

**CARBONATES AND ASSOCIATED SULFIDE RIMS IN CM CHONDRITES: COMPLEX FORMATIONAL HISTORIES.** Simone de Leuw<sup>1</sup>, Alan E. Rubin<sup>2</sup> and John T. Wasson<sup>1,2</sup>, <sup>1</sup>Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095-1567, USA, <sup>2</sup>Institute of Geophysics and Planetary Physics, University of California, Los Angeles, CA 90095-1567, USA (sdeleuw@ucla.edu).

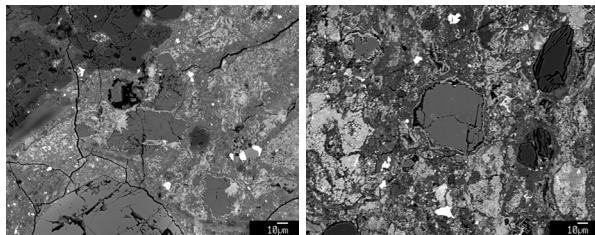
**Introduction:** Although CM chondrites are primitive solar-system materials, they have undergone a complex evolutionary history including extensive episodes of aqueous alteration and brecciation. In addition to nebular materials, CM chondrites contain abundant hydrous minerals, such as serpentine and tochilinite that probably formed by low-temperature aqueous alteration on the parent body [e.g., 1-3]. Carbonates are a minor alteration phase in CM chondrites, usually ranging between 2-3 vol%. Previous studies [e.g., 4-7] have shown that calcite ( $\text{CaCO}_3$ ) (possibly mixed with aragonite) is the dominant carbonate phase in CM chondrites, with minor amounts of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) also present. For simplicity, we refer to all  $\text{CaCO}_3$  grains as calcite. It is widely accepted that, within the alteration sequence, less-altered samples contain only calcite and that, with progressive aqueous alteration, dolomite crystals occur. Our investigations show that carbonate formation during aqueous alteration is more complex than previously thought.

**Samples and Techniques:** Polished and carbon-coated thin sections of the CM chondrites Y 791198, Cold Bokkeveld, QUE 93005, and MET 01070 were analyzed using the UCLA JEOL JXA-8200 electron microprobe (wavelength-dispersive element maps and quantitative analyses). Rubin et al. [8] classified these CM chondrites as petrographic subtypes 2.4, 2.2, 2.1, and 2.0, respectively.

**Observations:** The dominant petrographic characteristics of the four studied CM chondrites are presented in order of increasing aqueous alteration.

**CM2.4 Y 791198** contains 12-15 vol.% calcite grains [8]. Calcite is the only carbonate phase observed. It occurs as single crystals and as irregularly shaped aggregates up to 80  $\mu\text{m}$  in size. In some cases the calcite grains are intergrown with a material that seems to be PCP (poorly characterized phases consisting mainly of tochilinite-cronstedtite assemblages) (Fig. 1a). We analyzed 63 different spots: all of the calcite grains contain significant amounts of  $\text{MgO}$ ,  $\text{FeO}$ , and  $\text{MnO}$  (0.06-1.5 wt.%, 0.49-4.8 wt.% and 0.14-0.93 wt.%, respectively); calcite is concentrated in the PCP-rich regions. Most of the calcites in Y 791198 are surrounded by a thin sulfide rim (<1  $\mu\text{m}$ ) similar to the feathery rims observed in QUE 93005 (see description below).

**CM2.2 Cold Bokkeveld** is a breccia containing sub-cm-sized clasts that have experienced different degrees of aqueous alteration [9]. Calcite occurs mainly as single grains, 20-40  $\mu\text{m}$  in size. A minority of the calcite occurs as aggregates, 40-90  $\mu\text{m}$  in size, containing speckles of sulfides, similar to those in QUE 93005. Although we observed no dolomite in Cold Bokkeveld, previous studies reported rare occurrences [10]. Many carbonate grains in Cold Bokkeveld are surrounded by PCP-rich material. A minority of the individual calcite crystals are surrounded by a thin sulfide rim, similar to those in Y 791198 and QUE 93005 (Fig. 1b). About 50% of the analyzed calcite grains (total of 42 analyses) contain minor amounts of  $\text{MgO}$  and  $\text{MnO}$  (up to 0.25 wt.% and 0.68 wt.%, respectively); all of the analyzed grains contain significant amounts of  $\text{FeO}$  (between 0.10 and 2.6 wt.%).

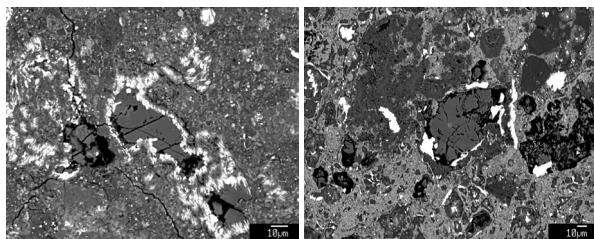


**Figure 1:** Backscattered electron images of (a) calcite in Y 791198, intergrown with PCP-rich material and (b) a typical calcite grain in Cold Bokkeveld, surrounded by a thin sulfide rim.

**CM2.1 QUE 93005** is highly aqueously altered; it does not appear to be brecciated [8]. It contains ~8 vol.% carbonate grains, ranging from 10 to 100  $\mu\text{m}$ . QUE 93005 is the only one of the four analyzed CM chondrites that contains both calcite and dolomite. Calcite occurs as irregularly shaped aggregates ranging between 50 and 100  $\mu\text{m}$  in size. Dolomite occurs as single crystals in the matrix, and in some rare cases as single crystals within larger calcite crystals. Dolomite is smaller than calcite and ranges from 10 to 30  $\mu\text{m}$  in size. A prominent feature in QUE 93005 is that every dolomite crystal is surrounded by a thin, feathery sulfide rim (Fig. 2a). In contrast most calcite aggregates contain patches of blocky sulfides within or at the rim of the crystal. Electron-probe analysis of sulfides indicates that the feathery rims around the

dolomite are almost exclusively pentlandite and that the blocky sulfides within or at the rim of the calcite are pentlandite, pyrrhotite, and “intermediate sulfides” containing moderate amounts of Ni [11]. All of the analyzed calcite and dolomite grains (total of 64 measurements) are complex carbonates containing significant amounts of MgO, MnO, and FeO; the dolomites have higher contents of MnO and FeO than the calcites (up to 5.0 and 8.0 wt.% and 1.1 and 0.91 wt.%, respectively).

*CM2.0 MET 01070* was classified as a CM1 chondrite in the *Meteoritical Bulletin* [12] and reclassified by [8]. It is the most highly aqueously altered sample of the four chondrites. The sample contains a large 12-mm-long PCP-rich lens (see [8] for description). MET 01070 contains about 4 vol.% calcite; no other carbonates are present. These grains are similar in shape and size to the calcite in QUE 93005 (Fig. 2b). In contrast to Y 791198, calcite is not concentrated mainly in the PCP-rich lens, but is heterogeneously distributed throughout the thin section. Some calcite grains contain blocky sulfides similar to those in QUE 93005. The calcite grains or aggregates are 10-60  $\mu\text{m}$  in size. About 50% of the measured carbonates (total of 22 measurements) show enrichments in MgO, MnO, and FeO (up to 0.20 wt.%, 1.1 wt.%, and 0.75 wt.%, respectively). A prominent feature of MET 01070 is that some regions contain large patches of fine-grained Mg-bearing calcite.



**Figure 2:** Backscattered images of (a) a typical dolomite grain in QUE 93005 surrounded by a feathery pentlandite rim and (b) calcite in MET 01070.

**Summary and Conclusions:** The present study shows that the formation of carbonates with increasing degrees of aqueous alteration is a more complex process than previously recognized. Zolensky et al. [13] reported that some carbonates in highly aqueously altered CM1 chondrites contain only calcite whereas other CM1 chondrites contain both dolomite and calcite. They also showed that completely hydrated CMs that contain both calcite and dolomite are carbonate poor compared to less-extensively aqueously altered samples. We confirm that the highly aqueously altered

MET 01070 chondrite has a much lower carbonate abundance than the less-altered samples Y 791198 and QUE 93005 (4 vol.% versus 12-15 vol.% and 8 vol.%, respectively). Zolensky et. al [13] concluded that there is a progressive increase in the modal proportions of carbonate from weakly to highly altered CM2 chondrites, but that the trend is reversed in carbonate-poor CM1 chondrites. The same trend holds for the formation of the more complex carbonates.

The sulfide rims around the carbonate phases in CM chondrites probably formed during aqueous reactions on the parent body. It is not yet clear if the rim sulfides precipitated on the carbonate surfaces or if the carbonates formed inside sulfide-lined cavities. The time sequence and formation processes of calcite, dolomite, and sulfide rims are key questions we are attempting to address. Browning and Bourcier [14] attempted to use geochemical modeling to explain similar rims around carbonates in CM chondrites, but they could not resolve the formation sequence based on their reaction progress models.

Because sulfide growth only requires recrystallization but no redox reactions, we suggest that it occurred first. Oxidation of carbonaceous matter to carbonate occurred at a lower rate, resulting in  $\text{CaCO}_3$  formation. The slower oxidation of sulfides to sulfate [15] led to  $\text{CaSO}_4$  formation at the expense of  $\text{CaCO}_3$  [16]. The liberated  $\text{CO}_3^{2-}$  probably formed fine carbonate grains in the matrix/PCP areas.

More detailed studies of carbonate-sulfide-assemblages in CM chondrites exhibiting different degrees of aqueous alteration are needed in order to resolve the complexities of carbonate and sulfide formation.

**References:** [1] Zolensky M. and McSween H. Y. (1988) In: *Meteorites and the Early Solar System*, pp. 114-143. [2] Zolensky M. et al. (1993) *GCA* 57, 3123-3148. [3] Clayton R. N. and Mayeda T. K. (1999) *GCA* 63, 2089-2104. [4] Brearley A. J. (1998) *LPS XXIX*, Abstract #1301. [5] Brearley A. J. et al. (1999) *LPS XXIX*, Abstract #1216. [6] de Leuw S. et al. (2007) *Meteorit. Planet. Sci.* 42, 5038. [7] de Leuw S. et al. (2007) *LPS XXXVIII*, Abstract #1361. [8] Rubin A. E. et al. (2007) *GCA* 71, 2361-2382. [9] Metzler K. et al (1992) *GCA* 56, 2873-2897. [10] Johnson C. A. and Prinz M. (1991) *LPS XXII*, Abstract #643. [11] Chokai J. et al. (2004) *LPS XXXV*, Abstract #1506. [12] Russell S. S. et al (2003) *Meteorit. Planet. Sci.* 38, A189-A248. [13] Zolensky M. E. et al. (1997) *GCA* 61, 5099-5115. [14] Browning L. B. and Bourcier W. L. (1999) *LPS XXIX*, Abstract #1533. [15] Jones C. L. and Brearley A. J. (2006) *GCA* 70, 1040. [16] Lee M. R. (1993) *Meteoritics* 28, 53-62.