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The Alkali Reserve of Interstitial Water at the Sites of Methane Emission in the Sea of Okhotsk

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Abstract—The chemical composition (alkalinity, pH, NH_4^+ , PO_4^{3-} , Si, H_2S , Cl^- , Ca^{2+} , and SO_4^{2-}) of interstitial water was studied in the sediments of the Sea of Okhotsk at sites of methane emission. Variations in alkalinity were observed in the sediments from a typical seawater value (2.3 mM/kg) to 63 mM/kg. It is demonstrated that they are caused by the processes of sulfate reduction and methane generation. Based on the balance relationships, an equation was constructed connecting changes in alkalinity with variations of Ca^{2+} , SO_4^{2-} , and NH_4^+ in interstitial solutions.

INTRODUCTION

In recent years, attention has been drawn to oceanic areas where cold gas emission, mainly of methane and hydrogen sulfide, takes place. Such lively interest in these occurrences is explained primarily by the existence of oases of intense biologic activity in the upper sedimentary layer near gas vents. It manifests itself in the development of bacterial mats and an abundance of specific benthos (polychaetes and bivalves) [1–3]. The biota in these places is maintained by chemosynthesizers and methanotrophic bacteria [4]. The bacterial activity results in changes in the chemical composition of interstitial solutions and seawater above gas vents. These changes may lead to the formation of various minerals. Carbonate concretions and barite were found at the sites of cold seeps [5, 6].

The alkali reserve or total alkalinity (TA) is a major-component characteristic of seawater. Hydrochemically, it is considered as an excess of strong bases over strong acids [7]. The relative value of TA (TA/Cl or TA/S) only slightly changes in the open parts of seas and oceans. However, such variations may be significant in the interstitial waters of reduced sediments [8]. A change in the balance between strong base and strong acid species is connected with the major-component composition of a solution and is controlled by a number of geochemical processes. Hence, alkalinity is one of the most important characteristics used in the construction of the general scheme of chemical transformations in interstitial water [8].

A detailed discussion of seawater alkalinity and its analytical definition, which is currently universally accepted, are given in [9]:

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] \\ & + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{HS}^-] \\ & + 2[\text{S}^{2-}] + [\text{NH}_3] + \dots - [\text{H}^+] \\ & - [\text{HF}] - [\text{H}_3\text{PO}_4] - [\text{HSO}_4^-], \end{aligned} \quad (1)$$

where the values in brackets are the concentrations of alkalinity components in moles per kilogram of solution. Equation (1) is widely used in the processing of potentiometric titration curves of alkalinity in a closed cell. It was found that for this procedure, the zero level of the proton corresponded to a dissociation constant of $10^{-4.5}$. However, if titration is performed by the Bruevich [10] method in an open cell in a flow of argon or air purified from carbon dioxide, the pH value at the final point, at which the indicator color changes, is equal to ~ 5.4 . In other words, the zero proton level in this method corresponds to pH 5.4. At this pH value, the concentrations of $[\text{H}_3\text{PO}_4]$, $[\text{HF}]$, $[\text{HSO}_4^-]$, $[\text{OH}^-]$, and $[\text{H}^+]$ can be ignored in Eq. (1) and it is reduced to the following form:

$$\begin{aligned} \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] \\ & + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] \\ & + [\text{HS}^-] + 2[\text{S}^{2-}]. \end{aligned} \quad (2)$$

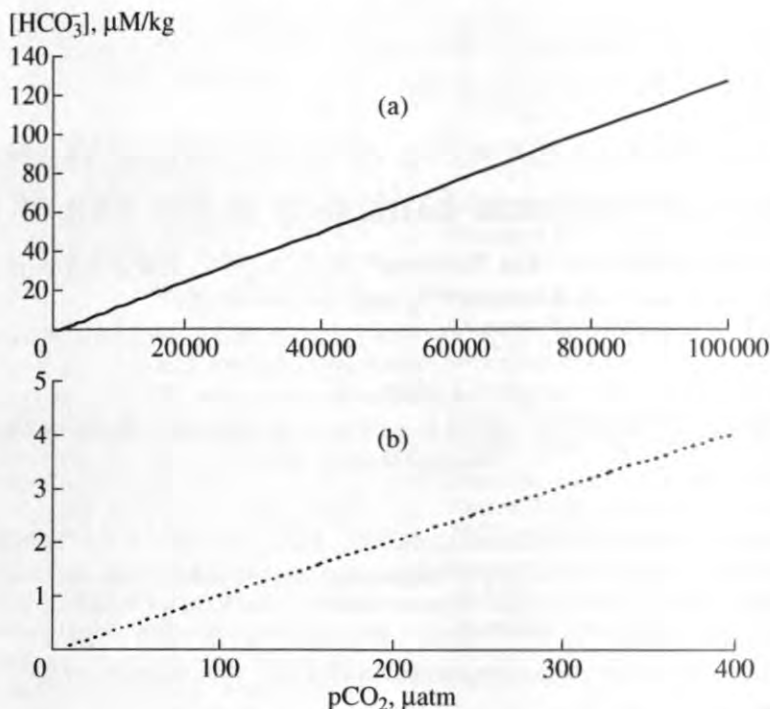


Fig. 1. Concentration of HCO_3^- as a function of the carbon dioxide partial pressure ($p\text{CO}_2$) at $t = 25^\circ\text{C}$, $S = 35\text{‰}$, and conditions of titration (a) in a closed cell at pH 4.5 and (b) in an open cell at pH 5.4.

Since titration in this method is carried out in a flow of inert gas, which removes volatile components from the solution, Eq. (2) does not include NH_3 .

We calculated the concentration of bicarbonate ions as a function of the carbon dioxide partial pressure at pH 4.5 (titration conditions in a closed cell) and pH 5.4 (final titration point in the Bruevich method). The results are shown in Fig. 1. Titration in a closed cell results in the complete transformation of carbonate alkalinity to carbonic acid and its dissolution in the titrated solution. At the equivalence point, the partial pressure of carbon dioxide ($p\text{CO}_2$) is $\sim 80000 \mu\text{atm}$. Figure 1a shows that at this carbon dioxide partial pressure, the concentration of bicarbonate ions is $\sim 100 \mu\text{M/kg}$ or about 4% of the total alkalinity in seawater, which results in underestimated values. On the other hand, the titration is performed at low pH and part of the acid is consumed for the protonization of F^- and SO_4^{2-} . The zero balance is established by processing the results of titration using the Gran method. In an open cell with flowing inert gas, $p\text{CO}_2$ is evidently lower. If $p\text{CO}_2$ is below $200 \mu\text{atm}$, the theoretical error of the Bruevich method is lower than 0.1% (Fig. 1b). It is evident that both methods yield similarly correct results if (1) electrodes in the method of potentiometric titration behave ideally, and the constants of all acid-base equilibria including protonization of F^- and SO_4^{2-} are selected correctly; and (2) the samples contain no volatile bases

such as NH_3 . The latter condition concerns the Bruevich method. The analysis of interstitial solution alkalinity by the potentiometric method does not exclude the possibility of hydrogen sulfide oxidation in the titration process, which results in underestimated results. An additional source of errors in the potentiometric titration could be the problem of electrode thermostating in microanalysis.

In this study, we used the Bruevich method, because it is convenient at low sample volumes and allowed us to eliminate errors due to hydrogen sulfide oxidation during titration.

In addition to the measurement of alkalinity, we analyzed the interstitial water for biogenic components (NH_4^+ , PO_4^{3-} , and Si), pH, H_2S , Cl^- , Ca^{2+} , and SO_4^{2-} . Based on these results, we estimated the contributions of each component to the total alkalinity and carried out balance calculations.

MATERIALS AND METHODS

Reduced sediments were sampled during cruise 28 of the R/V *Akademik M.A. Lavrent'ev* (August–September 1998) in the region of submarine gas emission on the northern slope of Sakhalin Island in the Sea of Okhotsk. The catalogue of four stations with coordinates and depths of sampling is shown in the table.

Gas vents were located by the Ocean Floor Observation System (OFOS) and the acoustic device Sargan-

Coordinates of stations studied in the region of gas vents on the northern slope of Sakhalin Island (Sea of Okhotsk, cruise 28 of the R/V *Akademik M.A. Lavrent'ev*, August–September 1998)

Station number	Date, GMT	Latitude and longitude	Sea depth, m	Core length, cm
St. 17-2	August 16, 1998	54°21.97 N; 143°58.88 E	385	82
St. 20-2	August 17, 1998	54°26.52 N; 144°04.09 E	685	575
St. 20-3	August 17, 1998	54°26.43 N; 144°04.12 E	685	300
St. 21-1	August 17, 1998	54°26.75 N; 144°04.94 E	705	210

EM-UDM. Gas chromatographic analysis of the bottom water showed high positive methane anomalies [11].

The drill cores of sediments were represented by reduced greenish gray mud with a hydrogen sulfide odor. After recovering the tubes, the pH's of the sediments were measured at ~4°C by the potentiometric method on the SWS scale. At the same temperature, interstitial water was squeezed through a membrane filter with a pore size of 0.2 μm. The analysis of biogenic species (PO₄³⁻, NH₄⁺, and Si) and H₂S was carried out by the spectral photometric method using routing procedures [12]. Chlorine was determined by the argentometer method using bichromate as an indicator [13]. The total alkalinity (TA) was measured in a nitrogen flow by titration of 1 ml of interstitial water with 0.02 N HCl solution in an open cell [14]. Calcium was determined onshore by complexometric EGTA titration [15]. In order to prevent CaCO₃ precipitation or consumption by bacteria during sample storage, the samples of interstitial water were acidified with hydrochloric acid to pH ~ 2. Sulfate ions (SO₄²⁻) were also analyzed onshore by ion exchange chromatography. The precision of the analyses of interstitial water sampled from a single horizon was ±0.1% (n = 8) for Ca²⁺, ±0.4% (n = 9) for TA, and ±0.2% (n = 15) for Cl⁻.

RESULTS AND DISCUSSION

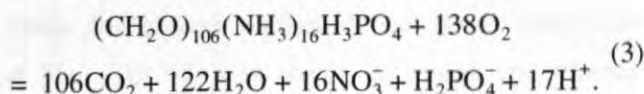
Figure 2 shows the vertical profiles of the distribution of alkalinity, calcium, SO₄²⁻, biogenic species (PO₄³⁻ and NH₄⁺), and H₂S in the interstitial water of the sediments sampled at the sites of gas emission.

Figure 2 demonstrates considerable changes in the chemical composition of interstitial water with depth. For instance, in comparison with the bottom water, the calcium concentration decreases by 60% at station 20-2, while the sulfate content falls to analytical zero. The interstitial water shows very high contents of ammonium nitrogen (6 mM/kg, station 20-2) and hydrogen sulfide (10 mM/kg, station 17-2). The concentration of these components are close to zero in normal seawater. The silicon content varies from 300 μM/kg (station 17-2) to more than 700 μM/kg in some horizons of other stations. At all stations, the alkalinity increases within the

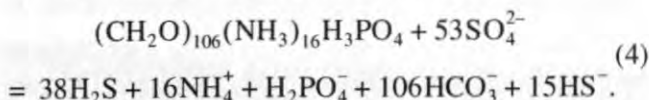
profiles up to 63 mM/kg (station 20-2). Using the data on TA and pH, we calculated the contributions of each component of Eq. (2) into the total alkalinity. Figure 3 demonstrates that residual alkalinity (RA), which is the alkalinity due to all components of Eq. (2) except the carbonate and bicarbonate species, is defined for more than 90% by sulfide alkalinity (SA = [HS⁻] + 2[S²⁻]). Thus, only the sulfide alkalinity is comparable with the carbonate alkalinity (CA = [HCO₃⁻] + 2[CO₃²⁻]). The role of other biogenic components in Eq. (2) is negligible.

In the deep horizons of marine sediments, changes in the composition of interstitial water are so high that it cannot be referred to as seawater. A problem arises on the nature of these changes. We believe that the composition of interstitial water was initially identical to that of seawater. This is supported by the fact that the chlorine content of interstitial water is constant and similar to the value observed in the bottom water. In our opinion, the main reason for changes in the chemical composition of interstitial water is the process of organic matter degradation. The decomposition of organic matter occurs through microbial activity and may proceed in various ways depending on the environmental conditions.

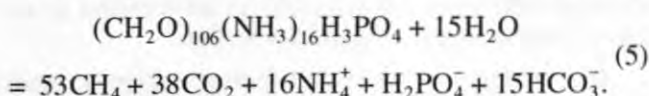
Aerobic oxidation:



Anaerobic oxidation (sulfate reduction):



Methane-generating decomposition of organic matter:



In these reactions, the "formula" for organic matter was used after the Redfield model. These equations demonstrate that the influence of organic matter decomposition on alkalinity depends on the environmental conditions. For instance, aerobic oxidation, (Eq. (3)) will

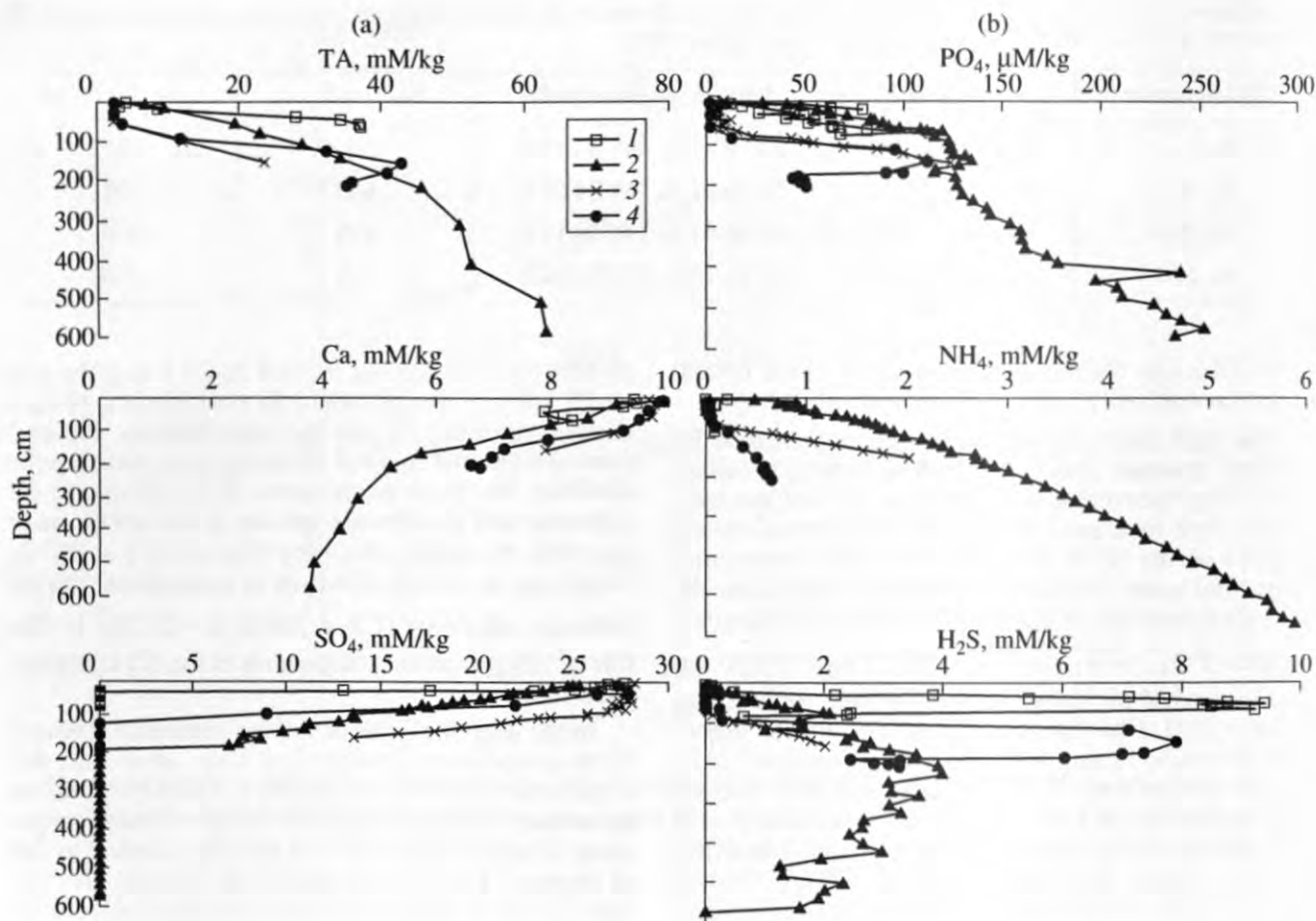


Fig. 2. Vertical distribution of hydrochemical parameters in the interstitial solutions of sediments from the northern slope of Sakhalin Island (Sea of Okhotsk, cruise 28 of the R/V *Akademik M.A. Lavrent'ev*, August–September 1998). Stations: (1) 17-2, (2) 20-2, (3) 20-3, and (4) 21-1. (a) Total alkalinity (TA) and concentrations of calcium (Ca) and sulfate ions (SO_4). (b) Biogenic components (PO_4 and NH_4) and H_2S .

reduce alkalinity. In such a case, the resulting protons will titrate HCO_3^- back to carbon dioxide and, consequently, the anions of weak acid (HCO_3^-) will be replaced by anions of strong acids (H_2PO_4^- and NO_3^-). Sulfate reduction (Eq. (4)) has the opposite effect. In this case, the anions of strong acid (SO_4^{2-}) are replaced by bicarbonate anions. Gases (CH_4 , NH_3 , and CO_2) are products of the methane-generating decomposition of organic matter (Eq. (5)). The interaction of carbon dioxide with ammonium results in an increase in the alkali reserve of the interstitial solution.

It is evident that anaerobic decomposition occurred in the sediments under investigation. In the upper horizons, the process of sulfate reduction was predominant. It resulted in an increase in the contents of biogenic components (NH_4^+ and PO_4^{3-}) in the interstitial solution and a significant increase in alkalinity. In accordance with reaction (4), the oxidation of each mole of

organic matter increases the alkaline reserve of the solution by 121 mol. Because of this, the maximum increase of alkalinity is observed in the upper horizons. However, such an increase is not terminated even in sulfate-free horizons, where sulfate reduction is impossible (lower horizons, station 20-2). We believe that in this region, the predominant process is methane generation in accordance with reaction (5). However, in this case, each decomposed mole of organic matter produces only 15 mol of alkalinity, which is almost an order of magnitude lower than in the process of sulfate reduction. In other words, the increase of alkalinity with depth should be expected to decline in this region along with constant enrichment in ammonium nitrogen, which was actually observed (Fig. 2a).

The maximum alkalinity of interstitial water is readily estimated in the following manner. The total alkalinity of aerated seawater is controlled by the thermodynamics of the carbonate system and equals ~ 2.4 mM/kg for a salinity of 35‰. Sulfate species of seawater are a resource for the increase of total alkalinity.

ity. Owing to sulfate reduction, the maximum alkalinity of the pore water will be $2.4 + 2 \times 28.24 \approx 59$ mM/kg ($S = 35\%$). There is an additional source of alkalinity, which is namely methane generation. It is less efficient than sulfate reduction, but it has no evident restrictions except for the amount of organic carbon in the sediment.

The process of chemical transformations of interstitial water is not limited to reactions (4) and (5). Rather, it is initiated by them. In our opinion, reactions (4) and (5) result in major-component changes in the composition of a solution and provide favorable conditions for mineral formation. This may be manifested primarily in sulfate and carbonate mineralization. Figure 4 shows that sulfide mineralization really occurred. On the H_2S versus SO_4^{2-} diagram, it is reasonable to expect a linear relationship with a slope of 45° (dashed line). However, this is not the case. In part, this could result from incomplete sulfate ion reduction. In our opinion, the main reason is the formation of iron sulfide minerals (pyrite and hydrotroilite). The formation of calcium carbonate minerals via the reaction



reduces the total alkalinity. A decrease in the content of dissolved calcium in interstitial water (Fig. 2a) is related to the authigenic formation of carbonate concretions. Indeed, concretions of varying shapes and sizes were found in the sediments of stations 21-1 and 17-2 [16].

Thus, the diagenesis of organic matter in sediments changes the alkalinity of the interstitial water, which is a characteristic of the cation-anion balance. Any changes in chemical compositions must be consistent with the principle of electric neutrality. This can be expressed by the equations

$$\sum_c z_c m_c^i = \sum_a |z_a| m_a^i, \quad (7)$$

$$\sum_c z_c m_c^f = \sum_a |z_a| m_a^f, \quad (8)$$

$$\sum_a |z_a| m_a^f - \sum_a |z_a| m_a^i = \sum_c z_c m_c^f - \sum_c z_c m_c^i, \quad (9)$$

where z is the ion charge and m is the ion molality (c denotes cation and a , anion). The superscripts i and f denote the initial pore water corresponding to the composition of bottom water and the final water, whose composition was altered by diagenetic processes. We believe that the contents of the following major ions are most sensitive: Ca^{2+} , NH_4^+ , HS^- , S^{2-} , HCO_3^- , CO_3^{2-} ,

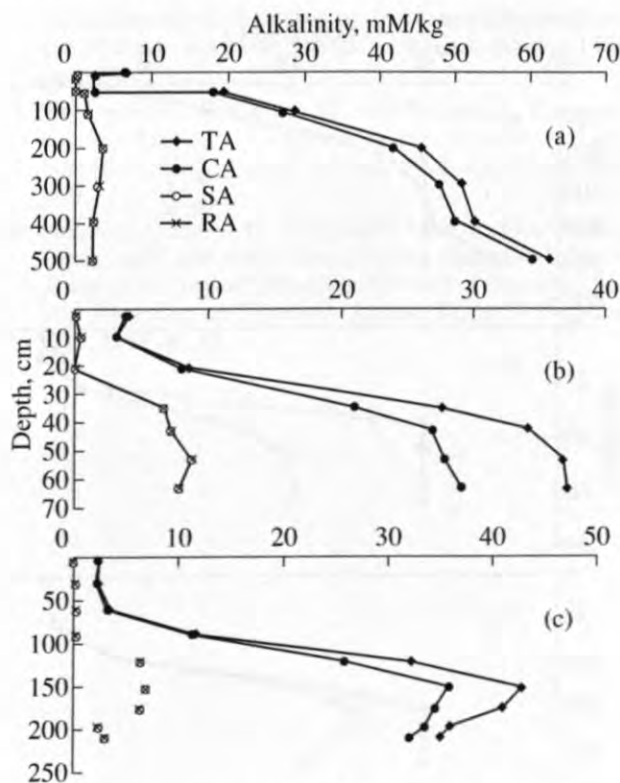


Fig. 3. Distribution of total alkalinity (TA), carbonate alkalinity (CA), sulfide alkalinity (SA), and residual alkalinity (RA) in the interstitial solutions of sediments. Stations: (a) 20-2 and 20-3, (b) 17-2, and (c) 21-1.

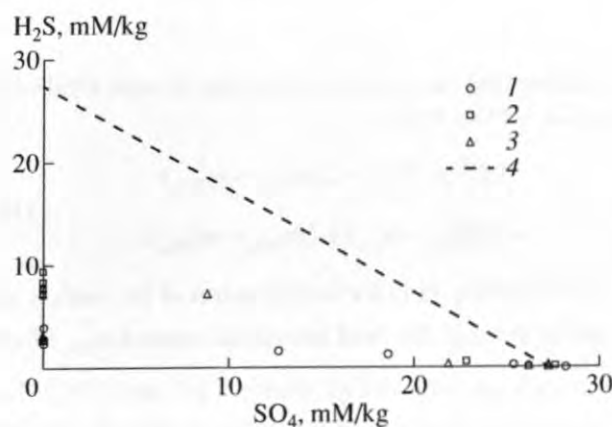


Fig. 4. Correlation of measured H_2S and SO_4 concentrations in the interstitial solutions of sediments from stations (1) 20-2 and 20-3, (2) 17-2, and (3) 21-3. The dashed line (4) shows the complete reduction of sulfates to H_2S .

and SO_4^{2-} . Then, Eq. (9) can be reduced to

$$\begin{aligned} & 2(m_{SO_4}^f - m_{SO_4}^i) + 2(m_{CO_3}^f - m_{CO_3}^i) + (m_{HCO_3}^f - m_{HCO_3}^i) \\ & + (m_{HS}^f - m_{HS}^i) + 2(m_S^f - m_S^i) \\ & = 2(m_{Ca}^f - m_{Ca}^i) + (m_{NH_4}^f - m_{NH_4}^i), \end{aligned} \quad (10)$$

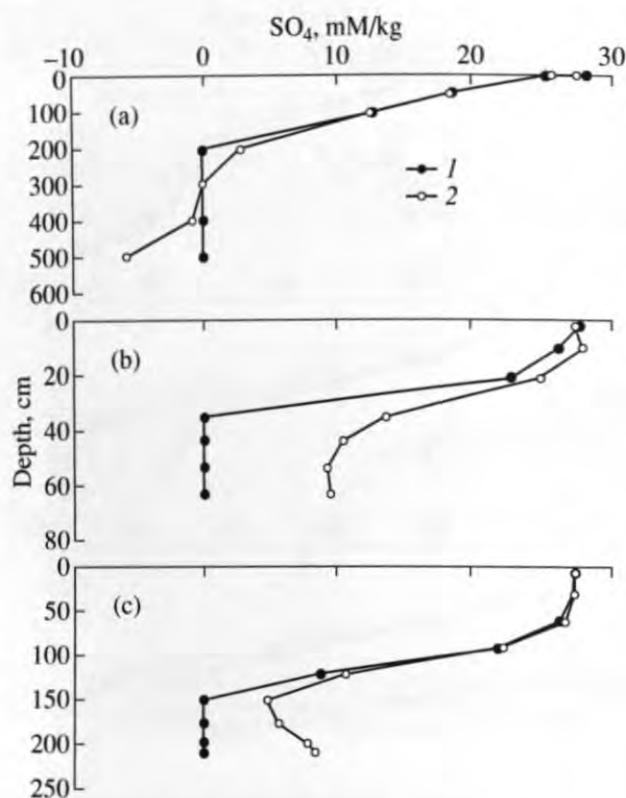


Fig. 5. Comparison of (1) measured and (2) calculated concentrations of SO_4^{2-} for stations (a) 20-2 and 20-3, (b) 17-2, and (c) 21-1.

or, taking into account the definition of total alkalinity, Eq. (2), we can write

$$\begin{aligned} \text{TA}^f &= \text{TA}^i - 2(m_{\text{SO}_4}^f - m_{\text{SO}_4}^i) \\ &+ 2(m_{\text{Ca}}^f - m_{\text{Ca}}^i) + (m_{\text{NH}_4}^f - m_{\text{NH}_4}^i). \end{aligned} \quad (11)$$

We used Eq. (11) for a calculation of the sulfate ion concentration in the final interstitial water ($m_{\text{SO}_4}^f$) from the measured values of alkalinity, Ca^{2+} , and NH_4^+ . The chemical composition of the solution near the surface of the sediments (0–3 cm) was used as the initial composition of the interstitial water. The calculated and measured concentrations are compared in Fig. 5. Three particular features can be inferred from this diagram. First, there is a general similarity in the shape of the calculated and measured curves of the sulfate ion concentration profiles. Second, good agreement is characteristic of the upper portions of the curves, where active sulfate reduction occurs. Third, there are discrepancies in the concentrations regions close to analytical zero. Despite the fact that the analytical uncertainty for the sulfate ion was rather high (about 5 mM/kg), we relate these discrepancies to processes that were not accounted for in the calculations. Equation (9) is

straightforward and includes no assumptions. It is one of the forms of the mass and charge conservation equation. In contrast, Eqs. (10) and (11) are based on the assumption of the invariable concentrations of Cl^- , Na^+ , K^+ , and Mg^{2+} with depth in the sediments. It is evident that this is not true for the magnesium ion, because it is coprecipitated with calcium carbonate, which forms magnesium-bearing calcite. Therefore, we relate the discrepancies for stations 17-2 and 21-1 with the formation of magnesium-bearing calcite. In station 20-2, we obtained negative sulfate concentrations, which is principally impossible. Such a result could be obtained if, in the horizons 300–500 cm, an increase in the $\text{SO}_4 : \text{Cl}$ ratio by 10% occurs relative to seawater: and this increase is not accounted for in the calculations. This issue requires additional investigation.

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