Hydrogen isotopic compositions and chemical structures of organic materials in Northwest Africa 801 CR2 chondrite: Implications for metamorphism histories of extraterrestrial organic materials. M. Hashiguchi[1] and H. Yurimoto[2], [1]Astromaterials Science Research Group, Institute of Space Astronautical Science, Japan Aerospace Exploration Agency (JAXA), Sagamihara 252-0510, Japan (hashiguchi@planeta.isas.sci.jaxa.jp), [2]Natural History Sciences, Hokkaido University, Sapporo 060-0810, Japan.

Introduction: Carbonaceous chondrites contain up to a few % of organic carbon, that mostly occur as insoluble organic materials (IOM) [1]. The IOMs show various hydrogen (H) isotopic composition [2, 3] and contain highly deuterium (D)-enriched organic globules [3-5]. It is almost universally accepted that the D-rich organic globules were formed in extreme cold environment in molecular clouds or outer region of protosolar nebula [e.g. 3-5]. D-enrichment of the meteoritic organic materials would be released by thermal metamorphism and aqueous alteration [2, 6-8]. Therefore, the D-rich organic globules are key materials for understanding of formation and evolution history of the extraterrestrial organic materials.

In our previous study, we analyzed D-rich organic globules embedded in matrix of Northwest Africa (NWA) 801 CR2 chondrite and revealed their various H isotopic composition (2,500–11,000‰) and various morphology [4, 8].

In the NWA 801 matrix, organic particles without large D-enrichment (less D-rich) also occur [4]. In this study, we investigate and compare H isotopic compositions and chemical structure of D-rich and less D-rich organic materials in the NWA 801 chondrite to understand their formation and evolution histories.

Sample and Methods: A polished thin section of NWA 801 chondrite [4, 8] was used in this study. The thin section was covered with a 30 nm thick carbon film for isotope and elemental analyses. H isotopes were measured on the thin sections by *in situ* quantitative isotope ratio imaging (isotopography) using HokuDai isotope microscope system (Cameca ims-1270 equipped with SCAPS [9]). The sample surface was homogeneously irradiated over a field area using a broad Cs^+ primary beam of ca. 60 μm in diameter. The primary beam was set to 20 keV and ca. 1 nA. A typical incident electron gun was utilized for charge compensation of the analysis area. We acquired the following negative secondary ion images (isotopographs) for each analyzing field as a sequence of $^{12}C^-$, H^-, D^-, H^- and $^{12}C^-$, typically. The selection criterion for distinguishing isotopically anomalous matter is that one of their isotopic ratios is 2 σ away from the 3 σ the distribution of the surrounding matrix. Identification and observation of D-rich and less D-rich organic materials were carried out by FE-SEM (JEOL ISM-7000F). Detailed information of the SIMS and FE-SEM analysis is described in our previous paper [4].

Elemental ratio of H and C of the organic materials were analyzed using secondary ion intensity of H^- and C^- by SIMS analysis, assuming that average H/C ratio of less D-rich organic materials is corresponding to that of CR2 IOM reported from a previous study [2].

Raman experiments were performed by Ranishaw Invia Reflex Raman microscope at the Open facility of Hokkaido University Sousei Hall. The laser power (Nd: YVO_4, 532 nm) on the sample was kept ca. 80 μW with spot size of ca. 1 μm. Raman spectra were acquired in the range 100-1800 cm^{-1} and the fluorescence background was subtracted assuming a linear baseline between 1000-1800 cm^{-1}.

Results and Discussion: Less D-rich organic particles in NWA 801 occur as sub-micron-sized globules with various morphology that can be classified as follows: ring globule, globule aggregate, round globule, irregular-shaped globule (Fig. 1), that are similar to D-rich organic globules in NWA 801 [4].

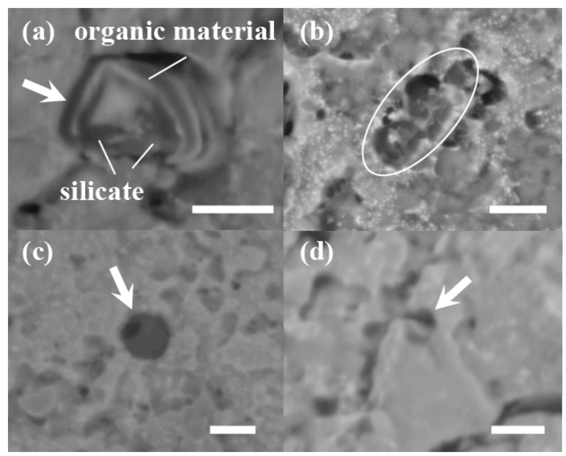

Fig. 1 Backscattered electron (BSE) images of less D-rich organic materials in matrix of NWA 801. Arrows or circle indicate the position of organic materials. They show various morphologies :(a) ring globule: a ring-shaped organic material that encloses silicate or oxide grains. (b) globule aggregate: aggregate of several organic globules. (c) round globule: a round shaped organic globule. (d) irregular-shaped globule. The classification is same as our previous study of D-rich organic globules in NWA 801 [4]. All scale bars show 0.5 μm.

Raman spectra from D-rich organic globules, less D-rich organic globule, and matrix showed D band (at ~1350–1400 cm^{-1}) and G band (at ~1550–1600 cm^{-1}). The D band and G band spectral parameters are linked to structure of organic matter [e.g. 10]. Fig. 2 shows ratio of peak intensity of the D band and G band (I_D/I_G) as a function of the full width half maximum of D band (FWHM-D). Less D-rich organic globules show similar Raman parameter to matrix organic materials, whereas D-rich organic globules can be distinguished from them. This figure indicates more metamorphosed structure of D-rich organic globules than that of less D-rich globules and matrix organics.

D-rich and less D-rich organic globules in NWA 801 showed similar H/C ratio, mostly less than 1.5 (Fig. 3). During thermal metamorphism and aqueous alteration, molecular structure of IOM is modified and their H/C ratio is decreased [2, 6]. Our observation indicates that the less D-rich organic globules in NWA 801 would not be attributed to release of D-enrichment from D-rich organic globules in same meteorite by metamorphism or alteration, despite of similarity of their morphology.

These results would mean that formation mechanism or environment, and alteration histories between D-rich and less D-rich organic globules are different. Furthermore, higher metamorphosed grade of D-rich organic globules than that of less D-rich organic globules and organics in matrix suggests that the D-rich organic globules have experienced thermal metamorphism individually.

Peak temperature during the metamorphism of D-rich organic globules is estimated about 200–400 ºC using Raman spectrum parameter ($T\ (^{\circ}C) = 931 - 5.1 \times \text{FWHM-D} + 0.0091 \times (\text{FWHM-D})^2$) reported by Busemann et al. (2007) [10]. Metamorphism with such temperature is feasible in the solar nebula or on the CR parent body [e.g. 11]. The D-rich organic globules are small (mostly sub-micron size) and distributed randomly in NWA 801 matrix coexisting with less D-rich organic globules [4, 8]. Therefore, it would plausibly be argued that metamorphism for such small D-rich organic globules have not selectively occurred on the parent body. Most possible scenario is that D-rich organic globules have been formed in ISM or outer solar nebula, and then they were metamorphosed in solar nebula at probably higher temperature than chondrite formation region (~ 3 AU) in the solar nebula. On the other hand, less D-rich organic globules have been probably formed on the parent body and experienced some degree of thermal metamorphism less than that of D-rich organic globules.

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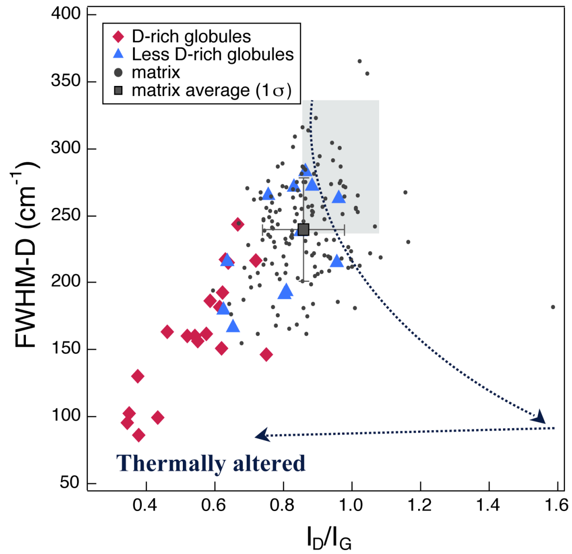

Fig. 2 Raman parameter of I_D/I_G plotted as function of FWHM-D. Arrows indicate Raman trends for thermal metamorphism, based on the data obtained from meteoritic IOM [10]. Gray area indicates range of IOM from CR2 chondrites (data from [10]).

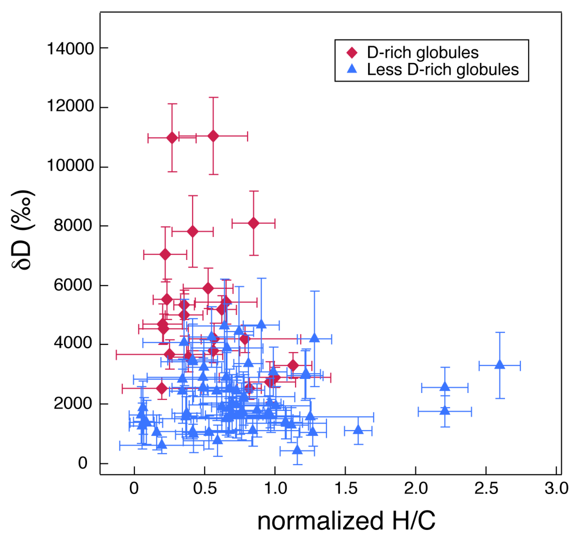

Fig. 3 Elemental ratio of H/C vs. H isotopic compositions of D-rich and less D-rich organic globules in NWA 801.