

Kinetics of CaCO_3 homogeneous precipitation in seawater

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Introduction

The stable supersaturation of CaCO_3 in surface seawater of many oceanic areas ranges from 2–3 to 6–7 times. Nevertheless the spontaneous precipitation of CaCO_3 is very retarded due to different inhibitors: dissolved organic matter [1,3], phosphates [3] magnesium [2,4].

During living activity of photosynthesized algae or the isolation of marine bacteria the great increase of pH take place. The achieved supersaturation usually may be about 10–15 and that is enough for spontaneous nucleation. The small amounts of suspended carbonate grains in pelagic area of oceans permits to suggest that only homogeneous nucleation may be the initial stage of CaCO_3 removal by phytoplankton biogenic activity.

We have been study the spontaneous nucleation of CaCO_3 in seawater at conditions simulating natural process as far as it was possible in laboratory during usual time scale.

Experimental

The natural Atlantic seawater aged two years and artificial seawater (ASW) (35‰ salinity) were filtered through membrane filter. The composition of ASW was changed with respect magnesium, sulfate, phosphates but ionic strength was constant $I = 0.7$. The experiments were conducted in a thermostatted glass vessel at $20 \pm 1^\circ\text{C}$. The CaCO_3 supersaturation achieved by adding Na_2CO_3 or NaOH then pH and total inorganic carbon were known. The main experimental kinetics parameter of homogeneous nucleation was induction period - t . It is the time required for the commencement of calcium carbonate formation. The observation of precipitate appearance were conducted visually (in stirred solutions) and using spectrophotometer in unstirred solution. The end of induction period coincides in the range of experimental error 10% with the pH dropping in solution that controlled by pH-meter. The reproducibility of experiments were about 20%, i.e. ± 0.10 logarithmic value of t .

The supersaturation $S = \{[\text{Ca}^{2+}][\text{CO}_3^{2-}]\}/K_s$ where $[i]$ - total concentrations, K_s - apparent solubility product of calcite or aragonite in

seawater - was calculated using initial measured pH value of supersaturated solution with known total carbon concentration.

Results

According to theory of homogeneous nucleation the logarithms induction time $\log t$ and supersaturation $\text{LOG } S$ shows the linear relationship:

$$\text{LOG } t = A - n \cdot \text{LOG } S \quad (1)$$

where t - induction period (minutes), A - constant value, n - the order of nucleation. The received experimental data were found to be fit well for equation (1).

I. The role of phosphates and hydrodynamic conditions. It was established that the stirring of solutions dramatically decreases the aragonite precipitation (by a factor of ten) both in natural and artificial seawater. In natural seawater with stirring the equation (1) turns out to be

$$\text{LOG } t = 8.20 - 4.58 \cdot \text{LOG } S \quad (2)$$

And in unstirred solution

$$\text{LOG } t = 9.28 - 4.78 \cdot \text{LOG } S \quad (S = 9-35) \quad (3)$$

In artificial seawater the rates of nucleation in 1.5-2 orders higher than (2):

$$\text{LOG } t = 6.32 - 3.761 \cdot \text{LOG } S \quad (S = 7-40) \quad (4)$$

It was necessary to point out that the dissolved phosphates are the major inhibiting factors of CaCO_3 precipitation in seawater. The induction period time in artificial seawater with 28 mkg P/l and natural seawater with 15 mkg P/l turns out to be very close (Fig.1).

II. The influence of magnesium and sulphate ions. It is usually proposed [2,4] that the magnesium ion must be the major inhibitor of CaCO_3 precipitation in seawater. This statement base on the data of homogeneous precipitation in the high supersaturated solution with induction periods less than 100 minutes.

Our experiments at low supersaturation with induction period up to 3000 minutes shows the very close kinetics of aragonite precipitation in normal seawater and calcite one in Mg-free seawater. On the Fig.2 the induction period of precipitation as the function of initial pH value at constant concentration of total carbon $C_t = 2.38$ mmole/l in all solutions is plotted. As it is seen

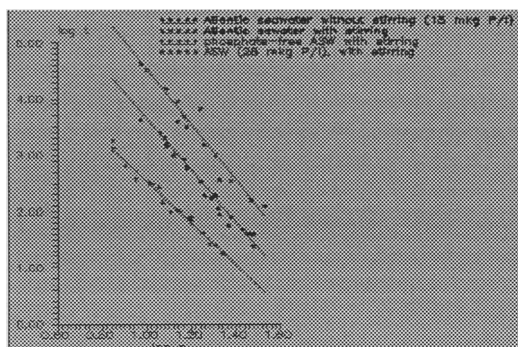


FIG. 1.

from Fig. 2, the differences are actually only in the range of great supersaturation (high initial pH value). Under usual conditions of CaCO_3 oceanic precipitation ($\text{pH} < 8.8$) there are no connection between induction period and Mg concentration in solutions with equal S value. In Mg-free seawater the equation (5) was established:

$$\text{LOG } S = 7.84 - 4.85 \cdot \text{LOG } t \quad (5)$$

In sulphate-free seawater the equation (1) converts into (6)

$$\text{LOG } S = 6.54 - 3.784 \cdot \text{LOG } t \quad (6)$$

which is very close to (4).

So it have been proven that the major ions of seawater do not act as inhibitors during CaCO_3 homogeneous precipitation in natural conditions.

Discussion

All receiving results are well explained by model of Ostwald step rule. The first precipitate consist of vaterite which recrystallize into aragonite and then calcite in water solution. The transformation aragonite - calcite is very retarded in seawater due to inhibition by dissolved magnesium ions where as vaterite - aragonite transformation occurs very quickly. This explains why the aragonite is the main precipitate during inorganic CaCO_3 crystallization from seawater.

Using established empirical equation one can estimate the values of induction period of precipitation in natural conditions. The extrapolation on average supersaturation 300% using equation (3) gives the time of precipita- tion

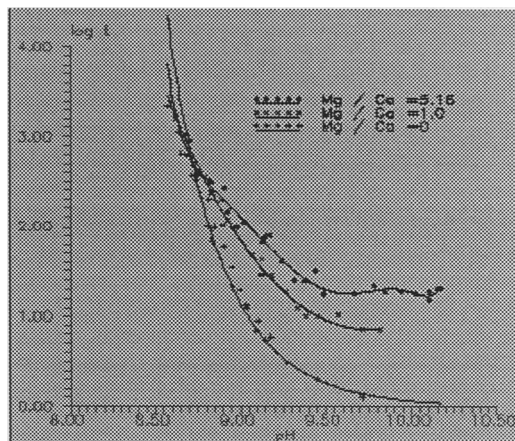


FIG. 2.

6000–10000 years in unstirred solutions that is close to the data of Pytkowicz (1973). This proves the impossibility of pure homogeneous CaCO_3 precipitation in surface seawater with average phosphorus concentration 30 mg P/l. However at conditions of strong stirring and decreasing of dissolved phosphorus concentration which is uptaked during photosynthesis this estimation may greatly diminish up to 1–2 years.

The absence of major inhibitor – phosphorus and small concentrations of dissolved organic matter (1.5–2 mg C/l) gives the real possibility of CaCO_3 spontaneous nucleation. In the well stirred warm surface water at $S = 6-7$ the induction periods of precipitation do not exceed several days. This process visually occur as whitening which take place on Great Bahama Bank or in the Persian Gulf.

References

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