

MODELING CM CARBONATE AND MAGNETITE COMPOSITIONS. C.M.O'D. Alexander, M. Telus. DTM, Carnegie Institution of Washington, Washington, D.C. 20015 (calexander@carnegiescience.edu).

Introduction: There is still no consensus about the conditions under which the CMs were altered, although at least two models have been proposed [1, 2]. Outstanding issues that remain unresolved include: the temperatures of alteration, water/rock ratios, the causes of variable degrees of alteration, water isotopic compositions, and closed vs. open system behavior. Here, we explore two simple alteration models to try to quantitatively explain CM bulk, magnetite and carbonate O isotopic compositions.

Assumptions common to all models: The CM chondrites accreted as homogeneous mixtures of anhydrous rock and ice. The bulk compositions of the anhydrous, $(\text{Mg}_2\text{FeSi}_2\text{O}_{(7-x)}\text{C}_{0.5}\text{H}_{0.35})$, where x is the fraction of Fe in metal) and altered $(\text{Mg}_2\text{FeSi}_2\text{O}_{(9+y/2)}\text{H}_4\text{C}_{0.5}\text{H}_{0.35})$, where y is the fraction of Fe as Fe^{3+}) rocks were chosen to crudely approximate those of the CMs, including IOM-like material, as well as anhydrous/hydrous serpentines. For simplicity, here x and y are set to zero. This means that the minimum atomic ratio of O in water/anhydrous rock, W/R_O , needed to achieve complete alteration is 0.286. The H in the IOM was assumed to have a $\delta D=3500\%$ and the water a $\delta D=-450\%$ [3]. With these compositions, both models are able to reproduce the range of bulk CM δD values [3], and there no need to invoke a heterogeneous admixture of D-rich interstellar water as suggested by [4]. The initial O isotopic composition of the anhydrous rock is assumed to be that of the Murchison anhydrous minerals [1]. The equilibrium O and H fractionation factors for water-serpentine [5], water-calcite [6] and water-magnetite [7] were used. The carbonates and magnetite are assumed to be trace components, and their isotopic compositions reflect equilibrium with the fluid compositions from which they formed (i.e., they do not continue equilibrating after formation).

Constraints: Successful models must reproduce the bulk O [1] and H [3] isotopic compositions, and bulk H contents [3]. They should also be able to reproduce the range of carbonate and magnetite O isotopic compositions [4, 8-13]. The ranges of carbonate compositions are quite similar, irrespective of the degree of alteration (e.g., Paris vs. ALH 83100) but they are not always identical even amongst CM1s [12]. Finally, the W/R_O should not exceed the solar ratio. Estimates of the solar W/R_O depend on how much C is apportioned to refractory organics, CO, CO₂ and CH₄. Using the solar composition of [14] and assuming ~10% of solar C in IOM and the rest in CH₄ gives the maximum water abundance with $W/R_O \approx 3.2$. However, CH₄ formation is kinetically inhibited and a more likely upper

limit is to assume all volatile C is in CO, in which case $W/R_O \approx 1.1$.

Model 1: Upon melting of the ice, differential compaction resulted in local variations in W/R_O . Alteration of the CMs then proceeded as closed systems, consuming all the available water. The initial O isotopic composition of the water was found by fitting to the bulk CM compositions. During alteration, it is assumed that the water and phyllosilicates remain in equilibrium, and that conditions are isothermal.

To reproduce the bulk O isotopic compositions of the most altered CMs (i.e., just enough water to fully alter them) the water must have an isotopic composition of $\delta^{17}\text{O} \approx 40\%$, $\delta^{18}\text{O} \approx 61\%$, $\Delta^{17}\text{O} \approx 8\%$. The model is able to roughly reproduce the range of calcite compositions and magnetite compositions in ALH 83100 after ~20% alteration (Fig. 1). This seems reasonable given that some alteration is necessary to release Ca. The results are insensitive to W/R_O . Nor are they very sensitive to temperature. Fig. 1 was calculated at 40°C, but temperatures as high as ~100°C can still reproduce the range of mineral compositions, consistent with estimates of the range of CM carbonate formation temperatures [15, 16].

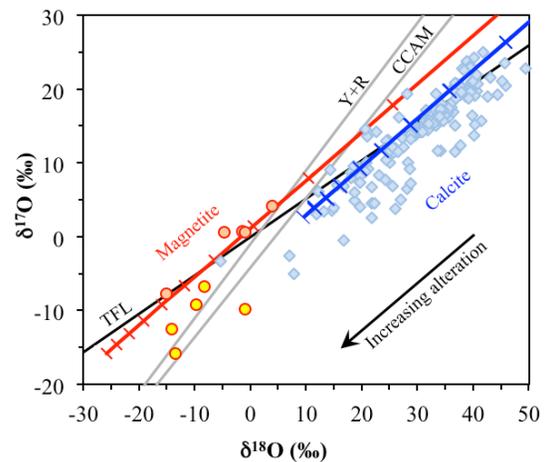


Fig. 1. Comparison of Model 1 results (red+blue lines) with a compilation of literature *in situ* calcite data, and magnetite data for ALH 83100 (orange fill) and ALH 84034 (yellow fill) [12]. The ticks are for 0-100% alteration in 10% increments.

An attractive aspect of Model 1 is its relative insensitivity to the assumed temperature and W/R_O . However, it cannot explain the magnetite and calcite compositions with low $\Delta^{17}\text{O}$, such as those in ALH 84034 and MET 01070) [12]. Also, the water O isotopic composition is mass fractionated well to the right of the Y+R

[2] and CCAM [1] lines. If nebular water formed close to either of these lines, it is not clear how such a fractionated composition could have been produced. This is because to fractionate it requires exchange with another major O reservoir, i.e., CO/CO₂ or silicates. High temperature exchange with silicates would produce little mass fractionation and there is little evidence for low temperature exchange with silicates in the nebula. At equilibrium, water is always isotopically lighter than CO and CO₂, which is opposite to what is required. Finally, there is not direct evidence for water with such a composition in any chondrites.

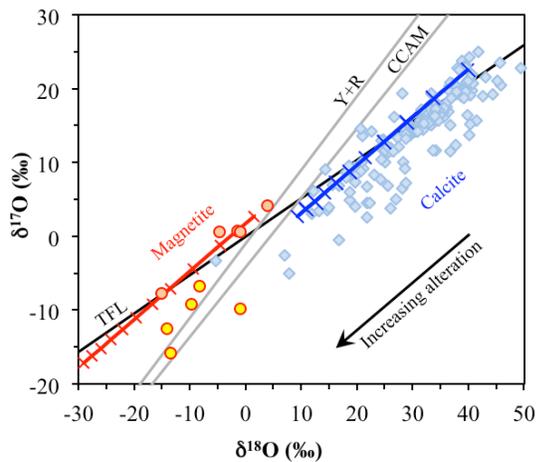


Fig. 2. Comparison of Model 2 in situ calcite and magnetite. Symbols are as in Fig. 1. The assume conditions were: $T=20^{\circ}\text{C}$, $W/R_0=0.8$, water $\delta^{17}\text{O}=7.5\text{‰}$, $\delta^{18}\text{O}=10.7\text{‰}$, $\Delta^{17}\text{O}=1.9\text{‰}$.

Model 2: The CMs acted as closed systems upon melting of the ice and during alteration. Their bulk compositions were determined by the extent of alteration and the subsequent loss of all the unreacted water. The water and altered rock are assumed to remain in isotopic equilibrium during alteration. The water was assumed to lie on the same slope 1 line as the anhydrous rock.

There are a range of W/R_0 , temperatures and water isotopic compositions that can reproduce the range of bulk CM compositions. However, assuming $W/R_0 \leq 1.1$ the water must have a composition $\delta^{17}\text{O} > 5\text{‰}$, $\delta^{18}\text{O} > 8\text{‰}$, $\Delta^{17}\text{O} > 0.7\text{‰}$. For a water composition $\delta^{17}\text{O} > 10\text{‰}$, $\delta^{18}\text{O} > 13\text{‰}$, $\Delta^{17}\text{O} > 3\text{‰}$, alteration temperatures must be below 0°C , which is inconsistent with estimates of carbonate formation temperatures [16]. Within this narrow range of water compositions, some fraction of the carbonate and magnetite compositions can be reproduced over a range of temperatures at different stages in the alteration. However, to reproduce

the full range of compositions at a single temperature requires that $T \leq 30^{\circ}\text{C}$ (Fig. 2).

As with Model 1, Model 2 can broadly reproduce the range of calcite and magnetite compositions, but not the full range. Model 2 is also more sensitive to assumed conditions than Model 1, particularly temperature that influences both the bulk and calcite/magnetite compositions. Given the high water contents of the starting material, it is surprising that there would not have been settling of the anhydrous rock as soon as the ice melted, which would have reduced the effective W/R_0 that the rock saw. Finally, it is unclear why there would have been a range of degrees of alteration, or how the unreacted water was lost without also losing salts dissolved in it.

Discussion: While the models can to first order explain the range of calcite and magnetite compositions, as already discussed, both have shortcomings and are still very simplistic. For instance, at the relatively low alteration temperatures experienced by the CMs it is not clear that the water and all altered material would have maintained equilibrium during alteration. Thus, it will be necessary to explore fractional alteration models. Also, it is assumed that the anhydrous rock had a uniform O isotopic composition. However, the Murchison anhydrous minerals composition must be dominated by chondrule and refractory inclusion material, as the matrix is entirely altered in this meteorite. It is possible that the anhydrous matrix had a different O isotopic composition to the anhydrous minerals separate. Indeed, a best fit to the CM fall bulk O isotope data suggests that the bulk anhydrous material had slightly higher $\Delta^{17}\text{O}$, implying that the matrix had an even higher $\Delta^{17}\text{O}$. If the first material to alter was matrix with slightly higher $\Delta^{17}\text{O}$, and after a certain amount of alteration then chondrules with lower $\Delta^{17}\text{O}$ became involved, this might explain the rapid decrease in $\Delta^{17}\text{O}$ in the highest $\delta^{18}\text{O}$ calcites [4, 11].

References: [1] Clayton R.N. & Mayeda T.K. (1999) *GCA* 63, 2089. [2] Young E.D. et al. (1999) *Science* 286, 1331. [3] Alexander C.M.O'D. et al. (2012) *Science* 337, 721. [4] Vacher L.G. et al. (2016) *ApJL* 827. [5] Saccocia P.J. et al. (2009) *GCA* 73, 6789. [6] Kim S.-T. & O'Neil J.R. (1997) *GCA* 61, 3461. [7] Zheng Y.-F. (1995) *Chem. Geol.* 121, 309. [8] Tyra M.A. et al. (2012) *GCA* 77, 383. [9] Tyra M. et al. (2016) *GCA* 175, 195. [10] Lee M.R. et al. (2013) *GCA* 121, 452. [11] Horstmann M. et al. (2014) *LPSC* 45, #1761. [12] Telus M. & Alexander C.M.O'D. (2017) *LPSC* 48, In Press. [13] Jenniskens P. et al. (2012) *Science* 338, 1583. [14] Asplund M. et al. (2009) *Ann. Rev. Astron. Astrophys.* 47, 481. [15] Alexander C.M.O'D. et al. (2015) *M&PS* 50, 810. [16] Guo W. & Eiler J.M. (2007) *GCA* 71, 5565.