The Nature and Classification of Organic-Associated Pores (OAP) Through Comparative Study on Marine, Transitional, and Continental Shales in Typical Areas, China*

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Abstract

Analyses of organic-rich shales from well cores that penetrated the marine, transitional and lacustrine shales developed in typical areas of China, were performed to evaluate the nature of organic-associated pores based on the comprehensive organic petrographic and SEM analyses. At least five types of organic macerals (alginate, bitumen, mineral bitumen groundmass, liptinite and vitrinite), four distinct OM occurrence pattern based on its correlation with surrounding minerals (free OM, mineral-adhered OM, clay-combined OM, intergrowth OM), and four subtypes of organic-associated pores based on genetic mechanism (hydrocarbon-bubble pore, hydrocarbon-dissolution pore, fossil-skeleton pore, OM-shrinkage pore) were identified in backscattered-image analyses. Mineral-adhered OM and clay-combined OM nearly corresponding to bituminite and mineral-bitumenous groundmass (MBG) respectively, are the primary OM occurrence patterns and usually exit in lacustrine shales in low maturation and marine shales in high maturation respectively. This is in contrast with the free OM generally as the particulate material with bio-texture (e.g. alginate, liptinite, vitrinite, fusinite and detritus of them) but mainly distributed in transitional shales for its abundance of vitrinite. Hydrocarbon-bubble pore is the most common and significant organic-associated pore type, which is generated by gas breakthrough out of the OM surface under the expansion force in gas window and widely developed in marine shales rich in free algnite and clay-combined OM. Hydrocarbon-dissolution pore is essentially the mineral-hosted pores accompanied with strong organic-acid corrosion caused by mineral-adhered OM or bitumen-coating in oil-window, and hereby is mostly developed in most of lacustrine shales but in small quantity. OM-shrinkage pore typically occurs along the conjunct edge between organic and inorganic constituents and is usually developed in the transitional shales due to OM occurrence. Fossil-skeleton pore usually distributed in organic detritus under certain pattern with specific geometric shape is less developed in all of the shales. In addition, a further study on the correlation between various OM occurrences and the evolution of organic-associated pores should be made, since the various associative relations between the organic matter and clay minerals could cause difference in their thermostability and further affected the hydrocarbon generation.

The nature and classification of organic-associated pores (OAP) through comparative study on marine, transitional, and continental shales in typical areas, China

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Outline

✓ **1 Introduction**

✓ **2 Samples and experiment methods**

✓ **3 Organic geological parameters**

3.1 kerogen type

3.2 OM maturity

✓ **4 OM identification**

4.1 OM classification

4.2 OM groups identification

4.3 OM subgroups identification

✓ **5 OAP development in different shales**

5.1 OAP classification

5.2 OAP developmental level in different shales

✓ **6 OAP development regularity**

✓ **7 Conclusions and outlooks**

1. Introduction

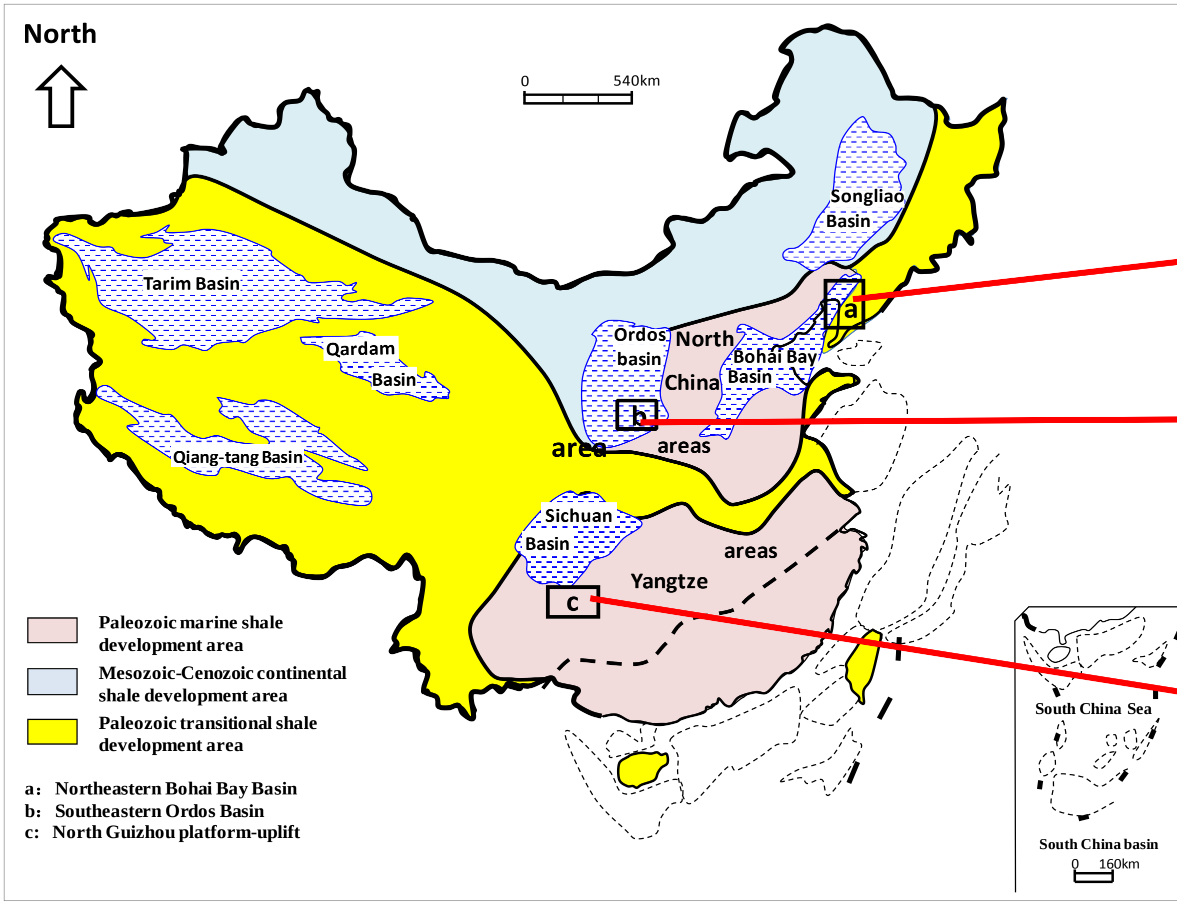
Organic pores have been confirmed since their first identification in the marine Barnett Shale, and they are believed to be generated within OM caused by gas-exsolution during the second thermal cracking stage. Such pores also have been discovered in China, such as the marine Lower Silurian Longmaxi shale and Niutitang Shale in the Upper Yangtze Plate.

Compared with the previous study on organic pores of shales, there are three different points in this study. Firstly, we involve in other pores whose formation is related to the OM in addition to the organic pores, and they are together defined as organic-associated pores (OAP). Secondly, shales from different sedimentary facies were involved, i.e., marine shale, lacustrine shale, and transitional shale, which allows a comprehensive and comparative study on the development difference of OAP. Thirdly, the identification of OM components and its in-situ occurrence under BIB-SEM that have never been involved before was also made in this study, which allows discerning, in which kind of OM that it is inclined to generate the OAP.

2. Samples and experimental methods

Sample sources

a. Liaohe depression in the Bohai Gulf Basin; b. Yanchang Oil Field in the Ordos Basin; c, North Guizhou Province in the Upper Yangtze Plate



Sedimentary facies	Age	Shale
Lacustrine	Es	Shahejie
Lacustrine	T_3	Yanchang
Transitional	P_1	Shanxi
Transitional	P_2	Longtan
Marine	S_1	Longmaxi
Marine	$\in_1$	Niutitang

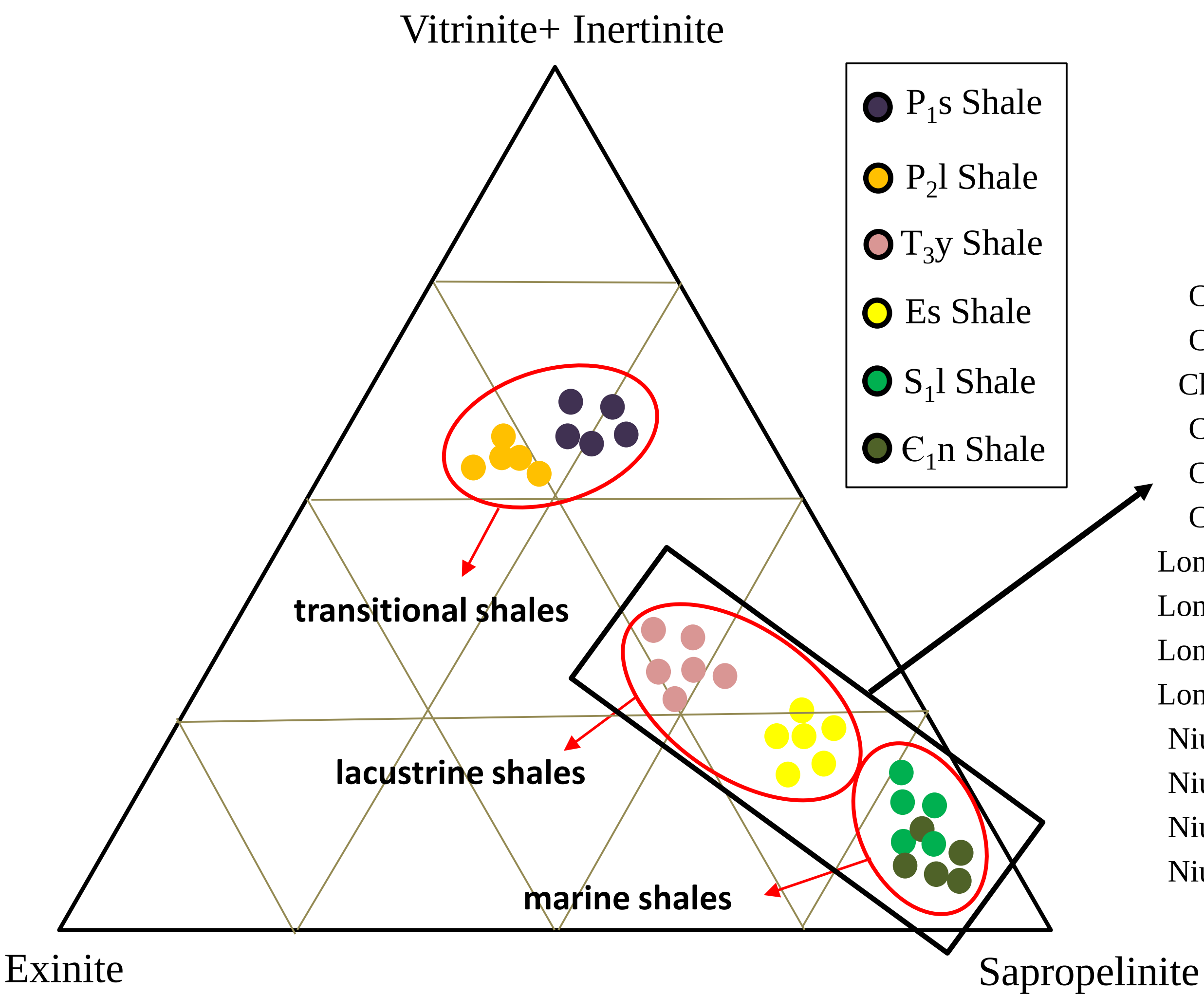
Shale distribution in China and sample locations of this study

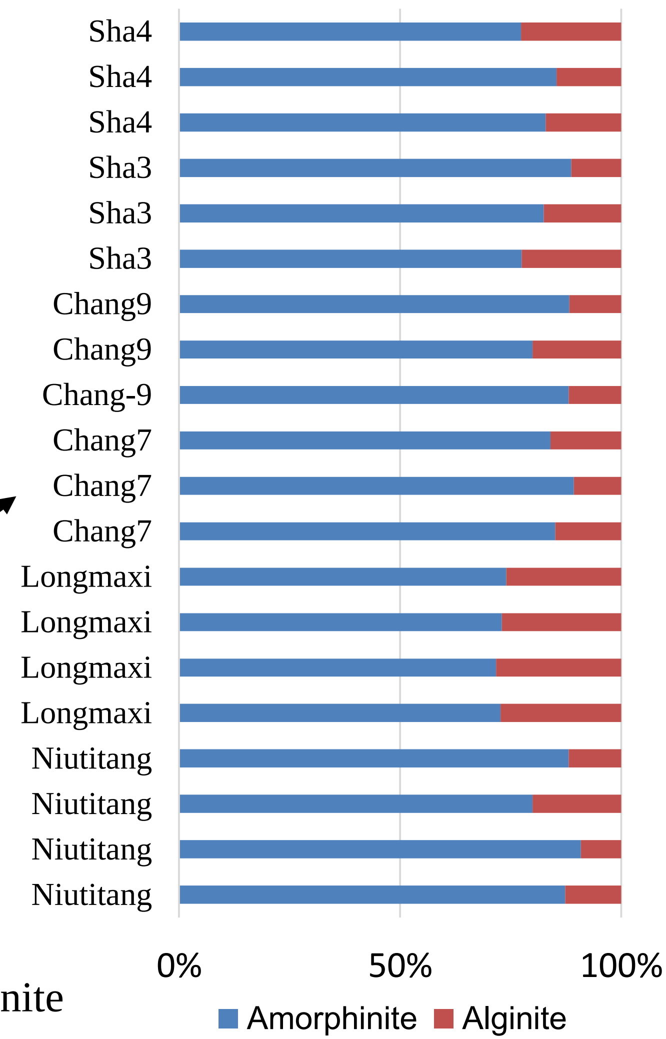
Experimental methods

Broad ion beam-scanning electronic microscope (BIB-SEM); N2 adsorption technique, and related organic geochemistry testing.

3 Organic geological parameters

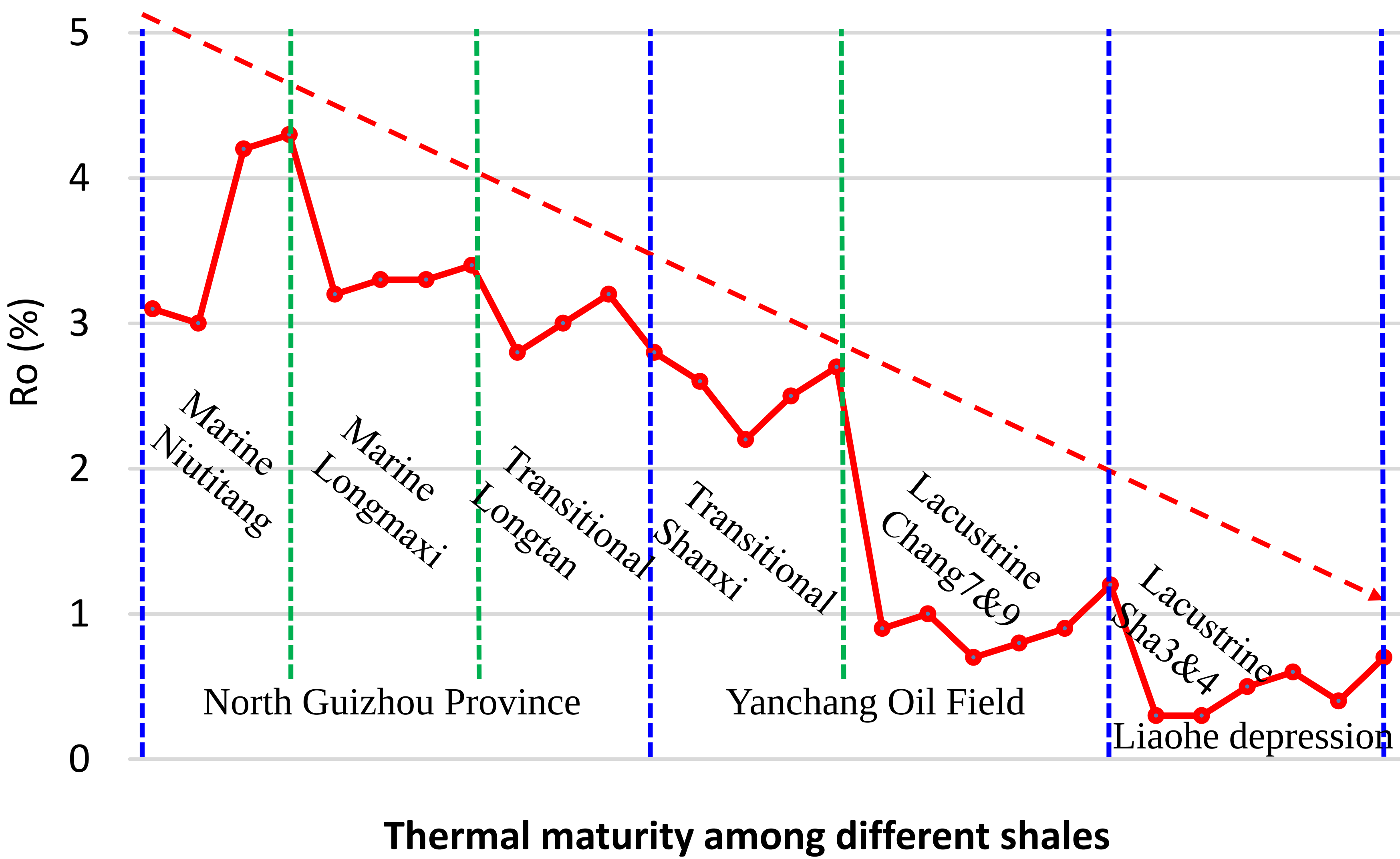
3.1 Kerogen type



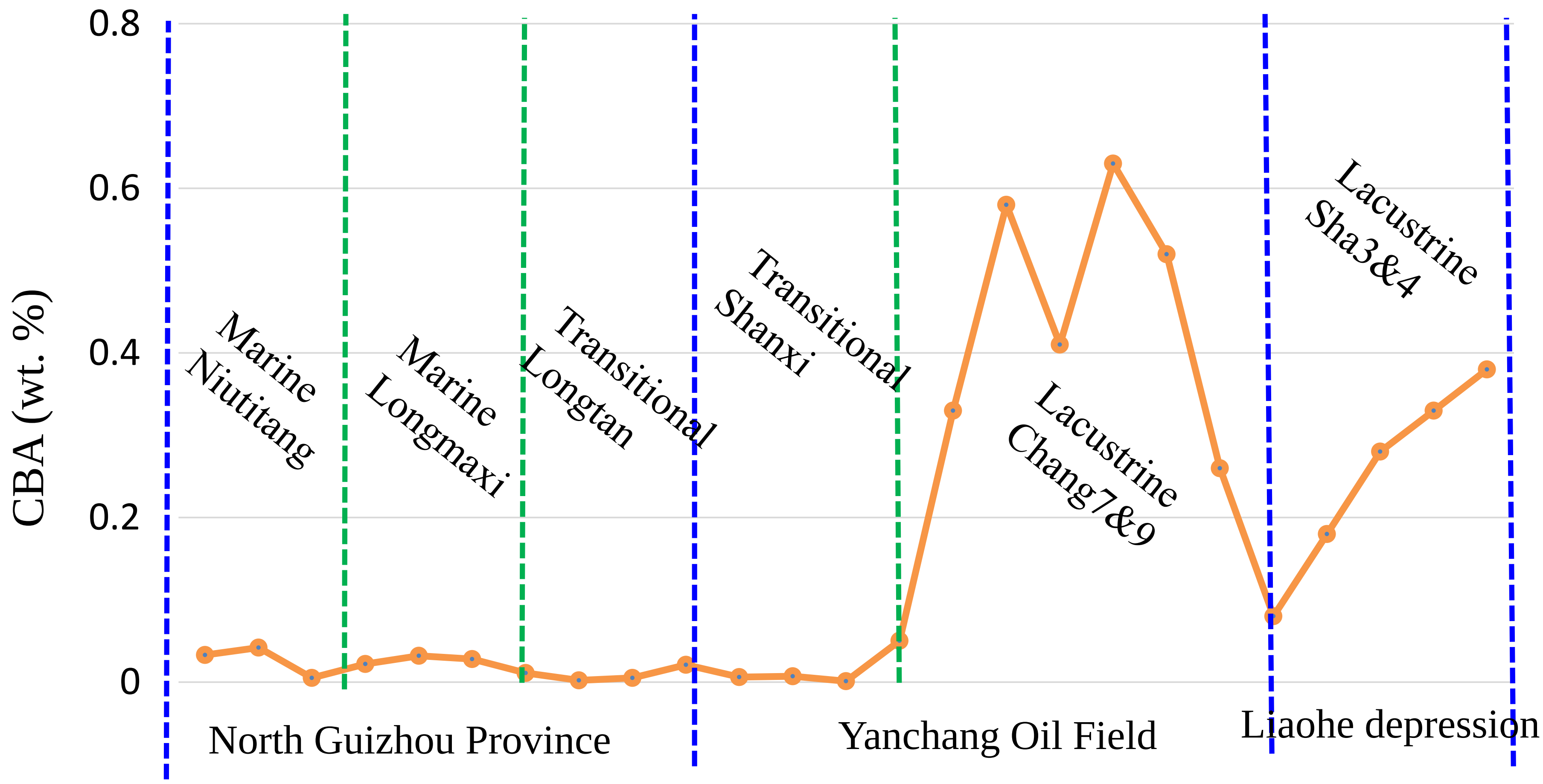


Kerogen type of the three sedimentary facies shales

3.2 Organic maturity



3.3 Chloroform bitumen “A” (CBA)



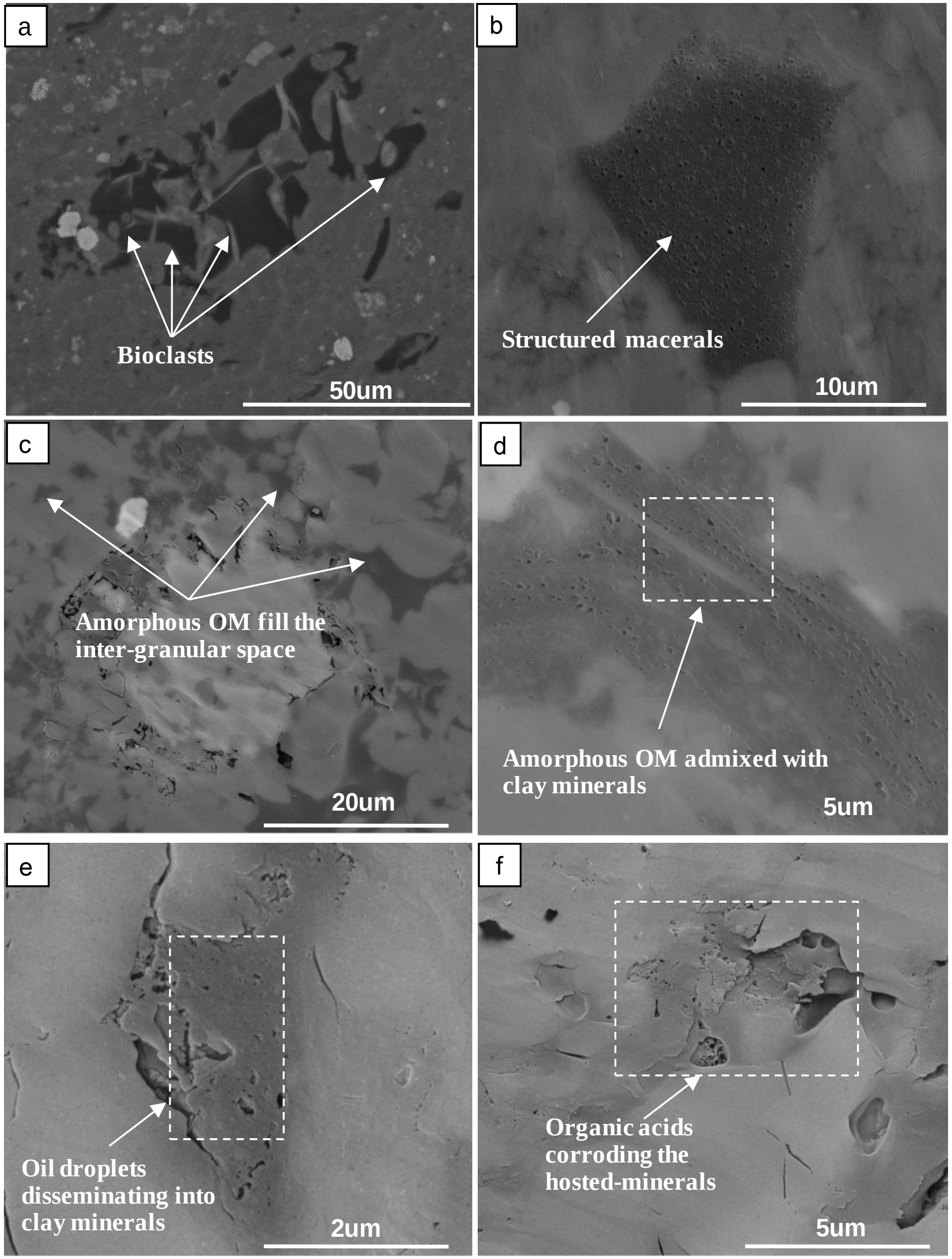
CBA content among different shales

4 OM identification under BSE images

4.1 OM classification from a morphological view

OM groups		OM components		Parental source	Frequency
Structured OM (SO)	Protogenetic SO	Bioclasts		Animal soft-tissue orphyto-detritus, such as graptolite, conodont, etc.	Rarely found in marine and terrestrial shales
	Epigenetic SO	**kerogen**	Inertinite	Fusinized products from xylem fiber in terrestrial higher plant	Commonly found in transitional shales
			Vitrinite	Gelatinized products from xylem fiber in terrestrial higher plant	
			Exinite	Epidermal tissue and secretion from terrestrial higher plant	Often found in terrestrial shales
			Alginite	Alginite without or with slight biodegradation	Rarely found in marine and terrestrial shales
Amorphous OM (AO)	Primary AO		Sapropelic amorphinite	Mycogenic products from lower aquatic organisms	Commonly found in marine and terrestrial shales
			Humic amorphinite	Biodegraded products of hydrogen-rich vitrinite and exinite	Only found in transitional shales in small quantity
	Secondary AO	**Solid bitumen**	Pre-oil solid bitumen	Early generation products from immature source rocks originally as very viscous fluids and later turn into solid by modification.	Only exist in immature shales in small quantity
			Post-oil solid bitumen	Products of the alteration of a once-liquid oil, generated from a mature source rock	Only exist in highly over mature shales in small quantity less than 25%
Thin-film OM (DO)		Liquid hydrocarbons	Oil droplets	Secondary products derived from a mature kerogen	Largely found in mature shales
			Organic-acids	Early generation products derived from immature to low maturity source rocks	Mainly exist in immature to low-maturity shales

4.2 OM groups identification using BSE images

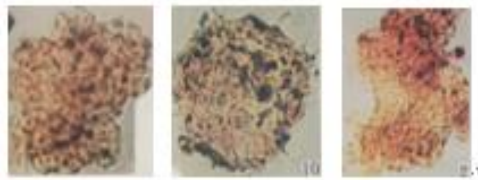
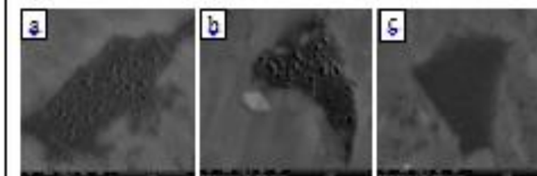
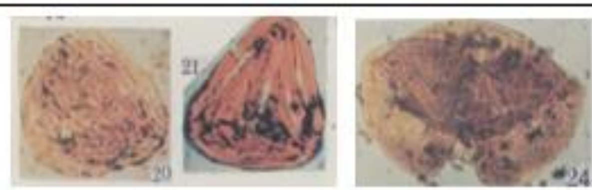
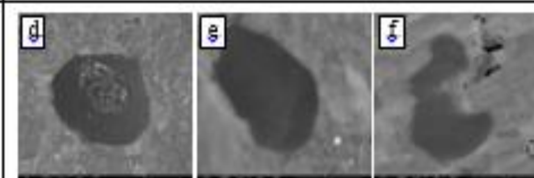
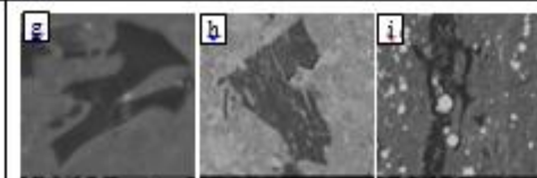
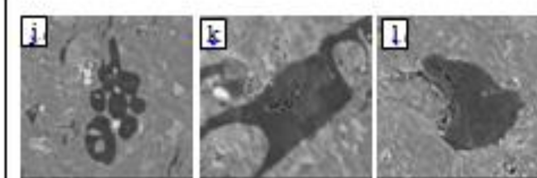


Structured OM with bio-texture have strong capacity to resist external compaction during deposition-diagenesis and thus usually present irregular shapes with well-defined boundaries in BSE images.

Amorphous OM (amorphinite and solid bitumen) are usually deformed into elongate or curly bodies and thereby usually fills into the inter-granular pores or admix with the clay minerals due to their high plasticity.

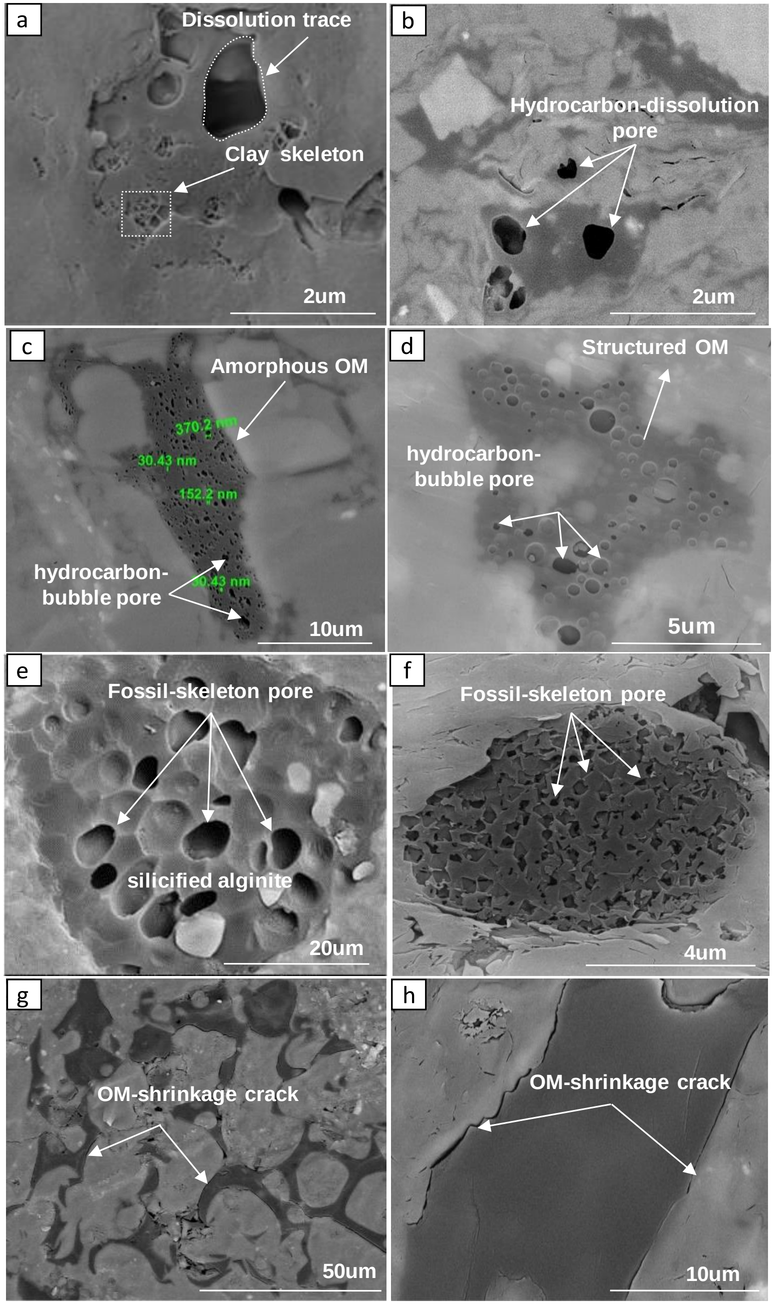
Thin-film OM have their own identifying characteristics in BSE images with lower grey value compared with the structured OM and the amorphous OM. They usually adhere onto or disseminate into the contacting minerals.

4.3 kerogen macerals identification using BSE images

Structured macerals	Morphological characteristics	Typical photomicrograph at different microscopes		
		Extracted morphology under optical microscope (Cao, 1984)	In-situ morphology under BIB-SEM	Zoom
Alginite	Variable contour with smooth boundary, generally showing oval or spindle morphology			>10000
Exinite	Regular contour with smooth boundary, showing globular or angular shape			×5000 ~10000
Vitrinite	Irregular contour with sharp boundary, showing stripped, clavate, or dendritic shape			×3000 ~5000
Inertinite	Irregular contour with sharp boundary, showing fragmentary or columnar shape			<×3000

5 OAP development

5.1 OAP classification based on the genetic mechanism



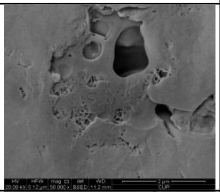
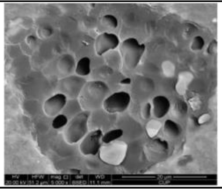
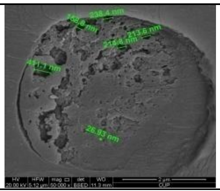
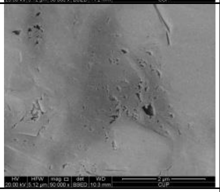
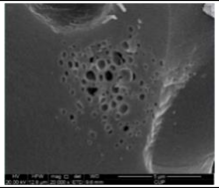
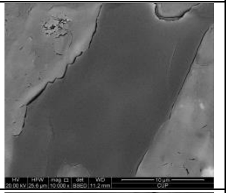
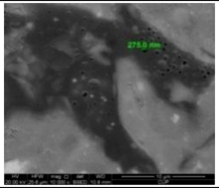
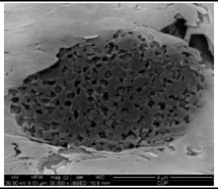
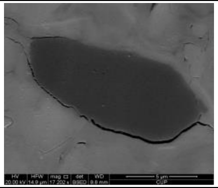
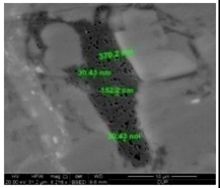
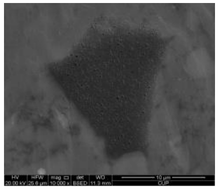
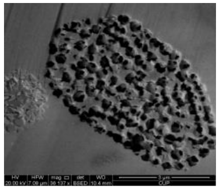
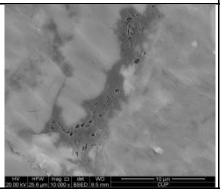
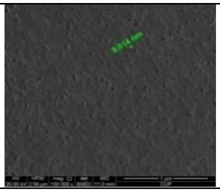
One is defined as hydrocarbon-bubble pores, which is exactly the organic pore previously defined and is believed to be generated within OM as a result of exsolution of gaseous hydrocarbons during the secondary thermal cracking. They generally present as ellipse shapes with wide spectrum of pore size from tens to hundreds of nanometers.

A small amount of OAP are developed in OM-adhering minerals bearing obvious dissolution trace and a large pore-size range from hundreds of nanometers to several microns. In fact, they are related to the corrosion of organic-acids and thereby we defined them as dissolution-related OAP.

The third identified is the shrinkage-related OAP, which typically occurs along the conjunct edge between the free OM and inorganic constituents. It is linear with a narrow width from several to hundreds of nanometers and the length generally reaching up to several ten microns.

The OAP within structure bioclasts are defined as “bioclast-skeleton pores” (BSP). To be specific, they usually exhibit specific geometric shapes, appearing to be hexagonal in plant tissues and round in silicified alginite with their pore size generally larger than 1μm.

5.2 OAP development level among different shales

	Shales	HBP		HDP	BSP	HSC
		In amorphinite otherwise solid bitumen	In structured macerals	In acids-disseminated minerals	In bioclasts	Around huminite
Terrestrial shales	Paleogene Sha-3& Sha-4	Not found	Not found			Scarcely found
	Triassic Chang-7& Chang-9	Not found			Not found	Scarcely found
Transitional shales	Permian Shanxi	Not found		Not found	Scarcely found	
	Permian Longtan	Not found		Not found		
Marine shales	Silurian Longmaxi			Not found		Scarcely found
	Cambrian Niutitang			Not found	Not found	Scarcely found

This table shows the overall development of OAP in the three sedimentary facies shales that have been classified.

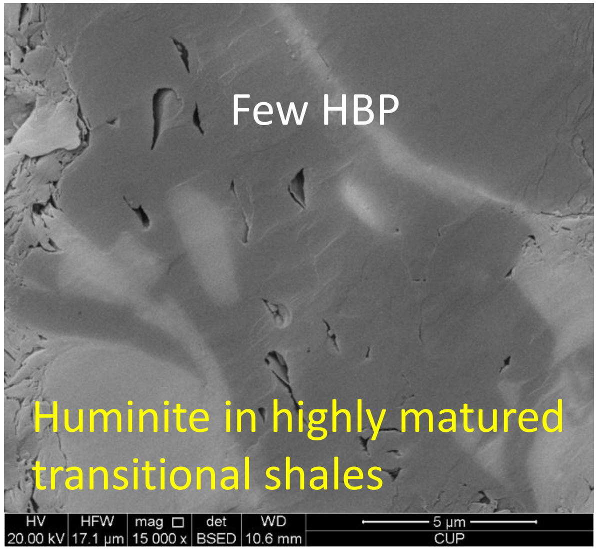
Table. Relative abundance of OAP classes in marine, transitional, and lacustrine shales based on observations. OAP are ranked by relative abundance in the main reservoir lithotype named for the six formation compared. 1=most abundant, 6=least abundant, HBP, Hydrocarbon-consumption pore; HDP, Hydrocarbon-dissolution pore; OSC: OM-Shrinkage crack.

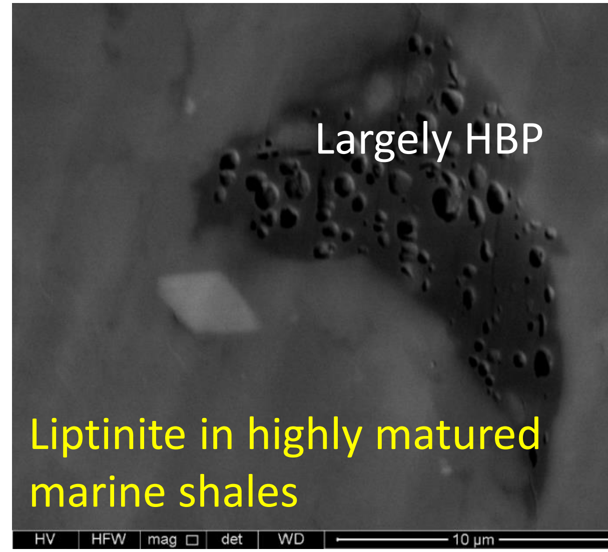
Formation	OAP composition (%)			OAP Rank
	HBP	HDP	OSC	
Sha-3&4	0	90	10	5
Chang-7&9	10	70	20	4
Shanxi	10	0	90	6
Longtan	20	0	80	3
Longmaxi	80	0	20	1
Niutitang	90	0	10	2

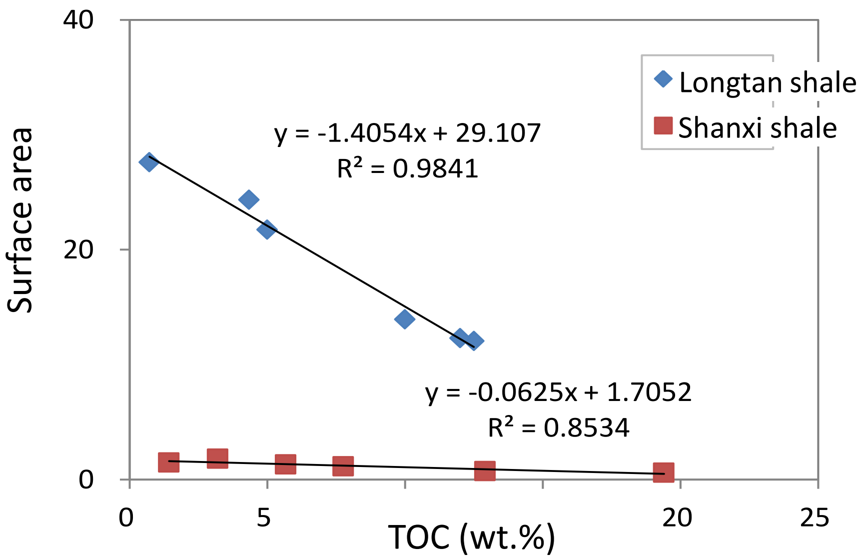
6 Hydrocarbon-bubble pores(HBP) development regularity

6.1 Control of maceral type on hydrocarbon-bubble pores

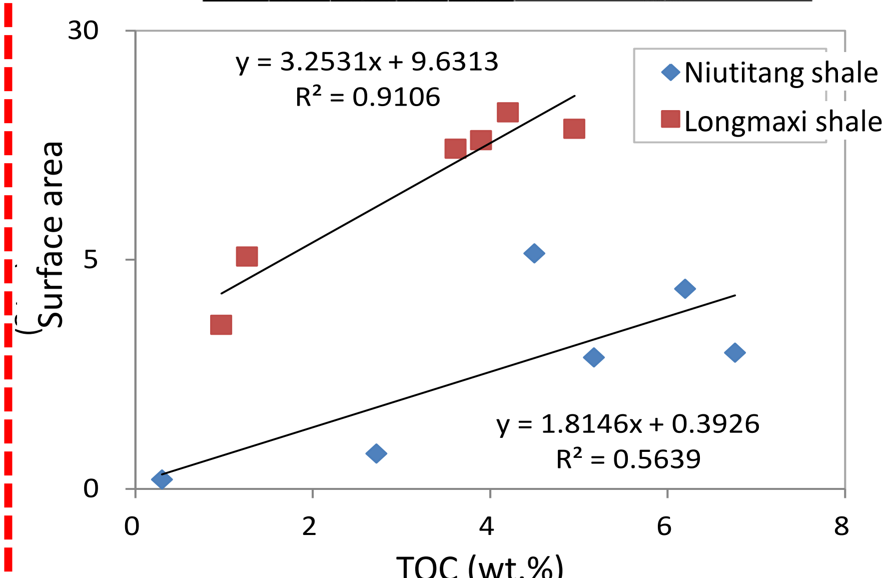
Liptinite is much more developed of HBP than humic macerals.





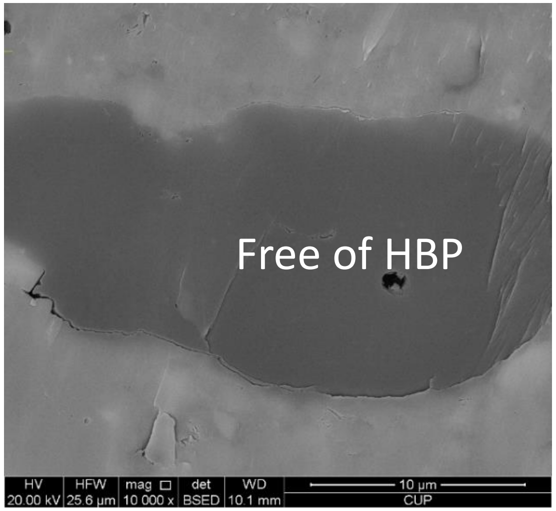


OM poorly develop the HBP so as to make negligible contribution to the surface areas

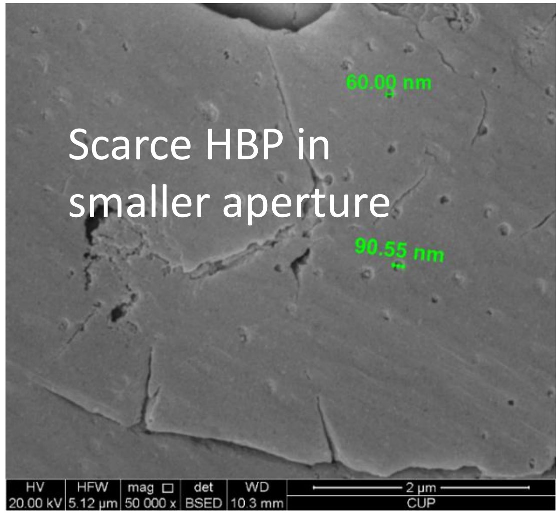


OM widely develop the HBP thus contribute mostly to the surface areas

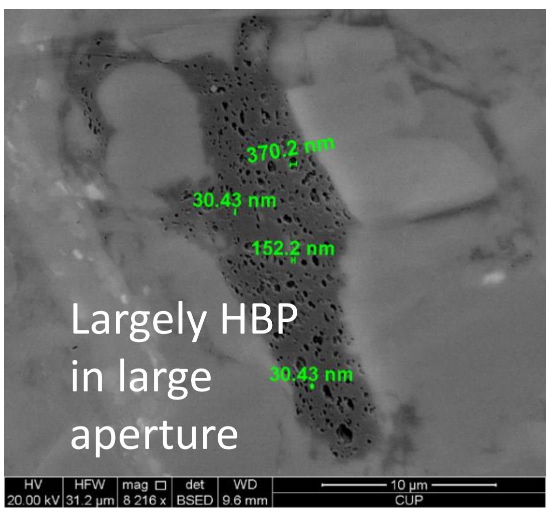
6.2 Control of organic maturity on hydrocarbon-bubble pores



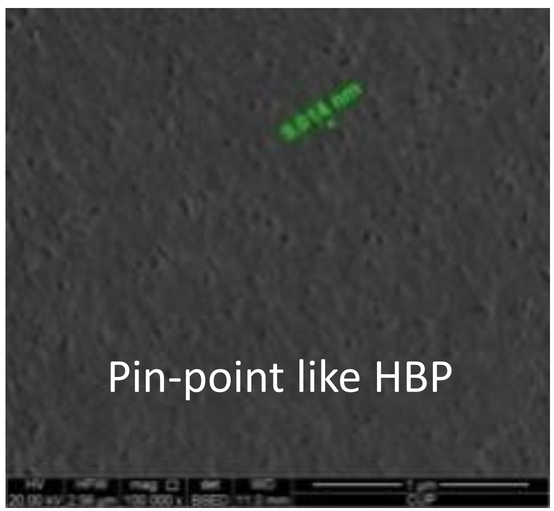
Immature Shahejie Shale



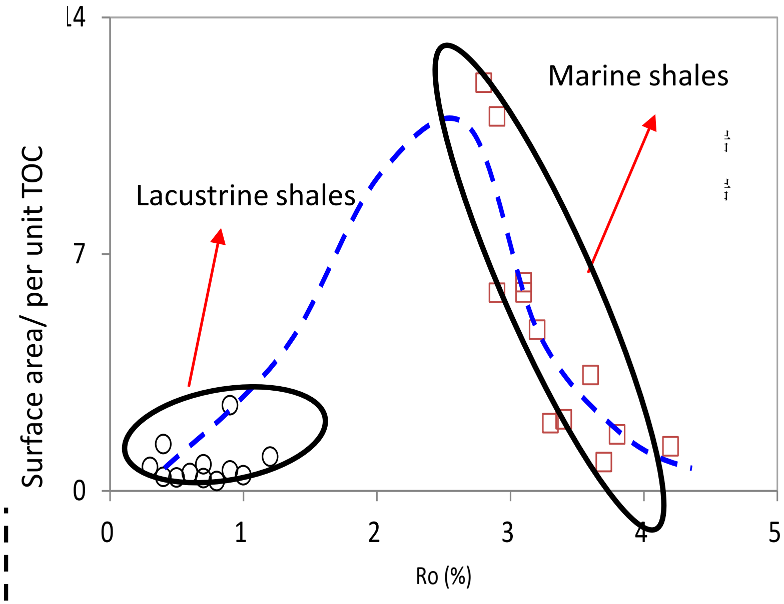
Low mature Yanchang Shale



Highly-over mature Longmaxi Shale

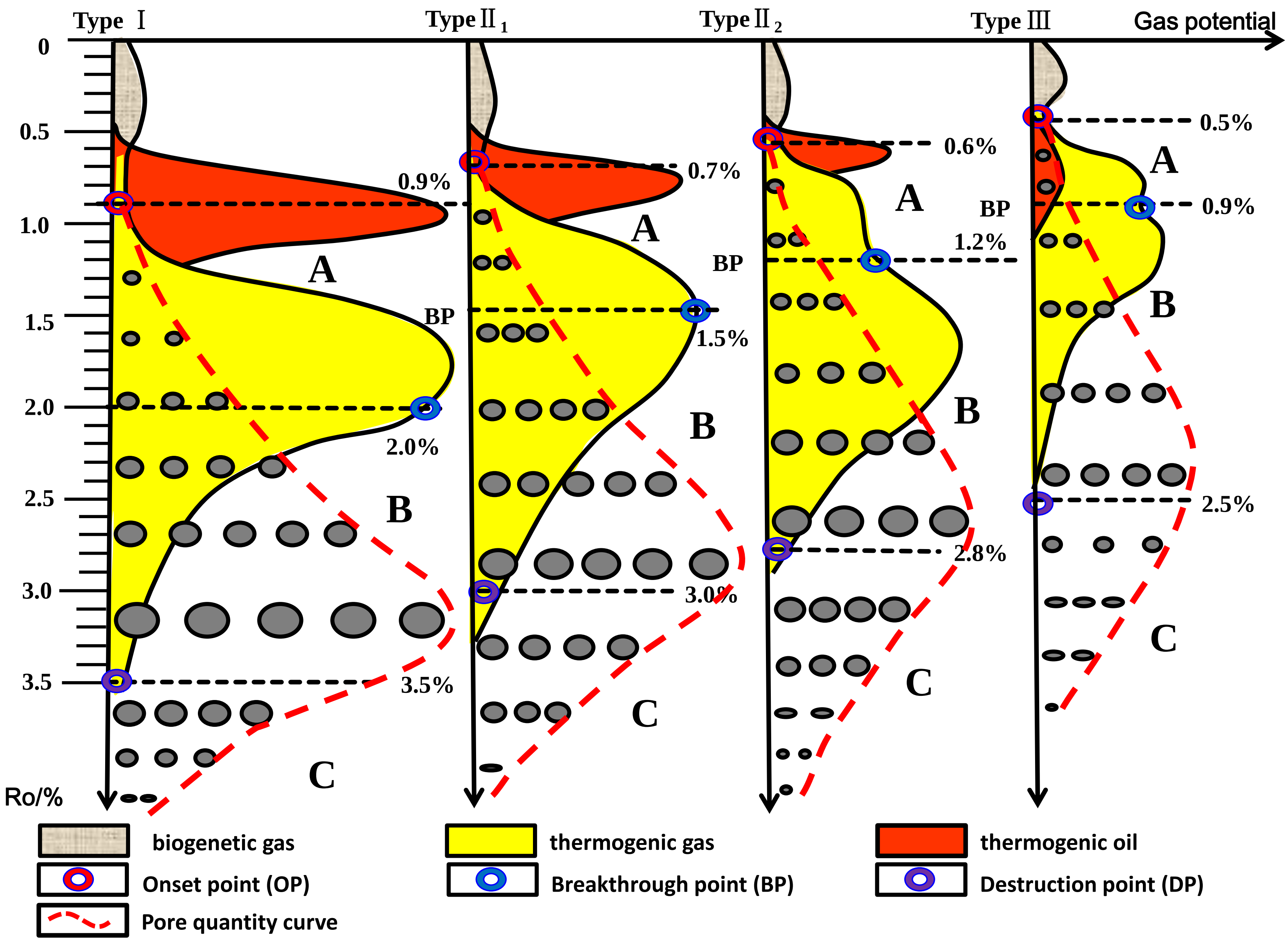


Niutitang Shale in Late over-mature stage



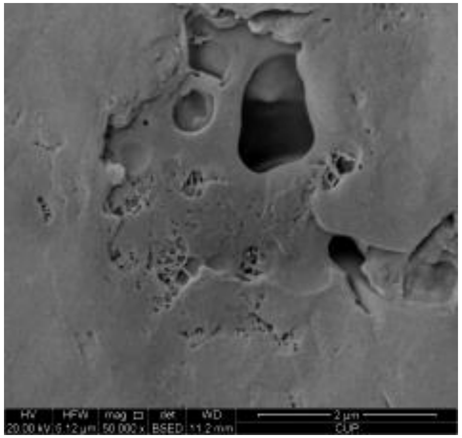
Positively correlated with the thermal maturity within limits (0-3.0 %Ro).

6.3 Development regularity of hydrocarbon-bubble pores

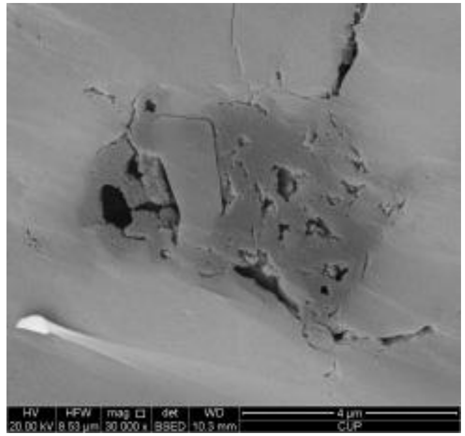


A: formation stage B: Development stage C: Destruction stage

7 Hydrocarbon-dissolution pores(HDP) development regularity



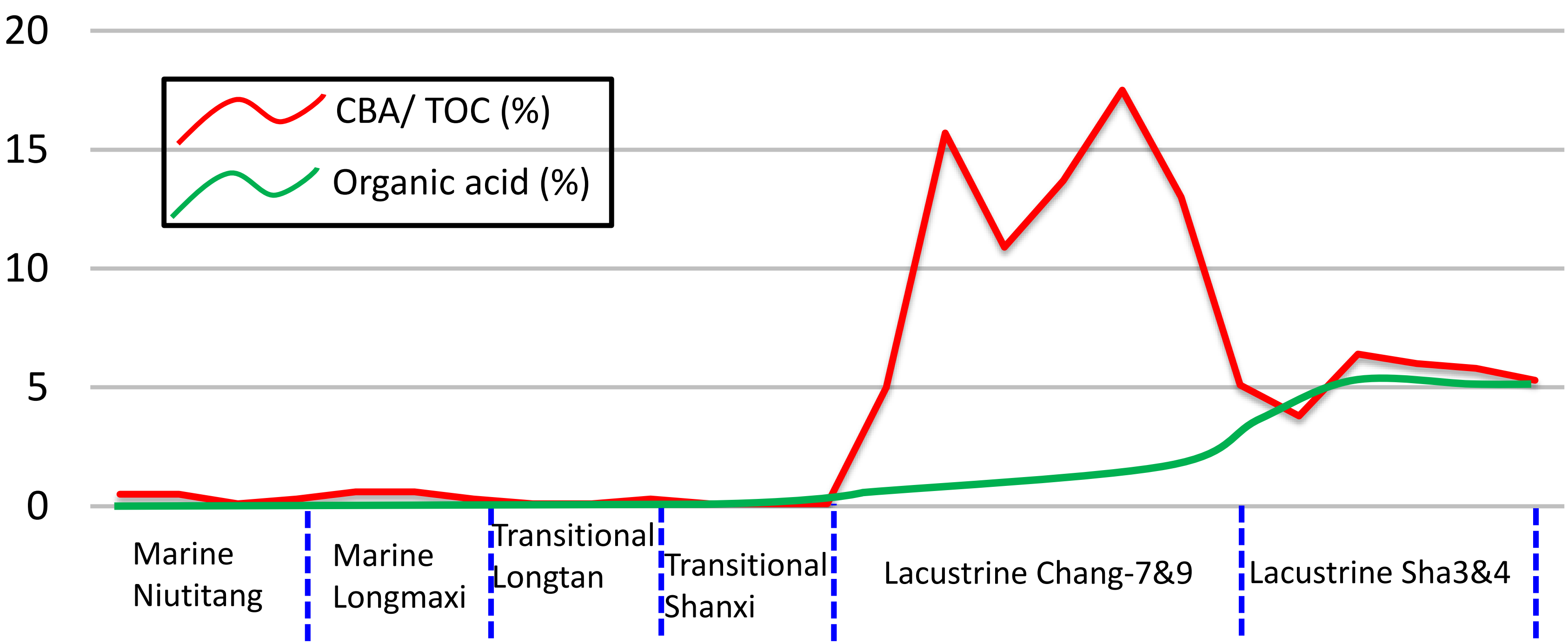
Immature Shahejie Shale



Low mature Yanchang Shale

Rarely found

Highly-over mature marine Longmaxi and Niutitang Shales

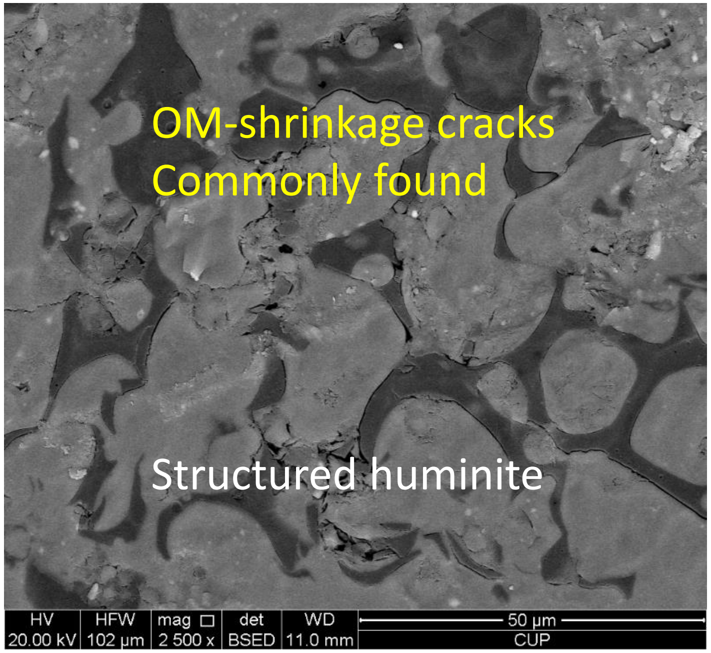


8 OM-shrinkage cracks development regularity

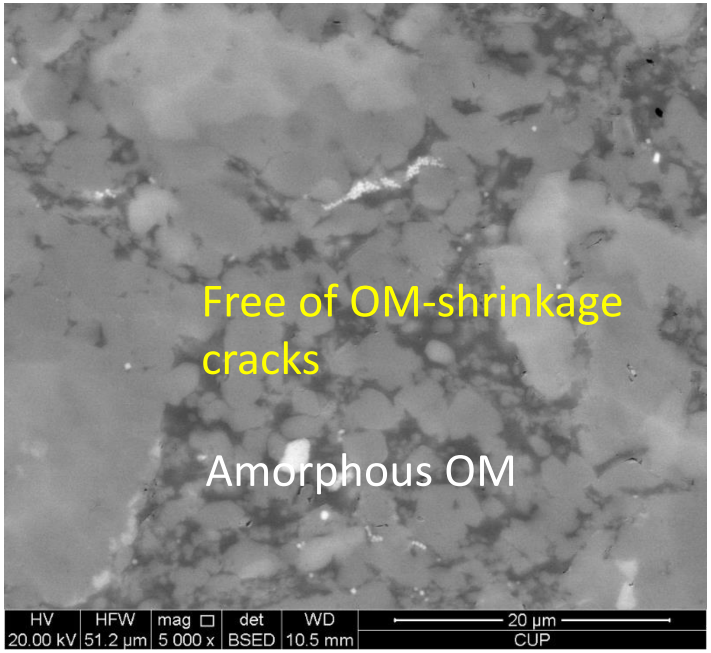
8.1 Development regularity of OM-shrinkage cracks

As discussed above, HSC are usually developed in transitional shales, while far less found in marine shales and terrestrial shales. Further, they are identified to mostly exist at the periphery of structure-stable huminite. Why ?

We deem that OM-shrinkage crack can be developed by hydrocarbon-generation, and it is related to thermal evolution and OM occurrence pattern.

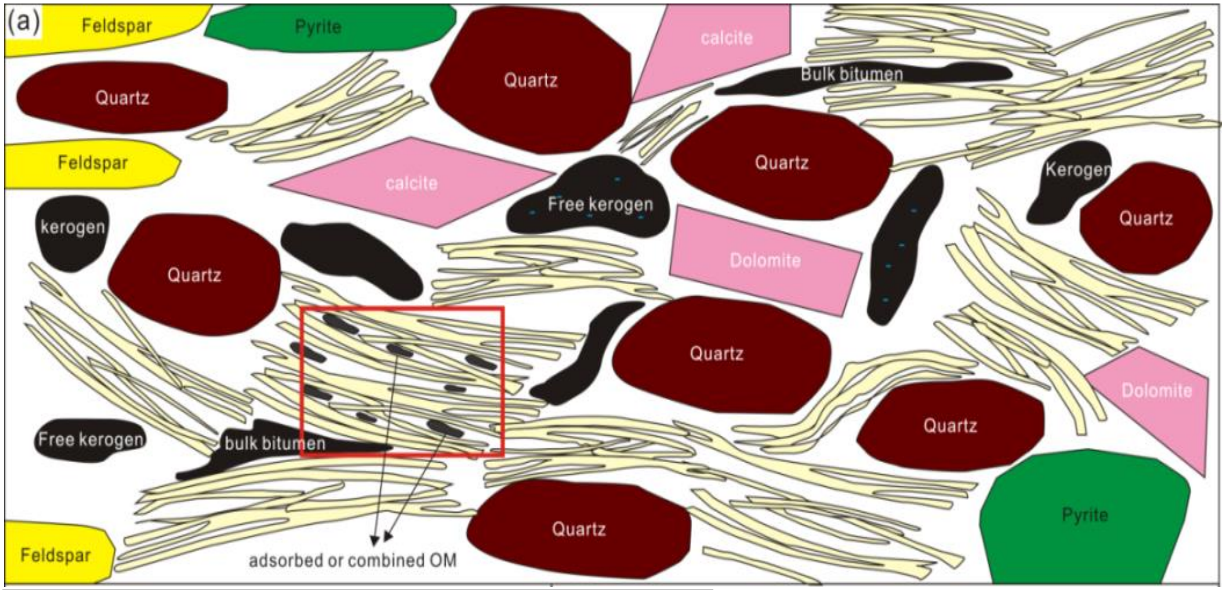


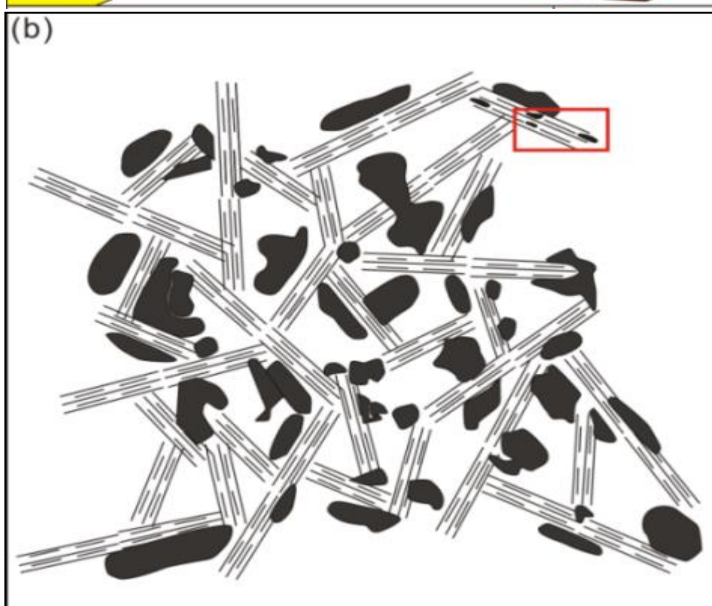
Structured huminite in transitional shales



Amorphous OM in transitional shales

8.2 Conceptual diagrams showing the OM occurrence pattern





In terms of the OM occurrence, structured OM are inclined to be isolated from the minerals, while the amorphous OM that have certain plasticity thus tends to mechanically admix with the surrounding minerals through filling in the cracks or intergranular pores associated with the surrounding minerals.

9 Conclusions and outlooks

Conclusions:

(1) OM can not only generate hydrocarbon-bubble pores (HDP) within OM but also can form hydrocarbon-shrinkage cracks (HSC) at the periphery due to volumetric contraction, and moreover can corrode the contact minerals in the form of organic acids leading to the formation of hydrocarbon-dissolution pores (HDP). In addition, some bioclasts with skeleton pores can be preserved thus retains these bioclast-skeleton pores (BSP).

(2) HBP are widely developed in over-mature marine shales that are rich in structure-alterable liptinite (alginite, amorphinite, exinite, solid bitumen). HDP are mostly developed in immature terrestrial shales containing certain amount of organic acids. HSC are commonly found in transitional shales rich in structure-stable huminite. BSP are in small quantity in all of the three sedimentary facies shales due to their amount.

Outlook:

(1) By means of morphology analysis of in-situ OM components and comparison with their primitive morphology under optical microscopy, the identification of OM under BIB-SEM was achieved, but still requires further refinement.

(2) A further study in the correlation between various OM occurrences and the evolution of organic-associated pores should be made, because various associative relations between the OM and clay minerals could cause difference in their thermosability an further affected the hydrocarbon generation.


Thank you!
Questions ?