

Maturity evaluation of source rocks using Raman and fluorescence spectroscopy

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Petroleum source rocks containing carbonaceous materials are called kerogens. There are some conventional methods to evaluate maturity of kerogens. For example, vitrinite reflectance ($R_0\%$) has been widely used to evaluate maturity of carbonaceous materials. However, vitrinite reflectance has a limitation in a spatial resolution (10 micrometers) and requires time-consuming sample preparations.

As a complementary method, Raman spectroscopy has been applied to evaluate maturity of carbonaceous materials. Kouketsu et al. (2014)^[1] proposed an analysis to separate Raman spectra of low-maturity carbonaceous materials into four bands (D1-, D2-, D3-, and D4-bands). However, it is extremely difficult to observe Raman spectra of much lower maturity carbonaceous materials because of fluorescence interference caused by functional groups and conjugated systems. This study aims to develop the versatile measure applicable to low-mature carbonaceous materials using complementary spectroscopic methods.

Kerogens extracted from cuttings and core samples from two wells (Shin-Ayukawa AK-1^[3] and MITI Yurioki-Chubu, Akita prefecture) were analyzed. It was reported that the maturity data^[3] of samples from Shin-Ayukawa increase drastically in the depth region (1550 m ~ 1950 m) because of dolerite intrusions (Waseda et al., 1995). The values of vitrinite reflectance data were measured over 100 points per sample. Raman spectra were measured on the same points where vitrinite reflectance values were measured using a 514.5 nm Ar⁺ laser for excitation with a power of 0.2 mW at the sample surface. Fluorescence spectra were obtained on a compact spectrometer (USB 2000, Ocean Optics) in a range of 515 nm ~ 850 nm. Infrared spectra of carbonaceous materials were obtained with a transmittance mode using an IR microscope. Mass spectra of hydrocarbons were extracted from cuttings samples.

Vitrinite reflectance data from Shin-Ayukawa ranged from 0.1% to 3.7% with increasing depth except for samples affected by dolerite intrusions. The slope values of Raman baseline decreased from 100 to 0.1 (counts / cm⁻¹) with increasing vitrinite reflectance values in the whole range (Fig. 1). The values of full width at half maximum (FWHM) of Raman D2-band decreased from 110 to 50 (cm⁻¹) with increasing vitrinite reflectance from 0.3% to 3.7%. The Raman bands of kerogens less than 0.3% of vitrinite reflectance cannot be detected. Fluorescence intensities of kerogens from Yurioki-chubu decreased with increasing vitrinite values reflectance from 0.1% to 0.6% (Fig.2). It should be noted that fluorescence spectra can apply for samples with low vitrinite reflectance where Raman bands cannot be detected. With increasing depth, intensities of infrared absorption bands assignable to amides and ethers became weak, while those of alkenes and aromatic rings became strong.

In summary, the fluorescence spectra inferred from the slopes of Raman spectra and its intensities show correlation with the vitrinite reflectance in the ranges of $R_0 = 0.1\% \sim 3.7\%$ and depth of 1050 m ~ 4900 m. This study proposes a spectroscopic method applicable to lower maturity carbonaceous materials.

[1] Kouketsu *et al* (2014), *Island Arc*. 23, 33-50.

[2] Koutetsu *et al* (2015), *JpGU*.

[3] Waseda *et al.* (1995), *Res. Org. Geochem.* 10, 1-5.

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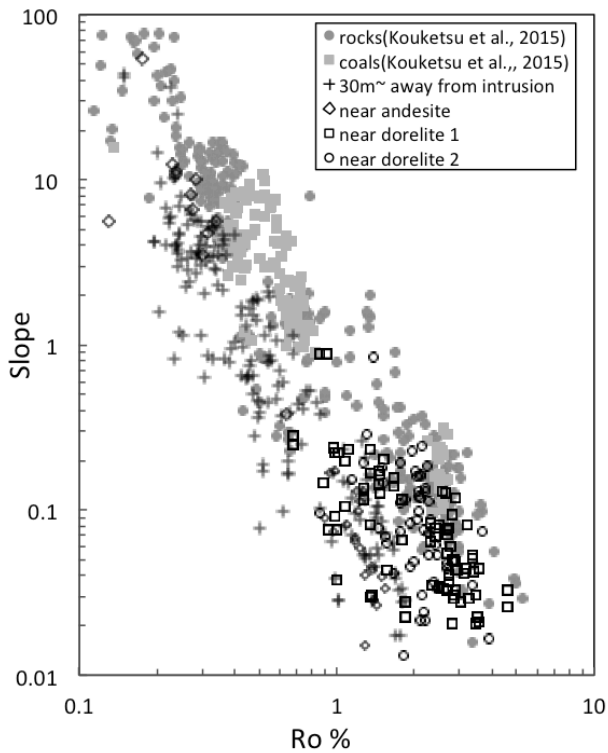


Fig.1 Correlation of vitrinite reflectance and slope of Raman baseline of kerogens from Shin-Ayukawa and previous study

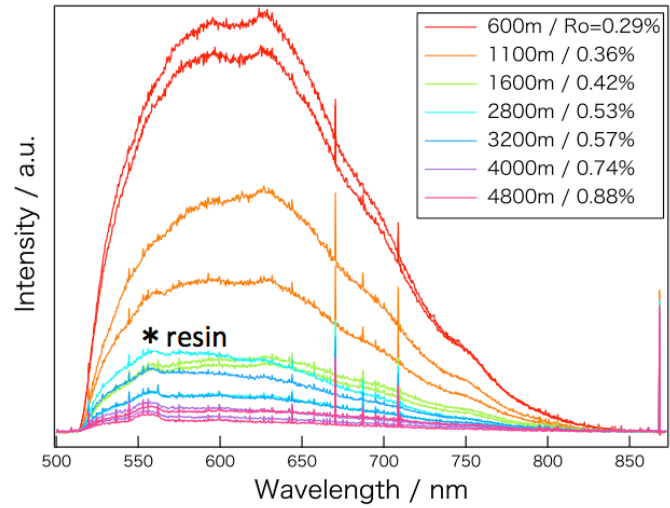


Fig.2 Fluorescence spectra of kerogens from Yurioki-Chubu