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Relationships between Organic Material and Thermal Maturity Derived from Coal and C-Shale Samples

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ABSTRACT

The purpose of this study is to characterize the relationship between organic material and thermal maturity during the process of evaluation of hydrocarbon potential. Samples studied include Miocene high volatile bituminous coal and coaly shale collected from outcrops and exploration wells in Hsinchu-Miaoli area, NW Taiwan, density centrifuge separated macerals, bituminous coal and anthracite from China, in addition to Woodford and Green River oil shale from the United States. Maceral composition analysis, elemental analysis, vitrinite reflectance measurement and Rock-Eval pyrolysis were performed for evaluation. The results of study show that: 1) coal samples from the Shiti Formation (middle Miocene) exhibit more vitrinite and less mineral matter contents than samples from the Nanchuang Formation (upper Miocene); H% is increased in exinite-enriched maceral mixtures with density < 1.25 g cm^{-3}, after density centrifuge separation. 2) A positive linear correlation between Tmax and Ro illustrates both Rock-Eval pyrolysis and vitrinite reflectance can be used as indicators of thermal maturity. 3) From the plot of H/C ratio vs. vitrinite reflectance, even though the depositional environments were different in Taiwan and China, their organic micelles exhibit a similar trend in the process of thermal maturation. As a whole, the curve has a turning point at Ro = 0.5% and H/C = 0.1 (atomic ratio 1.2) in this study. 4) A rather good correlation between S2 and TOC of samples studied indicates the contribution of S2 from TOC. 5) The highest HI occurred in certain maturities (Tmax and Ro) of samples studied, and not in the stages of less maturity or over-maturity. 6) Two different linear trends were observed in the cross plot of S1 vs. S2. Field outcropped shale or C-shale exhibits a steeper slope compared to that of coal samples which can be attributed to the compositional difference in their organic material. 7) A rather strong positive correlation for H% vs. S2 illustrates the contribution of H-containing macerals, especially exinite. As a result of this study, we expect to promote evaluation techniques for HC exploration; for instance, the development or improvement of evaluation methods for source rocks, reservoirs, structural evolution, and thermal maturity. Evaluations are expected to give more detail regarding local conditions, and be better quantified and more accurate.

Key words: Organic material, Thermal maturity, Coal

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1. INTRODUCTION

Evaluation of hydrocarbon potential is one of the most important aspects of oil exploration (Dow 1974). Its precision relates to the prediction of locations and reserves of prospect areas and the outcome of exploration projects (Magoon and Dow 1994). A hydrocarbon reserve can be generated by a proper combination of good source rock, depositional and tectonic structures, and thermal maturation (Otis and Schneidermann 1997). Therefore, "Material" and "Maturity" (M & M) of the hydrocarbon are the two important topics in evaluation.

The purpose of this study is to characterize the relationships between organic material and thermal maturity. 42 samples studied include Miocene high volatile bituminous

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coal and coaly shale plus kerogen and organic matters recovered from exploration wells in NW Taiwan, coal samples (aged from Devonian to Tertiary) from China, Green River (Eocene) and Woodford shale (Permian) from the USA, in addition to maceral mixtures prepared by density centrifuge separation of $ZnCl_2$ solution as proposed by Dormans et al. (1957). Maceral composition analysis, elemental analysis, vitrinite reflectance measurement and Rock-Eval pyrolysis were performed to evaluate the characteristics of organic materials and maturities.

2. LITERATURE REVIEW OF LOCAL GEOLOGIC SETTINGS

Taiwan is located in an active arc-continent collision zone between the Eurasian Plate and Philippine Sea Plate. The so-called Penglai Orogeny starting from Plio-Pleistocene led to the lifting of the Central Mountain Range and the exposure of small-sized hydrocarbon fields, especially on the northwestern part of the Western Foothills Belt of Taiwan. Three coal-containing cyclothems occurred in Miocene formations, namely the Nanchuang Formation, Shiti Formation and Mushan Formation, respectively from top to bottom. Various methods have been developed for oil and gas exploration in the past, such as thermal studies (Lin 2000), basin analyses (Chi et al. 1987), and tectonic structure studies (Hwang and Wang 1993). Chiu (1972, 1975) finished a detailed Miocene stratigraphic study in western-central Taiwan. Afterwards, a Cenozoic basin study of offshore Taiwan was done by Sun (1982, 1985). In addition, Liou and Hsu (1988) followed by Hsiao et al. (1991) completed thorough studies on the evaluation of hydrocarbon potential. Furthermore, Huang (1984, 1986) combined paleontology, stratigraphy and geodynamics to improve the understanding of local geologic settings.

3. METHODS

The material study starts from the collection of coal samples with maturity close to the early oil window, various maceral groups were then prepared by using density centrifuge separation. Rock-Eval pyrolysis and elemental (N, C, S, and H) analysis were then performed to evaluate the relationship between hydrocarbon potential and maceral composition. Secondly, for the collections of kerogen or organic matter having the same maturity but different hydrocarbon potentials, the maceral compositions were compared with the results of their pyrolysis and elemental analysis, so as to study the mechanism of hydrocarbon generation.

Furthermore, a maturity study was performed on the collections of coal or kerogen samples that showed maturity within the oil window and the relationship among their vitrinite reflectance and Rock-Eval pyrolysis were studied.

Maceral analysis and vitrinite reflectance measurements were performed on polished pellets using a Leitz MPV Compact Microscope, whereas elemental analysis and Rock-Eval pyrolysis were performed in the Precise Instrument Center of National Science Council and EDRI of Taiwan Chinese Petroleum Corp., respectively.

4. RESULTS

The analytic results of maceral composition, elemental (N, C, S, and H) composition, vitrinite reflectance and Rock-Eval pyrolysis from the 42 samples studied are listed in Table 1. Coal samples from the Shiti Formation (middle Miocene) exhibit more vitrinite and less mineral matter contents than samples from the Nanchuang Formation (upper

Table 1. Analytic results of the 42 samples studied. Sample #1 - 24: coals from Taiwan, (SF): Shiti Formation, (NF): Nanchuang Formation; #25 - 28: oil shales from the USA; #29 - 40: coals from China, (D): Devonian, (C): Carboniferous, (P): Permian, (J): Jurassic, (Cr): Cretaceous, (T): Tertiary; #41 - 42: coals from exploration well of Taiwan with depth (feet) in parenthesis, (MF): Mushan Formation. V, E, I, MM% stand for vitrinte, exinite, inertinte and mineral matter %, respectively in maceral analysis; N%, C%, S%, H% and H/C are from elemental analysis; Ro(%): vitrinite reflectance; Tmax, S1, S2, HI, TC, and IOC all from Rock-Eval Pyrolysis. Some of the elemental analysis and IOC were not detected due to cost.

(a) Description, petrographic, and chemical analyses results for samples #1 - 24.

NO #	Sample Name		V%	E%	I%	MM%	N%	C%	S%	H%	H/C	Ro (%)
1	Li Feng (SF)	1	60.6	5	29.6	4.8	1.05	73.18	0.72	4.77	0.065	0.739
2		2	95	1	0.8	3.2	1.20	61.37	0.15	5.32	0.087	0.529
3		3	68.8	2.4	0.2	28.6	1.39	66.18	2.36	4.93	0.074	0.582
4	Ming Deh (NF)	1	46.6	0.6	0	52.8	--	--	--	--	--	0.411
5		2	63.2	1.4	0	29.2	--	--	--	--	--	0.416
6		3	55.6	0.8	0.2	43.4	--	--	--	--	--	0.445
7		4	53.4	1.4	0.6	44.6	--	--	--	--	--	0.467
8		5	56.4	2.	0.2	41.4	--	--	--	--	--	0.47
9		6	71	0.8	0	28.2	--	--	--	--	--	0.462

Table 1. (Continued)

NO #	Sample Name		V%	E%	I%	MM%	N%	C%	S%	H%	H/C	Ro (%)
10	MT (NF)	1	58.2	0.8	0	41	--	--	--	--	--	0.497
11		2	43.2	1.2	0	55.6	--	-	--	--	--	0.425
12		3	36	4.2	1.8	58	--	--	--	--	--	0.339
13		4	51.2	1.8	0	47	--	--	--	--	--	0.418
14	Ming Deh (NF)	Wt	53.2	1.2	0	45.6	0.73	42.14	2.69	4.12	0.098	0.386
15		Wb	30.2	1.4	0	68.4	0.42	18.93	0.82	2.13	0.113	0.52
16		Et	66.2	0.6	0.2	33	0.82	45.39	2.4	4.08	0.090	0.518
17		Eb	3.8	0	0	96.2	0.16	2.2	0.34	0.34	0.155	0.357
18	Yu Feng (SF)	O	93.2	1.2	0.6	5	1.71	76.97	0.98	5.79	0.075	0.738
19		d < 1.25	84.	11.4	0	4.6	1.62	78.39	0.87	5.91	0.075	0.682
20		d > 1.25	92.8	4.4	0.2	2.6	--	--	--	--	--	0.707
21		1.25 < d < 1.35	93.2	3	1.6	2.2	1.69	77.61	0.83	5.20	0.067	0.747
22		d > 1.35	81.6	3.6	4.8	10	1.37	59.17	3.47	4.22	0.071	0.726
23	Heng Shan (NF)		95.4	0.4	0	4.2	0.3	57.24	0.39	5.12	0.089	0.23
24	Wu Chi Shan (NF)		33.2	1.2	0	65.6	1.73	73.26	0.83	6.75	0.092	0.356

(b) Rock-Eval Pyrolysis results for samples #1 - 24.

NO #	Tmax (°C)	S1 (mgHC/g)	S2 (mgHC/g)	HI (S2/TOC) mgHC/gTOC	TC (%)	TOC (%)	IOC (%)	S (%)
1	434	1.28	111.28	148.063	75.157	75.157	--	0.830
2	431	0.68	83.51	133.371	62.615	62.615	--	0.298
3	429	1.35	138.93	205.254	67.687	67.687	--	1.342
4	425	2.89	86.05	207.484	41.473	41.473	--	1.470
5	424	3.64	94.27	220.938	42.668	42.668	--	1.213
6	423	3.33	97.48	242.198	40.248	40.248	--	2.003
7	424	2.2	69.09	167.094	41.348	41.348	--	5.613
8	422	2.29	81.62	163.302	49.981	49.981	--	1.833
9	418	4.48	113.06	199.996	56.531	56.531	--	1.292
10	426	1.42	83.16	160.985	51.657	51.657	--	3.287
11	423	0.32	30.01	115.565	33.121	25.968	9.153	1.394
12	420	5.66	114.45	279.795	40.905	40.905	--	2.035
13	418	4.5	85.49	184.115	46.433	46.433	--	1.991
14	430	2.69	78.42	177.120	44.275	44.275	--	1.999
15	425	1.21	36.49	196.383	19.241	18.581	0.660	0.659
16	427	1.22	67.07	155.183	43.220	43.220	--	3.103
17	433	0.07	1.57	70.530	2.316	2.226	0.090	0.150
18	437	2.42	175.15	221.160	79.196	79.196	--	0.642
19	435	2.39	212.47	268.071	79.259	79.259	--	0.54
20	438	1.63	133.17	168.835	78.876	78.876	--	0.706
21	437	1.64	150.92	189.120	79.801	79.801	--	0.681
22	441	1.35	103.22	160.972	64.123	64.123	--	1.459
23	377	1.22	31.42	54.078	58.101	58.101	--	0.506
24	431	3.3	224	314.744	71.169	71.169	--	3.212

Table 1. (Continued)

(c) Description, petrographic, and chemical analyses results for samples #25 - 42.

NO #	Sample Name	V%	E%	I%	MM%	N%	C%	S%	H%	H/C	Ro (%)
25	Woodford Shale (P)	11.6	0.2	0.2	88	0.12	13.78	0.12	0.18	0.013	0.309
26	Green River (T)	12.8	0	0	87.2	0.94	33.21	1.42	3.76	0.113	0.281
27	Green River d < 1.25	0.6	16.8	0	82.6	0.92	33.04	0.64	3.98	0.120	0.214
28	Green River d > 1.25	4	10.2	0	85.8	0.79	29.65	0.94	3.53	0.119	0.184
29	Fu Shuan 1 (T)	87	4.6	0	8.4	1.17	66.32	0.78	4.61	0.070	0.543
30	Fu Shuan 2 (T)	88.2	9.4	0.6	1.4	1.4	70.54	0.25	5.62	0.080	0.594
31	Shui Cheng 1 (P)	80	10.8	8.8	0.4	0.98	37.74	0.40	3.70	0.098	0.58
32	Shui Cheng 2 (P)	69.4	24.8	3.6	2.2	1.15	75.49	0.15	8.02	0.106	0.392
33	Lu Chuan (D)	6.6	1.8	0	91.6	0.64	52.48	5.31	6.03	0.115	0.451
34	Jen Chiu 1 (C)	82.6	15.4	0.6	1.4	1.3	71.93	0.3	5.31	0.074	0.681
35	Jen Chiu 2 (C)	71.4	4.8	22	1.8	1.47	72.67	0.73	4.48	0.062	0.586
36	Shan Shi (C)	78	2.6	8.2	11.2	0.69	73.28	0.26	4.23	0.058	1.239
37	San Dao Ling (J)	61.2	6.8	32	0	0.8	70.59	0.35	4.49	0.064	0.717
38	Mao Ming (T)	1.4	0.8	0	97.8	0.58	6.16	1.11	3.43	0.557	0.174
39	Jiao Tsu (P)	--	--	--	--	--	--	--	--	--	4.6
40	Fu Shin (Cr)	88	2.8	5.6	3.6	1.27	67.21	0.65	4.67	0.069	0.54
41	Mu Shan (4852) (MF)	80	5.6	0	14.4	0.85	51.29	4.52	3.26	0.064	1.571
42	Mu Shan (4860) (MF)	73	3.4	0	23.4	1.12	59.63	3.43	3.43	0.057	1.562

(d) Rock-Eval Pyrolysis results for samples #25 - 42.

NO #	Tmax (°C)	S1 (mgHC/g)	S2 (mgHC/g)	HI (S2/TOC) mgHC/gTOC	TC (%)	TOC (%)	IOC (%)	S (%)
25	440	0.52	7.9	511.990	14.963	1.543	13.420	0.034
26	428	8.47	146.53	511.484	32.656	28.648	4.008	1.054
27	430	8.81	155.32	437.509	35.501	35.501	--	1.030
28	428	8.07	144.61	498.535	33.320	29.007	4.313	1.040
29	429	0.74	69.44	104.209	66.635	66.635	--	0.566
30	429	1.17	123.13	171.152	71.942	71.942	--	0.426
31	450	2.08	153.41	334.132	45.913	45.913	--	0.232
32	453	1.78	352.47	453.962	77.643	77.643	--	0.403
33	444	3.11	156.04	354.379	44.032	44.032	--	10.288
34	429	1.44	113.15	155.362	72.830	72.830	--	0.670
35	432	1.27	92.18	123.963	74.361	74.361	--	0.588
36	445	0.6	16.89	22.996	73.446	73.446	--	0.178
37	432	1.98	52.79	74.211	71.135	71.135	--	0.575
38	426	0.48	17.37	239.026	7.267	7.267	--	0.973
39	488	0.32	0.08	0.097	82.219	82.219	--	0.395
40	430	1.15	70.09	101.720	68.905	68.905	--	0.416
41	477	1.84	47.76	85.470	55.879	55.879	--	3.578
42	479	1.44	43.87	87.092	50.372	50.372	--	2.699

Miocene). In addition, H% is increased in exinite-enriched maceral mixtures with density < 1.25 g cm^{-3}, after density centrifuge separation. Most of the vitrinite reflectance measured falls in the range of 0.3 ~ 0.7%, close to the early oil window.

Furthermore, a positive linear correlation between Tmax and Ro can be found (Fig. 1), which illustrates both Rock-Eval pyrolysis and vitrinite reflectance can be used as indicators of thermal maturity. In addition, plotting a curve with H/C ratio vs. vitrinite reflectance (Fig. 2), we found that even though the depositional environments were different in Taiwan and China, their organic micelles exhibit a similar trend in the process of thermal maturation. As a whole, the curve has a turning point at Ro = 0.5% and H/C = 0.1 (atomic ratio 1.2) in this study.

After Person's correlation analysis, not surprisingly, TOC vs C exhibits a strong positive correlation, whereas TOC vs MM, Vitrinite vs MM, and C vs MM exhibit a strong negative correlation. More cross plots of note are further discussed as follows: A rather good correlation between S2 and TOC (Fig. 3) indicates the contribution of S2 from TOC. Both Figs. 4 and 5 illustrate that the highest HI occurs at certain maturities (Tmax and Ro), and does not occur in stages of less maturity or over-maturity. Furthermore, two different trends were observed in the cross plot of S1 vs. S2 (Fig. 6). Generally, field outcropped shale or C-shale exhibits a steeper slope compared to that of coal samples which can be attributed to the compositional difference in organic material. As for the plot of HI vs. TOC (Fig. 7), no significant trend can be found, although the Green River and Woodford oil shale from the U.S. exhibit the highest HI with not-so-much TOC contents. Finally, a rather strong positive correlation of H% vs. S2 was found in Fig. 8, which illustrates the contribution of H-containing macerals, especially exinite.

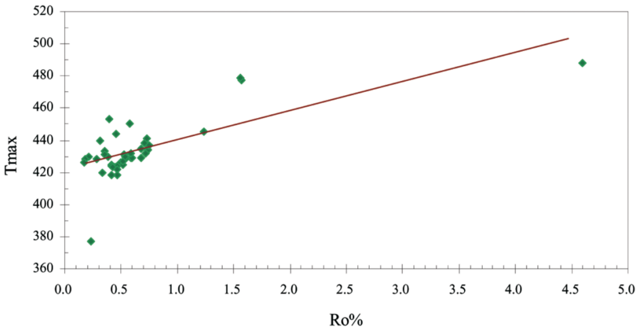

Fig. 1. The linear correlation between Tmax and Ro% in the samples studied.

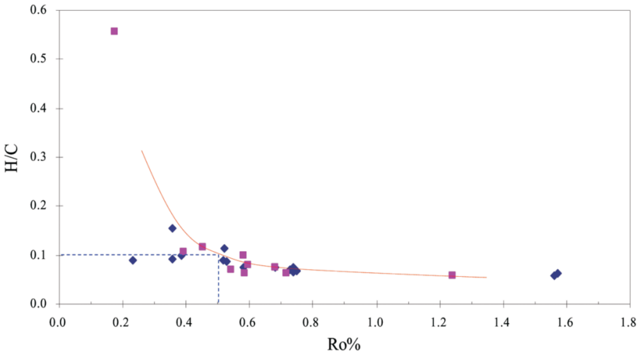

Fig. 2. H/C ratio vs. vitrinite reflectance curve of samples from China (■) and Taiwan (◆). Even though the depositional environments were different, their organic micelles exhibit a similar trend in the process of maturation. As a whole, the curve has a turning point at Ro = 0.5% and H/C = 0.1 (atomic ratio 1.2).

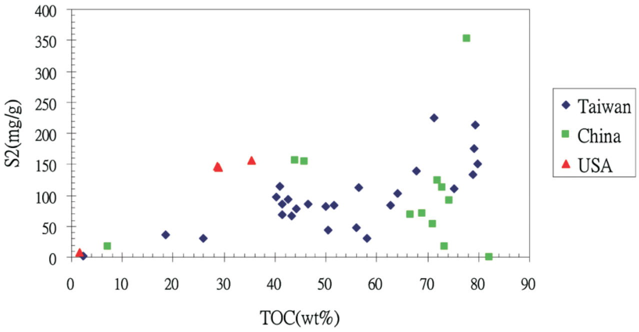

Fig. 3. Correlation between S2 and TOC of samples studied.

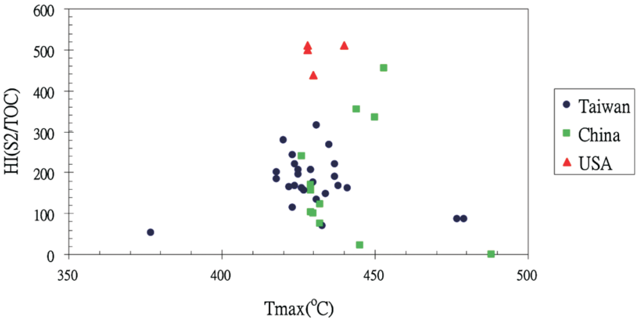

Fig. 4. Correlation between HI and Tmax of samples studied.

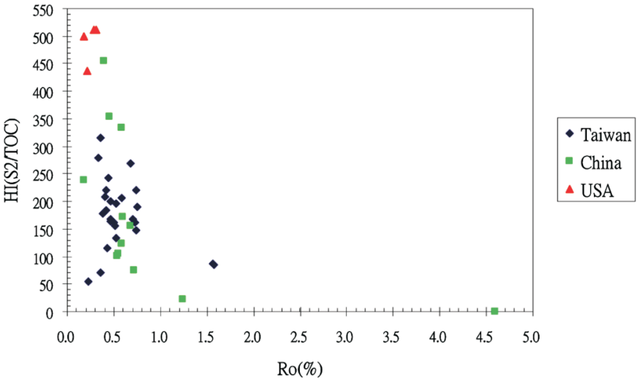

Fig. 5. Correlation of HI and Ro of samples studied.

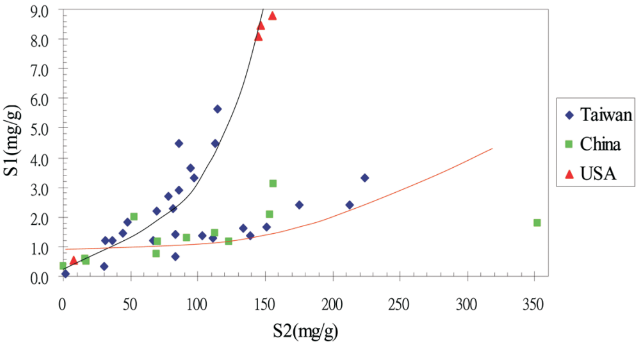

Fig. 6. Correlation between S1 and S2 of samples studied. Two linear trends with positive slope can be observed; black lines and red lines were drawn from C-shale samples and coal samples, respectively.

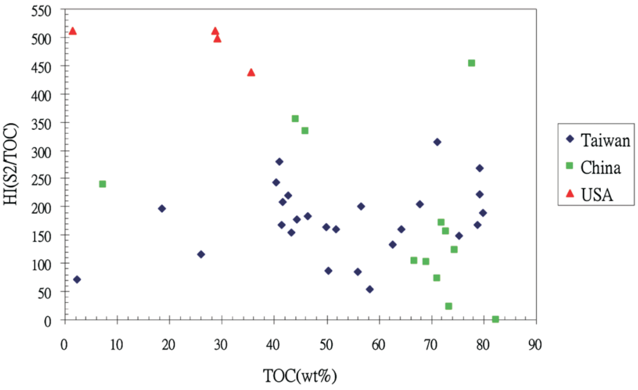

Fig. 7. Correlation between HI and TOC of samples studied.

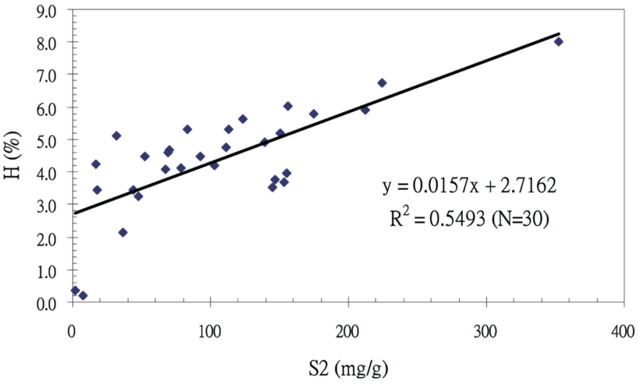

Fig. 8. Correlation of H and S2 of all samples studied.

5. CONCLUSION

(1) Coal samples from the Shiti Formation (middle Miocene) exhibit more vitrinite and less mineral matter contents than samples from the Nanchuang Formation (upper Miocene). In addition, H% is increased in exinite-enriched maceral mixtures with density < 1.25 g cm^{-3}, after density centrifuge separation.

(2) A positive linear correlation between Tmax and Ro illustrates both Rock-Eval pyrolysis and vitrinite reflectance can be used as indicators of thermal maturity.

(3) From the plot of H/C ratio vs. vitrinite reflectance, even though the depositional environments were different in Taiwan and China, their organic micelles exhibit a similar trend in the process of thermal maturation. As a whole, the curve has a turning point at Ro = 0.5% and H/C = 0.1 (atomic ratio 1.2) in this study.

(4) A rather good correlation between S2 and TOC of samples studied indicates the contribution of S2 from TOC.

(5) The highest HI occurred in certain maturities (Tmax and Ro) of samples studied, and not in the stages of less maturity or over-maturity.

(6) Two different linear trends were observed in the cross plot of S1 vs. S2. Field outcropped shale or C-shale exhibits a steeper slope compared to that of coal samples which can be attributed to the compositional difference in their organic material.

(7) A rather strong positive correlation of H% vs. S2 illustrates the contribution of H-containing macerals, especially exinite.

As a result of this study, we expect to promote evaluation techniques for HC exploration; for instance, the development or improvement of evaluation methods for source rocks, reservoirs, structural evolution, and thermal maturity. Evaluations are expected to give more detail on local conditions, and be better quantified and more accurate.

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