Compositions (mean and standard errors) of nodules from Gulf of Bothnia

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<tr>
<th>Composition</th>
<th>Mean ((\bar{x}))</th>
<th>s/(\sqrt{n})</th>
<th>2</th>
<th>s/(\sqrt{n})</th>
<th>3</th>
<th>s/(\sqrt{n})</th>
<th>4</th>
<th>s/(\sqrt{n})</th>
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<td>5.2</td>
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<td>0.02</td>
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Hydroxide phase represents acid-soluble fraction of nodule, dried at 100°C. Major elements given in weight%, trace elements in ppm of the hydroxide fraction. All mean values and standard errors were calculated from the original values, which subsequently were normalized such that \(\text{Fe} + \text{Mn} = 40\), using the factor \(f\) at the bottom of each column, see text. The original mean data can be retrieved by division of each set of metal values by

Silica shows a fairly large negative correlation with Al when the influence from IF, etc., is removed (Table IVb), suggesting that Si to a large extent occurs in separate phases (quartz, diatomaceous materials).

As and La also show positive correlations with Fe; the correlations between Fe—P and Fe—As are well known (Boström and Valdés, 1969; Calvert and Price, 1977). Apatite must be a minor source for P, however, since much less Ca is present than this would require. Furthermore, La is well correlated with Fe, see Table IVb.

Ba, Ni and Cu show pronounced correlations with Mn (Fig.12, Tables IVa and b); the correlations Mn—Ni and Mn—Cu are known from many studies of deep-sea nodules (Glasby, 1977). Our data furthermore corroborate the high Ni-values found by Manheim (1965) for Baltic nodules. The correlation Mn—Ba is less easy to explain. Ba is often present as barite in marine deposits (Arrhenius and Bonatti, 1965) but this is unlikely in this case because of the low sulfate content in the brackish waters of the Gulf of Bothnia. Data in Table IVb suggest that Ba occurs in minerals like psilomelane (Burns and
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<td>—</td>
<td>28</td>
<td>2</td>
<td>41</td>
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</tbody>
</table>

the corresponding f-value. The number of analyses used for the averaging is given by n.

Column 7 represents mean of nodules of all types, column 8 of all ellipsoidal and spheroidal nodules and column 9 of all flat nodules. $\bar{x}$ = arithmetic mean, $s$ = standard deviation and $s/\sqrt{n}$ represents standard error (Crow et al., 1960).

Burns, 1977), but we have no mineralogical data to support this assumption. Some elements show no distinct correlations. Thus, both Zn and Sr show a remarkably uniform content in the HF-fraction, independently of nodule-type. Ca and Mg show some but poor correlation with Al, and Na shows no distinct correlation with any other constituents.

We therefore conclude that the nodules contain the following components:

1. An acid-insoluble fraction, mostly consisting of silicates and other rockforming constituents.
2. Silica, representing leached quartz and diatoms.
3. Al, Ti, Sc, V, Cr, Ca and probably Na represent small amounts of silicate rock materials that have dissolved in the acid-leach, but which do not per se belong to the hydroxide phase.
4. A Mn-hydroxide component which includes Ba, Ni and Cu.
5. A Fe-hydroxide component, which includes P, La and As.
Fig. 4. Manganese content of flat nodules, uncorrected for diluting effect from terrigenous matter. Absence of flat nodules at a given site is indicated with —.

**Variations in element abundances in nodules of different shapes at a given site**

The mean data presented here show that the hydroxide composition of the nodules varies with their shapes, but this does not exclude that some flat nodules at a site occasionally may be richer in Ba and Ni than coexisting spheroidal nodules.

Several different types of coexisting nodules from stations 1976-19, 1976-26, 1977-22 and 1977-40B were analyzed to detect how the compositions of flat, ellipsoidal and spheroidal nodules vary: (a) at a given site; and (b) from area to area. The results show that there is a considerable compositional scatter, particularly at site 1976-19. Thus, the relation between insoluble matter and Mn (Fig. 13) shows that most spheroidal and ellipsoidal nodules are richer in Mn (HF) and poorer in insoluble matter than coexisting flat nodules. Likewise most rounded nodules are richer in Ni (HF) than coexisting nodules of other types. However, some flat nodules (site 1976-26) are richer in Mn (HF) and Ni (HF) than spheroidal nodules from Mn-Ni poor sites (1976-19). Furthermore, the largest compositional variations occur at site 1976-19 just off the coast, whereas nodules from site 1977-40B in the open Bothnian Bay show smaller scatter, probably reflecting a more homogenous local environment of formation.
Fig. 5. Manganese content in spheroidal and ellipsoidal nodules, uncorrected for diluting effect from terrigenous matter. Absence of nodules with this morphology at a given site is indicated with —.

Fig. 6. Acid insoluble fraction in nodules.
DISCUSSION

*Synoptic nodule patterns — enigmas and tentative explanations*

The nodule compositions in the Gulf of Bothnia display distinct latitudinal variations as Figs. 4—8 show and the relations in Figs. 9—14 and in Table IVa and b further substantiate. We have no simple explanation for this distribution. Since several major rivers dump much organic matter into the gulf, one would expect the sediments to be fairly reducing, not the least off the second largest Swedish river, Lule river. However, the nodule distributions, the distribution of manganese oxides versus iron oxides in the bottom sediments, and the distribution of oxidized species (nitrate) in the waters suggest that the Bothnian Bay is a considerably more oxidizing environment than the Bothnian Sea (Dahlin, 1977; Boström et al., 1978). Studies by Burman (1982a, b) show, however, that the Swedish rivers that drain to the Bothnian Bay are much more loaded with Fe, Mn and some trace metals than are the ones debouching into the Bothnian Sea; possibly this is the explanation for the latitudinal patterns seen here.

The distribution patterns agree with those by Winterhalter (1966). It is therefore likely that the samples from the Bothnian Sea are representative although they represent a smaller number of samples than those from the
TABLE III

Mean composition of sediments from Bothnian Bay

<table>
<thead>
<tr>
<th></th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
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<tr>
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<td>$x$</td>
<td>$s/\sqrt{n}$</td>
<td>$x$</td>
<td>$s/\sqrt{n}$</td>
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<tr>
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1. Mean composition of well-oxidized top layer of unconsolidated postglacial sediments, Bothnian Bay.
2. Mean composition of Mn-depleted deep layer of unconsolidated postglacial sediments, Bothnian Bay. (Data in column 1 and 2 after K. Boström and J. Ingri, ms. in prep.)
3. Difference between sediments in column 1 and 2, assuming Al and Ti to be conservative constituents. The loss of water, organic matter, manganese, etc., will lead to an apparent increase in the Ti and Al-values; hence the factor $f = \sqrt{\frac{Ti_1}{Ti_2} \times \frac{Al_1}{Al_2}}$ is used to correct all values in column 2 before the subtraction. Statistically insignificant changes are given as 0.
4. Mean spheroidal nodule, see Table II, column 8 this work. ($\bar{x}$, $s$ and $n$ are defined in Table II).

Bothnian Bay. A peculiar phenomenon is the distribution of irregularly shaped, flaky and very thin nodules, which Winterhalter (1966) called nodules of Korsö-type. We can here confirm this report; our data show that this type is occurring uniquitously over most of the Bothnian Sea, but is rare or missing in the Bothnian Bay and in the Baltic proper. The Korsö-type must represent special growth conditions that we do not yet understand (Winterhalter, 1966); the prevalence of such conditions over much of the Bothnian Sea may at least partly explain the differences in the nodule compositions in the Bothnian Bay and the Bothnian Sea. Another environmental indicator may be that Mesistothea entomon is much more common at nodule sites in the Bothnian Sea than in the Bothnian Bay.

Origin of nodules in the Gulf of Bothnia

The origin of shallow water nodules has been extensively discussed, i.e. there is no reason to recapitulate most of the arguments in the review articles
Fig. 8. Phosphorus content in the acid soluble fractions of all nodules after normalization of the analyses to Fe + Mn = 40%.

Fig. 9. Mean content of hydroxide phase (acid soluble fraction) and normalized Mn content. The symbols represent: rectangles = flat nodules; triangles = ellipsoidal nodules; circles = spheroidal nodules; solid symbols = open-sea nodules; open symbols = coastal nodules; bars = standard errors (see Table II).

The graph shows that the manganese content in the hydroxide phase increases as the total fraction of hydroxyl phase increases. Note that this normalization (see text) filters out the diluting effect from terrigenous matter, degree of hydration, etc.
TABLE IVa

Interelement relations in nodules in Gulf of Bothnia (hydroxide fraction). Correlation coefficients

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<th>Fe</th>
<th>Mn</th>
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<th>P</th>
<th>Ba</th>
<th>Zn</th>
<th>Ni</th>
<th>Cu</th>
<th>Y</th>
<th>La</th>
<th>Sc</th>
<th>Cr</th>
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</table>

Correlation coefficients (Snedecor and Cochran, 1967) for nodules from the Gulf of Bothnia. (IF = acid insoluble fraction; to become comparable, all IF-values are multiplied with the same f-constant as the elements). The correlation Mn—Fe already is fixed by the relation Fe + Mn = 40%. Correlations larger than ±0.27 are significant at the 1% significance level, those larger than ±0.20 at the 5% significance level (Crow et al., 1960).
Fig. 10. Relations between Mn and Al (from Table II). Low Mn-values (see Fig. 9) are associated with high detritus loads in the nodules, i.e. Al and insoluble matter are well correlated, see also Table IVb. For legend, see Fig. 9. Black squares = mean grouped data (columns 8 and 9, Table II).

Fig. 11. The relations between Al and Ti (from Table II) suggest that terrigenous detritus or authigenic clay minerals are attacked during the leaching, see also text and Table IVb. For legend, see Figs. 9 and 10.

by Calvert and Price (1977) and Calvert (1976), but some genetic aspects are of interest for further discussion.

A major controversy in the nodule growth debate has been whether the material largely derives from diagenetic processes in the sediments (Manheim, 1965) or from lateral migration of material, partly derived from rivers (Varentsov, 1973). Varentsov's (1973) conclusion is based on the assumption that only 0.2 m of sediment has accumulated since the last glaciation. This accumulation rate appears low; our echo-sounding recordings from several regions of the whole Baltic Sea suggest that postglacial clays cover some 40% of the floor of the Baltic with a thickness ranging between 5—25 m, 1 mm yr⁻¹ being a good order of magnitude estimate of the mean accumulation rate. These figures imply a mean sedimentation rate of 0.4 mm/yr⁻¹ for the total Baltic Sea or 3.2 m of sediments for the last 8000 yrs (Boström et al., 1982a).
TABLE IVb

Partial correlations

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</table>

Partial correlations (Snedecor and Cochran, 1967) based on relations in Table IVa. Correlation coefficients in the columns below IF, Al, etc., represent those, for which the influences from IF, Al, etc., are removed. Correlations larger than |±0.31| are significant at the 1% significance level, those larger than |±0.25| at the 5% level.

To test the diagenetic source model by Manheim one may compare the mean composition of well-developed nodules (Table II, column 8) with those of postglacial sediments (Table III, columns 1 and 2). The unconsolidated sediments are of two different types: (a) a reddish brown top layer, some 10—50 mm thick, resting over (b) a greenish-grey to almost black layer, which sometimes smells of hydrogen sulfide in freshly opened cores. These sediments differ in the contents of Mn, Ba, P and Ni, implying that the deeper sediments have lost these elements during diagenesis; such processes have been discussed by Bezrukov (1960), Lynn and Bonatti (1965), Bonatti et al. (1971), Holm (1978) and Lindström and Holm (1980). The least understood process is the pore-water migration of Ba (Boström, 1976), but microbiological processes may possibly release Ba from sulfates by reduction (Bolze et al., 1974). Preliminary studies (J.I.) suggest that the pore waters in the
sediments in Gulf of Bothnia may be rich in Ba, i.e. the migration of Ba in the sediments could be considerable. Processes of this nature are furthermore well developed also outside the Baltic Sea and have been observed in the Barents Sea (Boström et al., 1982b; Ingri, 1982).

Assuming that Al and Ti do not migrate during diagenesis, one may calculate what fraction of the oxidized sediments (Table III, column 1) are lost to
Fig. 14. Relations between Mn and Ni contents in nodules from the same dredge hauls; see legend and caption to Fig. 9. Rounded nodules tend to be richer in Ni and Mn than flat nodules.

form the reduced sediments (Table III, column 2). The difference (Table III, column 3) represents the material possibly available for nodule formation, which reveals a striking similarity with the mean nodule (Table III, columns 3 and 4). Iron is the element that most easily will reprecipitate upon reaching the oxidized zone. Normalizing the data such that the iron-values are identical, yields the element relations in Fig. 15, revealing that Fe and P are lost in the same proportions from the sediment as they are incorporated in the nodules, whereas proportionally more Si, Mn, Ba and Ni are released than the nodule growth requires. Suspended-matter studies show that Mn and Ba are preferentially lost from the Baltic Sea in suspended fines (Boström et al., 1981) and losses of dissolved Si from bottom sediments are widely occurring (Broecker, 1974).

The diagenetic origin hypothesis by Manheim (1965) thus is in good agreement with our quantitative relations. The data (Table III) show that a few centimeters of top sediment could indeed form much larger nodule fields than are actually observed. The results thus indicate that the nodules are repositories for only a fraction of the diagenetically mobilized material, and that the balance is leaving the Baltic Sea by currents, winnowing of suspended matter, microbiogeochemical processes and transport in higher organisms (Boström et al., 1981, 1982a).
Lost sediment fraction

Fig. 15. Compositional relations between mean spherical and ellipsoidal nodules and the diagenetically lost fraction of the sediments, see Table III, columns 3 and 4. Proportionally more Si, Mn, Ba and Ni are lost from the sediments than are incorporated in nodules; the formation of flat nodules would imply even larger separations between the Fe—P phase on the one hand and the Mn—Ba—Ni phase on the other.

There may yet be some salient points in Varentsov’s (1973) arguments; it is doubtful whether simple upward migration and redeposition alone explain the nodule growth. The nodules are rarely located on top of those sediments where the diagenetic processes occur, but mostly on isolated hills, located above the depth zone of permanent accumulation. A considerable lateral transport of mobilisates is thus occurring, most of it probably as suspended matter. However, considerable quantities of laterally transported matter are also delivered by rivers; N. Swedish rivers are rich in Fe, Mn, Ni, Cu and Ba (Burman, 1982a, b), i.e. rivers and diagenesis deliver similar products. The importance of these sources probably varies, nodules near the coast probably being formed primarily from river material whereas nodules in the open sea are predominantly diagenetic. More studies of these problems are needed.

In conclusion, a diagenetic source for much of the matter in the nodules is at present the best genetic model for nodule growth in the Gulf of Bothnia; however, aspects of this process are poorly known and should be further studied, particularly the migration of several transition metals and Ba in the sediments and in the bottom waters and the role played by settling suspended and biological matter which has so far been largely ignored.

ACKNOWLEDGEMENTS

We thank S. Brandlöf, B. Boström and J. O. Burman for analytical assistance and discussions of analytical problems and Dr. M. Kumpas and other crew members on R/V “Strombus” for assistance at sea, and Dr. G. Lithner of the Swedish Environmental Protection Board (SNV), who kindly gave us
some nodules. Funds from the Swedish Board of Technical Development (STU) and Swedish Natural Science Board (NFR) are gratefully acknowledged.

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SELECTIVE REMOVAL OF TRACE ELEMENTS FROM THE BALTIC BY SUSPENDED MATTER

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ABSTRACT

Suspended matter was collected at 30 stations in the Baltic and Kattegatt, at the thermocline and at the bottom, and analysed for Na, Ca, Mg, Si, Ti, Al, Fe, Mn, Ba, Sr, Ni and V. The composition of the suspended matter varies considerably, but can be described as a mixture of: (1) 12—25% terrigenous detritus with much Si, Al, Ti and Fe; (2) 75—88% biological matter with much Ni, V and Ba; and (3) some Mn-oxyhydroxide.

The annual efflux of water from the Baltic is about 460 km³, with a suspended load in the Baltic straits of ~1.2—3.6 mg psh material l⁻¹. These values imply that much Si, Ti, Al, Fe, Sr, Ni and V and particularly much Ba and Mn are lost from the Baltic in the suspended load.

The average suspended matter is richer in Mn (5X), Ba (2.5X), Sr (4X) and V (1.8X) than permanently depositing Baltic sediments. These constituents are relatively enriched in pelagic deposits, i.e. it is likely that much Mn, Ba and V in deep-sea sediments derive from the continents via suspended transport. This conclusion is supported by the similarity between suspended matter and average Atlantic pelagic sediment.

INTRODUCTION
Several studies have been made of the composition and flux of suspended matter in the hydrosphere (Lai, 1977; Sackett, 1978), but the number of multi-element analyses is still small (Hirsbrunner and Wangersky, 1975, 1976; Chester et al., 1978; Emelyanov and Pustelnikov, 1976; Krishnaswami and Sarin, 1976; Martin and Meybeck, 1979; Sholkovitz and Price, 1980).

These suspended phases normally show strong elemental variations, and many trace element abundances are remarkably high compared to the major components, possibly due to admixture of, for instance, adsorbed phases and biological matter. However, the study of suspended matter poses many problems of contamination during sampling and analysis, i.e. some data may be poor. Furthermore, some studies show results that differ considerably (Copin-Montegut and Copin-Montegut, 1972; Krishnaswami and Sarin, 1976) possibly due to geographical variations or shaking of the samples after their procurement (Hirsbrunner and Wangersky, 1975). There is consequently a need for additional studies of these problems, since transport of elements in particulate matter may influence several marine geochemical cycles, for instance, Mn and Ba (Böström, 1976; Sundby, 1977; Baker and Feely, 1978).
This paper reports on the elemental composition (Na, Ca, Mg, Si, Ti, Al, Fe, Mn, Ba, Sr, Ni and V) of suspended matter from the Baltic and its straits. The term 'Baltic' here refers to the entire Baltic Sea including the gulfs of Bothnia, Finland and Riga, whereas 'Baltic proper' stands for the area south of 60°N, excluding the gulfs. The Gulf of Bothnia is divided into the Bothnian Bay (to the north) and the Bothnian Sea (to the south).

METHODS OF COLLECTION AND ANALYSES

Sampling

Samples were collected in July, 1979 onboard the R/V "Strombus" and in November 1979 onboard the R/V "Argos", referred to as 'summer' and 'fall' stations below (see Fig. 1). At each station the position of thermocline...
and bottom were recorded by a bathythermograph and a depth-recorder. Subsequently, a plastic integrating 25-l water sampler was lowered to the appropriate depth; this sampler was a modification of a unit described by Nilsson (1971). Since the thermocline layer is not defined with any great precision, the sampler was allowed to continuously rise and sink (±3 m) around the steepest gradient in the temperature; because of the constricted efflux valve, the total samplings required about 5 min each.

Bottom samples were obtained by quickly lowering the container to within 2 m above the bottom, where it subsequently was left for 5 min. Because of the shallow depths, almost all water from the deep casts represents bottom water, as indicated by the ascending bubble train. However, at a few places with large water depths (e.g. east of Gotland) no bottom samples were collected. Furthermore, an integrated sample was taken from the 0—40 m layer at several fall stations where the thermocline was not defined. To obtain sufficient material, 25-l water samples were collected at each sampling point, but occasionally 50 l was procured. On deck, the samples were filtered in a millipore pressure filtering set-up (6 atm) on 0.45 µm filters and subsequently stored in plastic containers. During the filtering the sampling containers were not shaken, i.e. the amount of man-made aggregates must be small (Hirsbrunner and Wangersky, 1975). The filtered samples were not rinsed with distilled water to lessen the risk of contamination.

The following types of suspended loads were sampled:

1. loads from south-trending coastal currents along the Swedish east coast;
2. loads from waters passing over different sills located at several places in the Gulf of Bothnia and the Baltic proper;
3. loads from the current gyres in the Baltic proper.

Microscopic and microprobe studies

In the laboratory, all samples were examined under a binocular microscope to check for contamination, and four samples were analyzed in an electron microsond (JEOL) with a Keeves energy dispersive system. Fecal pellets, copepods, diatoms, coccoliths (?), fibers, eggs and crystalline particles (quartz, feldspars, micas, some with ferric hydroxide coatings) were noticed, but no metallic particles (e.g. from wire) could be observed. Paint and rust flakes from the ship were searched for in vain; thus no particles with measurable quantities of Mn, Pb, Cr, Ti or with much Fe were found. The abundant organic particles were easily recognized in the microsond by their morphologies, by their low counting rates and the presence of Na, Si, S, P and Cl.

Emission spectrometric analyses

To ensure a contaminant-free environment, a separate laboratory was used where handling of metal-rich samples such as ores was prohibited. Also,
### TABLE I

Comparison of different digestion procedures of suspended matter (μg l⁻¹)

<table>
<thead>
<tr>
<th>Method</th>
<th>Na</th>
<th>Sr</th>
<th>Si</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>V</th>
<th>Zr</th>
<th>Cr</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-HClO₄</td>
<td>6.3</td>
<td>0.06</td>
<td>2.2</td>
<td>29</td>
<td>1070</td>
<td>11</td>
<td>0.09</td>
<td>0.22</td>
<td>0.15</td>
<td>0.11</td>
<td>0.33</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>HNO₃-bomb</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>LiBO₂ fusion</td>
<td>10.3</td>
<td>0.08</td>
<td>64</td>
<td>1.7</td>
<td>28</td>
<td>820</td>
<td>11</td>
<td>0.07</td>
<td>0.19</td>
<td>0.15</td>
<td>0.14</td>
<td>0.28</td>
<td>0.50</td>
</tr>
<tr>
<td>(\bar{x})</td>
<td>8.3</td>
<td>0.073</td>
<td>1.95</td>
<td>28.5</td>
<td>920</td>
<td>10.3</td>
<td>0.08</td>
<td>0.20</td>
<td>0.15</td>
<td>0.13</td>
<td>0.32</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>S.D.</td>
<td>2.8</td>
<td>0.012</td>
<td>0.35</td>
<td>0.7</td>
<td>130</td>
<td>0.6</td>
<td>0.01</td>
<td>0.02</td>
<td>0.00</td>
<td>0.02</td>
<td>0.04</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>(S_{rel} (%))</td>
<td>34</td>
<td>16</td>
<td>18</td>
<td>2</td>
<td>14</td>
<td>5</td>
<td>18</td>
<td>10</td>
<td>0</td>
<td>16</td>
<td>13</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

The mean values (\(\bar{x}\)), standard deviations (S.D.) and relative standard deviations (\(S_{rel}\)) reveal a good agreement between the different methods to the extent a comparison is relevant (many silicate-bound elements do not dissolve in HNO₃). Repeated metaborate digestions show that Si can be determined with great precision. Similar studies of Ba (B. Boström, personal communication) show the same general precisions as those for Mn. Accuracies are good as is shown in Burman et al. (1978, 1979) and Burman (1979).
TABLE II

Test of analytical methods (all concentrations in weight-%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Analysis</th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
<th>Sr</th>
<th>Si</th>
<th>Ti</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Ba</th>
<th>Ni</th>
<th>V</th>
<th>Zr</th>
<th>Cr</th>
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</tr>
</tbody>
</table>


\(^a\) \(X_1\) and \(X_2\) represent the analyses of 10.7 and 3.6 mg aliquots of the standard rock. BR (a basalt), presented as unknown samples; corresponding recommended values are given in the row BR(RV).

\(^b\) \(Y_1\) and \(Y_2\) represent the analyses of 10.9 and 3.0 mg aliquots of the standard rock GSN (a granite), presented as unknown samples; corresponding recommended values are given in the row GSN(RV).

Recommended values from Roubault et al. (1970) and de la Roche and Govindaraju (1975); values for \(X_1\), \(X_2\), \(Y_1\) and \(Y_2\) tend to be slightly lower than the recommended values. This is probably due to some incorporation of moisture from air, causing a weight-increase before analysis. However, the mutual proportions between the elements are little affected.
Mean compositions of suspended matter in the Baltic and adjacent waters (given in % of ashed material). For distribution of stations see Fig. 1

<table>
<thead>
<tr>
<th>Sample type</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\bar{x})</td>
<td>S.D.</td>
<td>(\bar{x})</td>
<td>S.D.</td>
<td>(\bar{x})</td>
</tr>
<tr>
<td>Na(%)</td>
<td>10.2</td>
<td>1.3</td>
<td>8.2</td>
<td>1.9</td>
<td>22.3</td>
</tr>
<tr>
<td>Ca(%)</td>
<td>3.8</td>
<td>0.4</td>
<td>3.1</td>
<td>0.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Mg(%)</td>
<td>1.9</td>
<td>0.2</td>
<td>1.7</td>
<td>0.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Si(%)</td>
<td>17.2</td>
<td>1.7</td>
<td>18.8</td>
<td>2.2</td>
<td>8.1</td>
</tr>
<tr>
<td>Ti(%)</td>
<td>0.10</td>
<td>0.02</td>
<td>0.18</td>
<td>0.02</td>
<td>0.11</td>
</tr>
<tr>
<td>Al(%)</td>
<td>3.2</td>
<td>0.5</td>
<td>4.1</td>
<td>0.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Fe(%)</td>
<td>3.8</td>
<td>1.0</td>
<td>3.9</td>
<td>0.9</td>
<td>2.2</td>
</tr>
<tr>
<td>Mn(%)</td>
<td>0.20</td>
<td>0.03</td>
<td>0.18</td>
<td>0.04</td>
<td>0.13</td>
</tr>
<tr>
<td>Ba(%)</td>
<td>0.12</td>
<td>0.05</td>
<td>0.078</td>
<td>0.024</td>
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</tr>
<tr>
<td>Sr(ppm)</td>
<td>560</td>
<td>90</td>
<td>390</td>
<td>55</td>
<td>480</td>
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<tr>
<td>Ni(ppm)</td>
<td>54</td>
<td>38</td>
<td>26</td>
<td>4</td>
<td>33</td>
</tr>
<tr>
<td>V(ppm)</td>
<td>73</td>
<td>36</td>
<td>75</td>
<td>14</td>
<td>75</td>
</tr>
<tr>
<td>ST</td>
<td>TC(^b)</td>
<td>BL(^c)</td>
<td>TC</td>
<td>BL</td>
<td>TC</td>
</tr>
<tr>
<td>n</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>100 \cdot Mn/Al</td>
<td>6.3</td>
<td>4.4</td>
<td>5.7</td>
<td>2.8</td>
<td>5.9</td>
</tr>
<tr>
<td>100 \cdot Ba/Al</td>
<td>3.8</td>
<td>1.9</td>
<td>1.6</td>
<td>1.1</td>
<td>2.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample type</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\bar{x})</td>
<td>S.D.</td>
<td>(\bar{x})</td>
<td>S.D.</td>
</tr>
<tr>
<td>Na(%)</td>
<td>13.1</td>
<td>5.9</td>
<td>19.5</td>
<td>4.8</td>
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<tr>
<td>Ca(%)</td>
<td>2.8</td>
<td>0.8</td>
<td>2.7</td>
<td>0.7</td>
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<tr>
<td>Mg(%)</td>
<td>2.3</td>
<td>0.6</td>
<td>3.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Si(%)</td>
<td>16.2</td>
<td>5.0</td>
<td>11.9</td>
<td>4.9</td>
</tr>
<tr>
<td>Ti(%)</td>
<td>0.20</td>
<td>0.09</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>Al(%)</td>
<td>4.4</td>
<td>1.9</td>
<td>2.1</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Fe (%)</td>
<td>Mn (%)</td>
<td>Ba (%)</td>
<td>Sr (ppm)</td>
</tr>
<tr>
<td>---</td>
<td>--------</td>
<td>--------</td>
<td>--------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>0.15</td>
<td>0.058</td>
<td>360</td>
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<tr>
<td></td>
<td>2.3</td>
<td>0.06</td>
<td>0.024</td>
<td>85</td>
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<tr>
<td></td>
<td>1.1</td>
<td>0.19</td>
<td>0.021</td>
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<td></td>
<td>0.6</td>
<td>0.11</td>
<td>0.009</td>
<td>51</td>
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<td>0.70</td>
<td>0.15</td>
<td>0.023</td>
<td>266</td>
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<td></td>
<td>0.87</td>
<td>0.07</td>
<td>0.005</td>
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<td>2.3</td>
<td>0.16</td>
<td>0.047</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>0.02</td>
<td>0.022</td>
<td>90</td>
</tr>
<tr>
<td>ST</td>
<td>100 \cdot Mn/Al</td>
<td>3.4</td>
<td>9.0</td>
<td>6.5</td>
</tr>
<tr>
<td>BL</td>
<td>n</td>
<td>14</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>EW(^d)</td>
<td></td>
<td></td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>EW</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) NM = not measured; \(^b\) TC = from thermocline; \(^c\) BL = from bottom layer; \(^d\) EW = from extended water column.

\(\bar{x}\) and S.D. represent the arithmetic mean and standard deviation and \(n\) indicates the number of analyses used for averaging. Data for Na, Ca, Mg and Sr (?) are disturbed by sea salts, particularly the samples from the southern Baltic proper.

Columns 1 and 2 represent mean compositions of suspended matter from the Bothnian Bay (summer stations 1—4), columns 3 and 4 matter from the Bothnian Sea and Northern Baltic (summer stations 5, 6, 8—11, 13, 15 and 17—19). Column 5 shows the mean of data in columns 1 and 3, and column 6 the mean of data in columns 2 and 4. Column 7 represents fall stations 4, 5 and 7—11 and column 8 the fall stations 1—3 and 6. Column 9 represents the mean composition of suspended matter, based on grouped (weighted) data from columns 5—8.
TABLE IV

Load of suspended matter in Baltic and adjacent waters (μg l⁻¹ ashed material)

<table>
<thead>
<tr>
<th>Sample group</th>
<th>̄x</th>
<th>S.D.</th>
<th>n</th>
<th>Sample type</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.17</td>
<td>0.02</td>
<td>4</td>
<td>TC</td>
<td>Bothnian Bay</td>
</tr>
<tr>
<td>2</td>
<td>0.32</td>
<td>0.04</td>
<td>4</td>
<td>BL</td>
<td>Bothnian Bay</td>
</tr>
<tr>
<td>3</td>
<td>0.22</td>
<td>0.09</td>
<td>15</td>
<td>TC</td>
<td>Bothnian Sea and</td>
</tr>
<tr>
<td>4</td>
<td>0.38</td>
<td>0.24</td>
<td>15</td>
<td>BL</td>
<td>Northern Baltic</td>
</tr>
<tr>
<td>5</td>
<td>0.21</td>
<td>0.02</td>
<td>19</td>
<td>TC</td>
<td>Whole Gulf of Bothnia</td>
</tr>
<tr>
<td>6</td>
<td>0.37</td>
<td>0.02</td>
<td>19</td>
<td>BL</td>
<td>and Northern Baltic</td>
</tr>
<tr>
<td>7</td>
<td>0.53</td>
<td>0.17</td>
<td>9</td>
<td>EW</td>
<td>Open Baltic proper</td>
</tr>
<tr>
<td>8</td>
<td>1.16</td>
<td>0.74</td>
<td>6</td>
<td>EW</td>
<td>Straits area</td>
</tr>
<tr>
<td>9</td>
<td>0.43</td>
<td>0.29</td>
<td>53</td>
<td></td>
<td>Whole Baltic</td>
</tr>
</tbody>
</table>

* For further details on the various sample groups, see corresponding column number in Table III and Fig. 1.

unused filters were analyzed routinely, but their contributions to the measured element readings were insignificant.

Three digestion methods were studied (see Table I), namely: (1) an HF-HClO₄ dissolution; (2) digestion with HNO₃ in a teflon bomb; and (3), fusion of ashed material in LiBO₂ at 1000°C in a platinum crucible and subsequent HNO₃ dissolution. This last method is the most superior. An organic-matter-rich suspended phase from the Lule river was used for this study.

The analyses were performed with an emission spectrograph (ARL 33000), with an inductively coupled plasma (ICP) as excitation source. Repeated analyses of rock standards indicated good reproducibilities and accuracies in the methods, (Burman et al., 1978; Burman, 1979; Burman and Boström, 1979), not the least for the important elements Al, Ti, Fe, Mn and Ba, (Table II).

RESULTS

The variations in suspended matter composition and load are considerable (Tables III and IV; Fig. 2), variations that are real and not due to analytical errors. The suspended load in the straits is much larger than in the Gulf of Bothnia and northern Baltic proper, and loads at the thermocline are generally smaller than at the bottom. Chemical compositions likewise show variations; Ba and Fe for instance show higher values relative to Al in the Bothnian Bay than in the rest of the Baltic.

However, more data are needed for a detailed description of the different regions. Thus, in the Bothnian Bay the spring flood reaches a maximum in late May—early June, whereas the corresponding flood maxima are reached earlier further south. Hence, the Ba and Fe maxima in the loads from the Bothnian Bay may be caused by massive inputs of Fe-Ba-rich river waters during the sampling period, whereas such inputs had already taken place.
Fig. 2. Inter-element correlations for (a) Al and Ti, (b) Al and Si and (c) for Al and Fe. The correlation coefficients are significant at the 1% level; for further details, see text and Table VI. The solid lines represent the best-fit regression line, calculated with Al as independent variable: (○) samples from Bothnian Bay; (■) samples from Bothnian Sea and the main part of Baltic proper; and (▲) samples from the straits area.
### TABLE V

Composition of various suspended matters and pelagic sediments

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (%)</td>
<td>23</td>
<td>20</td>
<td>22</td>
<td>11</td>
<td>19</td>
<td>12.9</td>
<td>27.7</td>
<td>28</td>
<td>33</td>
</tr>
<tr>
<td>Ti (%)</td>
<td>0.26</td>
<td>~0.036</td>
<td>0.05</td>
<td>0.07</td>
<td>0.10</td>
<td>0.16</td>
<td>0.62</td>
<td>0.51</td>
<td>0.30</td>
</tr>
<tr>
<td>Al (%)</td>
<td>8.4</td>
<td>0.7</td>
<td>1.0</td>
<td>1.1</td>
<td>1.9</td>
<td>1.1</td>
<td>3.1</td>
<td>9.6</td>
<td>7.6</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>4.5</td>
<td>0.3</td>
<td>0.7</td>
<td>0.6</td>
<td>0.7</td>
<td>1.8</td>
<td>2.3</td>
<td>5.7</td>
<td>5.5</td>
</tr>
<tr>
<td>Mn (%)</td>
<td>0.34</td>
<td>0.02</td>
<td>0.06</td>
<td>0.06</td>
<td>0.08</td>
<td>0.10</td>
<td>0.16</td>
<td>0.090</td>
<td>0.45</td>
</tr>
<tr>
<td>Ba (ppm)</td>
<td>330</td>
<td>200</td>
<td>220</td>
<td>210</td>
<td>710</td>
<td>470</td>
<td>560</td>
<td>1100</td>
<td>1700</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>63</td>
<td>70</td>
<td>140</td>
<td>60</td>
<td>200</td>
<td>110</td>
<td>33</td>
<td>100</td>
<td>110</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>56</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>&lt;50</td>
<td>110</td>
<td>76</td>
<td>160</td>
<td>120</td>
<td>91</td>
</tr>
</tbody>
</table>

Baltic suspended matter: (1) rich in terrigenous material (Emelyanov and Pustelnikov, 1976); (2) rich in diatomaceous material (Emelyanov and Pustelnikov, 1976); (3) rich in organic material (Emelyanov and Pustelnikov, 1976); (4) mean values, suggested by Emelyanov and Pustelnikov, 1976; (5) mean values (Table III, this work).

River suspensates: (6) mean data for several major rivers (based on data in Martin and Meybeck, 1979).

Pelagic sediments: (7) sediments from Atlantic Ocean (mean of values from table 13, columns 1 and 2, Boström, 1976); (8) mean composition of Pacific Ocean sediments, deposited near the continents. Such sediments account for some 30% of all Pacific sediments (Boström 1976; region I in tables 1 and 2); (9) mean composition of all Pacific Ocean pelagic sediments (Boström, 1976; region L in Table 2).
when suspensions further south were sampled. Also sea-state controls the size of the suspended load. During the summer cruise the weather was abnormally calm with winds of less than 8 knots during most of the cruise, whereas the fall cruise took place in normal weather, i.e. seas were moderately rough and winds typically ranged from 20–30 knots. Hence, some of the chemical variations (Table III) may be of a seasonal nature and the large standard deviations in the means make it difficult to detect statistically meaningful differences for some of the chemical data.

The data (Tables III and IV) show an acceptable agreement with data from Emelyanov and Pustelnikov (1976), (Table V) who reported an average suspended load in the Baltic of some 3 mg l\(^{-1}\); our mean value (Table IV, sample group 9) would suggest about 1 mg l\(^{-1}\) dry (not ashed) weight. The discrepancy may well be due to the calm sea state during our sampling. The comparison of chemical data in Table III (column 9) and in Table V (column 4) requires a correction for the water and organic matter content of the data by Emelyanov and Pustelnikov (1976), roughly corresponding to a doubling of the values; data for Ti, Al, Fe and Mn then show good agreements. The high contents of Ba in the Fe–Al-poor suspendates (Table V, columns 1–3) furthermore suggest a high Ba value for the mean in Table V. These agreements suggest that the data (Tables III and IV) can be used for a geochemical balance study of the Baltic. Furthermore, the Baltic suspensions resemble those in oceanic waters close to Europe (off the Iberian peninsula; Copin-Montegut and Copin-Montegut, 1972).

Some authors, e.g. Lal (1977), have expressed concern about the large suspended loads reported by Russian investigators, but the data from the Baltic by Emelyanov and Pustelnikov (1976) appear to be largely correct.

DISCUSSION

Nature of suspended matter

To understand the element relations, some correlation calculations have been made. However, correlations within closed data sets often yield misleading results (Chayes, 1967); to realize whether an apparent correlation is meaningful frequently requires further model testing, as will be demonstrated here.

The inter-element relations (see Fig. 2) suggest correlations between Al and Ti, the correlation coefficient \( r \) being 0.62, between Al and Si \( (r = 0.78) \) and between Al and Fe \( (r = 0.74) \). These three \( r \)-values are significant at the 1% significance level and suggest that most of the Si, Al, Ti and Fe are present in a terrigenous component.

Manganese shows no significant correlation with Al \( (r = 0.00) \) or with Fe \( (r = 0.08) \) and the partial correlation coefficient for Fe–Mn with the influence from Al removed \( (r = 0.12) \) is not significant even at 5% level. Most Mn is, therefore, probably admixed in suspended matter as a non-terrestrial phase. Likewise, the correlation Al–Ni \( (r = 0.24) \) is insignificant,
TABLE VI

Input components and comparison between real and model suspensates

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.61</td>
<td>30</td>
<td>106</td>
<td>6</td>
<td>94</td>
</tr>
<tr>
<td>Ti</td>
<td>0.0037</td>
<td>0.38</td>
<td>106</td>
<td>3</td>
<td>97</td>
</tr>
<tr>
<td>Al</td>
<td>0.027</td>
<td>7.09</td>
<td>99</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>Fe</td>
<td>0.063</td>
<td>4.72</td>
<td>92</td>
<td>4</td>
<td>96</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0018</td>
<td>0.072</td>
<td>21</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>Ba</td>
<td>0.0041</td>
<td>0.062</td>
<td>68</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0013</td>
<td>0.0051</td>
<td>121</td>
<td>43</td>
<td>57</td>
</tr>
<tr>
<td>V</td>
<td>0.00039</td>
<td>0.0099</td>
<td>63</td>
<td>11</td>
<td>89</td>
</tr>
</tbody>
</table>

(1) Mean composition of plankton. In weight % on a dry matter (100 °C) basis. Based on 188 analyses (Boström and Boström, 1980); (2) mean composition of post-glacial Mn-poor clay from the Baltic. In weight % on a dry matter (100 °C) basis (Bostrom and Ingri, 1980); (3) the fraction (%) of the real suspensate that is explained by a model mixture of 75% biological matter (column 1) and 25% terrigenous matter (column 2) (see also Fig. 4c); only Mn is poorly explained by the model, suggesting the presence of an additional Mn-phase; (4) the fraction (%) of the model mixture that is biogenous; (5) the fraction (%) of the model mixture that is terrigenous.

Note that the pronounced terrigenous nature of Si, Ti, Al and Fe is in excellent agreement with data in Figs. 2a–2e.

Fig. 3. Schematic model of the sedimentation in the Baltic, particularly that of suspended matter (SM). Rivers, abrasion, resuspending processes and the biosphere will introduce SM into the system. SM may either exit or deposit in the transient deposits in deep basins. The permanent deposit will be devoid of highly oxidized constituents, such as Mn, which will therefore not end up in the sink below the redox boundary (see also Table VII, column 4a). Some of the remobilized components will return to the biosphere or directly to SM and will eventually leave the Baltic. Note that SM may change composition, as indicated by SM$_1$, SM$_2$ and SM$_3$. 
Fig. 4. Comparisons of elemental abundancies in Baltic suspended matter with: (a) those in Mn-poor sediments, depositing below the redox cline in the Baltic. The solid line represents the best fit between the conservative elements Al, Ti and Fe, the dashed line the departure from this fit with a factor of 1.2. Vertical bars show the spread (1 sigma) in the data in Table III, column 9; the graph shows that suspended matter is enriched in Mn, Ba, V, Sr, Mg, Ca and Na; many of these excess elements are due to the biological component in suspended matter (see Fig. 4c) or the presence of sea salts (Na, Ca and Mg); (b) mean composition of plankton (the poor agreements demonstrate that biogenous phases alone cannot explain the composition of suspended matter); (c) a model suspensate, assumed to consist of one part Mn-poor sediment and three parts plankton (BM = biological matter); see also Table VI, which shows how much of the Ba, Ni, Ti, etc. that are biogenous and minerogenous. The calculations of the best-fit proportions of BM and Mn-poor sediment is described in Boström et al. (1978b).

In all graphs, concentrations (given in logarithmic units) are normalized such that $\Sigma(Fe + Al) = 1.0$. 
suggesting that Ni is partly admixed as another phase, probably in biogenous matter, as will be shown below. The relations of Al—Ba, Mn—Ba etc., also demonstrate that much Ba must have a non-terrigenous matter source.

Suspended matter may be rich in biogenic matter (detritus) or in elements that have been enriched in the suspended matter by biological activities (Emelyanov and Pustelnikov, 1976; Krishnaswami and Sarin, 1976; Sholkovitz and Price, 1980). This study confirms these conclusions. It is likely that wave action and other hydrodynamic conditions during rough weather will resuspend clayey matter that has settled during calm weather. This resuspended matter may mix physically and chemically (adsorption) with biological matter, i.e. the resulting suspension should chemically be a mixture of clayey matter and biological matter. Some aggregation of clay and biological matter may also take place within the water column (Hirsbrunner and Wangersky, 1975).

Table VI shows the mean compositions of plankton and Baltic post-glacial, manganese-poor clay, typical for the sediments located below the shallow redox cline. These sediments largely consist of reworked tills (Boström et al., 1978 a, b, Boström and Ingri, 1980), the dominating surface deposit in Scandinavia. This implies that the inorganic detritus in Scandinavian rivers is essentially identical to the sediments below the redox cline. Another reason for this assumption is that much of the subsurface abrasion in the Baltic involves much erosion, reworking and redeposition of till materials (Winterhalter, 1966; Boström et al., 1978). The relations between various sources of suspended matter and other geological processes are schematically shown in Fig. 3. It is therefore likely that the suspended matter should be a mixture of these Mn-poor clays and biological matter (see Fig. 4). Note that clay or biological matter alone cannot explain the composition of the suspended matters (see also Table VI).

**Mass of suspended matter leaving the Baltic**

The annual discharge from the Baltic is 460 km$^3$ (Mikulski, 1970). Assuming the average load of suspended matter to be 1.2 mg (ashed) material per liter with the composition in Table III, column 9, yields the element losses shown in Table VII. However, it is probable that suspended matter transport through the straits will be higher in rough weather, but this effect is partly offset by the south-westerly winds that predominate over Scandinavia during strong storms, i.e. waters tend to be pushed into the Baltic. As a conservative estimate we will therefore assume a mean load in the straits of some 3.6 mg ashed material per liter, thus obtaining the data shown in Table VII, columns 2a and 2b.

**Quantity of elements lost in the biomass**

The mean productivity in the Baltic is close to 100 g C m$^{-2}$ y (Ackefors, 1978). Since the area of the Baltic is $3.66 \times 10^{11}$ m$^2$ and the volume is
TABLE VII

Geochemical balance of the Baltic

<table>
<thead>
<tr>
<th>Element</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>12.9</td>
<td>71 200</td>
<td>214 000</td>
<td>0.61</td>
<td>16 000</td>
<td>30</td>
<td>25 000 000</td>
</tr>
<tr>
<td>Ti</td>
<td>0.16</td>
<td>880</td>
<td>2 650</td>
<td>0.0037</td>
<td>96</td>
<td>0.38</td>
<td>320 000</td>
</tr>
<tr>
<td>Al</td>
<td>3.1</td>
<td>17 100</td>
<td>51 300</td>
<td>0.027</td>
<td>700</td>
<td>7.09</td>
<td>6 000 000</td>
</tr>
<tr>
<td>Fe</td>
<td>2.3</td>
<td>12 700</td>
<td>38 100</td>
<td>0.063</td>
<td>1 600</td>
<td>4.72</td>
<td>4 000 000</td>
</tr>
<tr>
<td>Mn</td>
<td>0.16</td>
<td>880</td>
<td>2 650</td>
<td>0.0018</td>
<td>47</td>
<td>0.072</td>
<td>60 000</td>
</tr>
<tr>
<td>Ba</td>
<td>0.047</td>
<td>260</td>
<td>780</td>
<td>0.0041</td>
<td>107</td>
<td>0.062</td>
<td>52 000</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0033</td>
<td>18</td>
<td>55</td>
<td>0.0013</td>
<td>34</td>
<td>0.0051</td>
<td>4 300</td>
</tr>
<tr>
<td>V</td>
<td>0.0076</td>
<td>42</td>
<td>126</td>
<td>0.00039</td>
<td>10</td>
<td>0.0099</td>
<td>8 300</td>
</tr>
</tbody>
</table>

(1) Composition of average suspended matter (in weight %, from Table III, column 9); (2) annual efflux of suspended matter from the Baltic, assuming average drainage to be 460 km$^3$ and the mean suspended load to be 1.2 mg l$^{-1}$ (column a) and 3.6 mg l$^{-1}$ (column b) (all values in tons); (3a) mean composition of plankton, given in weight-% on a dry basis; (3b) annual loss in biological matter by drainage in the straits (all values in tons) — this does not represent an additional loss but rather the biological fraction in the total suspended load, given in column 2; (4a) composition of post-glacial Baltic Mn-poor sediment, depositing permanently below the redox boundary; (4b) annual permanent accumulation below the redox boundary in Baltic sediments (all values in tons); (5) quantity of matter removed annually from the Baltic in suspended matter (from columns 2a and 2b) given in % of total sedimentation (from column 4b); (6) quantity of matter lost annually from the Baltic in biological matter (from column 3b) in % of total sedimentation (from column 4b). It should be realized that the removed biological matter shown here is admixed with the total suspended matter listed in column 5; i.e. this column shows how large a fraction of the total suspended matter is made up of biological products; (7) fraction of suspended matter that represents biogenous products, obtained from data in columns 2b and 3b.
of which 2.1% is drained annually (Mikulski, 1970), one finds that $7.7 \times 10^{11}$ g C is lost annually from the Baltic. One formula unit C corresponds to one unit CH$_2$O, assuming a simplified composition of the soft tissue in plankton. Furthermore, ash material usually makes up some 25%, of the dry weight (100°C) of plankton, that is, the total mass of plankton is 3.33 times larger than that of C. This means that $2.6 \times 10^{12}$ g plankton is lost annually from the Baltic, resulting in the element losses in Table VII, column 3b.

In these calculations, no losses of biogenous matter are assumed to take place within the Baltic as should be expected (Eppley and Peterson, 1979). However, much of the biogenous matter is returned to the biosphere by bacterial processes in the top layers of the bottom as is also shown by the composition of the permanently depositing sediments, (Table VI, column 2; Fig. 3).

**Total mass of elements lost in permanent sediments**

Wave action and currents create a constant stirring and resuspension of the bottom deposits in shallow regions of the Baltic, and only at depths exceeding ~65 m does permanent deposition of post-glacial sediments take place, where they accumulate at a rate of ~1 mm y$^{-1}$ (Hallberg et al., 1973; Bostrom and Ingri, 1980). Thus, the total mass of permanently depositing matter is $0.60 \times 0.1 \times 140 \times 10^7$ tons or $8.4 \times 10^7$ tons, assuming the density of dry matter uncompressed in situ to be 0.60 and knowing that water depths over 65 m cover 140 000 km$^2$ (Ehlin and Mattisson, 1976).

The post-glacial sediments in the Baltic are basically of two types, namely an oxidized brown upper layer, rich in Mn, and a lower grey reduced zone, poor in Mn. The top layer, however, is very thin (~2 cm) and clearly represents a transient deposit, which redox processes transform into the grey reduced type found below the redox cline; in some regions the latter is even located in the water mass, i.e. the brown top layers are missing. Some of these processes have been described by Hallberg et al. (1973) and Holm (1978); see also Fig. 3. To study the chemical balance of the Baltic, it is therefore necessary to know the composition and mass of this permanently depositing phase. Combining the mean sediment composition in Table VII, column 4a (Boström and Ingri, 1980) and the mass that permanently deposits in the Baltic yields the quantities in Table VII, column 4b.

**The total geochemical balance in the Baltic**

Obviously, several errors affect the results in Table VII, but the estimates here should be an aid in future research. The present model only shows overall losses; too little is known to permit a detailed balance to be established for each of the various subdivisions of the Baltic (Gulf of Bothnia etc.). The data do show clearly, however, that the suspended matter preferentially removes Mn, Ba, Ni and V from the Baltic compared to the major elements Si,
Much of this selective loss is explained by biological matter alone as data in Table VII (columns 3, 4 and 6) reveal. Comparing these values (column 7 in Table VII) with data in Table VI shows an excellent agreement. These results support the assumption that the average suspended load in the outstreaming waters in the straits might be closer to 4 mg l\(^{-1}\) than 1 mg l\(^{-1}\).

**Suspended matter as a source of pelagic sediments**

Particulate transport is probably of great importance for many elements that eventually end up in the pelagic sediments. The striking similarities between the suspended matter studied here, Atlantic pelagic sediments and Pacific pelagic sediments depositing near the continents (Table V, Fig. 5) support this assumption. Fairly large discrepancies are registered, however, for Ba, Mn and Ni when mean Pacific sediments are compared with suspended matter, but this is to be expected because of volcanic contributions of Mn and Ba in the Pacific, and the additional mobilization of elements because of redox processes in hemipelagic sediments (Bezrukov, 1960; Bonatti et al., 1971; Boström, 1976).

The mean world river particulates (Martin et al., 1979; and see Table V, column 6) show poorer resemblance with pelagic sediments than the Baltic suspendates do. This is probably due to the fact that coarse terrigenous matter in rivers will not travel far beyond the river mouth, and that debouching

![Fig. 5. Comparison of Baltic suspended matter with pelagic sediments: (▲) = mean Atlantic Ocean pelagic sediment (see Table V, column 7); (●) = mean Pacific Ocean pelagic sediments, formed close to continents (see Table V, column 8); (○) = mean data for total Pacific pelagic sediments (only shown for Mn, Ba, V and Ni since Al, Ti, Fe and Si values are similar). Before plotting all data have been normalized to a constant Σ(Al + Fe); all values in logarithmic abundances.]
fine terrigenous particles will probably pick up additional biogenic matter in the estuaries, i.e. they approach the Baltic suspendates and mean pelagic sediments in composition.

In this context, the geochemical behaviour of Mn is critical. Suspended matter is generally enriched in Mn relative to iron (Emelyanov and Pustelnikov, 1976; Krishnaswami and Sarin, 1976; Sundby, 1977; Baker and Feely, 1978; Buat-Menard and Chesselet, 1979; this work) but some suspended matter seems to be depleted in Mn, with Fe/Al ratios below the terrigenous average (Sholkovitz and Price, 1980). However, most studies show an excess of Mn; the authors therefore feel that the results above are of a general significance.

Unsolved problems

No balances for the subregions of the Baltic can be established because of insufficient data, but some questions may be noted. The sediments in the Bothnian Bay have higher Mn/Fe values than those in the Bothnian Sea (Boström et al., 1978a) but the suspended loads (Table II) suggest the opposite trend; some of the highest Ba values are found in the Bothnian Sea, whereas the suspended matter is richest in Ba in the Bothnian Bay. Obviously, more work is required to solve the problem of how suspended matter participates in the sedimentation processes in the Baltic. Furthermore, the model here ignores to what extent Mn-rich muds in the Baltic also partake in the formation of suspended matters (see Fig. 3). This simplification has no effect on the net loss of traces from the Baltic but implies an additional complication in the mechanisms that are involved when the suspended phases are formed.

CONCLUSIONS

Suspended matter in the Baltic is enriched in Ba, Mn, Ni and V compared to the permanently depositing post-glacial sediments. Losses of such suspended matter from the Baltic explain the paucity of Ba, Mn, Ni and V in Baltic sediments.

Biogenous constituents form a significant part of the suspended matter in the Baltic, in contrast to average world river suspendates which are richer in terrigenous constituents. Suspended matter of the Baltic "type" shows a far-reaching similarity with pelagic sediments in the Atlantic and Pacific oceans, suggesting a genetic relationship.

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A Geochemical Massbalance for the Baltic

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Abstract
The river discharge of most major and trace elements into the Baltic is vaguely known and only for a few components are good figures available for several rivers. Furthermore, most rivers are regulated, i.e., they are affected by human activities. Therefore, data obtained now do not necessarily reflect conditions in the past.

The suspended and dissolved load in the waters leaving the Baltic roughly equals the quantities delivered by rivers, except for a selective loss (compared to crustal abundances) of Mn, Ba, Ni, Cu and Zn. Only 2% of all Al and Ti in the Baltic element budget are lost from the Baltic, the corresponding figure for Mn is 16%; the balances end up in the permanently depositing sediments below the redox cline. The budget figures furthermore show that abrasion accounts for 50-95% of all recent sediments.

Several local cycles control the distribution of, e.g., As, P, Mn and Ba. Nodules cover extensive bottom areas in the Gulfs of Bothnia, Finland and Riga and explain much of the deposition of these elements. Redox processes likewise explain variations for other elements, e.g., for Mn and S, in the sediments.

A comparison of the metal abundance patterns for the Baltic with clean reference areas like the Barents sea do not suggest a severe degree of pollution, and the As/Fe or Ba/Fe ratios in Baltic nodules are similar to those in nodules from the World Ocean.

Introduction
The Baltic may be considerably polluted on a regional scale by heavy metals (Olausson et al., 1977), but post-depositional fractionation processes obscure or accentuate original element patterns (Suess, 1978). There are furthermore serious difficulties to determine low levels of, for instance, Hg, Pb and Cd (Roseman & De Laeter, 1980) and the knowledge of the geochemical element cycles in the Baltic and its drainage areas is incomplete. The presence of, e.g., 1000-2000 ppm As in geological products is not necessarily an indicator of pollution – the association P-As-Fe is well known in oxidized sediments and concretions (Goldschmidt, 1954; Boström & Valdés, 1969; Boström et al., 1982). Alternatively, the presence of such element associations may indicate that natural pollution-controlling mechanisms act efficiently.

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 S-106 91 Stockholm, Sweden
To partly alleviate this situation we have studied element transports into and out of the Baltic in dissolved and particulate form and studied to what extent some components accumulate permanently below the redox cline in the sediments. A more detailed report of these results will be given elsewhere. Although our data are still incomplete and approximative in character several selective losses of elements are now well documented.

We will first give an account of what is known about the transports of particulate and dissolved components. The water exchange in the Baltic is shown in Fig. 1.

**River Discharges**

Measurements in several Swedish rivers of five elements (Fe, Mn, Cu, Pb and Zn) over a period of two years were reported by Ahl (1975), but only few rivers that drain into the Baltic have been analyzed for a large number of elements on

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**Figure 1.** Map, showing the subdivision of the Baltic, the drainage areas and the water exchanges (after Falkenmark, 1976). Note that there is a considerable amount of salt water from Kattegatt entering the Baltic as a bottom current. The Gulf of Bothnia is the single largest fresh water supplier to the Baltic proper.
a long term basis, namely the Kalix, Torneå, Rånéa and Töre rivers (Burman, 1982, 1983). Data by both Ahl (1977) and Burman (1982, 1983) show that north Scandinavian rivers are significant sources of Fe and Mn.

Suspended matter from the Kalix, Torneå, Töre and Rånéa rivers differs much from suspended matters in other Baltic rivers (Burman, 1982, 1983), in which the Fe-Al ratio often is close to 0.5, whereas it is 5.0 in, e.g., the Kalix river. Iron-rich suspended matters have also been reported for other rivers, e.g., the Monongahela river (Kopp & Kroner, 1967), where Fe/Al is larger than 5.7 in the suspended phase; also the Nile has fairly iron-rich suspended loads (Martin & Meybeck, 1978). There is furthermore a close tie between the presence of iron-rich river suspensions and the iron-rich concretions, which occur in large abundances in the Northern Gulf of Bothnia, Gulf of Finland and Gulf of Riga. Possibly the whole Boreal region, which is characterized by coniferous forests and cold-continental climates, is a weathering region, where iron-rich suspended matter is preferentially produced. Southern Sweden and the areas of Central Europe that face the southern Baltic are dominated by semi-continental climates and mixed forests of the northern European plain-type. It is characteristic that adjacent regions of the Baltic are poor in iron-manganese nodules; likewise Ahl (1977) reported considerably lower iron contents in Swedish rivers from this region. Also, Burman (1982, 1983) filtered and then acidified his samples already in the field, whereas in other studies often no filtration was performed and acidification takes place first after prolonged transport. There are thus reasons to expect large variations in data from different authors, as was pointed out also by Livingstone (1963). Another reason for large regional variations is that most Baltic rivers are regulated; Kalix, Töre, Rånéa and Torneå rivers are among the few free-flowing ones. Ahl (1977) demonstrated that the Kalix river contains five times more iron than the regulated Luleå river, in spite of the fact that both drain geologically, botanically and climatically very similar regions. The Kalix river may therefore be fairly representative of an undisturbed system in northern Scandinavia. The river discharge figures in Table 1 represent mean estimates using several sources.

The annual discharge of river water into the Baltic is about 470 km$^3$, which equals the net drainage of the Baltic since evaporation and precipitation balance each other, see also Fig. 1.

**Composition of Baltic Sea Water**

**Suspended phases**

Baltic suspended matters have been studied by Emelyanov & Pustelnikov (1976), by Bostrom et al. (1981) and by Lisitsin & Emelyanov (1981); reported analyses show good agreements. The amount of suspended matter (ashed fraction) is frequently about 1 mg l$^{-1}$ in the southern Baltic and in the Sound, but values as high as 5.5 mg l$^{-1}$ have been reported by Krey (1974). It is reasonable to assume that a somewhat elevated value must be used for a balance calculation, since measurements are rarely made in stormy weather when the suspended load is highest; as in rivers it is likely that the material transport is most intense during periods of rapid water flow. We will here assume the values
Table 1. Material supplied annually by rivers to the Baltic Sea.

<table>
<thead>
<tr>
<th></th>
<th>From rivers draining to the Gulf of Bothnia; WF = 180 km$^3$ yr$^{-1}$</th>
<th>From rivers draining to the remaining Baltic Sea; WF = 290 km$^3$ yr$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SM in $10^6$ kg yr$^{-1}$</td>
<td>Mean comp. (µg l$^{-1}$)</td>
</tr>
<tr>
<td>Si</td>
<td>232</td>
<td>2243</td>
</tr>
<tr>
<td>Al</td>
<td>71</td>
<td>57</td>
</tr>
<tr>
<td>Ti</td>
<td>4.7</td>
<td>nd</td>
</tr>
<tr>
<td>Fe</td>
<td>188</td>
<td>300</td>
</tr>
<tr>
<td>Mn</td>
<td>5.0</td>
<td>21</td>
</tr>
<tr>
<td>Ba</td>
<td>0.81</td>
<td>7</td>
</tr>
<tr>
<td>Cu</td>
<td>0.12</td>
<td>6</td>
</tr>
<tr>
<td>Zn</td>
<td>0.46</td>
<td>6</td>
</tr>
<tr>
<td>Ni</td>
<td>0.094</td>
<td>0.4</td>
</tr>
<tr>
<td>Zr</td>
<td>0.22</td>
<td>nd</td>
</tr>
<tr>
<td>V</td>
<td>0.18</td>
<td>nd</td>
</tr>
</tbody>
</table>

Sources: For rivers draining to the Gulf of Bothnia: Burman (1982, 1983). For the other rivers the averages and other data are estimated using data in Martin & Meybeck (1978, 1979) and in Riley & Chester (1971).

SM = suspended matter     DM = dissolved matter     nd = no data     WF = net water flux
Table 2. Export of material through Northern Kvark, Southern Kvark and the Sound.

<table>
<thead>
<tr>
<th></th>
<th>N. Kvark; WF = 100 km³ yr⁻¹</th>
<th>S. Kvark; WF = 180 km³ yr⁻¹</th>
<th>Sound; WF = 470 km³ yr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SM composition (%)</td>
<td>DM (µg l⁻¹)</td>
<td>Total load (10⁶ kg yr⁻¹)</td>
</tr>
<tr>
<td>Si</td>
<td>19.9</td>
<td>520</td>
<td>72.0</td>
</tr>
<tr>
<td>Al</td>
<td>4.04</td>
<td>0.6</td>
<td>4.1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.15</td>
<td>nd</td>
<td>~0.15</td>
</tr>
<tr>
<td>Fe</td>
<td>3.63</td>
<td>16</td>
<td>5.2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.19</td>
<td>2.8</td>
<td>0.24</td>
</tr>
<tr>
<td>Ba</td>
<td>0.067</td>
<td>14.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Cu*</td>
<td>0.011</td>
<td>0.5</td>
<td>0.061</td>
</tr>
<tr>
<td>Zn*</td>
<td>0.036</td>
<td>2.0</td>
<td>0.24</td>
</tr>
<tr>
<td>Ni*</td>
<td>0.0060</td>
<td>0.5</td>
<td>0.056</td>
</tr>
<tr>
<td>Zr</td>
<td>0.0087</td>
<td>nd</td>
<td>0.009</td>
</tr>
<tr>
<td>V</td>
<td>0.0067</td>
<td>nd</td>
<td>~0.007</td>
</tr>
</tbody>
</table>

SM load = 1.0 mg l⁻¹  SM load = 1.2 mg l⁻¹  SM load = 1.7 mg l⁻¹

WF = net water flux; SM = suspended matter; DM = dissolved matter and TSM = fraction of total load transported in suspended matter;

* data for concentration levels (DM) of Cu, Zn and Ni in the Sound derive from Magnusson & Rasmussen (1981);

the other Cu, Zn and Ni values are assumed to be similar.
given in the lower part of Table 2 to be realistic figures, but the values may be too low, particularly in view of the difficulty in estimating bottom winnowing; Boström et al. (1981) used 3.0 mg as a mean for the suspended load in the Danish straits. The suspended phases are strongly admixed with biological matter, representing both nano-plankton and biological detritus, as is shown by microscope, microprobe and geochemical analyses (Boström et al., 1981). This is particularly the case with suspended matters near the surface, whereas bottom waters are richer in suspended matter with much lithogenic material present.

The data in Table 2 are based on results in Boström et al. (1981) and on additional measurements from 27 stations, distributed evenly in the Gulf of Bothnia, the Baltic Proper and in the Sound; this field work was performed in the summer and fall of 1981. The suspended matter shows considerable synoptic variations, primarily in the Fe/Al ratios. The elevated Fe/Al ratios in Gulf of Bothnia are most certainly caused by the river discharges of suspended matters. The mean suspended phase that leaves the various drainage areas is shown in Table 2.

Dissolved matter

As with river water, fine particulates are frequently not removed before analysis, i.e., sea water analyses often include fines. To alleviate the lack of data for Baltic water we collected a total of 85 water samples in 1979 and 1981, representing surface, intermediary depth (pycnocline) and bottom water samples. The stations were evenly distributed through the Gulf of Bothnia, the Baltic Proper and in the Sound. The results are reported in Table 2, where they are combined with data by other authors. The sea water abundances of Si, Ba, Ni, Cu and Zn clearly indicate that much of these elements exist as dissolved components. Fe, Al and Mn on the other hand are to a large extent present as very fine particles that are not easily collected on a 0.45 μm Millipore filter; otherwise it would be hard to explain the difference in, e.g., Fe-values reported by the Mg(OH)₂ precipitation procedure (Koroleff, 1980) used by us and by the extraction procedure used by Danielson & Westerlund (1978) and Magnusson & Rasmussen (1981).

The resulting transport figures for dissolved and suspended matter are given in Table 2.

Composition of Baltic Sediments

The floor of the Baltic is covered by a wide range of sediments, but it is primarily the presently forming postglacial deposits that concern us here. They are basically of three different types:

a) Brown, well oxidized Fe-Mn rich sediments that occur at the top of the sediment layer. These sediments are only a few centimeters thick and are of a transient type, i.e., microorganisms decompose organic matter at the same time releasing much Fe, S and P (Hallberg et al., 1972; Holm, 1978; Bågander, 1977; Martens, 1978; Lindström 1980) which subsequently may enter into new phases. A typical migrating element is Mn (Manheim, 1965; Suess, 1978).
b) Grey to greenish-grey reduced manganese-poor sediments, which are located below the oxidized stratum described above. They represent the permanently accumulating postglacial sediments in the Baltic after the redox processes have terminated. In areas where the redox cline is located in the water mass this sediment also forms the sediment-water interface.

c) Iron-manganese concretions. These are related to the oxidized sediments, but are primarily found on local elevations with little or no permanent accumulation of loose unconsolidated sediments. Concretions are very abundant in the Gulf of Bothnia (Fig. 2).

Figure 2. Distribution of iron-manganese nodules in Gulf of Bothnia (Winterhalter, 1966; Boström et al., 1982). The shaded region lacks nodules of any significant size or frequency except for dark brown to rust colored hydroxide films; this area broadly coincides with bottom depths of 50–60 m or less. The most manganese and trace metal rich nodules (Ni, Cu, As) occur in the Bothnian Bay. Similar distribution patterns are reported for Gulf of Riga and Gulf of Finland by Varentsov & Blashechishin (1976). The Baltic proper on the other hand is comparatively poor in nodules (K. Boström and J. Ingri, unpublished results).
The composition of these sediments (a–c) are given in Table 3, where also data for glacial sediments and their fine fractions are presented.

The accumulation rates of the sediments in the Baltic are reasonably well known. Winterhalter et al. (1981) found accumulation rates of 0.5–1.5 mm yr⁻¹ in several depressions but considered the mean accumulation rates to be close to 0.1 mm yr⁻¹; this value was also used by Voipio & Niemistö (1979). Boström et al. (1981) used a higher estimate of 0.38 mm yr⁻¹, assuming that sediment accumulating areas cover 38% of the surface of the Baltic and that sediments there accumulate at 1 mm yr⁻¹. This figure was derived from numerous echo-sounding profiles, which reveal that sediment thicknesses of 7–9 m are good mean values for the postglacial deposits which have formed the last 7000 years. An accumulation rate of 1 mm yr⁻¹ for the last centuries was also observed by Hallberg (1976).

Soft accumulation bottoms cover some 27% of the floor of the total Baltic (Winterhalter et al., 1981). Adding 3% for areas with mixed bottom types yields a conservative figure of 30% or 110000 km² of the Baltic as a recipient of recent sediments. These form at a rate of 0.11 km³ yr⁻¹ if an accumulation rate of 1 mm yr⁻¹ is accepted.

These water-rich sediments must have low dry in-situ uncompressed densities (= DISUD). In deep sea sediments DISUD-values as low as 0.60 have been reported (Boström et al., 1976). Hence, in Baltic sediment a similar value is a reasonable estimate, i.e., the dry matter deposition is about $6.6 \times 10^{10}$ kg. The more conservative accumulation estimate of about 0.1 mm for the total Baltic would lead to a total dry matter deposition of $2.2 \times 10^{10}$ kg yr⁻¹.

**Eolian Components**

Eolian sediment transport is important at low latitudes, where arid climate types prevail (Rex & Goldberg, 1958; Delany et al., 1967; Prospero & Bonatti, 1969). The climate in the Baltic region shows the opposite patterns. Eolian transport is therefore probably of minor significance for most major and trace metal balances of the Baltic, although cyclic salts, sulfur and carbon particles may be transported on a large scale. The claim by Soviet scientists that 70–80% of all metals are brought to the Baltic by the atmosphere (Carlberg, 1981) hence appears unlikely; nor does the data by Pakarinen (1983) support this claim.

**Mass-Balance Studies**

**Basic entries in the balance sheet**

Although the compositions and transport rates of the components that flow in and out of or accumulate in the Baltic are incompletely known, enough data are available for a sketch of the basic features of the Baltic mass-balance (Tables 1–4).

The efflux values given in Tables 2 and 4 are probably reasonably good as concerns the relative element proportions. Table 4 shows that much Si, Ti, Al, Fe, Mn, Zr and V is lost in suspended matter; this is particularly the case in the Northern and Southern Kvark. Much Ba, Ni, Cu and Zn on the other hand is discharged in dissolved form (Table 2).
Table 3. Mean composition of Baltic sediments.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td>s.e.</td>
<td>X</td>
<td>s.e.</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Si (%)</td>
<td>28.0</td>
<td>2.6</td>
<td>30.8</td>
<td>0.8</td>
<td>3.2</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Ti (%)</td>
<td>0.23</td>
<td>0.01</td>
<td>0.37</td>
<td>0.03</td>
<td>0</td>
<td>0.047</td>
<td>0.23</td>
</tr>
<tr>
<td>Al (%)</td>
<td>5.4</td>
<td>0.4</td>
<td>6.7</td>
<td>0.2</td>
<td>0</td>
<td>0.56</td>
<td>2.13</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>6.9</td>
<td>1.3</td>
<td>4.2</td>
<td>0.2</td>
<td>3.5</td>
<td>25.9</td>
<td>35.2</td>
</tr>
<tr>
<td>Mn (%)</td>
<td>4.9</td>
<td>1.2</td>
<td>0.07</td>
<td>0.01</td>
<td>4.8</td>
<td>14.1</td>
<td>4.8</td>
</tr>
<tr>
<td>P (%)</td>
<td>0.33</td>
<td>0.030</td>
<td>0.15</td>
<td>0.016</td>
<td>0.21</td>
<td>1.55</td>
<td>2.15</td>
</tr>
<tr>
<td>Ba (%)</td>
<td>0.11</td>
<td>0.012</td>
<td>0.062</td>
<td>0.003</td>
<td>0.060</td>
<td>0.23</td>
<td>0.12</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>123</td>
<td>23</td>
<td>51</td>
<td>2</td>
<td>82</td>
<td>330</td>
<td>200</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>32</td>
<td>5</td>
<td>37</td>
<td>4</td>
<td>0</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>63</td>
<td>6</td>
<td>99</td>
<td>8</td>
<td>0</td>
<td>112</td>
<td>166</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>134</td>
<td>27</td>
<td>135</td>
<td>19</td>
<td>0</td>
<td>330</td>
<td>340</td>
</tr>
<tr>
<td>Zr (ppm)</td>
<td>146</td>
<td>15</td>
<td>216</td>
<td>11</td>
<td>0</td>
<td>31</td>
<td>50</td>
</tr>
<tr>
<td>Yb (ppm)</td>
<td>3.0</td>
<td>0.4</td>
<td>4.0</td>
<td>0.1</td>
<td>0</td>
<td>5.5</td>
<td>7.9</td>
</tr>
</tbody>
</table>

n = number of samples analyzed

1. Mean composition of oxidized layers of postglacial clay from three cores in Bothnian Bay.
2. Mean composition of reduced sections from three cores in Bothnian Bay.
3. Released (lost) components when oxidized sediments are reduced, assuming Al to be a conservative element.
4. Mean composition of rounded and ellipsoidal nodules from Gulf of Bothnia.
5. Mean composition of flat and slab-shaped Fe-Mn concretions from Gulf of Bothnia.
6. Mean composition of glacial deposits, mostly dredged from shallow regions in the Gulf of Bothnia at depths of 40–60 m, i.e., in areas where transport processes dominate.
7. Mean composition of the fine fraction (wet-sieved, less than 0.040 mm) of the glacial deposits under point 6. The dredge samples were obtained on outcrops of stiff till and other glacial deposits, where coring or grab-sampling was impossible to perform. Nevertheless, a small amount of oxidized sediment (as a thin layer on top of the tills, etc.) was almost always admixed in the dredging material. To remove this contamination it was assumed that the Mn-data in column 7 was 0.14% too high. Removing this quantity of Mn and proportional quantities of Fe, Al etc., using the proportions in column 1, yielded a "cleaned" fine fraction. This was used in the plot in Fig. 6.

Data in columns 1, 2, 6 and 7 from Boström & Ingri, 1982; 270 additional analyses of core samples from Gulf of Bothnia and 100 core samples from Baltic proper confirm the trends displayed in columns 1, 2, 6 and 7 (see also Fig. 4 and 5). Data in columns 4 and 5 derive from Boström et al. (1982); similar data are reported by Manheim (1965) and Winterhalter (1966).
Table 4. Geochemical mass-balances for the Gulf of Bothnia and the Baltic sea (total).

<table>
<thead>
<tr>
<th>Element</th>
<th>Supply from rivers (10^6 kg yr⁻¹)</th>
<th>Permanently deposited Mn-poor sediments</th>
<th>Material lost through</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GB</td>
<td>BS</td>
<td>Composition (%)</td>
</tr>
<tr>
<td>Si</td>
<td>640</td>
<td>2100</td>
<td>30.0</td>
</tr>
<tr>
<td>Al</td>
<td>81</td>
<td>200</td>
<td>7.09</td>
</tr>
<tr>
<td>Ti</td>
<td>&gt; 4.7</td>
<td>~12</td>
<td>0.38</td>
</tr>
<tr>
<td>Fe</td>
<td>240</td>
<td>310</td>
<td>4.72</td>
</tr>
<tr>
<td>Mn</td>
<td>8.8</td>
<td>13</td>
<td>0.072</td>
</tr>
<tr>
<td>Ba</td>
<td>2.1</td>
<td>5.7</td>
<td>0.062</td>
</tr>
<tr>
<td>Cu</td>
<td>1.2</td>
<td>3.3</td>
<td>0.0037</td>
</tr>
<tr>
<td>Zn</td>
<td>1.6</td>
<td>7.8</td>
<td>0.014</td>
</tr>
<tr>
<td>Ni</td>
<td>0.17</td>
<td>0.56</td>
<td>0.0051</td>
</tr>
<tr>
<td>Zr</td>
<td>&gt; 0.22</td>
<td>nd</td>
<td>0.022</td>
</tr>
<tr>
<td>V</td>
<td>&gt; 0.18</td>
<td>~0.67</td>
<td>0.0099</td>
</tr>
</tbody>
</table>

River data from Table 1. Sediment data partly from Boström & Ingri (1982); partly from unpublished material. Quantities lost through S. Kvark and the Sound from Table 2. The relative loss (in %) is defined as EXP/(DEP + EXP) where EXP represents exported quantity and DEP the permanently deposited quantity for a given component.

GB = Gulf of Bothnia  BS = Baltic Sea (total)
Discussions of the mass-balance

Table 4 shows how well some balance entries are explained by other entries. Even if all river supplied material accumulated in the Baltic postglacial clays they could at most account for a minor fraction of the sediment accumulation rates.

It is obvious that the entries in Table 4 do not match each other. The sediment accumulation far exceeds the differences between influxing and effluxing quantities, i.e., no less than 90 to 96% of all accumulation is unexplained. This suggests that the main fraction of all postglacial clays have their source within the Baltic basin, being generated by submarine erosion; a process that is facilitated by the postglacial land up-lift.

Submarine erosion as a significant source of postglacial sediment has been pointed out by Winterhalter (1972), Boström et al., (1978a), Niemistö et al. (1978) and Winterhalter et al. (1981). Traces of such erosion have also been documented in the field by Winterhalter (1966), and dredging at numerous sites during 1976–1979 in the Gulf of Bothnia reveals lumps of till-like materials, partially covered by hydroxides (Boström et al., 1982). Such Fe-encrusted lumps and slabs are particularly common in the northern part of the Bothnian Sea, but have been observed by us also in coastal waters, e.g., near Luleå in the Bothnian Bay.

Geochemical and mineralogical studies of the sediments in the Gulf of Bothnia likewise suggest a considerable differentiation of previous tills and other glacial deposits (Boström et al., 1978a). In shallow regions fine fractions and sheet silicates are removed by the panning action of waves and currents, forming quartz-feldspar rich resistates, whereas hydroxide and mica-rich fractions are moved to deeper regions. The accumulations in the depressions are therefore enriched in, for instance, Fe, Ti, Mn and Ba, whereas the shallow regions are enriched in Si-rich sediments (see Fig. 3–5). Furthermore, data in Table 3, column 7 and Fig. 7 show clearly that the fine fraction in glacial deposits is identical in composition to the postglacial manganese poor sediments.

The element relations in suspended matter and in the Baltic postglacial clays are compared in Fig. 7, where the first component represents a phase that leaves the Baltic, whereas the latter one is an ultimate sink for elements in the Baltic. The graph clearly shows that Mn, Zn, Cu, V and probably Ba are present in excess quantities, whereas Zr shows no selective loss and Si, Ti and Ni only small, probably insignificant excesses; note that Fe and Al have been used to normalize the data. Much Si, Ba, Cu, Zn and Ni exist in dissolved form in sea water; it is therefore likely that also these are selectively lost from the Baltic, see also Table 4.

A complication is the poorly known trace metal load of the inflowing bottom current of 470 km$^3$ yr$^{-1}$; the net transport of dissolved Ba would be zero if the Ba-content is two times larger in this inflow than in the outflowing currents. However, that would require a Ba-content of about 30 μg l$^{-1}$, which is much higher than reported for ocean surface waters (Broecker, 1974) or observed in our analyses of deep waters in the straits. We therefore claim that Ba is selectively lost from the Baltic; similar arguments suggest that also Mn, Cu, Zn and Ni are selectively lost (see Table 4).
Figure 3. Concentration of quartz in the sediment surface in the Gulf of Bothnia (Boström et al., 1978a), given as height of the quartz-peak in standardized x-ray diffraction recordings. Each station is represented by a dot; commonly several samples were analyzed from each station. The 250 mm quartz peak is equivalent to 40 weight % quartz, 200 mm to 32 % and 150 mm to 24 %. The highest quartz concentrations are found in shallow areas, where quartz is enriched as a residual resistate after the fine fractions of tills and other glacial deposits have been removed by waves and currents. Dotted line represents the 50 m isobath.
Figure 4. Concentration of Fe₂O₃ (in %) in the sediment surface in the Gulf of Bothnia (Boström et al., 1978a). The iron content is highest in the deep depressions; sediments with 7.5% Fe₂O₃ or more largely represent postglacial deposits, the other ones are more or less reworked tills, glacial varved clays, etc. A similar distribution of Fe is reported for the Baltic proper by Blashchishin (1976). Some other major components (Ti, P) show the same tendency to be enriched in postglacial deposits (Blashchishin, 1976; Boström et al., 1978a; also, see Table 3).
Figure 5. Distribution of Ba in the sediment surface in the Gulf of Bothnia. Samples with less than 600 ppm Ba represent glacial deposits and reworked tills; stations with more than 750 ppm Ba are well developed postglacial deposits; see also Table 3. Similar distribution patterns were found also for Ba, Ni, Zr, Cu, V and Yb (Emelyanov, 1976; Boström et al., 1978a; and present work, see Table 4) in Gulf of Bothnia and the Baltic proper.
Figure 6. Relations between Mn-poor postglacial clay (Table 3, column 3) and the fine fraction of glacial deposits in the Baltic (Table 3, column 7), after correction for admixed Mn-rich layer.

Figure 7. Relative element distributions in Baltic postglacial manganese-poor sediment and in Baltic suspended matter (= BSM), after normalization, making $\Sigma (Fe + Al) = 1.0$. BSM is distinctly enriched in Mn, Zn, Cu, V and Ba, whereas Si, Al, Fe and Zr are conservative constituents.
Several geochemical subcycles may supply the excess quantities of Mn, Zn, etc. Much of these elements are probably tied in organic tissue already on land, as is shown by the pronounced enrichment of Ba and Mn in North European trees (Ehlin, pers. comm.). Another geochemical subcycle that delivers some of these elements is the reduction of oxidized postglacial clays, as shown in Table 3, columns 1–3; also, this is a process that liberates Si, Fe, Mn, P, Ba and Ni and probably some other elements as well. Several of the released elements are characteristic components in the iron-manganese nodules (Table 3, columns 4 and 5). However, not all released matter enters into nodules (Fig. 8), but are produced in excess during the reduction, i.e., not all released Fe and P will accrete in nodules. Hence, the mobile amounts of Ni, Ba, Si and Mn that are available for other geochemical processes are still larger.

The suspended phases that exit through the Danish straits probably are partly transported to the ocean, e.g., by bottom winnowing; this suspended phase is strikingly similar to mean Atlantic pelagic sediments in composition (Fig. 9). However, there is no reason to assume that the transport of suspended matter from estuarine areas to the deep sea is a simple process. Thus, Boström et al. (1978b) found that mixtures of mean terrigenous matter and mean marine biological matter could explain most types of pelagic sediments. Likewise, Boström et al. (1981) demonstrated that Baltic suspended matter could be described as mixtures of mean terrigenous and marine biological matter. Also, already within the Baltic suspended matters can display considerable topological variations.

Implications for the Geochemistry of Heavy Metal Pollutions in the Baltic

The results demonstrate a considerable mobility of some metals, such as Mn, Ba, Cu, Ni and Zn and that large fractions of these elements exit from the Baltic in suspended and dissolved phases. It is hence likely that several other components also disappear by the same mechanism; this is probably the case for Cd, which is relatively enriched in much marine biological matter also in the Baltic (Prosi, 1979; Boström & Boström, 1982). Additional studies of the removal of metals from the Baltic are needed, however, to confirm the results above, and to reveal to what extent Pb, Hg, As, etc. are lost by the same mechanisms.

Such removals of pollutants may partly explain the fact that most heavily polluted sediments are encountered in coastal areas, particularly narrow bays (Olausson et al., 1977). As such sediments are reworked by waves and currents, much of the pollutant-rich fines will be more easily suspended than other components and to a large extent incorporated in biological material, but the lower or undetectable pollution contents in the deep water deposits may also be due to dilution by fines from unpolluted regions. However, deep water concretions are likely to be important sinks for several metals like As, Ba and Ni (Boström et al., 1982). Other problems for the pollution research in the Baltic are related to analytical problems. For several elements reliable analyses are still hard to obtain; notorious elements in this respect are Pb, Cd and Hg (Roseman & De Laeter, 1980). Also sampling problems pose a considerable difficulty in pollution
Reduction loss

Figure 8. Relative element abundances (in logarithmic units), reduction loss fraction and mean Baltic nodules, after normalization such that Fe (in nodule) = Fe (in loss fraction). As Mn-rich sediments are reduced to Mn-poor sediments (Table 3, columns 1 and 2) a fraction of the sediment is lost, assuming Al to be the permanent component. Note that much Mn, Si, Ba and Ni are not incorporated in nodules after their release from the oxidized sediment (Boström et al., 1982).

Figure 9. Element relations in Baltic suspended matter and in Atlantic pelagic sediment (Boström, 1976; his Table 13, mean of data in columns 1 and 2). Both data sets are normalized such that \( \Sigma (\text{Fe} + \text{Al}) = 1.00 \), and presented in logarithmic forms. Based on data in Boström et al. (1981).

research. Very thin slices of material are commonly procured to detect anthropogenic contributions in the tops of sediment cores and to show how these additions grow annually. However, a drop in sample size from, e.g., 200 to 100 mg implies a considerable loss of precision (Moore, 1979). A study of the variance in reported results for rock standards is another sobering experience; a variation with a factor 3–4 is common for trace elements like Ba, Co, Cr, Cu, Zn, V, Zr and Yb and variations with a factor 10 or more are reported for La, Ni, Pb, Sn, Sr, Y and W (Govindaraju & de la Roche, 1977). This means that comparison of data by different analysts can yield highly misleading conclusions.
A consequence is that more inter-laboratory comparisons of results must take place and that for a given problem all analyses should preferably be made in the same laboratory. The results are then most likely to be comparable, having the same systematic errors. We would here like to stress that most phases involved in the discussion above have been analyzed in our laboratory in order to circumvent these difficulties, i.e. they should as a rule be well comparable.

Conclusions

Data in Tables 1–4 for the amounts of inflowing, outflowing and accumulating Si, Ti, Al, Fe, Mn, Ba, Ni, Cu, V, Zn and Zr in the Baltic vary much in quality. The accumulation rates of postglacial sediments amount to about $20-60 \times 10^9$ kg yr$^{-1}$ (all values here represent the sum of the oxides only of the elements listed above), whereas the amounts of inflowing and effluxing components are much smaller.

The postglacial sediments derive to 50–95% from a glacial deposits within the Baltic basin; the older deposits being reworked by waves, currents and ice in shallow regions, whereby fines are moved into deeper areas and coarse materials tend to accumulate in the shallow regions. Bed-loads in rivers may be an extra, but unknown, source.

In the deeper regions the first formed sediments often are well oxidized and rich in Fe, Mn, P, Ba and Ni, but microbial redox processes release much of these constituents, the mobilized matter partly entering into Fe-Mn concretions (which generally are rich in P, Ba and Ni) and partly into biological phases. Since both discharging waters and discharging suspended matters are enriched in Ba, Cu, Mn, and Zn compared to the permanently depositing sediments it appears that these elements are selectively lost from the Baltic. This would explain the low trace element contents of Baltic sediments. Preliminary data suggest that much Cd and Hg are lost by the same mechanism, whereas much As is incorporated in Fe-Mn-concretions.

Acknowledgements

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Paper 9
Geochemistry of ferromanganese concretions in the Barents Sea
by
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Abstract

Ferromanganese concretions from 10 stations in the Barents Sea have been analysed for 24 elements. The deposits occur as discoidal and flat concretions and as coatings. In the latter case on lithified or detrital material or as extensive pavements on the Svalbard shelf.

The concretions are compositionally similar to Baltic concretions but differ considerably from deep-ocean nodules particularly in Cu, Ni and Co contents. Statistical analyses reveal distinct correlation between Mn-Na-Ba-Ni-Cu; the Mn-rich coatings showed enrichment of Mo, Zn and possibly Co in a Mn-phase. The Fe-phase holds high concretions of P and As. Two Fe-rich concretions with high contents of P, Ca, Sr, Y, Yb and La were found east and north-east of Spitsbergen Banken, probably indicating upwelling of nutrient-rich, cold polar water along the Svalbard shelf.
Introduction

Since the Vega expedition (1878-1880) found ferromanganese nodules north of Dickson Island in the Kara Sea, several authors have reported concretions from the Northern Russian Seas (Samilov and Titov 1922, Rossolimo 1923, Gorshkova 1931, 1957, Klenova 1960). The Marine Scientific Institute of the U.S.S.R. organized several expeditions in the Barents Sea between 1921 and 1928 and the concretions recovered during these voyages have been investigated by Gorshkova (1931). Gorshkova's work still seems to be the only thorough study of Barents Sea concretions. Chemical analyses of nodules from this area are therefore sparse.

Furthermore, the Barents Sea area is interesting because it probably is relatively unpolluted except for some input of radioactive isotopes. Barents Sea concretionary deposits could hence provide background values for typical pollution elements in Baltic Sea nodules.

The "polar front", a boundary formed when the cold polar water meets the warm and saline Atlantic water, is an interesting feature in the Barents Sea. Upwelling of nutrient-rich polar water supports a luxurious flora of phytoplankton and a high abundance of polar cod and capeling on the Svalbard Shelf (The Mitchell Bently Atlas of the Oceans 1977). High availability of biogenic elements could strongly affect the composition of Fe-rich concretions in particular in this area.
Distribution and morphology

The field work was made onboard RV Norvarg of the Norwegian Polar Institute in 1980. All concretions were dredged in the vicinity of the large shelf area east and south-east of Svalbard (Fig. 1). South of 78°N, the recovered concretions are flat and irregularly shaped and range from more or less Fe-impregnated sediment fragments (up to 35% Fe) to coating on rock debris and lithified clay. These types of Fe-concretions are very common in the central and westerly parts of the Barents Sea (Gorshkova 1931). Lag deposits with Fe-coated gravel and pebbles are found on the slope east of Spitsbergen Banken and south of Björn Oya down to a depth of 400 m and locally the sea-floor is partly covered by an Fe-crust (Elverhøi and Kristoffersen 1978). Such a thin (~ 1 mm thick) crust developed at the sediment surface was recovered with a 1 m³ grab sampler at stn 19 during the Norvarg expedition and fragments dredged at stn 10 and 11 probably also originate from an extensive Fe-pavement on the bottom (Kristoffersen pers. comm. 1980).

The northernmost nodules (stn. 21, 26, 27, 28), on the other hand, are more Mn-rich (up to 23% Mn) and are discoidal in shape formed as a ring or rim around a visible nucleus of rock fragments or lithified sediment. This is a common growth form in lakes and shallow-marine environments and is often referred to as girdle concretions (Calvert and Price 1977). The ring-shaped concretions have clearly marked yellow-brown Fe-rich and black-brown Mn-rich growth rings; they are rather smooth, hard and
Figure 1. The type of concretions found in the Barents Sea. Unspecified stations are taken from Rossolimo 1923, Samoilov and Titov 1922, Samoilov and Gorshkova 1924 and Klenova 1960. Specified stations are from Gorshkova 1931 and marked stations represent this study.
yellow-brown on the underside and are black, rather porous and knobby on top. Flat concretions also show this layered structure occasionally but a homogeneous, yellow-brown veneer occurs more frequently. One large limestone boulder (26-1) and a basaltic pebble (26-6) from stn 26 with developed rims at the sediment-water interface also showed coatings as 1 to 2 cm broad brown and black bands with a thickness of approx. 1 mm. The porous and knobby black band is present above the brown band. Both are located above the rim. These bands have been analysed (Table 2), together with Fe-rich coatings from stn 19, 5, 12 and 16. At stn 12 and 16 the concretionary material appears as rather thick (5-6 mm) hard, yellow-brown coatings on rock fragments with a clayey surface.

Spherical or spheroidal concretions of the type frequently found in the Baltic Sea (Winterhalter 1966, Boström et al 1982) seem to be very rare in the Barents Sea. No concretions of this type was found during the Norvarg expedition and Gorshkova (1931) described no such nodules.

Sample preparation and analysis

Pebbles and sand impurities were removed from the concretions and the seemingly homogeneous oxyhydroxide phase was ground in an agate mortar and thereafter dried at 80°C. 500 mg of each sample was leached with 12% HCl together with a reducing agent (hydroxylammonium-hydrochloride). The oxyhydroxide phase dissolved after 4 hours at 80°C, leaving a grey residue. Emission spectroscopy, using an
Inductively Coupled Plasma (ICP) as source was used to analyse the acid-soluble fraction. Most elements were measured in an ARL 33000 sequentially reading unit and Yb, La, Sc, Co, Mo and P were determined in an ARL 35000 scanning unit (Burman 1979 and Burman et al. 1979, 1981). The residue and sediments were analysed for major elements together with Cr, Zr, Ba and Sr using a metaborate digestion procedure (Burman et al. 1978). Remaining trace elements in residue and sediments were dissolved in HF-HClO₄ and then analysed. K was analysed by Atomic Absorption.

Analytical checks, using two USGS standard deep-sea nodules (A-1 and P-1) (Flanagan et al. 1980) yielded good agreement between obtained and recommended values (Table 1). Due to the very low content of insoluble residue in the A-1 nodule, major elements together with Sr, Ba, Cr and Zr were determined on a fused and dissolved unleached sample of this concretion. Trace element contents in both nodules are, however, based on leached values as described above.

A concretion with a developed rim from stn 26 was studied using a JEOL Scanning Electron Microscope (SEM) equipped with a Kevex energy dispersive unit. Scanning profiles for Na, Si, Ca, P, Mn and Fe over alternating Fe and Mn layers in the nodule, together with point analyses, gave major element distribution within the concretion (Figs. 3, 4 and 5). X-ray diffraction work on the HCl-leached concretion residue and sediment was performed on a Phillips diffractometer using CuKα radiation.
Treatment of data

Some samples contain as much as 60% acid-insoluble silicate-rich detritus. To make the samples comparable, the influence of the insoluble fraction (IF) must be removed (Bischoff et al. 1981, Boström et al. 1982, Glasby and Thijssen 1982). Normalization by multiplying all values (in %) with a factor \( f_1 \), defined as \( f_1 = \frac{100}{100-\text{IF}} \) showed that the sum of Mn and Fe was close to 40% but not fully constant. Hence, acid-soluble values were subsequently multiplied with a factor \( f_2 \), where \( f_2 = \frac{40}{\text{Fe+Mn}} \). This relation makes Fe and Mn anticorrelated, an assumption that seems to be justified according to Fig. 4. The \( f_2 \) normalized values were used in the correlation matrix shown in Table 4. Partial correlations (Snedecor and Cochran 1967) were also calculated and selected portion of these correlations are shown in Table 5. However, closed sets of data often yield misleading correlations (Chayes 1967) and therefore the obtained associations must be carefully evaluated and compared to other information.

Results and discussion

The chemical composition of the concretions from the western Barents Sea is similar to other shallow-marine nodules found in the Baltic and elsewhere (Winterhalter 1966, Boström et al. 1982, Calvert and Price 1977) (Table 1). Low Cu, Ni and Co values, high P content and a variable aluminosilicate component are characteristic for both the Baltic Sea and Barents Sea concretions. However, the Barents
Table 1. Chemical composition of Barents Sea concretions and their shallow water - deep sea equivalents

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1) This study. Data represent total analyses of four discoidal concretions resp. five flat concretions. Co* and Mo* are HCl-leached values. Figures are all based on analyses of 0.5 g dried sample. Standard deviations are shown within brackets.

2) This study. Discoidal and flat values are averages of 13 concretions respectively. Data for SiO₂ to Cr, except P₂O₅, represent total analyses and Cu to Yb values are HCl-leached values of the same concentrations. See also Table 2 for comparison to Barents Sea HCl-leached values.
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3) Manheim 1965 (composite sample, Baltic proper).
4) Calvert and Price 1970 (analyses of core and rim from one concretion).
6) This study. Recommended or "best values" are not available for all elements. Values within brackets show figures obtained only by one or two laboratories, see Flanagan and Gottfried 1980.
Table 2. Composition of the HCl-soluble fraction in Barents Sea iron - manganese deposits

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Values for discoidal concretions represent averages of 12 and the flat figures of 10 concretions. All have been recalculated to 100% leachable fraction. * High values probably due to limestone contamination.
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Figure 2. Plots of original data, HCl-leached values. Filled circles represent discoidal nodules and the triangle flat concretions.
Figure 3. Point analysis with the microprobe, showing major element composition of a manganese layer and an iron layer from a discoidal concretion from station 26.
Figure 4. Microprobe scan profiles over alternating iron and manganese-rich layers in a discoidal concretion from station 26. Note the anti-correlation even within a manganese- or iron-rich layer.
Figure 5. Microprobe scan profiles over the same concretion shown in Fig. 4. Note the close correlation between iron and phosphorous and the small scatter for calcium.
Table 3. Element enrichment in Barents Sea concretions, compared to underlying sediment.

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<td>3.1</td>
<td>5.1</td>
<td>1.5</td>
<td>7.7</td>
</tr>
<tr>
<td>Fe₂O₃ %</td>
<td>21.9</td>
<td>0.1</td>
<td>22.0</td>
<td>22.1</td>
<td>0.4</td>
</tr>
<tr>
<td>MnO %</td>
<td>18.5</td>
<td>0.0</td>
<td>18.5</td>
<td>3.3</td>
<td>0.0</td>
</tr>
<tr>
<td>MgO %</td>
<td>2.0</td>
<td>0.1</td>
<td>2.1</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>CaO %</td>
<td>2.1</td>
<td>0.1</td>
<td>2.2</td>
<td>1.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Na₂O %</td>
<td>2.6</td>
<td>0.4</td>
<td>3.0</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>K₂O %</td>
<td>0.5</td>
<td>0.3</td>
<td>0.8</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Ba ppm</td>
<td>532</td>
<td>110</td>
<td>642</td>
<td>332</td>
<td>179</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>576</td>
<td>32</td>
<td>608</td>
<td>255</td>
<td>91</td>
</tr>
<tr>
<td>Cr ppm</td>
<td>33</td>
<td>32</td>
<td>65</td>
<td>33</td>
<td>51</td>
</tr>
<tr>
<td>Zr ppm</td>
<td>21</td>
<td>45</td>
<td>66</td>
<td>20</td>
<td>93</td>
</tr>
<tr>
<td>Soluble insoluble content %</td>
<td>71.3</td>
<td>28.7</td>
<td>100</td>
<td>44.5</td>
<td>55.5</td>
</tr>
</tbody>
</table>

Upper part of table shows total analyses of one discoidal respectively one flat concretion. Lower part shows HCl-leachable fractions from 4 disciformed and 3 flat concretions. Nodules and the sediment (grey, 10 cm depth) are from station 27. Values within brackets are standard deviations. *Compared to grey sediment. **Composite value of residues from 12 discoidal respectively 11 flat concretions. Recalculated by multiplying with residual values 37.2 respectively 47.9.
Sea nodules are 4 to 5 times richer in V and much poorer in Ba than corresponding ones from the Gulf of Bothnia. Two of the Fe-rich coatings (stn 16 and 12) are anomalous in comparison to the other concretions. These coatings are very high in P and Ca together with a pronounced accumulation of Sr, Y, Yb and La. In composition they more resemble the Fe- and P-rich nodules found in the upwelling areas of the East Australian shelf (Cook and Marshall, 1981) than "ordinary" shallow marine Fe-concretions.

Barents Sea concretions are essentially a mixture of an oxy-hydroxide component and admixed sediment or a lithogeneous phase. Leaching procedures partly destroy some silicates in the lithogenic fraction (Bischoff et al. 1981, Glasby and Thijssen, 1982, Boström et al. 1982) and element present in the acid-soluble fraction therefore derive from three major host phases, a Mn-rich phase, an Fe-rich phase and from a leachable detrital fraction.

**Detrital phase**

In the Barents Sea concretions Al, Sc, Cr, Zr, K and Mg clearly are correlated with the acid-insoluble residue (Tables 4 and 5). The close correlations between Sc and IF and Sc and Al are in agreement with the findings of van der Weijden et al. (1970) who showed a close relationship between Sc and Al and the illitic clay fraction in north Atlantic sediments. Some Sc values are though high in flat concretions and in the Fe-rich coatings (Table 2), i.e. Sc is probably present in the clay fraction but to some extent also in the Fe phase. Slight enrichments of Cr and Zr are seen in the Fe-rich
Table 4. Statistical significant correlations in Mn-Fe concretions from the Barents Sea.

<table>
<thead>
<tr>
<th></th>
<th>Discoidal</th>
<th>Flat+ discoidal</th>
<th>Discoidal</th>
<th>Flat+ discoidal</th>
<th>Discoidal</th>
<th>Flat+ discoidal</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF*-Al</td>
<td>0.93</td>
<td>0.49</td>
<td>Ti-Zr</td>
<td>0.76</td>
<td>Zr-Yb</td>
<td>0.82</td>
</tr>
<tr>
<td>IF-Mg</td>
<td>0.89</td>
<td>0.65</td>
<td>Ti-V</td>
<td>0.82</td>
<td>Zr-Sc</td>
<td>0.82</td>
</tr>
<tr>
<td>IF-K</td>
<td>0.83</td>
<td>-</td>
<td>Ti-Y</td>
<td>0.71</td>
<td>Zr-La</td>
<td>0.85</td>
</tr>
<tr>
<td>IF-Ti</td>
<td>0.68</td>
<td></td>
<td>Ti-Sc</td>
<td>0.68</td>
<td>Zr-Y</td>
<td>0.97</td>
</tr>
<tr>
<td>IF-Cr</td>
<td>0.92</td>
<td>0.71</td>
<td>Ti-Zn</td>
<td>0.82</td>
<td>Zr-Cu</td>
<td>0.71</td>
</tr>
<tr>
<td>IF-Zr</td>
<td>0.83</td>
<td>0.66</td>
<td>Ti-Ni</td>
<td>0.83</td>
<td>Zr-Ni</td>
<td>0.84</td>
</tr>
<tr>
<td>IF-Sc</td>
<td>0.98</td>
<td>-</td>
<td>Ti-Cu</td>
<td>0.88</td>
<td>Zr-Zn</td>
<td>0.85</td>
</tr>
<tr>
<td>IF-V</td>
<td>0.68</td>
<td></td>
<td>Ti-La</td>
<td>0.64</td>
<td>V-Zn</td>
<td>0.95</td>
</tr>
<tr>
<td>IF-Zn</td>
<td>0.63</td>
<td></td>
<td>Ca-Ba</td>
<td>0.72</td>
<td>V-Ni</td>
<td>0.91</td>
</tr>
<tr>
<td>IF-Cu</td>
<td>0.65</td>
<td>-</td>
<td>Ca-Sr</td>
<td>0.83</td>
<td>V-Cu</td>
<td>0.67</td>
</tr>
<tr>
<td>IF-Y</td>
<td>0.81</td>
<td>0.58</td>
<td>Si-Sr</td>
<td>0.68</td>
<td>V-Y</td>
<td>0.91</td>
</tr>
<tr>
<td>IF-La</td>
<td>0.88</td>
<td></td>
<td>Si-P</td>
<td>0.71</td>
<td>V-La</td>
<td>0.66</td>
</tr>
<tr>
<td>IF-Fe</td>
<td>-</td>
<td>0.67</td>
<td>Si-As</td>
<td>0.84</td>
<td>V-Sc</td>
<td>0.63</td>
</tr>
<tr>
<td>IF-Yb</td>
<td>-</td>
<td>0.51</td>
<td>P-As</td>
<td>0.69</td>
<td>V-Yb</td>
<td>0.84</td>
</tr>
<tr>
<td>IF-As</td>
<td>-</td>
<td>0.54</td>
<td>P-Sr</td>
<td>0.82</td>
<td>Ni-Zn</td>
<td>0.99</td>
</tr>
<tr>
<td>Al-Mg</td>
<td>0.90</td>
<td>0.68</td>
<td>Fe-Si</td>
<td>0.98</td>
<td>Ni-Cu</td>
<td>0.78</td>
</tr>
<tr>
<td>Al-K</td>
<td>0.90</td>
<td>-</td>
<td>Fe-Yb</td>
<td>0.67</td>
<td>Ni-Ba</td>
<td>-</td>
</tr>
<tr>
<td>Al-Ti</td>
<td>0.74</td>
<td>0.64</td>
<td>Fe-As</td>
<td>0.94</td>
<td>Ni-Na</td>
<td>-</td>
</tr>
<tr>
<td>Al-Cr</td>
<td>0.94</td>
<td>0.78</td>
<td>Fe-Y</td>
<td>-</td>
<td>Ni-Y</td>
<td>0.88</td>
</tr>
<tr>
<td>Al-Zr</td>
<td>0.81</td>
<td>-</td>
<td>Fe-Sc</td>
<td>-</td>
<td>Ni-La</td>
<td>0.70</td>
</tr>
<tr>
<td>Al-Sc</td>
<td>0.96</td>
<td>-</td>
<td>Fe-Cr</td>
<td>-</td>
<td>Ni-Yb</td>
<td>0.80</td>
</tr>
<tr>
<td>Al-Y</td>
<td>0.64</td>
<td>-</td>
<td>Fe-Zr</td>
<td>-</td>
<td>Cu-Zn</td>
<td>0.75</td>
</tr>
<tr>
<td>Al-La</td>
<td>0.71</td>
<td>-</td>
<td>Mn-Na</td>
<td>0.68</td>
<td>Cu-Ba</td>
<td>-</td>
</tr>
<tr>
<td>Al-Y</td>
<td>0.71</td>
<td>-</td>
<td>Mn-Ba</td>
<td>0.85</td>
<td>Cu-Na</td>
<td>-</td>
</tr>
<tr>
<td>Al-Cu</td>
<td>0.66</td>
<td>-</td>
<td>Mn-Ni</td>
<td>0.60</td>
<td>Cu-Y</td>
<td>0.69</td>
</tr>
<tr>
<td>Mg-K</td>
<td>0.97</td>
<td>0.81</td>
<td>Mn-Cu</td>
<td>0.58</td>
<td>Cu-La</td>
<td>0.73</td>
</tr>
<tr>
<td>Mg-Cr</td>
<td>0.81</td>
<td>0.58</td>
<td>Mn-Ca</td>
<td>0.55</td>
<td>Cu-Sc</td>
<td>0.69</td>
</tr>
<tr>
<td>Mg-Sc</td>
<td>0.91</td>
<td>-</td>
<td>Mn-Sr</td>
<td>0.49</td>
<td>Zn-Y</td>
<td>0.89</td>
</tr>
<tr>
<td>Mg-La</td>
<td>0.69</td>
<td>-</td>
<td>Cr-Zr</td>
<td>0.93</td>
<td>Zn-La</td>
<td>0.68</td>
</tr>
<tr>
<td>Mg-Ca</td>
<td>-</td>
<td>0.60</td>
<td>Cr-Y</td>
<td>0.77</td>
<td>Zn-Yb</td>
<td>0.81</td>
</tr>
<tr>
<td>K-Cr</td>
<td>0.78</td>
<td>-</td>
<td>Cr-Sr</td>
<td>0.93</td>
<td>Ba-Sr</td>
<td>0.65</td>
</tr>
<tr>
<td>K-Sc</td>
<td>0.87</td>
<td>-</td>
<td>Cr-La</td>
<td>0.80</td>
<td>Y-La</td>
<td>0.88</td>
</tr>
<tr>
<td>K-Ba</td>
<td>-</td>
<td>0.45</td>
<td>Cr-Yb</td>
<td>0.73</td>
<td>Y-Sc</td>
<td>0.76</td>
</tr>
<tr>
<td>K-Ca</td>
<td>-</td>
<td>0.61</td>
<td>Cr-Y</td>
<td>0.86</td>
<td>Y-Yb</td>
<td>0.90</td>
</tr>
<tr>
<td>Na-Ca</td>
<td>-</td>
<td>0.63</td>
<td>Cr-Cu</td>
<td>0.68</td>
<td>La-Sc</td>
<td>0.84</td>
</tr>
<tr>
<td>Na-Sr</td>
<td>-</td>
<td>0.53</td>
<td>Cr-Ni</td>
<td>0.69</td>
<td>La-Yb</td>
<td>0.73</td>
</tr>
<tr>
<td>Na-Fe</td>
<td>-</td>
<td>0.80</td>
<td>Cr-Zn</td>
<td>0.72</td>
<td>Yb-Sc</td>
<td>-</td>
</tr>
<tr>
<td>Ti-Cr</td>
<td>0.72</td>
<td>0.45</td>
<td>Zr-V</td>
<td>0.88</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Prior to the least-square correlation coefficient calculations all values were multiplied with the $f_2$ factor defined in the text. Values represent the HCl-leachable fraction and figures with absolute values greater than 0.77 and 0.63 (10 discoidal) and 0.56 and 0.44 (10 discoidal plus 10 flat concretions) are significant at the 1% and 5% levels respectively (Snedecor and Cochran, 1967). Notice that the correlation Fe-Mn already is fixed by the relation Fe+Mn = 40%. *IF represent HCl insoluble fraction.
Table 5.

Discoidal

Fe/
Mn

IF-A1

Selected partial correlations in Barents Sea concretions

IF

Flatt
disc-

Fe/

Si

Al

P

Ti

Mg

Ca

Na

K

oidal

Mn

IF

Si

AI

P

Ti

Hg

Ca

0.96

0.95

-

0.91

0.87

0.65

0.93

0.94

0.75

Mn-Na

-

0.96

0.94

0.94

0.93

0.94

0.96

0.90

IF-Sc

0.99

0.99

0.87

0.99

0.97

0.99

0.95

Mn-Ba

-

0.83

0;86

0.85

0.86

0.84

0.88

0.78

0.51

0.86

0.88

0.87 -0.04

0.75

0.87

0.85

-

Mn-Ni

-

0.62

0.60

0.63

0.58

0.59

0.61

0.55

0.17

0.57

IF-Cr

0.92

0.92

0.38

0.89

0.91
0.80 -0.32
0.86 0.95

0.98

IF-K

0.92

0.91

0.79

Mn-Cu

-

0.69

0.58

0.62

0.56

0.57

0.63

0.46 - 0 . 0 9

IF-Zr

0.83

0.82

0.38

0.78

0.67

0.87

0.86

0.82

Mn-Ca

-

0.70

0.56

0.62

0.62

0.53

0.72

IF-Mg

0.92

0.91

0.34

0.84

0.88

0.94

0.93

0.63

Mn-Sr

-

0.53

0.56

0.50

0.78

0.47

IF-Zn

0.61

0.62

0.32

0.49

0.20

0.86

0.78

0.68

0.86

Fe-IF

-

-

0.68

0.70

0.68

0.74

IF-Cu

0.7Z

0.70

0.18

0.48

0.20

0.52

0.32

0.61

0.61

Fe-Y

-

0.26

0.55

0.54

0.59

1F-Y

0.82

0.80

0.58

0.79

0.64

0.89

0.86

0.88

0.91

Fe-Sc

-

0.37

0.53

0.52

Sc-Zr

0.85 - 0 . 04

0.82

0.25

0.77

0.63

0.79

0.85

0.87

0.83

Fe-Cr

-

0.50

0.57

Sc-Cr

0.94

0. 31

0.97

0.78

0.88

0.87

0.78

0.93

0.92

0.82

Fe-Zr

-

0.50

0.72

Mg-K

0.97

0. 92

0.98

0.86

0.96

0.97

Al-Sc

0.96

0. 62

0.96

-

0.92

0.92

0.77

A1-T1

0.74

0. 45

0.75

-

0.54

-

0.82

Fe-Si

-

0. 90

-

0.91

0.86

0.91

0.91

P-Sr

0.77

0. 84

0.72

0.76

-

0.67

0.89

Fe-As

-

0. 96

0.78

0.95

0.92

0.95

0.95

As-Si

0.81

-

Ma

K

-

0.94

0.54

-0.13

0.52

0.51

0.03 -0.07

0.42

0.85

0.77

0.81

0.85

0.80

0.57

0.57

0.50

0.54

0.65

0.70

0.53

0.43

0.37

0.49

0.76

0.67

0.77

0.67

0.60

0.59

0.67

0.72

0.77

0.90

0.73

0.65

0.68

0.71

0.96

0.96

-

Fe-As

-

0.38

0.63

0.59

0.62

0.58

0.10

0.71

0.40

0.63

0.96

0.95

0.81

P-As

0.59

0.66

0.65

0.61

-

0.55

0.59

0.59

0.59

0.58

0.85

0.71

0.89

P-Sr

0.84

0.66

0.32

0.67

-

0.65

0.63

0.14

0.44

0.57

0.90

0.87

0.91

P-Si

0.74

0.71

-

0.73

-

0.79

0.73

0.68

0.76

0.72

0.90

0.79

0.88

Si-Sr

0.73

0.69

-

0.69

0.41

0.68

0.69

0.75

0.68

0.70

0.94

0.89

0.95

Ca-Sr

0.78

0.83

0.86

0.83

0.90

0.84

0.84

-

0.75

0.81

-0.11

0, 87

-

0.85

0.73

0.84

0.88

0.83

0.76

0.87

Mg-K

0.84

0.80

0.81

0.79

0.81

0.82

-.

0.70

0.82

As-P

0.58

0.84

0.43

0.85

-

0.79

0.72

0.68

0.48

0.69

Al-Ti

0.69

0.64

0.64

-

0.62

-

0.54

0.62

0.67

0.63

La-Y

0.87

0. 62

0.85

0.77

0.07

0.82

0.85

0.90

0.90

0.86

La-Y

0.84

0.86

0.83

0.79

0.82

0.75

0.83

0.83

0.84

0.83

La-Sc

0.86 -0. 30

0.89

0.77

0.38

0.77

0.70

0.84

0.87

0.85

La-Sc

0.74

0.73

0.77

0.70

0.73

0.69

0.74

0.77

0.76

0.75

La-Yb

0.72

0 .65

0.63

0.70

0.77

0.60

0.86

0.80

0.82

0.70

La-Yb

0.62

0.57

0.61

0.55

0.63

0.62

0.60

0.62

0.71

0.60

Y-Yb

0.88

0. 93

0.88

0.95

0.95

0.85

0.96

0.91

0.95

0.96

Y-Yb

0.76

0.76

0.83

0.81

0.84

0.86

0.85

0.85

0.85

0.83

V-Yb

0.81

0 76

0.87

0.83

0.90

0.78

0.84

0.82

0.89

0.85

V-Yb

0.54

0.63

0.64

0.63

0.65

0.63

0.66

0.58

0.56

0.65

-

V-Zn

0.97

0 92

0.96

0.93

0.95

0.85

0.95

0.95

0.95

0.95

V-Zn

0.70

0.59

0.61

0.59

0.57

0.61

0.62

0.62

0.69

0.61

Zn-Ni

0.99

0. 99

0.99

0.99

0.99

0.97

0.99

0.99

0.99

0.99

Zn-Ni

0.97

0.88

0.83

0.82

0,80

0.74

0.82

0.89

0.95

0.82

Partial correlations in discformed concretions with absolute values larger than |t0.80| and j±0.67|are significant at the U respectively 5% level. Partial correlations larger than |±0.58| and |±0.46|
are significant at the IX respectively 5% level for discoidal plus f l a t concretions. Correlation c o e f f i cients in the columns below Fe/Mn, IF etc. represent those, for which the influences from Fe/Mn, I F , Al
etc are removed (Snedecor and Cochran, 1967). Correlation coefficients used for the calculations are from
Table 4.


coatings (Table 2) but these elements are mainly detrital in origin. Ti is apparently exclusively associated with the lithogeneous fraction. High values of V in the residue (Table 3) and in the sediments in the Barents Sea, compared to the Gulf of Bothnia (Boström et al. 1983, 1984) indicate that parts of the V contents in the HCl-soluble fractions are leached from lithogeneous input, although the main part originates from the oxyhydroxide fraction.

X-ray diffraction studies of the acid-insoluble residue revealed the presence of quartz and feldspars, i.e. Si, Ca and Na are also associated with the residue (Table 3). Most of the lithogeneous Si occurs in the acid insoluble fraction (Fig. 2, Table 4 and 5) probably in the form of quartz as quartz has been shown to remain unaffected by the acid treatment used (Ingri, unpublished).

Manganese phase

Na, Ba, Ni and Cu are closely associated with manganese, Ca, Na and to a lesser extent Mg are enriched in discoidal concretions but not in flat concretions (Table 3). This can be explained by the association of Na with the manganese phase as stated above; it is also possible that Mg is enriched together with Mn, although primarily present in the lithogenic fraction. The excess of Ca in discoidal concretions could be explained analogously but electron microprobe investigations showed a close correlation between Fe, P and Ca in discoidal concretions (Fig. 5). This fact and the "excess" of Ca in Fe-rich coatings (Table 2) indicate that much of the non-residual Ca is present in the Fe-rich phase. The Sr correlation to
Mn is doubtful; Sr is very well correlated to P-Ca both in rim developed and flat concretions and the Fe and Mn rich coatings show a strong enrichment of Sr in the Fe-phase. Zn does not show any distinct correlation to any of the main phases but is definitely enriched in the Mn-rich coatings (Table 2). Co and Mo have only been determined in the coatings and in discoidal concretions (not included in the correlation matrix). Judging from the obtained values it is seen that Mo is enriched in the Mn-phase (Table 2) and it seems also as if Co is correlated to the Mn-phase.

Iron phase

P, Ca, Si, As, Sr, Y, La and Yb are clearly enriched in the Fe-coatings (Table 2). The correlation coefficient between Fe and P is weak in discoidal and flat type of concretions but the microprobe investigation on a discoidal nodule shows a strong association between Fe and P (Figs. 3 and 5). A clear correlation with Ca is also obvious but the enrichment of Ca in discoidal formed concretions is not seen in flat ones (Table 3). Si is enriched both in Fe-rich coatings and rim developed concretions (Tables 2 and 5, Fig. 2). A small but significant accumulation of Si with Fe has been shown also in Loch Fyne concretions and in the Gulf of Bothnia (Calvert and Price 1977, Ingri, unpublished) usually the Si enrichment in the Gulf of Bothnia is seen in concretions sampled close to the reduced-oxidized interface. The close correlation between Si and Fe in discoidal concretions from the Barents Sea (Fig. 2 and Table 5) could not be proved with the microprobe. The presence of detrital Si in all phases probably masks any preference to Fe. (The micro-
probe scan for Na did not show correlation with Mn, probably due to
the same incorporation of Na-terrigenous matter in all phases).

As is correlated to Fe in both concretionary types with absolute
figures mostly exceeding values found in deep-sea nodules, a feature
that seems to be typical for shallow-marine concretions (Calvert and
Price 1977). Yb, Y and La all show an enrichment in the Fe-rich
coatings. La, however, has no distinct correlation to any of the
major phases when flat and discoidal concretions are considered.
Y is 3 to 5 times enriched in the concretions compared to under-
lying sediment (Table 3) and shows a weak correlation to Fe whereas
Yb is closely associated with Fe throughout the material. V shows
no significant correlation to Fe nor to Mn and no clear association
with Mn or Fe in the coatings from stn 26 (Table 2). V is definitely
correlated to the oxyhydroxide-phase though (enrichment 3 to 6 times
compared to underlying sediment, Table 3), and the high V values
obtained in the Fe-coatings from stn 19 and 5 suggest a correlation
between acid-soluble V and Fe.

Ca-P concretions

The thick Fe-coating found on the slope of the Spitsbergen Banken
(stn 12) and at the shelf east of Svalbard (stn 16) have, as stated
earlier, a composition atypical of ordinary shallow-marine concretions.
X-ray diffraction data on the sample from stn 16 proved the presence
of an apatite phase, not usually encountered in shallow-marine
ferromanganese concretions (Calvert and Price 1977). The apatite
phase readily explains not only the strong accumulation of Sr, Y,
La and Yb, probably as an substitution for Ca, but also the enrichment of Ba in this manganese poor sample (Table 2) (Kolodny 1981).

The Mn and Fe source

Gorshkova (1967) suggested that the high Mn content in the top sediments of the Northern and North-Eastern Barents Sea could be explained by Mn-rich suspended matter from Ob and Yenisei; numerous islands in the Eastern Kara Sea force the waters westward into the North-Eastern Barents Sea. The high Mn/Fe ratio in the discoidal concretions compared to suspended matter ratios in rivers from the coniferous forest belt of Northern Sweden and Russia (Burman 1982, Konovalov 1959, Nesterova 1960) also indicates that, after settlement, this Mn rich fraction is redistributed and enriched in the top sediment owing to redox changes in the sediment (Bruevich 1938). River input to other parts of the Barents Sea is very limited.

Only one larger river, the Petchora River, supplies water directly into the south-eastern parts. Revers on the Kola peninsula and in Norway are small and drain into fiords. Hence the sediments in the central and southern Barents Sea and on the shelf areas around Svalbard and Novaya Zemlya consist of yellow-grey to grey sandy mud with gravel and outcropping relict sediments (Gorshkova 1931, Klenova 1960). Fe-rich flat nodules in the Central Barents Sea as well as the Fe-crusts formed on the Svalbard shelf probably originate from these relict sediments, low in Mn. The Fe content in the pore-waters of these sediments is sufficient for the formation of framoidal pyrite within the sediment (Elverhøi 1977).
and perhaps also sufficient to cause migration and precipitation of Fe at the sediment-water interface. Stains and coatings of Fe on till fragments and glacial clay creating low grade concretionary material probably originate directly from sea-water.

The two different current regimes reflected in the two main communities of fish within the Barents Sea (cod, haddock and plaice are caught in the warm Spitbergen and North Cape currents, whereas polarcod and capeline are abundant in the cold water flowing over the Svalbard shelf. The Mitchell Bently Atlas of the Oceans (1977) indicates that upwelling of cold nutrient rich waters along the Svalbard shelf could be a plausible explanation for the high Ca and P values found in some Fe-concretions at the shelf edge.

Conclusions

The iron-manganese concretions found in the Barents Sea are mainly of three types.

1) Mn-rich discoidal concretions; these are found in the Northern Barents Sea and have possibly been formed by diagenetic enrichment in the sediment of Mn-rich suspended matter. This suspended matter is probably derived from the coniferous forest belt of Northern Russia.
2) Flat concretions and coatings with varying Fe content; these are distributed all over the Barents Sea, and on the Svalbard shelf they occasionally form Fe-pavements on the sea-floor. These deposits may have been formed by diagenetic reactions in relict sediment poor in Mn and/or enriched from sea-water.

3) Fe-concretions very rich in Ca and P forming an apatite phase with much incorporated Y, La, Yb, Sr and Ba. These crusts more resemble marine phosphorites in composition than ordinary shallow-marine Fe-concretions and are possibly an indication of upwelling of nutrient rich cold polar water along the Svalbard shelf.

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