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Water desorption and aragonite–calcite phase transition in scleractinian corals skeletons

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Abstract

Several authors have reported lower temperatures for the aragonite–calcite phase transition for the skeleton of scleractinian corals, when compared with those observed in the mineral aragonite. This phenomenon has been attributed to the hydration of the coral aragonite.

Using differential scanning calorimetry coupled with thermogravimetry measurements, we have observed the existence of double endothermic peaks probably connected with two separate phenomena: water desorption, followed by the aragonite–calcite transition. Determination of the enthalpy of the first endothermic peak allowed us to predict the existence of hydrogen-bonding interactions between the oxygen atoms of the carbonate planes and the water molecules.

Keywords: Coral; DSC; Desorption; Phase transition; Water

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1. Introduction

Several authors [1,2] and one of us [3] have established that the aragonite constituting the skeleton of scleratinian corals and that of mineral origin present two different temperatures for the aragonite–calcite phase transition. These are approximatively located at 300°C for the corals [4,5] and 450°C for the mineral [6,7].

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The difference has been attributed to hydration of the coral [1,2,5]. Ganteaume et al. [1] have shown that water expulsion was concomitant with the process of transformation of the aragonite into calcite and could induce the phenomenon. Gaffey [8], using reflectance spectroscopy measurements in the visible and near-infrared on skeletal carbonates, concluded that these compounds contain liquid water in fluid inclusions, and that some carbonates contain, in addition to liquid water, bound water on calcium carbonate and/or calcium hydrate molecules. Differential scanning calorimetry associated with thermogravimetry enabled us to examine and confirm these previous results.

2. Methods

2.1. Preparation of the coral skeleton samples

The coral samples used for our experiments belonged to three species of Scleractinia from the Carribbean fauna, i.e. *Diploria strigosa* (Dana), *Agaricia agaricites* (Linneaus) and *Montastrea cavernosa* (Linneaus). The corals were collected by SCUBA diving on the reef of Petit Havre (Guadeloupe Island, French West Indies), at depths of between 3 and 5 m. Coral samples were bleached for 24 h in sodium hypochlorite solution, at the commercial concentration of 33% (wt/vol) and ambient temperature, in order to destroy the organic tissues. This treatment was repeated once more and the samples were rinsed for one hour in running tap water and then with distilled water, to ensure that the tissue was removed. Next, the coral skeletons were dried for 48 h at 60°C, and stored at 20°C in a dehydrated room.

2.2. Instrumental

Thermogravimetry (TG) experiments, associated with differential scanning calorimetry (DSC), were conducted with a Setaram TG-DSC 111 thermoanalyser, composed of a G11 pilot unit and a B111 micro-balance connected with a DSC111 calorimeter. These instruments were driven by an EPSON PC computer.

Temperatures were recorded to ± 0.5°C. The precision of the enthalpy measurements was about 5%. The thermo-balance gave results with a precision of 50 μg.

2.3. Calibration

The calorimeter was calibrated for temperature and enthalpy under static air using pure metal samples, whose purities were: 99.995% for indium, and 99.999% for tin and lead.

The heating rate used was 2 K min^{-1} up to 30-50 K above the melting point of the sample. Cooling rates were also 2 K min^{-1}.

2.4. Experimental

The dry coral skeleton samples (20-60 mg), kept entire, were introduced into alumina crucibles. The reference crucible was empty and the experiment was conducted in static air.

The increase in temperature, from 25 to 550°C, was recorded at a heating rate of 10 K min^{-1}. The maximum temperature was limited to 550°C in order to avoid chemical decomposition of the aragonite into calcium oxide (CaO) and carbon dioxide (CO_2). All the experiments were duplicated.

3. Results

The results of the experiments are listed in Table 1. The coral samples I, II and III belonged to the species *Diploria strigosa*, sample IV to *Agaricia agaricites*, and sample V to *Montastrea cavernosa*.The following features were noticed: 1. Samples IV and V presented DSC thermograms with, in some cases, a single peak (Figs. 1 and 2) and in

Table 1
Results of the analysis of the aragonite–calcite transition in five coral samples. Differential scanning calorimetry is coupled with thermogravimetry measurements

Sample	Form of the peak	T/°C	Enthalpy (kJ/kg coral)	Enthalpy (kJ/mol H_2O)	Loss of mass %	Deduced formula
I	Single	286.7	30.6	23.9	1.68	$CaCO_3{\cdot}0.095\ H_2O$
II	Single	285.5	33.1	26.4	1.69	$CaCO_3{\cdot}0.096\ H_2O$
II	Single	286.4	30.7	24.0	1.63	$CaCO_3{\cdot}0.092\ H_2O$
IV	Double(1)	281.8	23.3	23.3	1.45	$CaCO_3{\cdot}0.082\ H_2O$
	(2)	337.2	6.7			
IV	Single	281.8	30.4	23.7	1.45	$CaCO_3{\cdot}0.082\ H_2O$
V	Double(1)	285.5	24.9	24.9	1.50	$CaCO_3{\cdot}0.085\ H_2O$
	(2)	313.3	6.6			

For single peaks, the heats of H_2O desorption have been calculated by difference, taking the value 6.7 kJ mol^{-1} for the heat of the aragonite calcite phase transition.

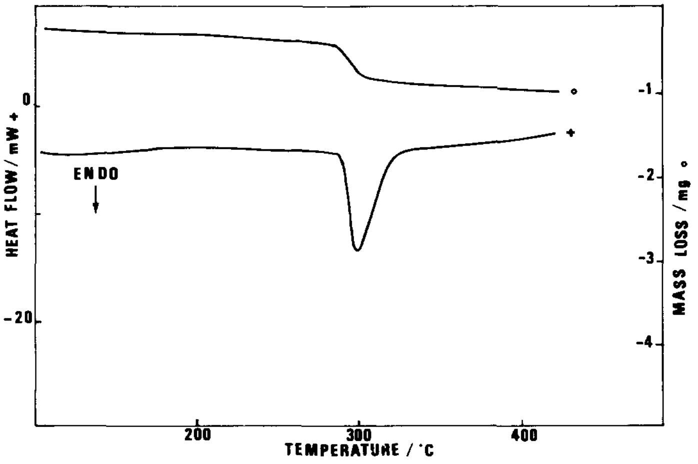

Fig. 1. DSC (+) and TG (o) thermograms for coral aragonite showing one endothermic peak. (sample I).

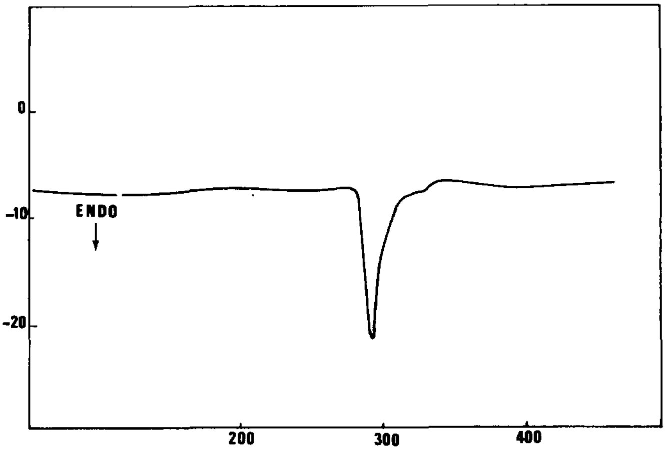

Fig. 2. DSC thermogram for the coral sample IV, showing one endothermic peak.

other cases, two peaks (Fig. 3) inside the range of temperature corresponding to the aragonite–calcite transition. But whatever the number of peaks, the total area under the endothermic curve remained constant for a given sample (Figs. 2 and 3). 2. The single peaks possessed a shoulder characteristic of multiple peaks found in differential calorimetry (Fig. 2).

The purity of a sample of mineral aragonite was verified by X-ray diffraction. DSC measurements on this sample (Fig. 4) gave the following results: 1. From the resulting thermogram, the aragonite–calcite phase transition does not produce any significant loss of mass of the sample. 2. The variation in enthalpy characteristic of the phase transition is equal to 6700 ± 100 J kg^{-1}, a value close to that given by Ganteaume et al. [1]: 7400 J kg^{-1}).

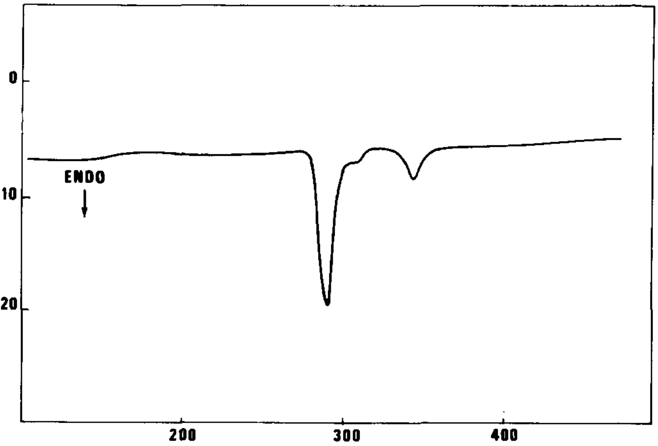

Fig. 3. Second DSC thermogram for the coral sample IV, showing two endothermic peaks.

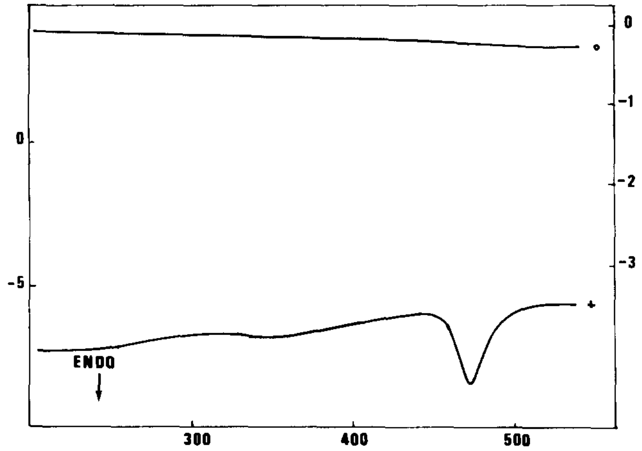

Fig. 4. DSC (+) and TG (o) thermograms for mineral aragonite sample.

4. Discussion

The percentage mass loss during the transition allows us to attribute the formula $CaCO_3{\cdot}0.1H_2O$ to the coral skeleton. Such a result was previously published by Ganteaume et al. [1,2].

The principal features of our experiments are the observation, in some cases, of double DSC peaks. We attribute this phenomenon to the separation of the dehydration stage from that of the aragonite–calcite transition. We think that the single peaks given by fine-grained coral become double when the grain size of coral aragonite increases.

The aragonite–calcite phase transition temperature was observed at 454°C in the mineral aragonite: this value was close to those observed by several authors [6,7]. However, for coral aragonite this transition is effectively observed at lower temperatures (286–337°C). This drop varies according to the coral species. The transition is induced by the expulsion of the water molecules present in the aragonite. The variation in enthalpy, associated with the first endothermic peak, can be attributed to the detachment of water molecules from the coral skeleton. The value, about 24 000 J per mole of water, corresponds to the desorption of the water. The variation in enthalpy corresponding to the second endothermic peak is close to the value obtained for mineral aragonite, 6.7 kJ mol^{-1}.

Gaffey [8], using reflectance measurements, concluded that scleractinian corals contain only fluid inclusions of liquid water. We do not agree with her interpretation. We expect that the endothermic peak would be more pronounced if it was associated with the vapourisation of the liquid water contained in the voids of the coral aragonite framework. We have measured the heat of dehydration of the coral skeleton as 24 kJ mol^{-1} of water, which is lower than the molar heat of vapourisation of liquid water. The reason for this difference is probably that the water clusters present in the aragonite /coral are smaller than the water clusters in liquid water. We suggest that neighbouring water molecules are linked by intermolecular hydrogen bonds. Since some of the water molecules have protons inside the cavities of the coral sample, hydrogen bonds are formed between the water molecules and the oxygen atoms of the carbonate planes. When heating the coral sample, it is possible that the breakage of the net of hydrogen bonds, followed by the evolving vapour, cause an increase in volume favourable to the aragonite–calcite transition; the molar volume of calcite is greater than that of aragonite. Future experiments using FTIR spectroscopy and TEM and SEM will permit us to complete this study.

5. Conclusions

DSC and thermogravimetry experiments confirm that the aragonite–calcite transition temperature is lower in aragonite corals (290°C) than in mineral aragonite (450°C). In scleractinian corals, water molecules are bound to the oxygen atoms of the carbonate planes by a hydrogen bond network. On heating, breaking the hydrogen bonds induces an increase in volume favourable to the aragonite–calcite phase transition.

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