MINERALOGICAL, SPECTRAL, AND COMPOSITIONAL CHANGES DURING HEATING OF HYDROUS CARBONACEOUS CHONDRITES.

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Introduction: Hydrous carbonaceous chondrites experienced hydration and subsequent dehydration by heating, which resulted in a variety of mineralogical and spectral features [e. g., 1-6]. The degree of heating is classified according to heating stage (HS) II to IV based on mineralogy of phyllosilicates [2], because they change, with elevating temperature, to poorly crystalline phases and subsequently to aggregates of small secondary anhydrous silicates of mainly olivine. Heating of hydrous carbonaceous chondrites also causes spectral changes and volatile loss [3-6]. Experimental heating of Murchison CM chondrite showed flattening of whole visible-near infrared spectra, especially weakening of the 3μm band strength [1, 4, 7].

In order to understand mineralogical, spectral, and compositional changes during heating of hydrous carbonaceous chondrites, we have carried out systematic investigation of mineralogy, reflectance spectra, and volatile composition of hydrated and dehydrated carbonaceous chondrites as well as experimentally-heated hydrous carbonaceous chondrites. In addition, we investigated reflectance spectra of tochilinite that is a major phase of CM chondrites and has a low dehydration temperature (~250°C).

Experimental: We performed synchrotron X-ray diffraction (XRD) analysis of 19 hydrated CM chondrites (LEW85311, LAP03718, GRA06172, GRO95566, LEW87022, LAP02333, DNG06004, LAP02269, MAC88176, LAP02336, LEW87148, ALH85013, MCY05230, MAC88100, LON94101, LAP031166, MET01072, Murchison, and Murray) and 6 dehydrated CM and CI chondrites (Y-793321 HS-II, Jbilet Winselwan HS-II, Y-982086 HS-II, Y-86720 HS-II, B-7904 HS-IV, DHO735 HS-IV and Y-980115 HS-II) in order to understand bulk mineralogy of fine-grained matrix material. For most of these samples, petrographic observation and quantitative chemical analysis were carried out by electron microscopes.

In addition, reflectance spectra of all samples were measured over the wavelength range of 0.4-15μm and under vacuum conditions using a Bruker VERTEX70v. Detailed results of the dehydrated chondrites are reported separately [8].

A large tochilinite grain from DNG06004 CM chondrite was analyzed by FE-SEM and reflectance spectra by micro FT-IR. Terrestrial tochilinite mineral samples from Pennsylvania and Cross Quarry (Quebec) were

was also investigated by the same procedure for comparison.

We performed heating experiments of Muchison and Tagish Lake meteorites at 400, 600, and 900°C for 50 hours under vacuum conditions at IW oxygen fugacity. Unheated samples and heated products were measured for chemistry and mineralogy by XRD, reflectance spectroscopy, and C isotope ratios and concentrations. Water contents were measured by stepped heating at 105, 200, 300, 400, 600, 800, and 950°C, using the Karl Fischer titration (KFT) method that can directly quantify water content. Some results of heating experiments of Murchison were already reported in [7].

Results and discussion: Petrographic observation of hydrated CM chondrites indicates that 17 CMs are classified to CM2.0 to 2.6 based on the existing classification scheme [9]. Synchrotron XRD analysis showed that serpentine is a major phase of all samples and (001) interlayer spacing range from 7.04 to 7.23Å, tochilinite is present in most of the samples except for those of low petrologic type (ALH85013 CM2.2, MAC88100 CM2.1, and LAP031166 CM2.1), and the mixed-layer tochilinite and serpentine (cronstedtite) phase was detected from many samples but not in the samples with no tochilinite. The shortest (001) spacing is detected from samples with the highest petrologic type, LEW85311 CM2.6 (7.06Å) and LAP03178 CM2.6 (7.04Å): the shorter spacing indicates higher rates of substitution of Si^{4+} by Fe^{3+} in tetrahedral layers in serpentine (thus more cronstedtite), suggesting serpentine in CM2.6 samples is enriched in Fe^{3+}, consistent with previous compositional analysis [e. g., 9].

Reflectance spectra of these 17 CMs plus Murray and Murchison showed that the 0.7μm absorption is observed in many samples, especially samples with 2.4 and higher petrologic type. On the other hand, the 3μm absorption is observed from all 19 samples and the peak position of the 3μm band (the the deepest absorption position) varies between samples from 2.70 to 2.84μm. This peak position positively correlates with petrologic type, as pointed out by [10], but the correlation is not obvious like that reported in [11]. In order to uncover the reason for the imperfect correlation, we focused the spectra of tochilinite (see also [3]). A large type-I TCI (200μm in size and dominated by tochilinite) in the DNG06004 CM2.4 sample showed the peak position of the 3μm band at 2.79μm, which is apparently higher than the serpentine-rich matrix (2.76μm) in the same

meteorite. This suggests that the deepest absorption position of bulk CM chondrite is affected by the tochilinite/serpentine ratio, in addition to the Mg/Fe ratio of serpentine which correlates with petrologic type.

Experimental heating of the Murchison sample shows mineralogical, compositional, and spectral changes with increasing temperature. S-XRD analysis of the Murchison samples shows that tochilinite and Fe-rich serpentine decompose at 400°C, serpentine decomposes completely and poorly-crystalline secondary olivine and taenite form at 600°C, and crystallization of secondary olivine and taenite progresses at 900°C. The mineralogical changes occuring at 400, 600, and 900°C correspond to mineralogical signatures observed in CM samples of heating stage II, III, and IV [2]. For example, Jbilet Winselwan (HS-II) shows XRD patterns similar to Murchison heated at 400°C.

Overall reflectance of the Murchison samples decreases from unheated to 400°C and then increases toward higher temperature: reflectivity at 2.5 µm is 0.1, 0.06, 0.07, and 0.19 for unheated, 400-, 600- and 900°C-heated Murchison, respectively, and the results are consistent with those of a previous study [4]. The increase of reflectance of the 900°C-sample is probably due to loss of carbonaceous material. Our C analysis indicates that approximately 80% of carbon is lost by 900°C heating, suggesting that the sample becomes brighter due to loss of low-reflectance IOM.

The 0.7µm band disappears at 400°C, indicating that Fe serpentine is decomposed. The 3µm band becomes shallower with heating, but never disappears at 900°C because of the presence of adsorbed and "rehydrated" water. The peak position of the 3µm band shifts with increasing heating temperature (unheated: 2.82 µm, 400°C: 2.74 µm, 600°C: 2.84 µm, 900°C: 2.89 µm). The broad shape of the 3µm band of 600 and 900°C samples apparently suggests the presence of adsorbed water that covers the sample surface when the heated samples were exposed to air after the heating experiments.

900°C-heated Murchison shows absorptions at 1, 1.3, 5.7, 6, 9.2 and 10 µm features attributed to olivine, suggesting secondary olivine formation. These absorptions are also observed in HS-IV samples such as DHO-735. In mid-infrared reflectance spectra, the Christiansen feature of unheated Murchison is located at 8.5 µm, and then shifts to longer wavelength up to 9.6 µm with increasing heating temperature. The strength of the 11.5µm phyllosilicate reststrahlen feature decreases and that of 12.5 µm olivine feature increases when temperature is increased like shown in [5].

Water content decreases with increasing heating temperature: from 9, 6, 1, 0.6 wt% for unheated, 400, 600, and 900°C-heated Murchison samples, respectively. This indicates dehydration occurs from tochilinite (mainly at 400°C) and serpentine (mainly at 600°C) during heating. We observed the presence of "rehydrated" water which was released at higher temperatures than adsorbed water. For example, in the case of 600°C-heated Murchison sample, more than 95% of the water is released below 600°C, although the sample has already been heated at 600°C for 50 hours. This indicates that most of water in this sample is rehydrated water, which seems to tightly bind with samples, because the largest release was observed at 400°C during stepped heating KFT analysis. The dehydrated water dominates also in the 900°C-heated Murchison sample.

We conclude that CM carbonaceous chondrite samples are almost completely dehydrated by 50 hour heating at 600°C, which is consistent with mineralogical and spectral changes indicating complete phyllosilicate decomposition and secondary olivine formation. In addition, CM samples that were once dehydrated at 600~900°C are "rehydrated" by atmospheric water when exposed to the lab atmosphere after experimental heating. In the same way, in the case of dehydrated carbonaceous chondrite samples that are classified to HS-III and HS-IV, water is dominated by adsorbed and rehydrated water.

Heating experiments of the Tagish Lake chondrite show mineralogical, compositional, and spectral changes basically similar to Murchison. The major difference is the decomposition temperature of hydrous phases: a major phyllosilicate of Tagish Lake is saponite that has a higher decomposition temperature than serpentine. Therefore, the 600°C-heated Tagish Lake sample still retains some saponite.

Based on Ar-Ar dating, the heat source for dehydration for three HS-IV samples was suggested to be solar radiation heating and/impact heating and not long-term [26]Al heating [12] because heating occurred relatively recently. The small grain size of recrystallized olivine and lack of Fe-Mg zoning in these HS-IV sample are also consistent with short-duration heating.

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