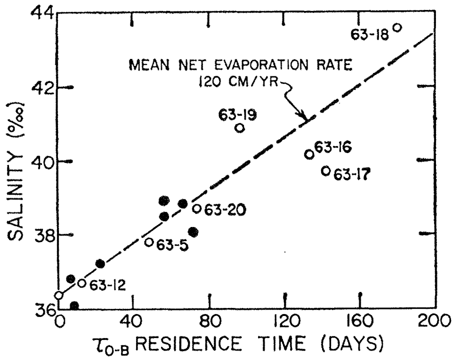

Fig. 2. Salinity versus residence time based on the results of Broecker and Takahashi (*6*). The samples marked with open circles are those for which Sr^{90} measurements were made.

from their bomb C^{14} content. The method is briefly summarized as follows: Waters flowing onto the bank from the adjacent open ocean contain only 10 percent as much bomb C^{14} as the atmosphere over the bank. Once the water is isolated on the shallow bank and hence is not subject to the rapid depletion of newly added bomb C^{14} through deep mixing, the C^{14}/C^{12} ratio grows toward equilibrium with that in the atmosphere. The rate of growth depends on: (i) the water depth (uniformly 4 m), (ii) the total dissolved inorganic carbon content of the water (uniformly 2.0 ± 0.2 mole/m^3), and (iii) the exchange rate of CO_2 between the atmosphere and ocean surface (8 ± 4 mole/m^2 yr) (*6*). Estimates of residence time made in this manner are summarized in the second column of Table 1. The uncertainty of 50 percent is due entirely to the permissible range of exchange rates. The range of residence times for the samples in this study was found to be 12 to 180 days.

Measurements of Sr^{90} were made by techniques given by Rocco and Broecker (*3*). Because the results average many tens of times higher than blank, uncertainties due to contamination are negligible. The amount of Sr^{90} accumulated by the sample was obtained by subtracting the value measured in adjacent surface ocean water (32 disintegrations per minute per 100 liters) from that observed in the sample. This was in turn converted to a deposition value per unit area by correcting for the mean water depth. These results, summarized in Table 1, show generally that the samples which had resided on the bank for longer times accumulated more Sr^{90} than the more recent ones, although a completely consistent increase in Sr^{90} content with time was not found. This has been attributed to short-term geographical differences in rainfall, which is not unlikely since the sampling stations were separated by tens of kilometers. This effect of local rainfall has been qualitatively corroborated by studying the salinities of the samples. As shown in Fig. 2, salinity increases with residence time on the bank; it corresponds to about 120 cm/yr net evaporation (indicated by the dashed line). The individual sample points, however, do scatter; in most cases they are sympathetically opposed to the Sr^{90} results. That is, unusually low salinity (for example, note sample 63-17) suggests a recent rain which would also result in an unusually high fallout value.

Conversely, of course, those salinity values which fall substantially above the average (sample 63-18) indicate periods of unusually high evaporation, and probably little if any recent precipitation in the immediate area of the sample. Lower Sr^{90} accumulation would, therefore, be anticipated in these cases. This effect is also qualitatively borne out in Table 1.

To compare the results with concurrent land fallout values, the average Sr^{90} deposition from all land sites in the AEC Health and Safety Laboratory's fallout network in the 20° to 30° north latitude band (*2*) was graphically integrated for the time periods corresponding to the residence times of the Bahama Banks samples. These data, also shown in Table 1, indicate substantial agreement.

Our results indicate that the waters of the Bahama Banks accumulate Sr^{90} fallout at a rate within a factor of 2 of that for the land masses between 20° and 30° north latitude. This conclusion is not in agreement with Bowen and Sugihara's (*1*) claim that fallout over the oceans is on the average several times higher than that over the continents.

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Magnesium Ions: Activity in Seawater

Abstract. *The activity of magnesium ions in seawater was determined from solubility data and found to be between the values determined by Platford and by Garrels and Thompson. Our value may result from extensive formation of magnesium sulfate ion pairs.*

We estimated the activity of magnesium ions in seawater by a simple procedure suggested by R. M. Garrels. The result may be compared with the value based on the work of Garrels and Thompson (*1*) and with the value obtained by Platford (*2*).

The activity of magnesium ions in seawater may be expressed in two ways. We used the conventional equation:

$$a_{Mg} = f_{Mg} \times (Mg^{+2}) \qquad (1)$$

where f_{Mg} is the activity coefficient and (Mg^{+2}) is the stoichiometric concentration. The activity coefficient f_{Mg} reflects nonspecific effects of ionic strength and specific interactions of magnesium with other ions or molecules present in seawater.

An alternative equation, implicit in the treatment of Garrels and Thompson, is

$$a_{Mg} = (f_{Mg})_u \times (Mg^{+2})_u \qquad (2)$$

where the subscript *u* refers to uncomplexed magnesium. Equation 2 is equivalent to Eq. 1 if the specific and nonspecific effects are separable. From single-salt solutions, Garrels and Thompson obtained activity coefficients that reflected the effects of ionic strength only. They estimated the concentrations of the uncomplexed ions by postulating that specific interactions resulted in ion pairs such as $MgSO_4{}^0$, $MgHCO_3{}^+$, and $MgCO_3{}^0$. For magnesium they found that $(f_{Mg})_u = 0.36$ and $(Mg^{+2})_u = 0.0470$ mole/kg at 25°C, chlorinity 19 per mill, and pH 8.1. Therefore, $a_{Mg} = 0.0169$.

We calculated a_{Mg} from Eq. 3:

$$a_{Mg} = K_{SP}/(a_{OH})^2 \qquad (3)$$

where K_{sp}, the thermodynamic solubility product of magnesium hydroxide, is 7.08×10^{-12} (*3*). The activity of hydroxyl ions, a_{OH}, was obtained from the pH of seawater samples at equilibrium with brucite at 23°C ± 0.1°C. This procedure involves an unknown error because pH measurements do not yield the thermodynamic activities of hydrogen and hydroxyl ions (*4*). However, the result is correct if applied to future work in which pH electrodes are also used.

The equilibrium pH values were obtained for Nevada massive buff and Quebec white platy brucites. The samples were ground and sifted in the 42- to 48-mesh range. Treatment with hydrochloric acid revealed no major carbonate impurities. The seawater, of chlorinity 18 per mill, was obtained off Oregon and filtered through a 0.45-μ Millipore R filter. The saturometer and the potentiometric circuit used for the equilibration and pH determinations have been described by Weyl (*5*). Preliminary experiments showed a drift that resulted from the entry of carbon dioxide into the seawater. This drift was eliminated by placing a large stopper, which held the reference electrode, snugly into the saturometer cup.

The average pH obtained after samples of seawater had been equilibrated with four Nevada and two Quebec brucites was 9.55 ± 0.01. The equilibrium pH was determined from the recorded electrode potential when this potential became stable within the sensitivity of our equipment. This sensitivity is ± 0.1 mv or ± 0.002 pH units. The average equilibration time was 30 minutes after addition of the brucite. The hydrogen ion activity calculated from the equilibrium pH, 2.82×10^{-10}, the dissociation constant of water, 8.3×10^{-15}, and the activity of water in seawater, 0.98, were used to calculate a_{OH} (*6*). The activity of the hydroxyl ions was found to be 2.9×10^{-5}. This value of a_{OH} and Eq. 3 yielded $a_{Mg} = 0.0084$; $(M_g{}^{+2})$, the concentration of magnesium ions, was 0.50 mole/liter. Therefore, f_{Mg}, the activity coefficient of the magnesium ions, was 0.17. This value of f_{Mg} reflects specific and nonspecific interactions.

A possible source of errors is the presence of impurities on the surface of the solid phase. Such impurities could alter the activity of the magnesium hydroxide. However, the resulting error should not be serious because equilibrium was approached from undersaturation. Such an approach should cause solution of the brucite sample and should prevent encapsulation of impurities into the near-surface layers of the sample. Preexisting impurities would have caused a significant difference between the results obtained with the two varieties of brucite.

Our value ($a_{Mg} = 0.0084$ at 23°C and chlorinity 18 per mill) is only half of the value based on the work of Garrels and Thompson ($a_{Mg} = 0.0169$ at 25°C and chlorinity 19 per mill). This discrepancy cannot be accounted for by the small differences in temperature and chlorinity. The difference in pH (9.55 in our case and 8.1 in the earlier work) cannot have such a large effect on the activity of magnesium ions either. The only pH-sensitive species are, in the ion-pair notation, $MgHCO_3{}^+$, $MgCO_3{}^0$, and $MgOH^+$. Bicarbonate and carbonate ions cannot affect the activity of magnesium ions by more than 5 percent because the sum of the concentrations of these two species is less than 5 percent of the magnesium ion concentration. Lyman (*7*) estimated that the apparent equilibrium constant for the reaction

$$Mg^{+2} + H_2O = H^+ + MgOH^+ \qquad (4)$$

in seawater is between $10^{-10.6}$ and $10^{-12.4}$. These values, at pH 9.55, mean that the ratio $(Mg^{+2})/(MgOH^+)$ is between 11 and 700. Therefore, complex formation with hydroxyl ions cannot affect a_{Mg} by more than 9 percent.

The effect of specific interactions is obtained by dividing our value of f_{Mg} by 0.36, the value of $(f_{Mg})_u$; the result is 0.47. In the ion-pair scheme this means that 47 percent of the magnesium ions are uncomplexed and 53 percent are complexed. For this estimate we assume, as Garrels and Thompson did, that the effects of specific and nonspecific interactions are separable.

Duedall determined the partial equivalent volume of magnesium chloride in seawater (*8*). The result was compared with the one calculated by Owen and Brinkley (*9*) for a sodium chloride solution of the same ionic strength as seawater. The volume in seawater was larger than that in the sodium chloride solution; the difference suggests less hydration of magnesium ions in seawater. This result may rule out hydration as the cause of the decrease in activity of magnesium in seawater relative to the value in a sodium chloride solution.

Up to 14 percent of the magnesium ions may be complexed to bicarbonate, carbonate, and hydroxyl ions. The other 39 percent are still unaccounted for at this point. Hydration appears to be ruled out. The ratio of sulfate to magnesium ions in seawater is 0.53 (*1*). Perhaps the low value of the activity that we obtained results from a formation $MgSO_4{}^0$ which is more extensive than that estimated by Garrels and Thompson. If this is the case, then 39 to 53 percent of the magnesium ions present in seawater form $MgSO_4{}^0$ ion pairs. This result is in rough agreement with that of Fisher (*10*), who found that the degree of magnesium sulfate association in a 0.02M magnesium sulfate solution was 0.386. Platford (*2*) estimated that only 3 percent of the magnesium in seawater is complexed to sulfate. Platford assumed in his calculation that, because $MgSO_4{}^0$ is an uncharged species, its activity is unity. However, the dipolar nature of this ion pair could cause interactions with the surrounding solution which would decrease the activity. This effect cannot be calculated at present. If Platford is correct, we must search for another cause of the low activity coefficient of magnesium ions in seawater. One possibility is that we have underestimated the effect of hydration in seawater.

Platford also calculated f_{Mg}, the activity coefficient of magnesium ions, from solubility measurements. However, his solubility determinations were made by adding sodium hydroxide to carbonate-free seawater and observing the pH at which a magnesium hydroxide precipitate was first formed. We found, by interpolation of Platford's results, that this pH, at chlorinity 18 per mill, is 9.89 and that the corresponding value of f_{Mg} is 0.065. It is difficult to explain why we obtained equilibration with added brucite at a lower pH, 9.55. The difference between our results and those of Platford is not due to the presence of calcium carbonate in our experiments. We also observed precipitation at *p*H values between 9.8 and 9.9 upon addition of base. Calcium carbonate, though supersaturated, does not appear to precipitate because the formation of nuclei is slow (*11*). The absence of coprecipitation of calcium with magnesium has been known for some time and is used for the separation of these ions in the analytical scheme of Pate and Robinson (*12*). Perhaps addition of a base causes initial supersaturation. In any event, our values for the activity coefficient of magnesium ions and those determined by Platford are lower than those determined by Garrels and Thompson.

Activities of single ions have thermodynamic significance, but they cannot be measured rigorously. The effect of the difference between our assumptions and those made by Garrels and Thompson cannot be evaluated at present.

Specific and nonspecific interactions probably differ only in a matter of degree. Also, these two types of interactions are not strictly separable because they are not independent of one another. Each ion added to seawater will affect the structure of the water and the environment and activity of the other ions present. Thus the interpretation of activities in terms of specific and nonspecific interactions is an idealization that provides only a preliminary insight into the structure of seawater.

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Recent Emerged Beach in Eastern Mexico

Abstract. *A bluff on the eastern coast of Mexico reveals a cross section through an ancient beach deposit now lying 4 meters above sea level. Radiocarbon dates on the shells within the deposit reveal an age of 1940 years. The deposit appears to be valid evidence for submergence greater than that of the present, but whether that submergence was due to a higher eustatic stand of the sea or whether there has been an uplift of the land since that time cannot yet be determined.*

The position of absolute sea level during the last 5000 years has recently been studied and debated by several workers (*1, 2, 3*). Although many of these workers have discredited the hypothesized absolute stands higher than the present one because of lack of evidence in areas they have studied, evidence from other areas (*4*) prevents me from disregarding the possibility entirely without further testing. I report here a previously undescribed beach deposit in eastern Mexico that contains shells whose C^{14} ages fall within the period in question and that now stands up to 4 m above sea level.

The deposit is located at longitude 97°46–47′W, latitude 24°29′30″N, on the south end of a southward projecting peninsula between Bahia Salada (also referred to as Bahia de los Algodores) and Laguna Madre in the state of Tamaulipas, Mexico (Fig. 1). It is exposed in an east-west trending bluff about 2 km south of the fishing village of La Carvajal. The south-facing bluff is a wave-cut cliff, the waves being generated by predominating southeasterly trade winds.

Figure 2 is a diagrammatic representation of exposure in the bluff. It trends perpendicular to the present coastline and is a cross section through deposits which strike parallel to the coast. The bluff contains three distinctive units.

The lowermost unit is a yellow-orange, clayey sand (24 to 30 percent clay, 56 to 68 percent sand) and continuously underlies all other units to an unknown depth. It is devoid of macrofossils but contains a few foraminifers and abundant calcium carbonate in the form of caliche. It is rather friable but distinctly more compact than the overlying units. The upper surface of this sand has two depressions, lower portions of which are 0.5 to 1.3 m above sea level (*5*), and these depressions are reflected in the present topography. The highest elevation of this surface is about 3.6 m; the unit is massive and shows no bedding whatsoever. Within this unit are two outcrops of beach rock, specimens of which have given C^{14} ages of 25,000 and 35,000 years. However, both specimens were highly recrystallized and contained shell material converted from aragonite to calcite, secondary sparry calcite cement, and grain-growth calcite. Thus, although it is improbable that the C^{14}-

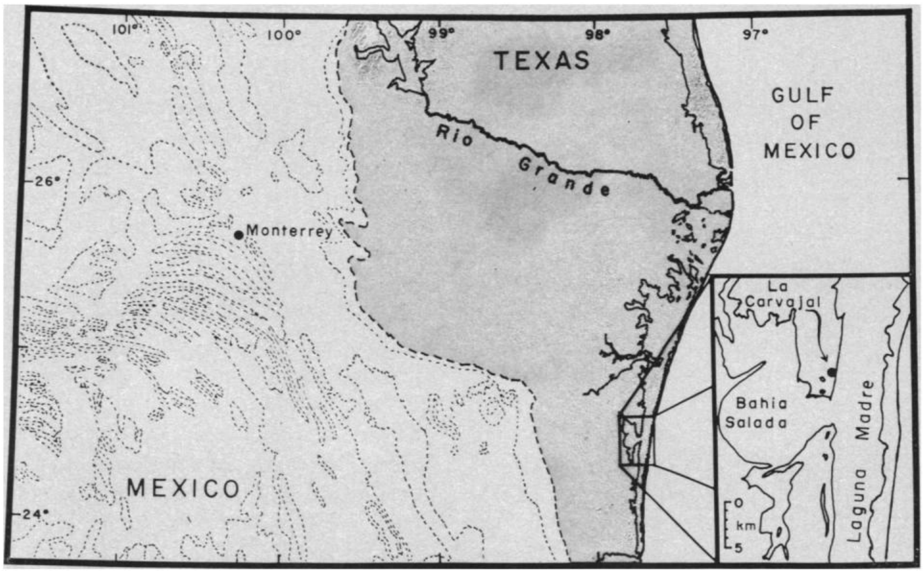

Fig. 1. Index map. Landward limits of Gulf Coast geosyncline indicated by extent of Eocene and younger sediments (shaded area). Structural trends indicated by strikes of contacts of Cretaceous formations (dashed lines).