

# Behavior of sedimentary organic matter in a closed system at high pressure and temperature



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## Abstract

Evolution of organic matter was discussed based on the experimental data of lignite-water in a closed system under the conditions of 373~973 K and 1~3 GPa. Geochemical parameters of saturated, aromatic hydrocarbons and carbon isotope ratios of individual *n*-alkanes for the original lignite and pyrolysates were determined. The experimental data indicated that high pressure significantly retarded maturation of organic matter, especially at lower temperature (<773 K), but favored cyclization, polymerization and aromatization of decomposed organic compounds and preservation of biomarkers and carbon isotopic records. Temperature effect on evolution of organic matter became more evident when temperature was higher than 873 K at high pressures. The biomarkers, petroleum compounds and carbon isotopic records were retained at the experimental conditions. The results indicate that gases and relative abundance of high molecular weight hydrocarbons and aromatic hydrocarbon may exist under the conditions of the lower lithosphere in the subduction zone, and also are significant for understanding the accumulation, preservation of petroleum in deep reservoirs and identifying early and extraterrestrial life.

## Sample and Experiment

### Sample

Lignite was collected from Eocene System in Nanning Basin, Guangxi, China, and is composed of 77% humics, 1.6% inertinite, 1.2% stable components, 18% clay mineral and 2.0% quartz with vitrinite reflectivity of 0.45% ~ 0.48%.



Fig.1 JY-3000T press

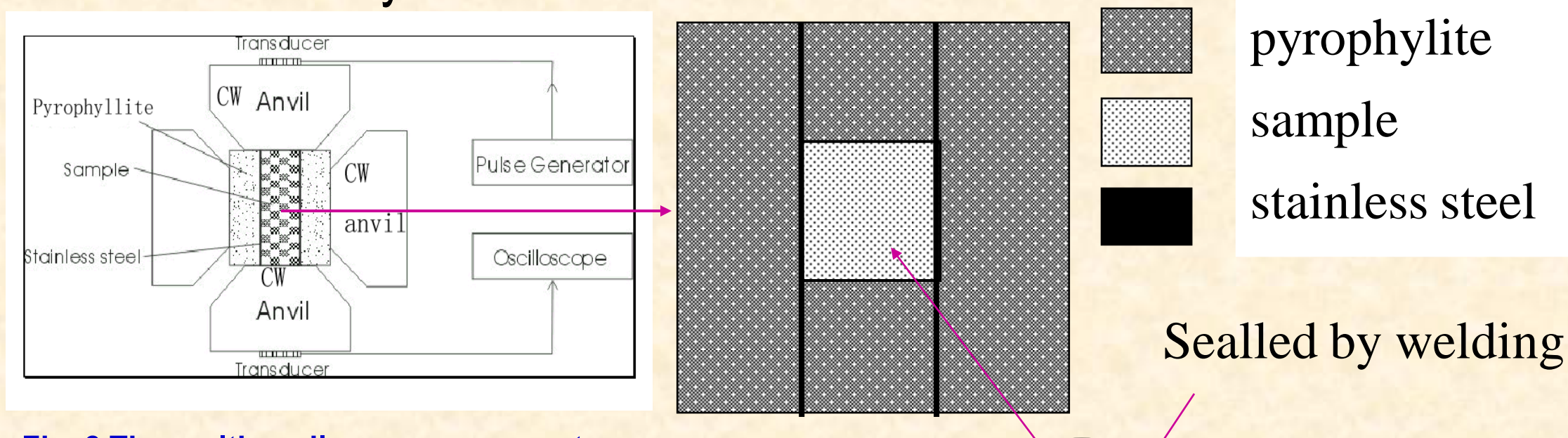


Fig.2 The multi-anvil pressure apparatus

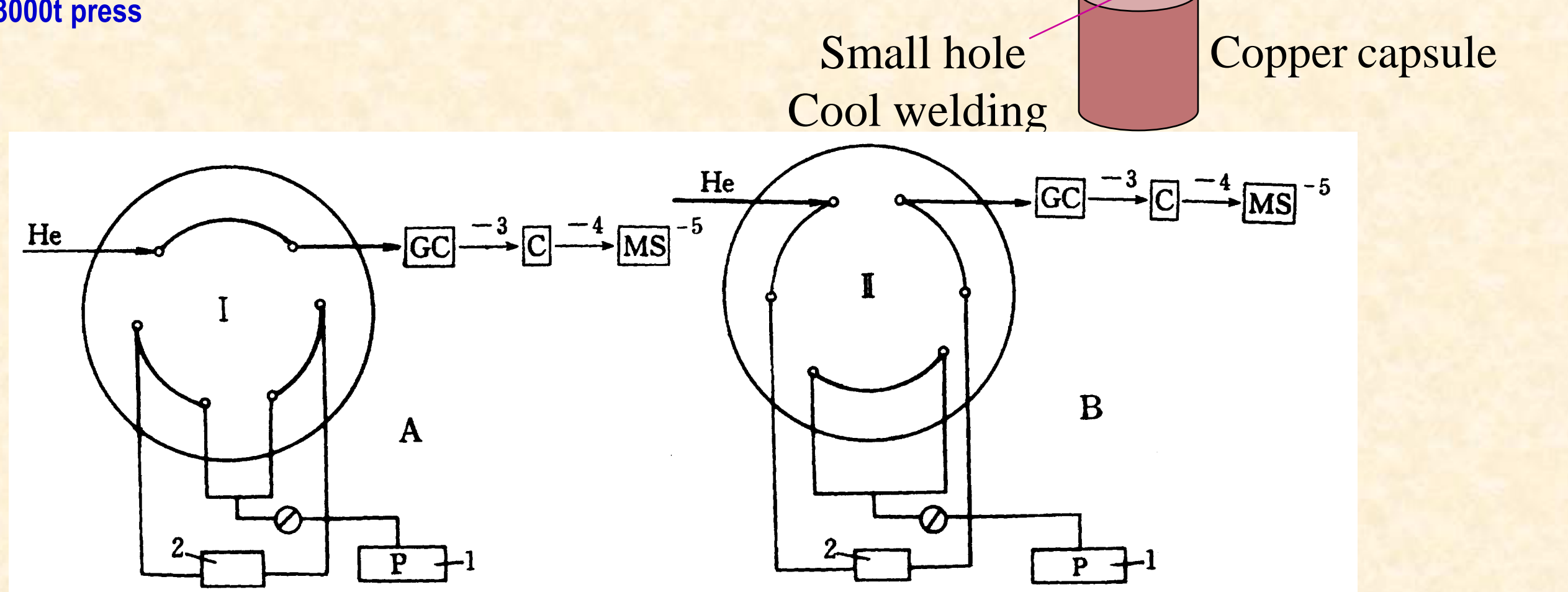


Fig.3 Diagram illustrating the online gas sample collection and analysis for carbon isotope compositions of experimental gas (Jiang et al., 2000). A. Sample collection by crushing the copper capsule of samples in a vacuum line; B. Sample injection and analysis for carbon isotope composition. States A and B are switched by a six-port valve (I and II). 1. Mechanical vacuum pump; 2. Obturation cell for crushing specimen copper capsule; 3. Gas chromatograph; 4. Combustion chamber; 5. MAT 52 Mass spectrometer. He was used as the carrier gas.

## Result and Discussion

### Carbon isotope compositions of gaseous hydrocarbons

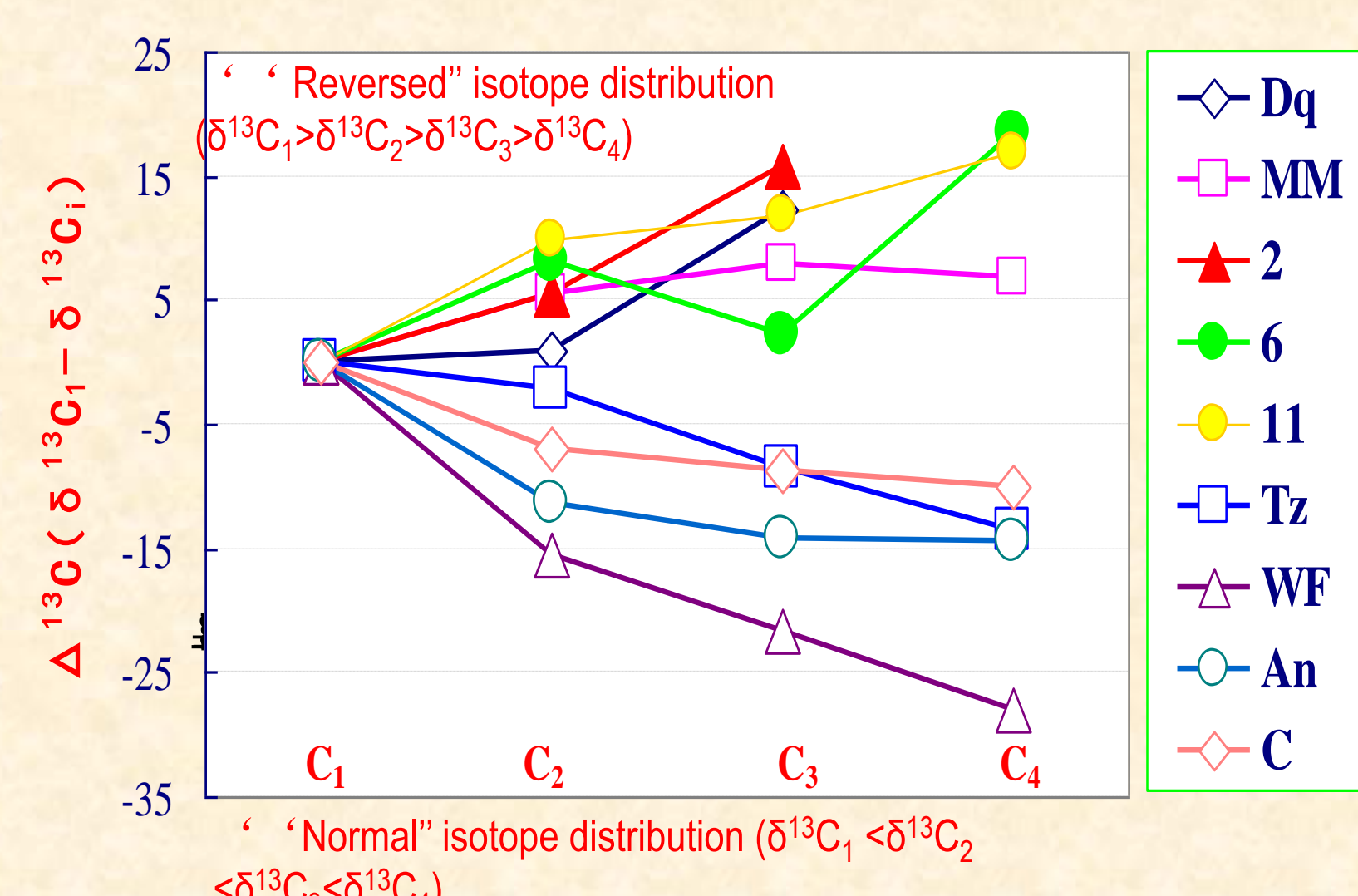


Fig.4 Differences between  $\delta^{13}C_2$  and  $\delta^{13}C_1$  in various gases thought to have biogenic and abiogenic origins. Dq—gas produced from the Daqing oil and gas field (Guo and Wang, 1994); MM—Murchison meteorite (Yuen et al., 1984); Sample Nos. 2, 6 and 11—HPT pyrolysates at pressures of 1, 2, 3 GPa (Du et al., 2003); Tz—Natural gas produced from the Tazhong-1 well in the Tarim Basin, NW China (Dai et al., 1997); WF—Gas from the drilling mud in the Wildmere field (Rowe and Muehlenbachs, 1999); An—Natural gas from Angola (Prinzhofer and Huc, 1995); C—Gases produce by low pressure pyrolysis of brown coal at 365 C (Andresen et al., 1995).

## Results and Discussion

### Alkanes

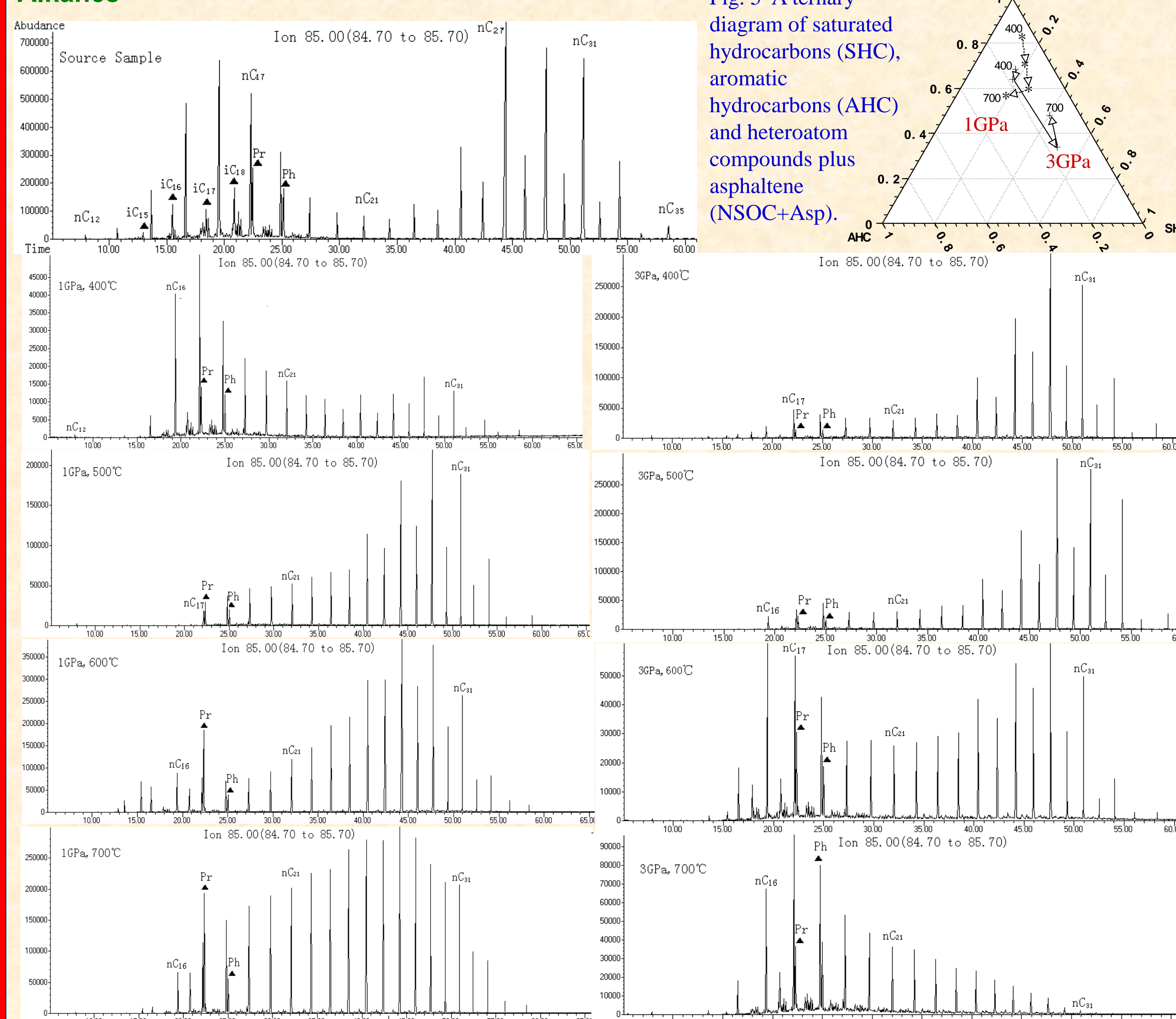


Fig.5 A ternary diagram of saturated hydrocarbons (SHC), aromatic hydrocarbons (AHC) and heteroatom compounds plus asphaltene (NSOC+Asp).

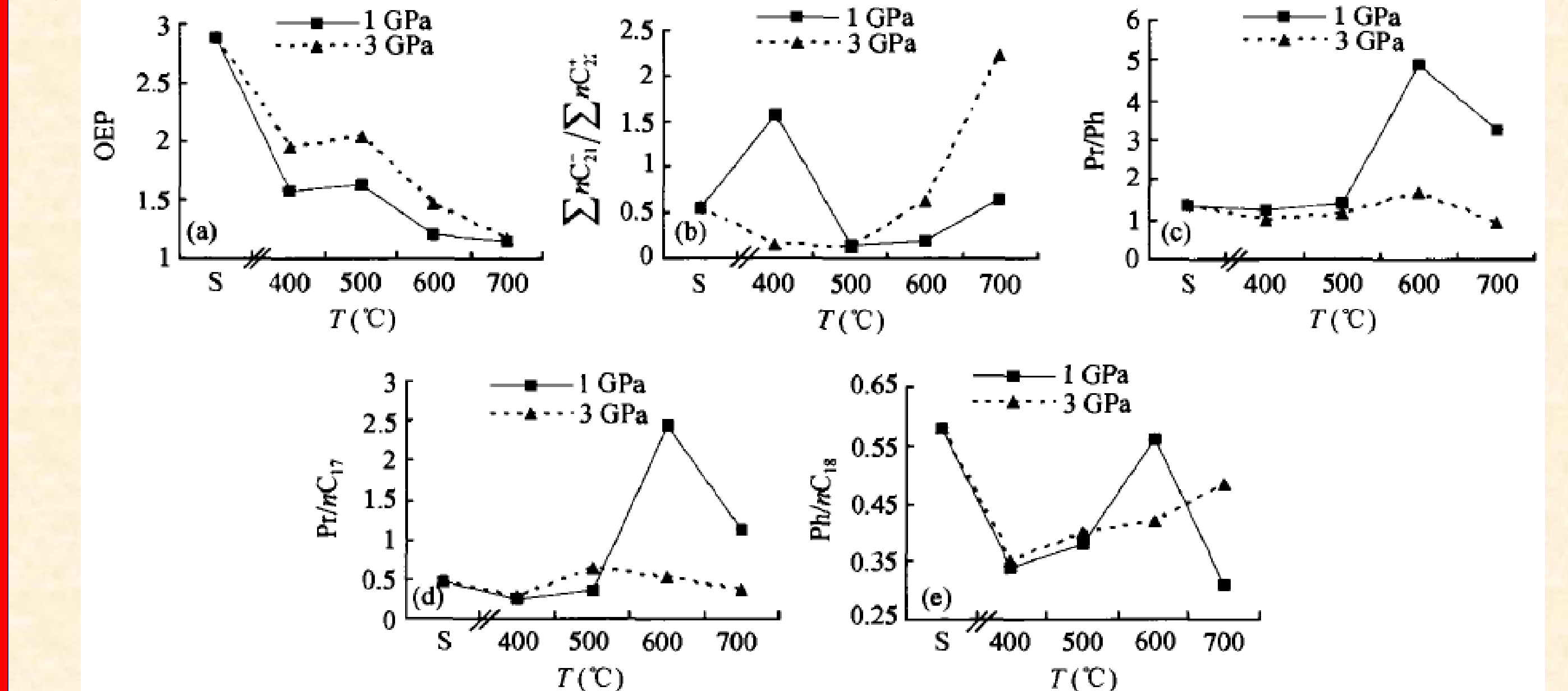


Fig.6 GC-MS chromatograms of *n*-alkanes extracted from the lignite and the HPT pyrolysates, showing the distribution patterns of acyclic alkane abundances at HPT. The abscissa denotes retention time(s) and ordinate presents relative intensity (mV). Pr—pristane, Ph—phytane, *n*-C<sub>i</sub> and *i*-C<sub>i</sub>—normal alkane and isomeric alkane with carbon number *i*.

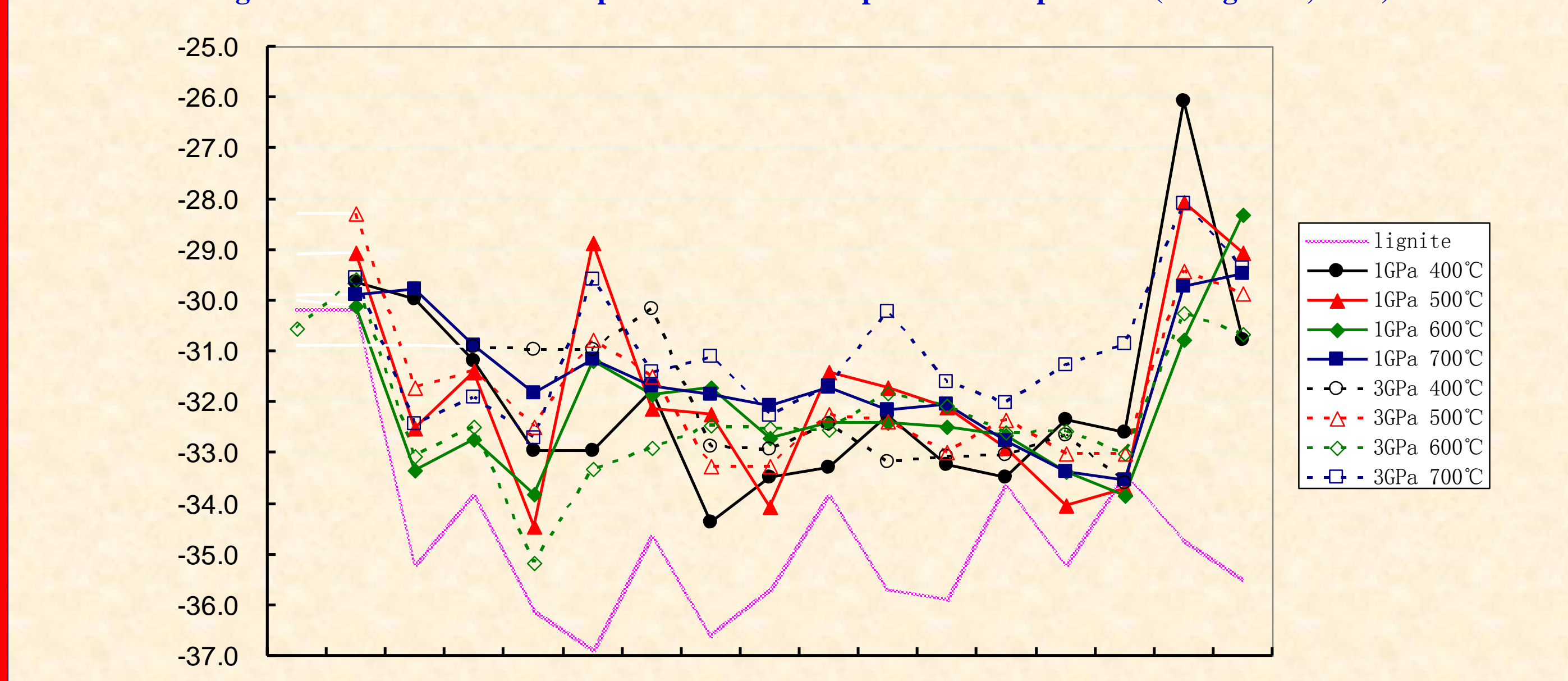


Fig.7 Variations of *n*-alkane parameters with temperature and pressure (Wang et al., 2006)

Fig.8 Carbon isotopic profiles of *n*-alkanes from the lignite and pyrolysates at 3 GPa and different temperatures

### Aromatic hydrocarbons

Table1 Variation in yield of chloroform bitumen "A" and its fractions and parameters of aromatic hydrocarbon at different temperatures and pressures

Chloroform bitumen "A"	Fractions (mg/g Sat TOC)	T (°C)	P (GPa)	Sample 400		Sample 500		Sample 600		Sample 700	
				1	3	1	3	1	3	1	3
Naphthalenes	MNR	1.8	1.5	3.4	1.0	2.5	0.8	1.1	1.0	1.4	1.1
	TeMN/TeMN	0.4	20	13.7	7.3	2.6	0.9	1.8	1.3	1.4	1.3
Phenanthrenes	1,2,5-/1,3,6-TMN	0.4	0.7	1.6	2.6	1.4	2.5	1.3	3.1	0.7	2.9
	MPI-1	0.13	0.27	0.38	0.27	0.65	0.48	0.68	0.65	0.88	0.63
	MPI-2	1.64	1.54	1.02	1.85	1.73	1.54	1.76	1.37	1.95	1.34
	MPI-3	1.00	0.86	0.58	1.08	1.04	0.86	1.09	0.82	1.15	1.12
Perylene	MPR	1.50	1.38	1.13	1.60	1.18	1.06	1.29	0.96	1.30	1.00
	MP/P	0.34	0.44	1.27	0.42	1.41	1.08	1.53	2.14	2.25	2.06
Perylene	Rc (%)	0.48	0.56	0.63	0.57	0.79	0.69	0.81	0.79	0.93	0.78
	PER/BFL	110	40.7	120	4.6	12.0	15.8	0.1	7.4	0.2	7.6
Perylene	PER/B(e)PY	110	58.1	100	3.8	19.4	25	0.3	25.8	0.2	24.9

a) Data of yield of chloroform bitumen "A" and its fractions cited from Wang et al.<sup>10</sup>; b) data of repeated experiments (700°C, 1 GPa). MN (methyl-naphthalene), TMN (Trimethylnaphthalene), TeMN (Tetramethylnaphthalene); P (phenanthrene), MP (methylphenanthrene); PER (perylene), BFL (benzofuranthene). B(e)PY (benzo[e]pyrene). MNR=β-MN/α-MN; MPI-1=1.5(3-MP+2-MP)/(P+9-MP+1-MP); Rc=0.6MPI-1+0.40; MPI-2=3(2-MP)/(P+9-MP+1-MP); MPI-3=(3-MP+2-MP)/(9-MP+1-MP); MPR=2-MP/1-MP.

Increasing temperature and pressure significantly affects organic matter metamorphism, resulting in the reduction of the Sat/Aro ratio and more abundant alkylphenanthene than phenanthrene. The mature parameters, such as MNR and MPI-1, are directly proportional to temperature, but inversely proportional to pressure.

## Conclusion

1. Gaseous hydrocarbons can be generated from organic matter under the HPT conditions of the lower lithosphere, particularly in subduction regions where sedimentary organic matter might be introduced into the mantle. The reversal in the stable carbon isotopes of gaseous hydrocarbons may not be an exclusive indicator of abiogenic gases. Therefore, isotope criteria commonly used to differentiate biogenic from abiogenic gases should be used with caution.

2. The relative abundance of high molecular weight alkanes could exist under the conditions of the lower lithosphere, which breaks through the traditional concept that alkanes mainly present at stage of "oil window".

3. High pressure significantly suppresses the thermal evolution of sediment organic matter especially at lower temperature, but favors the cyclization, polymerization and aromatization of pyrolysate. The pressure effect on maturation of organic matter is nonlinear. It can be inferred that sediment organic matters in the subducted slab could be retained in the deep lithosphere, and the results are also significant for understanding the accumulation and preservation of petroleum in deep reservoirs.

4. *n*-C<sub>12+</sub> hydrocarbons from biogenic sources could be preserved under the HPT conditions. Compounds, such as Pr and Ph, might preserve the carbon isotope signals inherited from biogenic sources. However, it needs farther work to trace the origins of organic matter in mantle rocks and extraterrestrial organic matter in meteorites using carbon isotopic compositions of the acyclic alkanes.

### References

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