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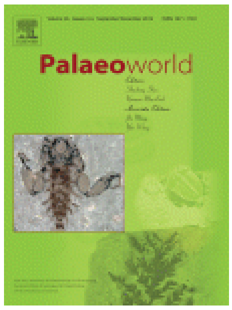

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Preservation of original aragonite structure in fossil corals (Scleractinia), demonstatred by microstuctural analysis of *Desmophyllum castellolense* from the Eocene basin of NE Spain

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Abstract Scleractinian corals produce an aragonite skeleton that is converted to calcite during diagenetic processes after death. However, examples belonging to five species that have preserved the original aragonite skeleton and its original microstructure have been found in the basin of Igualada (NE Spain). This study presents a mineralogical analysis and description of the species *Desmophyllum castellolense*. X-ray diffraction was used to confirm the skeletal aragonite and analyse the associated elements. The microstructure of the skeleton was described from polished and thin sections using scanning electron microscopy (SEM) and optical microscopy.

Keywords Corals – Scleractinia – Eocene – Aragonite – Calcite - Microstructure

Introduction

Scleractinian corals, with a few exceptions (Stolarski *et al.,* 2007) produce an exoskeleton of aragonite that remains stable during the life of the coral. On the death of the coral, this skeleton remains stable for the whole process of fossilization or can be transformed into calcite as a result of the action of external diagenetic agents.

Transformation into calcite may occur in two ways: by dissolution or by neomorphism:

Dissolution

The dead coral is buried by sediment brought by external agents. This sediment becomes compact as a result of diagenetic processes. As the aragonite coral skeleton is dissolved by water circulating in the zone, an empty space takes the outer form of the coral. This space remains empty or can be subsequently filled with calcite crystals

(Fig. 1. 1). The microstructure of the coral disappears completely in this diagenetic process.

Neomorphism

This is the transformation of aragonite into calcite as a result of polymorphism in the two minerals. The changes occur in the structure of the crystal passing from the orthorombic structure of aragonite to the trigonal structure of calcite. This transformation is governed by the interaction of pressure and temperature as shown in the diagram of equilibrium phases (Fig. 1. 3).

Calcite is more stable than aragonite in locations where the free energy of Gibbs (G) is lower in calcite (Gca) than in aragonite (Gar). By contrast, aragonite will be more stable in locations where Gar is lower than Gca. Likewise, given that entropy is greater in calcite than in aragonite, an increase in temperature at a constant pressure induces the formation of aragonite. The microstructure of the coral is preserved to a very high degree in this diagenetic process in which molecules of aragonite are transformed one by one into molecules of calcite. In low pressure conditions, aragonite is unstable, but as a result of the action of living organisms such as corals, it can form outside its stability field and remain unalterable for long geological periods. (Giménez et al., 1997).

Corals of the eocene basin of Igualada (NE Spain)

The corals of the Eocene basin of Igualada underwent diagenesis due to dissolution and most of them display a calcitic skeleton that replaces the original skeleton of aragonite (Fig. 1. 2).

Some samples howerer were outside the influence of diagenetic agents and preserved their original skeleton of aragonite. Such samples were covered with impermeable materials, mainly clays, which prevented water circulation and impeded the transformation of aragonite into calcite. Thus, their microstructure was preserved (Giménez et al., 1997) (Fig. 1. 4).

The samples that preserved the skeleton of aragonite belong to the following species: *Desmophyllum castellonense* Alvarez-Pérez, 1993; *Flabellum appendiculatum* (Brongniart, 1823); *Nicaeotrochus cyclolitoides* (Michelin, 1846); *Petrophylliella callifera* (Oppenheim, 1912) and *Funginellastraea barcelonensis* (Oppenheim, 1911).

This work is focused on a study of *Desmophyllum castellonense*, found in the outcrops of the Eocene basin of Igualada, located south of the Pyrenees, in the Ebro Basin. This is a foreland of the Pyrenees and Catalan Coastal Ranges (Fig. 2. 1).

Materials

The holotype of *Desmophyllum castellonense* is deposited in the Geological Museum of the Diocesan Seminary of Barcelona (MGSB), registered as N- 52.081. The thin sections (P) and the samples studied belong to the German Álvarez collection (GA).

Methods

A number of samples were placed in acrylic resin and the polished and thin sections were obtained. Some polished sections were attacked in 5% of HCL for 5 seconds and analyzed using scanning electron microscopy (SEM) JOEL, type 5SM-6300, equipped with EDAX to detect the elements present in the sample. Diffractions with X-ray were performed with a diffractometer INCAR-OXFORD. The thin sections were studied with a NIKON optical microscope of polarized light.

Identification and subsequent description of microstructural elements were based on the works of Alloiteau, 1957; Wells in Moore, 1967; Russo, 1976; Lazier et al.*,*1999; Sorauf, 1999 and Risk et al., 2002.

Lithostratigraphic units

The Paleocene-Eocene deposits of the basin of Igualada consisting of alternating marine and continental deposits were divided from bottom to top into the following formal lithostratigraphic units:

- ***Mediona Formation* attributed to the Late Thanetian (Anadón *et al.*, 1983).**

- ***Orpí Formation* attributed to the Ilerdian (Hottinger, 1960).**

- *Pontils Formation* attributed to the Late Ypresian (Anadón and Feist, 1981).

- *Santa Maria Group*:

- *Collbàs Formation* attributed to the Early Bartonian (Serra-Kiel *et al.*, 1997).

- *Igualada Formation* divided into two units:

  - "Castellolí Deltaic complex" attributed to the Late Bartonian (Serra-Kiel *et al.*, 1997).

  - "Castellolí Marl and Limestone" attributed to the Early Priabonian (Costa *et al.*, 2009).

- *Tossa Formation* attributed to the Middle Priabonian (Costa *et al.*, 2009).

- *Artés Formation* attributed to the Late Priabonian. (Anadón *et al.*, 1992)

(Table 1)

The samples studied in this work were collected at "Castellolí Marl and Limestone" in the proximity of "Can Llucià", "Casa Nova", "Can Francolí" and "Can Manyoses" located NE of Castellolí. They therefore belong to the Priabonian (Cascella and Dinarès-Turell, 2009; Costa *et al.*, 2009) (Fig. 2. 2).

Mineralogical analysis

Analysis with X-ray Diffraction

Three samples were selected for mineralogical analysis by X-ray Diffraction. The first sample was *Acropora cervicornis* (Lamarck, 1816), a recent coral with an aragonite skeleton. The second sample was *Desmophyllum castellolense*, a coral of Eocene age with a skeleton which we assume is aragonite. The third sample was *Cereiphyllia tenuis* (Reuss, 1868), a coral of Eocene age, with a calcite skeleton.

Qualitative analysis by means of X-ray Diffraction of a mixture of minerals enabled us to ascertain whether each coral had spectres of minerals forming part of the mixture (Meerssche, 1973; Gay, 1977). Accordingly, the diffractrogram obtained was compared with those of calcite and aragonite.

The minerals are identified in the diffractograms, taking the maximum intensity as the reference point (Jong, 1967). Calcite corresponds to the angle $2\theta = 29.399$ (Fig. 3. 1) and aragonite to the angle $2\theta = 26.223$ (Fig. 3. 2). This result appears in table (Fig. 3. 3) (Barraud, 1960; Ducros, 1971; Klein, 1997).

In the diffractogram of *Acropora cervicornis* (AA-G-1), the line of maximum intensity coincides with that of aragonite ($2\theta = 26.223$). The corresponding line for calcite ($2\theta = 29.399$) shows a relatively low intensity. Aragonite is therefore the dominant phase in the sample (Fig. 4. 1).

The diffractogram of *Desmophyllum castellolense* (AA-G-2), coincides with the previous sample, which suggests the presence of aragonite. Nevertheless, the calcite line is prominent. Aragonite proceeds from the coral skeleton and the calcite from the sediment. Calcite was not completely eliminated in the preparation of the sample for the X-ray study (Fig. 4. 2).

In the diffractogram of *Cereiphyllia tenuis* (AA-G-3), the line of maximum intensity coincides with that of calcite ($2\theta = 29.399$). The line of aragonite is very weak, which suggests a residual presence in the sample (Fig. 4. 3).

Energy Dispersive Spectroscopy (EDAX)

Scanning electron microscopy (SEM) equipped with EDAX (spectrograph of disperse energy) enabled us to detect the elements present in the sample. Thus, the presence of carbonates and other minerals could be confirmed in the sample. The presence of calcium (Ca), strontium (Sr) and sulphur (S) was detected in the *Desmophyllum castellolense* sample (Fig. 4. 4). Strontium is an isomorph of calcium in aragonite and its presence is therefore associated with that of this mineral. Sulphur in the form of sulphate (gypsum) is associated with the calcium of calcite. This is common in marine sediments such as those of the sample analysed (Giménez et al., 1997). The presence of foreign elements was not detected.

Description of skeletal elements

Desmophyllum castellolense is a solitary, cone-like long and cylindrical coral

(Figs. 5. 1,2,3-1). The base is strongly welded to the substrate in young individuals and less in adult individuals (Fig. 5. 2). Elliptical or circular calices (Figs. 5. 1,4,5). Septa are hexamerally arranged in five complete cycles and one incomplete sixth cycle. Between 96 and 129 septa were counted. Their length and thickness depend on the series to which they belong (Figs. 5. 1,4.5). The septa of the two first cycles are equal and are prominent in the calice.

The upper part of the septa is rounded owing to its fan-like arrangement of simple trabeculae that form the septum . The edges of the septa are smooth with a rhopaloid inner part (Figs. 5. 1,5). The lateral face of the two first cycles is smooth, whereas that of the remaining ones is covered with small spiniform teeth

(Fig. 5. 6). In the inner part of the calice, the septa fuse and form a pseudo-columella (Fig. 5. 5). Visible ribs in the whole extension of the coral. They are the continuation of the septa. They are therefore costosepta (Figs. 5. 2,3-1). Septothecal wall (Fig. 5. 5) Finely granulated exotheca that covers the outer space of the coral including the ribs (Fig. 5. 3).

The samples studied do not exceed 5 cm in height. The calical diameter varies between 0.5 cm and 2.5 cm (Álvarez Pérez, 1993, 1997).

Microstructure of basic elements

Sclerodermite

Constituted by a centre of calcification surrounded by acicular aragonite crystals. The aragonite crystals appear as fine needles in the transversal section, whereas they appear as small crystallised granules in the outer layer (Fig. 5. 7). In the thin section, the centre of calcification is generally dark and occasionally light and the aragonite crystals are always light (Fig. 5. 8).

Simple trabecula

Formed by a row of sclerodermites whose centres of calcification can be isolated or joined forming a central line. In the latter case, the acicular aragonite crystals are perpendicular to this line (Figs. 5. 9,10).

Stereome

Constituted by acicular aragonite crystals that are parallel, with no centre of calcification (Fig. 5. 11). They present a fibrous aspect in the longitudinal section (fibrous stereome) (Fig. 5. 12). They resemble small granules in close proximity to one another (granulated stereome) in the transversal section (Fig. 5. 13).

Structural elements of skeleton

Septa.

Formed by the union in the same plane of simple trabeculae that extend upwards in the form of a fan. This type of growth is observed in the lateral face of the septum in the form of concentric rings (Fig. 5. 6). The centres of calcification are aligned and dark (Figs. 6. 2,5-1) or light (Figs. 1. 4; 6. 1,3,4) in the transversal section. The aragonite crystals are perpendicular to these (Figs. 5. 10; 6. 1). The lateral faces are covered with layers of stereome that increase the thickness of the septum, giving it greater consistency (Fig. 6. 3-b).

Costae

Formed by simple trabeculae joined to the outer edge of the septum of which they are a continuation (Figs. 6. 4,5).

Wall

Constituted by simple trabeculae attached laterally to the neighbouring septa joining them together (Figs. 6. 4,5). The stereome laminae of the septa could be extended to cover its inner part (Fig. 6. 5).

Exotheca

Formed by layers of fibrous stereome covering the ribs and the wall (Fig. 6. 5-e). The aragonite crystals are in a horizontal position with the result that the granulated stereome appears externally (Fig. 5. 3).

Conclusion

In *Desmophyllum castellolense,* a fossil coral from the Eocene basin of Igualada, the original aragonite skeleton made up of simple trabeculae and stereome is preserved. The septae, ribs and the wall are constituted by laminae of simple trabeculae that grow in thickness as a result of successive layers of stereome. The exotheca consists of stereome layers.

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