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 (D1: ~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 N₂ and H₂ (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 D1- 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 D1- 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 ΓD 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 ΓD is certainly one of the suitable parameters for identifying metamorphic trends in chondrites. Hence, we selected the ΓD to further conduct kinetic analyses.

Kinetic analyses. We fitted the changes in ΓD with
an equation:
\[ \Gamma_D = \Gamma_0 - k \ln t \]  
where \( t \) is the time and \( \Gamma_0 \) 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 \( \Gamma_0 \) 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):
\[ \ln k = \ln A - \frac{E}{RT} \]  
where \( R \) is the gas constant (8.314 Jmol\(^{-1}\)K\(^{-1}\)). The \( \Gamma_0 \) shows linear correlations to the temperature; accordingly we also deduced the relationship between \( \Gamma_0 \) and temperature as:
\[ \Gamma_0 = \Gamma_1 - aT \]  
where \( \Gamma_1 \) and \( a \) are the constants. For the decreases in \( \Gamma_D \), the apparent activation energies were 16±11 kJmol\(^{-1}\).

The relationships between the heating time, the temperature and the \( \Gamma_D \) values can be described as:
\[ \log t = \log \left(\frac{\Gamma_0 - aT}{A\exp\left(\frac{E}{RT}\right)}\right) \]  

![Arrhenius diagram of thermal changes in the \( \Gamma_D \) values of the Murchison samples.](image)

Using eqs. 1 to 3. Combining these equations, time–temperature–transformation (T–T–T) diagrams of \( \Gamma_D \) 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 \( \Gamma_D \) 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 \( \Gamma_D \) 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 \( \Gamma_D \) (Fig. 4). Assuming the alteration period of \( \sim 10^7 \) years, the temperature could be \( \sim 900 \) 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., \( \sim 823-873 \) K [4], \( \sim 803-863 \) K [9], \( \sim 859 \) K [12], and \( \sim 834-876 \) K [13]. It justifies the validity of T–T–T diagrams of \( \Gamma_D \), 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 \( \Gamma_D \) as functions of the heating temperature and the time in thermally metamorphosed chondrites.

**Acknowledgments:** We would like to acknowledge Dr. Mike Zolensky for providing the meteorite samples. This study was supported by JSPS KAKENHI.