

MINERALOGIC AND O-ISOTOPE EVOLUTION IN CM CHONDRITES: ON THE NON-RELATIONSHIP BETWEEN BULK O-ISOTOPES AND DEGREE OF AQUEOUS ALTERATION. K. T. Howard¹, G. K. Benedix¹, P. A. Bland^{1,2,3}, J. Gibson⁴, R.C. Greenwood⁴, I.A. Franchi⁴ and G. Cressey¹. ¹Impacts and Astromaterials Research Centre (IARC), The Natural History Museum, Mineralogy Department, London, SW7 5BD, UK. ²IARC, Dept. of Earth Sci. & Eng., Imperial College, London, SW7 2AZ, UK. ³Dept. Applied Geol., Curtin University of Technology, GPO Box U1987, Perth WA 6845, Australia. ⁴ Planetary and Space Science Research Institute (PSSRI), Open University, Milton Keynes, MK7 6AA, UK. E-mail: kieren.howard@nhm.ac.uk

Introduction: In CM chondrites, the largest group of meteorites to have experienced extensive low temperature processing, bulk O-isotope compositions are expected to reflect exchange between isotopically light anhydrous components, plotting below the terrestrial fractionation line (TFL) in 3-isotope space, and isotopically heavy hydrous reservoirs (that plot above the TFL) [1]. The primary manifestation of aqueous alteration is serpentinisation, which is the formation of serpentine family minerals by hydration of primary anhydrous Fe,Mg silicates – mostly well crystalline olivine and pyroxene. Since the formation of serpentine involves incorporation of isotopically heavy water, its abundance and evolution provides critical constraints on O-isotope systematics. Position Sensitive Detector X-Ray Diffraction (PSD-XRD) allows us to quantify the abundance of serpentine and constrain its anhydrous precursors in CM chondrites, as well as to track the evolution of ever finer crystalline size domains during the progression of hydration [2,3]. This allows us to define the degree of aqueous alteration, using the total abundance of hydrous phyllosilicate for samples spanning the complete petrographic range from least to most altered (CM2-CM1) [2,3]. The same powders used in the XRD analyses, have also been analysed for bulk O-isotopes; here both datasets are combined to provide new constraints on the evolution of O-isotope compositions and the nature and settings of aqueous alteration. These data also appear to provide more evidence for heterogeneous O reservoirs in the early solar system.

Samples and methods: We studied fresh, fusion-crust free powders of CM2 falls (*Mighei (3)*, *Murray*, *Murchison*, *Nogoya (2)*, *Cold Bokkeveld (2)*), CM2 finds (*QUE97990*, *ALHA81002*, *Y791198*, *QUE93005 (2)*), CM1/2 (*ALH83100*), CM1 (*MET01070 (2)*, *SCO06043*), and C2/ung (*Essebi*). Modal mineralogy (0.2g samples) was determined by PSD-XRD and a pattern stripping technique [2,3]. O-isotope analyses were performed by laser fluorination following the method and in the same lab as described in [4]. Because of the high volatile content of CMs and the methods used to cope with this problem, relatively large analytical variations in replicate analyses are to be expected (see replicate data for Murchison below; Fig.1). Another potential cause of variations can relate

to sample heterogeneity. For example, spinel can have $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of -40, -40 ‰ [1], and spinel-rich CAIs are known to have variable abundances in CM2s [5]. However, our data show spinel is always <<1 vol% of the bulk mode [2,3] and no large CAIs were evident when preparing the sample powders (the same can be said for carbonate).

Results and discussion: Fig. 1 shows the 3-isotope plot with total phyllosilicate abundances for samples discussed herein (full modal data in [3]). Pristine CM2 falls exhibit a very limited range of total phyllosilicate abundance ($75\% \pm 1.3 \sigma$) [2,3], but show large variations in O-isotopic compositions (Fig. 1). In CM2 finds the situation is the same as in the falls: minimal variation in degree of alteration (total phyllosilicate abundance $74\% \pm 1.52 \sigma$); and significant variation in O-isotope compositions, e.g. $\delta^{18}\text{O}$ varies by >10‰. And even if we take the minor variation in abundance of alteration minerals to be significant, there does not appear to be a clear relationship with bulk O-isotope composition. This has previously been suggested on petrographic grounds for 3 CM2 falls (*Nogoya*, *Murchison*, *Murray*) [6]. We can now confirm the non-relationship between aqueous alteration and bulk O-isotope compositions across the entire petrographic range (see below) in both falls and finds.

Despite being significantly more hydrated [3], the CM2/1 and CM1s in this study (total phyllosilicate = 82-87%) are lighter in bulk O-isotopes than all CM2 samples except *QUE97990* and *Murray* (Fig. 1). This further demonstrates the lack of correlation in bulk O-isotope compositions and degree of alteration. Data for these same powders (and all of the samples in this study) shown in [7] rule out the possibility of terrestrial contamination as an explanation.

Many of these same samples were also analysed by [1,8], before accurate quantification of the degree of alteration provided by PSD-XRD. Their results show less variation because of the different analytical approach, but also show no systematic correlation in bulk O-isotope compositions and the degree of alteration. Rather data in [1,8] show *Mighei*, *Murray* and *Murchison* cluster closely (consistent with relatively uniform phyllosilicate abundances) and *Nogoya* and *Cold Bokkeveld* are slightly heavier (despite similar total

phyllosilicate abundances as the other CM2 falls). In [1,8] the more altered Antarctic CM2 QUE93005 and the transitional CM2/1 ALH83100 are lighter than the CM2 falls (Fig. 1) – contrary to model expectations and in line with our new data.

QUE97990 and Murray have bulk O-isotope compositions that plot in the field of the CO-CV-CK; as does 1 other CM2 we have not studied (Paris) [9]. The absence of other samples falling between these and the main CM population starting higher ($\delta^{18}\text{O} = 4\text{-}5\%$) on the CCAM and traversing slope 1/2 lines is surprising.

$\Delta^{17}\text{O}$ values for the suite of CMs range from -3.87 to -1.68, with 1σ errors ranging from 0.01 (ALH 81002) to 0.73 (Mighei). QUE97990 and Murray have the most negative $\Delta^{17}\text{O}$ values relative to the other CMs. As $\Delta^{17}\text{O}$ has been taken as a proxy for water/rock (w/r) ratio [1], this may suggest these samples formed under different w/r conditions than the other CMs. Perhaps in a region(s) of less water, where the anhydrous component was more dominant in the isotopic budget. As is to be expected given the data described above, there is no obvious relationship between $\Delta^{17}\text{O}$ and the degree of aqueous alteration.

For analysed samples with bulk O-isotope compositions within error of each other, the lack of correlation with composition and degree of alteration in Fig.1 can be explained by uncertainties in these data. But it is telling that there is no systematic correlation in bulk O-isotope composition, with data acquired using a different methodology [1,8], and degree of alteration. And many of our samples clearly have distinct compositions outside of analytical uncertainty. For example, Y791198, Murray and ALH81002 (Fig. 1): Y791198 is less altered than Murray, but heavier in O-isotope composition, ALH81002 is more altered than Y791198, but lighter. Before the apparently anomalous CM Paris [9], QUE97990 and Y791198 were regarded as the least altered CMs. Our data show they are very similar [3] in total phyllosilicate abundances (QUE97990 = 67%; Y791198 = 70%), but they have very different O-isotope compositions and Y791198 is enriched in $\delta^{18}\text{O}$ by almost 5‰ (Fig.1). Finally, the CM1s that we studied are lighter than almost all CM2s (Fig. 1). These observations highlight the non-correlation between O-isotope compositions and the degree of aqueous alteration.

Conclusion: Beyond uncertainties in these data, there is reason to question the existence of a simple, systematic relationship between bulk O-isotope compositions and the degree of aqueous alteration. To explain the observed non-correlation in bulk O composition and degree of aqueous alteration, 2 scenarios can be envisaged that are not mutually exclusive. The 1st

requires variable O-isotope compositions of the components involved: anhydrous phases and/or hydrous reservoirs (ice/water). In this scenario isotopic exchange during hydration is between light (anhydrous) and heavy (hydrous) reservoirs of varied compositions. Meaning that even after experiencing the same degree of hydration, bulk O-isotope compositions of 2 samples may differ as a result of a different initial composition. This is exactly as we see in the bulk modal mineralogy, where the initial abundance of Fe,Mg rich anhydrous precursors, and/or chondrule/matrix ratio (since matrix is more Fe-rich) controls the relative abundance of Fe and Mg rich serpentines after hydration [2,3]. We know that primitive meteorites accreted heterogeneous anhydrous compositions. Perhaps ices were also heterogeneous. Especially since kinetically, it is much easier to fractionate the O-isotope compositions of ice/water, relative to anhydrous Fe,Mg silicate components. The 2nd scenario requires that another process, most reasonably oxidation of Fe and S, is consuming water [7]. Variable oxidation is consistent with heterogeneous abundances of metal and sulfide in CMs [2,3] and may be contributing to the lack of correlation between O-isotope compositions and the degree of aqueous alteration – as is being explored in [7].

References: [1] Clayton R.N. & Mayeda T.K. (1984) *EPSL*, 67,151-161. [2] Howard K.T. et al. (2009) *GCA*, 73, 4576-4589. [3] Howard K.T. et al. (2011) *GCA*, in press. [4] Miller M.F. et al. (1999) *Rap. Comm. Mass Spect.*, 13, 1211-1277. [5] Rubin A.E. et al (2007) *MAPS*, 42, 1711-1726 [6] Velbel M.A. (2007) *MAPS*, 42, p.5177. [7] Alexander C. M. O'D. et al. (2011) *LPS 42*, in press. [8] Clayton R.N. & Mayeda T.K. (1999) *GCA*, 63, 2089-2014. [9] Bourout-Denise M. (2010) *LPS 41*, #1683.

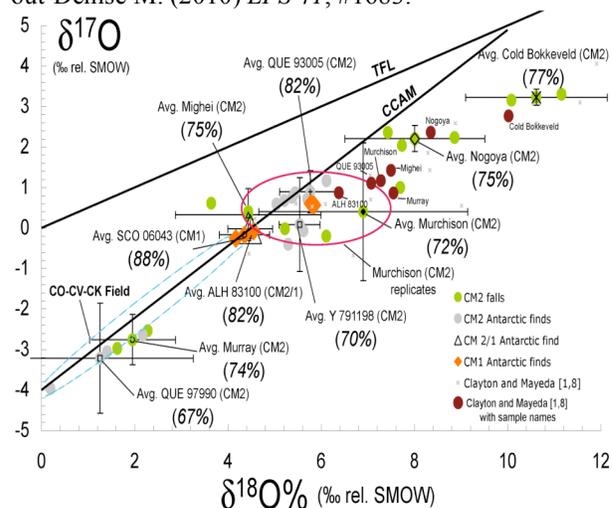


Fig. 1. $\delta^{18}\text{O}$ vs. $\delta^{17}\text{O}$ ‰ rel. SMOW. The value (%) under each sample is the total hydrous phyllosilicate abundance and defines the degree of aqueous alteration [2,3].