

FORMATION CONDITIONS OF CARBONATES IN CM CHONDRITES EVALUATED BY EQUILIBRIUM MODELLING. R. L. Haller and M. R. Lee, School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, United Kingdom (robin.haller@glasgow.ac.uk).

Introduction: Equilibrium modelling is used in terrestrial geology to understand many different environments. In contrast, meteoritic applications have mostly focused on the aqueous alteration of CI carbonaceous chondrites (e.g. [1]). Models for CM carbonaceous chondrite alteration are less common and have been undertaken for large parent bodies [2, 3] or have used older thermodynamic databases with limited number of phases (e.g. [4]). While both CI and CM chondrites are characterised by aqueously formed minerals, the former contain phases including saponite and dolomite while the latter typically contain calcite, tochilinite and cronstedtite. In contrast to the CIs, most CMs have been only partially altered. PHREEQC [5] is open-source software for geochemical modelling and offers the user a variety of thermodynamic databases. Recently, [6] created customised databases containing a large number of species. While these databases are missing some phases present in carbonaceous chondrites (e.g., pentlandite), they can be used for fluids of a wide range of temperature, pressure and ionic strength.

CM chondrites are the most abundant carbonaceous chondrite (CC) group but the nature of their anhydrous precursor (i.e., CM3) is still poorly constrained, although Asuka 12169 [7] is a potential candidate. Another CC group of interest as a proxy for a CM3 is the CO chondrites. Of particular note is Dominion Range (DOM) 08006. It is arguably the most pristine CO chondrite (petrologic type 3.00 [8]) and high-quality analyses are available for its mineralogy [9] and bulk chemistry [10]. The availability of DOM 08006 as a valuable CM3-proxy together with the new databases in PHREEQC were our main motivations to perform a series of equilibrium models in order to examine the aqueous alteration conditions for CM chondrites as a function of temperature, water to rock (W/R) ratio and fluid composition. We focused especially on mineral assemblages containing calcite, as it is one of the characteristic minerals for CM chondrites, as well as being well studied in terms of, for instance, precipitation ages [11] and composition and petrography [12]. Calcite-rich veins found on the B-type NEA Bennu [13] also show that this mineral is particularly informative regarding the aqueous processing of carbonaceous asteroids possibly related to CM chondrites. The overall aim of this study was to determine alteration conditions capable of forming calcite starting from a CO3.00, and compare the mineralogy of the modelled systems to published analyses of CM chondrites.

Methods: We used PHREEQC to simulate the reaction of a DOM 08006-like material with either pure

water, or a parent body fluid at different temperature and W/R ratio. The composition of this primordial fluid is poorly constrained but was likely not just pure H₂O, because conditions during accretion of the parent body in the outer solar system would have been cold enough to accrete ices of e.g., CO₂, CO, NH₃ or HCl. We chose to implement a fluid of variable concentration but fixed ratio of CO₂, NH₃, H₂S and HCl (Table 1) [1, 3, 14, 15]. Alteration temperatures are also rather poorly constrained, and we included a broad range of 1–150°C, although clumped isotopes suggest temperatures of ≤71°C for calcite precipitation [16]. W/R ratios are generally assumed to have been between 0.2–0.7 [17]; we decided to span a wider range (0.2–5.0) to account for local differences between microenvironments.

The database *diagenesis.dat* [6] was used with a few added phases from the database *core10.dat* [3]. While tochilinite, a characteristic mineral in CM chondrites, is absent from both databases, we included it using an ideal mixture of troilite and Fe-hydroxide as suggested by [18]. The formation of kinetically inhibited phases and minerals including pyrite or quartz was suppressed.

The system included the elements Al, C, Ca, Co, Cl, Cr, Fe, H, K, Mg, Mn, N, Na, O, P, S, Si; with the exception of H and N, their abundance in DOM 08006 has been determined by [8]. We attempted to create a starting mineralogy closely representing the elemental composition while also resembling the mineralogy of DOM 08006 identified by [7]. Minerals like olivine were represented as pure phases and it was therefore necessary to add minerals like tephroite or Co-spinel to account for minor elements. While DOM 08006 is supposed to be quite pristine, it experienced some terrestrial weathering [8] and likely also some incipient forms of alteration (metasomatism) which could have been responsible for the abundance of magnetite [19] and some chrysotile. Thus, these two minerals had been removed from the starting material and replaced mainly by native iron, Fe-sulphides and forsterite.

Table 1: Overview of the model input parameters and selected output (in italics). The parameter combinations result in a total of 245 different systems, 24 of them containing calcite.

Parameter	Minimum	Maximum
Fluid (CO ₂ , NH ₃ , H ₂ S, HCl) conc.	1, 0.1, 0.05, 0.005 M	10, 1, 0.5, 0.05 M
W/R ratio	0.2	5
Temperature	1°C	150°C
<i>pH calcite</i>	7.68	12.58
<i>pe calcite</i>	-10.92	-5.74

Results and Discussion: Calcite precipitates as a minor phase (max 1.85 vol.%) in only 24 out of the 245 modelled systems of different temperature, W/R ratio or

fluid composition. The corresponding fluids have 1–5 M CO₂, more commonly 1–2 M, moderate to low W/R ratios (0.2–1, more commonly 0.75–1), neutral to alkaline pH and low *p_e* (Table 1). Where calcite is absent, in its place is either ankerite at lower or dolomite at higher temperature, although it can coexist with these phases at the temperature extremes. Calcite precipitation at moderate temperatures (50–125°C) occurs at only two conditions: A 1 M CO₂ fluid with 0.75 W/R ratio, and a 2 M CO₂ fluid with 1 W/R ratio; the former is shown in Figure 1.

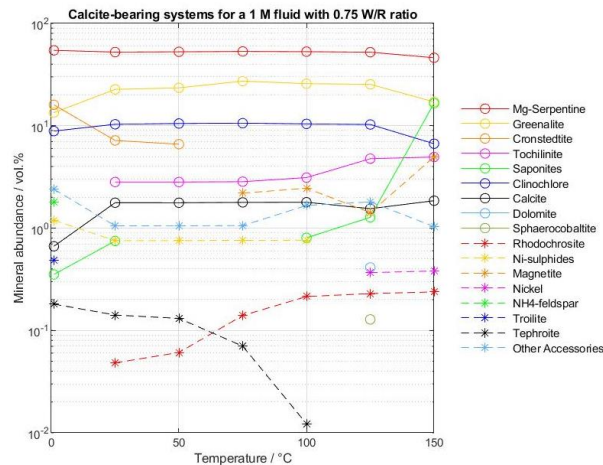


Figure 1: Volumetric abundance of minerals for calcite-bearing systems of constant fluid concentration and W/R ratio, and variable temperatures of 1, 25, 50, 75, 100, 125 and 150°C. Ni-sulphides are the sum of heazlewoodite and polydymite, while chromite, linnaeite, cobalt, andradite, riebeckite and hydroxyapatite are depicted as Other Accessories.

Most clumped isotope data [16] suggest calcite precipitation at temperatures of ~25°C; in Figure 1 this would correspond to an assemblage, in descending abundance, of: Mg-serpentine, greenalite, clinocllore, cronstedtite, tochilinite, calcite, Ni-sulphides, tephroite, rhodochrosite, and with accessories, hydroxyapatite, K-bearing saponite, chromite and linnaeite. Because kinetic effects were not considered, no primary olivine and pyroxene is preserved and all calcite-bearing systems contain >90% phyllosilicates, corresponding to a petrologic type of 1.0–1.1 [20] or subtype of CM2.0 [21]. Such an assemblage could be compared to a CM1 like Scott Glacier (SCO) 06043, although the model predicts more Fe-rich phyllosilicates than recorded [20].

Several vol.% of tochilinite forms at $\geq 25^\circ\text{C}$ for a large variety of fluid concentrations and W/R ratios. Since this mineral had been manually added to the database, we interpret this result with caution. Clinocllore is modelled to occur, but is uncommon in CM chondrites. It is expected as a sink for Al, while in reality Al is probably incorporated in minerals like serpentine [22]. The same accounts for Mn: In our

models, Mn can be present both as rhodonite (low T) and rhodochrosite (high T); this suggests that calcite of different composition could have precipitated at different temperatures. Assuming prograde reactions, Mn-free calcite would precipitate first at 1°C while gradually more Mn-rich calcite, reported by e.g., [23], would precipitate with rising temperature. Minerals like magnetite and dolomite, which are more common in CM1s than CM2s could also form from the same fluid when reaching temperatures of around 125°C. However, because all the models simulate a single fluid and do not take isotopes into account, carbonate precipitation and overall alteration could also have been caused by fluids from different parts of the parent body, as some meteorite samples suggest (e.g., [24]).

The main differences between the model mineralogy and analysed meteorites likely arises from the oversimplification of an equilibrium approach and the creation of microenvironments during aqueous alteration that cannot be captured with an equilibrium model. These shortcomings could be addressed with a kinetic model [25] which is more likely to be able to preserve olivine and pyroxene in the altered mineralogy.

To conclude, calcite in CM chondrites likely formed under moderate W/R ratios (0.75–1) from a diluted parent body fluid (1–2 M CO₂). The observed differences between samples of CM meteorites and modelled mineralogy could have evolved by heating or cooling a fluid of constant W/R ratio and CO₂ concentration.

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