Metamorphism Trend in Some Mongolian Coals Revealed by Raman Spectroscopy

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Raman scattering spectra of the representative samples from Mongolian low metamorphic coal deposits as of Sharyn-Gol, Baganuur, Nalaikh, Alagtolgoi and Dovt were measured. Total carbon content of these samples was measured by X-ray microanalysis method. An existence of graphite-like domains in vitrinite of the low metamorphism coals has been revealed by the Raman measurements. A Raman amorphous A band at 1342-1364 cm^{-1} is less intense and broader than that of a graphitic G band at 1560-1580 cm^{-1} for all studied samples. The graphitic G band is found to be shifted to higher frequencies within 1560-1580 cm^{-1} with a decrease of coal maturity, while the Raman amorphous-graphitic band intensity ratio $R=f_A/f_G$ is found to be increased.

I. INTRODUCTION

The energy sector of Mongolia based almost only on a coal mining represents both a significant economic hope and a considerable environmental threat for the country. Consequently, coal processing into clean charcoal or other refined products through proven, existing modern technology is highly required. In these circumstances, start of structural characterization analysis of all kinds of Mongolian coals also represents immediate task.

The high sensitivity Raman spectroscopy has been found useful for defining the level of organic metamorphism (LOM) in carbonaceous natural objects. For example, the degree of structural order of polyaromatic chains in coals can be characterized using Raman spectra, simply because spectral frequencies are principally assignable to carbonaceous functional groups.

In this work Raman spectra of five coal samples from the biggest Mongolian coal deposits were measured and used to characterize their LOM. Total carbon content of the four coal deposit samples determined by X-ray microanalysis method was used as references for the studied coal samples.

II. EXPERIMENTAL

Freshly broken surfaces of the coal samples from the Sharyn-Gol, Baganuur, Nalaikh, Alagtolgoi, and Dovt coal deposits were radiated by focused laser beam to excite Raman scattering spectra. Spectra were excited by 50 mWt power, 647.1 nm red light of an argon-ion laser (Innova 90) and recorded with a Horiba Jobin Yvon T 64000 spectrometer. The Raman spectra in the 4000-250 cm^{-1} range of wave number of each coal sample was recorded in an usual laboratory condition for 4 times by 1 sec data acquisition at each spectral position and then four spectra were averaged to reach the best possible signal-to-noise ratio. Spectra recorded from different spots standing within 1-3 mm each other on a sample surface were similar in background fluorescence wide band intensity, shape, and Raman narrow bands.

Raman bandwidth analysis was done using a standard curve resolution algorithm and a multiple point correction for background subtraction to distinguish the amorphous (f_A) and graphitic (f_G) Raman scattering clear bands of a carbonated molecular species in samples.

A total carbon content of four coals (Sharyn-Gol, Baganuur, Nalaikh, Alagtolgoi) was determined by scanning electron microscopy (LEO1455VP, Carl Zeiss, Germany) with X-ray microanalysis using energy dispersive SiLi-detector (Rontec, Germany) and the determined values were used as a measured maturity of the samples.

III. RESULTS AND DISCUSSION

It seems reasonable to expect an equal number of spectral frequencies of Raman scattering and infra-red absorption bands [1, 2] in organic matter, but for these coal samples a number of Raman bands is much fewer than a number of their FTIR bands [3-7]. For the coal samples studied, two intensive Raman bands of carbon in the wave number range of 1520-1600 and 1340-1370 cm^{-1} were well dominated (see Table 1) over broad weak shoulders in the region of 1900 and 2750-2850 cm^{-1}.

A Raman band around 1560-1580 cm^{-1} is from a CH bond stretching of all pairs of sp^2 atoms in both rings and chains labeled graphite-like (G) and a peak near 1342-1364 cm^{-1} is assigned to the breathing modes of sp^2 atoms in rings [8-12]

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labeled amorphous (*A*) or defect (*D*), which are typical to the Raman spectra of the bituminous coal.

Table 1: Raman frequencies in the some Mongolian coal samples

Coal sample name	Raman bands			
	ν, cm^{-1}	Band assignment	ν, cm^{-1}	Band assignment
Sharyn-Gol	1344		1560	
Baganuur	1357		1571	
Nalaikh	1364	Amorphous C-H bending	1578	Graphite-like C-H bending
Alagtolgoi	1363		1580	
Dovt	1342		1574	

The graphitic band shift to higher frequencies within 1560-1580 cm^{-1} means a disorder increase of carbon CH bonds in a coal vitrinite structure. It is generally observed for coals that the *A* band at 1342-1364 cm^{-1} is less intense and broader than the graphitic band *G* at 1560-1580 cm^{-1}. As shows in Figure 1 (spectrum 1 and 2), for the coals from Sharyn-Gol and Baganuur, *A* peaks are comparable or stronger than neighboring *G* peaks, which may be explained as a relatively increased number of disorder defects with an increased number of broken Raman transition rule in these samples. Similar behavior has been observed in Raman spectra of bituminous coal previously [13]. It is also found that during metagenesis and beyond, the intensity of the *G* band increases while the *A* band decreases with an increasing sample maturity [13]. This phenomenon has been also observed here and shows metamorphism level of the coals studied.

A band near 1900 cm^{-1} is clearly appeared on the shoulder of the graphitic bands of Sharyn-Gol and Baganuur coal samples (Figure 1, spectra *1* and *2*), while this band is negligible for the rest of the coals. Therefore, we assume that this weak band at 1900 cm^{-1} is from defect disorder-induced vibrations. Low intense broad band near 2800 cm^{-1} is usually attributed to CH stretching vibration. This band has been registered clearly on the spectra of Dovt coal (Figure 1, spectra *5*).
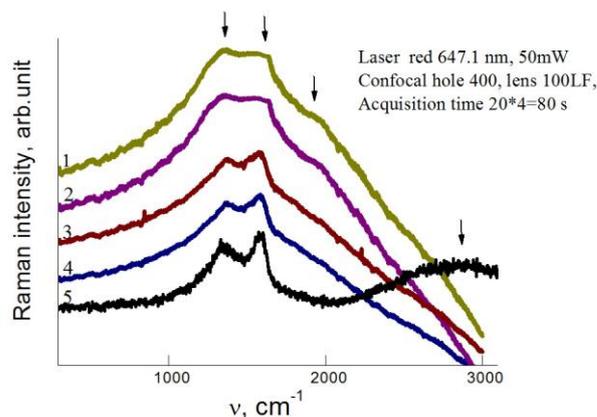

Figure 1: Raman spectrums of the coal samples (1– Sharyn-Gol, 2 – Baganuur, 3 – Nalaikh, 4 – Alagtolgoi, 5 – Dovt)

Images of fresh broken cleavage surface of coals from the optical microscope (Olympus) with a magnification of 100 were made to reveal heterogeneity in a structure of the studied coals. The typical image of Sharyn-Gol coal sample (Fig. 2) shows a thin (1-10 μm thick) yellowish-brown color inclusive of mostly oxidized organic matter included between coal vitrinite domains. Sharin Gol coal sample was the richest with this oxidized inclusive among studied coals, which indicate the lowest stage of metamorphism of the deposit.

Figure 2: Typical optical image of fresh broken surface of the Sharyn-Gol coal sample

In the table 2 it is given the band separation (*G-A*) and the Raman intensity ratio $R=f_A/f_G$ for the studied coals. Differences in the appearance of these bands well associated with the geological history of coals. Depending on a maturity of coals, both amorphous and graphitic bands might shift to the high frequency side. Consequently, two bands location have been shifted to a higher frequency up

to 20 cm^{-1} (Table 1). As shows direct X-ray determination and fresh broken surface optical images, coals from Sharyn-Gol has the lowest content of carbon and relatively enriched with inclusive of oxygen containing complexes.

Table 2: Carbon graphitic *A* and amorphous *G* bands separation *G-A* and intensity ratio $R=f_A/f_G$ (found by curve fitting) for the some Mongolian coals. Carbon mass content was measured using micro X-Ray analysis mode of a scanning electron microscopy

Coal sample	Carbon content, mass %	Raman band separation G-A, cm^{-1}	Raman intensity ratio, $R=f_A/f_G$
Sharyn-Gol	43.67	216	1.01
Baganuur	72.38	214	1.00
Nalaikh	81.76	214	0.96
Alagtolgoi	82.93	217	0.95
Dovt	≥ 80	232	0.90

The Raman graphitic and amorphous band separation and Raman band strength ratio for the studied coals are plotted below versus carbon content ranking in studied coals in the Figure 3a and 3b.

As shows in Figure 3a, the Raman *G-A* separation almost the same when the carbon content in coals increases approximately two times in the samples 1-4. However, the sample 5 shows the highest band separation alone. It has significantly different Raman bands from those of others. It has the lowest background fluorescence intensity and clear shaped Raman band with narrow width. From the unusual Raman spectra features of the sample 5a, here we note that a carbon content measurement of the sample 5 should have been measured again for the clarity.

The Raman amorphous-graphitic band intensity ratio $R=f_A/f_G$ drops slightly from 1 to 0.9 with an increase of carbon content in coals (Figure 3b). This behavior might be explained by a disappearance of oxygen rich inclusive and a simultaneous size growing of graphitic domains in vitrinite bulk of samples. The Raman intensity ratio, $R=f_A/f_G$ is the highest in the coal of Sharyn-Gol deposit, which indicates again less graphitic domains or less maturity of this coal among the studied five coals.
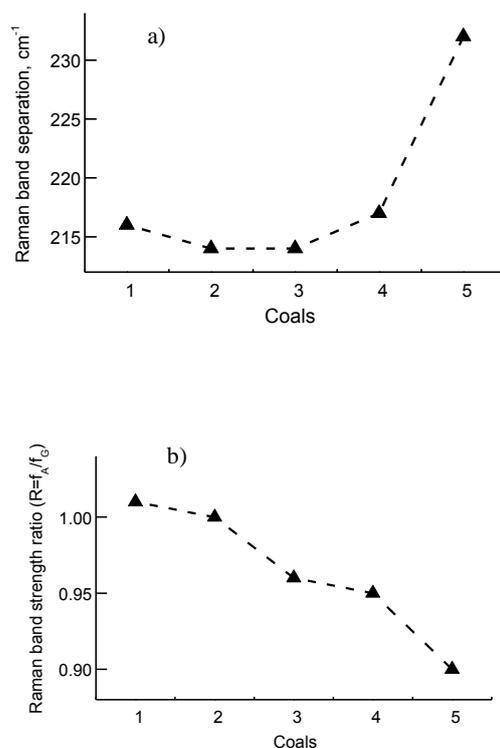

Figure 3: Raman band separation *G-A* (3a) and Raman amorphous/graphitic band intensity ratio, $R=f_A/f_G$ (3b) for the studied coal samples (1–Sharyn-Gol, 2 – Baganuur, 3 – Nalaikh, 4 – Alagtolgoi, 5 – Dovt)

IV. CONCLUSION

The present Raman measurements reveal an existence of graphite-like domains in vitrinite bulk of the low metamorphism coals studied. The amorphous *A* band at 1342-1364 cm^{-1} is less intense and broader than that of the graphitic *G* band at 1560-1580 cm^{-1} for all samples studied.

The graphitic *G* band is found to be shifted to higher frequencies within 1560-1580 cm^{-1} with a decrease of coal maturity, while the Raman amorphous/graphitic band intensity ratio $R=f_A/f_G$ is found to be increased.

The high sensitivity Raman spectroscopy can be an independent tool to reveal a metamorphism grade of coals.

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