

The Precipitation of Calcium and Magnesium from Sea Water.*

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With 2 Figures in the Text.

APPARENTLY calcium carbonate is precipitated in certain parts of the ocean by processes which are inorganic in so far as that the calcium does not first form a true constituent of organisms (Clarke, 1920, p. 128). The conditions governing solubility of calcium in sea-water have been reviewed by Johnston and Williamson (1916) with the conclusion that surface layers of the ocean are approximately saturated, and that slight natural changes, particularly in carbon dioxide tension, might suffice to cause precipitation.

The molar concentration of magnesium in sea-water is about five times that of calcium. In marine sediments magnesium carbonate is a constituent which varies in proportion according to the organic remains producing them (Clarke and Wheeler, 1922). It is a frequent constituent of shells, but much less abundant than calcium. The mode of formation of magnesium-containing deposits is often obscure.

Magnesium hydroxide is precipitated from sea-water by addition of small amounts of alkali. In fact, both magnesium and calcium are in a delicate equilibrium where slight changes in alkalinity and carbon dioxide tension may cause precipitation. The delicacy of these equilibria and the nearness of their points of maximum sensitivity to natural conditions make calcium and magnesium particularly subject to changes induced by organisms. Likewise they are two of the most important elements biologically, both in amount and specific effect. It is therefore significant to examine the solubility conditions for both elements together, and to determine the conditions for their precipitation.

* I wish to express to Dr. Allen my appreciation for the extension of laboratory facilities and material and helpful personal interest, and to Dr. Atkins and Mr. Harvey for many suggestions and practical help.

The solubility product constants for the two carbonates are, at 16 degrees—

- (1) $K_{MgCO_3} = 1.4 \times 10^{-4}$ (Johnston, 1915).
 (2) $K_{CaCO_3} = 0.98 \times 10^{-8}$ „ „

The solubility product constant for calcite is practically equal to that for calcium carbonate (Johnston and Williamson, 1916).

In sea-water at pH 8 the excess base, which is practically a measure of $[HCO_3^-]$ is about 2.5×10^{-3} N. From the equation

$$(3) [CO_3^{--}] = \frac{k_2 [HCO_3^-]}{[H^+]} \text{ by substitution}$$

$$[CO_3^{--}] = 1.35 \times 10^{-4}$$

From (2) $[Ca^{++}][CO_3^{--}] = 0.98 \times 10^{-8}$
 and, from (2) and (3)

$[Ca^{++}] = 0.73 \times 10^{-3}$ representing the solubility limit for $CaCO_3$ at pH 8 in sea-water.

By actual determination

$$[Ca] = 1 \times 10^{-2}$$

Therefore, sea-water at pH 8 is super saturated with $CaCO_3$.

The solubility product constants for magnesium hydroxide and calcium hydroxide are

- (4) $K_{Mg(OH)_2} = 1.2 \times 10^{-11}$ (Johnston, 1915).
 $K_{Ca(OH)_2} = 4.1 \times 10^{-6}$ „ „

In sea-water

$$[Mg] = 0.05.$$

Substituting in (4)

$$[OH^-] = \sqrt{\frac{1.2 \times 10^{-11}}{5 \times 10^{-2}}} = 1.6 \times 10^{-5}$$

pH 9.2 is attained by photosynthesis experimentally and probably naturally (Atkins, 1922), and *Ulva* can apparently produce a pH close to 10. It therefore appears that magnesium hydroxide might be precipitated under natural conditions. In these calculations no allowance is made for activity factors or for the influence of neutral salts.

Addition of alkali to pH 10 is known to produce a precipitate in sea-water. Qualitative examination of such a precipitate showed CO_2 , Ca, and Mg.

After preliminary tests, the two series reported in Tables 1 and 2 were made in which graded amounts of NaOH and Na₂CO₃, respectively, were added to samples of sea-water. After at least 24 hours shaking, the mixtures were filtered and a sample of filtrate analysed for Ca by McCruden's (1909-10) method with KMnO₄. The residue in the flasks was

TABLE 1.

ADDITION OF NaOH TO 200 ML. SEA-WATER.

Number	NaOH added gram molecules per liter.	pH	In precipitate.			
			Ca. gram molecules per liter.	Mg. gram molecules per liter.	% total Ca.	% total Mg.
11	0.00209	9.3	0.0002	0	10	0
12	0.00625	9.5	0.0003	0.00015	14	1.5
13	0.0174	10.0	0.00039	0.00161	19	16
14	0.0523	10.5	0.00039		19	
15	0.156	11.5	0.00083		38	
7b	0.278	11.6	0.00125	0.00857	57	86
Sea-water			0.00212	0.01		

TABLE 2.

ADDITION OF Na₂CO₃ TO 200 ML. SEA-WATER.

Number.	Na ₂ CO ₃ 2 added gram molecules per liter.	pH	In precipitate.			
			Ca. gram molecules per liter.	Mg. gram molecules per liter.	% total Ca.	% total Mg.
18	0.00285	9.1	0	0.0006	0	0.8
19	0.00855	8.5	0.000875	0.00005	3.8	0.5
20	0.0259	9.3	0.0017	0.00005	81	0.5
21	0.0740	10.0	0.00917	0.0004	95	4.0
22	0.134	10.6	0.00183	0.0042	86	40
17b	0.438	11.0	0.00193		91	
Sea-water			0.00212	0.010		

washed into the filter with a small amount of 70% alcohol, and the filter washed once with alcohol. The residue was dissolved in standardized H₂SO₄ and titrated with NaOH. The difference between H₂SO₄ and NaOH was equivalent to ([Mg]+[Ca]) in the precipitate. [Ca] being determined in the filtrate, [Mg]=([Mg]+[Ca])-[Ca].

This procedure for determination was worked out with suggestions from Mr. H. W. Harvey. Qualitative tests on the amount of 70% alcohol used for washing showed only traces of Ca and Mg. Willstätter's method was not noted until later. It is similar, but uses alcohol and acetone titrations to effect a separation.

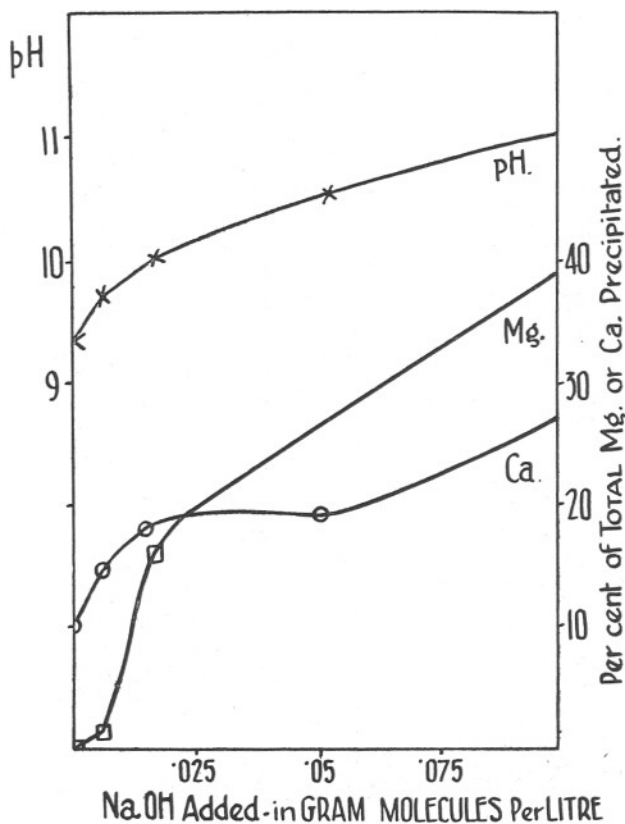


FIG. 1. Titration of sea-water with NaOH (part of curve from points given in Table 1).

Colorimetric pH determinations and Mg precipitated are consistent with many potentiometric titrations made in 1924.

Fig. 1 represents the lower part of the curve drawn from points given in Table 1, showing the relation of per cent Ca and Mg precipitated and pH against NaOH added. Fig. 2 shows data from Table 2 for Ca and Mg precipitation and pH against Na_2CO_3 . It is conspicuous that either with Na_2CO_3 or NaOH, Ca exceeds Mg in the precipitate. Na_2CO_3 precipitates much more Ca, and relatively little Mg up to pH 10. A

small amount of Mg is precipitated by Na_2CO_3 . These facts agree with the much greater solubility product of MgCO_3 . NaOH precipitates increasingly less Ca above pH 10, conforming with the greater solubility of $\text{Ca}(\text{OH})_2$ than of CaCO_3 .

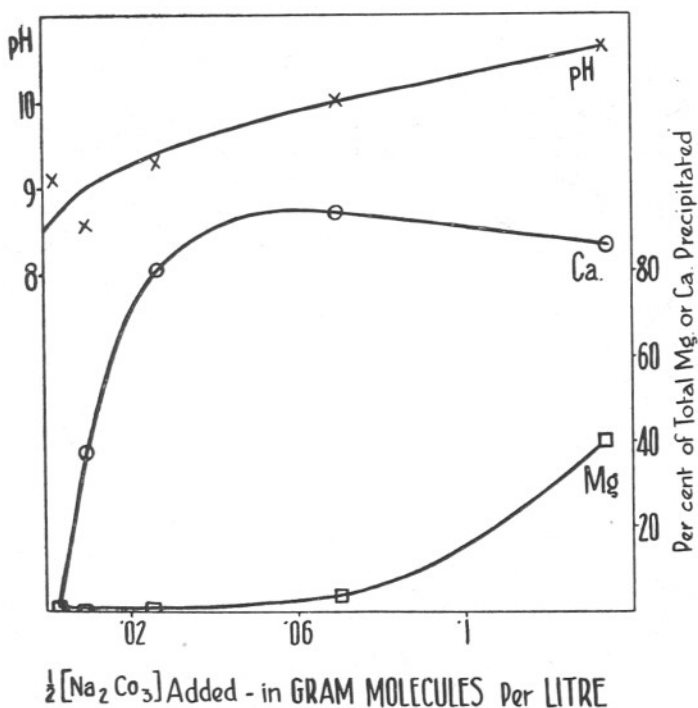


FIG. 2. Titration of sea-water with Na_2CO_3 .

Unfortunately, methodical uncertainty is greatest in the regions of low alkalinity and principal biological importance. The investigations show that Ca and some Mg may be precipitated under possible conditions of natural sea-water alkalinity, although it is another question as to how frequently this alkalinity is attained. The same conditions governing precipitation outside of the organism may explain the excess of Ca over Mg in organic "formed" precipitates, as alkalinity necessary for magnesium precipitation is much more difficult for the organism to attain, especially within its tissues.

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