

Figure 1. Geographic location and tectonic division of Upper Yangtze region, China. Cambrian, Silurian, and Permian shales were collected at the outcrop sites from Chengkou, Nanjiang and Jiange of Sichuan Province and Zunyi of Guizhou Province. One immature oil shale and one immature coal were also analyzed for comparative purposes.

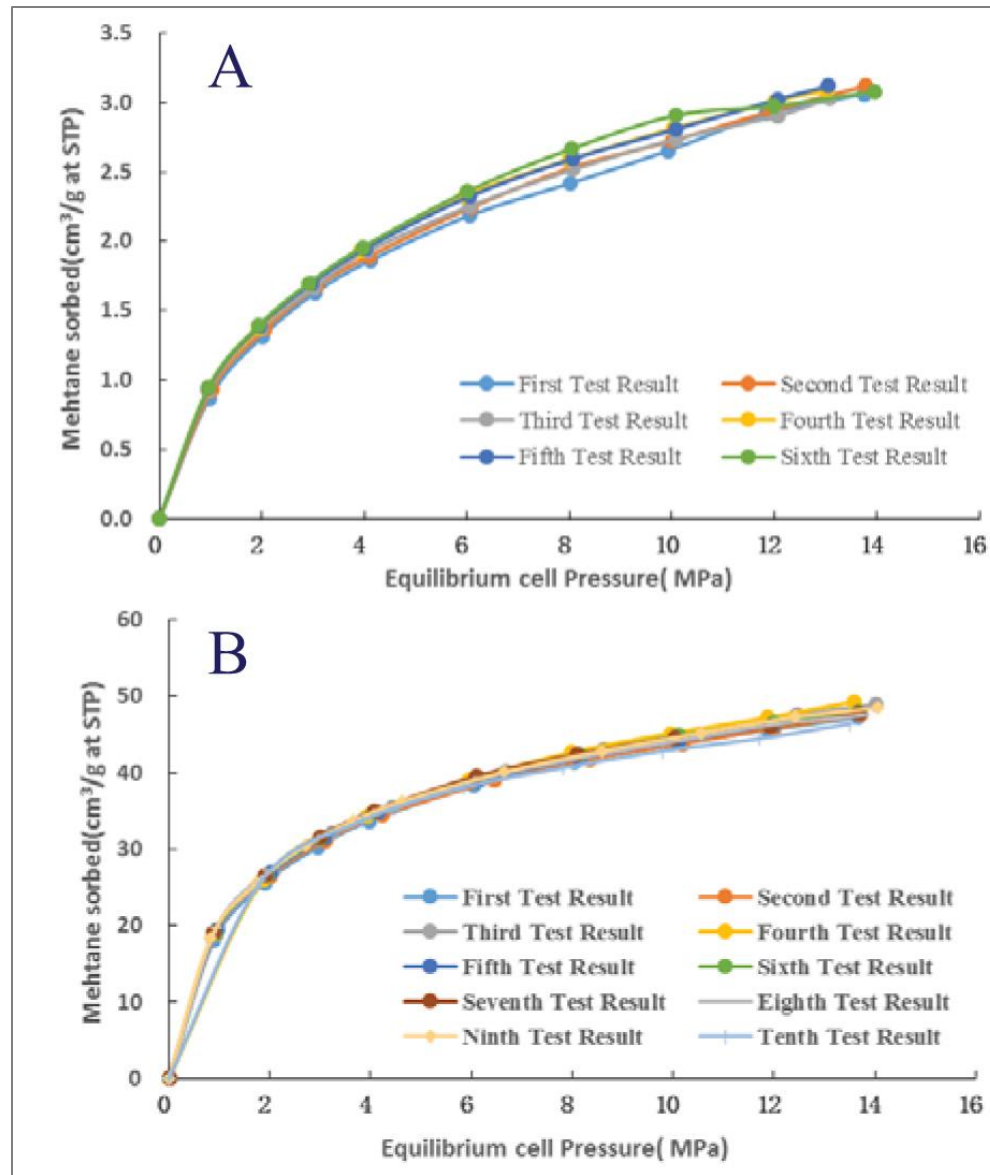


Figure 2. Sorption isotherms for repetitious tests. A: Six methane sorption isotherms of the same Silurian shale at 30°C. B: Ten sorption isotherms of the same kerogen of Silurian shale at 30°C. Methane sorption measurements on the powder samples of initial shales and extracted shales and kerogen were performed on a high pressure gas isothermal sorption instrument. The relative standard deviation of the sorption measurement on shale sample is 2.36% (A) and 1.62% for kerogen sample (B). It is obvious that the accuracy of data is very high and the differences of methane sorption of different samples can be compared.

Sample	Age	Location	Strata	Lithology	TOC (wt%)	HI(mgHC/ g _{TOC})	OI(mgCO ₂ /g TOC)	S ₁ (mg/g _{Rock})	S ₂ (mg/g _{Rock})	T _{max} (°C)
ZY-2	ε ₁	Guizhou Zunyi	Niu-ti-tang Fm.	Dark shales	2.84	0	42	0.00	0.01	505
ZY-3	ε ₁	Guizhou Zunyi	Niu-ti-tang Fm.	Dark shales	3.71	0	39	0.00	0.01	506
CK-1	ε ₁	Sichuan Chengkou	Qiong-zhu-si Fm.	Dark shales	4.74	1	3	0.10	0.04	n/a
NJ-2	S ₁	Sichuan Nanjiang	Long-ma-xi Fm.	Dark shales	3.59	2	6	0.04	0.08	606
NJ-5	S ₁	Sichuan Nanjiang	Long-ma-xi Fm.	Dark shales	2.76	2	3	0.22	0.05	606
NJ-6	S ₁	Sichuan Nanjiang	Long-ma-xi Fm.	Dark shales	3.68	1	20	0.01	0.03	602
JG-1	P ₂	Sichuan Jiange	Da-long Fm.	Dark shales	4.87	305	5	0.40	15.47	440
JG-4	P ₂	Sichuan Jiange	Da-long Fm.	Dark shales	4.87	269	5	0.57	15.86	434
Coal	T ₂	Guangxi Baise	He-kou Fm.	Coal	59.20	196	25	/	/	420
Oil Shale	E ₂	Guangdong Maoming	You-gan-guo Fm.	Brown oil Shale	13.60	566	26	0.69	86.42	427

Table 1. The geological and geochemical information of shale samples.

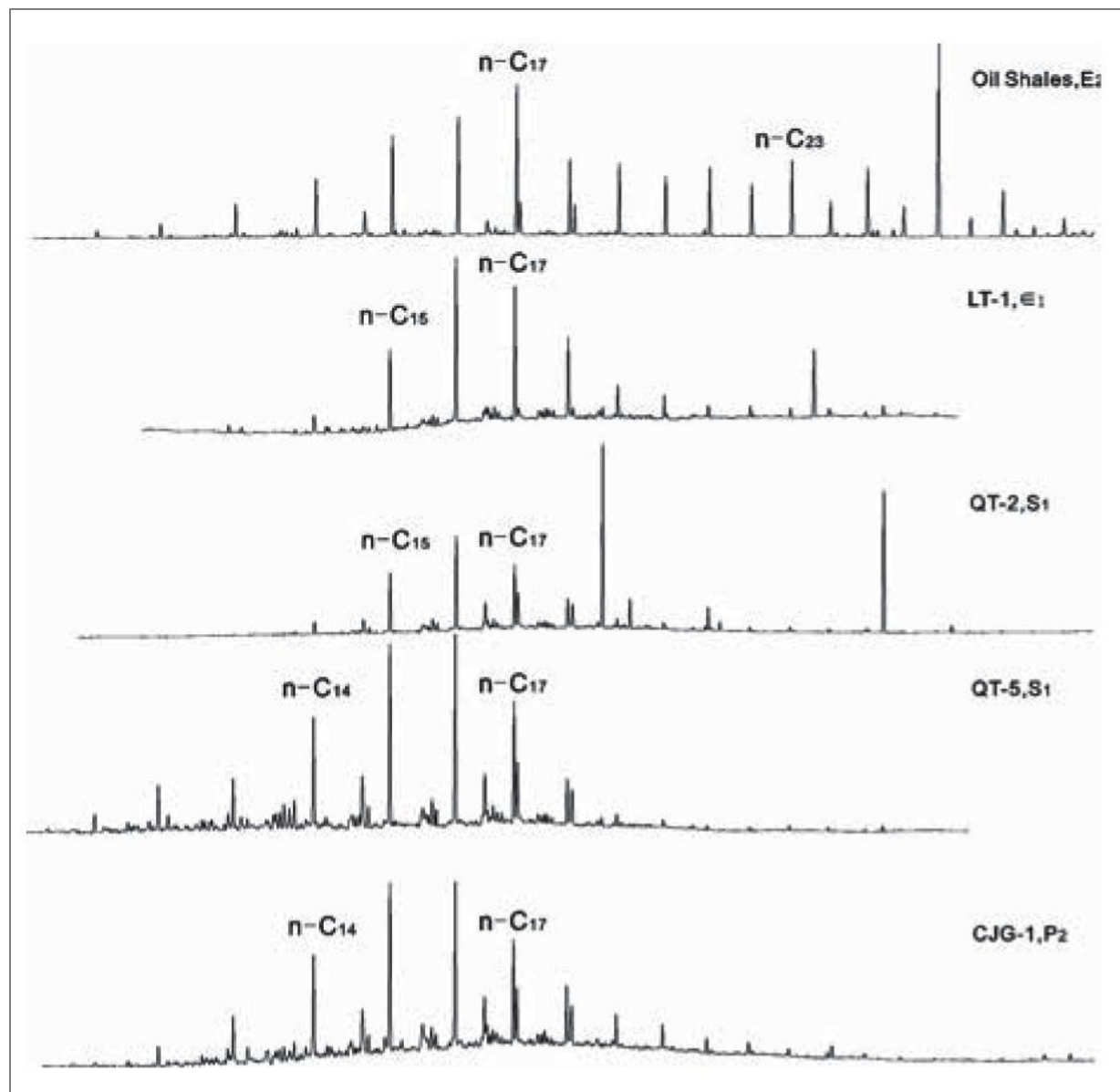


Figure 3. The chromatograms of aliphatic hydrocarbons in the Paleozoic shales from Upper Yangtze region and Paleogene oil shale of Maoming. While the chromatograms of aliphatic hydrocarbons in Permian shales are composed of a broader range of *n*-alkanes ranging from *n*-C₁₂ to *n*-C₂₆ with *n*-C₁₅ and *n*-C₁₆ as dominant peaks. The results show that the aliphatic hydrocarbons in Cambrian and Silurian shales are mainly composed of low carbon number *n*-alkanes ranging from *n*-C₁₁ to *n*-C₂₀ and dominated by *n*-C₁₅ to *n*-C₁₈ peaks.

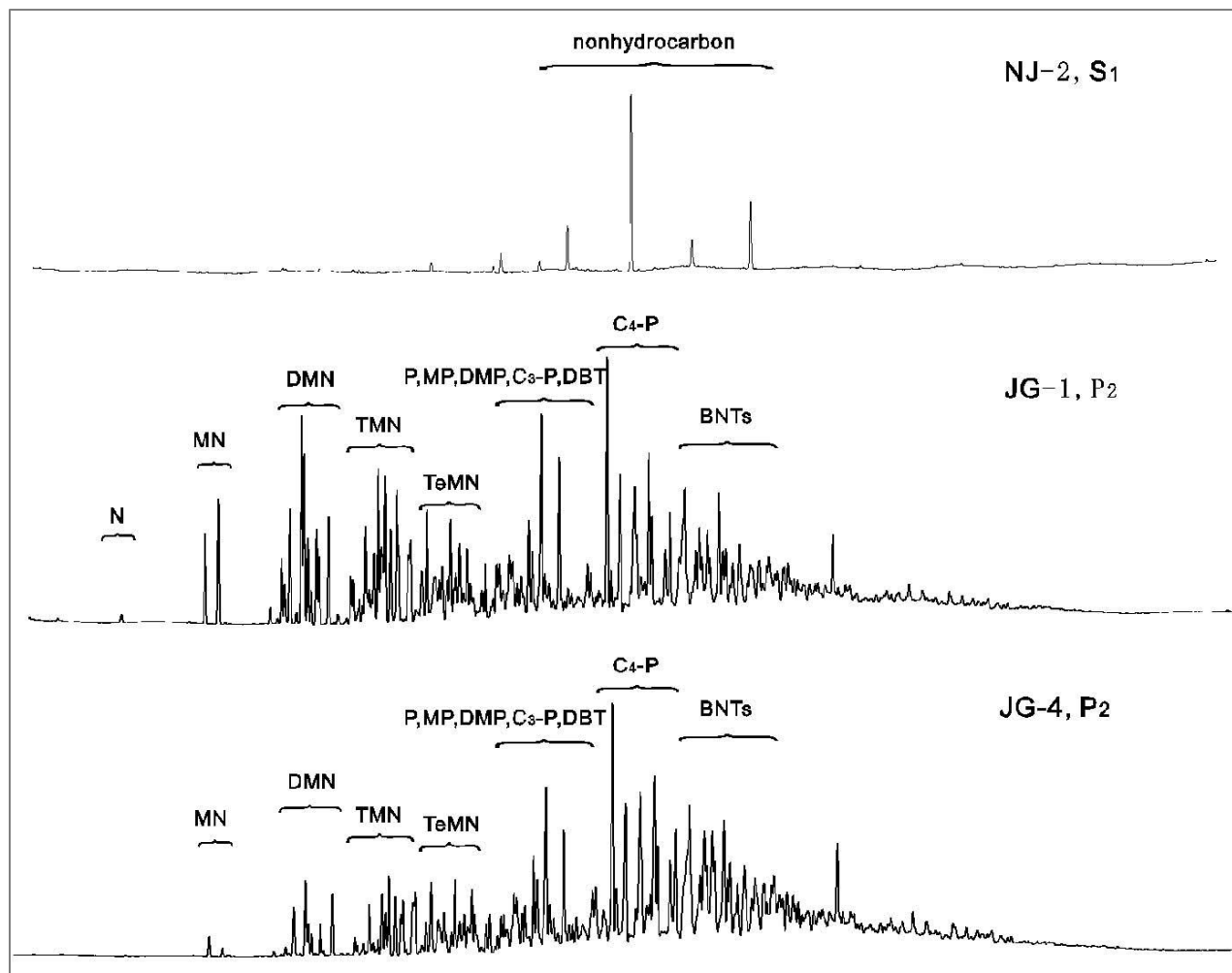


Figure 4. The chromatograms of aromatic hydrocarbon in the Paleozoic shales from Upper Yangtze. Phenanthrene and methylated isomers (i.e., P, MP, DMP, TMP and TeMP), benzonaphthalenes, trimethyl naphthalenes and tetramethyl naphthalenes are in relatively high abundance in the Permian shales of the Dalong Formation.

Samples	Age	TOC (wt. %)	Shales		Extracted Shales		MSC(extracted shale) - MSC(shale)	Percentage of impact SOM on MSC of total shale (%)	Kerogen		Percentage of kerogen MSC vs MSC of extracted shale (%)
			MSC(cm ³ /g , 12MPa) ^a	V _L (cm ³ /g)	MSC(cm ³ / g, 12MPa)	V _L (cm ³ /g)			MSC(cm ³ / g, 12MPa)	V _L (cm ³ /g)	
ZY-2	Є _{1n}	2.84	1.87	2.69	1.59	2.06	-0.28	-15	17.02	21.78	36
ZY-3	Є _{1n}	3.71	2.70	3.67	2.56	3.50	-0.14	-5	23.22	29.60	40
CK-1	Є _{1s}	4.74	1.40	2.33	1.62	2.11	0.22	16	14.48	29.14	50
NJ-2	S _{1L}	3.59	1.93	2.41	2.25	2.83	0.32	17	36.06	44.26	68
NJ-5	S _{1L}	2.76	1.37	1.74	1.05	1.32	-0.32	-23	15.50	28.05	48
NJ-6	S _{1L}	3.68	2.21	3.59	1.87	2.50	-0.34	-15	26.51	31.66	62
JG-1	P _{2d}	4.87	0.70	0.90	0.94	1.15	0.24	34	11.15	23.37	69
JG-4	P _{2d}	4.87	0.65	0.86	0.80	1.16	0.15	23	10.71	25.58	78
Coal	T _{2h}	59.20	8.40	11.88	/	/	/	/	12.68 ^d	/	/
Oil Shale	E _{2y}	13.60	4.95	8.53	4.74	7.74	-0.21	-4	10.94	19.62	37

Table 2. Langmuir fitting results for methane sorption for the bulk of shales, extracted shales and isolated kerogen samples.

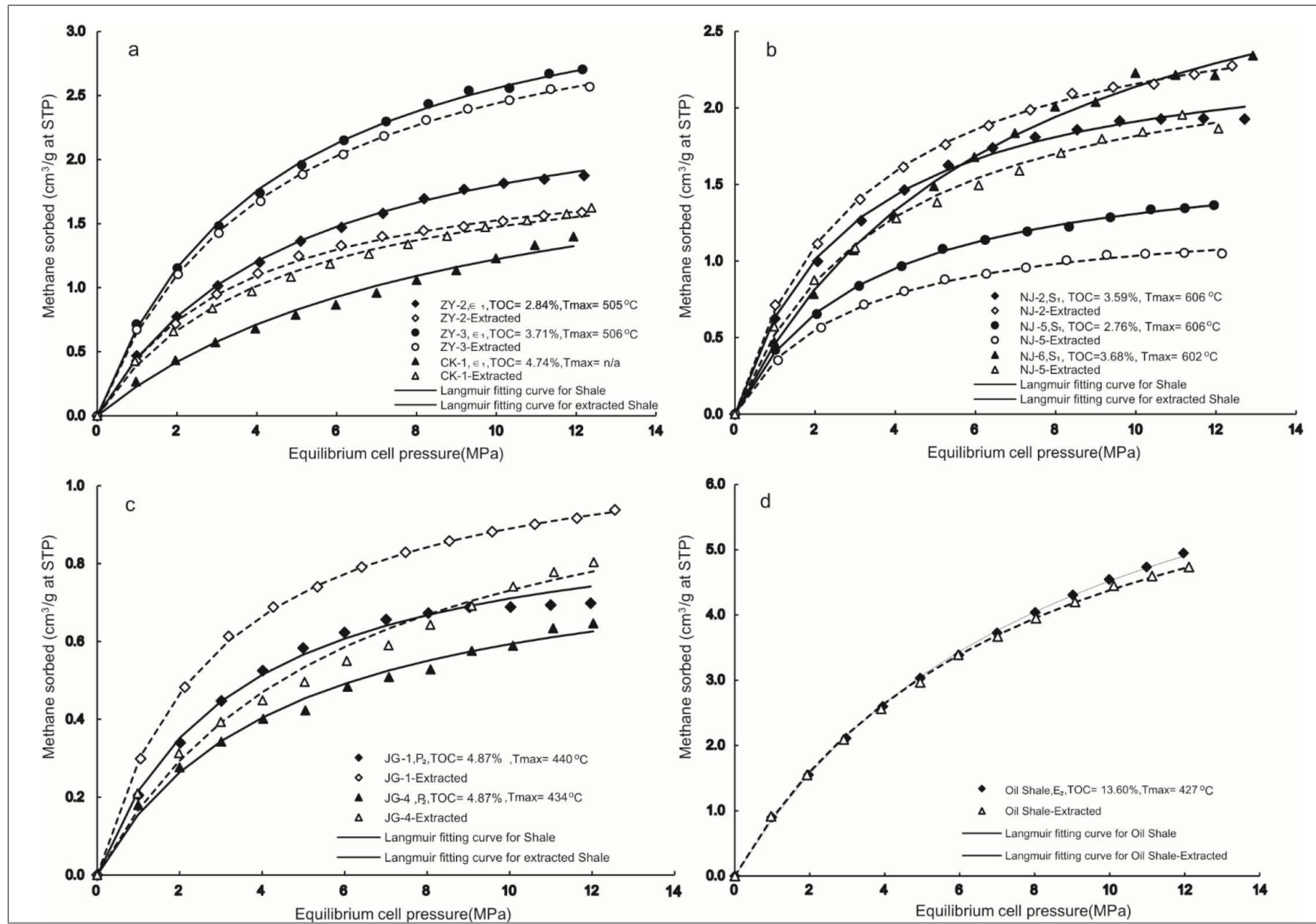


Figure 5. Representative sorption isotherms of shales and their extracted samples.

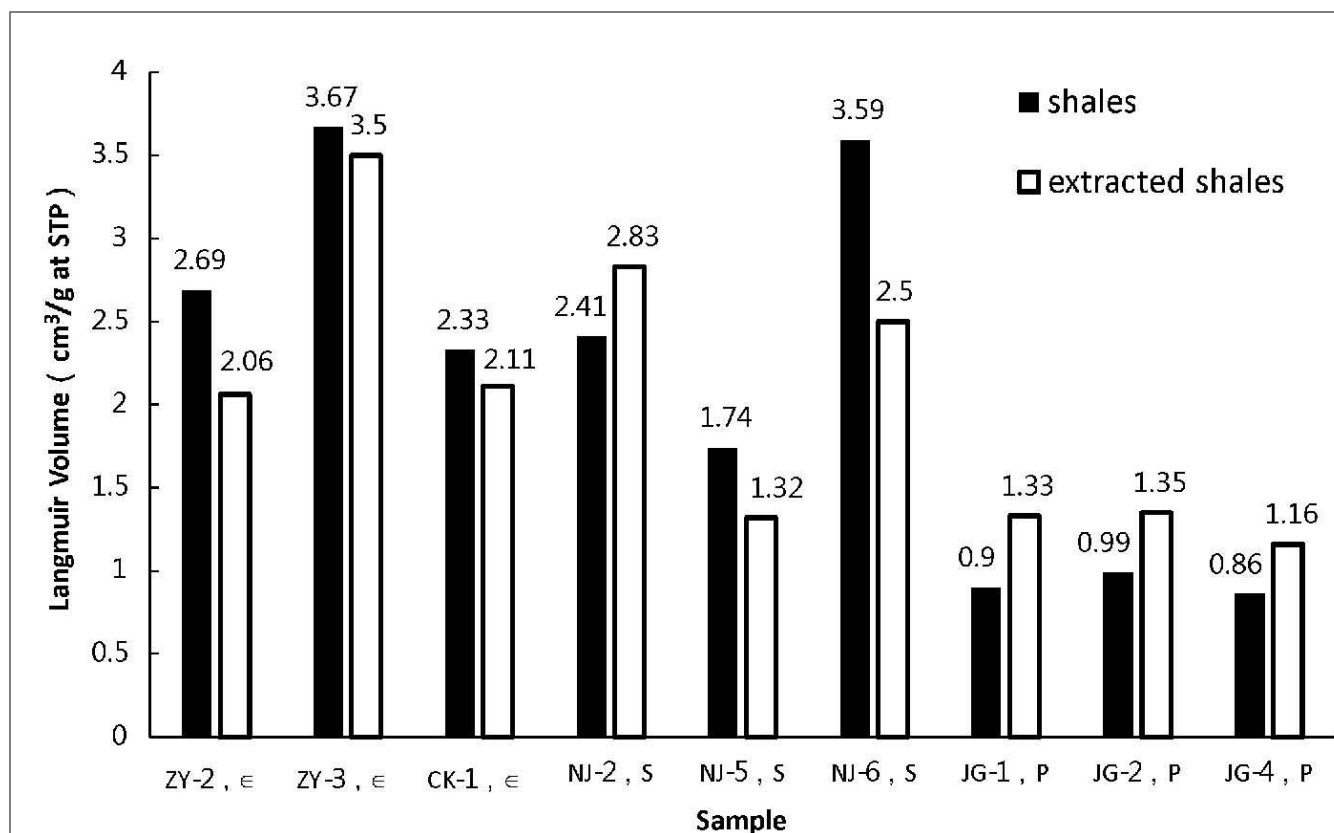


Figure 6. The comparison between Langmuir sorption volume of shales and their extracted samples. Almost all the Cambrian and Silurian extracted shales display reduced sorption capacity compared with initial shales. All the Permian and Paleogene extracted shales show increased sorption capacity compared with initial shales.

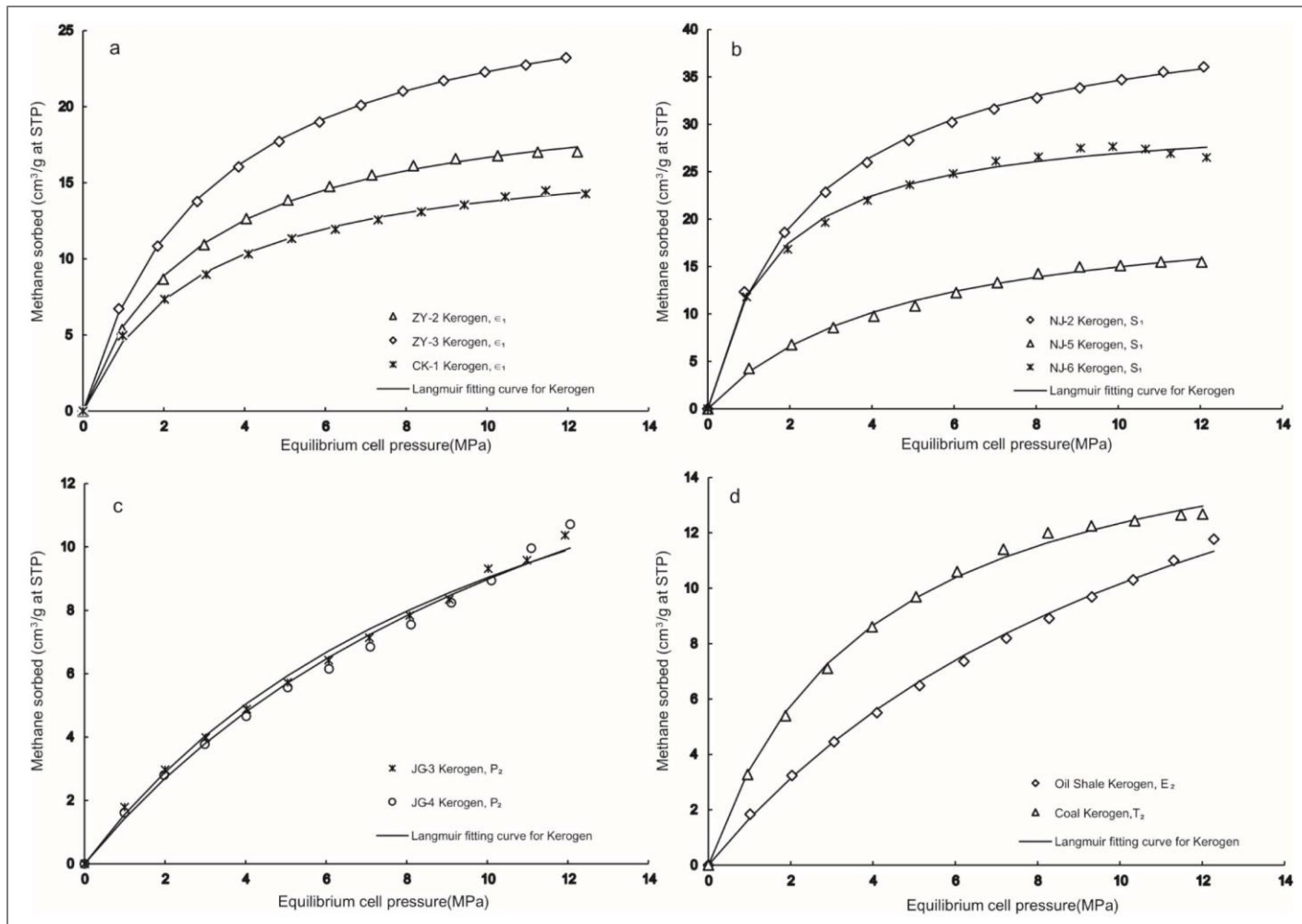


Figure 7. Representative methane sorption isotherms of shale kerogen and coal

Conclusion

The isotherms of high mature kerogen are similar to that of Triassic coal.
The methane sorption capacity of kerogen in Paleozoic shales was investigated.
The methane sorption capacity of kerogen in Paleozoic shales was investigated.