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Materials and Methods

Figs. S1 to S10

Tables S1 to S3

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A Cretaceous Scleractinian Coral with a Calcitic Skeleton

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It has been generally thought that scleractinian corals form purely aragonitic skeletons. We show that a well-preserved fossil coral, *Coelosmilia* sp. from the Upper Cretaceous (about 70 million years ago), has preserved skeletal structural features identical to those observed in present-day scleractinians. However, the skeleton of *Coelosmilia* sp. is entirely calcitic. Its fine-scale structure and chemistry indicate that the calcite is primary and did not form from the diagenetic alteration of aragonite. This result implies that corals, like other groups of marine, calcium carbonate-producing organisms, can form skeletons of different carbonate polymorphs.

Scleractinian corals belong to the taxonomic class of anthozoans and are among the most prolific biomineralizing organisms in nature (1). Their calcium carbonate skeletons form shallow- and deep-water reefs and are prominent in the fossil record as far back as 240 million years ago (Ma) (2). Living scleractinians produce entirely aragonitic skeletons (3, 4). An identification of calcite in calcification centers of the shallow-water scleractinian *Mussa* sp. (5) was not confirmed by subsequent analysis (6). Aragonite is metastable at ambient temperatures and pressures and is susceptible to diagenetic transformation to calcite, the stable form of calcium carbonate under ambient conditions. Most fossil scleractinians have therefore been dissolved or transformed to calcite, preserving only their macroscopic morphology. In these cases, the original mineralogy can be inferred on the basis of their Sr content and by analogy with living scleractinians (7). Although some studies have left open the possibility that the original

mineralogy of some fossil Scleractinia was calcitic (8–10), it has been generally accepted that the aragonitic skeletal mineralogy of scleractinians

was highly conserved throughout their evolution (11).

Here we show that a fossil scleractinian coral formed a calcitic skeleton. We studied a suite of fossil corals attributed to the caryophylliid genus *Coelosmilia*. Our specimens are from the Upper Cretaceous (Maastrichtian) deposits of Poland (fig. S1) and are similar, but not identical, to the fossils studied in (12) in which the calcite in the corals was inferred to have formed diagenetically. We have now used a variety of micro-analytical methods to show that the calcite is instead primary. The overall skeletal architecture of *Coelosmilia* is similar to that of modern deep-sea corals, such as *Desmophyllum* (Fig. 1) and *Javania* (fig. S2). *Coelosmilia* sp. has a conical calice with septa arranged into five full cycles forming a hexameral pattern. Our specimens are complete skeletons and well preserved. External

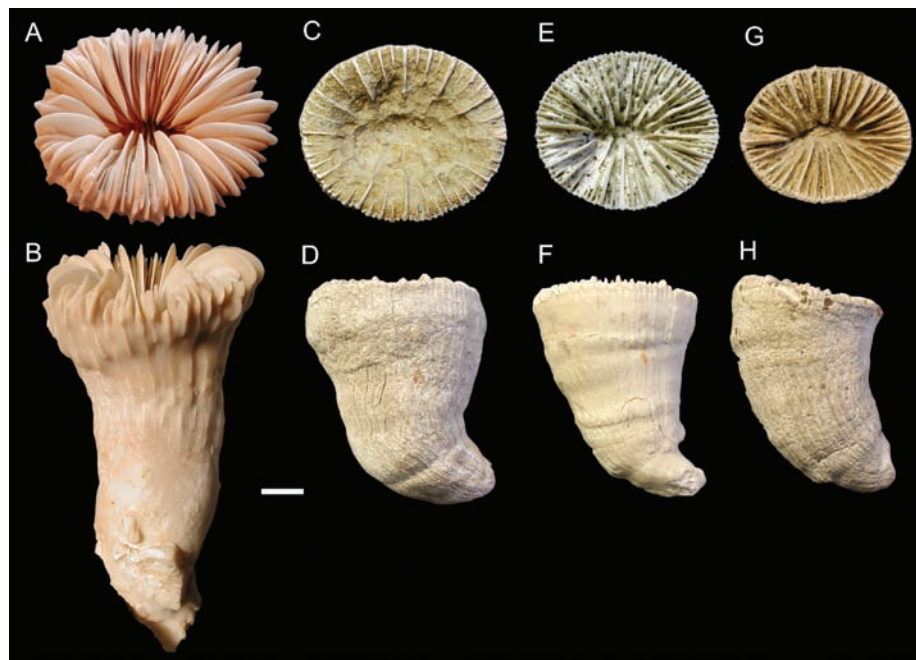


Fig. 1. Morphology of the modern aragonite *Desmophyllum* sp. and the Late Cretaceous calcitic *Coelosmilia* sp. (A and B) *Desmophyllum* sp. Relatively smooth septa, a thick septothecal wall, and a lack of pali are typical features of this solitary, azooxanthellate scleractinian coral. (C to H) *Coelosmilia* sp. resembles *Desmophyllum* sp. in all morphological aspects. Distal [(A), (C), (E), and (G)] and lateral [(B), (D), (F), and (H)] views are shown. Scale bar, 10 mm.

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microarchitectural details, such as fine granulations on septal surfaces and, in some specimens, desmocyte attachment scars are still visible (fig. S2). In contrast, shells of gastropods, phragmocones of cephalopods, and other scleractinian coral species (13), which occur with *Coelosmilia* sp. in the same deposits, are dissolved and preserved only as molds and casts.

The skeleton of the specimen *Coelosmilia* sp., which we present in detail here, preserves all the structural details intact throughout its ontogeny (Fig. 2, A to C). The septal ultrastructure is characterized by a central line of well-organized calcification centers and radiating fiber bundles, constructed by the sequential addition of micrometer-sized growth layers (14, 15). Longitudinal sections through the mid-septal zone reveal discrete vertical rods, similar to trabeculae in

modern Scleractinia (Fig. 2D). Individual half-moon-shaped growth segments in the thecal region correspond to the position of former growth fronts in the wall (Fig. 2E). In polarized light, bundles of fibers show simultaneous and complete light extinction, indicating a parallel arrangement of crystallographic axes. All of these features are identical to those of living scleractinians (14, 15). The structural similarity between *Coelosmilia* sp. and modern Scleractinia is strong, especially with the azooxanthellate members of the traditional suborder Caryophylliina, here represented by *Desmophyllum* sp. (Fig. 2, H to L).

Synchrotron radiation diffraction studies demonstrate that the *Coelosmilia* sp. skeleton is composed of calcite, without any trace of aragonite (Fig. 3A and fig. S6). In comparison to synthetic and geological calcite reference mate-

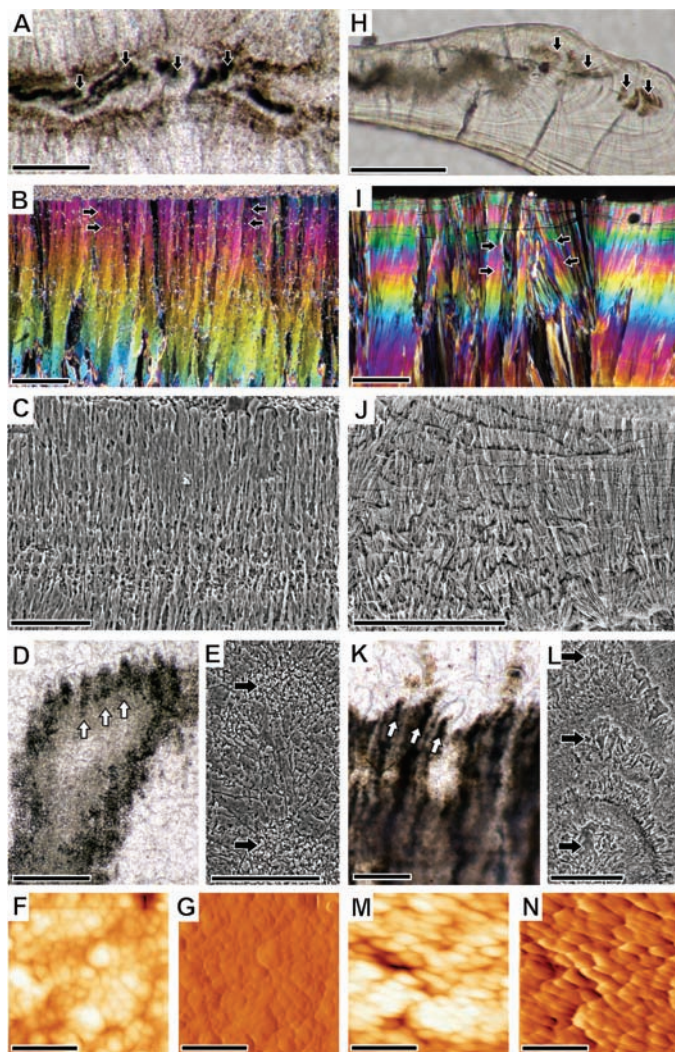
rials, the *Coelosmilia* sp. skeleton has broader Bragg peaks, indicating smaller crystallite sizes and/or larger microstrain fluctuations in the *Coelosmilia* sp. calcite. The inferred crystallite grain size is consistent with the size of individual calcite domains observed by atomic force microscopy (Fig. 2, F and G) and shows that, in analogy with modern corals, the *Coelosmilia* sp. skeleton is composed of crystallites typically 30 to 100 nm in linear dimension (15, 16). Slight shifts in the *Coelosmilia* sp. Bragg peaks relative to the reference calcite spectrum are consistent with the lattice parameter differences between biogenic and synthetic Mg-containing calcite (17, 18) (fig. S7).

The trace element composition of the *Coelosmilia* sp. skeleton is also consistent with a calcitic mineralogy. The fibrous (bulk) part of the skeleton has Mg/Ca and Sr/Ca ratios averaging about 15 and 0.7 mmol/mol, respectively (Fig. 3B). Typical Mg/Ca and Sr/Ca concentrations of modern aragonitic scleractinian corals are 1 to 5 and 7 to 10 mmol/mol, respectively. High-spatial-resolution (~200 nm) secondary ion mass spectrometry analyses (19) show that the Mg/Ca and Sr/Ca ratios oscillate in the *Coelosmilia* sp. skeleton across scales of a few micrometers, in a pattern similar to those observed in modern scleractinians (20).

We rule out the possibility that the calcite formed from the transformation of an originally aragonitic skeleton. The diagenetic transformation of aragonitic skeletons to calcite in fossil corals invariably involves complete reorganization of the skeletal ultrastructure. During diagenetic recrystallization, growing calcite cuts across septa and walls, leaving behind an irregular mosaic of calcite crystals, which eventually completely replaces the original ultrastructural organization of the skeleton (7). In contrast, in the *Coelosmilia* sp. skeleton, all ultrastructural elements are preserved and the crystals in the fiber bundles are well aligned, as demonstrated by the simultaneous and complete extinction of polarized light.

Cathodoluminescence observations of the fibrous part of the skeleton show no evidence of the cloudiness that is typically associated with recrystallization (fig. S3). The trace element chemistry also rules out a hypothetical aragonite-to-calcite transformation in which the crystal structure simply “flips” from aragonite to calcite, leaving all micrometer-scale features intact. During such a hypothetical transformation, the bulk chemistry of the skeleton would not change, because mass transfer (the dissolution and reprecipitation of carbonate) would not take place. However, the Mg/Ca and Sr/Ca ratios of the skeleton are different from typical aragonitic ratios, both by a factor of approximately 10, and the oscillatory pattern is inconsistent with simple equilibrium precipitation of carbonate from a supersaturated solution. In modern scleractinians, such trace element variations are driven by biological mechanisms involved in the biomineralization process (19, 20). We therefore conclude that *Coelosmilia* sp. is a scleractinian coral with a primary calcitic skeleton.

Fig. 2. Structural characteristics of the *Coelosmilia* sp. skeleton (left column) in direct comparison with the skeleton of *Desmophyllum* sp. (right column). (A and H) Optical microscopy transmitted-light images of a thin section through a septum perpendicular to the growth direction. Black arrows indicate successive growth steps in the zone of centers of calcification (COC), which appear darker than the surrounding fibrous skeleton. (B and I) Optical microscopy polarized transmitted-light images of a thin section through a septum perpendicular to the growth direction. The individual growth layers of the fibrous skeleton are clearly visible in both corals as optical layering (indicated by black arrows). (C and J) Scanning electron microscopy (SEM) images of the polished and etched surface of a septum perpendicular to the growth direction. Fiber bundles with individual growth layers are visible. (D and K) Optical microscopy transmitted-light images of a thin section through the midplane of a septum parallel to the growth direction and through the central axis of the COC. Successive COCs are organized as rods, or trabeculae, in the direction of growth, as indicated by white arrows. A slight undulating of the mid-septal zone trabecular centers make them appear and disappear from the plane of the cut section. (E and L) SEM images of the polished and etched surface of a cut through the thecal region parallel to the growth direction. Half-moon-shaped segments correspond to the position of organic enriched growth fronts in the wall. (F, G, M, and N) Atomic force microscopy images of skeletal fibers in height mode [(F) and (M)] and deflection mode [(G) and (N)], showing nanogranular structure. Scale bars in (A) to (E) and (H) to (L), 100 μ m; in (F), (G), (M), and (N), 200 nm.



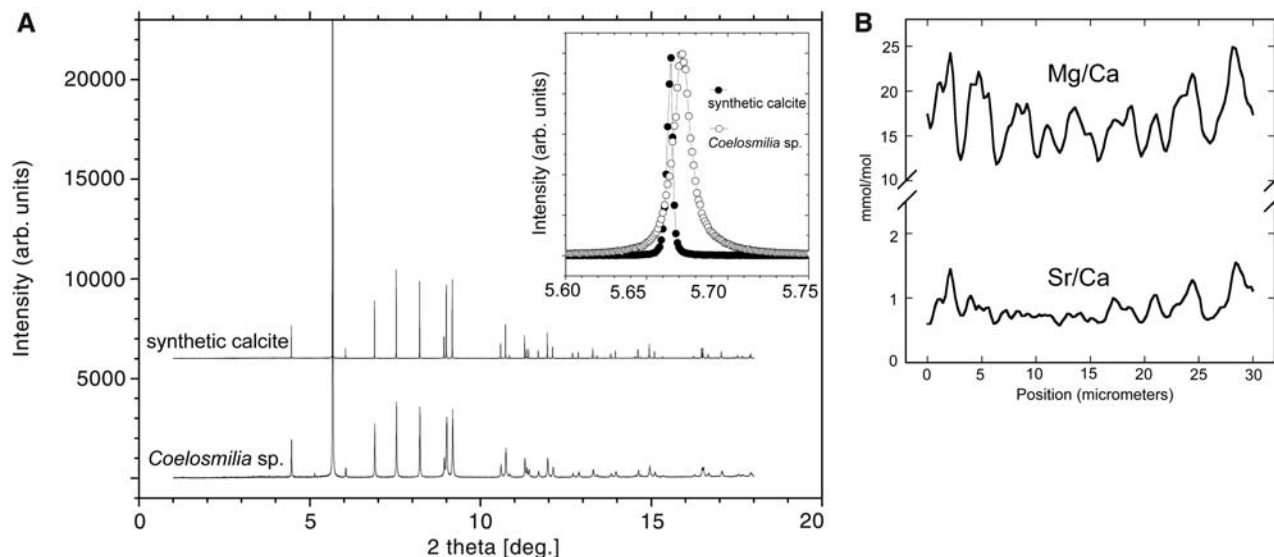


Fig. 3. Crystal structure and chemical composition of the *Coelosmilia* sp. calcitic skeleton. **(A)** High-resolution synchrotron radiation powder diffraction patterns of *Coelosmilia* sp. skeleton (lower trace) and synthetic calcite (upper trace). The most intense (104) Bragg peak is shown in the inset. The Bragg peaks

of *Coelosmilia* sp. are broader than those of synthetic calcite. **(B)** Typical NanoSIMS ion microprobe transect across the layered fibrous part of the *Coelosmilia* sp. skeleton. The observed variations in Mg/Ca and Sr/Ca ratios are similar in wavelength and amplitude to those observed in modern scleractinians.

It has been suggested that hypercalcifying organisms, including corals, are sensitive to the Mg/Ca ratio of seawater, which has changed through geologic history in response to variations in the plate tectonic cycle (21). According to this model, hypercalcifying aragonite-producing organisms (including corals) flourish during periods in which seawater has a Mg/Ca ratio greater than 2, whereas hypercalcifying calcite-producing organisms flourish when the Mg/Ca ratio is less than 2 (in the modern ocean Mg/Ca = 5.2). The *Coelosmilia* sp. lived in the Late Cretaceous when the inferred Mg/Ca ratio of seawater was below 2. Our findings may thus appear to support the recently proposed idea that seawater composition can even change the skeletal mineralogy of scleractinians (22). However, other aragonitic scleractinians lived at about the same time as the *Coelosmilia* sp. specimens studied here (16, 23), and other studies have shown that the chemical and isotopic composition of scleractinian skeletons is under strong biological control (15, 19, 20, 24–26). Therefore, it seems more likely that the capability of scleractinians to produce either aragonitic or calcitic skeletons is genetically determined. In any case, skeletal mineralogy can no longer be considered a conservative feature among scleractinians throughout their evolution.

Scleractinians first appear in the fossil record in the Middle Triassic (~240 Ma), 12 to 14 million years after the Permian mass extinction, which exterminated an already weakened population of Paleozoic rugosan (calcitic) corals. The Permian mass extinction possibly resulted from the synergistic effects of environmentally linked stresses on marine organisms, perhaps including hypercapnia: the direct physiological effects of an increased partial pressure of CO₂ (27). The

scleractinians represent the first corals in the fossil record after the extinction (2). Increased atmospheric CO₂ levels may increase the acidity of seawater, leading to the decalcification of carbonate skeletons and the formation of naked corals that can survive and resume calcification when atmospheric CO₂ levels decrease again (28). Our result, although from a much younger fossil, is consistent with the idea that scleractinians derive from naked corals or anemone-like ancestors, which survived the Permian mass extinction (29). When the scleractinians appeared in the Triassic, they abruptly formed a taxonomically robust and diverse group (30), consistent with having a substantial evolution and origin in the Paleozoic before the Permian mass extinction (31). Previously, the notion of a deeper evolutionary origin and a potential link between rugosans and some Mesozoic “scleractiniamorphs” [“aberrant scleractinians” (11)] was weakened by the presumed difference in skeletal mineralogy, but as we have shown here, this is no longer the case.

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Figs. S1 to S7
References

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