

NON-PROGRESSIVE AQUEOUS ALTERATION OF CM CARBONACEOUS CHONDRITES: THE PERSPECTIVE OF MODAL MINERALOGY AND BULK O-ISOTOPES. K. T. Howard^{1,2,3}, G. K. Benedix⁴, P. A. Bland⁴, J. Gibson⁵, R.C. Greenwood⁵, I.A. Franchi⁵ and G. Cressey³. ¹Kingsborough Community College, City University of New York. ²American Museum of Natural History. ³The Natural History Museum, London. ⁴Curtin University of Technology, West Australia. ⁵WA Museum, West Australia. ⁶Open University, Milton Keynes, UK. E-mail: kieren.howard@kbcc.cuny.edu

Introduction: Here we test 2 of the major hypotheses in the study of aqueous alteration of carbonaceous chondrites (CCs), by combining mineral abundance and bulk O-isotope data for the same sample powders.

Hypothesis 1: A systematic increase in the relative abundance of Mg-rich serpentines is expected to accompany increasing degrees of aqueous alteration [1]. This is the rationale used by many authors [e.g. 2,3] when adapting the model of [1] to create progressive alteration sequences. This model is a consequence of mineral reactivity: Fe-rich phases alter most rapidly during earlier stages of hydration (forming Fe-rich serpentines). Mg-rich phases (mostly in chondrules) alter slower to form more Mg-rich serpentines. At the same time as Mg-rich serpentines are forming from anhydrous components, Fe-rich serpentines recrystallize to more Mg-rich serpentines.

Hypothesis 2: Bulk O-isotope compositions of CCs are expected to become progressively richer in ¹⁸O, with increasing degrees of hydration. This expectation is because compositions of hydrous CCs are understood to be a product of exchange between low $\Delta^{17}\text{O}$ (light) anhydrous components, and hydrous reservoirs (presumably ices) with high $\Delta^{17}\text{O}$ (heavy) compositions that were established prior to accretion [4,5].

We find little evidence to support either of these hypotheses. This is reconciled with an asteroidal environment where flow and fluid supply were restricted.

Classification using total phyllosilicate: If the rationale for assigning a petrographic subtype is to define the relative degree of hydration, then total phyllosilicate abundances and bulk OH content are the only assumption free indicators. These parameters correlate and the OH results are being communicated elsewhere. Accurate determination of the degree of hydration is critical to allow meaningful comparisons with other data sets, like bulk O-isotopes. We propose the following classification scheme. We assign a value of 1.0 to a sample with 100% phyllosilicate and a value of 3.0 to a sample with 0% phyllosilicate. A type 2.0 sample in our classification contains 50% phyllosilicate, consistent with the intentions of the traditional 1-3 scheme [6]. Being based on total phyllosilicate (vol%) means that all aqueously altered CCs can be placed on the same scale.

Sample selection and analytical techniques: Using our Position Sensitive Detector X-ray diffraction

(PSD-XRD) technique [7], we have determined a complete modal mineralogy for all phases >1wt% in more than 30 CMs, including finds and falls. We have classified them all using total phyllosilicate abundances. We reported initial bulk O-isotope data on some of these samples in [8]. Initial results were surprising, data showed little evidence for any relationship between the degree of hydration and bulk O-isotope compositions determined by us [8] or [4,5]. We've now repeated earlier analyses, and it is clear that pre-fluorination reactions can lead to systematic underestimation of the ¹⁸O component. To reduce the affects of low temperature reactions between phyllosilicates and BrF₂, 2 new analytical protocols have been developed. This means we have now performed more than 60 bulk determinations, from 15 meteorites, by 3 approaches. Here we report on results relevant to the hypotheses.

Results: Data show no systematic differences between fall and find samples. The influence of weathering can be excluded from discussion.

Modal Mineralogy: The outstanding feature of bulk CM mineralogy is the dichotomy in diffraction intensities amongst serpentines- this is only evident in PSD-XRD patterns of large volumes of bulk powders. As previously [e.g. 7], we interpret the high intensity diffraction peaks to correspond to relatively well crystalline Fe-rich serpentines and the contrasting diffuse hk reflections to correspond to more Mg-rich serpentines. In XRD patterns of the most altered samples, decreasing crystallite sizes and increasing structural complexities, consistent with recrystallization, are evident.

Total phyllosilicate abundances (vol%) in CMs range from just less than 60% to almost 90%. On our scheme this corresponds to a range in subtypes from 1.8–1.3. Even the most altered samples still contain anhydrous components (minimum olivine + pyroxene =7-8%), meaning the supply of H₂O was exhausted (this is also true for CI). Abundances of other minor phases are typically as follows: metal=<1%; sulphides =1-5%, magnetite=1-8%, carbonates=1-4%, sulfates =<2%. Variations in the relative abundances of Fe-rich serpentines (Avg.=28%, 1 σ =12%) and Mg-rich serpentines (Avg.=47%, 1 σ =16%) are far greater than variations in total phyllosilicate abundances (Avg.=75%, 1 σ =7%). Central to hypothesis 1, there is no correlation ($r^2=0.03$) in the abundance of Mg-serpentine vs. total phyllosilicate (or petrographic type). An extreme

example of this non-relationship comes from comparison of very similarly altered samples (e.g. types 1.3 and 1.4, with 77% and 73% total phyllosilicate), in which the relative abundances of Mg-serpentine differ by more than 30%.

Bulk O-isotope compositions: Even where variations in alteration are minimal, variations in O-isotopes are often significant, in an expression of the analytical uncertainties. For example, average $\delta^{18}\text{O}$ varies by >8% between 2 fall samples of type 1.5 (Murray and Murchison). For samples with bulk O-isotope compositions that are within error, potential relationships between bulk O-isotope compositions and the degree of alteration are masked by analytical uncertainties.

For samples with clearly distinct bulk O-isotope compositions and similar degrees of hydration (types 1.4-1.6), the data scatter: there is no evidence for a systematic relationship between bulk O-isotope compositions and minor variations in phyllosilicate abundances. For samples with distinct bulk O-isotope compositions, and very different degrees of alteration, comparisons are more revealing. The most altered samples (e.g. SCO06043 and ALH83100: types 1.2/3 or CM1/2) can have lighter bulk O-isotope compositions than the least/much less altered samples. Despite being nearly completely hydrated, SCO06043 and ALH83100 preserve bulk O-isotope compositions falling on the Carbonaceous Chondrite Anhydrous Mixing line (CCAM) in 3 isotope plots; implying that hydration was without apparent mass dependent fractionations. $\Delta^{17}\text{O}$ values for the suite of samples range from -1.66 to -4.05, with 1σ errors ranging from 0.01 to 0.48. $\Delta^{17}\text{O}$ shows no evidence for a relationship to the degree of alteration and can't easily be related to water:rock ratios as is usually suggested [e.g. 3,4,5]

Discussion: Progressive evolution of more Mg-rich serpentine compositions during alteration is not obvious in the bulk mineralogy of CMs. This indicates that it is not variations in the degree of alteration that are controlling the observed bulk abundances of different serpentine polytypes. We interpret this to indicate that: 1) the relative abundances of Fe- and Mg-rich serpentines reflect the relative abundances of Fe, Mg rich anhydrous precursors alone. Likely chondrule: matrix ratio was an important control on the relative production of Fe-rich vs. Mg-rich serpentines (since matrix is more Fe-rich). 2) There was no significant mixing or homogenization of fluid compositions (e.g. little to no flow) that would result in the evolution of progressively more Mg-rich serpentines predicted by [1] (as a consequence of contrasting reactivity's of Fe-rich matrix vs. Mg-rich chondrule components). The model [1] explains succession of hydration in any single sample.

The fact that we cannot observe the expected progression in comparison of bulk samples can be explained by an absence of fluid flow cf. [9].

These observations can explain bulk O-isotope systematics. We observe that by the time CCs are $\frac{3}{4}$ hydrated (75% phyllosilicate), their bulk O-isotope compositions are much more ^{18}O -rich than anhydrous separates from CMs [4,5] and the bulk compositions of anhydrous CCs (i.e. CO/CV/CKs). This is consistent with incorporation of heavy ^{18}O -rich H_2O into serpentines. Our data can't exclude variable heavy H_2O compositions [8] that would be consistent with the scatter in O-isotope compositions. As the supply of ice is exhausted, supply of ^{18}O -rich H_2O ceases and water:rock ratios become very low, with the remaining H_2O probably confined to grain boundaries. Ultimately, this H_2O is consumed in reactions, forming serpentines with final isotopic compositions reflecting the initial relative contributions of anhydrous components and fluid.

As fluid becomes limited it becomes increasingly enriched in ^{16}O . Alteration continues and during hydration of anhydrous components, serpentines undergo recrystallization, releasing isotopically light fluid. Therefore, late stage hydration will form serpentines that are isotopically lighter than the earlier generation(s) and this brings the whole-rock value back towards the initial sum of the water and rock contributions. Samples subjected to most late stage fluids and/or recrystallization (CM1s) may contain greater proportions of light phyllosilicates. Less altered samples escaped interactions with late stage ^{16}O -rich fluids that may have been lost by de-volatilisation, explaining their heavier bulk O-isotope compositions, despite lower total phyllosilicate volumes.

Conclusion: Modal abundances of Fe- and Mg-rich serpentines, and bulk O-isotope compositions of CMs, reflect the compositions and abundances of the anhydrous precursors. Variations in degrees of aqueous alteration can be explained by variations in proportions of chondrules, matrix and ices at the point of accretion. Little evidence for progressive evolution of CM bulk mineralogy's on their parent bodies exists: hydration may have been without flow in a static environment.

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