

The carbonate system in hypersaline solutions: Alkalinity and CaCO_3 solubility of evaporated seawater

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Abstract

Changes in total alkalinity and in pH during the evaporation of seawater in the laboratory were studied for an evaporation range extending between 1.1 and 26 (as defined by the concentration ratio of Mg in the evaporated sample relative to mean ocean water).

The evaporation experiments were performed with and without suspended aragonite. The results of the two experimental sets define an alkalinity field for evaporated, marine-derived brines. Data from naturally formed marine brines fall within the experimental field. Deviations therefrom can be explained by changes in alkalinity unrelated to CaCO_3 precipitation/dissolution reactions.

The chemical evolution of seawater upon evaporation has been studied mainly in relation to major ion composition (e.g. Borchert 1965; Herrmann et al. 1973). Evaporation progresses in well defined steps at which distinct mineral precipitations are detected. The early precipitation of CaCO_3 is followed by gypsum precipitation at about threefold evaporation and by halite precipitation when the volume is reduced to about a tenth of the original seawater. It is also generally recognized that evaporation of seawater should affect the carbonate system in various ways. CO_2 solubility should decrease, due to the salting-out effect (Li and Tsui 1971), and the apparent dissociation constants of carbonic acid as well as the apparent solubility product of CaCO_3 should vary as the ionic composition and ionic strength change (Lyman 1956; Ben-Yaakov and Goldhaber 1973; Sass and Ben-Yaakov 1977).

The characterization of the behavior of the carbonate system in evaporated seawater is important for several reasons. It should result in a better understanding of CaCO_3 precipitation from lagoons and other evaporated seawater bodies as well as of organic and inorganic precipitation associated with biological activities such as photosynthesis and respiration. It should also help in estimating the amount

of CaCO_3 precipitating from evaporating seawater in enclosed basins and lagoons and should provide important information pertinent to the fauna and flora of brines.

However, most research on the behavior of the carbonate system during evaporative processes is restricted to limited seawater evaporation progress only or to the evaporation of nonmarine solutions (Al-Droubi et al. 1980; Stumm and Morgan 1981).

Our objective was to investigate the effect of evaporation on seawater alkalinity and CaCO_3 solubility by running evaporation experiments in the laboratory and measuring the ionic composition, pH, and alkalinity of seawater samples evaporated to various degrees. CaCO_3 solubility was evaluated by running parallel experiments on samples in which aragonite powder was suspended.

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Experimental

The solutions investigated consist of natural seawater samples which were evaporated to various degrees under laboratory conditions. Surface Mediterranean seawater, sampled off the Tel Aviv coast during June and August 1980 was used in the D/674 and D/675 series. The

Table 1. Chemical composition.

Sample No.	EP*	DE†	I‡	pH	TA§	Na	Mg	Ca	Cl	SO ₄	10 ² ×TA:		
						g·liter ⁻¹					Mg (meq·liter ⁻¹)	Na:Mg (g·liter ⁻¹)	Cl:Mg (g·liter ⁻¹)
Without aragonite													
Seawater		1	0.7	8.10	2.30	11.0	1.32	0.423	19.8	27.7	2.12	8.33	15.0
D/674		1.1	0.8	8.07	2.72	11.9	1.45	0.485	22.3	—	2.28	8.21	15.4
D/679		1.1	0.8	8.03	2.58	—	1.47	0.484	—	—	2.13	—	—
D/674/1	1	1.5	1.1	7.90	3.81	15.8	1.97	0.610	30.3	—	2.35	8.02	15.4
D/674/2	3	2.0	1.4	8.10	4.71	20.1	2.57	0.812	39.2	—	2.23	7.82	15.3
D/674/3	6	3.2	2.4	7.62	4.78	33.8	4.18	1.20	63.3	—	1.39	8.09	15.1
D/674/4	9	3.7	2.7	7.61	3.90	38.3	4.78	1.25	70.2	—	0.99	8.01	14.7
D/674/5	12	6.7	4.8	7.49	4.59	67.9	8.40	1.03	124.5	—	0.66	8.08	14.8
D/674/6	17	8.2	5.7	7.65	5.36	85.0	10.1	0.733	152.9	—	0.64	8.42	15.1
D/674/7	26	9.6	6.6	7.73	6.85	97.9	11.7	0.567	179.3	—	0.71	8.31	15.3
D/674/8	34	14.7	7.4	7.64	10.7	91.7	18.0	0.320	189.9	26.1	0.72	5.09	10.6
D/674/9	45	17.6	7.7	7.58	12.5	85.8	21.5	0.260	186.0	30.9	0.71	3.99	8.7
With aragonite													
D/679/5/a		0.5	0.4	8.05	1.30	—	0.72	0.230	—	—	2.19	—	—
D/679/a		1.1	0.8	7.74	2.20	—	1.44	0.460	—	—	1.86	—	—
D/679/2/a	24	1.5	1.1	7.76	2.19	—	1.99	0.615	—	—	1.34	—	—
D/679/3/a	21	2.4	1.7	7.60	2.39	—	3.10	0.955	—	—	0.94	—	—
D/679/1/a	26	3.7	2.7	7.54	2.27	—	4.73	1.33	—	—	0.58	—	—
D/679/4/a	37	5.6	4.0	7.59	3.22	—	7.10	1.01	—	—	0.55	—	—
D/679/6/a	31	9.8	6.8	7.49	9.75	—	12.0	0.425	—	—	0.99	—	—
D/679/7/a	31	10.9	6.9	7.64	10.6	—	13.3	0.358	—	—	0.97	—	—
D/675/4/a	41	15.2	7.4	7.49	12.8	—	18.6	0.352	—	26.2	0.84	—	—
D/675/5/a	52	26.7	8.8	7.51	24.1	—	32.5	0.190	—	45.4	0.90	—	—

* Evaporation period (days).

† Degree of evaporation (*see text*).

‡ Ionic strength.

§ Total alkalinity (meq·kg⁻¹ H₂O).

seawater for series D/679 was sampled from the surface of the northern tip of the Gulf of Elat (Aqaba), Red Sea, in February 1981.

Evaporation procedure—Seawater was evaporated in a continuously ventilated fume hood, at 25°C ± 3° in open Pyrex beakers, in the presence or absence of aragonite; the solutions were homogenized several times per day by manual stirring with glass rods. After the desired degree of evaporation was attained, the solutions, including precipitated salts, were quantitatively transferred to tightly sealed polyethylene bottles and stored until analysis in a thermostatic shaking bath at 25°C ± 0.1°. Evaporation times of the different runs are detailed in Table 1.

An excess of a Red Sea coralline aragonite powder with no X-ray-detectable calcite peak was added to each aragonite-bearing run (designated "a" in Table 1).

Analytical procedure—A carbonate titration system computerized at Ben Gurion University was used for the analysis of the carbonate system parameters (Ben-Yaakov et al. 1982). The alkalinity titration was monitored by a Commodore PET personal computer which also activated the motor-driven burette and handled data processing. The experimental solution was filtered with a 50-ml all-glass syringe, via a 25-mm-diameter 0.45-μm Millipore membrane filter. Fifty milliliters of the filtrate were titrated with a 0.5 N HCl solution (BDH concentrated volumetric solution) in a covered, thermostatically controlled, Metrohm model EH-88 titration vessel at 25°C ± 0.1°. A Metrohm model EA-121 combined glass pH electrode was used throughout. The acid was delivered by a computer-controlled Metrohm Multi-Dosimat E-415 motor-driven piston system. Complete

system control was provided by four programmed routines: 1—pH electrode calibration against NBS-based standards; 2—individual sample pH measurement; 3—complete titration cycle monitoring and raw data recording; 4—data processing and carbonate system parameter computation. Na, Mg, and Ca were analyzed by atomic absorption spectrometry with a Perkin-Elmer model 460 spectrophotometer. An air-acetylene flame was used for Na and a N₂O-acetylene flame for Ca and Mg. Chloride ion concentrations were measured by potentiometric titration using a Radiometer model PHM 64 electrometer equipped with a Metrohm EA-246 combined massive silver electrode. Sulfate was determined gravimetrically as BaSO₄. The error estimates on these determinations are (relative SD) ±2% for Na, Mg, and Ca, and ±0.5% for Cl and SO₄ analyses.

Computation procedure

The alkalinities were calculated from the titration data by a modification of Sass and Ben-Yaakov's (1977) calculation procedure in which the carbonate system is completely described during the titration by

$$\frac{1}{V_o} \left[TA \cdot V_o + \frac{a_{H^+}}{\gamma_{H^+}} (V_o + V_a) - N_a \cdot V_a \right] = C \frac{K'_1 a_{H^+} + 2K'_1 K'_2}{a_{H^+}^2 + K'_1 a_{H^+} + K'_1 K'_2} \quad (1)$$

where V_o is the volume of the sample before titration, V_a is volume of hydrochloric acid added, N_a is normality of hydrochloric acid, γ_{H^+} is activity coefficient of the hydrogen ion, TA is total alkalinity, C is total concentration of CO₂, and K'_1 , K'_2 are first and second dissociation constants of carbonic acid.

The right-hand term in Eq. 1 represents the charged carbon species in the solution. At sufficiently low pH values beyond the equivalence point, the concentrations of these species become very small and, after we neglect the right-hand term, Eq. 1 is reduced to a simple Gran-type equation (Gran 1952):

$$a_{H^+}(V_o + V_a) = -TA \cdot V_o \gamma_{H^+} + N_a \cdot \gamma_{H^+} \cdot V_a. \quad (2)$$

In Eq. 2, the product $a_{H^+}(V_o + V_a)$ is a linear function of the titration variable V_a . For any given titration point below the equivalence point, a_{H^+} can be calculated from the measured pH, and $V_o + V_a$ are known. Hence, the total alkalinity of the sample and γ_{H^+} can be calculated from the line slope and intercept, which are obtained by linear regression analysis on several titration points in this region. In practice, we used titration data obtained in the pH region below 1 pH unit under the inflection point.

The analytical concentrations of the dissolved species were transformed to molal concentration units by applying an empirical density-to-magnesium-concentration equation and density-concentration equations for evaporated seawater solutions (Starinsky 1974; density = 0.997 + 0.74 × 10⁻⁶ × TDS). The degree of evaporation (DE) is henceforth defined as the ratio between the molal concentrations of magnesium in the evaporated solution and that in "mean" seawater (Riley and Skirrow 1965).

Results and discussion

The major ion composition, pH, DE, and alkalinities measured in the experiments are given in Table 1. Normalization of ion concentration and alkalinity-to-magnesium concentration, which was conservative throughout our experiments, is helpful in evaluating the relative ionic composition as evaporation progresses (Table 1). The normalized concentrations clearly show the various stages of precipitation along the evaporation path. Gypsum precipitation commences at about DE = 3.5. After this, Ca²⁺ concentration decreases (Fig. 1), declining to about 7 mmol·kg⁻¹ H₂O for DE values >9. Halite precipitation is detected at about DE = 10, after which sodium and chloride are no longer conservative (Table 1, Fig. 2). The fact that the concentration of the major ions for the runs with and without aragonite are sim-

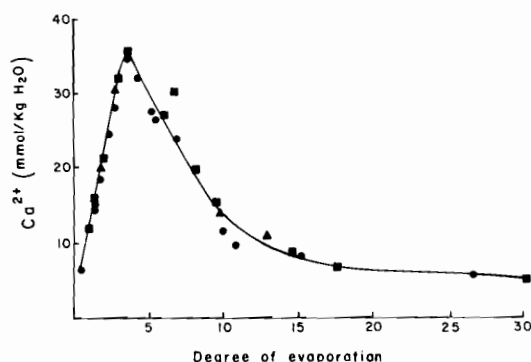


Fig. 1. Plot of the molal Ca^{2+} concentration vs. the degree of evaporation of seawater; ●—evaporation of seawater in the presence of aragonite; ▲—untreated evaporation experiment; ■—untreated evaporation experiment (from Starinsky 1974).

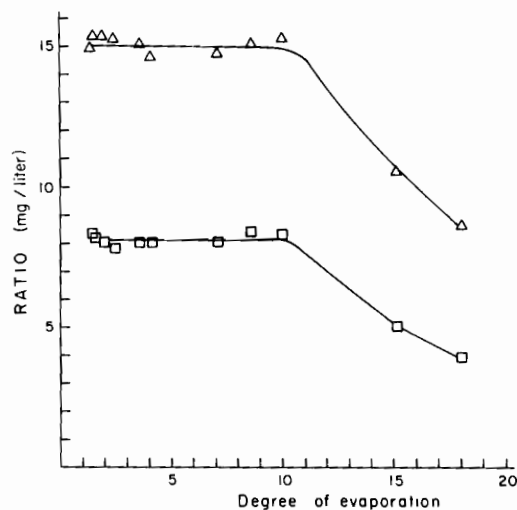


Fig. 2. Variation of $\text{Na}^+:\text{Mg}^{2+}$ (□) and $\text{Cl}^-:\text{Mg}^{2+}$ (Δ) during evaporation of seawater. Data from untreated evaporation experiments.

ilar suggests that the carbonate reaction does not markedly affect the major ion concentrations.

The alkalinity of the samples in which no aragonite was added increases at first (Table 1, Fig. 3) until a local maximum is reached at about $\text{DE} = 2.5$. Beyond this evaporation level, alkalinity decreases until fourfold evaporation is reached. From this point on, alkalinity increases conservatively. This implies that active carbonate precipitation takes place over the relatively narrow range $\text{DE} = 2.5-4$. This behavior is also apparent from the shape of the Mg-normalized alkalinity vs. DE function (Fig. 4). Over this range, the normalized alkalinity drops from about 2.2 to about 0.68. The alkalinity lost from 1 liter of original seawater (TA_{lost}), can thus be estimated from

$$\text{TA}_{\text{lost}} = \text{Mg}_{\text{sw}} \left[\left(\frac{\text{TA}}{\text{Mg}_{\text{sw}}} \right) - \left(\frac{\text{TA}}{\text{Mg}} \right) \right] \quad (3)$$

where Mg_{sw} is magnesium concentration in seawater, $\text{TA}/\text{Mg}_{\text{sw}}$ is magnesium-normalized alkalinity of seawater, and TA/Mg is magnesium-normalized alkalinity of the sample.

The alkalinity lost can be related to CaCO_3 precipitation by applying the fact that each equivalent of alkalinity lost is due to the precipitation of 0.5 mole or 50

g of CaCO_3 . Hence, the corresponding amount of carbonate that precipitates out is

$$\text{CaCO}_3 \text{ p (mole)} = 0.5 \text{ TA}_{\text{lost}} (\text{eq}), \quad (4)$$

or

$$\text{CaCO}_3 \text{ p (g)} = 50 \text{ TA}_{\text{lost}} (\text{eq}). \quad (5)$$

Alkalinity concentrations in evaporated seawater that was in contact with aragonite are clearly affected by intimate contact between solid aragonite and the brine (Fig. 3). CaCO_3 precipitation begins earlier (as compared to the runs without aragonite) and the normalized alkalinity (Fig. 4) increases beyond a DE value of 6 and seems to level off beyond a DE of 10. This implies that the presence of aragonite triggers CaCO_3 precipitation at an earlier evaporation stage and causes aragonite dissolution at the evaporation range of about $\text{DE} = 6-10$ (Fig. 4). It is thus apparent that evaporated seawater that is not in contact with solid carbonate is undersaturated with respect to aragonite. For example, comparison of the two alkalinities at about $\text{DE} = 9.8$ (Table 1) shows a deficiency of about $3 \text{ meq kg}^{-1} \text{ H}_2\text{O}$ of the run without aragonite below that of the brine in contact with ara-

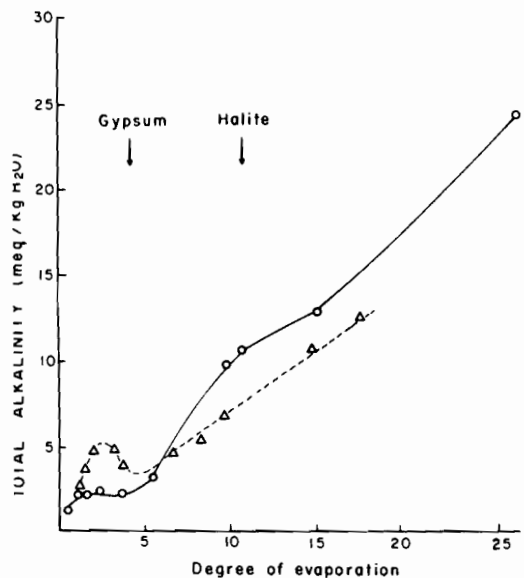


Fig. 3. Change in total alkalinity with the progress in evaporation of seawater (○—with aragonite; △—without aragonite).

gonite. This would imply that 1 kg of the brine that was not in contact with solid CaCO_3 could dissolve 150 mg of aragonite. An interesting question arises in this connection as to whether this undersaturation can redissolve the carbonate that has been precipitated at an earlier stage, assuming that it is in intimate contact with the brine. This question is best answered by comparing the magnesium-normalized alkalinity of the aragonite runs to its value in normal seawater (Fig. 4). This comparison reveals that, despite the dissolution at high DE, TA exhibits a net loss. By applying Eq. 3, one can calculate, for example, that the net alkalinity loss from 1 liter of seawater, evaporated to about DE = 10, taking into account dissolution at high DE, is

$$\text{TA}_{\text{lost}} = 108.6(2.12 - 0.99) \times 10^{-3} = 1.2 \text{ meq.} \quad (6)$$

The corresponding net amount of CaCO_3 that had precipitated out (Eq. 5) is 60 mg.

The pH values of the evaporated seawater with and without aragonite show

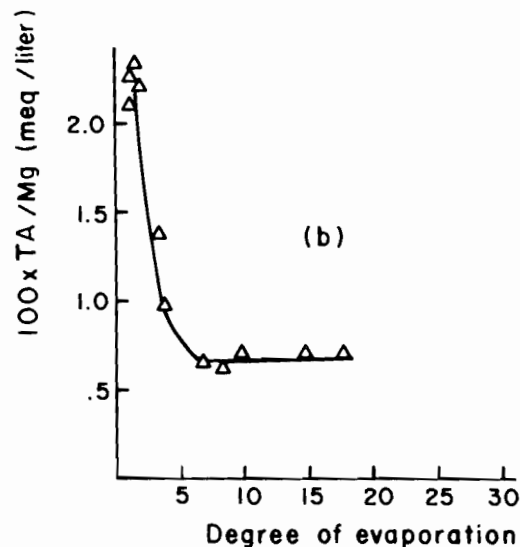
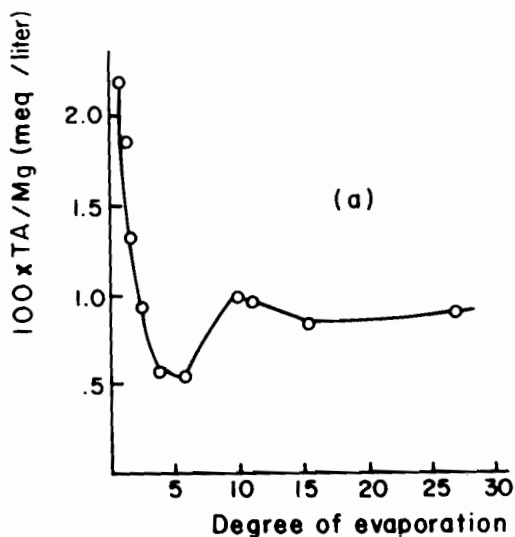


Fig. 4. Normalized alkalinity change during the evaporation of seawater (a—with aragonite; b—without aragonite). Positive, negative, and zero slopes indicate CaCO_3 dissolution, precipitation, and conservative behavior.

similar trends (Fig. 5). Most of the change occurs during the first evaporation stage when the pH drops from the seawater value (ca. 8.2) to about pH 7.5 at DE = 5. Beyond this, the pH levels off, except for a small maximum (pH = 7.75) around DE = 12. The pH values measured during our experiments seem to correlate

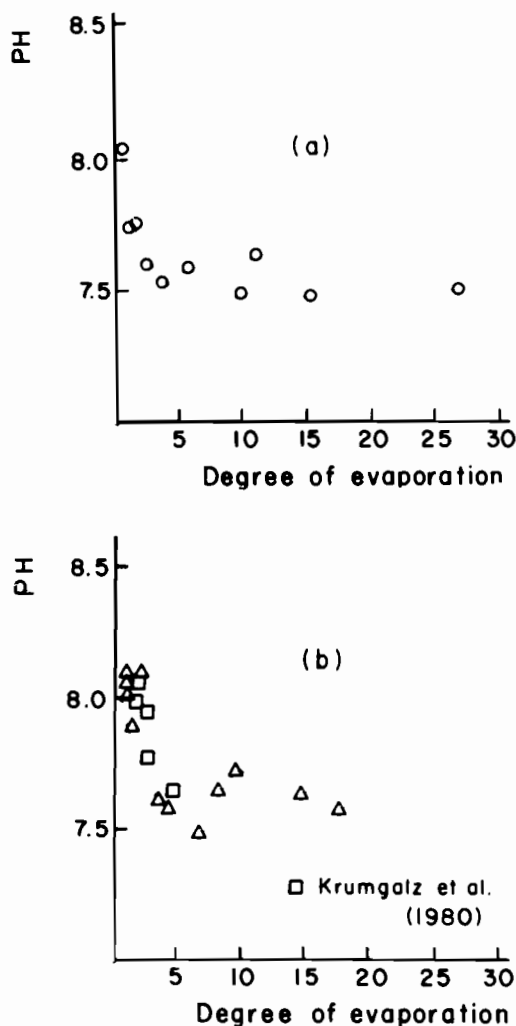


Fig. 5. Plot of pH vs. degree of evaporation of seawater (a—with aragonite; b—without aragonite).

well with those in the evaporation of Mediterranean Sea water reported by Krumgalz et al. (1980) (Fig. 5b). Because their experiment was done in the absence of aragonite, its results are more similar to our runs in which no aragonite was present. The pH variations probably reflect the change in the first and second dissociation constants of carbonic acid as the ionic composition and ionic strength change along the evaporation path (Ben-Yaakov and Goldhaber 1973; Ben-Yaakov

and Sass 1977; Sass and Ben-Yaakov 1977). The reason for the small maximum at DE = 10 (beginning of halite precipitation) which seems to be more pronounced for the runs without aragonite (Fig. 5b) is still unknown.

It is customary to express carbonate solubility in seawater in terms of the apparent solubility product (McIntyre 1965; Ben-Yaakov and Goldhaber 1973; Ingle et al. 1973)

$$K'_{sp} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] \quad (7)$$

where brackets denote total concentration of free and complexed species.

The derivation of K'_{sp} is possible if the first and second apparent dissociation constants of carbonic acid in the experimental solution are known. Since the numerical value of these constants for evaporated seawater are not known, the apparent dissociation constant of aragonite in our experiments cannot be evaluated. An alternative approach to evaluate CaCO_3 solubility is to cite the total amount of CaCO_3 dissolved in the solution, in contact with an excess of solid carbonate, or, expressed differently, the total amount of CaCO_3 that will precipitate from such a solution, upon complete evaporation, assuming CO_2 exchange with the atmosphere. This parameter can be derived in a straightforward manner, in the present experiments, by examining the alkalinity of the brines in which aragonite powder was suspended. If borate alkalinity is neglected, total dissolved CaCO_3 in $\text{mol} \cdot \text{liter}^{-1}$ is approximately related to total alkalinity (expressed in $\text{equiv} \cdot \text{liter}^{-1}$) by

$$S_{\text{CaCO}_3} = \frac{\text{TA}}{2}. \quad (8)$$

Figure 3 shows that in the aragonite runs the mass of CaCO_3 dissolved for a given volume of brine generally increases along the evaporation path. For example, at DE = 25, the solubility of aragonite is about tenfold higher than in normal seawater. Part of this increase could be due to the decrease in pH (Fig. 5) which should tend to reduce the con-

centration of the carbonate ion in solution and, hence, increase CaCO_3 solubility. A better insight into the pH effect can be obtained by considering the functional relationship between the apparent solubility product K'_{sp} and the solubility S as defined here. Following Riley and Chester (1971):

$$[\text{CO}_3^{2-}] = \frac{\text{CA}}{\frac{a_{\text{H}^+}}{K'_2} + 2} \quad (9)$$

where CA is carbonate alkalinity, K'_2 is the second apparent dissociation constant of carbonic acid, and a_{H^+} is activity of the hydronium ion on the practical pH scale ($a_{\text{H}^+} = 10^{-\text{pH}}$). Assuming, as before, that

$$\text{CA} \cong \text{TA}, \quad (10)$$

one obtains from Eq. 7, 8, and 9:

$$K'_{sp} = [\text{Ca}^{2+}] \times \frac{2S_{\text{CaCO}_3}}{\frac{a_{\text{H}^+}}{K'_2} + 2}, \quad (11)$$

or

$$S_{\text{CaCO}_3} = \left(\frac{a_{\text{H}^+}}{K'_2} + 2 \right) \times \frac{K'_{sp}}{2[\text{Ca}^{2+}]}. \quad (12)$$

Two solubility ranges can be distinguished: one in which $a_{\text{H}^+} > K'_2$ (or $\text{pH} < \text{p}K'_2$) and the other in which $a_{\text{H}^+} < K'_2$ (or $\text{pH} > \text{p}K'_2$).

For the range in which $\text{pH} > \text{p}K'_2$:

$$S_{\text{CaCO}_3} \cong \frac{K'_{sp}}{[\text{Ca}^{2+}]}; \quad (13)$$

and for the range in which $\text{pH} < \text{p}K'_2$:

$$S_{\text{CaCO}_3} \cong \frac{a_{\text{H}^+} K'_{sp}}{2K'_2 [\text{Ca}^{2+}]}. \quad (14)$$

Sass and Ben-Yaakov (1977) showed that the $\text{p}K'_2$ of Dead Sea brine is about 7 as compared with $\text{p}K'_2 = 9$ for normal seawater (Lyman 1956; Mehrbach et al. 1973). This was attributed to a high degree of ion pairing which tends to reduce the concentration of free carbonate ion. Preliminary determination of $\text{p}K'_2$ by the method of Sass and Ben-Yaakov (1977) suggests that the $\text{p}K'_2$ values for evaporated seawater should be between 7 and

8. These results are not reported here in detail because of large data scatter which has not yet been resolved or explained. However, these preliminary indications and extrapolation of tabulated $\text{p}K'_2$ values (Lyman 1956; Mehrbach et al. 1973) toward high salinities suggest that the $\text{p}K'_2$ value for evaporated seawater should be much smaller than its value in normal seawater. Consequently, the CaCO_3 solubility for the measured pH range, and certainly for values higher than pH 8.5, should be rather independent of pH. Thus, a large increase in pH due, for example, to photosynthesis, will not drastically decrease the solubility of CaCO_3 as measured here (Eq. 13). Should a lower pH range ($\text{pH} < \text{p}K'_2$) be reached, the solubility S_{CaCO_3} should be proportional to a_{H^+} and a decrease of 1 pH unit should increase the solubility tenfold.

Geochemical implications

The pH values measured during the present experiments are in good accord with field data from the Bardawil Lagoon (eastern Mediterranean) as reported by Krumgalz et al. (1980). The similarity between the Ca^{2+} concentrations and pH values of the lagoon waters and our experimental results supports the conjecture that the present laboratory study simulates the natural carbonate system behavior in the lagoon. The similarity between the pH values seems to indicate an equilibrium between the lagoon brine and atmospheric CO_2 and that respiration and photosynthesis probably play a minor role in determining the pH of the lagoon waters. This is not surprising, taking into account the fact that the lagoon is very shallow (ca. 2 m) and is probably well mixed. It thus appears that our general conclusions concerning CaCO_3 solubility apply not only to this lagoon but probably to other shallow, evaporated seawater bodies.

Our experimental results set limits to the expected carbonate alkalinity in natural, seawater-derived brines. If alkalinity is controlled only by carbonate precipitation and dissolution, it should be kept between the values measured in the

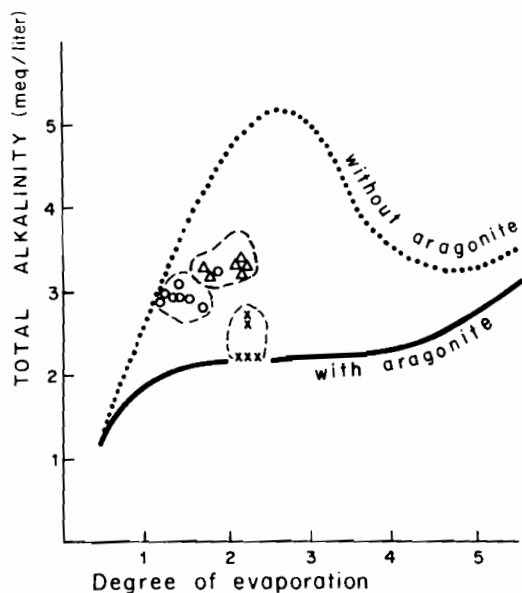


Fig. 6. Total alkalinity vs. degree of evaporation of Mediterranean seawater in the Bardawil Lagoon. (Data recalculated from Levy 1972.) \times —Inner lagoon; Δ —main lagoon; O —western arm. Curves represent the experimental variation in alkalinity with evaporation of seawater (see Fig. 3).

experiments with and without aragonite. Indeed, examination of the field data seems to support this observation. The alkalinity of the Bardawil brines, as measured by Levy (1972), seems to fall between the alkalinity measured for the two experimental conditions (Fig. 6). Furthermore, it is apparent that the alkalinity of the older, inner lagoon waters, which are in better contact with solid carbonate—as would be expected—approaches the values measured for the aragonite runs. The alkalinity of open Mediterranean water (El Arish) coincides well with the expected value of slightly evaporated normal seawater, while the western arm waters (one of the lagoon inlets) deviates slightly from conservative behavior (Fig. 6).

Further support for the possible applicability of our results is gained from examination of the alkalinity of solar pond brines, whose origin is believed to be Gulf of Elat seawater (Eckstein 1970; Aharon 1974). Alkalinity measurements

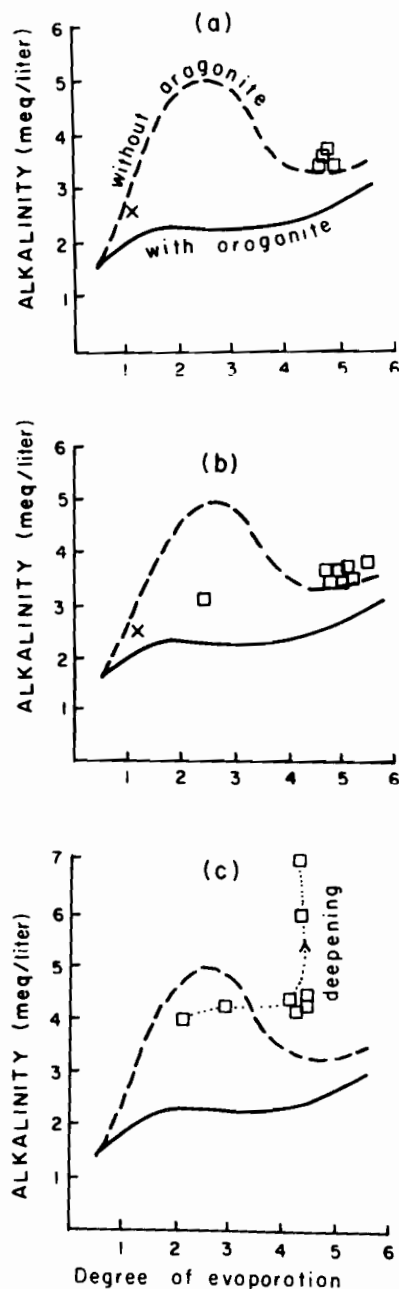


Fig. 7. Total alkalinity vs. degree of evaporation of Red Sea water in a natural solar pond. (Data recalculated from Aharon 1974.) \times —Open sea. Curves indicate the variation in total alkalinity with the evaporation of seawater. a—Sampled August 1972; b—sampled October 1972; c—sampled February–March 1973.

during August (Fig. 7a) and October 1972 (Fig. 7b) are in good agreement with the expected alkalinity. The alkalinities measured during February–March 1973, however, in sulfide-bearing brines (Fig. 7c) are much higher than our experimental results. This is not surprising considering that bacterial sulfate reduction, which is probably responsible for the sulfide buildup, increases the alkalinity of the system (Ben-Yaakov 1973). This mechanism could be responsible for the slightly higher alkalinity observed in Fig. 7a and b over the experimentally derived one, in which no other reaction besides carbonate precipitation and dissolution caused alkalinity changes. It thus appears that the deviation in the alkalinity of natural seawater-derived brines from the values reported here can be interpreted as an indication of additional alkalinity reactions, aside from the expected carbonate reaction.

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