

**UNRAVELLING THE AQUEOUS ALTERATION HISTORY OF CM CHONDRITES BY KINETIC 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](mailto:robin.haller@glasgow.ac.uk)).

**Introduction:** In contrast to the CI carbonaceous chondrites, most CM carbonaceous chondrites are partially aqueously altered; however, the exact reasons why water/rock reactions did not go to completion are poorly constrained (e.g. [1]). While equilibrium models have been used in planetary science, including for understanding CI chondrites (e.g. [2]), kinetic models, which would address the incomplete alteration in CM chondrites more realistically, have rarely been applied [3]. One reason could be the scarcity of kinetic data in thermodynamic databases, although [4] recently compiled reaction rates of many minerals for the geochemical software PHREEQC [5].

We have created a series of kinetic models for CM chondrite aqueous alteration in PHREEQC. They build on the previous equilibrium models presented in [6] that have been inspired by the pristine CO 3.00 chondrite Dominion Range (DOM) 08006 [7] as a proxy for a CM3 chondrite, and the newly available kinetic data from [4] in a new database built by [8]. We modelled variations in temperature and W/R ratios in an attempt to reproduce CM chondrites of different petrologic types, and to examine which parameter (temperature or W/R ratio) is more likely to have been responsible for their incomplete aqueous alteration.

**Methods:** We used the same starting material and a similar script as in [6]. Kinetic modelling, however, requires descriptions of the dissolution rates of minerals, which are further influenced by the surface areas of mineral grains and moles of the minerals in the initial rock. While the database contains rate expressions for many minerals, especially silicates, phases in our starting mineralogy like iron metal and gehlenite are missing. In such cases we used the dissolution rate of a similar mineral (chemically and/or crystallographically) as a proxy.

The surface area (SA) of a mineral can be approximated as a function of its grain size for a known grain shape, although the specific SA is mineral dependent and would ideally be evaluated by analysis of the sample using techniques such as 2D- or 3D-imaging [9] or gas adsorption [10]. Reported specific SAs in the literature focus mostly on terrestrial rock-forming minerals and can show orders of magnitude differences depending on the study and analysis technique (e.g. [9]). Thus, as a first approximation, we calculated the specific SA of the initial phases based on a trimodal grain size distribution depending on whether the phase is predominantly present in chondrules (20  $\mu\text{m}$ ), as fine-grained material (FGRs and matrix, 0.1  $\mu\text{m}$ ) or either in both of these materials or in refractory inclusions (RIs, 0.5  $\mu\text{m}$ ). Using a formula described by [10] with

parameters for quartz, yields specific SAs of 0.2, 50 and 10  $\text{m}^2/\text{g}$  for the three grain sizes, respectively. To obtain SAs in  $\text{m}^2$  for PHREEQC, the specific SAs are further multiplied by the molar mass and abundance (in moles) of the initial phases.

Another parameter to consider is a correction factor which typically accounts for differences of field compared to laboratory rates and often takes values of around 10–20 to compensate for effects like weathering or cementation of natural samples. We implemented a correction factor of 10 for pyroxenes to account for their lower abundance than olivine in most altered CM chondrites [11] despite having a lower dissolution rate.

Based on results from preliminary runs, we modelled a time interval of  $10^{-5}$  to  $10^5$  years, with incremental time steps of 0.5 log units. It was necessary to use PHREEQC's implicit solver *cvoid* to ensure convergence with dissolution rates of different orders of magnitude. Furthermore, we simplified the starting system by removing phases containing elements of minor abundance (Co, Cr, K, Mn, Na and P) to ensure faster and more stable simulations. We modelled variations in temperature (1–125°C) and W/R ratios (0.2–2). The fluid was modelled as water containing 1, 0.1, 0.05 and 0.005 molal  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  and HCl, respectively.

**Results and Discussion:** A timespan of  $10^{-5}$ – $10^5$  years produced the continuous dissolution of most primary phases, causing precipitation of secondary minerals, mostly hydrous, until a steady state is eventually reached, equivalent to an equilibrium model. An example for 25°C and a 0.75 W/R ratio, producing a calcite-bearing CM-like mineralogy, is shown in Figure 1 with primary and secondary phases as solid and dashed lines, respectively. In general, the pH increased and  $p_e$  decreased during ongoing alteration, which is reflected by early precipitation of oxidised minerals like nontronite. Primary Fe-silicates dissolved faster than their Mg-bearing counterparts; this probably led to the early precipitation of Fe-rich minerals like daphnite or minnesotaite, which would dissolve again once the fluid became more Mg-rich. Ankerite also forms early, in the first 0.1 years, but seems to be later replaced by calcite. The early breakdown of Fe-rich phases provides enough Fe for andradite to form, which in turn decreases the abundance of calcite due to limited amounts of Ca in the system. However, dissolving andradite, probably due to the late growth of tochilinite, again increases the abundance of calcite.

A mildly altered CM-like mineralogy could have formed before an incremental time of 10 years is reached for the system in Figure 1. This rock would

have ~15 vol.% forsterite and enstatite, and some remaining sulphides and metal, in addition to around 22% Mg-serpentine and cronstedtite, 13% clinochlore, 3% magnetite and andradite and 1% calcite. These quantities do not quite match typical CM mineralogies (e.g. [11]); nonetheless, it is an improvement on an equilibrium model, and the prediction of Fe-phases that are uncommon in the CMs like andradite could be explained by the rather Fe-rich initial mineralogy of DOM 08006. However, if earlier formed Fe-minerals like daphnite or ankerite are preserved due to factors such as non-negligible dissolution rates or clogging of pore spaces, less andradite and magnetite would be expected to form.

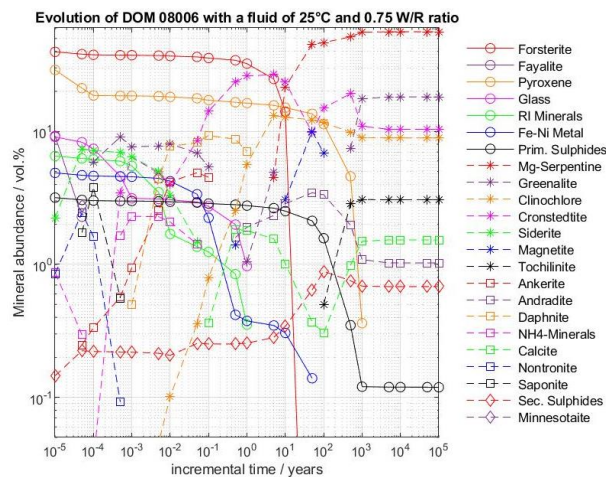


Figure 1: Evolution of the volumetric abundance of primary (solid) and secondary minerals (dashed lines). Timesteps are 0.5 log units and the total time can be calculated as the sum of all previous time steps.

An overview of the influence of T and W/R ratio is in Figure 2, which shows the evolution of petrologic type as defined by [11]. Variation of temperature had a notable effect on the timing and mineralogy of alteration (volumetric abundance of dissolved primary and precipitated secondary minerals), while differences in W/R ratio would rather influence the stability and volumetric abundance of secondary minerals. CM chondrites analysed by [11] are of type 1.7–1.2; these petrologic types can be reached in as little as ~4.5 days with a fluid of 125°C but can also take as much as 10<sup>4</sup> years if temperatures remain low. However, this is still a much shorter time than the suggested duration of aqueous alteration, for instance based on <sup>53</sup>Mn/<sup>53</sup>Cr ages of carbonates [12]. One possible reason for this difference in timescale could be that precipitation of phyllosilicates significantly decreases pore-accessible permeability, thus preventing further water/rock interaction and potentially produces only mildly altered CM chondrites. In our sampled systems, dolomite only formed at 125°C and usually at higher W/R ratio,

although it is also produced as an early metastable phase in some cases for lower W/R ratios. While olivine dissolution and Mg-serpentine precipitation overlap in time for lower temperatures, they are more temporally distinct at 125°C; in other words, primary silicates could dissolve fast enough before pore spaces were blocked by phyllosilicates, leading to CM chondrites of lower petrologic type. However, we cannot rule out the possibility of some kind of fluid mobilisation by e.g. meteorite impacts which might also produce CM chondrites of lower petrologic type.

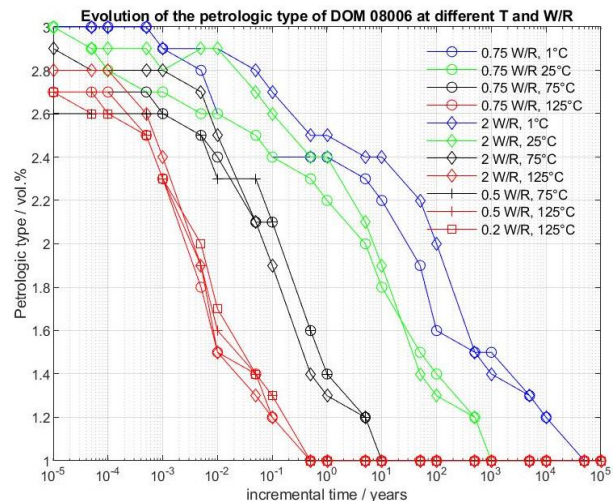


Figure 2: Evolution of the petrologic type defined by [11] for systems of different temperature and W/R ratio.

**CONCLUSIONS:** Our kinetic models can successfully form CM chondrites of different petrologic types from the CO3.00 DOM 08006 for various combinations of temperature and W/R ratio. As can be expected, temperature has a large influence on the rate of dissolution and seems likely to be responsible for differences in the extent of aqueous alteration between CM meteorites. As this work is still in progress, future versions of the model including more sophisticated dissolution rates and SAs, for instance, might be able to give a better insight into the mechanisms of CM chondrite aqueous alteration.

**References:** [1] Suttle M. D. et al. (2021) *GCA*, 299, 219–256. [2] Zolotov M. Y. (2012) *Icarus*, 220, 713–729. [3] Kopp R. E. and Humayun M. (2002) *GCA*, 67, 3247–3256. [4] Zhang Y. et al. (2019) *Comp. & Geosc.*, 133, 104316. [5] Parkhurst D. L. (1995) US Geological Survey. [6] Haller R. L. and Lee M. R. (2023) *LPS LIV*, this issue. [7] Davidson J. et al. (2019) *GCA*, 265, 259–278. [8] Zhang G. et al. (202) *Comp. & Geosc.*, 143, 104560. [9] Beckingham L. E. et al. (2017) *GCA*, 205, 31–49. [10] Brantley S. L. and Mellot N. P. (2000) *Am. Min.*, 85, 1767–1783. [11] Howard K. T. (2015) *GCA*, 149, 206–222. [12] Fujiya W. et al. (2012) *Nat. Commun.*, 3, 1635.