# Ionic macrocomponents of the interstitial waters of Puck Bay

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## Abstract

The article analyses the principal ionic components in the sediment interstitial waters of Puck Bay. It was found that the vertical and horizontal distributions of chloride, sulphate and bicarbonate anions, and sodium, potassium, magnesium and calcium cations are affected by underground inflows of fresh water, the hydrostatic pressure of the seawater above the sediment, sulphate reduction and oxidation of organic matter, ion exchange reactions as well as mineral formation and decomposition. Differentiation of ion concentration is most marked in the western part of the Bay, where the proportion of underground inflows in interstitial waters is as high as 90%. Chloride and sodium ions dominate in interstitial waters; the next most abundant anion is either bicarbonate or sulphate, depending on the stage of sediment diagenesis and the proportion of fresh water. The same applies to magnesium and calcium among the cations. The interstitial waters of Puck Bay were classified into three groups representing composition and genesis: sea, mixed, and saline waters, and three subgroups: magnesium-bicarbonate, magnesium-sulphate and calcium-sulphate waters.

## 1. Introduction

The difference in chemical composition of interstitial water as compared with the overlying near-bottom water was noticed for the first time during the 'Challenger' expedition. It was found that the composition of interstitial water filtered from globigerina ooze differed from that of the near-bottom water (Murray and Irvine, 1895). The composition of interstitial water reflects chemical interactions between the solid sediment and the overlying solution. Since the ratio of the dissolved substances to those in the

solid state is very small for most sediment components, reactions and pro-
cesses difficult to analyse in the solid components can be easily investigated
in interstitial water. Interstitial water analysis also provides information on
the early stages of sediment diagenesis.

Grippenberg (1934) and Kullenberg (1952) are the pioneers of studies
on the interstitial water of Baltic Sea sediments. These studies are being
continued with new techniques of interstitial water collection.

The analyses of interstitial water from Gulf of Gdańsk sediments are
at a very early stage (Gursky $et$ $al.,$ 1987; Bolałek, 1988; Jankowska and
Bolałek, 1990). Gursky $et$ $al.$ (1987) analysed 21 samples of interstitial
water from 5 sediment cores collected in the north-eastern part of the Gulf
of Gdańsk and described the stages by which the chemical composition of
interstitial water was built up. Bolałek (1988) described the concentrations
of $Cl^-$, $HCO_3^-$, $SO_4^{2-}$, $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ ions in the interstitial
water of a special sediment profile in Puck Bay. He discussed the drainage
effect of underground water from the proglacial valley of the river Reda on
the basic ion composition of the interstitial water. Jankowska and Bolałek
(1990) analysed differences in chloride ion concentrations in the interstitial
waters of Puck Bay.

The present article discusses the results of studies commenced in 1987 of
the macroconstituents of the interstitial waters in Puck Bay (Bolałek, 1988;
Jankowska and Bolałek, 1990).

Puck Bay is the shallow western part of the Gulf of Gdańsk, 2 m deep
at its western most end and 40–50 m deep in the centre of the entrance to
the Gulf of Gdańsk. Like the bottom bathygraphy, the sediments are highly
diverse. The western part of the bottom is covered with medium- and
coarse-grain sand; this type of bottom also extends along Hel Peninsula.
Small-aleuronic and aleuronic-pelite loams fill the depression of the Bay
(Musielak, 1984).

The Kashubian Lake District upland, genetically related to the Baltic
glacier, forms the western border of the Bay. The upland is dissected by the
proglacial stream valleys of the rivers Reda and Płutnica, the depth of the
troughs varying from 20 to 130 m (Cyberski and Jankowska, 1984). These
valleys give rise to major inflows of underground waters, which amount
to about 14 000 $m^3$ $h^{-1}$ (Cyberski and Jankowska, 1984). These waters by
Alekin's clasification (Alekin, 1956) belong to the second type of the calcium
group of bicarbonate class ($C_{II}^{Ca}$) and the equivalent concentrations (r) of
dissolved salts in these waters form the following series (Bolałek, 1988):
$rHCO_3^- < rCa^{2+} + rMg^{2+} < rHCO_3^- + rSO_4^{2-}$.

The article analyses the distribution of chloride, bicarbonate, sulphate,
sodium, potassium, calcium and magnesium ion concentrations and the in-

tercorrelations between the ions in the interstitial waters of Puck Bay. Concentration changes are discussed in the light of the chemical composition of the water overlying the bottom sediments in the Gulf of Gdańsk, Puck Bay and the Polish sector of the Baltic Sea. Comparison of the data from various locations and depths yields an indication of the geographical differentiation of the ionic macrocomponents of the interstitial waters. Data analysis was used to determine the factors influencing the chemistry of the region's interstitial waters. The chemical composition and information on sediment genesis determined the classification of interstitial waters.

## 2. Materials and methods

Sediment cores were collected at 26 sampling stations located in Puck Bay (Fig. 1) in 1987. The cores were taken with a GOIN corer from on board r/v ' Oceanograf 2 '. The cores, from several to 110 cm in length were immediately sectioned into 5 cm segments, and kept at 4°C until further laboratory processing (about 6 h after sampling).

Interstitial water was squeezed out in the laboratory by a low pressure gas-mechanical method (Bolałek, 1989) in an apparatus based on the principle described by Robbins and Gustinis (1976). The squeezing operation was carried out a few hours after the core sampling. The squeeze water was analysed for chloride, total alkalinity, sulphate, sodium, potassium, calcium and magnesium, in accordance with the well-established methods of determining interstitial water composition (Sayles and Manheim, 1975; Shishkina, 1966, 1972):

- Chloride – by titration with 0.005 M $AgNO_3$ with potassium dichromate indicator (analysis error 0.3%). Bromide and iodide ions are included in this determination, though their concentrations are so low that the chlorinity equivalent can be assumed equal to the concentration of chloride ions.

- Total alkalinity – titration with 0.05 M HCl with methyl orange indicator. Under aerobic conditions, characteristic for most sediments, total alkalinity is the sum of bicarbonate alkalinity, borate alkalinity and the alkalinity of other weak acids ($Alk_x$) (Lakhin, 1979). Taking into account $Alk_x$ caused by ammonia and phosphate ions, the fact that borate alkalinity is a constituent of importance at pH $> 8$ (Ivanoff, 1975) and that in seawater of pH 7–8, over 90% of inorganic carbon is present in the form of bicarbonate (Horne, 1969), total alkalinity was expressed in terms of bicarbonate ion concentration. Hydrogen sulphide was detected in over 15% of samples and $HS^-$ ion alkalinity can reach tenths of mmol $dm^{-3}$, and in extreme cases, *e.g.*
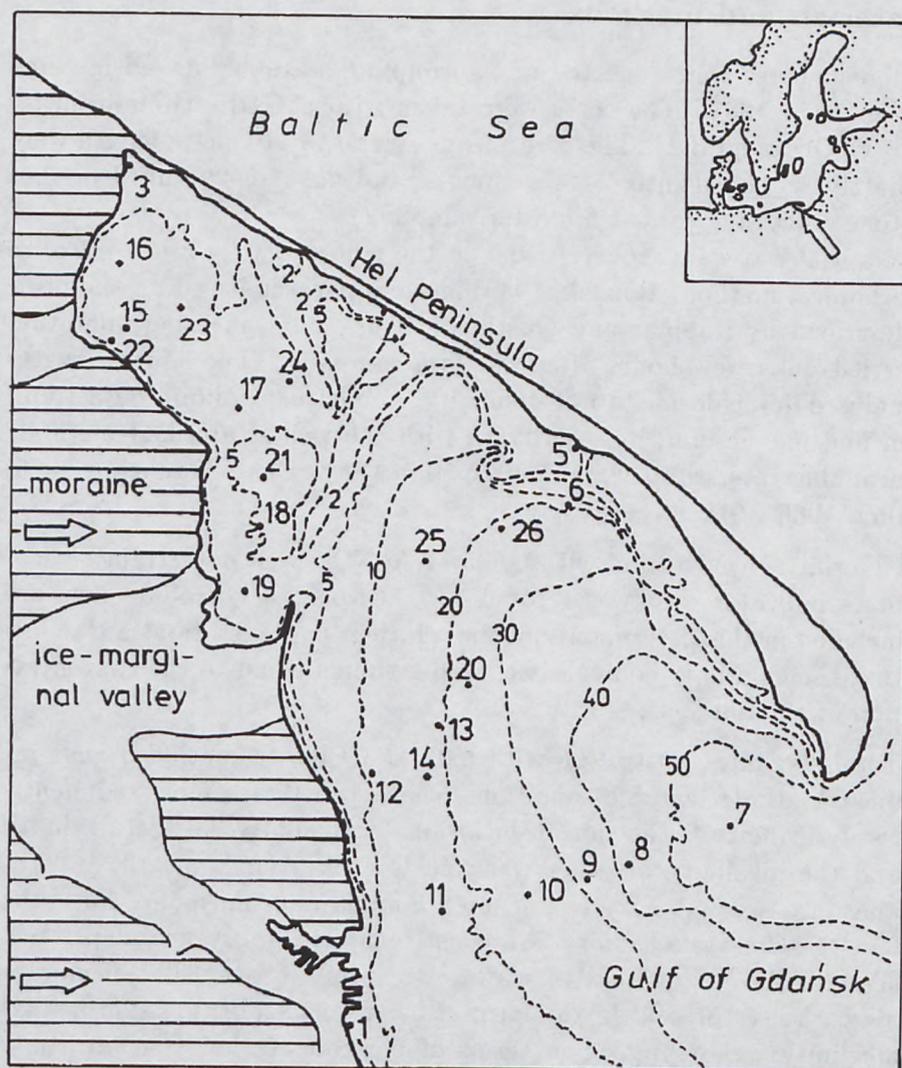
Fig. 1.  Map of sampling stations in Puck Bay

in the Black Sea, even 3 mmol dm$^{-3}$ (Volkov, 1979). The error of the alkalinity determination was 2%.

- Sulphate – nephelometric measurement of barium sulphate suspension absorption in an acidic medium, analytical error – 3%.
- Sodium and potassium – atomic emission spectrometry with an error of about 3%.
- Calcium – complexometric titration with 0.02 M EDTA, murexide indicator, analytical error – 3–5%.
- Magnesium and calcium – complexometric titration with 0.02 EDTA and eriochrome black T indicator. The magnesium concentration was calculated as the difference between the sum of calcium and magnesium, and individual calcium determinations. Analytical error – about 2%.

## 3. Results

Interstitial water from Puck Bay sediments differs from the near-bottom water of the Bay, from Gulf of Gdańsk water and from Baltic Sea water (Tab. 1–3) with respect to macrocomponent concentrations and the ratios

**Table 1.** Concentrations of ionic macrocomponents of near-bottom and interstitial waters of Puck Bay

| Component | $Cl^-$ | $HCO_3^-$ | $SO_4^{2-}$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
|---|---|---|---|---|---|---|---|
| Near-bottom water | | | | | | | |
| n | 263 | 16 | 16 | 16 | 16 | 16 | 16 |
| min | 1.85 | 100 | 560 | 2.03 | 68 | 104 | 252 |
| max | 5.05 | 137 | 649 | 2.25 | 84 | 130 | 278 |
| mean | 3.86 | 112 | 612 | 2.14 | 77 | 114 | 266 |
| SD | 0.22 | 13 | 30 | 0.80 | 7 | 10 | 10 |
| Interstitial water | | | | | | | |
| n | 183 | 181 | 161 | 171 | 173 | 177 | 175 |
| min | 0.37 | 45 | 0 | 0.20 | 9 | 52 | 14 |
| max | 4.28 | 1065 | 1109 | 2.49 | 127 | 281 | 387 |
| mean | 3.12 | 328 | 280 | 1.73 | 79 | 112 | 202 |
| SD | 0.88 | 274 | 240 | 0.55 | 30 | 51 | 82 |

Abbreviations as in Table 2.

**Table 2.** Ionic macrocomponent concentration changes versus chloride concentration in the interstitial waters of Puck Bay

| $Cl^-$ | Estimator | $HCO_3^-$ | $SO_4^{2-}$ | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ |
|---|---|---|---|---|---|---|---|
| 4.0<Cl<4.5 | min | 95 | 0 | 2.16 | 84 | 88 | 231 |
| n = 15 | max | 1037 | 588 | 2.49 | 126 | 156 | 316 |
| | mean | 599 | 128 | 2.31 | 104 | 108 | 264 |
| | SD | 331 | 212 | 0.12 | 13 | 22 | 24 |
| | | | | | | | |
| 3.0<Cl<4.0 | min | 71 | 0 | 1.53 | 55 | 6 | 146 |
| n = 116 | max | 1065 | 1109 | 2.23 | 127 | 140 | 387 |
| | mean | 347 | 308 | 2.01 | 92 | 102 | 247 |
| | SD | 268 | 263 | 0.16 | 15 | 20 | 39 |
| | | | | | | | |
| 2.0<Cl<3.0 | min | 45 | 165 | 1.10 | 36 | 52 | 95 |
| n = 25 | max | 340 | 1026 | 1.80 | 91 | 180 | 202 |
| | mean | 207 | 345 | 1.42 | 65 | 102 | 137 |
| | SD | 85 | 227 | 0.20 | 17 | 42 | 27 |
| | | | | | | | |
| 1.0<Cl<2.0 | min | 74 | 118 | 0.67 | 17 | 60 | 15 |
| n = 18 | max | 301 | 731 | 1.13 | 59 | 281 | 126 |
| | mean | 155 | 235 | 0.85 | 32 | 150 | 72 |
| | SD | 49 | 163 | 0.14 | 11 | 62 | 33 |
| | | | | | | | |
| Cl<1.0 | min | 109 | 112 | 0.20 | 9 | 104 | 19 |
| n = 8 | max | 173 | 218 | 0.48 | 20 | 172 | 56 |
| | mean | 140 | 175 | 0.31 | 14 | 132 | 34 |
| | SD | 21 | 34 | 0.08 | 4 | 22 | 12 |

$Cl^-$ and $Na^+$ – concentrations in g dm$^{-3}$, other concentrations in mg dm$^{-3}$,
n            – number of analysed samples,
min         – minimum concentration,
max         – maximum concentration,
mean       – arithmetic mean,
SD          – standard deviation.

of particular ions to chloride. The ion to chloride ratio is a good tool for observing compositional changes in interstitial water at various stages (Tab. 2). The ion concentration ratio shows the most significant changes in water with a chloride concentration below 2 g $Cl^-$ dm$^{-3}$. Bicarbonate, sulphate and calcium concentrations differ greatly as compared with the Bay's near-bottom water, magnesium differs somewhat less. The least changeable are the sodium to chloride and potassium to chloride ratios.

**Table 3.** Empirical relationships between ionic macrocomponent concentrations in waters of Puck Bay

| Chloride ion concentration [g dm$^{-3}$] | Estimator | $\frac{HCO_3^-}{Cl^-}$ | $\frac{SO_4^{2-}}{Cl^-}$ | $\frac{Na^+}{Cl^-}$ | $\frac{K^+}{Cl^-}$ | $\frac{Ca^{2+}}{Cl^-}$ | $\frac{Mg^{2+}}{Cl^-}$ |
|---|---|---|---|---|---|---|---|
| **Puck Bay – near-bottom water** | | | | | | | |
| Cl<4.04 | min | 0.025 | 0.145 | 0.537 | 0.018 | 0.027 | 0.068 |
| | max | 0.036 | 0.172 | 0.560 | 0.021 | 0.035 | 0.069 |
| | mean | 0.030 | 0.159 | 0.552 | 0.020 | 0.030 | 0.069 |
| | SD | 0.004 | 0.008 | 0.008 | 0.001 | 0.003 | 0.001 |
| **Puck Bay – interstitial water** | | | | | | | |
| Cl<4.24 | min | 0.016 | 0.000 | 0.503 | 0.012 | 0.019 | 0.011 |
| n = 183 | max | 0.357 | 0.438 | 0.650 | 0.036 | 0.298 | 0.099 |
| | mean | 0.107 | 0.109 | 0.556 | 0.025 | 0.048 | 0.063 |
| | SD | 0.064 | 0.074 | 0.028 | 0.005 | 0.053 | 0.012 |
| 4.0<Cl<4.24 | min | 0.025 | 0.000 | 0.537 | 0.021 | 0.021 | 0.057 |
| n = 16 | max | 0.247 | 0.146 | 0.591 | 0.031 | 0.037 | 0.076 |
| | mean | 0.134 | 0.032 | 0.562 | 0.025 | 0.026 | 0.064 |
| | SD | 0.079 | 0.053 | 0.020 | 0.003 | 0.005 | 0.006 |
| 3.0<Cl<4.0 | min | 0.019 | 0.000 | 0.526 | 0.021 | 0.018 | 0.048 |
| n = 116 | max | 0.289 | 0.312 | 0.626 | 0.032 | 0.039 | 0.099 |
| | mean | 0.095 | 0.084 | 0.552 | 0.026 | 0.028 | 0.068 |
| | SD | 0.071 | 0.071 | 0.021 | 0.003 | 0.005 | 0.009 |
| 2.0<Cl<3.0 | min | 0.016 | 0.071 | 0.519 | 0.017 | 0.019 | 0.045 |
| n = 25 | max | 0.138 | 0.336 | 0.650 | 0.036 | 0.086 | 0.081 |
| | mean | 0.085 | 0.135 | 0.573 | 0.026 | 0.042 | 0.056 |
| | SD | 0.036 | 0.080 | 0.035 | 0.007 | 0.018 | 0.008 |
| 1.0<Cl<2.0 | min | 0.036 | 0.073 | 0.503 | 0.012 | 0.033 | 0.011 |
| n = 18 | max | 0.238 | 0.455 | 0.639 | 0.032 | 0.207 | 0.073 |
| | mean | 0.104 | 0.156 | 0.556 | 0.021 | 0.103 | 0.045 |
| | SD | 0.037 | 0.106 | 0.038 | 0.005 | 0.048 | 0.018 |
| Cl<1.0 | min | 0.150 | 0.236 | 0.507 | 0.018 | 0.144 | 0.044 |
| n = 8 | max | 0.459 | 0.438 | 0.564 | 0.032 | 0.289 | 0.080 |
| | mean | 0.268 | 0.312 | 0.533 | 0.025 | 0.241 | 0.058 |
| | SD | 0.105 | 0.058 | 0.017 | 0.005 | 0.049 | 0.011 |
| Gulf of Gdańsk[*] | | 0.043 | 0.144 | 0.551 | 0.021 | 0.033 | 0.067 |
| southern Baltic Sea[**] | | 0.020 | 0.141 | 0.554 | 0.021 | 0.026 | 0.067 |
| Ocean[***] | | 0.007 | 0.140 | 0.556 | 0.021 | 0.021 | 0.067 |

[*]    Młodzińska, 1975,
[**]   Trzosińska, 1977,
[***]  Culkin, 1965.
Abbreviations as in Table 2.

The chloride ion concentration in the near-bottom water of Puck Bay was about half as much as that in the surface water of the open sea, and ranged from 1.85 to 5.05 g $Cl^-$ $dm^{-3}$; values below 3.50 g $dm^{-3}$ and over 4.51 g $dm^{-3}$ were recorded in only 15 samples, *i.e.* they made up only about 6% of all the results obtained (Fig. 2). The most frequent concentration range was 3.51–4.00 g $Cl^-$ $dm^{-3}$ (70.3% of the result set). The $Cl^-$ concentration in such water was higher in the deeper part of the Bay, and lower in the shallow area (Fig. 4a), the reason being the inflow of more saline water from the Gulf of Gdańsk into the deeper region of the Bay.

Chloride concentrations in interstitial water ranged from 0.37 to 4.25 g $dm^{-3}$ (Tab. 1). The proportion of lower concentrations was greater in relation to near-bottom water: 18% of results were found in the 3.01–3.51 g $dm^{-3}$ range, and only 41.5% in the 3.51–4.00 g $dm^{-3}$ range (Fig. 2). Vertically, chloride ion concentration decreased in interstitial water with depth (Fig. 3). In the 0–5 cm layer chloride concentration decreased from 4.28 to 2.43 g $dm^{-3}$. The lowest chloride concentrations were detected in the near-shore zone in the vicinity of Władysławowo and at the mouth of the river Reda; the highest, over 4.00 g $dm^{-3}$, were found in the north-eastern area of the basin (Fig. 4). The 2.00 g $dm^{-3}$ isochlore appeared in the chloride distribution in interstitial water of the 20–25 cm sediment layer near the entrance to the proglacial valleys of the rivers Reda and Płutnica; concentrations of 4.00 g $dm^{-3}$ were found solely along Hel Peninsula. At depths of 40–45 cm interstitial water contained still lower amounts of chloride, particularly in sediments adjacent to the upland shore-line. The 1.00 g $dm^{-3}$ isochlore was found in this profile, and concentrations of 4.00 g $dm^{-3}$ and higher were not detected (Fig. 4c). In general, the chloride concentration increased in all sediment layers from the western shore of Puck Bay towards the east. Interstitial waters have been classified as follows: sea – with a chloride concentration close to that of the near-bottom water $Cl^-$ > 3 g $dm^{-3}$, mixed (2 < $Cl^-$ < 3 g $dm^{-3}$) and saline ($Cl^-$ < 2 g $dm^{-3}$).

Bicarbonate ion concentration in the near-bottom water of the Bay varied in a rather narrow band from 0.025 to 0.036 g $dm^{-3}$ (Tab. 1).

Interstitial water bicarbonates here were found to range widely from 0.045 to 1.065 g $dm^{-3}$ (Tab. 1). The largest number of results (45.8%) lay within the 0.100 to 0.200 g $dm^{-3}$ concentration range. Over 50% of results exceeded the maximum bicarbonate concentrations in the near-bottom water of the Bay. 30.5% of results lay within the 200 to 500 mg $dm^{-3}$ range, and concentrations over 500 mg $dm^{-3}$ made up 17.4% of results. Bicarbonate concentration in the interstitial water varied in both horizontal and vertical profiles. In the vertical profiles (Fig. 3), the bicarbonate concentration changes were not so explicit as those of chloride. In most

cases an increase in bicarbonate concentration with depth was observed. The distribution of bicarbonate concentrations indicated a relationship with the sediment type and clearly reflected the effects of underground and sea water inflows. The effect was noticeable at all levels analysed (Fig. 5). The maximum bicarbonate concentrations were found in pelite and aleurite sediments, where the interstitial water yielded chloride concentrations of $> 3$ g dm$^{-3}$. Concentrations close to near-bottom sea water levels were noted in the sandy sediments of the coastal region.

The bicarbonate-chloride ratio in Puck Bay's interstitial waters ranged from 0.016 to 0.357 (Tab. 3). High values of the ratio were found for waters with chloride concentrations $> 3$ g dm$^{-3}$. Bicarbonate concentrations were related to chloride concentrations by the following equation:

$$HCO_3\,(g\,dm^{-3}) = -0.01184 + 0.1090\,Cl\,(g\,dm^{-3}). \tag{1}$$
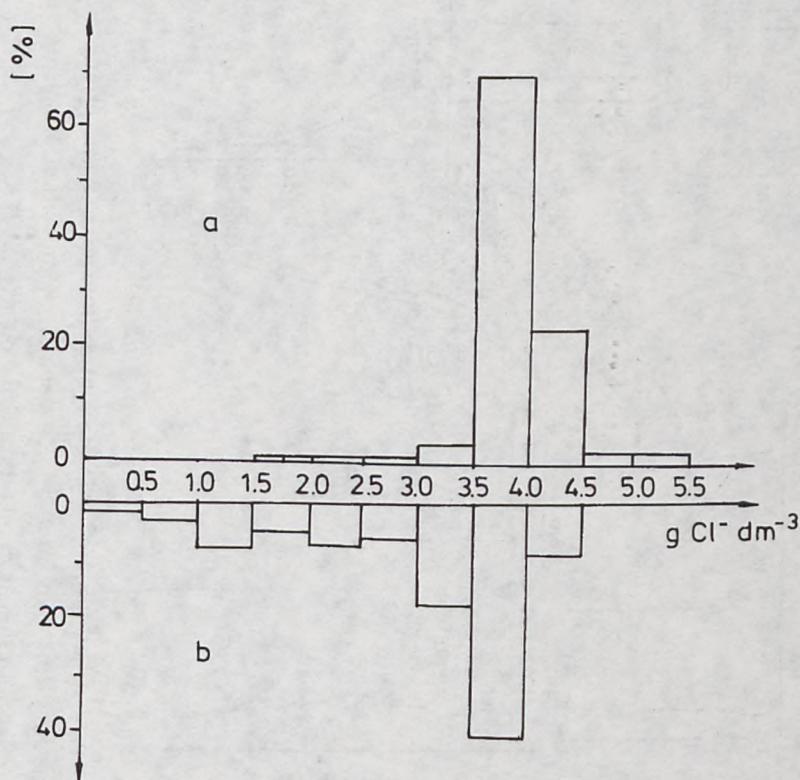


Fig. 2.  Chloride ion concentration histogram in near bottom (a) and interstitial water (b)
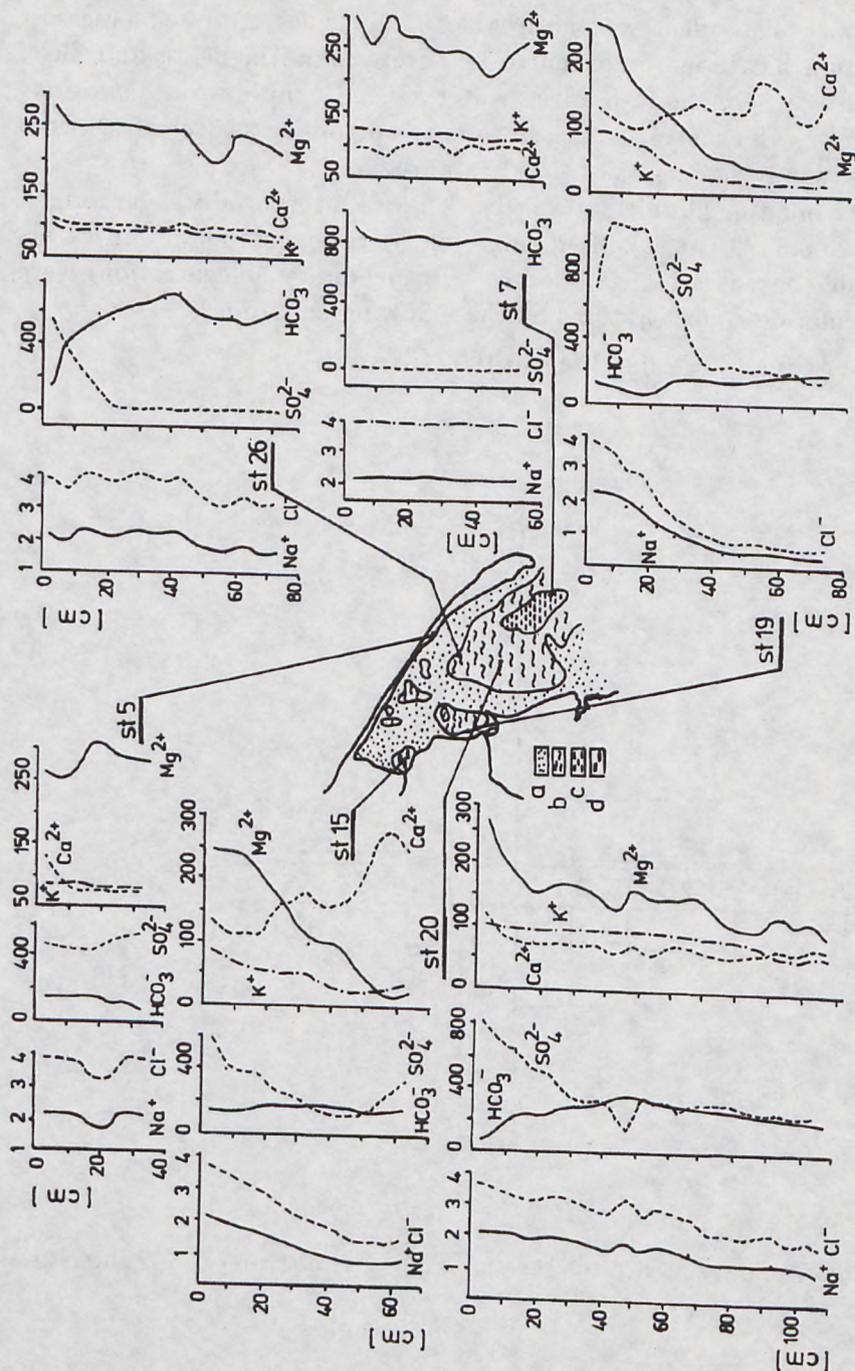
Fig. 3. Vertical distribution of chloride and sodium ions [g dm⁻³] and bicarbonate, sulphate, calcium and magnesium ions [mg dm⁻³] in interstitial waters *vs.* composition of surface sediments of Puck Bay: a – sand, b – aleurite, c – pelite, d – peat (Jankowska and Bolałek, 1990)
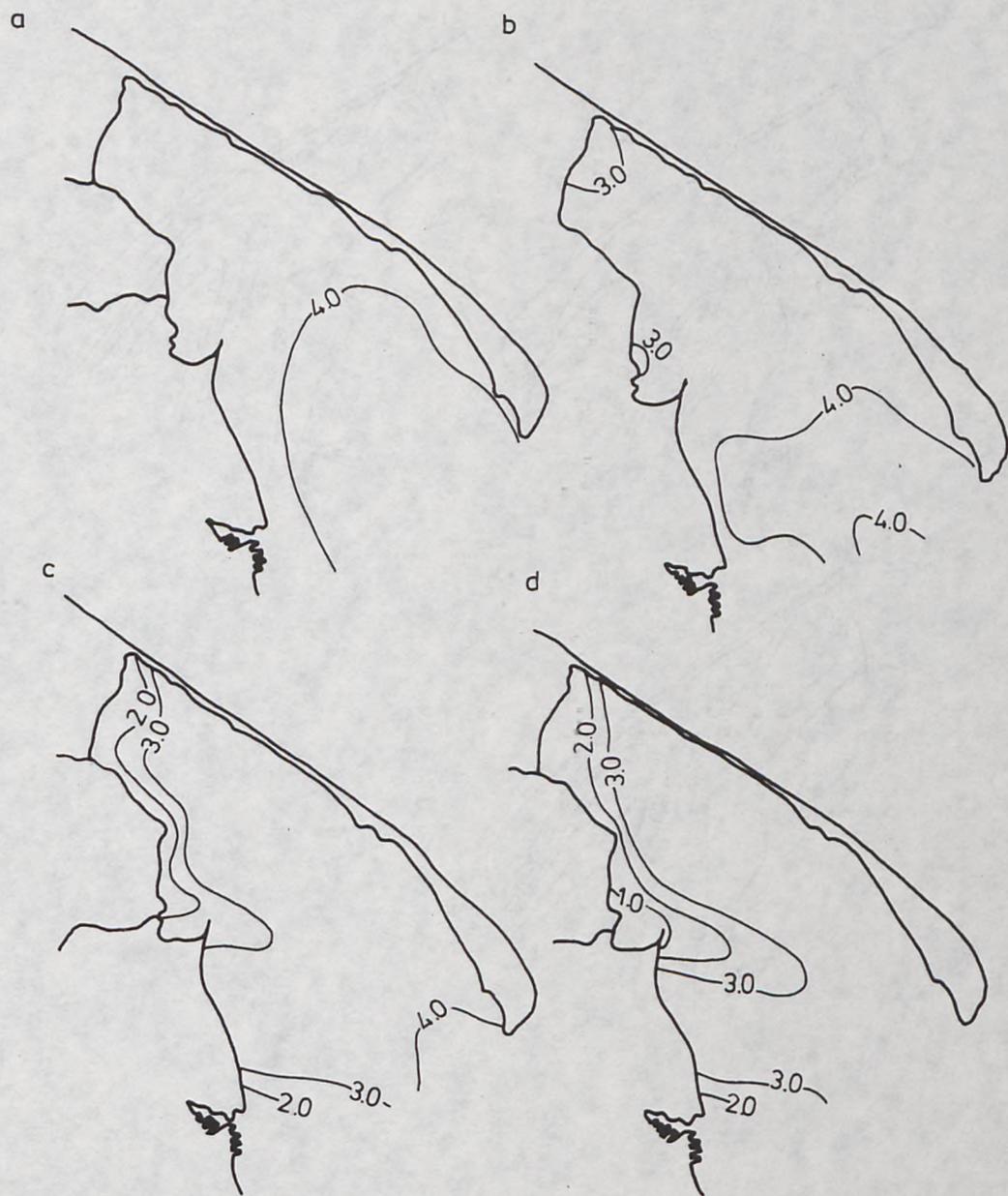
Fig. 4.   Chloride ion distribution [g dm$^{-3}$] in near-bottom (a) and interstitial water from depths of 0–5 cm (b), 20–25 cm (c) and 40–45 cm (d) in Puck Bay
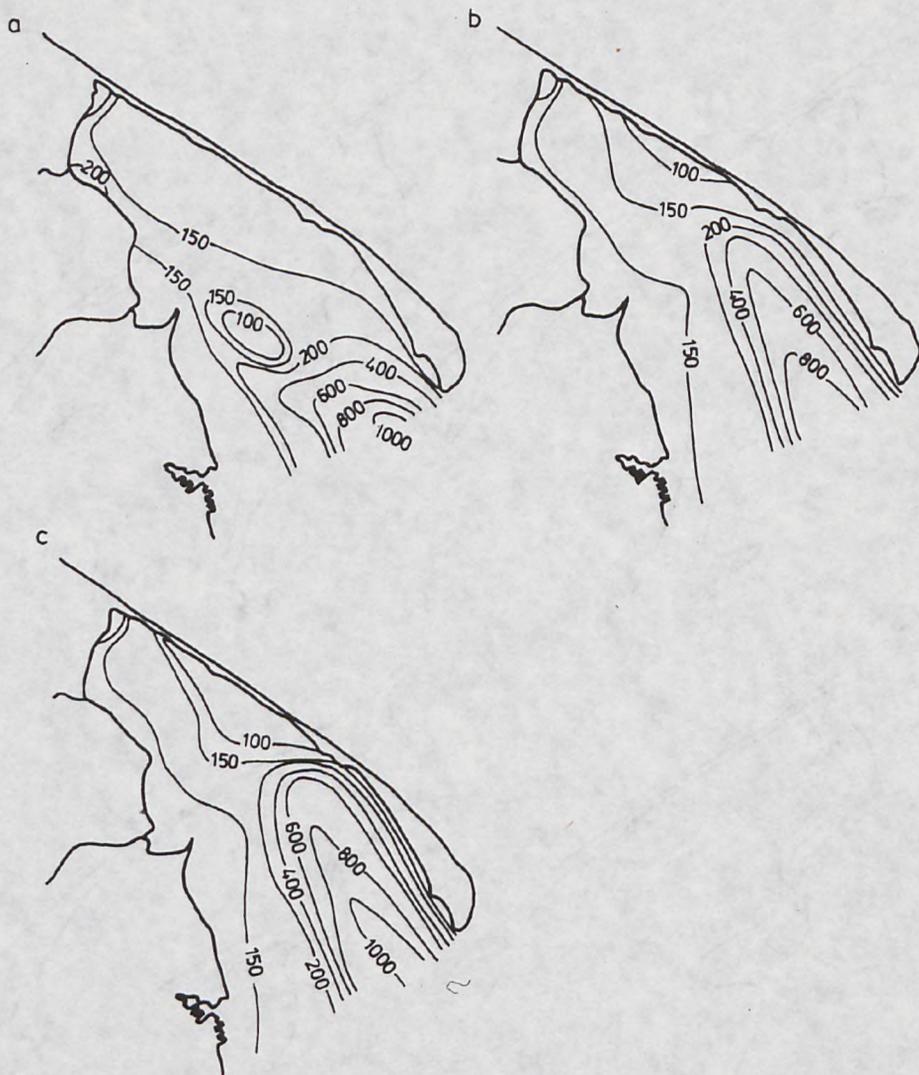
Fig. 5.   Bicarbonate ion distribution [mg dm$^{-3}$] in interstitial water from depths of 0–5 cm (a), 20–25 cm (b) and 40–45 cm (c) in Puck Bay

Like bicarbonates, sulphate ions showed considerable variability, depending on the sediment type and proportion of fresh water. Sediments with a large pelitic or aleurite-pelitic fraction and considerable amounts of bicarbonates contained few, if any, sulphates. By contrast, the sandy sediments adjacent to Hel Peninsula contained large quantities of sulphates at every depth (Fig. 6). The observed concentrations corresponded closely to the levels found in the near-bottom water of the Bay. Generally, sulphates were found within the 0–1109 mg dm$^{-3}$ range. The majority of results (80%) were lower than the minimum concentrations detected in the near-bottom water. The class of low concentrations – <100 mg dm$^{-3}$ – comprised 26% of the results.

The ratio of sulphate to chloride concentrations also varied considerably – from 0.000 to 0.438 (Tab. 3). The lowest $SO_4^{2-}$ : $Cl^-$ values were found for water of high chloride content.

Sulphate concentration was related to chloride concentration by

$$SO_4 \, (g\,dm^{-3}) = 0.224 + 0.0193 \, Cl \, (g\,dm^{-3}). \tag{2}$$

Sodium ion concentration in the near-bottom water of the Bay varied from 2.03 to 2.25 g dm$^{-3}$ and displayed a variability following the chloride pattern. The weight ratio of sodium to chloride ions changed only slightly (Tab. 3) – from 0.537 to 0.560, with the mean of 0.552 equal to the mean value determined for Gulf of Gdańsk water (Młodzińska, 1975).

The interstitial waters of the Bay contained sodium ions within the range from 0.20 to 2.49 g dm$^{-3}$. 43.9% of the results were found in the 2.01–2.50 g dm$^{-3}$, and 29.8% in the 1.51–2.00 g dm$^{-3}$ ranges. Concentrations < 1.00 g dm$^{-3}$, not detected in the near-bottom water at all, made up 14.6% of the results. Vertically, sodium ion concentration decreased in the interstitial water with depth (Fig. 3).

The vertical and horizontal distributions of sodium concentration in the interstitial waters closely resembled the distributions of chloride ion concentrations. In regions of lower chloride concentrations, the sodium-to-chloride ratio increased in the interstitial waters with depth. The following relationship between sodium and chloride ions was found for the entire set of results:

$$Na \, (g\,dm^{-3}) = 0.0203 + 0.5499 \, Cl \, (g\,dm^{-3}). \tag{3}$$

The Na-Cl correlation coefficient, equal to 0.99 (Tab. 4), supported the strong relationship between these ions.

Potassium concentrations in the near-bottom water of Puck Bay varied little, from 0.068 to 0.084 g dm$^{-3}$ (Tab. 1). The mean concentration was 0.077 g dm$^{-3}$, and the mean ratio of potassium to chloride ion concentration was 0.02, as in the Gulf of Gdańsk (Tab. 3).
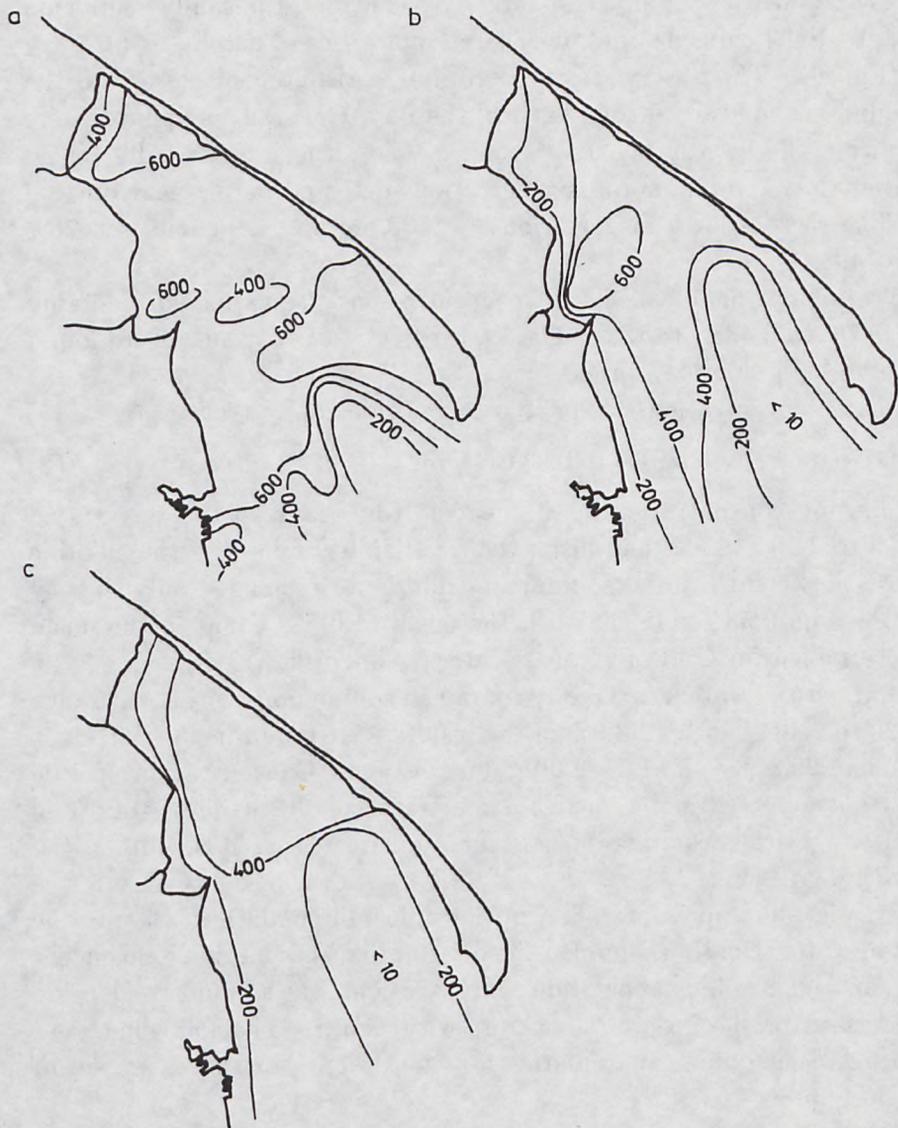
Fig. 6. Sulphate ion distribution [g dm$^{-3}$] in interstitial water from depths of 0–5 cm (a), 20–25 cm (b) and 40–45 cm (c) in Puck Bay

**Table 4.** Correlation coefficients of ionic macrocomponent concentrations of the interstitial waters of Puck Bay

| | $Cl^-$ | $HCO_3^-$ | $SO_4^{2-}$ | $Na^+$ | $K^+$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|
| $Cl^-$ | 1.0000 | | | | | |
| $HCO_3^-$ | 0.3954 | 1.0000 | | | | |
| $SO_4^{2-}$ | 0.0814 | -0.6816 | 1.0000 | | | |
| $Na^+$ | 0.9901 | 0.4341 | 0.1087 | 1.0000 | | |
| $K^+$ | 0.8666 | 0.4992 | 0.0326 | 0.8779 | 1.0000 | |
| $Ca^{2+}$ | -0.3256 | -0.2730 | -0.0273 | -0.3636 | -0.3893 | 1.0000 |
| $Mg^{2+}$ | 0.8563 | 0.2894 | 0.0912 | 0.8795 | 0.6911 | -0.0934 |
| | | | | | | 0.3256* |

hyperbolic correlation.

Potassium concentration in the interstitial waters of the Bay varied widely – from 0.009 to 0.127 g $dm^{-3}$ (Tab. 1). The greatest number of results was found in the 0.080 to 0.100 g $dm^{-3}$ (31.2%) and in the 0.101 to 0.120 g $dm^{-3}$ (26.0%) ranges.

Like the distribution of sodium, that of potassium in the interstitial waters of the Bay's sediments in both vertical and horizontal profiles closely resembled the distribution of chloride ions (Fig. 3). The relationship between the two ions was expressed by

$$K\,(g\,dm^{-3}) = -8.8 \times 10^{-4} + 0.0259 Cl\,(g\,dm^{-3}). \qquad (4)$$

The K–Cl correlation coefficient was 0.87, and the coefficient with sodium was 0.88; the correlations with other macrocomponents were weaker.

The calcium concentration in the near-bottom water of the Bay fluctuated from 104 to 130 mg $dm^{-3}$ (Tab. 1).

The interstitial waters contained from 0.52 to 281 mg $dm^{-3}$ calcium (Tab. 1). At station 1 at a depth of 15–20 cm, the calcium concentration was as high as 513 mg $dm^{-3}$; this amount was attributed more to the accumulation of calciferous shells than to the intrusion of water of different chemical composition. 44.4% of results were found in the 50–100 mg $dm^{-3}$ range, 43.8% in the 100-150 mg $dm^{-3}$ range, and concentrations > 150 mg $dm^{-3}$, not detected in the near-bottom water, comprised 11.8% of the data set.

The maximum amounts of calcium were found in the vicinity of the Reda and Płutnica proglacial valleys (Fig. 7), the concentrations gradually diminishing towards the east.

The peak values were measured at stations 1 and 15. The core from station 15 contained 281 mg $dm^{-3}$ calcium at a depth of 55–60 cm. Certain subsurface samples showed a significantly higher calcium content than expected from the analysis of the surface sediment layer (0–5 cm).
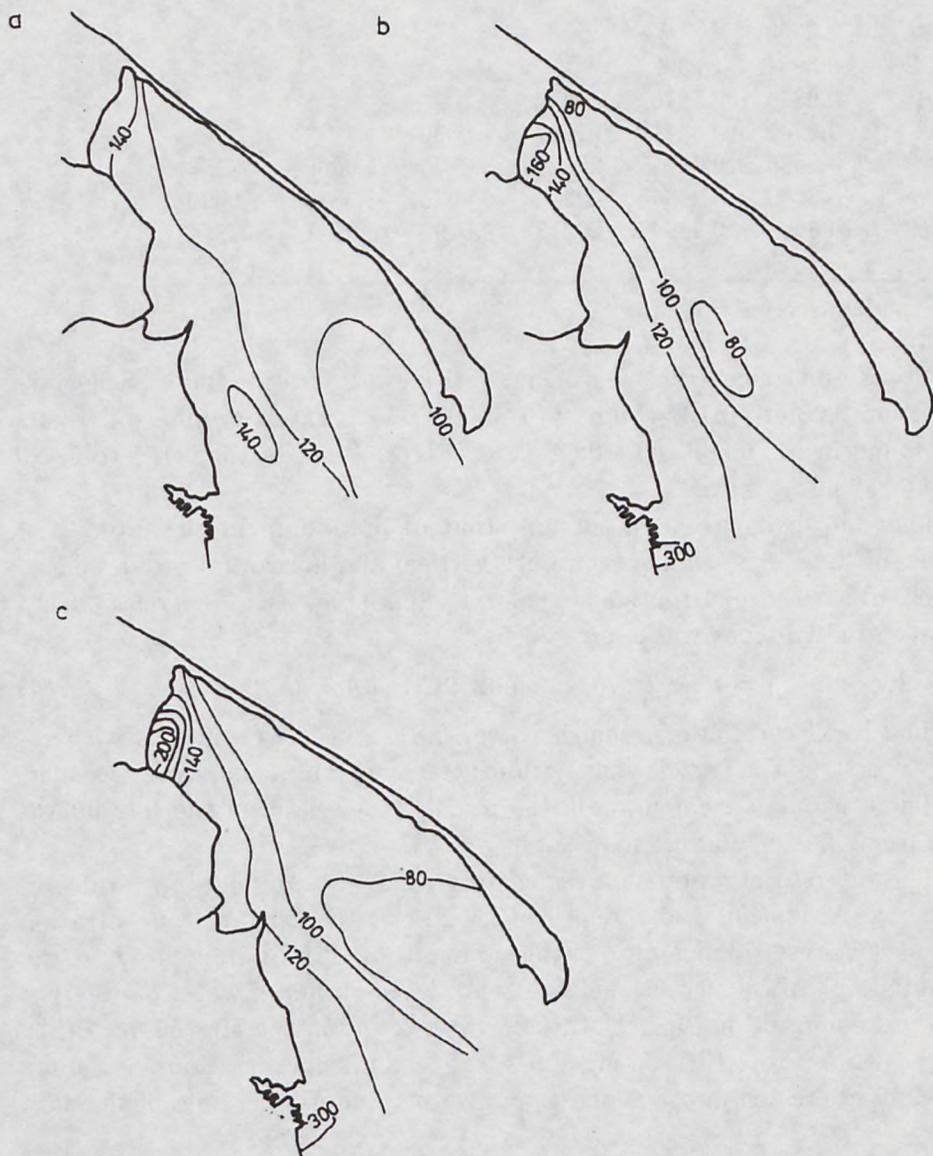
Fig. 7.   Calcium distribution [mg dm$^{-3}$] in interstitial water from the depths of 0–5 cm (a), 20–25 cm (b) and 40–45 cm (c) in Puck Bay

The Ca:Cl ratio hardly varied with depth in the northern and north-eastern part of the Bay (stations 5, 7, 8, 9), approximating to the mean of the near-bottom water (Tab. 3). In the central area of the Bay, at station 20, the calcium-to-chloride ratio remained stable down to 80 cm, *i.e.* to the depth where the chloride concentration fell sharply. The maximum values of the calcium-to-chloride ratio were recorded in the western part of the Bay, *e.g.* at station 19. The ratio increased nearly tenfold with depth (Fig. 8), this probably being the effect of calcium inflow with underground waters.
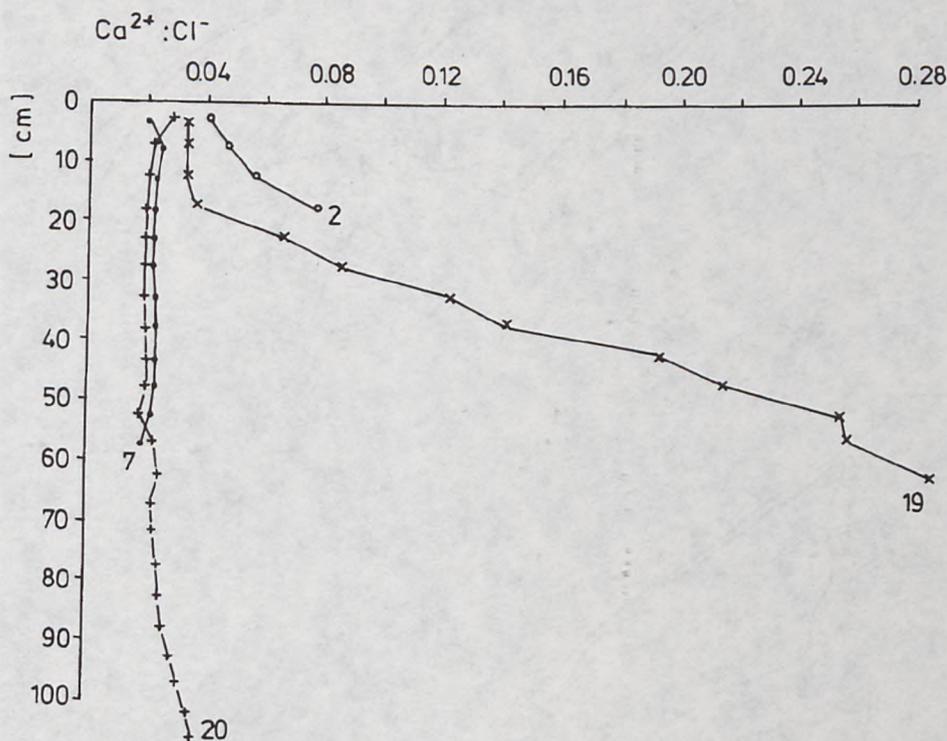
Fig. 8. Changes of the calcium-to-chloride concentration ratio in interstitial water

Calcium appeared in the underground waters of the regions adjacent to the Bay in concentrations of 60–100 mg dm$^{-3}$, *i.e.* the same level as in seawater, though its ratio to chloride ions extended to over several thousand.

The following equation was found to describe the calcium-to-chloride ion relationship:

$$Ca\,(g\,dm^{-3}) = 0.1656 - 0.0165\,Cl\,(g\,dm^{-3}). \qquad (5)$$

The magnesium concentration in the near-bottom water of the Bay showed little variability (Tab. 1). The mean concentration was 266 mg dm$^{-3}$,
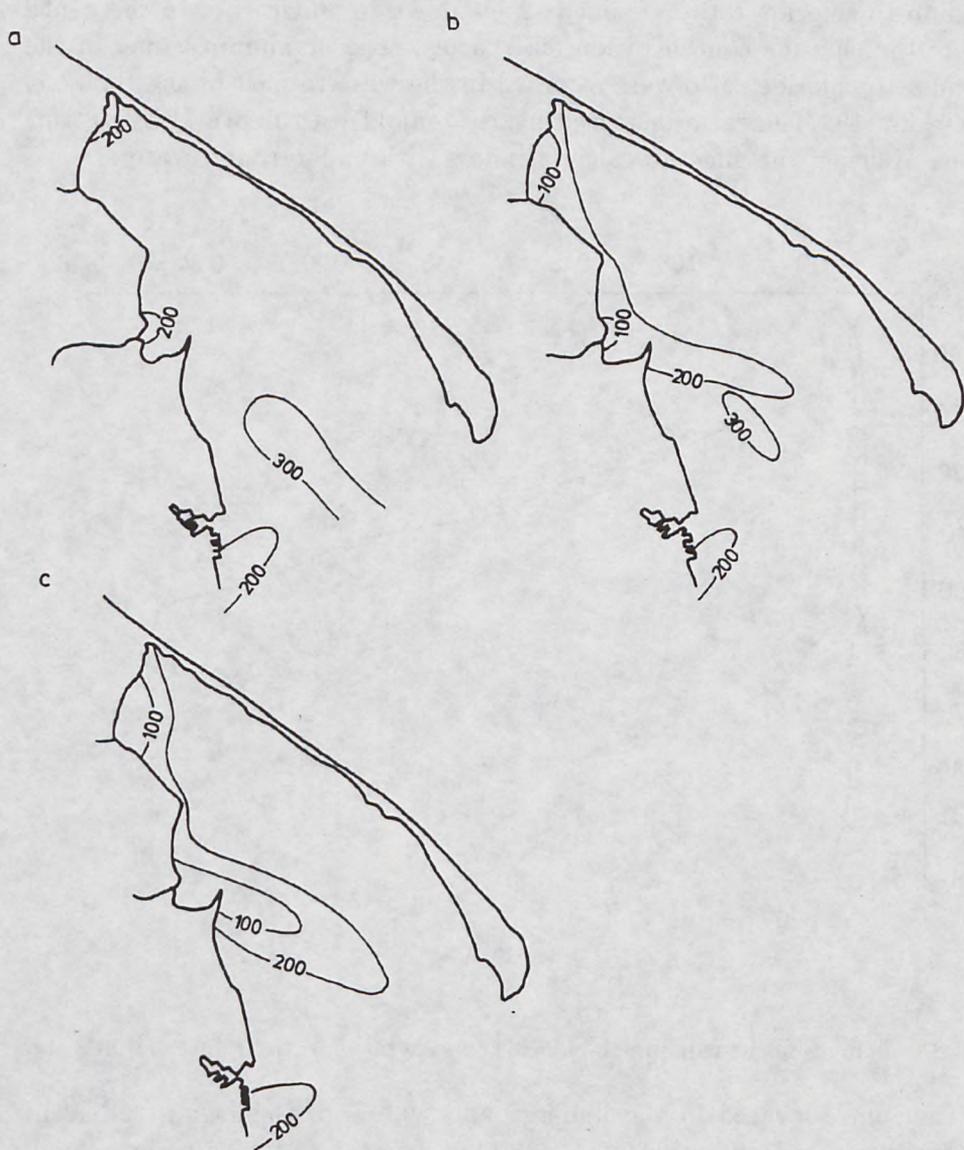
Fig. 9.  Magnesium distribution [g dm$^{-3}$] in interstitial water from depths of 0–5 cm (a), 20–25 cm (b) and 40–45 cm (c) in Puck Bay

and the ratio of magnesium to chloride ion concentration reached 0.069, a value similar to that of the Gulf of Gdańsk (Tab. 3).

The magnesium concentration in the interstitial waters of the Bay's sediments varied over a wide range – from levels close to zero (14 mg dm$^{-3}$) to one exceeding seawater concentrations (387 mg dm$^{-3}$). 58.8% of the results were in the 200–300 mg dm$^{-3}$ class, 6% of results exceeded the upper limit. Magnesium concentrations decreased with sediment depth (Fig. 3). The vertical distribution of magnesium followed the distribution pattern of chloride ions. The lowest concentrations were measured in the western part of the Bay (Fig. 9). The relationship between magnesium and chloride concentrations is described by

$$Mg\,(g\,dm^{-3}) = -0.01632 + 0.07057\,Cl\,(g\,dm^{-3}). \tag{6}$$

The magnesium-to-chloride ratio ions varied between 0.011 and 0.99. In interstitial water with a chloride concentration $< 3$ g dm$^{-3}$ (Tab. 2) the magnesium concentration was found to be lower than that indicated by the mean Mg:Cl ratio in the near-bottom water or in the surface 0–5 cm sediment layer.

## 4. Discussion

The chemical composition of interstitial water in marine sediments is usually very complex and depends on a variety of conditions: geographical (distance from land or from watercourses), geological (minerals present in sediments, sediment type), sedimentation, hydrogeological (underground water intrusions), physico-chemical (redox and sorption processes, hydrostatic pressure of seawater), biological (bioturbation, organic matter input in the form of detritus) and anthropogenic. The main role is attributed to the hydrochemical relationship between interstitial waters and sediments. This group of mechanisms includes the mixing of water masses, the mineralization of organic matter in sediments, and the adsorption of elements on sediment particles. The complex action of these processes results in a physico-chemical balance between the interstitial water and the surrounding sediment.

The main factors influencing the chemical composition of the interstitial water in Puck Bay seem to be:

- intrusions of underground water,
- the hydrostatic pressure of seawater,
- reduction of sulphate and oxidation of organic matter,
- ion exchange reactions,
- reverse weathering.

Chloride is a good indicator of water inflow of different chemical composition, because it is an active hydrochemical migrant. It does not form insoluble salts with seawater macrocomponents, neither does it take part in adsorption processes. Chloride distribution does not depend on either the chemical or the biogeochemical composition of the sediment. Owing to the good solubility properties of chlorides, 97 to 99% of the chloride concentration is found in interstitial water. The chloride concentration is affected by diffusion processes, and by migration processes caused by compaction and intrusions of underground water of different composition. For these reasons, chloride ion concentration has been applied as an indicator of the proportion of underground water in interstitial water. If $\eta$ is taken to be the mixing coefficient of underground waters of different composition (Ovchinnikov, 1963)

$$\eta = Q_F \times Q_S^{-1} = (a - c) \times (c - b)^{-1}, \tag{7}$$

where

$Q_F$ – volume of underground water in the mixture,

$Q_S$ – volume of sea water in the mixture,

$a$   – chloride ion concentration in the near-bottom water of Puck Bay at a given sampling station,

$b$   – chloride ion concentration in the underground water (calculations were done for the maximum concentration 0.05 g dm$^{-3}$),

$c$   – chloride ion concentration in the interstitial water.

The mixing coefficient $\eta$ ranged from 0.0 to 10.94. The percentage of underground water was calculated from

$$Q_F(Q_F + Q_S)^{-1} \times 100\% = (1 + \eta^{-1})^{-1} \times 100\%. \tag{8}$$

and varied from 0 to 92%. Underground water was found to have made the greatest contribution in regions stretching away from the proglacial valleys of the rivers Reda and Płutnica. Underground water made up 50% of the interstitial water at depths of 10–15 cm (stations 1 and 2) (Fig. 10) and 20–40 cm (stations 15 and 19), the latter about 2 km off shore.

Sea water prevailed in the interstitial waters at other stations. Figure 11 illustrates the analysis of chloride ion concentration 3 g dm$^{-3}$ and indicates that the height of the water column over the sediment influences the depth of the isochlore. The interstitial water, a syngenetic water, could not be pushed out by drainage water flowing in from land because of the hydrostatic pressure of the water over the sediment.

The chemical composition of interstitial water of marine origin is influenced by sulphate reduced (desulphatation) by organic carbon. A decrease in sulphate concentration in interstitial water is frequently observed in marine sediments as resulting from bacterial reduction processes (Berner et al.,
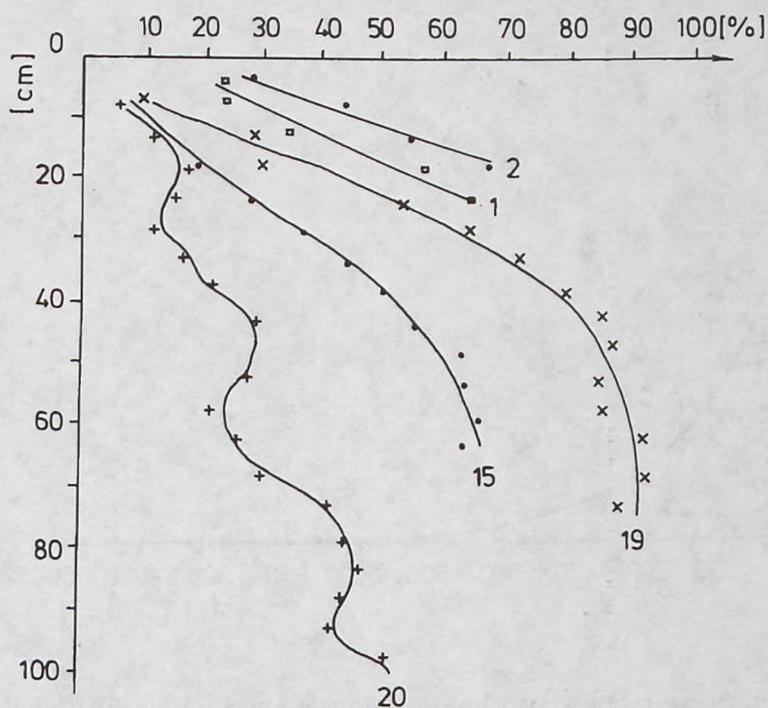
Fig. 10.  Percentage of underground fresh water in the interstitial waters of Puck Bay
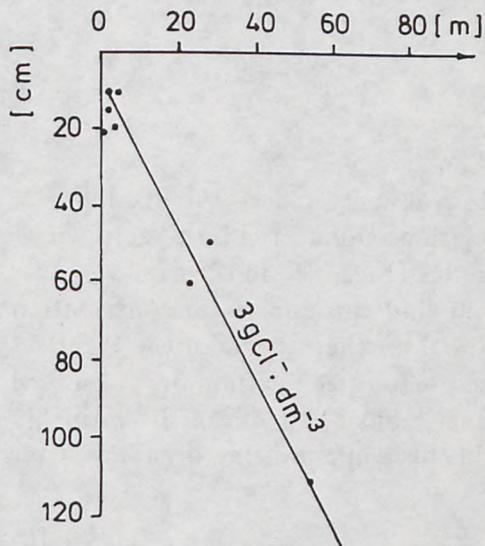


Fig. 11.  Relationship between the depth [cm] of chloride ion presence in interstitial water and the height [m] of the water column above the sediment
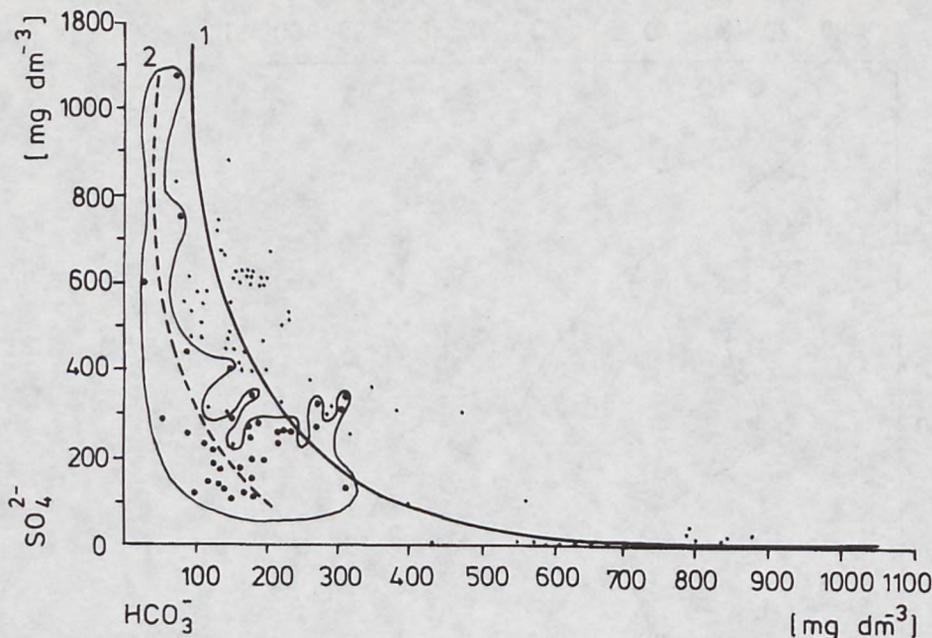
Fig. 12. Sulphate concentration versus bicarbonate concentration in interstitial waters ( 1 – Cl⁻ > 3 g dm⁻³, 2 – Cl⁻ < 3 g dm⁻³)

1970; Bischoff and Ku, 1970, 1971; Nissenbaum *et al.,* 1972; Sayles and Manheim, 1975; Shishkina *et al.,* 1980, 1981). The following reaction presents a generalized description of this process:

$$2\,CH_2O + SO_4^{2-} \rightarrow H_2S + 2\,HCO_3^-, \tag{9}$$
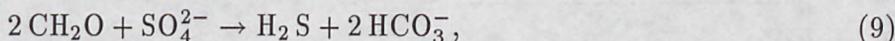
where
$CH_2O$ – denotes the model organic carbon source.

The bicarbonate ions formed in this reaction increase the alkalinity of the interstitial water. Sulphate concentrations equal or close to zero correspond to high concentrations of bicarbonates (Fig. 12). This correlation was especially marked in the region where the underground water contribution was negligible, *i.e.* in the north-eastern and northern parts of the Bay.

Increased sulphate concentrations, as related to bicarbonates, observed in interstitial waters with chloride concentrations > 3 g dm⁻³, are probably the result of sulphide being oxidized by bacteria mineralizing organic matter with oxygen from underground waters

$$H_2S + 2\,O_2 \rightarrow SO_4^{2-} + 2\,H^+. \tag{10}$$

Bicarbonate ions are also utilized in other reactions and for this reason their concentration decreases to a greater extent than the equivalent increase of sulphate concentration. The relationship between bicarbonate

and sulphate anions and the sum of calcium and magnesium is presented in Figure 13. $\triangle$ denotes the difference between the real concentration of the ion in the interstitial water $(X_{iw})$ and its concentration calculated from the ratio of this ion to the chlorinity equivalent in the near-bottom water $(k)$:

$$\triangle X = (X_{iw} - kCl_{iw}),\tag{11}$$

where   $Cl_{iw}$ chloride ion concentration in the interstitial water.
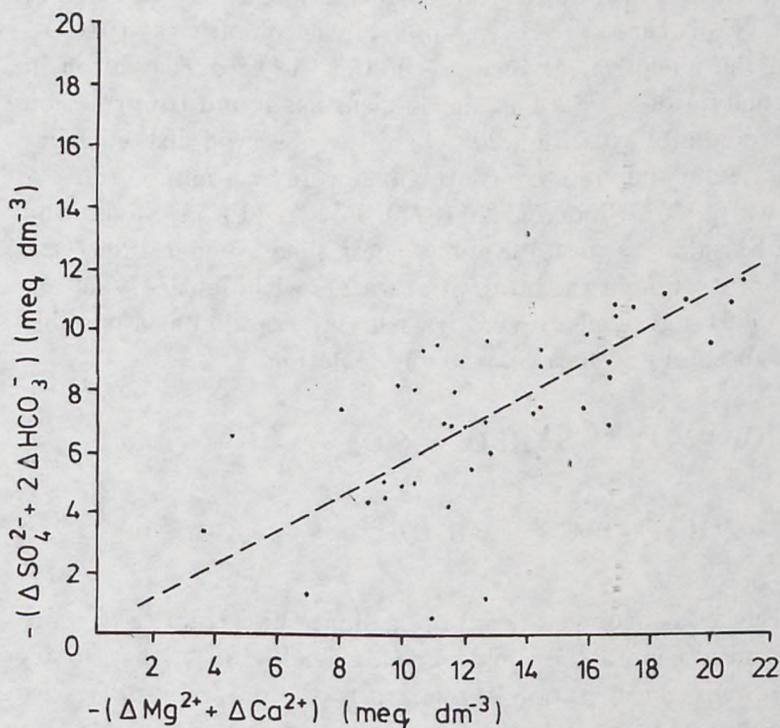


Fig. 13.   Relationship between the sum of bicarbonate and sulphate ion concentrations, and calcium and magnesium in interstitial water (see text)

A literature review of biogenic sediments from coastal areas (Sayles and Manheim, 1975) helps to explain the relationship between calcium, magnesium, sulphate and carbonate ions. In principle, they are biogenic calcite dissolution and recrystallization on the one hand and dolomitization on the other:

$$2\,(Ca_x, Sr_{1-x})CO_3 \; + \; Mg^{2+} \rightarrow CaMg(CO_3)_2 + $$
$$+ \; (2x - 1)Ca^{2+} + 2\,(1 - x)Sr^{2+}.\tag{12}$$
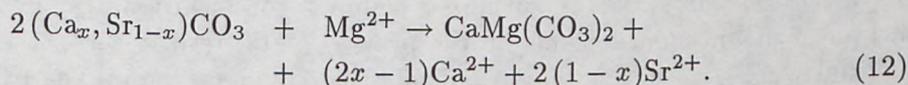
When dissolved, calcite increases concentrations of $Ca^{2+}$ and $Sr^{2+}$, as it contains trace amounts of strontium. A considerable amount of $Mg^{2+}$

and a certain quantity of $Ca^{2+}$ are precipitated as dolomite, so there is a surplus of $Ca^{2+}$ and $Sr^{2+}$ in the water.

The lack of $HCO_3^-$ to balance $SO_4^{2-}$ and the decrease in magnesium concentration can be explained by the following reaction:

$$CaCO_3 + Mg^{2+} + 2\,HCO_3^- \rightarrow CaMg(CO_3)_2 + CO_2 + H_2O. \qquad (13)$$
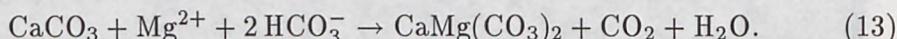
Bicarbonate ions formed in the oxidation of organic matter by sulphates are incorporated into dolomite during calcite recrystallization (Sayles and Manheim, 1975). This is the source of the unbalanced quantities of $HCO_3^-$ and $SO_4^{2-}$ and of the unequivalent increase in the $Ca^{2+}$ concentration in relation to the depletion of $Mg^{2+}$. This mechanism has found confirmation in the presence of dolomite at station 20, where the observed discrepancies between bicarbonate and sulphate concentrations were at a maximum.

Bischoff and Ku (1970), Bloomquist (1977), Powers (1957), Sayles and Manheim (1975), Shishkina et al. (1981) have described a general decrease in magnesium concentration in the interstitial waters with depth. MacKenzie and Garrels (1966) suggested a reverse weathering reaction as a possible mechanism of magnesium and bicarbonate ion depletion:

$$Al_2Si_2O_5(OH)_4 + 5\,Mg^{2+} + 10\,HCO_3^- + SiO_2 \rightarrow$$
(kaolinite)
$$Mg_5Al_2Si_3O_{10}(OH)_8 + 10\,CO_2 + 3\,H_2O.$$
(chlorite) $\qquad (14)$
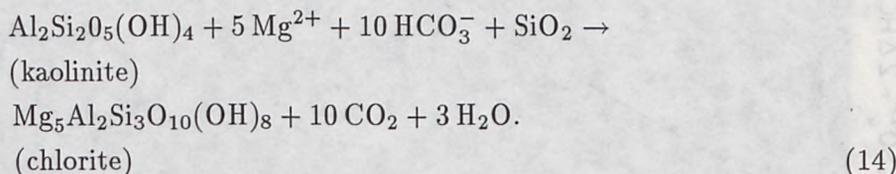
Because the Puck Bay sediments contain kaolinite and chlorite (Trimonis et al., 1987) and also potassium feldspar (Musielak, 1984), the greater decrease of magnesium concentration in relation to the potassium decrease probably comes about as a result of the following reaction:

$$2\,KAlSi_3O_8 + 8\,H_2O + 5\,Mg^{2+} \quad \rightarrow \quad Mg_5Al_2SiO_{10}(OH)_8 + 8\,H^+$$
feldspar                                       chlorite
$$2\,K^+ + 3\,SiO_2. \qquad (15)$$
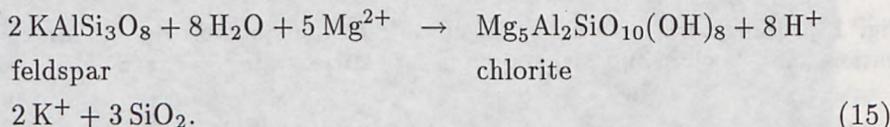
The information on minerals in Puck Bay has recently been supported by studies carried out by the Department of General and Marine Geology of Gdańsk University.

Sodium is the leading cation in the interstitial water of the Puck Bay sediments and chloride is the leading anion. Potassium shows the lowest equivalent concentration. A surplus of sulphate or bicarbonate ions and calcium or magnesium depends on the proportion of fresh water in the interstitial water on the one hand and on the sediment type on the other. Seawater ($Cl^- > 3$ g dm$^{-3}$) in pelitic and aleurite-pellitic sediments contains an excess of bicarbonates over sulphates. As the coarse fraction in the

**Table 5.** Classification of the interstitial waters of Puck Bay

| Interstitial water | | Series | |
| Group | Subgroup | Cations | Anions |
| --- | --- | --- | --- |
| seawater | Mg-HCO$_3$ | rNa$^+$ >rMg$^{2+}$ >rCa$^{2+}$ >rK$^+$ | rCl$^-$ >rHCO$_3^-$ >SO$_4^{2-}$ |
| | Mg-SO$_4$ | rNa$^+$ >rMg$^{2+}$ >rCa$^{2+}$ >rK$^+$ | rCl$^-$ >rSO$_4^{2-}$ >HCO$_3^-$ |
| mixed water | Mg-SO$_4$ | rNa$^+$ >rMg$^{2+}$ >rCa$^{2+}$ >rK$^+$ | rCl$^-$ >rSO$_4^{2-}$ >HCO$_3^-$ |
| | Ca-SO$_4$ | rNa$^+$ >rCa$^{2+}$ >rMg$^{2+}$ >rK$^+$ | rCl$^-$ >rSO$_4^{2-}$ >HCO$_3^-$ |
| saline water | Mg-SO$_4$ | rNa$^+$ >rMg$^{2+}$ >rCa$^{2+}$ >rK$^+$ | rCl$^-$ >rSO$_4^{2-}$ >HCO$_3^-$ |
| | Ca-SO$_4$ | rNa$^+$ >rCa$^{2+}$ >rMg$^{2+}$ >rK$^+$ | rCl$^-$ >rSO$_4^{2-}$ >HCO$_3^-$ |

Mg-HCO$_3$ – magnesium-bicarbonate water,
Mg-SO$_4$   – magnesium-sulphate water,
Ca-SO$_4$   – calcium-sulphate water.

sediment increases in quantity, the anion predominance is reversed. The interstitial water in these sediments contains cations in amounts following the seawater pattern: magnesium precedes calcium. The same sequence of cations and anions is observed in mixed the interstitial waters of aleurites with chloride concentrations from 2 to 3 g dm$^{-3}$. Owing to good filtration conditions in small-grain sands those waters contain greater quantities of calcium than magnesium, and the sulphate equivalent concentration is slightly higher than the bicarbonate concentration. Interstitial waters with a significant fresh water content (Cl$^-$ < 2 g dm$^{-3}$) in sandy sediments contain higher concentrations of calcium than of magnesium. Only aleurites exhibit a certain excess of magnesium over calcium. The interstitial waters of Puck Bay have been classified into three groups and three subgroups based on the equivalent concentrations of the predominant magnesium or calcium, and sulphate or bicarbonate ions (Tab. 5):

- group   I – sea water (of sea water origin) with a chloride concentration > 3  g  dm$^{-3}$,

- group  II   – mixed water with a chloride concentration from 2 to 3 g dm$^{-3}$,

- group III   – interstitial water with a significant fresh water content (originating from land) and a chloride concentration < 2 g dm$^{-3}$,

- subgroup A – magnesium-bicarbonate water,

- subgroup B – magnesium-sulphate water,

- subgroup C – calcium-sulphate water.

Subgroup A appears solely in group I, while subgroup C in groups II and III; water of subgroup B occurs in every group.

## 5. Conclusions

The chemical composition of the interstitial waters of the Puck Bay sediments differs from both that of the near-bottom water and that of sea water from the Gulf of Gdańsk and the Baltic Sea. The differences are in the concentration levels, the ratios of individual ions to chloride concentration and the relationships between particular cations and anions. The interstitial waters have been classified into six types according to the dominating ion – calcium or magnesium, and sulphate or bicarbonate:

1. Magnesium-bicarbonate waters of seawater origin ($Cl^- > 3$ g $dm^{-3}$),
2. Magnesium-sulphate waters of seawater origin ($Cl^- > 3$ g $dm^{-3}$),
3. Mixed magnesium-sulphate waters ($2 < Cl^- < 3$ g $dm^{-3}$),
4. Mixed calcium-sulphate waters ($2 < Cl^- < 3$ g $dm^{-3}$),
5. Magnesium-sulphate waters originating from land ($Cl^- < 2$ g $dm^{-3}$),
6. Calcium-sulphate waters originating from land ($Cl^- < 2$ g $dm^{-3}$).

The vertical and horizontal distributions of macrocomponent concentrations are closely related to sediment type and reflect the interrelationships of various processes influencing the composition of the interstitial waters.

In Puck Bay, the following factors influence the composition of the interstitial waters:

- inflows of underground water from the western border of the Bay,
- the hydrostatic pressure of sea water,
- sulphate reduction by bacteria and oxidation of organic matter,
- ion exchange reactions,
- reverse weathering.

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