Experimental simulations of the influence of early marine diagenesis on the geochemical records (Sr/Ca and U/Ca ratios) of past climates by Porites corals

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The geochemical analyses (Sr/Ca, U/Ca and stable isotopes) of fossil and modern corals are very powerfull tools to study the variability of past climates since the last interglacial period. Moreover, in the last decades, their use has been greatly promoted by the advances of analytical techniques (precision of <0.5°C in the estimation of Sea Surface Temperature with the Sr/Ca palaeothermometer; Beck *et al.*, 1992). At the same time, sedimentologic studies of fossil and modern corals have shown that marine diagenesis begins very soon after the death, or even during the growth-history of the corals. For example, Potthast (1992) has shown that 10–20 year old Porites colonies exhibit various secondary microstructures resulting in overgrowths onto primary biogenic crystals and intraskeletal pores surfaces. Moreover, it has been demonstrated that this very early marine diagenesis does not alter the aragonitic mineralogy of the corals (Porites: Potthast, 1992; *Acropora*: Ribaud *et al.*, 1997). In spite of these works, palaeoclimatic or palaeoenvironmental reconstructions based on geochemical analyses of skeletal aragonite, generally rely only on the evidence of the lack of mineralogical alteration of aragonite to calcite, thus neglecting the possible effects of early aragonitic marine diagenesis. However, some recent works have demonstrated that the geochemical signatures of corals (e.g. δ11B, Sr/Ca ratio) can be altered by these very early diagenetic processes (Gaillardet and Allègre, 1995; Ribaud *et al.*, 1997). In the study of Holocene *Acropora* corals, Ribaud *et al.* (1997) have shown that this alteration of the geochemical signal can even reach in some cases a level at which the Sr/Ca results can no longer be used in terms of palaeotemperatures.

The purpose of the work presented here is thus to evaluate the effects of early diagenesis on the geochemical signatures of biogenic carbonates, using an experimental approach.

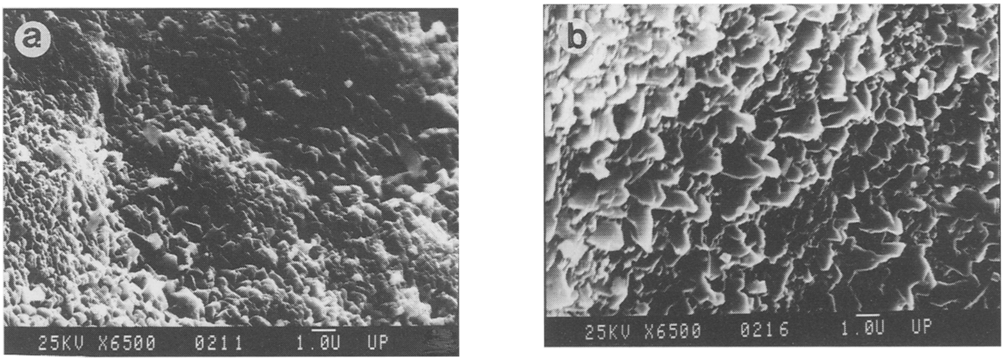

FIG. 1. SEM pictures (same scale, ×6500) of single aragonite grains surfaces, (a) starting material, (b) after experiments.

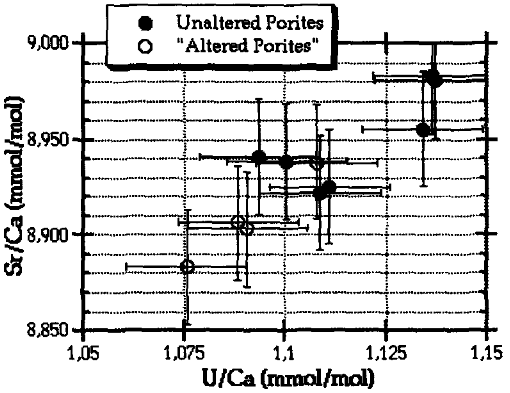

FIG. 2. Sr/Ca ratio in function of U/Ca ratio of the starting material (unaltered Porites) and of the overgrown seeds ('altered Porites').

Materials and methods

Aragonite overgrowths were precipitated from an artificial seawater (S= 35‰) prepared according to Pytkowicz (1973), with a Sr concentration of 4 ppm, (half of that of natural seawater). This low concentration has been chosen to magnify the effect of aragonite overgrowths on the Sr/Ca ratios of the bulk aragonite powder. Aragonite powder has been prepared by soft grinding a modern Porites colony from Noumea (New Caledonia, provided by ORSTOM), free from secondary microstructures. The organic matter has been removed by overnight leaching with hydrogen peroxyde. Then, the powder has been sieved to separate the 150–200 μm fraction and cleaned ultrasonically to remove the fine particles. This relatively large size fraction has been selected to allow the recognition of the Porites ultrastructure on single grains with scanning electron microscopy.

The precipitation of aragonite overgrowths onto biogenic aragonite seeds has been performed in the mixed flow reactors. The aqueous solution of known composition is introduced at a controlled flow rate in a 0.250 L polypropelene vessel immersed within a thermostated bath (30 ± 0.5°C). The mineral growth occurs under steady state conditions as monitored by pH and alkalinity analysis of the output solution.

Sr, U and Ca concentrations of bulk aragonite powders were determined on 0.1 to 0.5 mg samples with a VG Sector 54-30 Thermal Ionization Mass Spectrometer at CEREGE, Aix-en-Provence. The reproducibility of the Sr/Ca and U/Ca ratios, estimated from replicated analyses, are respectively 0.06 and 0.03 mmol/mol (2σ).

Results

The experiments have been conducted for a duration of 6 days, resulting in variations of pH between 8.41 (input) and 8.05 (output), and of alkalinity between 2.38 10^{-3} and 1.93 10^{-3} $\mathrm{mol.l^{-1}}$. These conditions of the input solution correspond to the saturation index of aragonite equal to 6.1 as calculated according to Mucci (1983).

The weight of aragonite precipitated during the experiment (Δm, g) can be calculated from the mass balance of dissolved carbon at the steady state conditions:

$$\Delta m = \Delta\Sigma CO_2 \, D \, t \;\; 100$$

where $\Delta\Sigma CO_2$ is the difference in the total dissolved inorganic carbon concentration between input and output solution calculated on the basis of measured alkalinities and pH, D is the flow rate in liters per minute and t is the elapsed time in minutes. Precipitation of 0.0515 g overgrowths, representing 5.1% of the initial weight of aragonite powder, were obtained during these first experiments. SEM observations of aragonite single grains show that the surface of the aragonite grains becomes more granular and more rugose than in the starting material (Fig. 1 a and b), due to the growth of drusic aragonite crystals of 1 to 2 μm on their surfaces (Fig. 1b).

The results of Sr, U and Ca analyses of bulk aragonite powders before and after the experiments are shown in Fig. 2. Analyses of the initial biogenic aragonite show some scatter (Fig. 2), in spite of the homogeneous grinding. This is likely due to the presence in the sample of skeletal aragonite grains from different growth bands from the Porites colony, related to the seasonal variation of sea surface temperature. Nevertheless, the analyses corresponding to bulk powders issued from the experiments show a decrease of the Sr/Ca and U/Ca ratios (Fig. 2), associated with the precipitation of about 5% of inorganic aragonite overgrowths onto the biogenic aragonite seeds.

Such a variation of Sr/Ca and U/Ca ratios within natural samples could have been interpreted as an increase of the sea surface temperature, if the diagenetic perturbation had been ignored. These preliminary results are thus in good agreement with the works by Ribaud *et al.* (1997) and Gaillardet and Allègre (1995), questioning the validity of geochemical results on fossil and modern corals. The experimental approach initiated here may help to calibrate a correction method for the effects of early marine diagenesis on the geochemical signatures in aragonitic fossil and modern corals.