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The Distribution of Iodine and Bromine in the Sediments of the Southwestern Barents Sea

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ABSTRACT

In 42 surface sediments from the southwestern Barents Sea, iodine and bromine ranged from 60 to 828 p.p.m. and 12 to 257 p.p.m., respectively. In the surface environment, both I and Br are related to organic matter; the dependence of halogens on the grain size of the sediment is small. With depth, all sediments showed a marked decrease in I and Br and in I/C and Br/C ratios; the ratios often reach a constant value. This decrease is caused by a loss of halogens during the burial of the sediments. The rate of decrease in I concentration per unit length in the cores has provided a means of estimating the accumulation rates in the sediments.

Introduction. In recent years there has been a growing interest in the mobility of many minor metals in Recent sediments and in their importance in diagenesis and the formation of secondary minerals (Strakhov 1966). Most of these investigations have been concerned with deep-water sediments, and little is known about the diagenetic movement of elements in open-shelf sediments. Of the elements that have been considered (e.g., the transition elements), most of them appear to be partitioned between the more chemically resistant fraction of the sediment (e.g., clays and sands) and the more mobile phases (i.e., the organic and oxide fraction of the sediment). Thus, for a particular element, the contribution made by any one fraction of the sediment is difficult if not impossible to estimate.

It is known that, unlike sedimentary rocks, Recent marine sediments contain high concentrations of I with respect to seawater and show some of the highest concentrations of I in geological materials. Likewise, Recent sediments contain much higher contents of Br than sedimentary (excluding some evaporites) and igneous rocks (Vinogradov 1939). This implies that the presence

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of halogens in Recent sediments is not due to a direct contribution of inorganic detritus entering a basin of deposition but is largely controlled by some other mechanism.

This paper attempts to discover the geochemical and sedimentary controls that govern the distribution, both lateral and vertical, of I and Br in the sediments of the southwestern Barents Sea.

_Bathymetry and Geological History._ The Barents Sea is a wide and relatively deep shelf sea lying between northern Norway and the U.S.S.R., Spitsbergen, and Novaya Zemlya (Fig. 1). The floor comprises a series of troughs, 300 to 400 m deep, separated by ridges (e.g., The Central Elevation) and bordered on the northwest and south by a series of shallower banks and platforms.
The area was apparently above sea level during the Tertiary. Atlantic waters flooded the area in the early Pleistocene during a period of tectonic warping that produced the troughs and platforms seen today (Klenova 1960).

Sediments. The depressions generally contain muds and fine-grained silts, and the elevations are covered with sands, silty sands, and gravel (Klenova 1960). The surface sediments south of 76°N are usually grey-green in color while those to the north are characteristically brown. Occasionally a thin brown surface layer, rarely exceeding 5 cm in thickness, is seen in some southern sediments; this, together with hydrographic data (Zenkevitch 1963), suggests that the surface sediment is oxidizing. The finer-grained sediments are generally, but not always, richer in organic matter than the sands (Gorshkova in: Zenkevitch 1963). The color, composition, and geochemical properties of the sediments at depth sometimes indicate a well-defined subsurface contact between the dominantly grey-green sediment and the underlying bluish-grey sediment (Klenova 1960). Sediments above this horizon are considered by Klenova to represent Recent detritus.

Materials and Analytical Methods. Sediment samples were collected by gravity coring at 42 stations in the southwestern Barents Sea (Fig. 1) during May 1968 on cruise 4 of the R/v ERNEST HOLT. The cores, recovered in 6-cm-diameter plastic tubes, were frozen on board.

The uppermost centimeter of each core, plus 5-cm sections at 5-cm intervals of selected cores, were subsequently sampled and dried at 50°C. The drying did not cause loss of halogens from the sediment (D. H. Doff, personal communication).

I and Br were analyzed by means of X-ray emission spectrometry, using a Philips P.W. 1212 Spectrometer with a tungsten anode at 80 kV and 20 mA, a LiF (200) analyzing crystal, and a scintillation detector. The precision of the method was found to be ± 3% for I and ± 4% for Br. In addition, chlorine contents were determined by X-ray emission methods and were subsequently used to determine the salt content in the dried sediments. The analyses of I and Br were then recalculated on a salt-free basis. In the case of the adjustment for Br, it was assumed that the Br/Cl ratio of the interstitial water was the same as that of seawater.

Organic carbon was determined by dry combustion in a Leco² Carbon analyzer after removing carbonates from a sediment subsample with warm dilute HCl. The precision of the method was ± 2% of the amount present.

Results. The variation in iodine in the surface sediments (i.e., within the interval 0 to 1 cm) was considerable, showing values within the range 60 to

828 p.p.m. The range in values of bromine in the same sediments was 12 to 257 p.p.m.

Because of the small number of surface samples available from such a large area, the areal variation in I and Br was investigated by trend-surface analysis. The distribution of I is shown in Fig. 2; the distribution of Br is similar. Low iodine values are seen in the extreme southwestern and southeastern platforms, especially in areas close to the Norwegian and Russian coasts, with a slight increase in the vicinity of the Murman Bank. Sediments having the highest I and Br contents were found in the Central Depression and in the Western Trough. Intervening areas showed lower I (and Br) levels, and in the cases of the Central Elevation there was a gradual decrease in I and Br
southwestward. Within the Western Trough, both I and Br reached maxima on the northern slope. This is different from the distribution of sediment grain sizes, which show a clear correlation with water depth (Klenova 1960). Hence, the northern slope of this trough is sandy, due to movement of coarser material downslope from the Bear Island-Spitsbergen Bank (Klenova 1960).

Vinogradov (1939, 1959) has suggested that the I (and Br) content of Recent sediments is related to both the grain size and the organic-matter content of a sediment. That is, clayey and organic-rich sediments contain more I and Br. The high I and Br contents of the sandy sediments on the northern flanks of the Western Trough of the Barents Sea may imply that the distribution of halogens in such sediments is not governed by the mechanical composition of the sediment. Furthermore, both I and Br show good correlations with organic carbon in the sediments (Figs. 3, 4). Greater scatter in the Br/C relationship may be due to error introduced by correcting for salt content of the dry sediment.

Although Figs. 3 and 4 show that there is an overall covariance between the halogens and organic matter, this need not imply that the I/C ratio is entirely independent of the mechanical composition of a sediment. A plot of I/C (or Br/C) ratios against organic carbon should show a constant I/C (or Br/C) ratio in sediments of varying carbon content and grain size if there is no dependency of halogen content on the grain size. Fig. 5 shows that muds (high carbon) do have slightly higher I/C ratios (~ 320) than sands (~ 270). We shall show below, when we consider the I/C of the sediments at depth, that the differences in ratio between surface sands and muds can, in fact, be neglected.

Both I and Br show decreasing concentrations with depth in all cores. Some cores, such as EH 59, 71, and 72 (Table I), show a regular pronounced decrease in halogens with depth, often having substantial amounts of I at depth.
The organic carbon values for these cores are relatively constant, with perhaps a slight loss with burial. Other cores (e.g., EH 57, 67, 73, 79, 85) show an abrupt decrease in I and Br values and a relatively uniform or a marked decrease in organic carbon with depth. Below this abrupt change, which occurs at different depths in the cores, the halogen contents are relatively constant.

As in the case of I and Br, the I/C ratio shows either a uniform decrease with depth or an abrupt change at varying levels within the sediment, below which a relatively constant but very low I/C ratio is found. The level at which
Table I Distribution of iodine, bromine, and organic carbon in selected sediment cores from the southwestern Barents Sea. All analyses on salt-free basis. I and Br in p.p.m., organic C in weight % dry sample. Iodine/carbon ratios as $I/C \times 10^4$.

<table>
<thead>
<tr>
<th>Core no.</th>
<th>EH 57</th>
<th>EH 59</th>
<th>EH 67</th>
<th>EH 71</th>
</tr>
</thead>
<tbody>
<tr>
<td>(74°22'N, 30°31'E)</td>
<td>(73°30'N, 30°30'E)</td>
<td>(70°15'N, 38°13'E)</td>
<td>(71°17'N, 43°30'E)</td>
<td></td>
</tr>
<tr>
<td>Depth in core (cm)</td>
<td>I</td>
<td>Br</td>
<td>C</td>
<td>I/C</td>
</tr>
<tr>
<td>0-1</td>
<td>388</td>
<td>102</td>
<td>1.33</td>
<td>292</td>
</tr>
<tr>
<td>0-5</td>
<td>168</td>
<td>50</td>
<td>1.28</td>
<td>131</td>
</tr>
<tr>
<td>10-15</td>
<td>23</td>
<td>8</td>
<td>1.32</td>
<td>17.4</td>
</tr>
<tr>
<td>20-25</td>
<td>22</td>
<td>5</td>
<td>1.35</td>
<td>16.3</td>
</tr>
<tr>
<td>30-35</td>
<td>26</td>
<td>7</td>
<td>1.31</td>
<td>19.8</td>
</tr>
<tr>
<td>40-45</td>
<td>17</td>
<td>10</td>
<td>0.33</td>
<td>26</td>
</tr>
<tr>
<td>50-55</td>
<td>51</td>
<td>25</td>
<td>5</td>
<td>0.39</td>
</tr>
<tr>
<td>60-65</td>
<td>31</td>
<td>12</td>
<td>0.44</td>
<td>77</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Core no.</th>
<th>EH 72</th>
<th>EH 73</th>
<th>EH 79</th>
<th>EH 85</th>
</tr>
</thead>
<tbody>
<tr>
<td>(72°00'N, 44°10'E)</td>
<td>(72°32'N, 42°50'E)</td>
<td>(73°24'N, 33°32'E)</td>
<td>(70°45'N, 35°22'E)</td>
<td></td>
</tr>
<tr>
<td>Depth in core (cm)</td>
<td>I</td>
<td>Br</td>
<td>C</td>
<td>I/C</td>
</tr>
<tr>
<td>0-1</td>
<td>828</td>
<td>257</td>
<td>2.35</td>
<td>352</td>
</tr>
<tr>
<td>0-5</td>
<td>802</td>
<td>270</td>
<td>2.63</td>
<td>305</td>
</tr>
<tr>
<td>10-15</td>
<td>648</td>
<td>240</td>
<td>2.73</td>
<td>237</td>
</tr>
<tr>
<td>20-25</td>
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<td>188</td>
<td>2.16</td>
<td>252</td>
</tr>
<tr>
<td>30-35</td>
<td>530</td>
<td>195</td>
<td>2.19</td>
<td>242</td>
</tr>
<tr>
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<tr>
<td>50-55</td>
<td>443</td>
<td>178</td>
<td>2.00</td>
<td>221</td>
</tr>
<tr>
<td>60-65</td>
<td>465</td>
<td>165</td>
<td>2.05</td>
<td>227</td>
</tr>
</tbody>
</table>

this abrupt fall in ratio takes place does not always relate to the mechanical composition of the subsurface sediments and suggests that the grain size of a sediment is not the controlling factor governing this change. If we assume that the environment of sedimentation has remained essentially constant during the deposition of the uppermost 100 cm or so of sediment, the decrease in I/C (or Br/C) ratios with depth must imply postdepositional removal of I (and Br) from the sediment. Sediments having a uniform decrease in I/C ratio with depth are generally found within the broad depressions of the Barents Sea while those displaying an abrupt change in this ratio are found on and around the banks.

Discussion. The range of I and Br concentrations in the Barents Sea sediments determined here is greater than that given by Vinogradov (1939), who quoted ranges of 30 to 300 p.p.m. I and 25 to 70 p.p.m. Br. Although those
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differences may be caused in part by different analytical methods, it is more probable that they are due to the sandy nature of Vinogradov's samples, since the latter were collected on the Southeastern platform. Furthermore, his samples may not have come from the surface of the sediment.

The considerably higher I/C ratios (~ $3 \times 10^2$) compared with the Br/C ratios (~ $8 \times 10^3$) in all surface samples demonstrate the marked enrichment of I relative to Br in marine sediments (Vinogradov 1939), especially since the concentration of I in seawater (~ 0.05 p.p.m.) is three orders of magnitude lower than that of Br—65 p.p.m. (Harvey 1960).

Marine organisms, in particular algae, are known to concentrate both I and Br from seawater (Shaw 1962). In a few instances (e.g., Laminariae and Phyllophorae), the I and Br contents may be high. Most marine organisms, however, rarely contain more than 100 to 300 p.p.m. I and Br. A comparison of the high halogen contents relative to organic matter (Figs. 3, 4) in the Barents Sea sediments with algal matter suggests that the amount of halogens contributed by the fallout of algal material onto the seabed is small. This, together with the constant areal relationship of halogens to organic matter in the sediments of an area with a highly diversified and variable fauna and flora (Zenkevitch 1963), suggests that the concentration of I and Br in the organic matter of marine sediments is due to some factors other than a simple algal concentration.

Vinogradov (1939) made preliminary investigations of the I contents of near-surface muds from several marginal seas. This work, together with an investigation of the iodine contents of interstitial waters in sediments of the Caspian Sea, the Black Sea, and the Bering Sea (Tageyeva and Tikhomirova 1962), constitutes all the available information on the geochemistry of I and Br in shallow-water sediments. Shishkina and Pavlova (1965), who measured the I distribution in deep-sea muds and their interstitial waters, concluded that there is a general relationship between the content of organic matter, the amount of clay-sized material, and the I (and Br) content of a sediment. Moreover, there is often a general decrease in the I and Br with depth in a sediment, although some sediments (Vinogradov 1939: table 4) have shown no such change. Tageyeva and Tikhomirova (1962), Mun and Bazilevich (1964), and Shishkina and Pavlova (1965) have shown for several marine and nonmarine areas that I in interstitial waters increases in concentration with depth. Much of this water-soluble I is likely to migrate into the overlying waters so that sediments lose I upon burial.

From these observations and from those obtained in the Barents Sea, it is clear that early diagenesis, which also causes marked changes in the composition of organic materials in sediments (Degens et al. 1961, 1963), is the most important control in the distribution of I and Br in sediments.

Data on the distribution of I and Br with depth in a sediment are scant. In order to provide a basis for comparison, we have analyzed the I and C con-
Figure 6. Variation in I/C ratio with depth in core L-66 from the Gulf of California (see Calvert 1966).

tents of a 5-m-long core from the Gulf of California, an area of reducing sediments having a relatively constant accumulation rate of 0.23 m/10³ years (Calvert 1966).

The I/C ratio decreases regularly from a surface value of 139 to approximately 35 at 2.5 m depth (Fig. 6). Below this level, the I/C ratio remains relatively constant. The decrease in I/C ratios in the upper part of the core follows an exponential rather than a linear trend, with greater losses occurring...
in the topmost 40 cm of sediment than elsewhere. Therefore, in areas of continuous sedimentation, a regular loss of I relative to C occurs during the burial of sediments. The I/C ratio is reduced to a low but relatively constant value below a particular level within a given sediment.

In the Barents Sea, sediments that show a regular decrease in halogens and I/C ratios to minimal values (e.g., EH 59, 71, 72; Table I) have been deposited under relatively constant conditions. Alternatively, sediment cores showing abrupt changes at particular levels indicate breaks in sedimentation during the deposition of the core. For example, there is a break in sedimentation between 5 and 15 cm in core EH 57 and between 20 and 35 cm in cores EH 67 and 73 (Table I). Furthermore, the I/C ratios in the upper parts of cores EH 57, 67, 73, 79, 85 (Table I) suggest a period of continuous post-glacial sedimentation overlying glacial or possibly early postglacial sediments. The plane at which this break in sedimentation occurs must represent either an unconformity, with concomitant erosion, or at least a long period of non-deposition. The rate of decrease in I/C ratios with depth in a given area of similar sedimentation (oxidizing) may, in broad terms, be time related, such that in rapidly accumulating sediments the decrease in I/C ratio per unit depth will be less than in sediments having low accumulation rates. Assuming that the break in I/C ratio is a synchronous time plane, sediments that have deep I/C discontinuities would have similar rates of decline in I/C ratio per unit length of core, and this loss would be less than in those sediments where the sedimentation break is closer to the sediment surface. This is borne out by the data in Table I. On these grounds we tentatively suggest that differences in the fall of I/C ratio per unit length in the various cores from the Barents Sea provide relative figures of accumulation rates.

Some indication of the regional trend in the accumulation rates has been attempted by separating all cores in Fig. 1 into four categories on the basis of I loss with depth (Fig. 7). The categories used are arbitrary and cannot at this stage be referred to any other more direct measurement of sediment accumulation in this area. However, the trends indicated in Fig. 7 are in close agreement with those of Klenova (1960). Little or no sediment is accumulating on the upper slopes of the western part of the Spitsbergen—Bear Island Bank and on parts of the southern slopes of the Western Trough. Areas showing low accumulation rates are largely confined to the shallower regions—the Murman Bank, the Southeastern Platform, and parts of the Central Elevation. Higher rates of accumulation occur in troughs, notably in the Central Depression and in the Western Trough. In the latter case, sediment accumulation rates are low in the western end. The highest rates of accumulation occur on the lower slopes of the northern edge of the Southeastern Platform. Klenova (1960) has also indicated, by mechanical analyses of sediments, that high accumulation rates occur on this slope; she believes this is due to the extensive supply of sediments moving northward off the platform.
Figure 7. The areal variation in sedimentary accumulation rates in the Barents Sea on the basis of the rate of decrease in I/C ratio with depth in the cores. Accumulation rates: A - very low, B - low, C - high, D - very high.

Conclusions. The concentrations of I and Br in 42 surface oxidizing sediments from the southwestern Barents Sea range from 60 to 828 p.p.m. and from 12 to 257 p.p.m., respectively. These values demonstrate the marked enrichment of I relative to Br in marine sediments. The cause of these enrichments is not known, but it must be some factor(s) besides the incorporation of halides by marine organisms. In the surface sediments, I and Br are related to the organic matter in the sediments; the correlation of halogen content with grain size of the sediment is very small.

With depth, all cores studied show a decrease in I and Br contents and in I/C and Br/C ratios to a fairly constant value that is caused by a loss of halogens
during the burial of the sediments. Although reducing sediments have lower I and I/C ratios compared with oxidizing sediments, the same trend with depth is observed (Fig. 6).

I/C ratios in the Barents Sea sediments show, with depth, either a regular fall to a constant value or an abrupt change in ratio at a particular level below which the I/C ratio is again constant. These trends indicate either continuous accumulation of sediments or a break in sedimentation at a particular level in a core. The rate of decrease in I/C ratios with depth may in broad terms be time related; low I/C ratios per unit depth may imply high rates of accumulation, and vice versa. This reasoning has been used to estimate the various rates of accumulation in the Barents Sea. High accumulation rates occur in the troughs and on the northern slope of the Southeastern Platform; low rates occur on the more elevated areas (Fig. 1). This variation is in close agreement with previous findings (Klenova 1960).

Future studies may show that other elements that are related to the organic matter of sediments (for instance, nitrogen and phosphorus) may behave in a similar way to the halogens. If this is so, the measurement of sediment accumulation rates will be of considerable importance in assessing the regeneration of nutrient elements from sediments into overlying seawater.

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