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## EVOLUTION OF CARBONATE MINERALIZATION IN THE CM2 CARBONACEOUS CHONDRITES.

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**Introduction:** Aragonite, calcite and dolomite are volumetrically minor products of aqueous alteration of the CM2 carbonaceous chondrites. However they are important tools for exploring the histories of their host rocks because of all the alteration products carbonates carry a record of fluid evolution that is the easiest to read. Chemical and isotopic analysis of carbonate grains within any one meteorite can provide information on fluid compositions and temperatures, and *via* the Mn-Cr system yield a crystallization age. Comparisons of the carbonates within different meteorites can additionally provide insights into the temporal evolution and/or spatial variability of fluid compositions e.g. [1-3], and the longevity of aqueous system [4]. These comparative studies assume that: (1) fluid compositions during carbonate mineralization were homogeneous on the scale of an individual meteorite, and (2) the chemical and isotopic composition, and mineralogy, of carbonates within any one meteorite changed with ambient conditions (i.e. the carbonates maintained equilibrium with the aqueous system). If these assumptions are valid, then each member of a suite of meteorites that have been altered to different extents should contain a distinct but mineralogically and compositionally homogeneous carbonate population that provides a 'snapshot' of local alteration conditions.

Here we have sought to test these assumptions by asking whether individual CM2s contain a single population or multiple generations of carbonates. If multiple generations are present we then ask whether equilibration was prevented by physical inhomogeneities in the aqueous system sluggish reaction kinetics. The presence of multiple carbonate generations will also offer an opportunity to track the evolution of aqueous systems over the length scale of an individual meteorite.

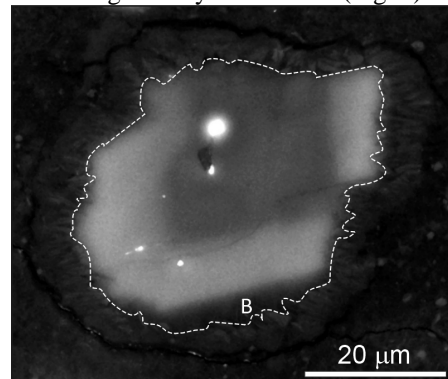
This study has used a suite of CM2s with different magnitudes of aqueous alteration, as expressed using the scheme of Rubin et al. [5]. Carbonate grains were located and characterised by backscattered electron and cathodoluminescence (CL) imaging, and X-ray mapping and microanalysis using a Zeiss Sigma field-emission SEM equipped with an Oxford Instruments INCA microanalysis system. Aragonite was distinguished from calcite by Raman spectroscopy using a Renishaw inVia Raman microscope operated with a 514 nm laser.

**Calcite and aragonite-bearing CM2s:** The CM2s examined with relatively low magnitudes of aqueous alteration were LON 94101, Mighei, Murchison (CM2.5), Murray (CM2.4/2.5), Nogoya (CM2.2) and

Pollen. All of these meteorites contain both aragonite and calcite, and it is most likely that calcite crystallized first. This calcite is uniformly distributed throughout the matrix whereas aragonite crystals are clustered in small areas. The calcite is inferred to have survived replacement by aragonite owing to compartmentalisation of the aqueous system, with aragonite crystallizing within isolated patches of fluids, probably during contraction of the aqueous system.

**The dolomite-bearing CM2 QUE 93005:** This meteorite is one of the most highly altered of the CM2s (classified as CM2.1 by [5]). It contains four compositionally distinct carbonates: breunnerite, calcite, dolomite and an iron-rich carbonate with a composition between dolomite and breunnerite, here termed 'calcian breunnerite'. These carbonates are intergrown in various combinations to make three types of polymineralic grains (described below). As these grain types are homogeneously distributed on the millimeter- to centimeter-scale, this disequilibrium assemblage is not explicable by fluid compartmentalisation, rather by incomplete reaction of existing minerals with fluids of different compositions.

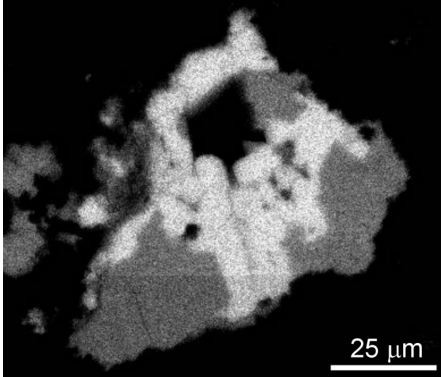
**Dolomite-breunnerite grains.** The oldest carbonate is dolomite, whose composition determined here ( $\text{Ca}_{51.9}\text{Mg}_{36.2}\text{Fe}_{7.4}\text{Mn}_{4.4}$ ) is very similar to that obtained from QUE 93005 dolomite by [6]. This dolomite occasionally shows trace element zoning and crystal terminations are overgrown by breunnerite (Fig. 1).



**Figure 1:** CL image of a carbonate grain in QUE 93005, whose edges are outlined by a dashed white line. The grain contains a zoned dolomite crystal, one termination of which is overgrown by breunnerite (B, non-luminescent).

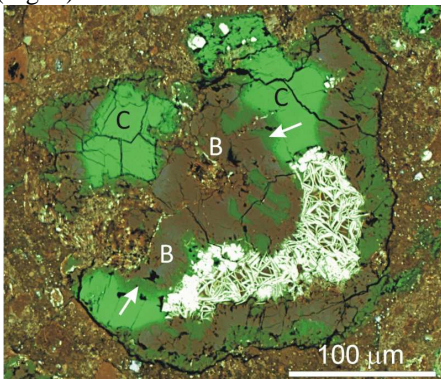
**Dolomite-calcite grains.** The dolomite may also be intergrown with calcite, and the relationships between these two minerals indicates that calcite has replaced

dolomite (Fig. 2). This reaction was hypothesised by [6] on the basis of a greater proportions of calcite relative to dolomite in the most highly aqueously altered CMs. The two types of dolomite-bearing grains therefore indicate a mineralization sequence of dolomite-breunnerite-calcite.



**Figure 2:** Calcium X-ray map of a dolomite grain (grey) partially replaced by calcite (white).

*Breunnerite-calcian breunnerite-calcite grains.* These carbonates occur together within concentric layered grains and crystallized from their margins inwards in the order breunnerite ( $\text{Ca}_{3.9}\text{Mg}_{57.2}\text{Fe}_{35.6}\text{Mn}_{3.2}$ ), calcian breunnerite ( $\text{Ca}_{43.1}\text{Mg}_{44.0}\text{Fe}_{11.5}\text{Mn}_{1.3}$ ) then calcite. The breunnerite was partially dissolved prior to calcian breunnerite crystallization, and also partially replaced by calcian breunnerite. Terminations of calcian breunnerite crystals were also etched prior to calcite cementation (Fig. 3).



**Figure 3:** False colour multi-element X-ray map of a QUE 93005 grain containing breunnerite (brown, B) and calcite (C, green), with calcian breunnerite (dark green) between (arrowed). The breunnerite has been partially replaced by pentlandite (white).

Overall, the three types of polyminerals grains in QUE 93005 suggest crystallization in the order of dolomite-breunnerite-calcian breunnerite-calcite, with significant hiatuses before crystallization of both the calcian breunnerite and calcite.

**Discussion:** All of the CM2s examined contain two or more generations of carbonates, demonstrating incomplete equilibration of earlier carbonates with evolving fluid compositions. In the aragonite- and calcite-bearing CM2s the two minerals are preserved because the change in fluid compositions coincided with, and was probably connected to, a reduction in fluid volumes so that existing calcite grains were not exposed to the solutions from which aragonite crystallized. QUE 93005 contains four carbonate generations, but does have evidence for partial equilibration of earlier formed carbonates as conditions changed (i.e. etching of both breunnerite and calcian breunnerite, and partial replacement of breunnerite by calcian breunnerite and dolomite by calcite). This may be expected if QUE 93005 had a much higher water/rock ratio during carbonate mineralization so that earlier carbonates were in contact with solutions of changing composition.

The carbonates in QUE93005 are compositionally unusual and to our knowledge this is the first time that breunnerite, and a carbonate with a composition equivalent to the 'calcian breunnerite', have been described from a CM2. This 'calcian breunnerite' is however very similar in composition to some carbonates in the paired CM1s ALH 84051/84034 [7].

The multiple carbonate generations the CM2s enable an assessment of the nature of fluid evolution between different parent body regions. Previous studies have assumed that owing to their relatively low degree of alteration, the calcite-rich CM2s did not reach the point of dolomite precipitation, whereas the dolomite-rich CM2s have progressed from calcite through to dolomite. In QUE 93005 however dolomite was the first and calcite the last mineral to crystallize. These findings suggest that fluid compositions evolved differently between CM2s with contrasting magnitudes of alteration, which was possibly due to contrasts in their fluid/rock ratios and/or temperatures.

**References:** [1] Johnson C. A. and Prinz M. (1993) *Geochim. Cosmochim. Acta*, 57, 2843–2852. [2] Ricci-puti L. R. et al. (1994) *Geochim. Cosmochim. Acta*, 58, 1343–1351. [3] Benedix G. K. et al. (2003) *Geochim. Cosmochim. Acta*, 67, 1577–1588. [4] de Leuw S. et al. (2009) *Geochim. Cosmochim. Acta*, 73, 7433–7442. [5] Rubin A. E. et al. (2007) *Geochim. Cosmochim. Acta*, 71, 2361–2382. [6] de Leuw S. et al. (2010) *Meteoritics & Planet. Sci.*, 45, 513–530. [7] Tyra M. A. et al. (2010) *LPS XLI*, Abstract #2687.

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