

# Aragonitic scleractinian corals in the Cretaceous calcitic sea

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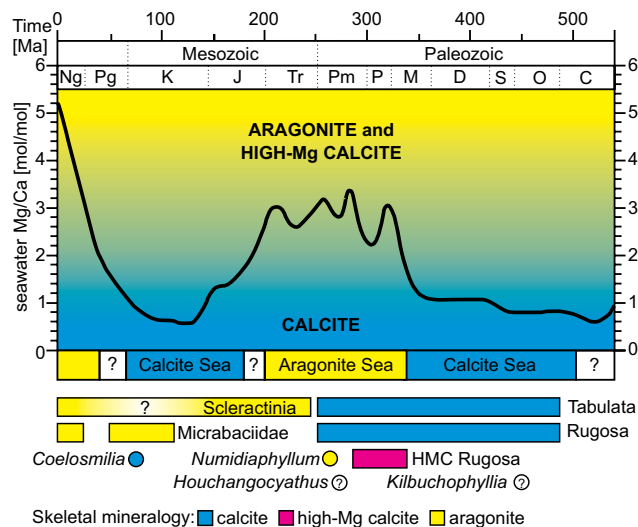
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## ABSTRACT

Changes in seawater chemistry have affected the evolution of calcifying marine organisms, including their skeletal polymorph (calcite versus aragonite), which is believed to have been strongly influenced by the Mg/Ca ratio at the time these animals first emerged. However, we show that micrabaciids, a scleractinian coral clade that first appeared in the fossil record of the Cretaceous, when the ocean Mg/Ca ratio was near the lowest in the Phanerozoic (thus a priori favoring calcitic mineralogy), formed skeletons composed exclusively of aragonite. Exceptionally preserved aragonitic coralla of *Micrabacia* from the Late Cretaceous Ripley Formation (southeastern USA) have skeletal microstructures identical to their modern representatives. In addition, skeletons of *Micrabacia* from Cretaceous chalk deposits of eastern Poland are clearly diagenetically altered in a manner consistent with originally aragonitic mineralogy. These deposits have also preserved fossils of the scleractinian *Coelosmilia*, the skeleton of which is interpreted as originally calcitic. These findings show that if changes in seawater Mg/Ca ratio influenced the mineralogy of scleractinian corals, the outcome was taxon specific. The aragonitic mineralogy, unique skeletal microstructures and ultrastructures, and low Mg/Ca ratios in both fossil and living micrabaciids indicate that their biomineralization process is strongly controlled and has withstood major fluctuations in seawater chemistry during the past 70 m.y.

## INTRODUCTION

Variation in seawater chemistry is thought to have played an important role in the evolution of skeleton-forming marine organisms and in the composition of their skeletons. The Mg/Ca ratio of seawater in particular has varied dramatically throughout the Phanerozoic (Stanley and Hardie, 1998; Porter, 2010). Abiotic precipitation experiments with seawater analogs have shown that precipitation of different CaCO<sub>3</sub> polymorphs is mainly controlled by the Mg/Ca ratio and temperature (Morse et al., 1997). At ~25 °C, present-day seawater ionic strength, and atmospheric CO<sub>2</sub> concentrations, the Mg/Ca ratio separates a regime of low-Mg calcite precipitation (Mg/Ca < 2) from a regime of aragonite/high-Mg calcite precipitation (Mg/Ca > 2) (Hardie, 1996). Based on the composition of early diagenetic carbonate cements and oolites (Sandberg, 1983), fluid-inclusion data (e.g., Lowenstein et al., 2001; Horita et al., 2002), and modeling of Mg/Ca fluctuations linking the chemical composition of the oceans with rates of oceanic crust formation (Hardie, 1996), the Phanerozoic has thus been divided into periods of calcitic and aragonitic seas, respectively (Fig. 1). It was suggested that the carbonate polymorph of hypercalcifying marine organisms was dictated by the seawater Mg/Ca ratio: during periods with high Mg/Ca ratio, aragonite-forming organisms dominated, whereas during periods with low Mg/Ca ratio, calcite-secreting organisms flourished (Stanley and Hardie, 1998). Furthermore, it was proposed that the skeletal mineralogy of newly evolved, CaCO<sub>3</sub> biomineralizing organisms was



**Figure 1. Ocean Mg/Ca ratio fluctuations throughout Phanerozoic and mineralogy of corals.** Black curve represents inferred oscillations of the Mg/Ca seawater ratio. Following Balthasar and Cusack (2015), a gradient from yellow (upper part) to blue (lowermost part) indicates a soft transition between aragonitic and calcitic conditions, instead of the sharp transition previously suggested to exist at the threshold Mg/Ca = 2 (Stanley and Hardie, 1998). Early Mesozoic and Cenozoic Scleractinia had aragonitic mineralogy (yellow bar), but the rarity of well-preserved Late Cretaceous scleractinians has not permitted unambiguous establishment of the carbonate polymorph of skeletons from this period, which was characterized by the lowest Mg/Ca ratios during the Phanerozoic. The aragonitic micrabaciid skeletons described in this study and the calcitic *Coelosmilia* (Stolarski et al., 2007) partially fill this gap (adapted from Porter, 2010; Ries, 2010; Holt et al., 2014). HMC—high-Mg calcite.

determined by the Mg/Ca ratio at the time of their origin (Porter, 2007, 2010). For nonhypercalcifiers, groups of organisms that appeared during aragonitic sea conditions would continue to produce aragonitic structures even in subsequent times of calcitic seas, but their calcification rate would be reduced, and vice versa (Stanley and Hardie, 1998; Porter, 2010).

Balthasar and Cusack (2015) demonstrated that temperature plays a key role in controlling abiotic calcite versus aragonite precipitation. Calcite precipitation is inhibited under aragonitic sea conditions at temperatures >20 °C, whereas during calcitic sea conditions, coprecipitation of aragonite and calcite can occur at temperatures >20 °C. According to this work, a pure calcitic sea condition (<1% of aragonite in CaCO<sub>3</sub> abiotic precipitates) would be rare in the geological past and constrained to temperatures <20 °C. During the same periods, in warm-water settings, abiotic precipitates could contain a significant fraction of aragonite (>50%). The modern seawater Mg/Ca ratio is ~5.2 mol/mol and all adult scleractinian corals, including deep- and/or cold-water species, form aragonitic skeletons (Cairns, 1995, p. 30).

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Some consider that scleractinian corals exert only partial control over their skeletal mineralogy (e.g., Holcomb et al., 2009). Accordingly, changes in the seawater Mg/Ca ratio should affect the CaCO<sub>3</sub> polymorph of their skeletons (Ries et al., 2006). The fossil coral record, which covers an ~460 m.y. period during which the ocean Mg/Ca ratio is inferred to have changed dramatically (from <1 to 5.2 mol/mol), provides a great opportunity to test the impact of seawater chemistry on coral calcification. In general, the evolution of corals, both Rugosa (Webb and Sorauf, 2002) and Scleractinia, indicates that variations in the Mg/Ca ratio might have influenced their skeletal composition (Fig. 1).

The calcitic scleractinian *Coelosmilia* reported from the upper Cretaceous chalk deposits seems to conform to the model of calcite versus aragonite seas (Stolarski et al., 2007). However, although this period of the fossil coral record is relatively poorly represented (Fig. 1), there is evidence for aragonitic coral skeletons from this period (Sorauf, 1999), suggesting a more complex influence of seawater chemistry on coral biomineralization. Recently, well-preserved skeletons of small solitary corals of the Micrabaciidae family were found in Cretaceous outcrops, including those in which the calcitic *Coelosmilia* skeletons were discovered, permitting a direct comparison of skeletal mineralogy and ultrastructure of two very different scleractinian taxa. Micrabaciids emerged in the fossil record in the Early Cretaceous (Baron-Szabo and Cairns, 2016), when the seawater Mg/Ca molar ratio was inferred to be the lowest during the Phanerozoic (<1 mol/mol). It is remarkable that unique macrostructural and microstructural features, which are not shared by any other group of Jurassic and Triassic scleractinians, are consistent with the hypothesis that micrabaciids appeared by skeletonization of some soft-bodied basal hexacorallians (Janiszewska et al., 2015). (The complete lack in the fossil record of possible deep-water skeletal-producing ancestors is an alternative, albeit less likely, scenario.) From the known groups of Scleractinia, the micrabaciids are therefore particularly suitable for examining the effect of seawater geochemistry on coral skeletons appearing *de novo*.

## MATERIALS AND METHODS

The fossil corals used in this study consisted of skeletons of *Micrabacia* from the Upper Cretaceous (ca. 70 Ma) deposits of eastern Poland and from the Cretaceous Ripley Formation (also ca. 70 Ma), Georgia,

USA, known for preservation of aragonitic fossils (Wade, 1926). Other materials used for comparison included skeletons of Miocene, Pliocene, and Holocene Micrabaciidae (Table DR1 in the GSA Data Repository<sup>1</sup>). Various analytical tools were used to compare structural and geochemical features of modern and fossil samples; details of scanning electron microscopy, scanning X-ray microscopy, Raman confocal microscopy, cathodoluminescence microscopy, and nanoscale secondary ion mass spectrometry (NanoSIMS) are provided in the Data Repository.

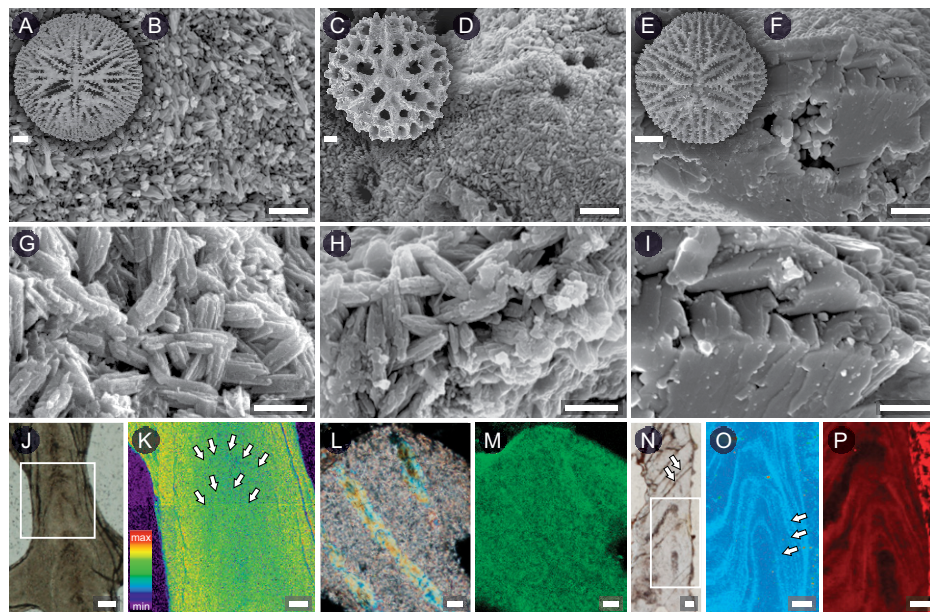
## RESULTS

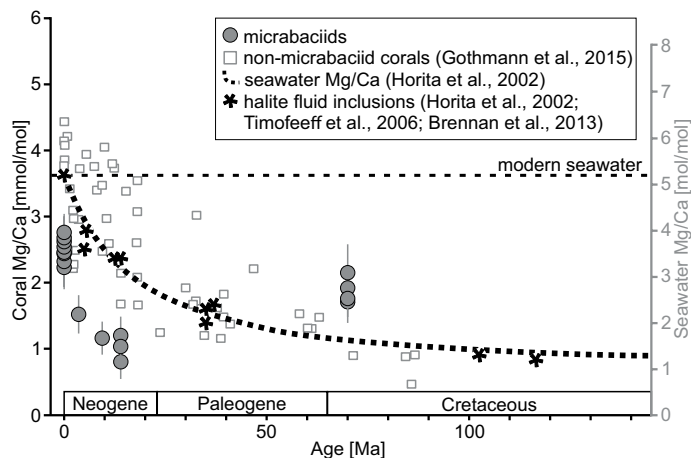
The micrabaciids from the Cretaceous Ripley Formation were exceptionally well preserved (Fig. 2C). Micro-Raman maps (lattice mode at 205 cm<sup>-1</sup>) of sectioned septa showed that they are composed entirely of aragonite (Fig. 2M). NanoSIMS mapping showed that the distribution of Mg is homogeneous throughout the septum (Fig. DR1), similar to the Mg distribution within septa of extant micrabaciids (Janiszewska et al., 2011). The Mg/Ca and Sr/Ca ratios of Cretaceous *Micrabacia* from the Ripley Formation were ~1.8 mmol/mol and 12.9 mmol/mol, respectively, i.e., similar to extant micrabaciids (Fig. 3; Fig. DR3). The pristine condition of the skeleton in these fossils was supported by microstructures identical to those observed in modern specimens (cf. Figs. 2D and 2H, and 2B and 2G). For example, distinct thickening deposits consisting of small (1–2 μm) chip-like bundles of fibers forming irregular meshwork within septa (Figs. 2D and 2H) are typical for extant micrabaciids.

In contrast, skeletons of *Micrabacia* sp. from the chalk deposits of eastern Poland are completely diagenetically altered, despite preservation of micromorphological details such as tiny granulations on septal flanks (Fig. 2E). Micro-Raman spectrometry of these skeletons revealed a purely calcitic mineralogy (Fig. 2P), and ultrastructurally they consisted of a mosaic of coarse crystals without preservation of the original microstructure in thickening deposits (Fig. 2F). Consistent with this, the Mg/Ca and Sr/Ca ratios of these skeletons averaged ~15 mmol/mol

<sup>1</sup>GSA Data Repository item 2017094, detailed methodology, Figures DR1–DR4, Table DR1 (locality information), and additional references, is available online at <http://www.geosociety.org/datarepository/2017/> or on request from editing@geosociety.org.

**Figure 2. Morphology and structural features of Holocene and Cretaceous micrabaciids. Left column: recent *Stephanophyllia* (A, B, G) and *Letepsammia* (J, K). Middle column: Cretaceous, juvenile *Micrabacia* (aragonitic skeleton) from the marls of the Ripley Formation (Georgia, USA). Right column: upper Cretaceous *Micrabacia* (calcitic skeleton) from the chalk deposits of eastern Poland. Distinct skeletal features of extant micrabaciids, i.e., star-like pattern of septa (A) and chip-like bundles of fibers of thickening deposits (B, G) are recognized in the perfectly preserved aragonitic skeletons of *Micrabacia* from the Ripley Formation (C, D, H). In the diagenetically altered calcitic skeletons of *Micrabacia*, overall morphological features are preserved (E), but the skeleton is fully recrystallized (F, I) and shows calcite cleavage lines (N, arrows). The distribution of sulfur (S<sup>VI</sup>) in *Micrabacia* (O, arrows) resembles laminar patterns in recent *Letepsammia* (K, arrows), but it correlates with Mn enrichment and bright orange cathodoluminescence (Fig. DR2; footnote 1) that suggest a diagenetic origin. J and N are thin sections in transmitted light; K and O are scanning X-ray microscope two-dimensional microfluorescence maps (of J and N, respectively); L is a thin section in polarized light; M is a micro-Raman map (of L) showing the aragonite composition of *Micrabacia* from Ripley Formation (aragonite lattice mode at 205 cm<sup>-1</sup>); P is a micro-Raman map (of O) at 281 cm<sup>-1</sup> showing the entirely calcitic mineralogy of *Micrabacia* preserved in Polish chalk. Scale bars: A and E are 1 mm; C is 100 μm; B, D, F are 10 μm; G–I: 5 are 5 μm; J is 50 μm; K–P are 20 μm.**





**Figure 3. Mg/Ca ratio of micrabaciid skeletons and other aragonite-preserved scleractinians for the past ~100 m.y. Despite the significantly different Mg/Ca ratios of the Cretaceous and modern ocean, the average Mg/Ca ratio of micrabaciid skeletons remains relatively low.**

and 0.7 mmol/mol, respectively. Scanning XRF (X-ray microscope two-dimensional microfluorescence) and WDS (wavelength-dispersive spectroscopy) maps showed Mg- and sulfur-enriched bands (Fig. 2O; Fig. DR2B) an order of magnitude wider than in modern scleractinians (Cuif and Dauphin, 2005; Meibom et al., 2008) and positively correlated with Mn (Fig. DR2D). Manganese, which is the main activator of cathodoluminescence in calcite and which does not occur in aragonite skeletons of extant scleractinians, is generally considered an element of diagenetic origin in the skeletons (Gothmann et al., 2015). Accordingly, the correlation of  $S^{VI}$  (Fig. 2O) with bright orange cathodoluminescence (Fig. DR2C) and enrichment in Mn (Fig. DR2D) suggest a diagenetic origin of sulfur in these fossil skeletons. Together these observations strongly indicate that the skeletons of *Micrabacia* sp. from the chalk deposits of eastern Poland were originally aragonitic and have been diagenetically altered into calcite, whereas *Micrabacia* sp. from the Ripley Formation have preserved their original purely aragonitic skeletons. The pristine preservation of aragonite in Ripley Formation micrabaciids allowed for direct comparison of skeletal Mg/Ca ratios with unaltered aragonite skeletons of other fossil and modern corals (Fig. 3; Fig. DR3). Skeletal Mg/Ca ratios of ~1 mmol/mol in Miocene micrabaciids were lower than other coral fossil skeletons of that age. The Sr/Ca ratio of *Micrabacia* from the Ripley Formation was similar to values in coral skeletons from the Pierre Shale Formation (ca. 71 Ma), i.e., between 13 and 14 mmol/mol (Fig. DR3).

Coral skeletal Mg/Ca is generally influenced by seawater temperature (Reynaud et al., 2007). However, the Mg/Ca ratios of extant Micrabaciidae skeletons average ~2.5 mmol/mol, regardless of the seawater temperature, and are usually lower than nonmicrabaciid Mg/Ca ratios from the same sites (Fig. DR4).

## DISCUSSION

The exceptionally preserved aragonitic coralla of *Micrabacia* from the Late Cretaceous Ripley Formation exhibit all structural and geochemical properties observed in modern representatives of Micrabaciidae (Fig. 2). In the Cretaceous chalk deposits of eastern Poland, skeletons of *Micrabacia* are diagenetically altered in a manner consistent with original aragonitic mineralogy. However, these aragonitic skeletons coexisted with *Coelosmilia* skeletons, the mineralogy of which is inferred to have been originally calcitic, based on well-preserved ultrastructures and consistent geochemical compositions (Stolarski et al., 2007). The co-occurrence in upper Cretaceous chalk deposits of two scleractinian taxa with different skeletal mineralogy indicates taxon-specific biomineralization control.

Laboratory experiments have shown that the  $CaCO_3$  polymorph can be strongly affected by the presence or absence of organic molecules (e.g., De Yoreo and Dove, 2004). In the calcification process of scleractinian corals, the taxon-specific composition of such molecules may influence the threshold at which seawater Mg/Ca can induce polymorphic change, as observed in mollusks (e.g., Falini et al., 1996). Higuchi et al. (2014) observed partially calcitic (~20%) primary skeletons produced by juvenile *Acropora* incubated in low Mg/Ca seawater from the larval stage. Nevertheless, the majority of the initial and post-initial skeleton was still aragonitic, suggesting that either some corals have both aragonite- and calcite-forcing organic matrix genes (Higuchi et al., 2014), the expression of which is less controlled and modulated during early ontogenetic development (note that many bryozoans and molluscs are capable of controlling  $CaCO_3$  polymorphism within a single shell; e.g., Sandberg, 1975; Marin et al., 2008), or the initial stages of *Acropora* calcification are generally less controlled, permitting essentially induced biomineralization of certain carbonate structures to take place (Gilis et al., 2015).

For extant coral species, general relationships between the skeletal Mg/Ca ratio, the Mg/Ca ratio of seawater (Ries et al., 2006; Cohen and McConnaughey, 2003; Gothmann et al., 2015), and water temperature (Reynaud et al., 2007) have been reported. The lowest Mg/Ca values are in cold-water species (see Fig. DR4). Oscillating around 2.5 mmol/mol across a broad range of seawater temperatures (2–16 °C), Mg/Ca ratios of extant micrabaciid skeletons are systematically lower than in most of the other modern scleractinians (Fig. DR4); this is consistent with very slow growth of the skeleton (Brahmi et al., 2012), but also suggests strong physiological control on the concentration of Mg in the skeleton formation process.

Studies of well-preserved aragonite corals show a general trend toward higher skeletal Mg/Ca and lower Sr/Ca ratios between the Cretaceous and today (Fig. DR3), consistent with data obtained from other fossil calcifiers and seawater ion concentration curves inferred from inorganic cements and inclusions in halite (Gothmann et al., 2015). However, despite the significant difference between concentration of Mg between the Cretaceous and the modern ocean, Mg/Ca ratios of Micrabaciidae skeletons remain relatively low (Fig. 3). The fact that micrabaciids first emerged in the Early Cretaceous fossil record (Baron-Szabo and Cairns, 2016) raises the possibility that the low Mg/Ca ratio of their skeleton represents the physiological relict of low Mg/Ca calcitic seawater.

In any case, the calcite-promoting conditions of the Cretaceous sea did not dictate the  $CaCO_3$  polymorph of the micrabaciid skeletons, which appeared at this time as entirely aragonitic. This is inconsistent with the hypothesis that the mineralogy of new (coral) clades was controlled by the seawater chemistry at the time they first evolved skeletons (Porter, 2007). The aragonitic *Acropora* lineage that emerged in the Paleocene (Mg/Ca < 2) represents similar evidence against this hypothesis (Stolarski et al., 2016). All findings of purely aragonitic Cretaceous corals (see also Sorauf, 1999) support the conclusion of Kiessling et al. (2008) that large-scale patterns of coral skeletal mineralogy seem more affected by sudden external disturbances, such as mass extinction events, than by slower changes to the Mg/Ca ratios of the global oceans.

In summary, this study fills a hitherto poorly documented phase in the fossil coral record. It is shown that, despite inferred low seawater Mg/Ca ratios during the Cretaceous, the micrabaciids appeared with aragonitic skeletons (Figs. 1 and 2) characterized by low Mg/Ca ratios, which have changed relatively little since and seem (among extant micrabaciids) relatively insensitive to water temperature (Fig. DR4). Collectively, these observations suggest a high level of biological control over the skeletal formation process, which has rendered at least this coral group unresponsive to major changes in ocean water composition.

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