

PSD-XRD MODAL MINERALOGY OF TYPE 3.0 CO CHONDRITES: INITIAL ASTEROIDAL WATER MASS FRACTIONS AND IMPLICATIONS FOR CM CHONDRITES. K. T. Howard^{1,2,3}, C.M.O.'D Alexander⁴ and K.A. Dyl⁵. ¹Kingsborough Community College of the City University of New York. ²American Museum of Natural History. ³The Natural History Museum, London. ⁴Department of Terrestrial Magnetism, Carnegie Institute of Washington. ⁵Curtin University of Technology, West Australia. Email: kieren.howard@kbcc.cuny.edu

Introduction: Mineral abundance data for meteorites aids relating these to asteroid surfaces and provides clues about the make-up of their parent bodies. An ability to target asteroids and interpret their mineralogy is more important than ever as we enter an age of asteroid sample return and consider capturing these objects. Since many of the most primitive meteorites are composed mainly of alteration products, we seek to define the conditions under which alteration took place on asteroids; accurate modal abundances are essential in understanding these primitive environments. Here mineral assemblages observed at different degrees of bulk hydration are compared to bulk H contents [1] and models of aqueous alteration [2,3]. One of the main questions we hope to resolve is the initial ice/water mass fraction of hydrous asteroids.

We present the first Position Sensitive Detector X-ray Diffraction (PSD-XRD) mineral abundance data for a suite of type 3.0 COs. Included in this quantification are amorphous Fe-bearing silicate abundances; which are a major component of CO 3.0s. We use the determined bulk mineralogy of these primitive COs as the starting point for our model of aqueous alteration. COs have been suggested as likely related to CMs on the basis of petrographic criteria, e.g., chondrule sizes; a CO-CM connection is also supported by similarities in O-isotope compositions between bulk CO samples and anhydrous separates extracted from CMs [4]. Oxygen isotope compositions have been determined for the same CM powders used in these XRD studies [5]. In 3 O-isotope space a trend line ($R=0.9$) through CM bulk compositions is very close to intersecting the main CO population ($\delta^{17}\text{O}=-3.68\pm 0.68\delta^{18}\text{O}$). Therefore, it cannot be ruled out that COs are precursors to classified CMs and that differences in CM and CO bulk O-isotope compositions are the result of aqueous alteration. (To the contrary, nano diamond and organic abundances are higher in CMs than COs, but for now we consider only bulk mineralogy). PSD-XRD patterns for COs and CMs are similar except for lesser peak intensities from olivine and pyroxene in CMs (because of alteration) and the absence of phyllosilicate diffraction peaks in COs; an expected correlation given the hypothesized CO-CM connection.

Methods: We quantify mineral abundances for phases present in amounts >1 wt.% by PSD-XRD using a pattern fitting technique [6]. Determinations for

CMs were based on 200 mg of powder; CO measurements were for 100 mg. Using Cu radiation makes it possible to determine the abundance of Fe-rich amorphous material as it induces X-ray fluorescence from Fe-bearing materials resulting in elevated backgrounds in XRD patterns that can be quantified [7]. Fe-rich amorphous materials in carbonaceous chondrites are known to include: Fe-(Ni)-sulfides, Fe-oxides, and $\text{FeO(OH)}\pm\text{H}_2\text{O}$ in addition to Fe,Mg silicates. Chondrule mesostases can also contain FeO at % levels but is more often compositionally similar to plagioclase. For some COs reported here, mass balance considerations and petrography (where studies exist) exclude >30% contributions to X-ray counts from sulfide, and/or Fe-oxide/hydroxides. Better matches to bulk compositions use materials with bulk Fe contents approximate to ferrous olivine.

Sample selection: more than 30 CMs in [1] and the following COs are used in this work: DOM 08006; DOM 08004; MIL 07193; MIL 03442; MIL 03377; MIL 05024; MIL 07182; MIL 090038; MIL 07709; MIL 05013 and DOM 10104.

Results: Modal mineralogy of COs is approximated as the following (vol.%): total olivine (29-50%); pyroxene (10-24%); feldspar (0-1.5%) magnetite (5.5-8.2%); sulfide (4.7-6.7%); metal (0.2-1.0%); phyllosilicate (0-3.3%); Fe-bearing amorphous (23-37%). In pattern fitting COs olivine was modelled with a Fo_{80} standard: olivine compositions are variable in COs but low incident beam angles (used to resolve phyllosilicate) and fluorescence complicate further deconvolutions (work is on-going). The following are modal abundances (vol.%) for CMs (some reported previously in [6]): olivine (3-23%); pyroxene (0-23%); cronstedtite (10-50%); MgFe-serpentine (22-82%); magnetite (0.5-8.4%); sulfide (0.6-5.4%); calcite (0.5-4.2%); gypsum (0-9.3%); metal (0-0.5%). Figure 1 shows abundances for CMs relative to the degree of hydration as defined by the ratio of phyllosilicate/(total olivine+pyroxene) [1,6].

Discussion: COs here contain pyroxene in greater abundances than reported in reflectance studies [8]. Below, we use the changes in mineral assemblages as a function of the degree of hydration to infer the dominant overall reactions at different degrees of hydration.

Low bulk hydration (<10 vol.% total phyllosilicate): Oxidation of metal forms magnetite ($3\text{Fe}_{(s)} + 4\text{H}_2\text{O}_{(1,g)} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_{2(g)}$). This is evidently a very

early stage reaction given that COs with <5 vol.% resolvable phyllosilicate contain >5 vol.% magnetite. Alteration in these COs is cryptic, only faint reflections from phyllosilicates (<5 vol.%) can be observed and perhaps these form during lithification. If COs were CM precursors, magnetite was destroyed in early hydration reactions, e.g., by conversion to cronstedtite.

Medium bulk hydration (50-75 vol.% total phyllosilicate): Hydration of amorphous FeMg-silicates and matrix olivine along with the oxidation of metal forms cronstedtite, e.g., $2\text{Fe}_{(\text{metal})} + (\text{Fe}^{2+}, \text{Mg})_2\text{SiO}_4 + 5\text{H}_2\text{O}_{(\text{l})} \rightarrow (\text{Fe}, \text{Mg})_2\text{Fe}^{3+}_2\text{SiO}_5(\text{OH})_4 + 3\text{H}_2$. During formation of cronstedtite, if sulfur is present, tochilinite [$6\text{Fe}_{0.9}\text{S} \cdot (\text{Mg}, \text{Fe}^{2+})(\text{OH})_2$] also forms. Subsequently, hydration of Mg-rich olivine and pyroxenes, including those in chondrules, forms MgFe-serpentine [$(\text{Mg}, \text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$] and tochilinite reacts, forming Fe, Ni-sulfides such as pentlandite. This explains XRD detection of tochilinite in only the least altered CMs. As hydration progresses, these reactions systematically increase abundances of MgFe-serpentine (Fig. 1). In contrast, cronstedtite abundances cluster at ~35 vol.% early in hydration and remain constant/decline slightly as hydration increases; magnetite abundances steadily increase with hydration (Fig. 1). These variations can be explained by exchange of Mg in fluid for Fe in cronstedtite, yielding MgFe-serpentine plus magnetite.

High bulk hydration (>80 vol.% total phyllosilicate): Saponite is not abundant enough to be detected in XRD patterns until late stage alteration, once pyroxene begins to contribute more to the hydrating fluid, increasing activities of Si and Al. Its abundance is difficult to resolve, but if saponite were to host all Al, a maximum 5 vol.% is possible in a bulk CM. Dissolution of sulphide and reaction of cronstedtite adds S and Fe to fluid leading to further increases in the abundances of Fe-oxides (e.g., magnetite; Fig. 1) and possibly also sulfates and ferrihydrite, i.e., CI like [9,10].

Observations: Abundances of total phyllosilicate and the relative proportion of FeMg-serpentine best indicate relative differences in hydration. An open question is if the 'end point' of aqueous alteration would be 100 vol.% phyllosilicates, or a more diverse mineralogy similar to CIs [9,10]. All samples preserving anhydrous silicates indicate that the fluid supply ceased; explaining why requires defining the initial water contents of parent bodies.

Mineral evolution, measured vs. model: The sequence of mineral evolution revealed by bulk mineral abundances agrees with models [2,3], indicating that the consequences of contrasting mineral reactivity are being accounted for. Our data emphasize the need to consider amorphous silicates in hydration reactions; this may be the main component of pristine matrices.

Initial water mass fraction: At inferred parent body temperatures (0-50°C), cronstedtite is not predicted to form until the water mass fraction reaches ≥ 0.5 and is more efficiently formed at even higher water mass fractions ≤ 0.8 [2]. A water mass fraction of 0.5 is the upper limit for typical asteroidal materials [2,4]. However, if only matrix is involved in the initial reactions, the effective water/rock ratios could be much higher than the bulk and allow cronstedtite to form early.

A bulk water mass fraction of 0.5 yields an asteroid with a bulk H content of 5.5wt%, more than twice the typical content of unheated CMs [1]. Oxidation and loss of H_2 during hydration reactions to produce a typical CM mineralogy can account for only ~60% of the initial H. If the initial water mass fraction was 0.5, >40% of the initial H must be lost by means other than mineral forming reactions, e.g., possibly by degassing.

Amorphous Fe-silicate abundances (~30 vol.%) in COs are close to the cronstedtite abundances in CMs, leading to another (testable) hypothesis: *the precursor to cronstedtite is mostly amorphous FeMg-silicate*. If the thermodynamic stability of amorphous silicate allows its reaction to cronstedtite at water mass fractions <0.5, bulk CM mineralogy could be reconciled with lesser initial water mass fractions and volatile losses.

Conclusion: Modal data for COs are a convenient starting point to consider aqueous alteration from (even if not proto CM materials). The importance of defining initial water mass fractions in asteroids and the origin of amorphous silicate and cronstedtite is greater than explaining sample mineralogy. Violent degassing might have rendered asteroids cavernous, loosely consolidated rubble piles: hard to land on or capture.

References: [1] Alexander C.M.O'D. et al. (2013) *GCA*, 123, 244-260. [2] Zolotov M. (2014) *Icarus*, 228, 13-26. [3] Dyl K. et al. (2006) *LPS 37th*, Abstract #2060. [4] Clayton R.N. & Mayeda T.K. (1999) *GCA*, 63, 2089-2014. [5] Howard K.T. et al. (2013) *LPS 44th*, Abstract #2520. [6] Howard K.T. et al. (2011) *GCA*, 75, 2735-2751. [7] Howard K.T. et al. (2010) *GCA*, 74, [8] Cloutis E.A. et al. (2012) *Icarus*, 220, 466-486. [9] Scott E. et al. (1999) *Science*, 286, 1331-1335. [10] King A. et al. (2014) *LPS 45th*, in press.

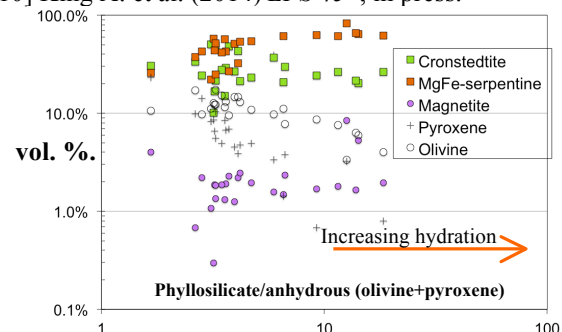


Fig. 1. Evolution of CM bulk mineralogy