CARBONATES IN THE CM1 CHONDRITE ALH84034: MINERAL CHEMISTRY, ZONING AND MNCR SYSTEMATICS

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Introduction: The CM carbonaceous chondrites are a complex group of primitive meteorites that record a variety of nebular and parent body processes. One of the major challenges in studying this group of meteorites is to distinguish between these different processes and establish where and when they occurred. Aqueous alteration is one of the most pervasive processes that has affected the CM chondrites, and has resulted in formation of variety of secondary phases [1,2]. The variation in the degree of alteration exhibited by different CM chondrites has led to the concept of progressive alteration within a parent body environment [1,3]. Alternatively, it has been argued that significant alteration of the CMs occurred prior to accretion within the solar nebula or within small, ephemeral parent bodies that broke up prior to accretion of the final CM parent body [4].

In order to gain further insights into the nature of the alteration of CM chondrites, we have been studying the detailed characteristics of carbonates in CM chondrites ranging from weakly to highly altered. We wish to understand exactly how the carbonate mineralogy, chemistry and isotope systematics evolve as a function of increasing degrees of alteration. Date for Murchison shows that complex and variable chemical zoning is recorded in the carbonates [5]. For comparison with Murchison, we have been studying the chemistry and zoning characteristics of carbonates in the CM1 chondrite, ALH 84034 using SEM techniques (BSE, CL) and EPMA. In addition, in order to understand the timing of carbonate formation, we have also studied the Cr isotopic composition of carbonates in ALH 84034 using the LLNL Cameca ims-3f ion microprobe and following techniques discussed by [6]. Standards included natural and synthetic silicate and carbonate minerals.

ALH 84034 is an CM1 chondrite that was not described [7]. Like the other CM1 chondrites [7], ALH84034 is characterized by the complete pseudomorphic replacement of chondrules and CAIs by serpentines, chlorites, oxides, sulfides etc.

Observations. Although we originally suggested that ALH 84034 was essentially unbrecciated [8,9], new observations [9] show that ALH 84034 contains clasts and fragments of unaltered material mixed in with the completely altered material. Unlike other CM1s [7], carbonates are relatively abundant in ALH 84034 and are distributed throughout the meteorite in a variety of different petrographic settings. We estimate that they occur at the 2-3 percent level. The carbonates occur both as individual grains and as irregularly shaped aggregates of crystals. The carbonates almost invariably occur external to altered chondrules, although there are rare occurrences of carbonates within chondrules. In contrast, carbonate is always abundant within altered CAIs.

EPMA studies show both calcite and dolomite are present. The two phases always occur separately, except within altered CAIs where they can coexist. Calcite is much less abundant and occurs largely as inclusion-free, single crystals or as subrounded clusters of grains. Most calcite grains are ≤50 µm in size, although rare, larger grains occur. Dolomite is much more abundant and typically occurs as angular to subrounded aggregates of grains up to 150 µm in size. Individual grains within the aggregates are also angular and have a size of 20-50 µm. Most aggregates have a highly fractured appearance indicating that they may have been crushed during brecciation. Intergrown within dolomite aggregates are serpentines and sulfides, typically pentlandite.

We studied several of the larger carbonate grains by CL and EPMA. These grains were selected because of their suitability for Mn-Cr dating by ion microprobe. Of the two calcites examined, one showed only weak variations in CL intensity, whereas a second, angular grain had extremely intense CL in the core region. The first calcite has MgCO₃, SrCO₃ and MnCO₃ contents all < 0.05 mol%, FeCO₃ contents are somewhat higher (0.2-0.4 mol%). Although the core compositions are homogeneous, there are slight increases in FeCO₃, MgCO₃ and MnCO₃ contents within 10 µm of the rim and CaCO₃ decreases. The second grain is asymmetrically zoned consistent with it being a fragment of a larger grain. The high CL region of the grain has flat zoning with MgCO₃, SrCO₃ and MnCO₃ < 0.05 mol% and FeCO₃ <0.3 mol%. However, in the low CL rim region MgCO₃, FeCO₃ and MnCO₃ all increase significantly to 0.6-2.0 mole%, but SrCO₃ shows no change.

The CL characteristics of the dolomite grains are significantly different from the calcites. Dolomite aggregates with a fragmental appearance show essentially indistinguishable, but complex CL behavior. These grains consist of domains with low, patchy CL intensity that correspond to the individual grains or subgrains within the aggregates. Each of the individual grains has extremely thin rims, a few microns wide, that exhibit much higher CL intensity than the core regions. Fractures that crosscut individual grains also show higher CL intensity than the cores of the grains.

The variability in the CL characteristics of the dolomites reflects considerable compositional variation within individual grains. Previous studies [7, 10] reported dolomite compositions from CM chondrites that contained up to 18 mol% (FeCO₃+MnCO₃). Dolomites in ALH 84034 appear to be especially Fe-rich with FeCO₃ contents varying between 5 and 20 mol%, higher than has been reported previously. MnCO₃ contents are lower (<4 mol% MnCO₃) and less variable. The dolomites also show considerable variations in their Ca/Mg ratios and are subcalcic, a feature that has been reported in CI and CM1 chondrites [7,10]. The MgCO₃ excess ranges up to 10 mol%, larger than previously reported [10].

Compositional profiles across these dolomite aggregates are extremely complex. We have not been able to determine unambiguously the compositional characteristics of the high CL rims on individual dolomite grains. However, Ca and Mg contents vary significantly and antithetically across the aggregates. In general, the CaCO₃ content of the grains appears to be highest at individual
grain edges. Mn and Fe also vary antipathetically, but in a nonsystematic fashion from one grain to another. Grains in the same aggregate can have both low and high Mn cores. However, in general, Fe is lower at the edges of the grains and higher in the cores where it effectively quenches the CL. Mn is elevated in the very narrow rim regions.

A single irregularly shaped grain was found that shows concentric zoning. The core has moderate CL intensity that is overgrown by a low CL zone and finally, an outer zone that has much higher CL. This grain, although fractured, shows no development of the high CL veins that are typical of other dolomites. EPMA profiles show that the CL corresponds to strong compositional zoning, with elevated MnCO$_3$ contents (1-2 mol%) in the core and rim where the CL is highest.

A comparison of the substitutional behavior of the major cations in the carbonates shows that there are significant differences between this symmetrically zoned grain and the typical fractured dolomite aggregates in ALH84034. In the latter, FeCO$_3$ and MnCO$_3$ show a weak negative correlation with similar compositional ranges, whereas in the zoned grain the correlation is positive and well developed and the compositional range is much more restricted. Other substitutional pairs also reveal significant differences. This evidence indicates that this grain grew in a different environment from other dolomites in ALH84034 and was mixed in at a late stage of alteration as a result of brecciation.

The Cr isotopic composition of several carbonates was studied by ion microprobe. Large variations in Mn/Cr during analyses reflect (inadvertent) spattering of Cr-rich inclusions or matrix located in fractures. Ion imaging was used to locate regions free of extraneous Cr and with high Mn/Cr; the SIMS data show, however, that ALH84034 carbonates contain substantially more Cr than carbonates in two other CM chondrites, Nogoya and Y791198. Two regions in dolomite #10 exhibit enrichments in $^{53}$Cr with $^{55}$Mn/$^{53}$Cr values ranging up to ~60‰. The magnitudes of the $^{53}$Cr excesses are linearly correlated with the respective $^{55}$Mn/$^{53}$Cr ratios, indicating in situ decay of $^{53}$Mn and demonstrating that short-lived $^{53}$Mn was extant at the time of carbonate formation. The slope of the correlation line on a $^{53}$Mn - $^{55}$Cr evolution diagram (Fig. 1), determined by a weighted least squares fit, corresponds to an initial $^{55}$Mn/$^{53}$Cr ratio of $(5.0 \pm 1.5) \times 10^{-6}$.

**Conclusions**: Like other CM1 chondrites, dolomite, rather than calcite is the most abundant carbonate phase in ALH84034. The dolomites record a complex history, rather than calcite is the most abundant carbonate phase. Although there is evidence that aqueous activity may have been episodic and involved periods of dissolution and reprecipitation, suggesting that water played an important role in the chemical/mineralogical evolution of primitive planetary bodies over an extended period of time, at least 15 Ma. Our studies of carbonates in ALH84034 and Murchison suggest that the history of carbonate formation was extremely complex and probably involved periods of dissolution and reprecipitation, suggesting that aqueous activity may have been episodic and involved fluids of different compositions.

The initial $^{53}$Mn/$^{55}$Mn ratio inferred for ALH84034 carbonates is approximately a factor of two lower than the value found for Kaidun carbonates [11] and comparable to the value found for carbonates in two other CM chondrites, Nogoya and Y791198. Carbonates in both Kaidun and ALH84034 appear to preserve their Cr isotope compositions despite pervasive aqueous alteration of surrounding lithologies. Assuming a solar system initial $^{53}$Mn/$^{55}$Mn ratio of $\sim 3 \times 10^{-7}$ [12,13], the difference in $^{55}$Mn/$^{53}$Mn$_{\text{core}}$ corresponds to a time interval of $\sim 10$ Ma between the formation of CAIs and carbonates in CM chondrites. Bremnerite (Fe-Mn-carbonate) in CI chondrites and fayalite in CV chondrites formed $\sim 3$ - 4 Ma after CM carbonates. The extended period of time between CAI and carbonate formation supports the view that formation of these secondary minerals most plausibly occurred in an asteroidal setting, consistent with our mineralogical observations [6]. It appears that water played an important role in the chemical/mineralogical evolution of primitive planetary bodies over an extended period of time, at least 15 Ma. Our studies of carbonates in ALH84034 and Murchison suggest that the history of carbonate formation was extremely complex and probably involved periods of dissolution and reprecipitation, suggesting that aqueous activity may have been episodic and involved fluids of different compositions.