

# **Analysis of Geological Effects on Methane Adsorption Capacity of Continental Shale: A Case Study of the Jurassic Shales in the Tarim Basin, Northwestern China\***

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Search and Discovery Article #10746 (2015)

Posted June 30, 2015

\*Adapted from extended abstract prepared in conjunction with poster presentation at AAPG Annual Convention & Exhibition 2015, Denver, Colorado, May 31-June 3, 2015. AAPG © 2015

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## **Abstract**

The geological effects on methane adsorption capacity for the Jurassic continental shales in the Tarim Basin, Northwestern China, have been investigated in this paper compared to the marine gas shales in the North America and the South China. The methane adsorption capacity ranges from 0.58 cm<sup>3</sup>/g to 16.57 cm<sup>3</sup>/g and the total organic carbon (TOC) content is between 0.5 wt% and 13.5 wt%. The organic maturity measured by Tmax is between 410°C (immature) and 499°C (overmature). The methane adsorption capacity of the Jurassic continental shales in Tarim Basin is affected by many geological factors, including the TOC content, organic matter maturity, mineral composition, surface area, pore size distribution, etc. The TOC content is the most significant factor with a positive effect on the adsorption capacity of the Jurassic shales, and the influence varies piecewise according to the TOC content. The TOC content contributes much more to the methane adsorption capacity of organic-rich shale samples (TOC content > 0.7 wt%) than to the organic-lean samples (TOC content < 0.7 wt%). The mineral composition is a secondary factor, and the abundance of clay content has a positive effect on the methane adsorption capacity despite its relatively weaker adsorption ability compared to TOC. The pore size distribution has different effects on surface area and pore volume. Mesopores and micropores provide the major surface area and are mainly derives from TOC and illite, which has a positive influence on the adsorption capacity. Mesopores and macropores offer the major pore volume and are mainly formed by illite, which is the major contributor for pore volume rather than surface area. Besides, the TOC and illite contents of the Jurassic shales in Tarim Basin are closely related to the origin, maturity and diagenesis evolution of the shale: 1) both TOC and illite contents variations are related to the different provenances and depositional environments of shale; 2) the decrease of TOC content with increasing maturity is also partly attributed to hydrocarbon generation; and 3) the increase of illite content with increasing maturity is due to illitization in the diagenesis of shale.

## **Introduction**

The Tarim Basin is about 1,400 km long, 520 km wide and 56×104 km<sup>2</sup> area, and is the largest inland-superimposed basin in China. It is located in the south of Xinjiang Province, Northwestern China, and tectonically in the western Sino-Korean and Tarim Paraplatforms, bounded by Tianshan Mountain, Kunlun Mountain, and Altun Upfaulted Block and Qaidam Basin from north, southwest and southeast, respectively

(Figure 1). The Tarim Basin is divided into seven first-level tectonic units and further subdivided into about 30 secondary structure units. The Jurassic shale in the Tarim Basin is a set of typical continental source rock and mainly deposited in the swamp and semi-deep to deep lakes environments, occurring in the piedmont depressions such as Kuqa Depression, Southwest, Northeast and Southeast areas of Tarim Basin.

### Methane Adsorption Capacity

Methane adsorption capacity of 50 samples varies between 0.58 to 16.57 cm<sup>3</sup>/g and the TOC content ranges between 0.05 and 17.02 wt%. Although the methane adsorption capacity increases apparently along with the increasing TOC content (Figure 2A), variations still exist between samples with similar TOC contents, indicating other potential factors are affecting the methane adsorption capacity. The decreasing methane adsorption capacity with the increasing maturity is due to the decreasing TOC content (Figure 2B and C). The TOC content relates with maturity because: 1) the consumption of TOC for hydrocarbon generation; and 2) the evolution of mineral matter with maturity along the diagenesis. The shales contain kerogen types II1, II2 and III, and the type II2 is the most common kerogen in the data suite (Figure 3). A positive correlation exists between HI and methane adsorption capacity (Figure 4A). However, a negative relationship exists between HI and methane adsorption capacity after the methane adsorption capacity is normalized to TOC (Figure 4B). The negative relationship between HI values and methane adsorption capacity normalized to TOC indicates that samples with lower HI values have a higher methane adsorption capacity on a per unit TOC volume basis. This observation is a further evidence for the primary effect of TOC content on methane adsorption capacity. Although the TOC content is the dominating effect on methane adsorption capacity, the prominent effect varies with the TOC content. Shale samples with higher TOC content (> 0.7 wt%) has a clearer positive relationship between the TOC content and methane adsorption capacity compared to the samples with lower TOC content (< 0.7 wt%) (Figure 5). There is a much higher straight line's slope between the TOC content of the organic-rich samples (TOC content > 0.7 wt%) and their methane adsorption capacity while there is a more gentle relationship within the organic-lean samples (TOC < 0.7 wt%). Thus, the TOC content contributes more to the methane adsorption capacity of organic-rich samples than to the organic-lean shale.

### Tarim Basin Shales

The Jurassic shales in the Tarim Basin consist of quartz, clay minerals, and to a lesser extent, other minerals (accounting for 1%~46% of total mineral content) such as potassium feldspar, potash feldspar, calcite, dolomite, hematite, pyrite and siderite. The clay minerals include kaolinite, chlorite, illite and interstratified illite/montmorillonite. The methane adsorption capacity has a slight trend with the total clay content and a relatively more apparent trend with the illite content (Figure 6). In the TOC range of 0 wt% ~ 0.7 wt%, a relatively apparent negative relationship exists between the TOC and illite contents (Figure 7), which is related to the effects from organic matter maturity on TOC content and the accompany diagenesis on illite content (Figure 8). Besides, the sediment provenance and deposit environment of the shale can influence the TOC and clay contents originally.

The pore surface area ranges from 0.16 m<sup>2</sup>/g to 12.51 m<sup>2</sup>/g for mesopores, 0 m<sup>2</sup>/g ~ 2.49 m<sup>2</sup>/g for micropores, and 0 m<sup>2</sup>/g ~ 0.11 m<sup>2</sup>/g for macropores; the pore volume is 0.0005 cm<sup>3</sup>/g ~ 0.017 cm<sup>3</sup>/g for mesopores, 0 cm<sup>3</sup>/g ~ 0.001 cm<sup>3</sup>/g for micropores, and 0.0002 cm<sup>3</sup>/g ~ 0.002 cm<sup>3</sup>/g for macropores. The pore surface area mostly (96.13%~100%) derives from the mesopores and micropores, while the majority of total pore volume (80.95%~100%) is from mesopores and macropores in Jurassic shales. Shale samples have a larger surface area in mesopores than

in micropores (Figure 9) is because: 1) the hydrocarbon generation consumes TOC (Figure 2B), increases the primary pore size and reduces the amount of micropores; and 2) the increasing illite content with maturity generates more surface area in mesopores than micropores (Figure 10).

Shale samples with high methane adsorption capacity have higher microporous and mesoporous surface area (Figure 10A). Specific to the micropores and mesopores, samples with a higher methane adsorption capacity have more mesoporous surface area than microporous surface area of their own respectively. Both microporous and mesoporous surface areas increase with the TOC content (Figure 10B). However, a more apparent positive trend can be observed between the TOC content and the microporous surface area compared to mesoporous surface areas. Illite content is also a contributor to the micropore and mesopore structure of shale (Figure 10C), and has a stronger relationship with mesoporous surface area than microporous surface area. The illite content contributes much more to the mesoporous surface areas than to the microporous surface areas (Figure 10C). However, the TOC content contributes more to microporous surface areas (Figure 10B). The stronger relationship between illite content and surface area in mesopores compared to micropores (Figure 10C) is because: 1) along with evolution, the increase of illite accompanies the micropores reduction as the TOC loss (Figure 7); and 2) the adsorption capacity of illite is weaker than organic matter and shale samples with lower TOC content cannot prominently obtain surface area from organic matter (Figure 5C).

### Conclusions

There is an overall positive correlation between total clay content and pore volume (Figure 9A) and surface area (Figure 9B) for pores with different diameters. The pore volume and surface area vary in different diameters, indicating that both volume and surface area of pores larger than 10 nm diameters are more strongly affected by clay content compared to TOC content while that of pores smaller than 10 nm diameters are more strongly influenced by TOC content (Figure 9A and B). The interrelationship among TOC, kerogen types, maturity and micropores are complex due to their interactions. The increasing microporous and mesoporous surface areas with maturity reflect the relationship between surface area and the amount of TOC and illite contents: 1) microporous surface area increases with the TOC content (Figure 10B), and 2) the mesoporous surface area increases with the illite content (Figure 10C).

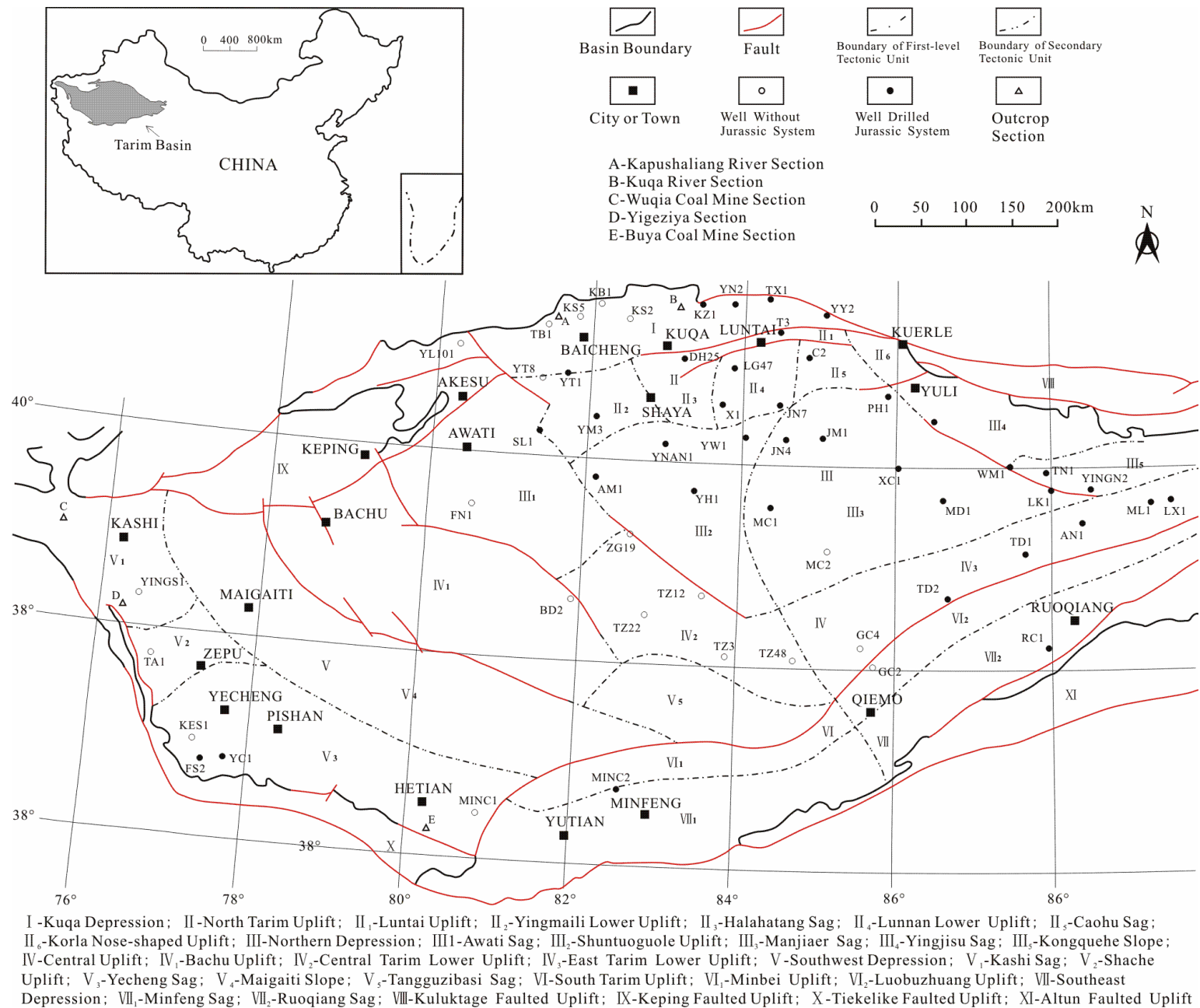


Figure 1. Location of study area, sampled wells and sections (inset shows location with respect to Tarim Basin).

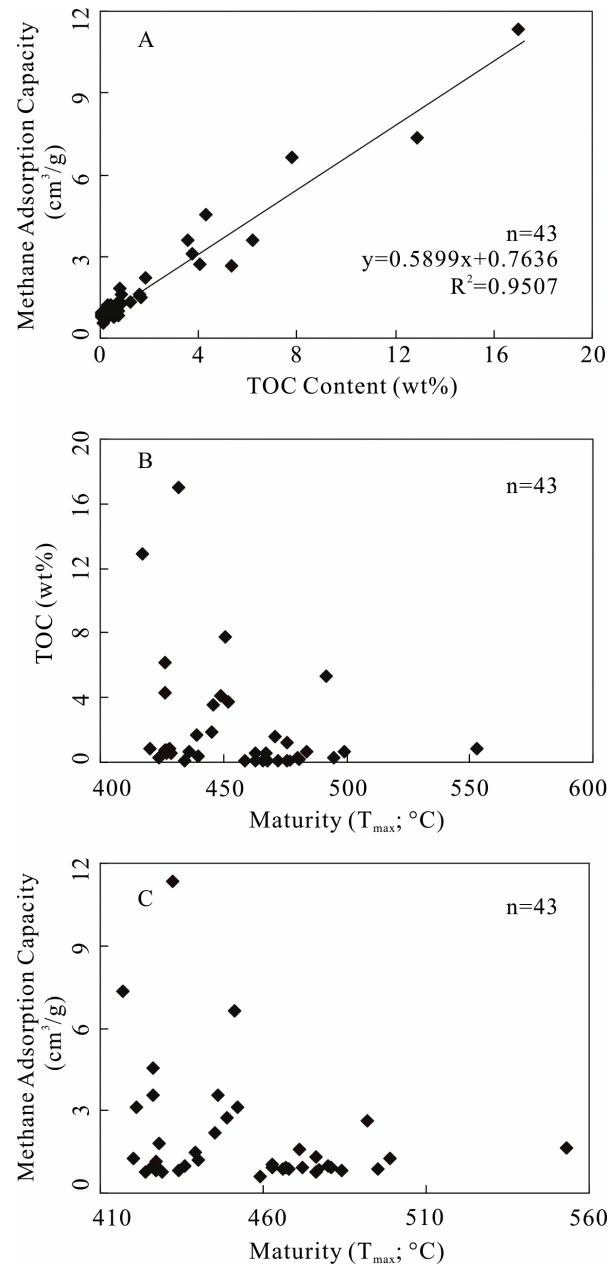


Figure 2. The relationship between TOC content and (A) methane adsorption capacity, (B) maturity and TOC content, and (C) maturity and methane adsorption capacity.

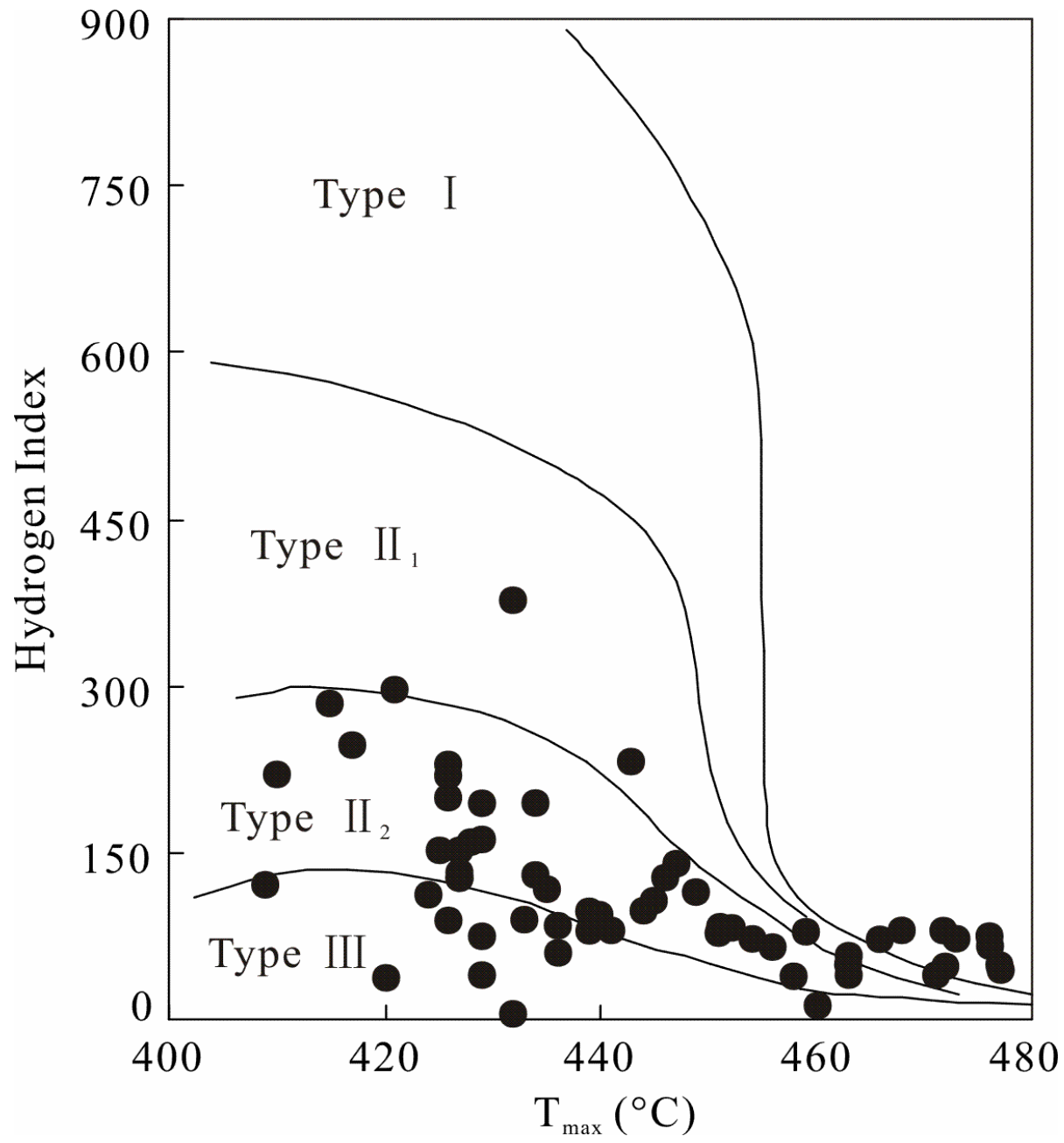


Figure 3. Diagram showing the kerogen type for all samples analyzed by the Rock-Eval analysis. Type II<sub>2</sub> is the most common kerogen type.

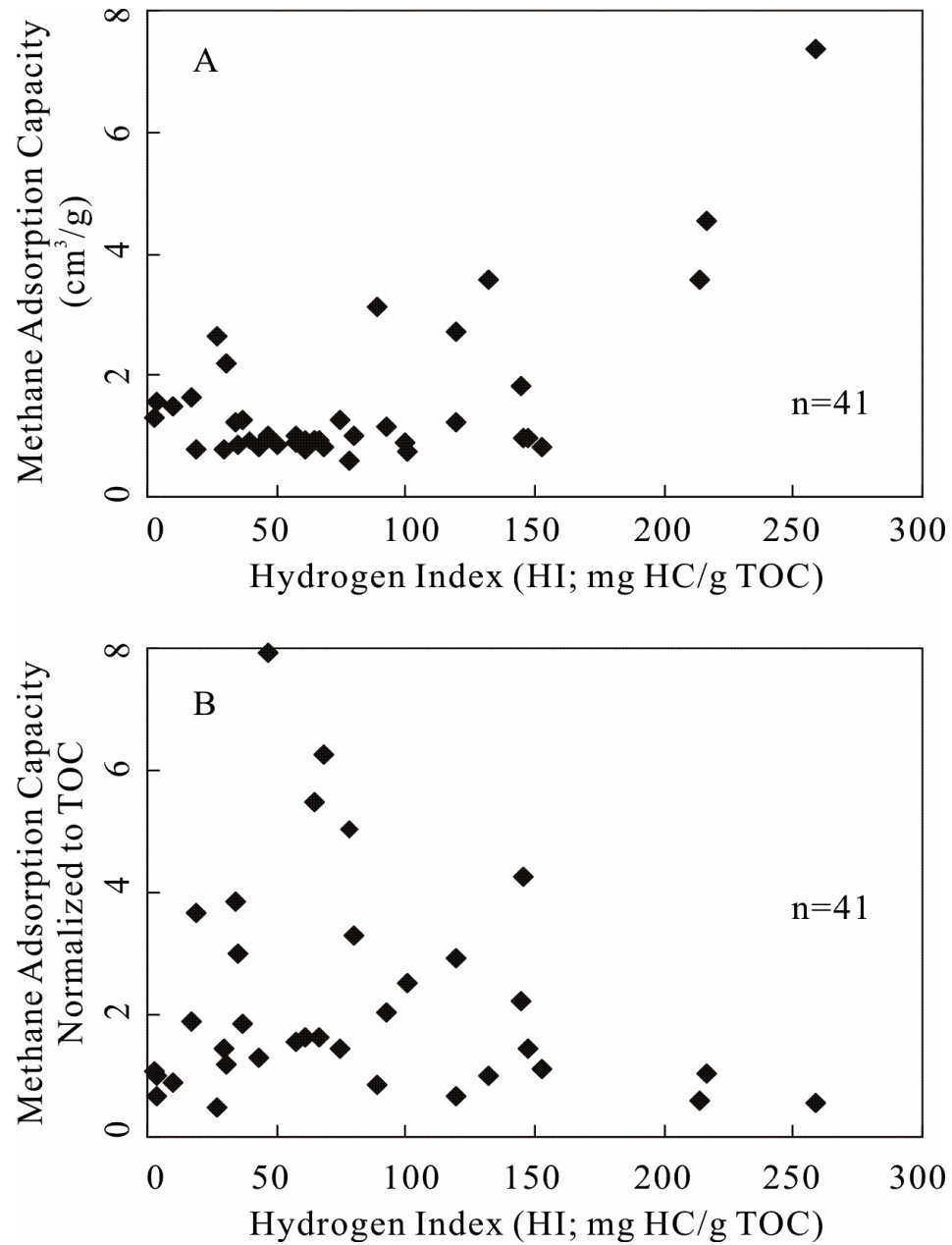


Figure 4. The relationship between hydrogen index (HI) and methane adsorption capacity (A) and HI and methane adsorption capacity normalized to TOC (B).

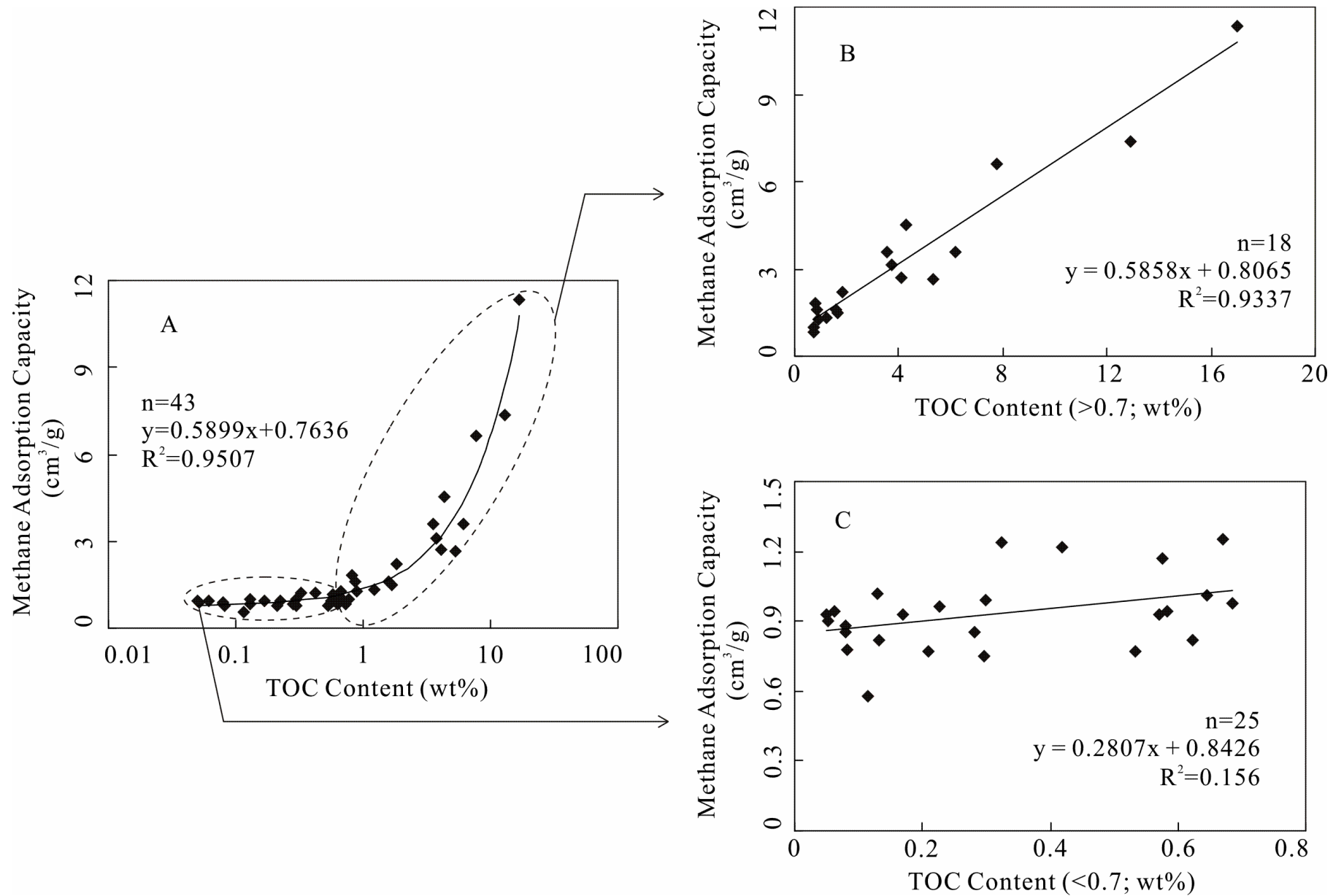


Figure 5. The piecewise fitting relationships between TOC content and methane adsorption capacity (A). The slope of the fit line between TOC content and methane adsorption capacity is much higher for the organic-rich shale samples with TOC content > 0.7 wt% (B) and more gentle for the samples with TOC content < 0.7 wt% (C).



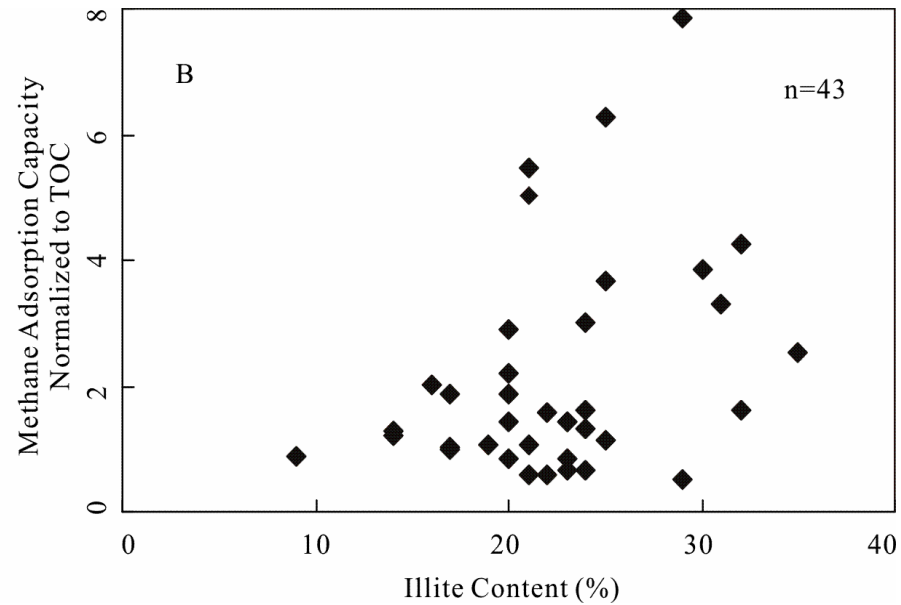
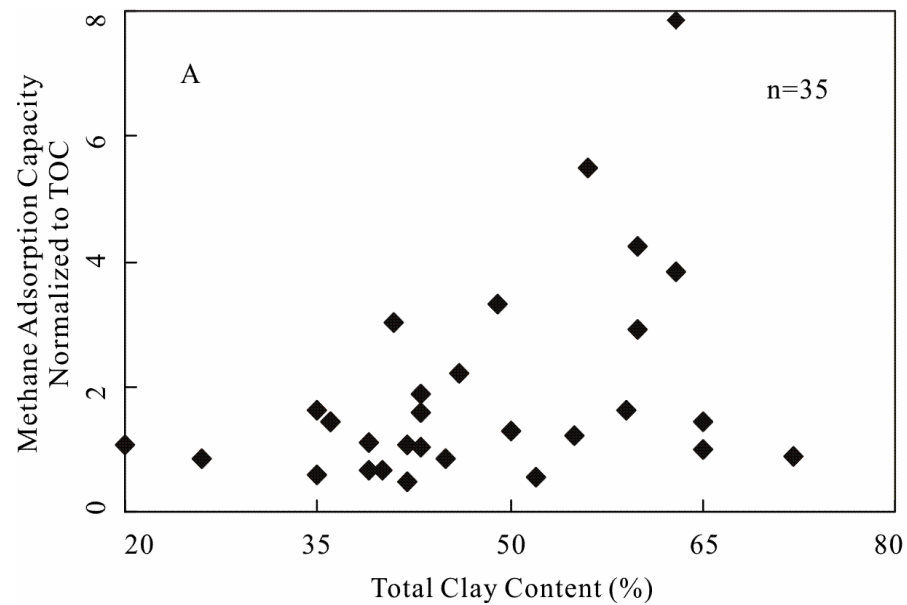


Figure 6. The relationship between methane adsorption capacity normalized to TOC and total clay content (A) and illite content (B).

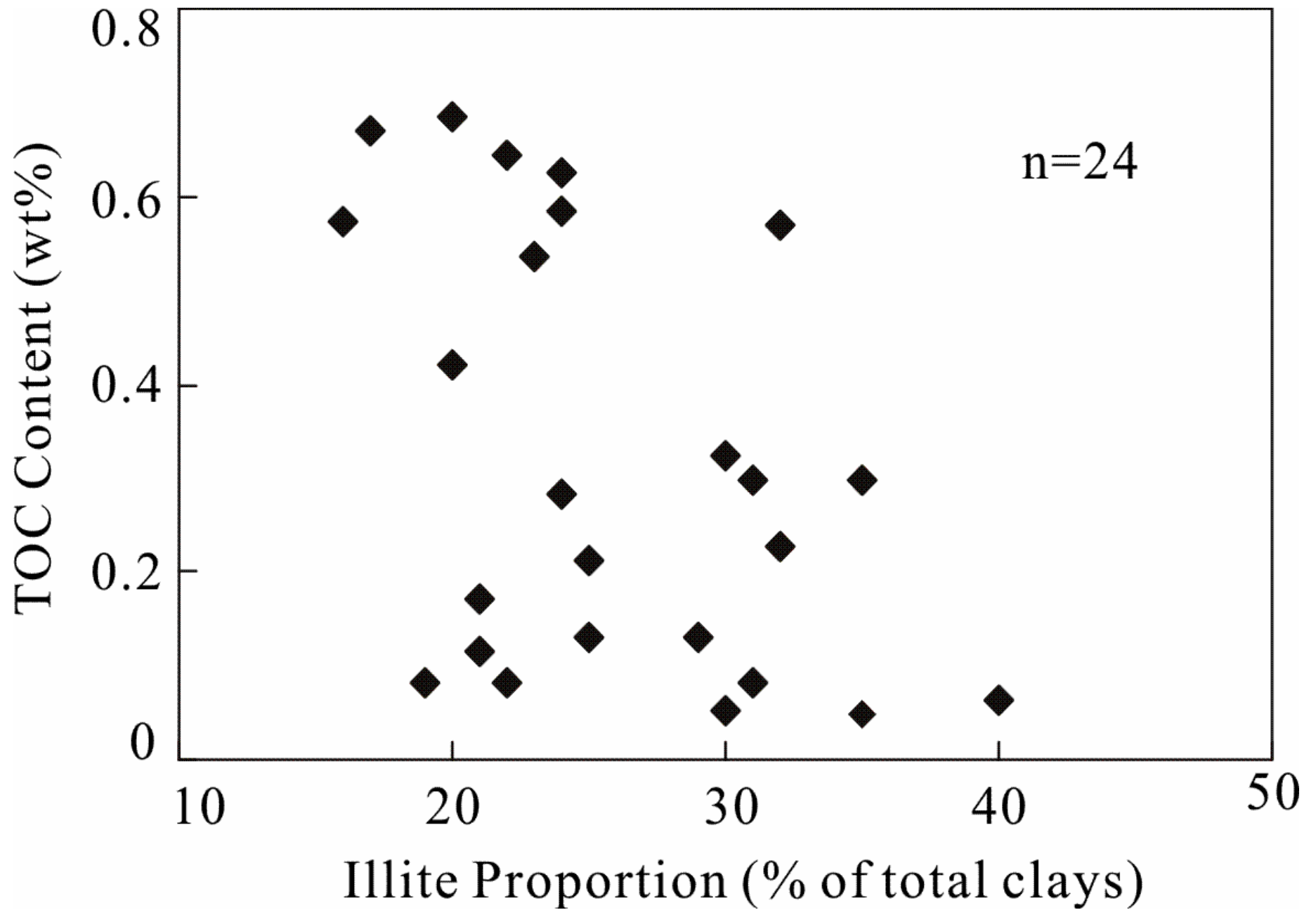


Figure 7. The relationship between TOC and illite content of shale samples with TOC content < 0.7 wt%.

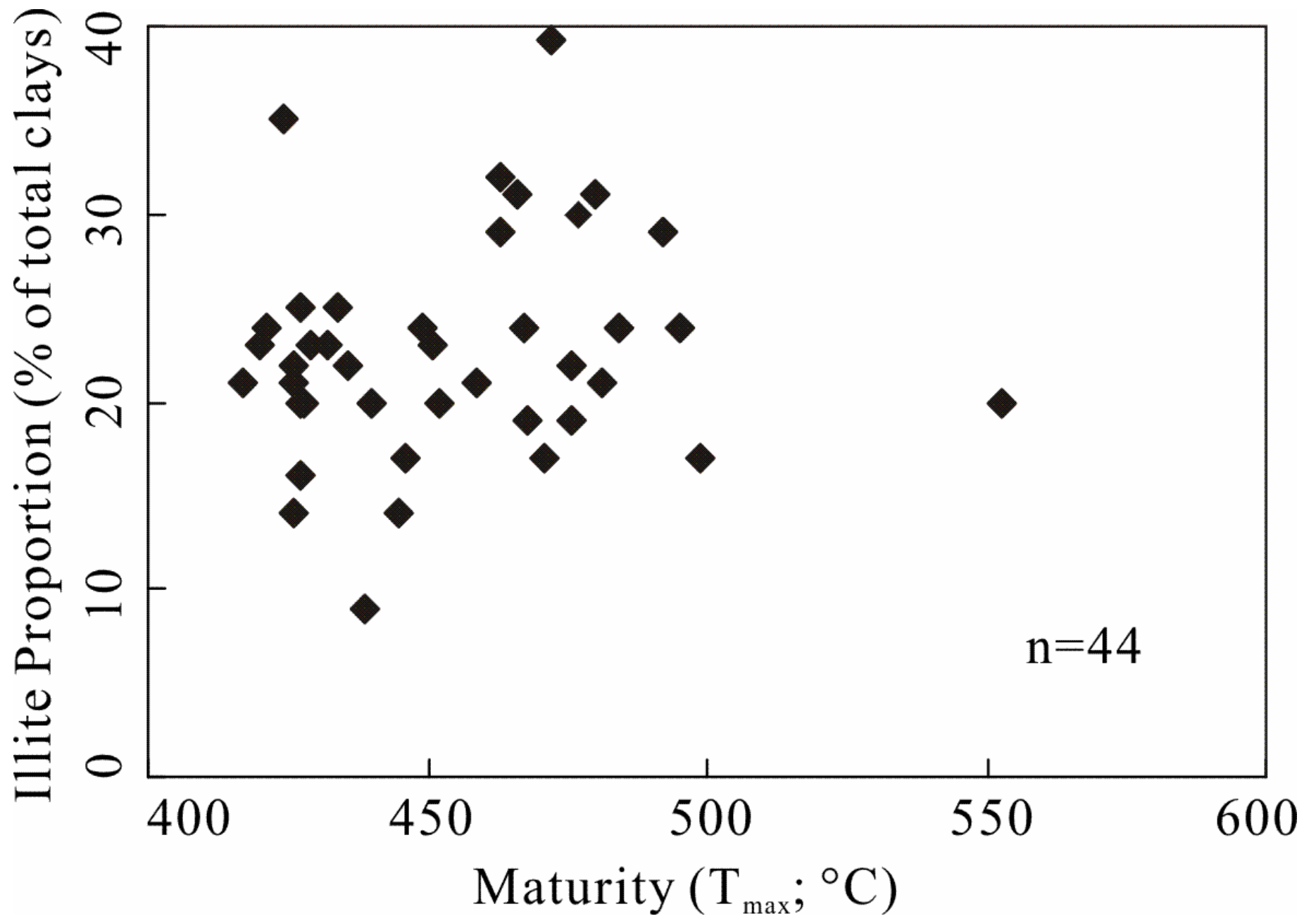


Figure 8. Plot of the illite proportion as a percentage of total clay content and maturity.

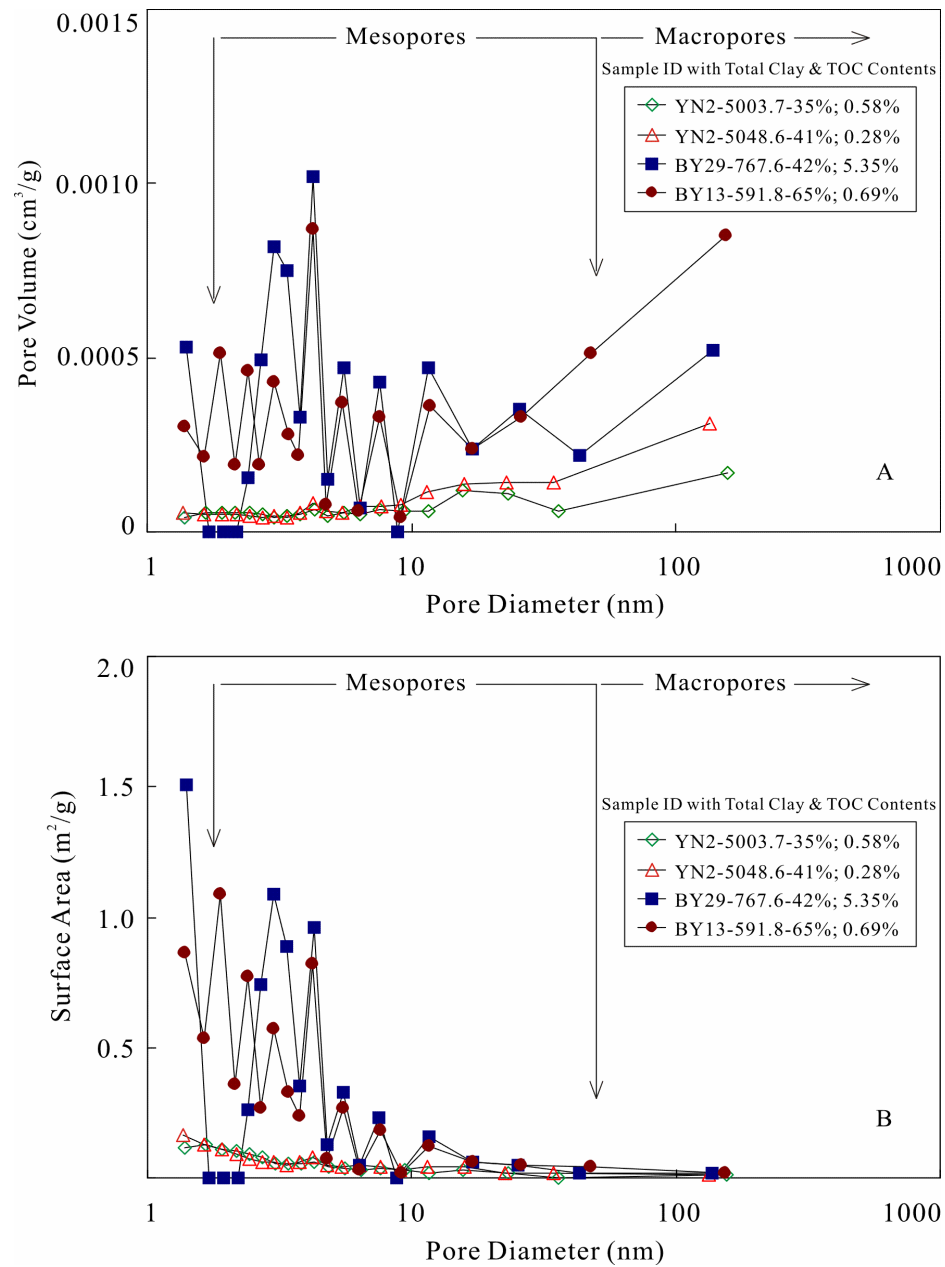


Figure 9. Pore size distribution of selected samples with varying clay and TOC contents. The pore volume generally increases with increasing pore diameters (A) while the pore surface area decreases with increasing pore diameters (B).

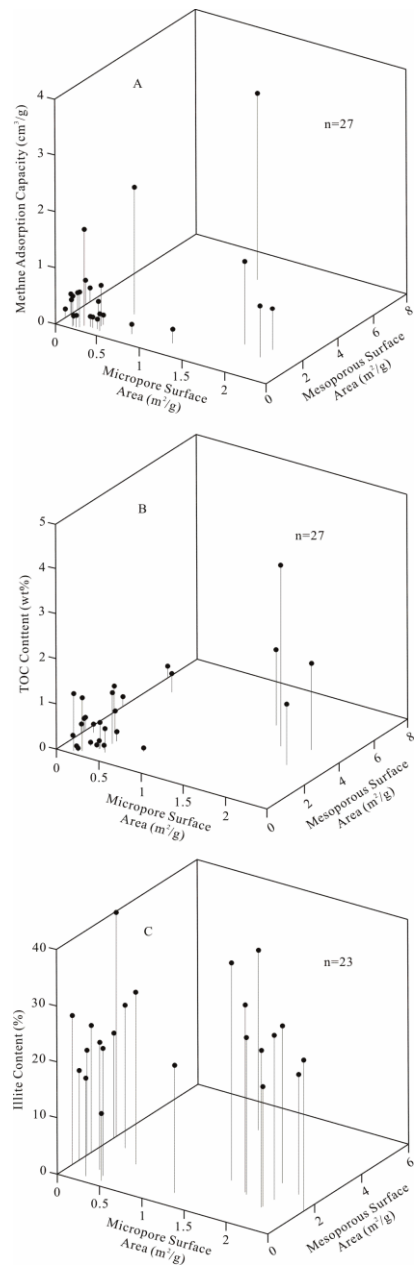


Figure 10. Relationship among mesoporous and microporous surface areas and methane adsorption capacity (A), TOC content (B) and illite content (C).