Kinetics of calcium and magnesium phosphates precipitation from seawater

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The precipitation of authigenic calcium phosphate (apatite) is generally believed to be major sink of oceanic phosphorus (P) in marine sediments(Froelich *et al.*, 1982; Savenko, 1992). The initial stage of apatite precipitation is nucleation process that could not be studied under natural conditions due to the large time scale required for this process and the number of biological processes affecting its formation in sediments. In contrast to those studies aimed at the characterization of calcium phosphate nucleation from Mg-free solutions of low ionic strength (i.e. Nancollas and Tomazic, 1974; Koutsoukos *et al.*, 1980), few attempts have been made to study the homogeneous nucleation of phosphates in Mg-rich solutions and the main factors controlling the kinetics of this process (Van Cappelen and Berner, 1989, 1991). This study addresses the homogeneous nucleation of Ca and Mg phosphates from modified seawater solutions.

Methods

The induction period (τ) which is the amount of time between the preparation of the supersaturated solution (without seed crystals) and the onset of spontaneous precipitation was determined at 20 ± 1°C for different solution composition. The end of the induction period was monitored using a spectrophotometer with an uncertainty $\pm 15\%$. Reagent grade chemicals were used to prepare the artificial seawater with a salinity of 70‰ containing all major components including bromides. To test the effect of magnesium on the nucleation kinetics, the $[Mg^{2+}]/[Ca^{2+}]$ ratio in artificial seawater varied from 0 to 10 at a fixed ionic strength of 0.7 M. Supersaturated solutions were made by a mixing of equal volumes of this 70‰ phosphate-free seawater with a Na_2HPO_4 solution (0.008 M) at different pHs. The first portion of the precipitated solid was immediately separated from solution by filtration through a 0.45 µm membrane filter, rinsed in H_2O, dried at 50°C, and analysed for Ca, Mg, and P content.

Results and discussion

The measured values of τ show a strong dependence on dissolved phosphate and magnesium concentration (Fig. 1).

At a constant pH of 7.95 ± 0.05, the following linear equation was obtained:

$$\log \tau[\text{min.}] = -14.23 - 4.87 \cdot \log[PO_4^{3-}]_t + 0.0214 \cdot [Mg^{2+}]_t$$

where $[i]_t$ is the total dissolved concentration (mM). As it is seen in Fig. 1, a slope of $\log \tau - \log[PO_4^{3-}]_t$ dependence does not depend on $[Mg^{2+}]/[Ca^{2+}]$ ratio in solution indicating that similar mechanisms control the nucleation process of phosphates in supersaturated solutions. Decreasing of the pH from 8 to 7.2 leads to an increase of τ due to a decrease in solution supersaturation:

$$\log \tau[\text{min}] = 16.93 - 4.83 \cdot \log[P]_t - 3.76 \cdot \text{pH}.$$

The addition of fluoride ($0-3 \cdot 10^{-4}$ M) and carbonate ($0-3.6 \cdot 10^{-3}$ M) did not influence the kinetics of phosphates homogeneous nucleation.

XRD analysis of the precipitated solids shows the presence of amorphous or semi-amorphous solid phases in solutions having a $[Mg^{2+}]/[Ca^{2+}]$ ratio from 0 to 1. In contrast, Mg-free solution produces a highly crystalline precipitate of hydroxylapatite. Analysis of phosphorus in the solids revealed a (Ca+Mg)/P molar ratio close to 1.5–1.6 in Mg-free seawater and to 1.3 in normal seawater. The relative content of Mg in solids decreases rapidly with increasing $[Mg^{2+}]/[Ca^{2+}]$ ratio in solution (Fig. 2). At a $[Mg^{2+}]/[Ca^{2+}]$ from 4 to 10, the Mg content in

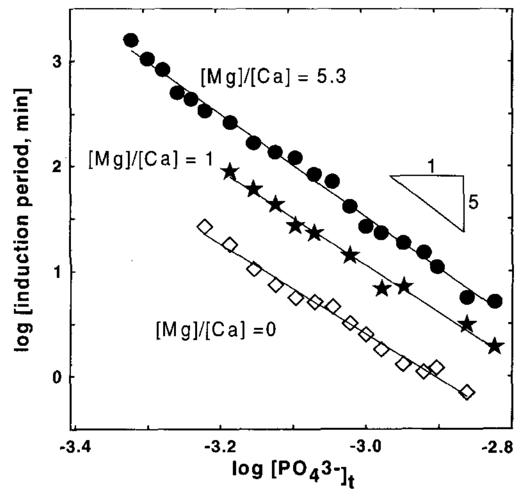

FIG. 1. Induction periods (τ) for spontaneous nucleation as a function of total dissolved phosphorus concentration in solutions with different Mg/Ca ratio at a constant pH 7.95 ± 0.05.

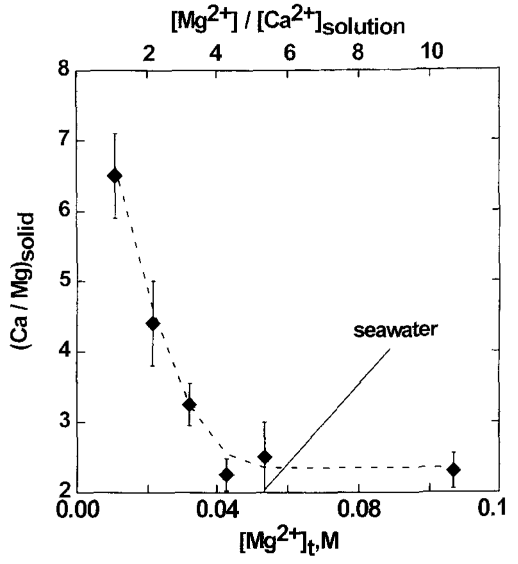

FIG. 2. Chemical composition of calcium-magnesium phosphates precipitated from modified seawater.

the solid does not depend on the total Mg concentration in solution indicating a possible maximum amount magnesium incorporated in the solid phase. No precipitation of a solid phase was observed in Ca-free 'seawater' solutions within the time scale needed for Ca-Mg phosphates precipitation in normal seawater. Based on these data, we suggest that the solid phases precipitated homogeneously from solutions with different [Mg^{2+}]/[Ca^{2+}] ratios are presented by metastable mixed (interlayed) amorphous phosphates of Ca and Mg such as octa calcium-magnesium phosphates with a stoichiometry of $(Ca,Mg)_4H(PO_4)_3 \cdot xH_2O$. In normal 35‰ seawater, the composition of precipitated solids corresponds to a Ca/Mg = 2.5 ± 0.4. This ratio does not depend on pH (6.4–9.1) and [PO$_4^{3-}$]$_t$ (10^{-3}–10^{-2} M) indicating that similar mechanisms are responsible for Ca and Mg fractionation in the course of phosphates homogeneous nucleation within a broad range of supersaturation degrees.

The results of this study are comparable with those of Van Cappelen and Berner (1991) on the growth of fluorapatite (FAP) from modified seawater solutions. In particular, the presence of Mg in normal seawater relative to Mg-free solutions leads to a decrease of the rate of FAP crystal growth and nucleation of mixed Ca-Mg phosphates by a factor of 20. This effect may be explained by the blocking of growth or nucleation sites of initial Ca phosphate by adsorbed Mg ions. When the experimental values for nucleation rates are corrected for average phosphorus concentration in modern upwelling marine environments (0.2–0.3 mg/l) and pH 8, these predict that τ for Ca-phosphate precipitation from seawater is of the order of 10^5 years. This indicates that the spontaneous inorganic precipitation of phosphorites is kinetically retarded and other mechanisms such as local bacterial decomposition of organic matter or the release of soluble P by microorganisms are responsible for the observed precipitation of apatite in natural environments.

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