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Raman Spectrum Characteristics of Lower Paleozoic Carbonaceous Shale in Middle Yangtze Region

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1 Introduction

Scholars have paid more attention to the rule of organic nanopores changing with the thermal evolution degree since Loucks et al. (2009) showed the importance of organic nanopores in storing the hale gas to oil and gas researchers with the help of argon ion polished technique of sample preparation and high-resolution field emission scanning electron microscope. Meanwhile, characterization of geology temperature with Raman spectrum characteristics of carbon-containing material has become a focus again. Bernard et al. (2012) studied the maturity of early Triassic carbonaceous shale in northern Germany with Raman spectrum, and considered nanopores to be formed by the secondary cracking of kerogen in the high mature stage. Romero-Sarmiento et al. (2014) evaluated the thermal evolution degree of the Barnett Shale with Raman spectrum characteristics; Moroz et al. (2014) reported the Raman spectrum characteristics of carbonaceous shale in Russian Eastern Siberia. Liu Dehan et al. (2013) conducted the vitrinite reflectance test and corresponding Raman spectroscopy test of coal and asphalt samples with different ranks, and established the linear fitting relationship between vitrinite reflectance and the difference of peak location and height of G-band and D-band. However, marine carbonaceous shale is mainly developed in lower Paleozoic in the South China which is more ancient than shale studied by previous scholars with Raman spectroscopy, therefore it is more mature. There is a great difference between the characteristics of Raman D and G bands of the shale and low mature shale. Second-order peak D' is generally developed which needs a separate study to evaluate the thermal evolution degree with Raman spectrum characteristics.

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2 Samples and Analytical Methods

Samples for this study include Lower Paleozoic Carbonaceous Shale samples of the edge of the basin and the nappe zone in Middle Yangtze Region. Raman analyses were performed using a JY Horiba LabRam HR800 spectrometer, equipped with a frequency doubled Nd: YAG laser (532.06 nm) whose output laser power is 45 Mw, a 50× long-work-distance Olympus objective with 0.5 numerical aperture, and a 300 grooves/mm grating. The aperture of the confocal hole is of 200 μm.Spectra were collected in the range of ~100-4000 cm-1. The acquisition time was about 10~40 seconds with two

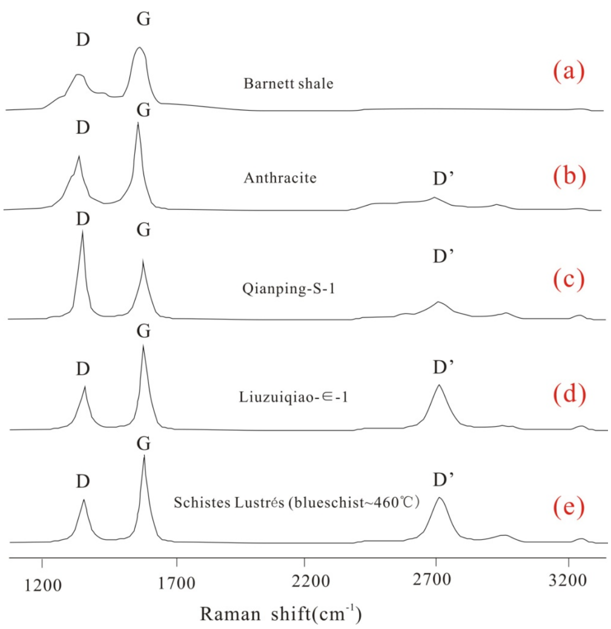

Fig.1 Comparison of Raman spectra of carbon geological samples with different thermal evolution degrees
(a) Raman spectra of Barnett shale (Romero-Sarmiento et al., 2014)
(b) Raman spectra of anthracite (Liu et al., 2013)
(c) Raman spectra of Silurian shales in Qianping
(d) Raman spectra of Cambrian shale in Liuzuiqiao
(e) Raman spectra of blueschists mineral carbonization(Beyssac et al., 2002)

Table1 Raman spectrum characteristic parameters of Lower Paleozoic Carbonaceous Shale in Middle Yangtze Region

Sample	Peak designation	Frequency (cm^{-1})	Height	Width	Area	Peaks distances (G-D)	R2
	D	1330.14	35274.2	135.29	2.01E+06		
Tianxinwu-S-1	G	1597.64	45935.5	49.20	962626	267.50	0.68
	D′	/	/	/	/		
	D	1328.65	33736.9	128.98	1.84E+06		
Lujiatai-S-1	G	1592.76	40660.4	49.14	852069	264.11	0.68
	D′	/	/	/	/		
	D	1331.72	50147.5	79.85	1.70E+06		
Qianping-S-2	G	1586.62	36362.2	55.28	856597	254.90	0.66
	D′	/	/	/	/		
	D	1334.80	43579.4	85.99	1.59E+06		
Qianping-S-1	G	1589.69	37097.5	55.28	873918	254.89	0.65
	D′	/	/	/	/		
	D	1351.34	39992.8	67.73	1.15E+06		
Banshan-S-1	G	1597.62	24912.5	67.73	716121	246.28	0.62
	D′	/	/	/	/		
	D	1334.80	42992.4	98.27	1.79E+06		
Liuzuiqiao-O-1	G	1583.54	33005.9	67.56	948874	248.74	0.65
	D′	/	/	/	/		
	D	1345.18	31524.8	67.73	905718		
Sanxigou-Є-1	G	1591.46	19777.9	67.73	568521	246.28	0.61
	D′	/	/	/	/		
	D	1345.18	29293.1	43.10	537310		
Liuzuiqiao-Є-3	G	1579.15	35177.8	36.94	553674	233.97	0.36
	D′	2699.70	16025.9	61.57	417243		
	D	1340.94	30425.9	42.99	558131		
Liuzuiqiao-Є-2	G	1571.26	49858.4	30.71	654482	230.32	0.29
	D′	2689.09	23988.4	67.56	686637		
	D	1343.12	11980.6	49.85	250973		
Liuzuiqiao-Є-1	G	1567.44	29866.2	31.16	392023	224.32	0.27
	D′	2685.93	9028.06	81.00	303768		

Note: R2=D/(G+D+D′), area ratio.

accumulations for each spectrum. The peak intensities of Raman signals were determined by using GRAMS32/AI software.

3 Preliminary results and discussion

The results show the Raman temperature parameter of lower Paleozoic Cambrian and Silurian samples from the nappe zone(Liuzuiqiao\Banshan) is lower than that of the contemporary samples(Sanxigou\Tianxinwu) near the basin(Raman parameter R2，R2=D/（G+D+D′）area ratio). The parameter of over mature carbonaceous shale in the middle Yangtze region decreases from 0.68 to 0.27 as the maturity increases. The spacing of D-band and G-band (G-D) of over mature carbonaceous shale declines from 267.50 to 224.32 as the maturity goes up. The width of D-band and G-band gradually goes down as the maturity raises . The width of D-band reduces from 135.29 to 42.99, and that of G-band drops from 67.73 to 30.71, but the change rule of G-band is not obvious (Table 1). Contrast Raman spectrum characteristics of Barnett shale, anthracite, Silurian shale and Cambrian shale in the middle Yangtze region and carbon-containing mineral in the greenschist facies terrane (Figure 1), it is shown that the peak width of the first order Raman G-band is smaller, and the second order Raman D′-band is obviously developed in carbonaceous shale in the nappe zone and other metamorphism regions. For example, the Raman spectra of Cambrian Liuzuiqiao-∈-1 is very similar to that of Schistes Lustrés reported by Beyssac et al. (2002). The metamorphic temperature of Schistes Lustrés is about 460°C. The peak height and peak area of the first order Raman D-band and G-band of Silurian Qianping-S-1 are larger. According to the research of carbonized minerals by Beyssac et al. (2002) and Lahfid (2010) studied, D-band is higher than G-band in the range of 420°C to 440°C and its peak height decreases quickly. D′-band becomes higher in the experiment. However, Liu Dehan et al.(2013) suggested that the change rule of D′-band of coal samples in the high evolution stage is less obvious than that of D′-band of lower Paleozoic carbonaceous shale in the middle Yangtze region. It may be caused by kerogen type. The kerogen type of coal samples type III, and that of lower Paleozoic carbonaceous shale in the middle Yangtze region is mainly type II or I. Bao Fang et al. (2012) noted the difference of peak width and frequency of D-band and G-band of different maceral. Beyssac et al. (2002) pointed out that the range of application of geology temperature of Raman temperature parameter R2 is 330–640°C. On the basis of a large number of samples, Ran Jing et al. (2013) confirmed the difference of peak location of Raman D-band and G-band of sedimentary organic matter in the middle the Yangtze region that it decreases with the maturity when Ro is more than 2.9. This is contrary to the relationship when Ro is less than 2.4. The Paleozoic carbonaceous shale in the middle Yangtze region is mainly in the over mature stage whose Raman spectrum characteristics are different from that of low-high mature carbonaceous shale.

4 Partial Conclusion

Raman peak temperature parameter R2 and the difference of peak location of D-band and G-band can be employed to evaluate the thermal evolution degree of the lower Paleozoic carbonaceous shale in the middle Yangtze region. In the over mature stage, (G-D) and R2 both decrease with the increase of thermal evolution degrees. There are differences between Raman spectrum characteristics of different types of organic matter, and organic matter type should be determined before quantitatively comparing the thermal evolution degree of carbonaceous shales with Raman spectrum characteristics.

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