Rhombic Calcite Microcrystals as a Textural Proxy for Meteoric Diagenesis

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Abstract

Numerous Phanerozoic limestones are characterized by diagenetic calcite microcrystals formed during mineralogical stabilization of metastable carbonate sediments in various diagenetic environments. Laboratory experiments show that calcite precipitating under conditions similar to those that characterize meteoric settings (impurity-free, low supersaturation, high fluid:solid ratio) exhibits the rhombic form, whereas calcite precipitating under conditions similar to those that prevail in marine burial settings (impurity-rich, high supersaturation, low fluid:solid ratio) exhibits non-rhombic forms. This prediction is tested here using new and previously published textural and geochemical data from the rock record. These data show that the vast majority of Phanerozoic limestones characterized by rhombic microcrystals also exhibit petrographic and/or geochemical evidence (depleted $\delta^{13}$C, $\delta^{18}$O, and trace elements) indicative of meteoric diagenesis. In contrast, non-rhombic forms are associated with marine burial conditions, suggesting that rhombic calcite microcrystals may provide a valuable textural proxy for meteoric diagenesis in Phanerozoic limestones.

Introduction

Numerous Phanerozoic limestones are characterized by low-Mg calcite (calcite) microcrystals that typically measure between 1 and 9 µm in diameter and comprise both carbonate matrix and allochems\(^1\). There is a general consensus that calcite microcrystals are diagenetic in origin and form during mineralogical stabilization of metastable phases such as aragonite and high-Mg calcite sediments, which is a replacement process whereby metastable minerals dissolve and calcite precipitates\(^2\).

Calcite microcrystals exhibit a wide range of crystal forms including rhombic, polyhedral (multi-faceted), rounded, subrounded, anhedral, and scalenohedral\(^1,3,4,5\). The vast majority of calcite microcrystals in Phanerozoic limestones are non-rhombic\(^1\), and exhibit geochemical signatures compatible with precipitation from marine-derived pore fluids during shallow burial\(^6\).

Previous experimental work shows that calcite crystals precipitating from impurity-free solutions that are slightly supersaturated with calcite (near-equilibrium) exhibit the rhombohedral form\(^7,8,9,10,11\) (Fig. 1a). Similarly, experiments show that aragonite reacted in distilled water converts to rhombic calcite microcrystals\(^12\). In contrast, calcite exhibits non-rhombic forms (scalenohedral, polyhedral, anhedral, etc.) when precipitation occurs in solutions that are highly supersaturated\(^7\), with high $a_{\text{Ca}^{2+}}/a_{\text{CO}_3^{2-}}$ (a is activity) or pH\(^7,13\), or in solutions containing various organic and inorganic impurities\(^8,10\). Likewise, calcite stabilized from aragonite in fluids containing $\text{Mg}^{2+}$, $\text{SO}_4^{2-}$, or excess $\text{Ca}^{2+}$, or under low fluid:solid ratios exhibits polyhedral (non-rhombic) and anhedral crystals\(^12\).

Given the above experimental observations, we propose that the uncommon rhombic calcite microcrystals in Phanerozoic limestones form exclusively in meteoric settings because fluids here are generally devoid of the conditions that have been shown to produce non-rhombic forms. Meteoric
diagenetic environments are generally characterized by (i) freshwater with lower [Mg], [Ca], and [SO₄] compared to seawater₁⁴,₁⁵, (ii) active oxidation of organic matter by O₂ and SO₄²⁻ (reference 15 and 16) (iii) undersaturation or low degree of supersaturation with respect to calcite₁⁴, and (iv) high fluid to solid (i.e., water/rock) ratios. The above hypothesis is tested using a global compilation of new and previously published textural and geochemical data from Phanerozoic limestones.

Results

Of the 31 microcrystalline limestone studies (Supplementary Table S1), 11 report rhombic crystals (Table 1). New and previously published stable isotope data from microcrystalline limestones are reported in Figure 3. δ¹³C measurements range from -6 to +5 ‰ and δ¹⁸O range from -9.40 to -3.20 ‰ VPDB (Fig. 3). All the limestones exhibit depleted δ¹⁸O values, and all but the Thamama Gp. calcites exhibit depleted δ¹³C values compared to the isotopic composition of age-equivalent marine calcites (Fig. 3). Previously published and new SEM images of natural and laboratory synthesized calcite microcrystals are reported in Figure 1. Representative SEM images from the three limestones studied here are reported in Figure 2. Textural and isotopic data for all samples studied here are summarized in Supplementary Table S2.

Our results from Mallaca limestone show that the dominant calcite crystal form is the rhombic (Fig. 2a) but polyhedral crystals are also observed (Supplementary Table S2). It is also observed that the sample with the most negative δ¹³C is primarily characterized by rhombic crystals whereas the sample with the least negative δ¹³C exhibits a mixture of rhombic and polyhedral crystals (Supplementary Table S2). Similarly, samples from Stuart City Trend with negative δ¹³C exhibit rhombic calcite crystals whereas those with positive δ¹³C contain mostly non-rhombic crystals (Supplementary Table S2). All Thamama Gp. samples have enriched δ¹³C and most exhibit non-rhombic forms (Fig. 3 and Supplementary Table S2).

Discussion

The textural and geochemical data compiled from the literature in Supplementary Table S1 are in agreement with previous global studies of Phanerozoic limestones that report that most calcite microcrystals are non-rhombic¹ and form during burial diagenesis from marine fluids⁶. We propose here that the rare rhombic microcrystals form exclusively in meteoric diagenetic environments. Discussed below are the lines of evidence in support of this hypothesis.

A large body of experimental observations demonstrate that calcite precipitating under conditions similar to those that characterize meteoric settings (impurity-free, low supersaturation, high fluid: solid ratio) exhibits the rhombic form⁷,⁸,⁹,¹⁰,¹¹,¹² (Fig. 1A), whereas calcite precipitating under experimental conditions similar to those that characterize marine or marine burial settings (impurity-rich, high supersaturation, low fluid: solid ratio) exhibits non-rhombic forms⁷,⁸,¹⁰,¹²,¹³ (Fig. 1B-D). Given that crystal form is dictated by the internal crystal structure and the external growth conditions⁹, the experimental
observations imply that the rhombic form is the structural form of calcite, and is dictated by its rhombohedral crystal system, whereas non-rhombic forms are growth forms, and are the result of various growth conditions. That is, the absence of the growth conditions that interfere with the growing calcite crystals in meteoric settings allows crystals to achieve their structural rhombic form, and the prevalence of those growth conditions in marine and marine burial settings leads to the various non-rhombic growth forms.

Growth conditions may interfere with calcite crystal forms in various ways. Impurities, such as Mg$^{2+}$, have been shown to adsorb on calcite growth steps, altering their orientation, and thus changing calcite crystal morphology from rhombic to elongated, multi-faceted crystals$^{8,17}$. Similarly, the occlusion of some organic additives such as amino acids into calcite crystals has been shown to distort the crystal form by creating heterogenous strains throughout the lattice$^{10}$. In the case of high supersaturation and high $a_{\text{Ca}^{2+}}/a_{\text{CO}_3^{2-}}$, the observed alteration in crystal morphology from rhombic to non-rhombic has been attributed to a disproportional change in the growth rate of crystal faces$^7$, whereas in the case of high pH (>12), the change in crystal morphology was attributed to the presence of OH$^-$ ions which has been suggested to stabilize the polar scalenohedral crystal faces$^{13}$. Several of the factors that influence crystal form of calcite precipitating directly from a solution have also been shown to influence calcite stabilized from aragonite$^{12}$. However, besides the aforementioned factors, stabilization experiments have shown that lowering fluid/solid ratio (solution volume/aragonite reactant mass) leads to the formation of polyhedral and anhedral calcite crystals rather than euhedral rhombic crystals, which has been interpreted to be the result of the increased competition of the growing crystals for space$^{12}$.

The meteoric-rhombic hypothesis is also consistent with direct observations from Holocene carbonate sediments in the Bahamas currently undergoing stabilization to rhombic calcite in a freshwater setting$^{18}$ (Fig. 1E) as well as calcite precipitating from freshwater in various modern environments$^{17}$. In contrast, polyhedral (non-rhombic) calcites in Neogene sediments are interpreted to have formed via stabilization in the marine realm based on marine stable isotope values$^{19,20,21}$ (Fig. 1F).

Phanerozoic limestones characterized by rhombic calcite microcrystals (Table 1; Fig. 2) commonly exhibit sedimentologic and petrographic evidence, such as paleosols, exposure surfaces, and clay-filled karstic cavities$^{4,22}$, and geochemical evidence, such as low trace element concentrations and depleted stable isotope values, indicative of meteoric diagenesis (Fig. 3). Of the 11 studies that report rhombic calcite microcrystals, 7 attribute the origin of the rhombic crystals to diagenesis in meteoric fluids, 3 to either meteoric or marine, and only 1 to marine diagenesis (Table 1). Often cited is a depletion in both $\delta^{13}C$ and $\delta^{18}O$ with respect to the inferred isotopic signature of age-equivalent marine calcites, known as the inverted J trend$^{6,23}$, which is observed in all but one of the case studies examined here (Fig. 3).

Interestingly, with rare exceptions, observations from the two limestone units examined here (Mallaca and Stuart City Trend) that exhibit the inverted J trend indicate that samples with the most depleted $\delta^{13}C$ are also characterized by rhombic crystals whereas samples with less depleted or enriched $\delta^{13}C$ are largely
characterized by non-rhombic crystals (Supplementary Table S2). The third limestone unit examined here (Thamama Gp.) is not inconsistent with our hypothesis but it reveals a more complicated story.

Samples from the Thamama Gp. are dominated by non-rhombic forms with a rare occurrence of rhombic crystals (Fig. 1C). We examined 12 samples from the Thamama Gp. from 5 wells, of which only one sample was characterized by rhombic crystals (Supplementary Table S2). Thamama has depleted $\delta^{18}$O and trace element concentrations$^{24,25}$, but seemingly normal marine $\delta^{13}$C (Fig. 3). Moshier (1989b) cited these values to argue that the calcite microcrystals formed via stabilization in the marine burial realm. He reasoned that the $\delta^{13}$C likely reflected marine fluids, and suggested that the low (< 200 ppm) Sr content observed in the calcite microcrystals of Thamama (Shuaiba Fm.) either reflects a low-Sr calcite-rich precursor sediment, or multiple episodes of recrystallization in an open system. Using similar data, Budd (1989) interpreted the calcite microcrystals in the Thamama to reflect diagenetic stabilization in meteoric fluids. Budd (1989) noted that although depleted $\delta^{13}$C is common in carbonates precipitated in meteoric settings, this is not always the case. He argued that meteoric fluids would not become $\delta^{13}$C depleted if there was little organic carbon in sediments, which would be the case in arid depositional settings. He also argued that the initially depleted $\delta^{13}$C signature of freshwater can trend toward normal marine as mineral-water reactions push the fluids to become rock buffered. Budd (1989) further suggested that the depleted $\delta^{18}$O and trace elements (Mg, Sr, Fe, and Mn) were more consistent with meteoric fluids.

While the diagenetic environment of the calcite microcrystals in Thamama Gp. has been debated, the depleted $\delta^{18}$O and trace elements are consistent with meteoric diagenesis, and its positive $\delta^{13}$C values are not inconsistent with this interpretation. The presence of rhombic microcrystals in the Thamama suggests to us that it was exposed to meteoric fluids during its diagenetic history. However, the observation that other forms of calcite are present in the Thamama (Fig. 1C) implies that the exposure to meteoric diagenesis was perhaps limited or it was preceded and/or followed by diagenesis in marine burial settings, which can also explain the positive $\delta^{13}$C values.

Statistics from published global studies are also generally consistent with the meteoric-rhombic hypothesis. In a global study of Phanerozoic limestones, the vast majority (~ 93%) of calcite microcrystals were interpreted to form in the marine burial realm$^6$. The remaining 7% exhibit geochemical evidence of meteoric fluids (Table 1). Interestingly, the rhombic form represents only ~ 10% of calcite microcrystals in Phanerozoic limestones$^1$, suggesting that mineralogical stabilization in the meteoric realm is less common than marine burial.

The data suggest that although rhombic crystals may form exclusively during meteoric diagenesis, meteoric fluids may not always produce rhombic crystals. This is because meteoric settings are not immune to the multitude of factors that can interfere with the form of the growing crystals. For example, it was suggested in a few studies that subhedral rhombic crystals or polymorphic textures containing some rhombic crystals formed during meteoric diagenesis$^{26,27}$, or during meteoric or marine diagenesis$^3$.$^28$. If microcrystals in these studies formed in the meteoric realm, several hypotheses can
explain why the crystals did not become perfectly rhombic. The subhedral rhombic crystals reported by Ahr (1989) were observed on surfaces and interiors of ooids. Aragonite ooids have been shown experimentally to stabilize to polyhedral calcite crystals rather than rhombic, possibly due to the presence of organic matter\(^\text{12}\).

It is also possible that rhombic calcite initially formed in a meteoric setting is altered by later diagenesis, thus obscuring the original form. For example, Lambert et al. (2006) proposed that partial dissolution during burial diagenesis could cause rhombic and polyhedral calcite microcrystals to become rounded, a phenomenon documented in laboratory experiments\(^\text{35}\). It has also been suggested that compaction and cementation during burial could alter calcite crystal form\(^\text{3,4}\). Therefore, later diagenesis may obliterate the initial morphological signature imparted by meteoric diagenesis, similar to geochemical resetting.

The meteoric-rhombic model has several implications. Calcite microcrystals host a significant proportion of microporosity\(^\text{1}\), and thus understanding their diagenetic history is a step towards accurate prediction of microporosity in limestones. Further, the link between calcite microcrystal texture and diagenetic environment provides an independent line of evidence to interpret the sedimentary rock record. Textural criterion for the meteoric environment is especially desirable given the equivocation of stable isotopes and trace elements in differentiating between diagenetic environments\(^\text{16,24,25}\). Notably, 12 out of 31 (39%) of the studies compiled here (Supplementary Table S1) invoked more than one diagenetic environment for the origin of calcite microcrystals based on isotope and trace element data, attesting to the inconclusiveness of these proxies. Lastly, the hypothesis that rhombic calcite microcrystals form exclusively in meteoric settings implies that their chemical signatures do not reflect marine conditions and thus are not suitable for palaeoceanographic reconstructions.

**Conclusions**

Petrographic and geochemical data presented here suggest that rhombic calcite microcrystals observed in Phanerozoic limestones most commonly form via mineralogical stabilization during meteoric diagenesis. This interpretation is supported by experimental evidence demonstrating that calcite precipitating under conditions similar to those characterizing meteoric settings (impurity-free, low supersaturation, high fluid:solid ratio) exhibits rhombic form, whereas calcite precipitating under conditions similar to those that prevail in marine burial settings (impurity-rich, high supersaturation, low fluid:solid ratio) exhibits non-rhombic forms. The hypothesis that rhombic calcite microcrystals form exclusively in meteoric environments implies that this form may be a useful textural proxy for meteoric diagenesis.

**Methods**

Textural and geochemical data from 31 studies of microcrystalline limestones are compiled in Supplementary Table S1. New textural observations and stable isotope data from three of these, the
Miocene Malacca Limestone, Indonesia\textsuperscript{25,29}, Cretaceous Stuart City Trend, Texas, USA\textsuperscript{30}, and Cretaceous Thamama Gp., U.A.E.\textsuperscript{14,25}, are reported in Supplementary Table S2 and Figs. 2 and 3.

Imaging was performed on a JEOL 7500 Field Emission SEM using an accelerating voltage of 5 kV and a working distance of 6 ± 0.2 mm. Samples were coated with 10 nm of osmium. Microcrystals are defined as crystals with a diameter between 1 and 10 µm\textsuperscript{1}. Rhombic refers to euhedral rhombohedral crystals with 6 rhombuses, whereas polyhedral refers to multi-faceted crystals having > 6 faces. The terms euhedral, subhedral, and anhedral refer to crystals with well-defined, moderately defined, and poorly defined crystal faces, respectively.

Stable carbon and oxygen isotopes were measured by placing ~10 µm of pure carbonate samples in a stainless steel boats. Samples were then reacted at 77° ± 1°C with anhydrous phosphoric acid in a Finnigan MAT Kiel IV preparation device coupled directly to the inlet of a Finnigan MAT 253 triple collector isotope ratio mass spectrometer. O\textsuperscript{17} corrected data were corrected for acid fractionation and source mixing by calibration to a best-fit regression line defined by NBS 18 and NBS 19 standards. Data are reported in ‰ notation relative to VPDB. Analytical precision is maintained at better than 0.1‰ for both δ\textsuperscript{13}C and δ\textsuperscript{18}O.

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Declarations

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Author contributions

M.S.H. and S.E.K. conceived the study. M.S.H collected and interpreted the data, drafted figures, and wrote the manuscript. S.E.K. supervised data interpretation and contributed to manuscript writing and editing.

Ethics declarations

Competing interests
The authors declare no competing interests.

### Tables

#### Table 1. Studies that report rhombic calcite microcrystals in Phanerozoic limestones.

| Study (reference) | Geologic Unit | Age | Location | Interpretation of Diagenetic environment |
|-------------------|---------------|-----|----------|------------------------------------------|
| This study        | Malacca Limestone, Stuart City Trend, and Shuaiba Fm. | Miocene and Cretaceous | Indonesia; Texas, US; UAE | Meteoric based on depleted $\delta^{13}$C and $\delta^{18}$O (except $\delta^{13}$C in Shuaiba Fm.) |
| Steinen 1982 (18) | Modern sediments | Holocene | Bahamas | Meteoric based on the observation that the sediments are residing in meteoric water |
| Moshier 1989a (29) | Malacca Limestone | Miocene | Indonesia | Meteoric based on depleted $\delta^{13}$C and $\delta^{18}$O |
| da Silva et al. 2009 (22) | Campo | Mid-Paleocene | Spain | Meteoric based on exposure surfaces and petrographic observations |
| Perkins 1989 (31) | Stuart City Trend | Cretaceous | Texas, USA | Meteoric or marine burial based on depleted $\delta^{18}$O isotopes and trace elements |
| Loucks et al. 2013 (30) | Stuart City Trend | Cretaceous | Texas, USA | No specific environment was inferred |
| Loucks et al. 2017 (32) | Calvin and Winn carbonates | Cretaceous | Louisiana, USA | Meteoric or shallow marine based on petrographic observations |
| Budd 1989 (14) | Thamama Gp. | Cretaceous | UAE | Meteoric based on low concentration of trace elements and depleted $\delta^{18}$O |
| Moshier 1989b (25) | Thamama Gp. | Cretaceous | UAE | Marine burial based on normal $\delta^{13}$C and depleted $\delta^{18}$O |
| Holail and Lohmann 1994 (33) | Bahariya Oasis Chalks | Cretaceous | Egypt | Meteoric based on depleted $\delta^{13}$C and $\delta^{18}$O, low concentration of trace elements, and petrographic observations |
| Deville de Periere et al. 2011 (4) | Mishrif Fm. | Cretaceous | Iraq; Qatar | Meteoric based on depleted $\delta^{13}$C and $\delta^{18}$O, and petrographic observations (clay-filled karstic features, dissolution molds, sparry cement), and proximity to an exposure surface |
| Dickson and Kenter 2014 (34) | Bashkirian & Visean | Carboniferous | Kazakhstan | Meteoric based on depleted $\delta^{13}$C and $\delta^{18}$O and petrographic observations |

### Figures
Figure 1

SEM images showing calcite microcrystals from various experimental and natural samples. (A) Rhombic microcrystals from aragonite to calcite stabilization experiments in distilled water and high fluid to solid ratio. (B) Polyhedral (multi-faceted) crystals from experiments in the presence of SO4^2- ([Na2SO4] = 28 mM). (C) Polyhedral crystals from experiments in the presence of Mg2+ ([MgCl2] = 5 mM). (D) Polyhedral and anhedral crystals from experiments at low fluid to solid ratio (0.3 mL/g) (A, B, C, and D are modified after reference 12). (E) Rhombic calcite crystals among aragonitic needles in Holocene sediments from the Bahamas, interpreted to have precipitated from freshwater (modified after reference 16). (F) Polyhedral and anhedral calcite microcrystals from Clino well (1769 ft) drilled on the western edge of the Great Bahama Bank, interpreted to have precipitated from marine-derived pore fluids (modified after reference 21). (G) Rhombic calcite microcrystals from the Lower Cretaceous Stuart City Trend interpreted to have formed during meteoric diagenesis. (H) Polyhedral calcite microcrystals from a carbonate reservoir in the Middle East interpreted to have formed during marine burial diagenesis. All scale bars are 5 µm.

Figure 2

SEM images of rhombic calcite microcrystals from (A) Mallaca limestone, (B) Stuart City Trend, and (C) Thamama Gp. Note that Thamama is characterized by a mixture of rhombic and polyhedral crystals. All
scale bars are 5 µm.

- This study - Indonesia - Miocene
- This study - Texas - Cretaceous
- This study - UAE - Cretaceous
- Budd (1989) - UAE - Cretaceous
- Moshier (1989a) - Indonesia - Miocene
- Moshier (1989b) - UAE - Cretaceous
- Perkins (1989) - Texas - Cretaceous
- Holail and Lohmann (1994) - Egypt - Cretaceous
- Develle de Periere et al (2011) - Iraq - Cretaceous
- Dickson and Kenner (2014) - Kazakhstan - Carboniferous

Figure 3

$\delta^{13}C$ and $\delta^{18}O$ from Phanerozoic limestones characterized by rhombic calcite microcrystals (Table 1). Gray boxes represent the estimated isotopic composition of marine calcite adopted from reference 6. Gray arrows point to data from samples shown in Figure 2.

Supplementary Files

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