KINETIC APPROACHES TO THE THERMAL HISTORY OF CHONDRITES BASED ON RAMAN SPECTRA OF ORGANIC MATTER.

K. Kiryu[1], Y. Kebukawa[1], M. Igisu[2], T. Shibuya[2] and K. Kobayashi[1], [1]Graduate School of Engineering Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan, [2] Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan.

Introduction: A variety of chondrites contain organic matter (OM) mainly in the form of insoluble organic matter (IOM) [e.g., 1], which is composed of carbon skeletons as polycyclic aromatic hydrocarbons (PAHs) with aliphatic side chains, carboxyl, hydroxyl, and carbonyl groups [2]. The final molecular structure of OM in chondrites strongly reflects the parent body processes [e.g., 3, 4], and therefore it is an effective index for aqueous alteration and/or thermal metamorphism in the parent bodies. We made use of the nature of OM which is susceptible to heat for the sake of establishing the way to evaluate the thermal history of chondrites.

Kinetic expressions are powerful ways to predict the thermal history of OM in chondrites [e.g., 5, 6]. Raman spectral features of OM in chondrites change depending on the thermal metamorphic conditions in the parent bodies, and thus often used as an indicator of metamorphic temperatures [e.g., 7-9], but kinetic studies are limited [10]. In this study, we combined Raman spectroscopy with kinetic expression, since the changes in disordered (D_1: ~1350 cm^{-1}) and graphite (G: ~1590 cm^{-1}) bands of Raman spectra, which originate from aromatic structures, is irreversible and thus could be used as the indicators of the extent of the thermal processes. Raman spectroscopy is a useful tool for assessing the thermal history of chondrites that particularly experienced high temperature and/or long duration heating. We performed a series of heating experiments of the Murchison meteorite and kinetic analyses based on their Raman spectral parameters.

Methods: The Murchison powders were subjected to heating under low oxygen atmosphere using a gas mixture of N_2 and H_2 (99:1, v/v) for 3-48 h at 600-900°C in a vacuum gas replacement furnace. After heating, Raman spectra were collected using a Raman spectrometer with a 532 nm laser (RAMANtouch; Nanophoton), at least ten different spots for each sample to average the local heterogeneity. All of the heated Murchison showed D_1- and G-bands in the Raman spectra. We determined five Raman spectral parameters: the full width at half maximum (FWHM, Γ), the peak position (ω), and the peak intensity ratio (I_D/I_G) of the D_1- and G-bands by peak fitting to the Lorentzian and Breit-Wigner-Fano (BWF) model [11] with a linear baseline correction. The unheated Murchison and two carbonaceous chondrites with different metamorphic conditions—Allende (CV3) and Tagish Lake (C2-ung)—were analyzed with the same method, for comparison to the heated Murchison.

Results: *Raman spectra of the heated Murchison.* The five Raman spectral parameters of the heated Murchison variously changed with time at each temperature. The Γ_D appears to constantly decrease depending on the temperature and time compared to the other four Raman spectral parameters (Fig. 1, 2). Busemann et al. [9], which examined IOM extracted from 51 unequilibrated chondrites utilizing Raman spectroscopy, revealed that Γ_D is certainly one of the suitable parameters for identifying metamorphic trends in chondrites. Hence, we selected the Γ_D to further conduct kinetic analyses.

Kinetic analyses. We fitted the changes in Γ_D with

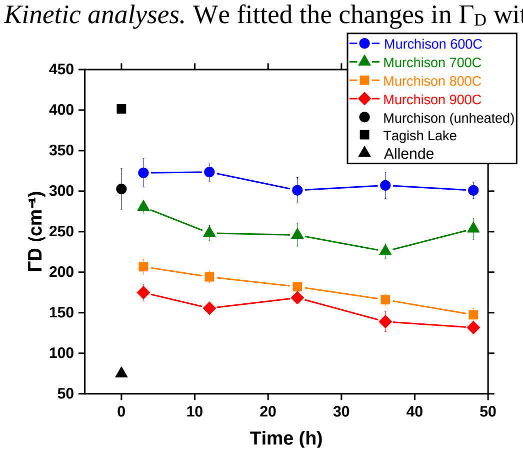

Fig. 1. Changes in the Γ_D values with time by heating at 600-900°C.

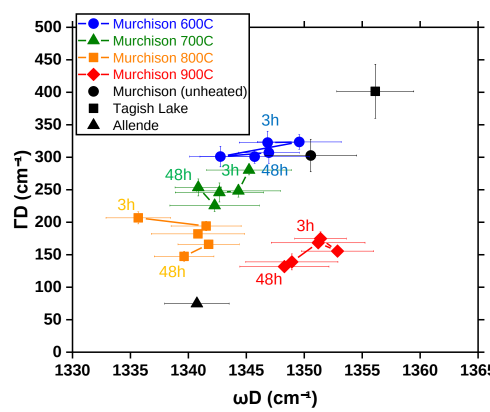

Fig. 2. Comparison of D_1-band parameters of the heated Murchison samples to those of the unheated Murchison and two carbonaceous chondrites samples.

an equation:

$$\Gamma_D = \Gamma_0 - k\mathrm{Ln}t \quad (1)$$

where t is the time and Γ_0 is the intercept which depend on the temperature T. Eq. 1 is log-linear behavior suggested by the phenomenological rate expression [5]. The apparent rate constants k and Γ_0 were obtained in this manner. Then, the apparent activation energy E and the apparent frequency factor A were determined by the Arrhenius equation (Fig. 3):

$$\ln k = \ln A - E/RT \quad (2)$$

where R is the gas constant (8.314 $\mathrm{Jmol^{-1}K^{-1}}$). The Γ_0 shows linear correlations to the temperature; accordingly we also deduced the relationship between Γ_0 and temperature as:

$$\Gamma_0 = \Gamma_i - aT \quad (3)$$

where Γ_i and a are the constants. For the decreases in Γ_D, the apparent activation energies were 16±11 $\mathrm{kJmol^{-1}}$.

The relationships between the heating time, the temperature and the Γ_D values can be described as:

$$\log t = \log \frac{\mathrm{Ln}[(\Gamma_i - aT)/\Gamma]}{A\exp(\frac{-E}{RT})} \quad (4)$$

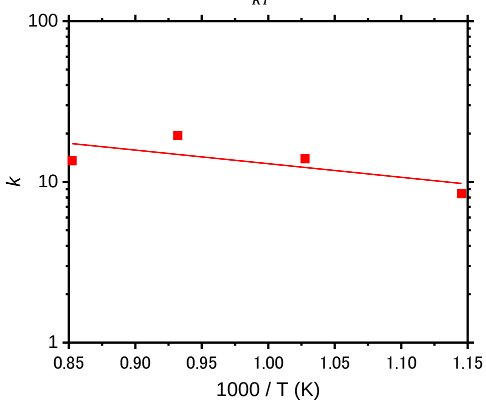

Fig. 3 Arrhenius diagram of thermal changes in the Γ_D values of the Murchison samples.

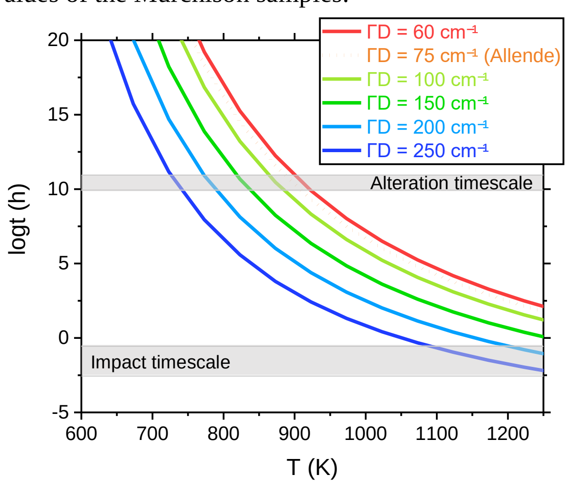

Fig. 4. Time-Temperature-Transformation (T-T-T) diagrams for various Γ_D values (60-250 $\mathrm{cm^{-1}}$) in the case of utilizing log-linear model. The calculation of Γ_D value of the Allende meteorite (75 $\mathrm{cm^{-1}}$) is shown in a dotted curve.

using eqs. 1 to 3. Combining these equations, time–temperature–transformation (T–T–T) diagrams of Γ_D can be generated (Fig. 4).

Discussion: We discussed the validity of the result through referring to Cody et al. [5] and Kebukawa et al. [6], which similarly estimated the thermal history of OM in chondrites adopting kinetic expressions. Compared to the values reported by the two previous studies [5, 6], in fact, T-T-T diagrams of Γ_D given by this study can be better tools in chondrites that especially underwent higher temperature and longer duration heating in the parent bodies. To the contrary, they might be insufficient in the estimation for a range of lower temperature and/or shorter duration heating. The trend shows that Γ_D tends to not change with heating as much as other indicators such as exciton intensity [5] and aliphatic C-H [6].

In order to check the result of this study in detail, we calculated the thermal history of Allende on the basis of T-T-T diagrams of Γ_D (Fig. 4). Assuming the alteration period of ~10^6-10^7 years, the temperature could be ~900 K for Allende (Fig. 4). The value is in agreement with peak metamorphic temperatures (PMT) for Allende investigated by previous studies to some extent, e.g., ~823-873 K [4], ~803-863 K [9], >859 K [12], and ~834-876 K [13]. It justifies the validity of T-T-T diagrams of Γ_D, allowing for the fact that the experiments were performed in shorter duration conditions compared to asteroids. The result of this study enables us to utilize Γ_D as functions of the heating temperature and the time in thermally metamorphosed chondrites.

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