Calcium distribution in the world ocean waters

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ABSTRACT

The calcium/chlorinity ratio is known to be a very useful tool for studying some phenomena occurring in natural marine systems, such as water mass circulation, mixing and diffusion through coastal and open sea water, geochemical and biological precipitation of calcium carbonate, etc. Therefore numerous determinations of calcium/chlorinity ratios have often been carried out on a regional basis. However, a complete analysis of all the existing data has been almost entirely lacking.

A consecutive statistical analysis of all existing literature data from 1884 to 1980 concerning calcium/chlorinity ratios in different locations all over the world showed that this ratio for open seas and oceans is equal to $0.021\,28 \pm 0.000\,15$ g.kg^{-1}(Cl‰)$^{-1}$. The value obtained practically coincides with the value earlier suggested by Culkin and Cox in 1966.

In addition, in this work, the calcium distribution in the nearshore waters of the Gulf of Elat (Aqaba) has been determined. The seawater samples were collected along the shore of the Sinai Peninsula at 13 stations in the vicinity of a coral reef. The calcium/chlorinity ratios of the nearshore waters of the Gulf of Elat ($0.020\,83 \pm 0.000\,05$) were found to be considerably less than those for water masses of open seas and oceans. This fact was explained by the biological precipitation of calcium carbonate from the adjacent surface waters of the gulf.

Oceanol. Acta, 1982, 5, 1,121-128.

RÉSUMÉ

La distribution du calcium dans les mers et océans du monde

Il est bien connu que le rapport calcium/chlorinité est un excellent instrument pour l'étude de certains phénomènes rencontrés dans le milieu marin, tels que la circulation des masses d'eau, le mélange et la diffusion entre les eaux côtières et les eaux de haute mer et la précipitation géochimique et biologique du carbonate de calcium. En conséquence, de nombreuses déterminations du rapport calcium/chlorinité ont été effectuées sur une base régionale. Cependant une interprétation générale de toutes les données existantes manque presque complètement.

L'analyse statistique des données publiées de 1884 à 1980, concernant les rapports calcium/chlorinité en différents endroits à travers le monde a montré que, pour les mers et océans, ce rapport est égal à $0.021\,28 \pm 0.000\,15$ g.kg^{-1}(Cl‰)$^{-1}$, valeur qui coïncide pratiquement avec celle suggérée antérieurement par Culkin et Cox en 1966.

Le présent travail examine la distribution du calcium dans les eaux, proches du rivage, du golfe d'Eilat. Les échantillons d'eau ont été prélevés à 13 stations situées sur la côte du Sinaï au voisinage d'un récif corallien. Les rapports calcium/chlorinité des eaux du golfe d'Eilat sont nettement inférieurs à ceux des mers et océans. Ce fait s'explique par la précipitation biologique du carbonate de calcium des eaux superficielles venant des régions avoisinantes du golfe.

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INTRODUCTION

Marcet (1819) was the first to suggest that the major components of seawater occur together in constant proportions. This hypothesis has been corroborated by Forchhammer (1865), who analyzed hundreds of water samples, and by Dittmar (1884), who analyzed 77 samples of seawater collected by the Challenger Expedition from oceans around the world. Dittmar concluded that the ratio of alkaline earth elements to chlorinity is nearly constant in all open oceans. It is now commonly accepted that in most of the seas and oceans, the ratios of all major ions to salinity (or chlorinity) are constant within the analytical precision of proper ion determination (Culkin, 1965; Culkin, Cox, 1966; Riley, Tongudai, 1967; Riley, Chester, 1971; Whitfield, Turner, 1979). However, modern precise analytical procedures have shown that although the hypothesis of constant ionic composition is largely correct, some variations occur in the composition of sea water bodies from different regions. Some conflicting evidence concerning variability in the ratios of some major ions to chlorinity (salinity) has recently appeared. These phenomena have been observed especially in some closed lagoons (Krumgalz et al., 1980), in the Baltic Sea region with its large inflow of river waters (Zarins, Ozolins, 1935; Gripenberg, 1937; Anderson, Dyrssen, 1981), in the Red Sea with its hot brines (Brewer et al., 1965; Miller et al., 1966; Brewer, Spencer, 1969; Danielsson et al., 1980), etc. As the analytical precision of different ion determinations in seawater is improved, new information concerning some chemical processes in the water bodies of oceans can be obtained.

Seawater (up to saturation depth) is known to be practically saturated with respect to calcium carbonate in the form of calcite or aragonite (Sillen, 1961; Schmalz, Chave, 1963; MacIntyre, Platford, 1964; Pytkowicz, 1969, 1970; Lyakhin, 1971; Tsunogai et al., 1971; Ben-Yaakov et al., 1974; Bezborodov et al., 1978; Morse et al., 1979). This fact is in agreement with some observations on the supersaturation with calcium carbonate of surface seawater (Cloud, 1962; MacIntyre, Platford, 1964; Wells, Illing, 1964; Groot, 1965; Broecker, Takahashi, 1966; Pytkowicz, Fowler, 1967; Lyakhin, 1968; Chave, Suess, 1970; Edmond, Gieskes, 1970; Alekin, Katunin, 1974). However, the delay of calcium carbonate precipitation from sea water can probably be explained by some kinetic factors: the effects of some inorganic ions (Simkiss, 1964; Pytkowicz, 1965; 1973; Weyl, 1965; Bischoff, 1968; Lippman, 1973; Berner, 1975), phosphates (Raistrick, 1949; Reddy, Nancollas, 1973; Berner et al., 1978) or naturally occurring organic compounds (Chave, 1965; Kitano, Hood, 1965; Chave, Suess, 1967; 1970; Meyers, Quinn, 1971; Berner et al., 1978) on the rate of $CaCO_3$ nucleation from natural saline waters. Therefore calcium ions can be considered as a quasi-conservative constituent of seawater, but sometimes, under certain conditions, calcium carbonate precipitation does occur. Recently such a phenomenon has been observed for some natural systems: the Persian Gulf (Wells, Illing, 1964), small hard-water lakes (Wetzel,
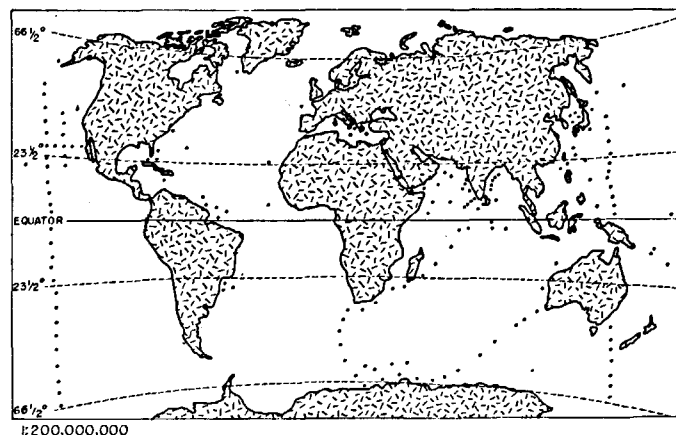

Figure 1

Map of the station location for calcium determination in seawater.

1966), shallow carbonate marine environments (Broecker, Takahashi, 1966) and the Great Lakes (Strong, Eadie, 1978). Thus, changes in the calcium/chlorinity ratio can characterize some natural processes occurring in seawater, such as calcium carbonate precipitation, the mixing of river water with sea water (since the calcium/chlorinity ratio for river water is much higher than that of seawater — Hutchinson, 1957), and the assimilation of calcium from seawater by various kinds of marine organisms to form calcareous shells, etc. Freemantle et al. (1978) tried to use Ca^{2+} ion distribution in the Gulf of Elat (Aqaba) to study seawater pollution by phosphate rock. Therefore numerous determinations of calcium/chlorinity (salinity) ratios have often been carried out on a regional basis. Figure 1 presents the location of the sampling station where seawater samples were taken during different expeditions for calcium determination. However, a complete analysis of all data concerning the calcium distribution in the world ocean waters has been almost entirely lacking. In this article we try to conduct such an analysis.

RESULTS AND DISCUSSION

All available data concerning calcium content for different seas and oceans from 1884 to 1980 are presented in Table 1. It should be emphasized that in many cases, the experimental literature data were recalculated by us to common units $g.kg^{-1}(Cl\%_{oo})^{-1}$ with seawater density computed from the equation of state of seawater (Millero et al., 1976).

The results shown in Table 1 can be divided into three groups: 1) the first group, with a calcium/chlorinity ratio equal to $0.02586 \pm 0.0013 \ g.kg^{-1}(Cl\%_{oo})^{-1}$, includes the Baltic Sea, the Gulf of Finland and the Gulf of Bothnia; 2) the second group includes hot brines in the Red Sea, with calcium/chlorinity ratios equal to $0.0308 \pm 0.0018 \ g.kg^{-1}(Cl\%_{oo})^{-1}$; 3) the third group includes all other data, ranging from 0.02033 to $0.02258 \ g.kg^{-1}(Cl\%_{oo})^{-1}$, with mean value 0.02137. The question is whether the difference between these three groups is significant, or whether they can be considered as coming from the same population. The t-

Table 1
Calcium/Chlorinity ratios throughout the world oceans and seas.

Location	$Ca^{2+}/Cl^{\circ}/_{oo}$, $g \cdot kg^{-1} (Cl^{\circ}/_{oo})^{-1}$	References	Remarks and coordinates
Group 1			
Baltic Sea:		Zarins, Ozolins, 1935	
surface water	0.02648 ± 0.00006		
bottom water	0.02426 ± 0.00007		
Baltic Sea:		Gripenberg, 1937	57°22'-59°46'N; 18°26'-20°24'E.
surface water	0.02619 ± 0.00024		
bottom water	0.02420 ± 0.00034		
Gulf of Bothnia	0.02649 ± 0.00017	Gripenberg, 1937	60°11.5'-65°38'N; 17°52'-23°47'E. The $Ca^{2+}/Cl \%_{oo}$ ratios were identical for surface and bottom waters (distances from bottom were 1-27 m and maximum depth was 175 m).
Gulf of Finland		Gripenberg, 1937	59°21'-60°31'N; 22°59'-28°48'E.
surface water	0.0277 ± 0.0013		
bottom water	0.0257 ± 0.0008		
Baltic Sea	–	Anderson, Dyrssen, 1981	The authors obtained the following relation, which should be valid for the Danish Sounds as well as the Baltic Sea: $Ca(g/kg) = 0.0204 \ Cl\%_{oo} + 0.0225$. This equation is identical to the formula presented by Gripenberg (1937).
Group 2			
Hot brines in the Red Sea:			
a) Discovery Deep	0.0303	Brewer *et al.*, 1965	
	0.0330	Brewer, Spencer, 1969	
	0.0298	Danielsson *et al.*, 1980	The Ca/Cl $\%_{oo}$ ratio was calculated by us from their graphical data.
b) Atlantis II Deep	0.0330	Miller *et al.*, 1966	
	0.0330	Brewer, Spencer, 1969	A layer with temperature 56°C.
	0.0309	Brewer, Spencer, 1969	A layer with temperature 44°C.
	0.0289	Danielsson *et al.*, 1980	An intermediate brine.
	0.0302	Danielsson *et al.*, 1980	A deep brine.
c) Chain Deep	0.0282	Brewer, Spencer, 1969	
Group 3			
All oceans	0.02128	Dittmar, 1884	Only four samples.
North Pacific Ocean	0.02115	Thompson, Wright, 1930	
Pacific Ocean	0.02135	Kirk, Moberg, 1933	
Western Pacific Ocean	0.02120	Miyake, 1939	
Tokyo Bay	0.02130	Matida, 1950	
Pacific Ocean (Gulf of Alaska);		Chow, Thompson, 1955	
surface water	0.02196		
5 000 m depth	0.02188		
Atlantic Ocean	0.02122	Carpenter, 1957	Samples were from open ocean water.
Bahamas Bank	0.02063	Carpenter, 1957	Samples were from a region of active precipitation of $CaCO_3$ on the Bahamas Bank. 48°12'N, 127°17'W.
Pacific Ocean:		Pate, Robinson, 1958	
surface water	0.02141		
1 559 m depth	0.02133		
Pacific Ocean	0.0218 ± 0.0010	Sugawara, Kawasaki, 1958	
Indian Ocean	0.0220 ± 0.0004	Sugawara, Kawasaki, 1958	
Antarctic seas	0.0222 ± 0.0002	Sugawara, Kawasaki, 1958	The results obtained were characteristic of total Ca^{2+} and Sr^{2+} content in seawater. The $Ca^{2+}/Cl \%_{oo}$ ratios were calculated
Labrador Sea	0.0217	MacIntyre, Platford, 1964	
Great Bahama Banks	0.02068 ± 0.00025	Broecker, Takahashi, 1966	by us. Considerable $CaCO_3$ precipitation was observed by the authors.
North Pacific Ocean	0.02128	Culkin, Cox, 1966	Approximately 70 samples from major oceans and seas were carefully analyzed.
South Pacific Ocean	0.02128	Culkin, Cox, 1966	A year later, Riley and Tongudai (1967)
North Atlantic Ocean	0.02128	Culkin, Cox, 1966	applied other methods for the analysis of
South Atlantic Ocean	0.02120	Culkin, Cox, 1966	the same seawater samples. The results
Northern seas	0.02121	Culkin, Cox, 1966	obtained by these two groups of scientists
Southern seas	0.02130	Culkin, Cox, 1966	were in excellent agreement. Therefore, for
Indian Ocean	0.02124	Culkin, Cox, 1966	statistical analysis, only the 1966 values
Mediterranean Sea	0.02131	Culkin, Cox, 1966	were taken.
Red Sea	0.02115	Culkin, Cox, 1966	
Persian Gulf	0.02123	Culkin, Cox, 1966	
North Sea	0.02118	Culkin, Cox, 1966	
Baltic Sea	0.02127	Culkin, Cox, 1966	
Indian Ocean	0.02152	Dietrich *et al.*, 1966	
Atlantic off South Coast of Brazil	0.02156	Kato, 1966*a*	The author suggested that a biogeoche-
Lagoon of Cananeia (Brazil)	0.0206	Kato, 1966*b*	mical precipitation of dissolved calcium took place in the lagoon water.

Table 1 (continuation)

Location	$Ca^{2+}/Cl°/_{oo}$, $g.kg^{-1}$ $(Cl°/_{oo})^{-1}$	References	Remarks and coordinates
Coastal water of Cananeia (Brazil)	0.021 68	Kato, 1966 b	
Gulf of Trieste	0.0218±0.0005	Mameli, Mosetti, 1966	
Atlantic Ocean:		Fabricand et al., 1967	
a) surface water	0.0218		18°59′N, 22°30.5′W.
3 250 m depth	0.0210		
b) surface water	0.0209		10°56′N, 49°30′W.
4 750 m depth	0.0211		
Straits of Florida:		Traganza, Szabo, 1967	
a) at the edge of Great Bahama Bank	0.021 13		
b) on the Great Bahama Bank	0.020 33		
Northern Adriatic Sea	0.021 24	Mameli, Mosetti, 1968	44°56.5′N, 13°25.4′E to 44°58.2′N, 12°38.0′E.
Otranto Channel	0.021 27	Mameli, Mosetti, 1968	39°52.1′N, 18°34.2′E to 39°51.2′N, 19°18.1′E.
A region between Greece and the Island of Crete	0.021 14	Mameli, Mosetti, 1968	36°17.2′N, 22°35.5′E to 35°30.2′N, 23°19.6′E.
Mediterranean Sea	0.021 16	Mameli, Mosetti, 1968	
Western North Pacific Ocean:			
a) the Oyashio region		Tsunogai et al., 1968 a	
surface water	0.021 21±0.000 04		
depth > 1 000 m	0.021 32±0.000 03		
b) the Kuroshio region			
surface water	0.021 08±0.000 03		
depth 500-1 000 m	0.021 20±0.000 05		
Pacific Ocean		Tsunogai et al., 1968 b	38°01′N, 143°58′E.
surface water	0.022 17		The author noted that the values obtained characterized the total amount of Ca^{2+} and Sr^{2+} in seawater.
Sargasso Sea	0.020 68±2.79%	Billings et al., 1969	32°10′N, 64°30′W. A strong temporal variation throughout the water column (up to 2 600 m) was discovered.
Western Pacific Ocean	0.0214		The Ca^{2+}/Cl ‰ ratios ranged from 0.021 07 to 0.021 74.
		Sagi, 1969	
Western Atlantic Ocean (near South America)		Lyakhin, 1971	
surface water	0.021 55±0.000 24		
5 000 m depth	0.022 0		
Indian Ocean			
surface water	0.021 04	Tsunogai et al., 1971	
Antarctic Ocean		Tsunogai et al., 1971	
surface water	0.021 16		
deep water	0.021 16		
South China Sea	0.0215	Chen, Jeng, 1972	The Ca^{2+}/Cl ‰ ratios ranged from 0.020 53 to 0.022 29. The precision of calcium determination was ±2.2 %.
Caribbean Sea (south of Puerto Rico)		Atwood et al., 1973	17°38′N, 67°00′W.
surface water	0.020 8		
depth 1 500 m	0.021 0		
Pacific Ocean		Tsunogai et al., 1973	
surface water	0.021 04		
deep water	0.021 26±0.000 6		
mean of the whole Pacific Ocean	0.021 23		
South Pacific Ocean		Horibe et al., 1974	There is depth distribution. The stations occupied were in the western boundary region of the South Pacific between American Samoa and Tonga.
surface water (up to 500 m)	0.021 34±0.000 03		
deep water (from 500 to 5 200 m)	0.021 49±0.000 04		
Central Ionian Sea		Magazzu, Corigliano, 1974	
surface water	0.021 53		
depth 1 000-4 000 m	0.021 45		
Eastern coasts of Sicily		Magazzu, Corigliano, 1974	
surface water	0.022 58		
Tropical North Atlantic Ocean	0.021 20±0.000 04	Lebel, Poisson, 1976	
Bashi Channel (near Taiwan)	0.020 5±0.004	Li, Chen, 1976	The precision of calcium determination was ±2.0 %.
Equatorial Pacific Ocean		Almgren et al., 1977	The authors could explain the relation between Ca/Cl ‰ and A/Cl ‰ by including the acid produced by the oxidation of peptides and fatty acids.
surface water	0.021 36		
depth 1 100 m	0.021 54		
Northern Indian Ocean Arabian Sea (nearshore waters of Goa)	0.021 3±0.001 9	Naik, 1978	Calcium concentration of nearshore waters showed significant seasonal variations; therefore these data were not included in the statistical calculations.

Table 1 (end)

Location	$Ca^{2+}/Cl°/_{oo}$, $g.kg^{-1} (Cl°/_{oo})^{-1}$	References	Remarks and coordinates
Northern Indian Ocean:			
a) Bay of Bengal			
surface water	0.021 90	Sen Gupta et al., 1978	In the Bay of Bengal this ratio is influenced
depth 3000 m	0.021 96		by river runoff.
b) Gulf of Mannar			
surface water	0.021 93		
c) Arabian Sea			
surface water	0.021 93		
depth 2000 m	0.021 96		
Laccadive Sea:	0.021 68 ± 0.000 02	Naqvi, Reddy, 1979	
Kavaratti Lagoon	0.021 45 ± 0.000 04		
Minicoy Lagoon	0.021 42 ± 0.000 05		
Red Sea	0.022 3	Danielsson et al., 1980	The Ca/Cl %o ratio was estimated by us from their graphical data.
Pacific Ocean:		Kanamori, Ikegami, 1980	26°11'N, 136°42'E.
depth 4244 m	0.021 54		
Mediterranean Sea:		Krumgalz, Holzer, 1980	34°29'89"E, 32°59'04"N.
surface water	0.021 23		
depth 1130 m	0.021 26		
Mediterranean Sea:		Krumgalz·et al., 1980	
a) Haifa Beach	0.021 1 ± 0.000 2		
b) 1.5 km from Haifa Beach	0.021 3 ± 0.000 3		
Great Bitter Lake		Krumgalz et al., 1980	
(30 m offshore)	0.021 47		
North Pacific	0.021 16 ± 0.000 12	Shiller, Gieskes, 1980	There are depth and longitudinal distributions.

test can be used to compare the difference between two averages, both of which have a degree of uncertainty:

$$t = \frac{\overline{X}_1 - \overline{X}_2}{s\sqrt{1/n_1 + 1/n_2}}, \qquad (1)$$

where:

$$s = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}. \qquad (2)$$

In these equations, $\overline{X}_i$ is the average value of a number of observations, n_i is the number of observations in a group, and s_i is the standard deviation in the proper group. When comparing the calcium/chlorinity ratios for the first and third groups ($\overline{X}_1 = 0.025\,86$, $\overline{X}_3 = 0.021\,37$, $n_1 = 7$, $n_3 = 86$, $s_1 = 0.001\,3$, $s_3 = 0.000\,40$) and for the second and third groups ($\overline{X}_2 = 0.030\,8$, $n_2 = 9$, $s_2 = 0.001\,8$), the t values are equal to 8.89 and 14.42, respectively.These values are larger than the critical t value equal to $t_{0.001}$ $(n_i + n_3 - 2) = 3.40$. This means that the probability is greater than 0.999 that the average values for the calcium/chlorinity ratios of the abovementioned groups are significantly different according to the Student t-test for the difference between two means.

Some physical explanations could be suggested for such significant differences in calcium/chlorinity ratios. If there is a non-marine water source in any ocean or sea having ionic concentration significantly different from that of sea water, then the major element/chlorinity ratios after the mixing of these water bodies would be considerably different from those in sea water. The Baltic Sea region and the hot hypersaline brines found in the central region of the Red Sea provide excellent examples of this phenomenon. For the Baltic Sea region, the calcium/chlorinity ratio is larger than that of other seas and oceans. This is due to the inflow of a large amount of continental river freshwater enriched by Ca^{2+} ions. The

abnormally high calcium/chlorinity ratios in the hot brines of the Red Sea can be explained by the nature of the water masses taking part in their formation.

These brines are known to be formed by hot, highly saline water with temperatures of 45-62°C (Riley, 1967; Pugh, 1969; Ross, 1969; Danielsson et al., 1980) and salinities of 255-326 %o (Brewer et al., 1965; Riley, 1967; Brewer, Spencer, 1969) entering the sea through fissures in the sea floor. The mixture of these waters, enriched by some elements including calcium, with ordinary seawater leads to the unusually high calcium/chlorinity ratios characterizing the hot brines in the Red Sea. Brewer et al. (1965) observed, in addition, a mixed water layer where calcium/chlorinity ratios gradually changed from anomalous values characteristic of these brines to values representative of ordinary sea water.

In an analysis of the third group of calcium/chlorinity ratio values using the t-test, it can easily be shown that not all values of the calcium/chlorinity ratios in this group belong to the same population. Variation of the calcium/chlorinity ratio in seawater is expected to occur with the depth and other hydrological conditions. The reasons for this are: (1) the effect of river waters enriched by calcium; and (2) uptake of calcium from the surface seawater by calcareous organisms and re-dissolution of the calcareous shells of dead organisms sinking to the deep water. We have found by consecutive t-tests of all cited literature data that the calcium/chlorinity ratios for waters of open seas and oceans is equal to $0.021\,28 \pm 0.000\,15$ $g.kg^{-1}(Cl\%o)^{-1}$. The value obtained practically coincides with the value $0.021\,2_6$ obtained by Culkin and Cox (1966). As more new data concerning calcium/chlorinity ratios in seawater for different locations become available, more precise calcium/chlorinity ratios for waters of open seas and oceans can be obtained. For all 86 locations analyzed, 59 locations have calcium/chlorinity values characteristic of open seas and oceans. The other 27 locations have
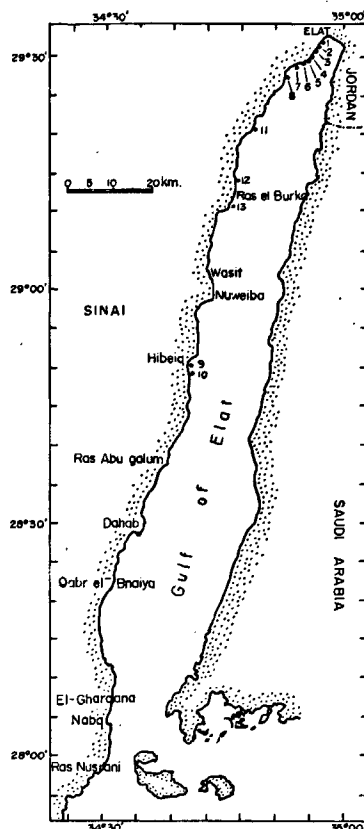
Figure 2
Map of the Gulf of Elat with station locations.

precipitation of calcium carbonate, etc. In water bodies with intensive coral production, interesting information can be obtained by the study of calcium distribution. The Gulf of Elat (Aqaba), with its numerous coral reefs, could be a natural model for studying the influence of coral growth on the calcium/salinity ratio. This study has been conducted on the calcium distribution in the Gulf of Elat / water body in the vicinity of a coral reef during September-October 1979.

Samples of seawater were collected along the shore of the Sinai Peninsula at 13 stations indicated in Figure 2. The samples were collected from the surface layer at a distance of 20-50 m from shore. The calcium content of the seawater samples was determined by potentiometric titration with ethyleneglycol bis-(β-aminoethyl ether)-N-N'-tetraacetic acid (EGTA). For the potentiometric titration, a digital titration system — DTS-833 (precision ± 0.1 mv) with a calcium electrode (F2110 Ca) and a saturated KCl-calomel reference electrode (K 401) was used. A detailed description of the procedure used has been given previously (Krumgalz, Holzer, 1980). Salinity values were determined by a salinometer, Autosal Model 8 400 having an accuracy of $\pm 0.003°/_{oo}$ after instrument calibration with standard seawater of 35.002 %$_{oo}$ salinity. The results obtained are presented in Table 2. The chlorinities of these samples were calculated from experimentally measured salinities using the equation:

$$Cl\%_{oo} = \frac{S\%_{oo}}{1.806\,55}. \qquad (3)$$

As can be seen from Table 2, calcium/chlorinity ratios are practically constant and are equal to $0.020\,83 \pm 0.000\,05$ g.kg^{-1}(Cl%$_{oo}$)$^{-1}$.

It is very interesting to compare the calcium distribution in the Gulf of Elat with the calcium content in other world oceans. The average calcium/chlorinity ratio found for the samples of seawater from the Gulf of Elat, $0.020\,83$ g.kg^{-1}(Cl%$_{oo}$)$^{-1}$, is much smaller than those found for open sea waters. This is the result of biological precipitation of calcium carbonate by some marine organisms, including corals, which deplete calcium in surface waters by the deposition of $CaCO_3$ in their skeletons. D. Dyrssen, in his review of this article, noted

calcium/chlorinity values either smaller or larger than those for open seas and oceans.

The smaller values in some cases can be explained by geochemical or biological precipitation of calcium carbonate (Carpenter, 1957; Broecker, Takahashi, 1966; Kato, 1966 b). On the other hand, the larger values in some cases can be explained by the influence of a strong river inflow (Sen Gupta et al., 1978). Since almost every different water body has a characteristic calcium/chlorinity ratio which depends on its hydrological conditions, the variations in calcium/chlorinity ratios can provide information on some natural processes occurring in the particular water body, such as water mass circulation, mixing and diffusion through coastal and open sea water, geochemical and biological

Table 2
Calcium ion distribution in the Gulf of Elat (Aqaba).

Station (*)	Calcium concentration, g Ca^{2+}/kg seawater	Salinity, (%$_{oo}$)	Calcium/chlorinity ratio, g.k^{-1}(Cl%$_{oo}$)$^{-1}$
1	0.468 0 ± 0.001 7	40.626	0.020 81 ± 0.000 07
2	0.468 4 ± 0.000 2	40.677	0.020 81 ± 0.000 01
3	0.467 6 ± 0.001 1	40.652	0.020 78 ± 0.000 05
4	0.469 3 ± 0.001 2	40.700	0.020 83 ± 0.000 05
5	0.468 9 ± 0.001 2	40.666	0.020 83 ± 0.000 05
6	0.469 3 ± 0.000 6	40.678	0.020 85 ± 0.000 02
7	0.466 2 ± 0.001 4	40.658	0.020 72 ± 0.000 07
8	0.469 6 ± 0.001 0	40.656	0.020 87 ± 0.000 04
9	0.469 8 ± 0.001 0	40.736	0.020 83 ± 0.000 04
10	0.471 0 ± 0.003 8	40.793	0.020 87 ± 0.000 16
11	0.469 8 ± 0.001 0	40.766	0.020 81 ± 0.000 04
12	0.472 2 ± 0.002 5	40.787	0.020 92 ± 0.000 11
13	0.471 2 ± 0.000 8	40.801	0.020 87 ± 0.000 04

(*) Stations 1-10, September 1979; Stations 11-13, October 1979.

that his data concerning the Red Sea and the Gulf of Aden also confirm that the low values of the $Ca/Cl‰$ ratio are due to the activity of coral reefs. There now exists a significant body of literature alluding to calcium depletion in coral reef waters as inferred from alkalinity depletions. However, in our article we did not review this field of research, and therefore the studies using the indirect alkalinity approaches were omitted.

REFERENCES

Alekin O. A., Katunin I. M., 1974. Saturation with calcium carbonate of the surface oceanic water, Okeanologiya, 14, 269-273.

Almgren T., Dyrssen D., Strandberg M., 1977. Computerized high-precision titration of some major constituents of seawater on board the R. V. Dmitry Mendeleev, Deep-Sea Res., 24, 345-364.

Anderson L., Dyrssen D., 1981. Excess calcium and alkalinity in the Baltic and Southern Kattegatt, Oceanol. Acta, 4, 1, 3-6.

Atwood D. K., Froelich P. N., Kinard W. F., 1973. Temporal and depth study of alkaline earth chlorinity ratios in seawater at a single station south of Puerto Rico, Limnol. Oceanogr., 18, 771-783.

Ben-Yaakov S., Ruth E., Kaplan I. R., 1974. Carbonate compensation depth: relation to carbonate solubility in ocean waters, Science, 184, 982-984.

Berner R. A., 1975. The role of magnesium in the crystal growth of calcite and aragonite from sea water, Geochim. Cosmochim. Acta, 39, 489-504.

Berner R. A., Westrich J. T., Graber R., Smith J., Martens C.S., 1978. Inhibition of aragonite precipitation from supersaturated seawater: a laboraty and field study, Am. J. Sci., 78, 816-837.

Bezborodov A. A., Khlystov A. Z., Martynova N. G., 1978. On the saturation of waters of the Lyons and the Genoa Gulfs with calcium carbonate and calcium phosphate, Okeanologiya, 18, 822-826.

Billings G. K., Bricker O. P., MacKenzie F. T., Brooks A.L., 1969. Temporal variation of alkaline earth element/chlorinity ratios in the Sargasso Sea, Earth Planet. Sci. Lett., 6, 231-236.

Bischoff J. L., 1968. Kinetics of calcite nucleation: magnesium ion inhibition and ionic strength catalysis, J. Geophys. Res., 73, 3315-3322.

Brewer P. G., Spencer D. W., 1969. A note on the chemical composition of the Red Sea brines, in: Hot brines and recent heavy metal deposits in the Red Sea, edited by E. T. Degens and D. A. Ross, Springer-Verlag, 174-179.

Brewer P. G., Culkin F., Riley J. P., 1965. The chemical composition of the hot salty water from the bottom of the Red Sea, Deep-Sea Res., 12, 497-503.

Broecker W. S., Takahashi T., 1966. Calcium carbonate precipitation on the Bahama Banks, J. Geophys. Res., 71, 1575-1602.

Carpenter J. H., 1957. The determination of calcium in natural waters, Limnol. Oceanogr., 2, 271-280.

Chave K. E., 1965. Carbonates: association with organic matter in surface seawater, Science, 148, 1723-1724.

Chave K. E., Suess E., 1967. Suspended minerals in seawater, Trans. N.Y. Acad. Sci., 29, 991-1000.

Chave K. E., Suess E., 1970. Calcium carbonate saturation in seawater: effect of dissolved organic matter, Limnol. Oceanogr., 15, 633-637.

Chen J.-C., Jeng W.-L., 1972. Geochemical studies of sea waters from the South China Sea, Acta Geol. Taiwan., 15, 129-139.

Chow T. J., Thompson T. G., 1955. Flame photometric determination of calcium in seawater and marine organisms, Anal. Chem., 27, 910-913.

Cloud P. E., 1962. Environment of calcium carbonate deposition west of Andros Island, Bahamas, Prof. Pap. US Geol. Surv., 350, 138 p.

Culkin F., 1965. The major constituents of seawater, in: Chemical oceanography, vol. 1, edited by J. P. Riley and G. Skirrow, Academic Press, 121-161.

Culkin F., Cox R. A., 1966. Sodium, potassium, magnesium, calcium and strontium in seawater, Deep-Sea Res., 13, 789-804.

Danielsson L.-G., Dyrssen D., Graneli A., 1980. Chemical investigation of Atlantis II and Discovery brines in the Red Sea, Geochim. Cosmochim. Acta, 44, 2051-2065.

Dietrich G., Duing W., Grasshoff K., Koske P. H., 1966. Physikalische und Chemische Daten nuch Beobachtungen des Forschungsschiftes "Meteor" im Indischen Ozean 1964/65, "Meteor" Forschungsergeb., Reihe A, 2.

Dittmar W., 1884. Report on researches into the composition of ocean water, collected by HMS Challenger, Challenger Rep., Phys. Chem., 1, 1-251.

Edmond J. M., Gieskes J. M. T. M., 1970. On the calculation of the degree of saturation of sea water with respect to calcium carbonate under in situ conditions, Geochim. Cosmochim. Acta, 34, 1261-1291.

Fabricand B. P., Imbimbo E. S., Brey M. E., 1967. Atomic absorption analyses for Ca, Li, Mg, K, Rb and Sr at two Atlantic Ocean stations, Deep-Sea Res., 14, 785-789.

Forchhammer G., 1865. On the composition of sea water in different parts of the ocean, Philos. Trans. R. Soc. Lond., A 155, 203-262.

Freemantle M. H., Hulings N., Mulqi M., Watton E. C., 1978. Calcium and phosphate in the Jordan Gulf of Aqaba, Mar. Pollut. Bull., 9, 79-80.

Gripenberg S., 1937. The calcium content of Baltic water, J. Cons., Cons. Perm. Int. Explor. Mer, 12, 293-304.

Groot K. de, 1965. Inorganic precipitation of calcium carbonate from seawater, Nature, 207, 404-405.

Horibe Y., Endo K., Tsubota H., 1974. Calcium in the South Pacific, and its correlation with carbonate alkalinity, Earth Planet. Sci. Lett., 23, 136-140.

Hutchinson G. E., 1957. A treatise on limnology, John Wiley.

Kanamori S., Ikegami H., 1980. Computer-processed potentiometric titration for determination of calcium and magnesium in seawater, J. Oceanogr. Soc. Jpn, 36, 177-184.

Kato K., 1966 a. Studies on calcium content in seawater. II. Distribution of calcium in the Atlantic water off south Brazil, Bol. Inst. Oceanogr. Saõ Paulo, 15, 29-39.

Kato K., 1966 b. Studies on calcium content in seawater. III. Calcium in the waters of Cananeia Lagoon and its adjacent regions, State of Sao Paulo, Brazil, Bol. Inst. Oceanogr. Saõ Paulo, 15, 41-45.

Kirk P. L., Moberg E. G., 1933. Micro-determination of calcium in sea water, Ind. Eng. Chem., Anal. Ed., 5, 95-98.

Kitano Y., Hood D. W., 1965. The influence of organic material on the polymorphic crystallization of calcium carbonate, Geochim. Cosmochim. Acta, 29, 29-41.

Krumgalz B. S., Holzer R., 1980. On the determination of Ca^{2+} ion concentration in seawater, Limnol. Oceanogr., 25, 367-370.

Krumgalz B. S., Hornung H., Oren O. H., 1980. The study of a natural hypersaline laggon in a desert area (the Bardawil Lagoon in Northern Sinai), Estuarine Coastal Mar. Sci., 10, 403-415.

Lebel J., Poisson A., 1976. Potentiometric determination of calcium and magnesium in seawater, Mar. Chem., 4, 321-332.

Li H.-W., Chen J.-C., 1976. Distribution of Na, Mg, Ca, K, Sr and Li in sea waters from the Bashi Channel, Acta Oceanogr. Taiwan, 6, 61-76.

Lippman F., 1973. Sedimentary carbonate minerals. Springer-Verlag.

Lyakhin Y. I., 1968. Calcium carbonate saturation of Pacific water, Oceanology (USSR), 8, 44-53.

Lyakhin Y. I., 1971. Calcium and magnesium in the waters of the western part of the tropical Atlantic, Oceanology (USSR), 11, 535-540.

MacIntyre W. G., Platford R. F., 1964. Dissolved calcium carbonate in the Labrador Sea, J. Fish. Res. Board Can., 21, 1475-1480.

Magazzu G., Corigliano F., 1974. Rapporti ionici Ca/Cl e Mg/Cl con la profondita nel mar Ionio, Boll. Pesca, Piscic. Idrobiol., 29, 169-178.

Mameli D., Mosetti F., 1966. Un nuovo metodo di marcatura delle acque di Mare costiere. Il contenuot in calcio e magnesio quale indicatore del mescolamento di acque continentali in acqua marina, Boll. Geofis. Teor. Appl., 8, 294-308.

Mameli D., Mosetti F., 1968. Some new investigations on the Ca and Mg content in sea water, Boll. Soc. Adriat. Sci., Trieste, ser. B, 55, 27-38.

Marcet A., 1819. On the specific gravity and temperatures of sea waters in different parts of the ocean and in particular seas: with some account of their saline contents, Philos. Trans. R. Soc. Lond., A 109, 161-208.

Matida Y., 1950. On the chemical composition of the sea water of Tokyo Bay, J. Oceanogr. Soc. Jpn, 5, 105-110.

Meyers P. A., Quinn J. G., 1971. Interaction between fatty acids and calcite in seawater, Limnol. Oceanogr., 16, 992-997.

Miller A. R., Densmore C. D., Degens E. T., Hathaway J. C., Manheim F. T., McFarlin P. F., Pocklington R., Jokela A., 1966. Hot brines and recent iron deposits in deeps of the Red Sea, Geochim. Cosmochim. Acta, 30, 341-360.

Millero F. J., Gonzalez A., Ward G. K., 1976. The density of seawater solutions at one atmosphere as a function of temperature and salinity, J. Mar. Res., 34, 61-93.

Miyake Y., 1939. Chemical studies of the western Pacific Ocean. I and II, Bull. Chem. Soc. Jpn, 14, 29-35; 55-58.

Morse J. W., Kanel J. de, Craig H. L. Jr., 1979. A literature review of the saturation state of seawater with respect to calcium carbonate and its possible significance for scale formation on OTEC heat exchangers, Ocean Eng., 6, 297-315.

Naik S., 1978. Calcium and magnesium concentration in the nearshore waters of Goa, Mahasagar-Bull. Nat. Inst. Oceanogr., 11, 185-189.

Naqvi S. W. A., Reddy C. V. G., 1979. On the variation in calcium content of the waters of Laccadives (Arabian Sea), Mar. Chem., 8, 1-7.

Pate J. B., Robinson R. J., 1958. The (ethylenedinitrilo) tetraacetate titration of calcium and magnesium in ocean waters. 1. Determination of calcium, J. Mar. Res., 17, 390-402.

Pugh D. T., 1969. Temperature measurements in the bottom layers of the Red Sea brines, in: Hot brines and recent heavy metal deposits in the Red Sea, edited by E. T. Degens and D. A. Ross, Springer-Verlag, 158-163.

Pytkowicz R. M., 1965. Rates of inorganic calcium carbonate precipitation, J. Geol., 73, 196-199.

Pytkowicz R. M., 1969. Chemical solution of calcium carbonate in seawater, Am. Zool., 9, 673-679.

Pytkowicz R. M., 1970. On the carbonate compensation depth in the Pacific Ocean, Geochim. Cosmochim. Acta, 34, 836-839.

Pytkowicz R. M., 1973. Calcium carbonate retention in supersaturated sea water, Am. J. Sci., 273, 515-522.

Pytkowicz R. M., Fowler G. A., 1967. Solubility of foraminifera in sea water at high pressures, Geochem. J., 1, 169-182.

Raistrick B., 1949. The influence of foreign ions on crystal growth from solution. I. The stabilization of the supersaturation of calcium carbonate solutions by anions possessing O-P-O-P-O chains, Disc. Faraday Soc., 5, 234-237.

Reddy M. N., Nancollas G. H., 1973. The crystallization of calcium carbonate. III. Calcite crystal growth inhibition of phosphonates, Desalination, 12, 61-73.

Riley J. P., 1967. The hot saline waters of the Red Sea bottom and their related sediments, Oceanogr. Mar. Biol., 5, 141-157.

Riley J. P., Chester R., 1971. Introduction to marine chemistry, Academic Press.

Riley J. P., Tongudai M., 1967. The major cation chlorinity ratios in seawater, Chem. Geol., 2, 263-269.

Ross D. A., 1969. Temperature structure of the Red Sea brines, in: Hot brines and recent heavy metal deposits in the Red Sea, edited by E. T. Degens and D. A. Ross, Springer-Verlag, 148-152.

Sagi T., 1969. The concentration of calcium and the calcium chlorosity ratio in the western North Pacific Ocean, Oceanogr. Mag., 21, 61-66.

Schmalz R. F., Chave K. E., 1963. Calcium carbonate: factors affecting saturation in ocean waters off Bermuda, Science, 139, 1206-1207.

Sen Gupta R., Naik S., Singbal S. Y. S., 1978. A study of fluoride, calcium and magnesium in the Northern Indian Ocean, Mar. Chem., 6, 125-141.

Shiller A., Gieskes J. M., 1980. Processes affecting the oceanic distributions of dissolved calcium and alkalinity, J. Geophys. Res., 85, 2719-2727.

Sillen L. G., 1961. The physical chemistry of sea water, in: Oceanography, edited by M. Sears, American Association for the Cultivation of Science, 549-582.

Simkiss K., 1964. The inhibitory effects of some metabolites on the precipitation of $CaCO_3$ from artificial and natural seawater, J. Cons., Cons. Int. Explor. Mer, 29, 6-18.

Strong A. E., Eadie B. J., 1978. Satellite observations of calcium carbonate precipitations in the Great Lakes, Limnol. Oceanogr., 23, 877-887.

Sugawara K., Kawasaki N., 1958. Strontium and calcium distribution in western Pacific, Indian and Antarctic Oceans, Rec. Oceanogr. Works Jpn, spec. no., 2, 227-242.

Thompson T. G., Wright C. C., 1930. Ionic ratios in water of the North Pacific Ocean, J. Am. Chem. Soc., 52, 915-921.

Traganza E. D., Szabo B. J., 1967. Calculation of calcium anomalies on the Great Bahama Bank from alkalinity and chlorinity data, Limnol. Oceanogr., 12, 281-286.

Tsunogai S., Nishimura M., Nakaya S., 1968a. Calcium and magnesium in sea water and the ratio of calcium to chlorinity as a tracer of water masses, J. Oceanogr. Soc. Jpn, 24, 153-159.

Tsunogai S., Nishimura M., Nakaya S., 1968b. Complexometric titration of calcium in the presence of larger amounts of magnesium, Talanta, 15, 385-390.

Tsunogai S., Yamazaki T., Nishimura M., 1971. Calcium in the Antarctic Ocean, J. Oceanogr. Soc. Jpn, 27, 191-196.

Tsunogai S., Yamahata H., Kudo S., Saito O., 1973. Calcium in the Pacific Ocean, Deep-Sea Res., 20, 717-726.

Wells A. J., Illing L. V., 1964. Present-day precipitation of calcium carbonate in the Persian Gulf, in: Developments in sedimentology, vol. 1, Deltaic and shallow marine deposits, edited by L. M. J. U. van Straaten, Elsevier, 429-435.

Wetzel R. G., 1966. Productivity and nutrient relationships in marl lakes of northern Indiana, Verh. Int. Verein. Limnol., 16, 321-332.

Weyl P. K., 1965. The solution behaviour of carbonate minerals in seawater. in: Proc. Int. Conf. Tropical Oceanogr., Miami Beach, Florida, 178-228.

Whitfield M., Turner D. R., 1979. Water-rock partition coefficients and the composition of seawater and river water, Nature, 278, 132-137.

Zarins E., Ozolins J., 1935. Untersuchungen uber die Zusammensetzung des Meerwassers im Rigaschen Meerbusen und an der Letzlandischen Kuste des Baltischen Meeres, J. Cons., 10, 275.