**THE COMPARATIVE STUDY FOR AQUEOUS ALTERATION AND THERMAL RECORDS IN CR CHONDRITES BY RAMAN SPECTROSCOPY.** M. Komatsu[1,2], T. J. Fagan[2], A. Yamaguchi[3], M. Yasutake[3,4], M. Kimura[3], T. Mikouchi[5], and M. Zolensky[6]. [1]SOKENDAI, The Graduate University for Advanced Studies, Japan (komatsu_mutsumi@soken.ac.jp), [2]Dep. of Earth Sciences, Waseda University, [3]National Institute for Polar Research, [4]Japan Synchrotron Radiation Research Institute, [5]University Museum, The University of Tokyo, [6]ARES, NASA Johnson Space Center, Houston, USA.

**Introduction:** CR chondrites are a primitive group of carbonaceous chondrites that preserve records of the formation of their components in the solar nebula [e.g., 1-3]. Although they do not show much evidence for thermal metamorphism, they have been affected by variable degrees of aqueous alteration [4]. We have been investigating the petrologic variations among the CR chondrites in the NIPR Antarctic meteorite collection. In this study, we focus on the petrology and Raman characteristics of chondrules and matrices in CR chondrites in order to understand the secondary processing of the CR chondrite parent body(-ies).

**Samples and methods:** Polished thin sections of nine CR chondrites Y-790112, Y-791498, Y-792518, Y-793261, Y-793495, Y 982405, A-8449, A-881828, and A-881595 were studied using JEOL JSM-7100F FE-SEM. The extent of aqueous alteration was estimated from the preservation of glass in chondrule mesostasis, textural replacement of chondrule phenocrysts.

The degree of thermal metamorphism of the meteorites was examined using Raman spectra of matrix grains collected with a JASCO NRS-1000 Raman Spectrometer at NIPR. Tagish Lake (C2-ungr), Murchison (CM2), ALH-77307 (CO3.0), Efremovka (CVred), and Allende (CVox), were also examined for comparison. Raman spectra were acquired with similar conditions of [5-7] from polished thin sections under atmospheric conditions in the spectral region 1000–1800 $cm^{-1}$. The Raman constraint on metamorphic temperature is based on the G- and D-bands (associated with graphite and defects, respectively) in the carbonaceous matter. The first-order carbon bands were fitted with two components, a Lorentzian profile for the D band, and Breit-Wigner-Fano (BWF) profile for the G band, with Origin 2020b software.

**Results and Discussion:**

*Aqueous alteration of CR chondrites*

CR chondrites are composed of chondrules, refractory inclusions, mineral fragments, and fine-grained matrix. They show variable degrees of aqueous alteration that resulted in the replacement of chondrule glass and matrix by phyllosilicates, and of Fe,Ni-metal by magnetite and Fe-sulfides; olivine and pyroxene phenocrysts in chondrules are also replaced by Fe-rich phases in the heavy altered samples as suggested by [8].

Many chondrules in CR chondrites have rims composed of Fe-rich phases. In the samples with weak aqueous alteration, clear boundary rims around chondrules are easily recognized and may have two distinct layers (Fig. 1a, b). This type of smooth two-layered rim is also described in slightly altered CR samples QUE 99177, MET 00426, and LAP 02342 [8]. In some cases, the rim consists of a layer with "honeycomb" structure described by [8] (Fig. 1a) and silica-rich layer [9; Fig. 1b]. Boundary layers become less clear in the samples with mild aqueous alteration (Fig. 1c), and are not observed in the sample with heavy aqueous alteration (Fig. 1d). Sample Y 982405 exhibits only little aqueous alteration, but boundary layers on chondrules were not observed. In this sample olivine grains in chondrules show Fe-enrichment on grain boundaries, suggesting the Fe introduction probably due to thermal processing.

Based on these characteristics and previous observations of amoeboid olivine aggregates [10], we classified the CR chondrites into four groups as follows (Table 1):

1. Little aqueous alteration: Y-791498, A-881828
2. Early to intermediate aqueous alteration: Y-8449, Y-792518, Y-793261, Y-790112
3. Heavily aqueous alteration: Y-793495, A-881595
4: Little aqueous alteration, mild thermal metamorphism: Y 982405

Here we compare the sequence of increasing aqueous alteration in CR chondrites and their Raman tracers focusing on the D-band, which is more sensitive to thermal processing than the G-band [11].

*Examination of Raman tracers*

Raman parameters of the observed D and G bands of carbon in the matrix of the carbonaceous chondrites (the coefficient of determination $R^2$>0.90) are shown in Table 1 and Fig. 2. Raman spectra of CR chondrites show variable intensities of fluorescence background, which results in a fitting error (low value of $R^2$) especially for the G-band in some cases.

Raman parameters obtained from CR2 samples show a large scatter (Fig. 2). Wide D-bands in the CR chondrites except Y 982405 are characteristic of highly disordered carbonaceous materials [11]. The relatively narrow bandwidth of the D-bands observed in Y 982405 is probably caused by thermal metamorphism, such as in Efremovka [7, 11].

Regarding the degree of aqueous alteration, petrologically primitive CRs (Y-791498 and A-881828) have relatively high values of peak position of D-band compared to other CRs, but no visible relationship between the Raman tracers and degree of aqueous alteration is observed. Indeed, it is suggested that there is little or no correlation between Raman parameters of IOM and the degree of aqueous alteration of CM2 chondrites [11]. Our observation of CR chondrites supports the conclusion of [11] that the record of aqueous alteration is not visible in the Raman tracers.

We do not observe any correlation between the maturation grade and the degree of aqueous alteration among CR chondrites, however, the metamorphic trends of D and G bands observed in this study are the same as determined from previous studies of matrix raw grains or extracted IOM [5, 6, 7, 11]. The low thermal maturity of the organic matter indicated by Raman spectra from datasets in [5-7] and [13] show that most CR chondrites did not undergo thermal metamorphism to the same extent as most ordinary, CO and CV chondrites, supporting the primitive nature of CR chondrites.

**References:** [1] Weisberg M. K. et al. (1993) *GCA*, *57*, 1567-1586. [2] Krot A.N. et al. (2002) *MaPS*, *37*, 1451-1490. [3] Komatsu et al. (2018) *PNAS*, 1722265115 [4] Brearley A. J. (2006) *MESS II*, 584-624. [5] Quirico et al. (2003) *MaPS*, *38*, 795-881. [6] Bonal L. et al. (2006) *GCA*, *70*, 1849-1863. [7] Bonal L. et al. (2007) *GCA*, *71*, 1605-1623. [8] Harju E.R. et al. (2014) *GCA*, *139*, 267-292. [9] Krot A.N. et al. (2004) *MaPS*, *39*, 1931-1955. [10] Komatsu et al. (2017) *The 8th Symp. on Polar Science*, OA_0050_01. [11] Busemann H. (2007) *MaPS*, *42*, 1387-1416.

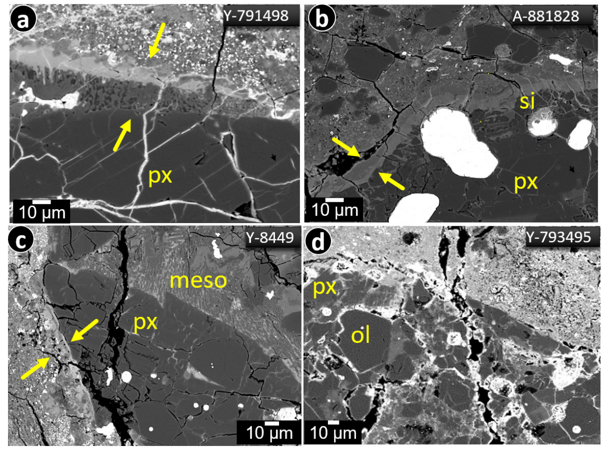


Fig. 1. BSE images of chondrule rims from CR chondrites in this study. (a, b) Chondrule rims from the sample with little aqueous alteration. (c) Chondrule with a mild aqueous alteration. (d) chondrule with a heavy aqueous alteration.

Table 1. Petrologic characteristics of CR chondrites in this study and their Raman tracers.

| | Aqueous alteration | FWHM-D | $I_D/I_G$ |
|---|---|---|---|
| Y-791498 | Little | 294.3±28.9 | 1.148±0.081 |
| A-881828 | Little | 204.7±30.2 | 0.764±0.069 |
| Y-8449 | Early to intermediate | 267.3±36.3 | 0.868±0.122 |
| Y-792518 | Early to intermediate | 335.4±37.2 | 1.177±0.063 |
| Y-793261 | Early to intermediate | 298.9±29.1 | 0.935±0.181 |
| Y-790112 | Early to intermediate | 304.9±3.0 | 0.870±0.017 |
| Y-793495 | Heavy | 312.7±37.9 | 1.260±0.082 |
| A-881595 | Heavy | 289.0±18.6 | 1.010±0.087 |
| Y 982405 | Little (Thermally altered) | 181.0±34.6 | 1.261±0.029 |

*Uncertainties are 1σ standard deviation of the mean.

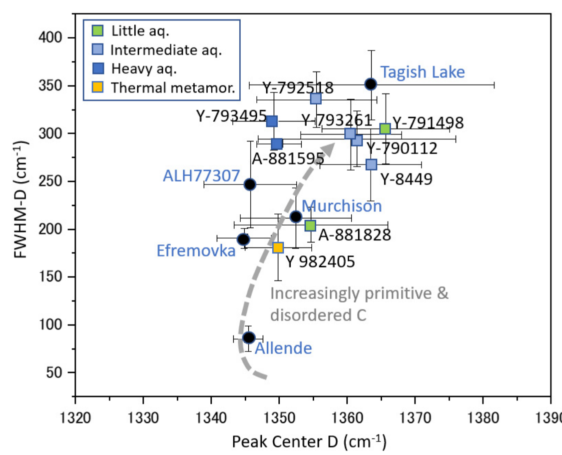


Fig. 2. D band parameters of CR chondrites in this study. Filled circles (Tagish Lake, Murchison, ALH-77370, Efremovka, and Allende) are plotted together for comparison. The trend of disordered carbon is derived from [7].