

Detecting shale oil hidden in nanopores using a novel electron microscopy method

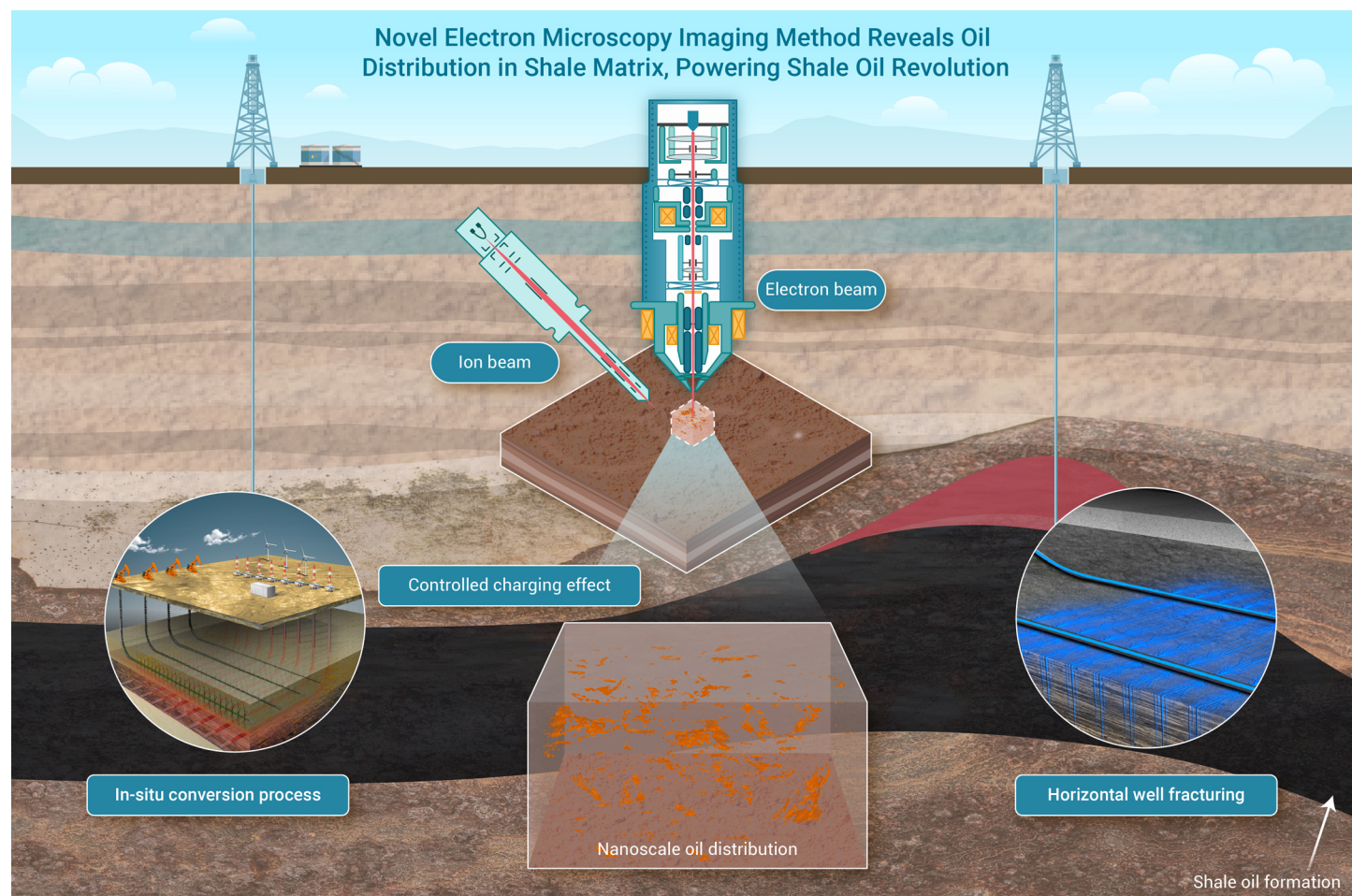
Xiaoqi Wang,¹ Siwei Meng,^{1,3} Mehdi Ostadhassan,^{2,3} Xiwei Li,⁴ Shujun Bao,⁵ Jiaping Tao,^{1,3} Xiaodan Liu,¹ Chenjun Zhang,¹ Man Shen,¹ Huaqing Xue,¹ Bo Liu,^{2,3,*} Xu Jin,^{1,3,*} and Wenzhi Zhao¹

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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Oil in shale matrix can cause local charging effect during high resolution electron microscopy imaging.
- Shale oil reserved in nano pores with small amount of below pmol can be detected by controlled charging imaging.
- High resolution large-area 2D controlled charging imaging provides a powerful tool for highly anisotropic samples.
- Microscopic 3D imaging reveals the spatial distribution of shale oil and its relationship with pore system.

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Shale oil has revolutionized the global energy landscape, mostly existing in nanopores. However, there is no method for directly characterizing such a small oil cluster. This paper proposes a novel method for the direct characterization of shale oil at the nanoscale via controllable local charging imaging using electron microscopy. With this method, the potentially movable hydrocarbons of below one pmol (10^{-12} mol) reserved in nanopores can be detected. The distribution of the shale oil clusters can be obtained through large-area two dimensional (2D) and three dimensional (3D) visualizations. Additionally, the amount of these resources can be calculated. Comparative analyses were conducted on reservoir samples from typical shale oil blocks in China and the US, and the results indicate the universality of the novel method, paving the way for accurate evaluation of shale oil resources and reasonable choice of exploitation technologies such as hydrofracturing and underground *in-situ* conversion processing.

INTRODUCTION

Shale plays have become an essential resource worldwide, and the future of global energy relies heavily on the effective exploration and development of shale oil and gas, especially in North America and China.¹⁻⁵ The global shale oil geological resources are 936.84 billion tons, with 61.85 billion tons technically recoverable.¹ Although the total amount is considerable, the development and exploitation of shale oil are extremely difficult because of the extremely low porosity and permeability of shale reservoirs. Generally, hydraulic fracturing is used to exploit shale oil resources, and the fracture network formed by hydraulic fracturing and natural fractures will significantly promote the percolation of shale oil (Figure 1). However, the rapid decline of production rate is still a bottleneck. To get out of this dilemma, we need to solve the macroscopic engineering problem through microscopic technologies. This is because abundant nanosized pores and throats are extensively distributed in shale matrix and organic particles, leading to an extremely complex pore structure.⁶ Such very fine pores host large quantities of hydrocarbons—oil in particular. Therefore, the pore abundance, pore connectivity, and spatial oil distribution in the reservoir space play a crucial role in determining the amount and discharge rate of shale oil. The whole system should be systematically characterized, which is important for assessing

the recoverable volume, economy of product, and development programs in shale oil.^{4,7,8}

Conventional geochemical methods such as pyrolysis can effectively obtain quantitative data on residual oil in a core sample.⁹⁻¹¹ However, to finely characterize the pore-throat system and the oil present in the matrix in shale in 2D and 3D, various approaches were developed.¹²⁻²⁶ In recent years, several cutting-edge characterization imaging techniques, commonly adopted in material and biological sciences, were applied to shale research and have led to the development of highly effective methods. Some examples of these methods include microcomputed tomography (micro-CT),^{12,14,19} nanocomputed tomography (nano-CT),^{12,15,16} field-emission scanning electron microscopy (FE-SEM),^{13,16-23} focused ion beam SEM (FIB-SEM),^{14,16,19,20} transmission electron microscopy (TEM),²¹⁻²² and multiple ion beam microscopy.¹²⁻²⁶ Such methods focused on evaluating the pore network at the nanoscale but failed to reveal the spatial distribution and accumulation mechanisms of the oil in the pores. To determine the location and distribution of residual oil, these imaging methods should be accompanied by other analytical techniques such as environmental SEM (E-SEM) with energy dispersive spectroscopy (EDS), magnetic resonance imaging (MRI),²⁷ and computed tomography (CT). However, each method has its own drawbacks and advantages. For example, E-SEM-EDS protects the light components of the crude oil from being carried away by the vacuum system and allows direct observation of droplets, layers, and other forms of the oil. However, the reduced resolution due to the low-vacuum mode results in the failure to observe micropore and nanopore throats. In addition, during high-acceleration voltage imaging, the highly penetrating electron beams cause difficulty in identifying the oil layer from kerogen particles. Thus, determining the relative location of the crude oil in the accumulation space from the E-SEM images becomes difficult. Low-field MRI can help obtain 2D and 3D occurrences of residual oil but with a low resolution. The use of micro- and nano-CT 3D imaging to differentiate residual oil and organic material from the pore space of the sample is based on the CT gray variance, which is so small that it can lead to major experimental errors. This is because there are resolution-related issues.²⁷⁻²⁹ High-resolution fluorescence microscopy imaging, widely applied in bioimaging, is also used as a potential method for determining the existence of oil in nanopores. Some examples of this imaging method include stimulated emission depletion, photo-activated localization, and stochastic optical reconstruction microscopies. Nevertheless, given the variation in the fluorescence properties of mineral and organic particles, these technologies fail to identify oil in the pores. In summary, effective and new analytical methods and technologies are needed to improve detection and reveal the spatial distribution of crude oil in fine pore throats.

Despite the drawbacks, studies have shown that electron microscopy remains the most prominent method for observing oil in micro- and nanopores because of its high resolution, although this method demands modifications to better suit the requirements. During the SEM imaging of oil-bearing shale samples, charging accumulation was easily observed on an uncoated rock sample surface. The nonconductive surface forms a static electric field, leading to image distortion, brightness, contrast abnormalities and image drift.³⁰⁻³⁷ However, the charging effects are not a complete disadvantage. If the degree of charging is controlled, such effects may generate

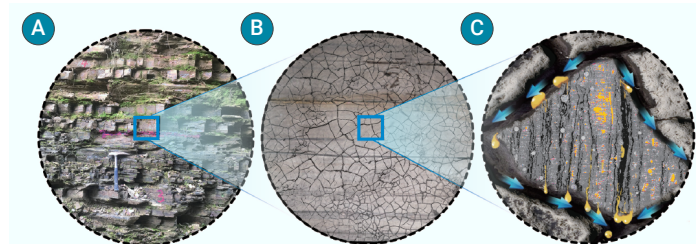


Figure 1. Pathway of a movable oil cluster composed of hydraulic fractures and natural microcracks (A) three dimensional (3D) fractures network produced by weathering in shale outcrop, an analogy to those obtained after underground hydraulic fracturing; (B) schematic diagram of natural fracture network inside shale matrix; (C) schematic diagram of matrix shale oil being extracted into surrounding microcracks.

Table 1. Information and organic geochemical data of samples.

Sample Name	Region	Formation	Lithology	TOC	R_o	T_{max}	S_1	S_2	$S_1 + S_2$	S_1/TOC	HI	Chloroform bitumen A
				%	%	°C	mg/g	mg/g	mg/g	mg/g TOC	mg/g TOC	%
H317	Ordos Basin	Yanchang Formation (T_{3y})	Black shale	13.6	1.07	459	2.06	17.07	19.13	15.15	125.51	0.54
Y56	Ordos Basin	Yanchang Formation (T_{3y})	Black shale	10.1	0.99	448	3.73	46.87	50.6	36.93	464.06	0.64
H269	Ordos Basin	Yanchang Formation (T_{3y})	Oil-bearing siltstone	0.76	0.86	443	0.46	0.85	1.31	60.52	111.84	0.49
J174	Junggar Basin	Lucaogou Formation (P_2l)	Black mudstone	6.42	0.71	443	1.02	48.01	49.03	15.89	747.82	0.07
Pu53	Songliao Basin	Qingshankou Formation (K_2qn^1)	Black mudstone	5.67	0.76	448	5.09	41.71	46.8	89.77	735.63	1.04
Bakken	Williston Basin	Lower Bakken Formation (BK lower)	Black shale	9.21	0.89	440	4.1	16.68	20.78	44.52	181.11	0.91

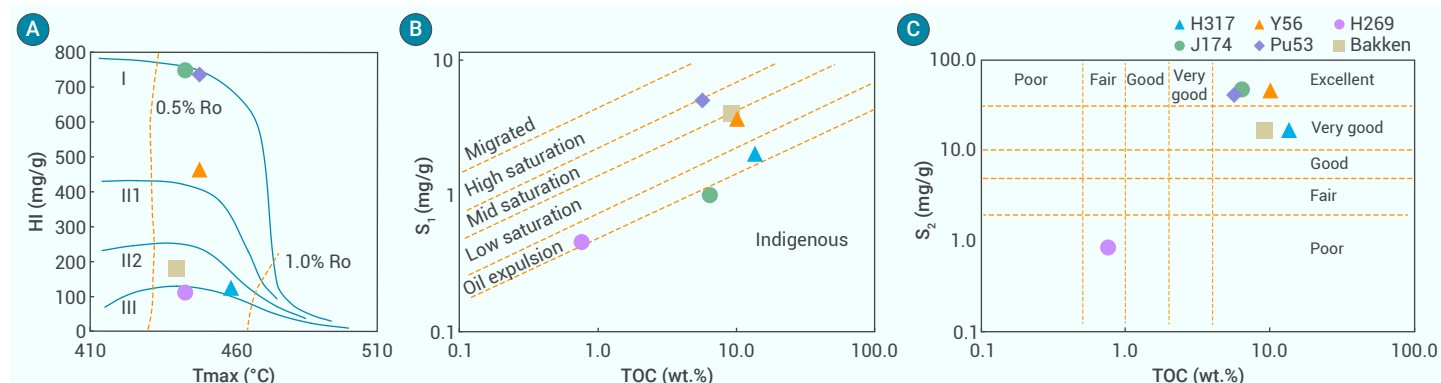


Figure 2. Organic geochemical characteristics of samples (A) cross plot of Rock-Eval HI (hydrogen index) data versus T_{max} showing the range in thermal maturity of shale samples and hydrocarbon generative (kerogen) types for various samples; (B) plot of S_1 (amount of free hydrocarbon in the sample) versus TOC (total organic carbon); (C) correlations between TOC and the amount of pyrolyzate released from kerogen (S_2) showing the generative source-rock potential.

more information for analysis of the samples and provide meaningful results.³⁰ In this study, the occurrence of crude oil in micro- and nano-pores is directly identified based on the local charging effects via an innovative approach in large 2D and 3D spaces for oil-bearing shale samples from China and the United States. The 2D large-area stitching imaging can easily scale up from the pore to the core scale, which can pave the way for shale oil resource evaluation and revocability evaluation.

MATERIALS AND METHODS

Samples

Six shale oil samples were studied (Table 1), three of which were collected from the Yanchang Formation in Ordos Basin. The other three were each collected from the Lucaogou Formation in Jungar Basin, the Qingshankou Formation in Songliao Basin, and the lower Bakken Formation in Williston Basin.

Geochemical analyses

Organic geochemical analyses were conducted on selected samples, including the total organic carbon content (TOC) content, kerogen maturity (vitrinite reflectance, R_o), temperature of maximum hydrocarbon generation (T_{max}), amount of free hydrocarbon (S_1), amount of pyrolyzate released from kerogen (S_2), hydrocarbon generation potential ($S_1 + S_2$), oil saturation index (OSI), hydrogen index (HI), and chloroform bitumen A content.

Local charging electron beam imaging

Samples were mechanically cut, polished, and subjected to surface ion milling using an RES102 argon ion polishing machine from Leica Company (voltage: 4 kV; beam current: 2.2 mA; ion gun dip angle: 2.5°; duration: 4 h). A Helios 650 FIB-SEM from Thermo Fisher Scientific was employed, using a through-the-lens backscattered electron detector TLD-BSE with Mode II: Immersion Mode. The parameter settings for the electron beam imaging were as follows: accelerating voltage: 2 kV; beam current: 0.8 nA; electron beam dwell time: 20–30 μ s. Images with local charging were obtained. To

ensure the stability of the parameters during each experiment, standard samples were used for instrumental calibration before the experiment. FEI MAPS software was used to create large-area 2D mosaics. Samples were coated with a conductive layer, and automatic 3D imaging was conducted using FEI Auto Slice and View software. The parameter settings for ion beam etching were as follows: accelerated voltage: 30 kV; beam current: 0.79 nA; interlayer distance: 20 nm. VSG Avizo Fire was applied for the processing and phase segmentation of the images. The total pore and charging area were extracted and quantitatively calculated.

Specimen current (I_{sc}) analysis and Duane–Hunt limit (DHL) testing

A Helios 650 FIB-SEM with a built-in I_{sc} meter from Thermo Fisher Scientific and an Oxford X-MAX N80 energy dispersive spectroscopy (EDS) detector was used. The incident beam energy was 2 kV, the work distance was 4 mm, the beam current was 0.8 nA, and the accurate actual beam current was tested using a Faraday cup. For spot and frame specimen current tests, the sample was continuously exposed to an electron beam, using the spot scan or frame scan mode, and the data were collected approximately every 5 s. The DHL tests were performed using EDS spot analysis under 2 kV without coating the sample with a conductive layer. The samples were exposed for 200 s, the EDS spectrum was collected, and the portion of the spectrum in the range of 1.8–2.0 KeV was linearly fitted.

Vacuum-induced weight loss tests

A corundum ceramic (Al_2O_3) crucible was used as the sample container. The crucibles were first ultrasonically flushed for 15 mins using ethyl alcohol and heated for 1 h at 400°C in a muffle furnace. All *n*-hexadecane, *n*-octadecane, *n*-eicosane, *n*-docosane, crude oil, bitumen A, white vaseline, paraffin, asphalt, and rock pieces were then loaded into the crucibles, one component at a time, weighed on a Mettler Toledo XS205 Dual Range analytic balance, and placed in vacuum chambers. To avoid damaging the lens cone during FIB-SEM, we used two chambers. The experiment was conducted in two steps: first, prevacuuming in the chamber of a Leica ACE600 vacuum coater

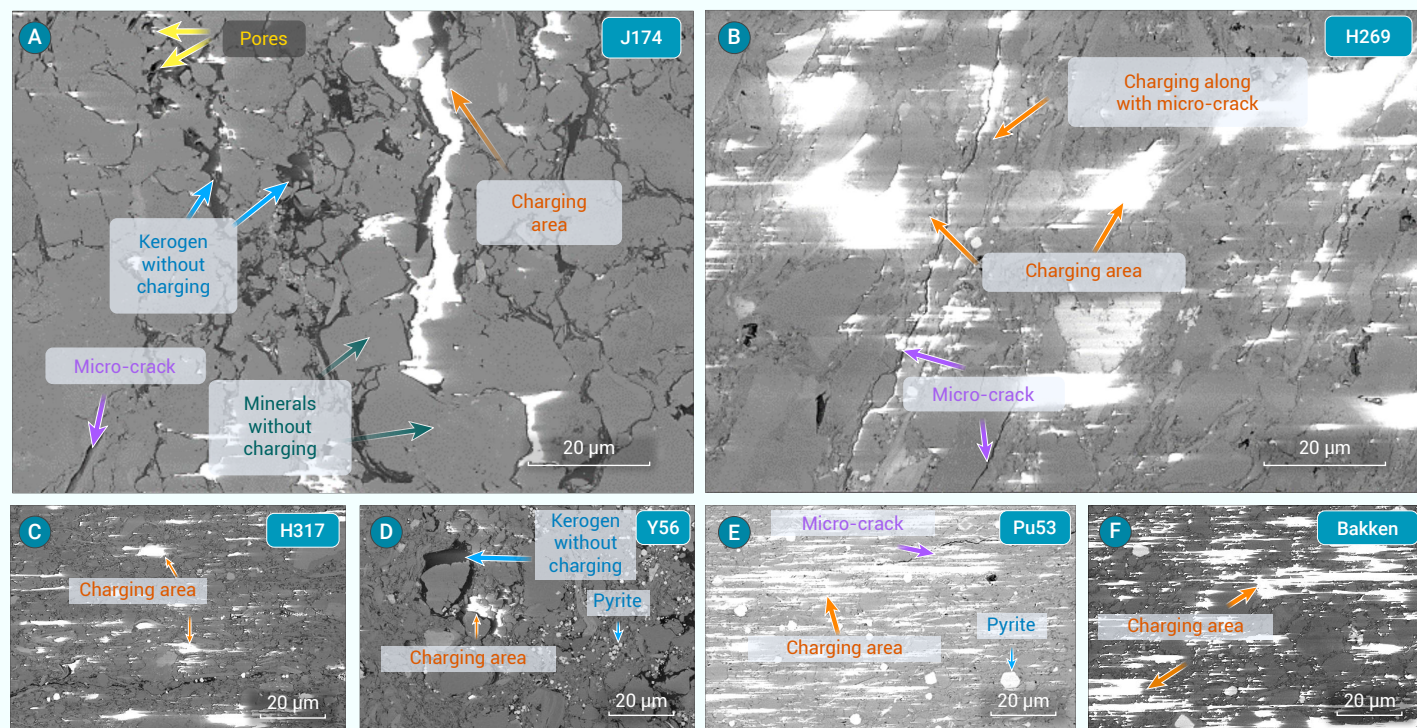


Figure 3. Local charging effects observed in the samples during electron microscopy (A) J174; (B) H269; (C) H317; (D) Y56; (E) Pu53; (F) Bakken.

for 12 h with 1.5×10^{-3} Pa chamber pressure, and then vacuuming in a Thermo Fisher Apero SEM chamber for 1 h with 3.9×10^{-4} Pa chamber pressure. Next, weights were measured again, and the weight loss percentage was calculated.

RESULTS AND DISCUSSION

Organic geochemical characteristics of samples

The results are listed in Table 1 and Figures 2A-C. These data enable us to assess the organic abundance, a key parameter for assessing the hydrocarbon generation potential of source rocks and an important indicator for assessing shale oil reservoirs.³⁵

As shown in Table 1, these six samples tested presented notable differences in the amount of residual movable hydrocarbon (S_1 and Chloroform bitumen A value) and potential ($S_1 + S_2$) for hydrocarbon generation. Except for the H269 sample, the other five samples were categorized as ideal source rocks with a high hydrocarbon generation potential (Figure 2C).³⁸ The Bakken Shale sample, a marine source rock, exhibited similar organic chemistry characteristics as the H317, Y56, and Pu 53 samples. The H269 sample is oil-bearing siltstone, even though the final detected total organic carbon (TOC) content was low (0.76%), and the S_1 and S_2 values were much lower than the source-rock samples. Furthermore, a high chloroform bitumen A value implies that a large amount of oil was expelled and migrated into the reservoir during the later stages of the basin evolution.

Note that shale samples always show an extremely high microscopic anisotropy and horizontal textures are observed in the centimeter-scale sample, which may cause a production drop during shale oil exploitation. Because the samples need to be pulverized into powder before various geochemical analyses, therefore, the findings obtained through geochemical analyses on powders would provide oil-containing information but would fail to represent the characteristics of oil distributions in the rock, which may mislead the evaluation of the percentage of recoverable oil.

Local charging effects of rocks bearing movable hydrocarbons

Local charging analysis was conducted on the samples via electron microscopy, and all the shale oil samples at the oil generation window showed notable local charging effects (Figures 3A-F). Pores and microcracks are shown in black, organic matter particles or bitumen streaks in gray-

ish-black, inorganic minerals such as quartz and feldspar in gray, and heavy element-bearing minerals such as pyrite in white. The brightness due to the charging effects was much higher than conductive minerals like pyrite, which made it easy to identify the phenomenon.

A closer look at the charged surfaces indicated that organic matter particles (Figures 3A & D) associated with free hydrocarbons were distinct. This phenomenon indicates the heterogeneity of organic matter at the micron scale. The kerogen particles dispersed in the same sample presented various phases of hydrocarbon generation, whereas the degree of charging varied for multiple samples. For the H269 sample, a charging area along with microcracks was also observed (Figure 3B), indicating oil accumulation in microcracks. These results imply that for various shale samples, the generated oil gets distributed in matrix pores and microcracks or gets absorbed in organic matter particles. For these oil samples from various locations, the difficulty of development seemed unique; therefore, the development plan should be customized.

In previous SEM research on various types of rocks with the same imaging parameters, the charging effect rarely happened on low-maturity source rocks, postmature shales at the gas window, and nonoil-bearing rock samples.³⁰ In contrast, the effect was easily recognized in oil-bearing source rocks in the oil-generating maturity window, oil-bearing tight sandstones, oil-bearing carbonates, and those containing oil in pores.

For further verifications, initially, a physical simulation experiment was conducted. When coating the ceramic surface with extracted chloroform bitumen A from shale, the charging effect happened; however, it disappeared after the coating was removed by heating. A similar phenomenon was proposed to correspond to the existing residual oil in the samples in the previous studies.^{30,31} Thereafter, the charging effect before and after the chemical removal of the residual oil was evaluated. For instance, sample H317 was treated with a mixture of dichloromethane and alcohol (9:1) for 96 h via Soxhlet extraction to remove all contaminations and existing hydrocarbons in the pores and was subjected to SEM imaging. The results showed that local charging (Figure S1) disappeared entirely from the sample surface owing to oil removal, and an extremely slight change in kerogen was observed on the sample surface. Microcracks were generated inside the kerogen or at the contact edge between the kerogen and the mineral, i.e., a micropore network was formed inside the organic matter, with traces of

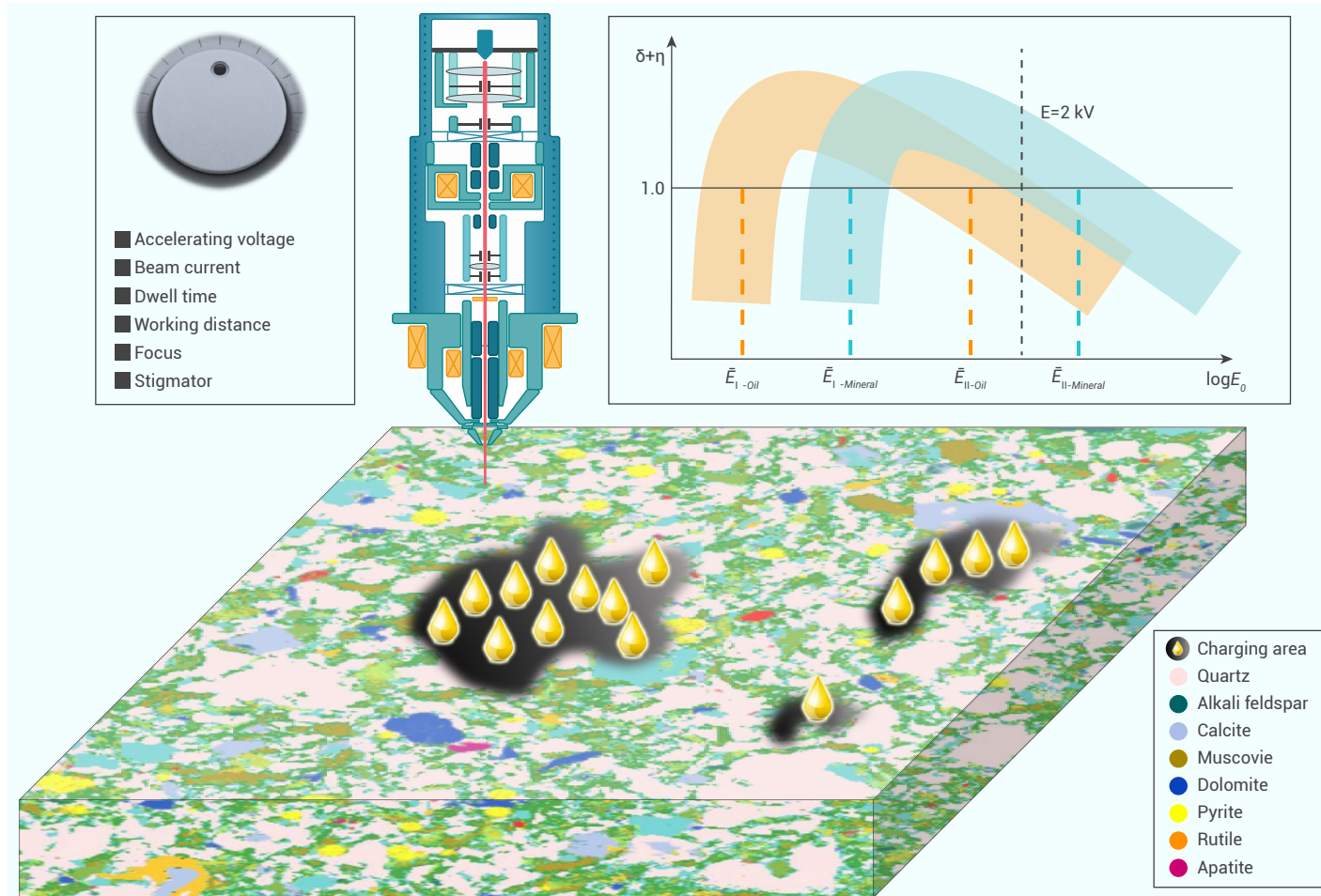


Figure 4. Schematic of charging effect and key parameters that affect the degree of charging

residual oil in the micropore network. The organic matter can be extracted using a polar solvent, such as chloroform bitumen A. All this evidence indicates that the charging effects originate from the residual oil in the samples.

Origins of the local charging effects

The charging effects of various constituent components in a natural rock are mainly dependent on two factors: the conductivity difference and the electron emission ability of each component. The relationship between the primary electron beam (incident on the specimen, I_B), the produced backscattered electrons current (I_{BSE}), the produced secondary electrons current (I_{SE}), the specimen current (I_{SC}), and the rate of build-up charging electrons ($\Delta Q/\Delta t$) can be described using the following equation:

$$I_B = I_{SC} + \frac{\Delta Q}{\Delta t} + I_{SE} + I_{BSE}$$

I_B can be measured using a Faraday cup standard sample combined with a galvanometer. I_{SC} is related to the electroconductivity of the sample and can be directly recorded by a galvanometer. In the shale sample, minerals, organic matter particles and oil have different electroconductivities. When an electron beam is irradiating the surface and $I_B - I_{SC}$ is larger than $I_{SE} + I_{BSE}$, then $\Delta Q/\Delta t > 0$, which leads to a specific amount of charging appearing on the surface particle.

Tests of I_{SC} values. For surface scanning, using certain incident beam current I_B , the I_{SC} can reflect the overall electroconductivity and electron emission capability of a rock sample. We aligned the beam and set the acceleration voltage and beam current to 2 kV and -1330 pA, respectively, to test the I_{SC} values of different samples (Figure S2 and corresponding electron micrographs in Figure S3). For the aluminum metal sample, the I_{SC} value was -1320 pA, which is quite close to the set of -1330 pA, and the difference was

possibly attributed to the thin layer of aluminum oxide from surface oxidation. For the H317-C sample, the I_{SC} value was exactly measured at -1330 pA, indicating good electroconductivity; no charging effect was observed, but organic matter and microcracks were clearly observed (Figure S3A). Among the uncoated samples, the J174 sample exhibited the highest absolute value of I_{SC} , indicating a relatively good average conductivity and slight charging effects (Figure S3E). The H317, H269, and Pu 53 samples showed similar I_{SC} values, while the Bakken sample was showed with the lowest I_{SC} value, along with the highest charging effect.

Next, I_{SC} was examined at the spot scanning mode of each sample (Figure S4), reflecting the impact of heterogeneity on charging behavior. For different spots, the J174 sample (Figures S4A & E) showed similar average I_{SC} values, approximately -1050 pA. Spot 1 corresponds to mineral particles, while spot 4 is located on the edge of pyrite and oil-bearing organic particles, resulting in different I_{SC} values. Spots 2 and 5 were in the charging zone, showing low I_{SC} values of approximately -800 pA. Interestingly, spot 3, corresponding to an organic matter particle, displayed good electroconductivity, implying that if oil remains undesorbed on the organic matter, the I_{SC} value can be as high as that of the minerals. Considering the Pu 53 sample (Figures S4B & F), spots 1 and 2 were in the charging zone, resulting in relatively lower I_{SC} values. Because spots 3~5 corresponded to quartz and pyrite minerals, they showed similar I_{SC} values around -600 pA, while no charging effect was detected. In the Bakken sample (Figures S4C & G), all five spots represented low I_{SC} values, and the entire surface exhibited considerable charging effects, with a small change in the I_{SC} values. This indicates that the overall electroconductivity of the sample is very low, and the surface electronic field is strong, possibly because of the high volumes of movable hydrocarbons preserved in the pores or adsorbed on the organic matter. The H317-C sample (Figures S4D & H), because of conductive carbon coating, was not illuminated at all,

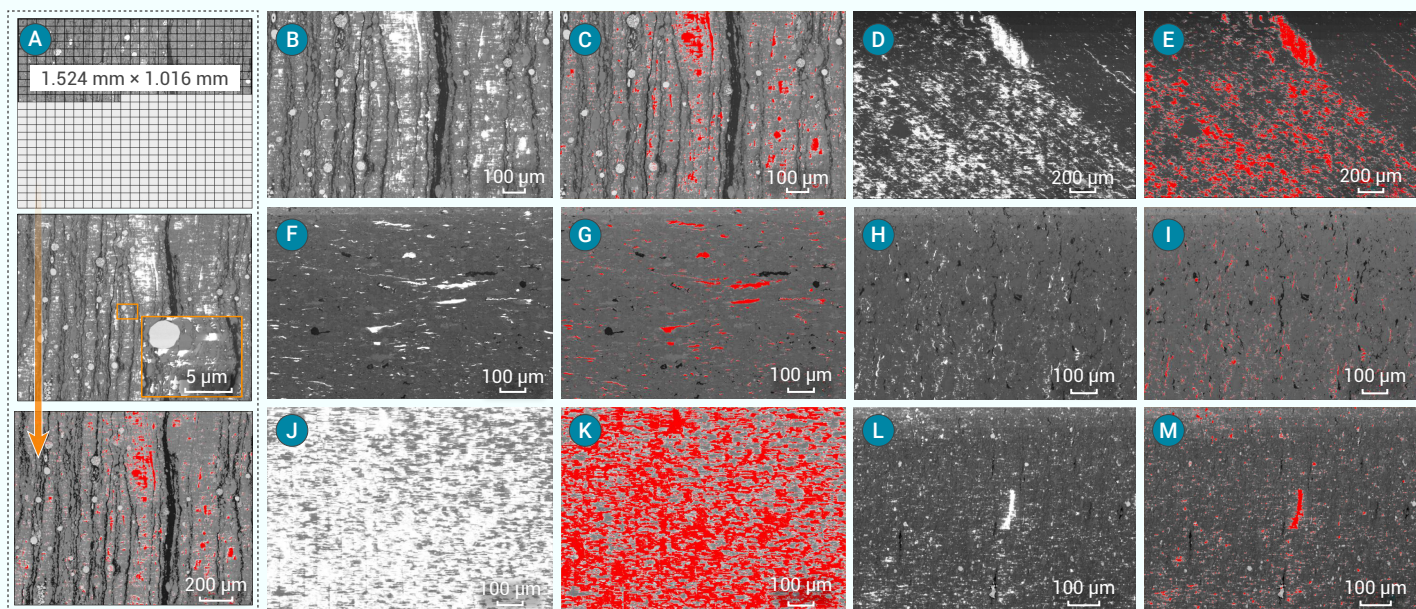


Figure 5. Charging distribution of samples obtained from a large-area image mosaic at the millimeter scale (A) schematic of the 2D large area mosaic imaging and segmentation; (B–M) large-area primary mosaic image with the charging effect and the extracted charging area after image processing of each sample; (B & C) H317; (D & E) Y56; (F & G) H269; (H & I) J174; (J & K) Pu53; (L & M) Bakken.

and no local charging was observed.

Tests of Duane–Hunt limit energy values. From the theory of electron microscopy, every material displays a certain electron emission curve when exposed to an electron beam, and two distinct energy values, E_I and E_{II} , exist (embedding curve in Figure 4).^{32–35} We used wide curves because shale oil is a mixture, and the shale matrix comprises various minerals. The x-axis represents the incident electron beam energy (E_0), and the y-axis represents the electron yield of the material, i.e., the sum of the secondary electron yield (I_{SE}/I_B , δ) and BSE electron yields (I_{BSE}/I_B , η). When E_0 is between E_I and E_{II} , $\delta + \eta > 1$, the emitted electron number becomes larger than the incident electron number, the sample is positively charged, the Duane–Hunt limit energy E_{DHL} (the high energy cutoff of the bremsstrahlung X-ray emitted from the sample) shifts to a value greater than E_0 , and charging effects do not appear.^{31,32} When E_0 is $< E_I$ or $> E_{II}$, $\delta + \eta < 1$, negative charges will accumulate on the sample surface and produce charging effects, and E_{DHL} shifts to a value smaller than E_0 . If E_0 is exactly equal to E_I or E_{II} , the surface of the material is neutral, no charging is observed, and E_{DHL} equals E_0 without a shift.³⁷ Herein, minerals, organic matter, and oil have different electron yields under the same incident electron beam energy of 2 keV.

To further confirm the local charging phenomenon, E_{DHL} values were obtained for J174 and H269 as representative samples for various charged zones (Figure S5). Results inferred that, collectively, organic and inorganic particles without charging can be defined with the E_{DHL} value ≥ 2 keV. On a negatively charged area, the organic particles that contain movable hydrocarbons usually have an E_{DHL} value < 2 keV.

When E_0 is 2 keV—in most of the minerals—because of relatively good electroconductivity and electron emission capability, the charging effect is not expected. However, in oil-bearing organic matter in the sample, larger negative charges were accumulated on the surface, creating a local charge field and leading to the inversion of a portion of the electrons that are emitted from the beam and received by the TLD-BSE detector, causing electron charge areas in the BSE images. Areas where organic matter adsorbed liquid hydrocarbons can cause local charging. This charging can be so strong in some cases that it can distort the image if the sample is free of surface coating.

Therefore, by adjusting parameters such as accelerating voltage, beam current, and dwell time, the charging effect can be effectively controlled, which allows it to occur only in oil-adsorbed zones. The possible influencing factors are listed in Supplementary Information.

2D large-area charging characterization

Following controlled experiments, we developed a procedure to extend this idea and examine a large area for the distribution of residual oil, considering the heterogeneity of shale oil samples at the centimeter scale. Because mud–sand layers were widely distributed in shale, the accuracy of assessing if the samples contained movable hydrocarbons might be compromised if the analysis area was extremely small to obtain high-resolution images. Specifically, after large-area ion polishing, centimeter-scale local charging imaging of the sample could be obtained using high-resolution image mosaicking. Figure 5 shows the charging distribution analysis results of various samples based on the large-area image mosaic method developed in this study (Figure 5A).

Figures 5B & C explain the process and present the results from Sample H317 in an area of 1.524×1.106 mm². Organic matter was observed in bitumen streaks, and charging effects occurred sporadically without any significant charging. Instead, electron charges were scattered on the surface associated with small organic particles. The results showed that a large amount of smaller organic matter particles associated with clay minerals generate hydrocarbons in a restricted area, creating charged zones instead of the elongated bitumen streaks. Based on the segmentation of the larger images, we could separate these charged areas to assess the content and distribution of movable hydrocarbons in the occupied 3.86% of the entire area.

A similar procedure was applied to all samples, as shown in Figures 5D–M. In the Y56 sample (Figures 5D & E), almost every organic particle surface was charged to 11.14%. Therefore, in this sample, almost all organic particles have adsorbed hydrocarbons, causing such intense charging. The H269 sample (Figures 5F & G), where minerals had a nonuniform size distribution and organic matter was mostly distributed along beddings without bitumen streaks, exhibited charged microcracks filled with movable hydrocarbons; this part was 2.68% of the total surface. The J174 sample (Figures 5H & I) was mainly composed of muddy carbonatite, with charging occurring mainly on the surface of micron-size organic particles associated with clay minerals; the area percentage was approximately 2.43%. For the Pu53 sample (Figures 5J & K), considerable charging was observed, without any specific relationship between the organic matter/minerals and charging distribution of 51.71%. In the Bakken sample (Figures 5L & M), the charging effects were observed on the surface of scattered organic particles with varying sizes; the area percentage of the charging was 4.48%.

The results indicated that not all organic particles in the source rocks will equally adsorb hydrocarbons, even on the micrometer scale, because of the

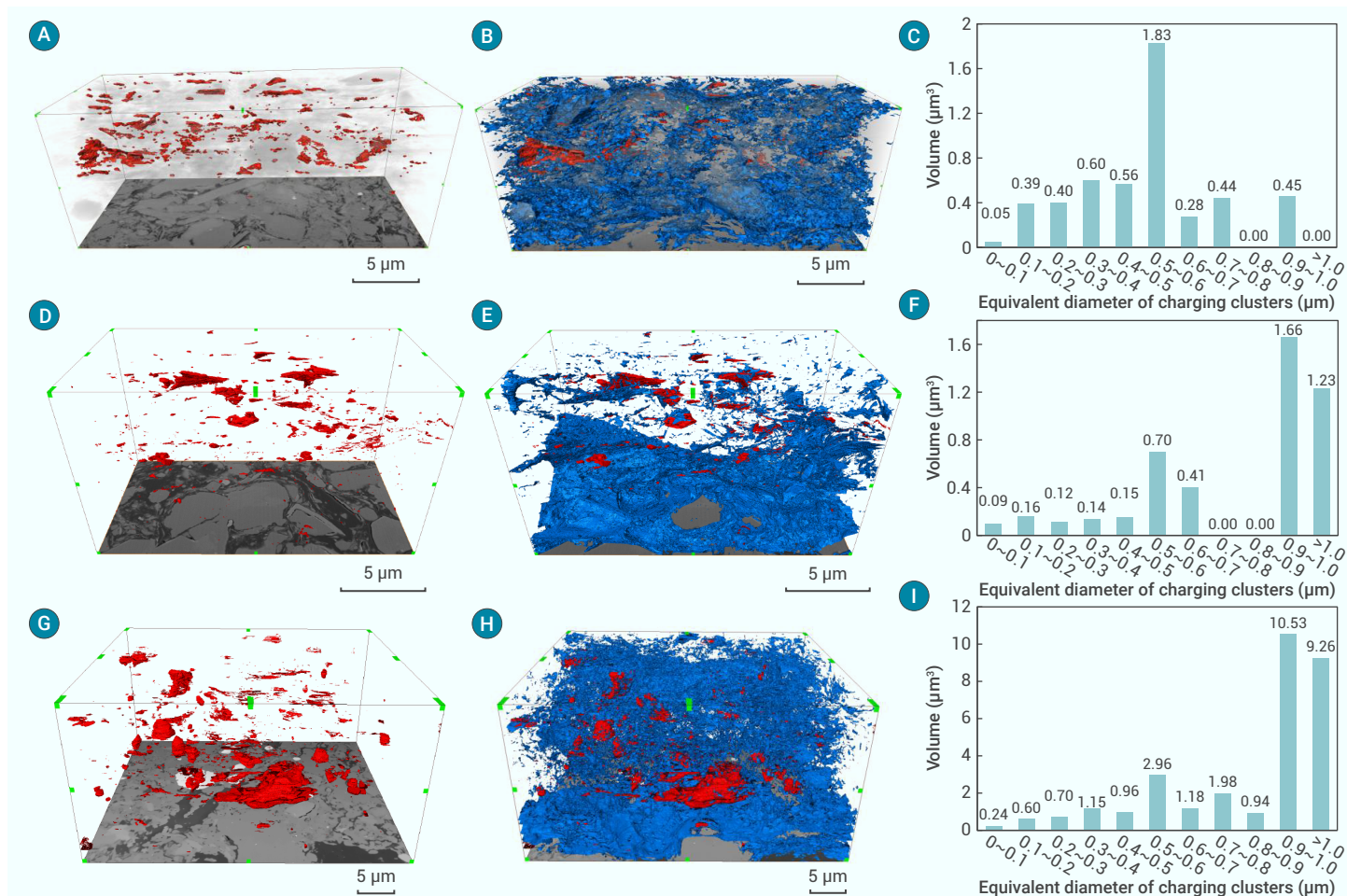


Figure 6. 3D charging distribution of residual oil in samples Red shades indicate the charging zone, where crude oil is concentrated, and the blue zone is the organic matter and pores free of charging. The histogram represents the diameters of charged clusters. (A–C) H317; (D–F) J174; (G–I) Pu53.

thermal progression of the organic matter. Using 2D large-area charging characterization, the oil distribution at the millimeter scale or even at the centimeter scale was visually observed, wherein the fine details at the nanoscale resolution were preserved. Large-area stitching revealed statistical information for oil abundance evaluation and was an important supplement experimental test for the conventional geochemical test. An advantage of this approach is that shale formation can be quantitatively and visually assessed at the same time.

3D distribution of electron charges

So far, we presented how the distribution of liquid hydrocarbons can raise areas with high electron charges in a large sample surface. Next, we would like to propose another method to assess movable hydrocarbons in a 3D domain, enabling us to understand migration pathways and fluid flow direction in the reservoir system at a small scale essential to better understand flow mechanism in tight formation. As a result, the 3D spatial distribution of movable hydrocarbons was done in a $25 \times 15 \times 12 \mu\text{m}^3$ space via the slice imaging and segmentation method.

Considering sample H317 as an example, the charging effect was observed where micron-size organic particles were concentrated adjacent to the clay minerals. As shown in Figures 6A–C, movable hydrocarbons were highly scattered in the organic matter network of particles of various sizes. The network of these organic particles containing the liquid hydrocarbons was not strong and without much communication. Such formation can create an unfavorable flow network, causing trapper/adsorbed liquids to be retained in the pores/organic matter and affecting production. However, a large quantity of movable hydrocarbons is expelled from intercrystalline pores during the pyrolysis test of the sample, showing that the existing pores and spatial distribution of the organic material within the rock matrix can

provide a proper pathway for movable hydrocarbons if appropriate methods are applied. As mentioned earlier, Figures S1C & D explain the occurrence of cracks within the organic particle and in the boundary of minerals and organic particles after polar solvent treatment, indicating that large quantities of movable hydrocarbons were absorbed in organic particles. These recoverable hydrocarbons can be extracted using polar solvent, leading to volume shrinkage after extraction.^{39–43} Figures 6D–I reveal the distributions of movable hydrocarbons in the J174 and Pu53 samples, showing that small quantities of movable hydrocarbon are associated with organic matter.

The 3D spatial distribution of movable hydrocarbons in various samples shows multiple degrees of aggregation (Figures 6A–B, D–E, G–H), and the equivalent diameter of charging clusters and volume show clear differences (Figures 6C, F, I). Therefore, the development plan and stimulation procedure should be customized for multiple shale formations with distinct oil spatial distributions.

Unlike other samples, H269, which is an oil-bearing siltstone (Figures 7A–C), displays movable hydrocarbons in intergranular microcracks with the least amount of organic matter (Table 1), indicating that to access such trapped hydrocarbons, proper stimulation methods such as hydraulic fracturing are required to create a network of connected fractures and increase the volume. Per the SEM image, the minimum thickness of the oil layer was approximately 53.5 nm (Figure 7C).

CONCLUSION

In order to directly visualize the occurrence of oil with high resolution, this study proposed a novel 2D/3D visualization method for detecting retained oil in shale samples. This method revealed that local charging effects can directly indicate the location and distribution of movable hydrocarbons adsorbed in organic particles or stored in nanopores or microcracks. This

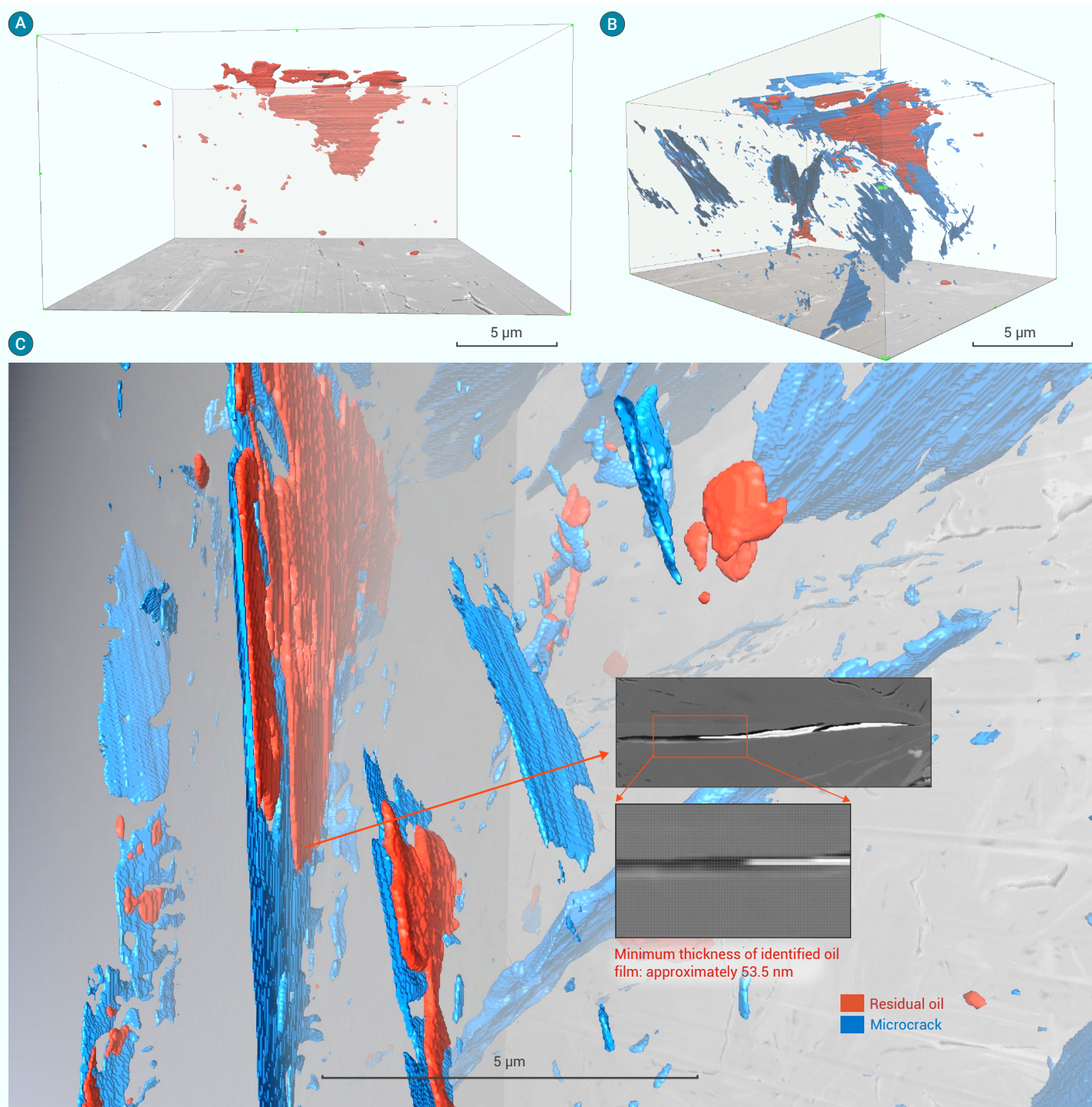


Figure 7. 3D charging distribution of residual oil in the H269 sample (A) distribution of the residual oil in the sample; (B) distribution of the residual oil and the kerogen network; (C) nano-oil film identification, with a minimum film thickness of approximately 53.5 nm, showing a high resolution.

method enables a nanoscale spatial resolution, with the limit of detection <1 pmol (10^{-12} mol). In terms of resolution, this method is superior to FE-SEM, ultrahigh-resolution fluorescence microimaging, MRI, and other existing methods for detecting movable hydrocarbons in rocks. This method can complement conventional geochemical analyses that can provide general information about the presence of hydrocarbons in the sample. Centimeter-scale analysis can be realized by increasing the number of stitched images and prolonging the time for acquisition, providing a powerful solution for macroscopic imaging of highly anisotropic samples. The related methods proposed and developed in this study potentially assess the hydrocarbon generation potential, movable hydrocarbon amount, and expulsion pathways

in 2D and 3D.

This method demonstrates broad applicability when applied to six typical shale samples from Ordos Basin (3), Jungar Basin (1), Songliao Basin (1), and Williston Basin (1). This method is suitable for either continental or marine samples and for either low-mature or high-mature samples. For the samples categorized as ideal source rocks, strong charging effects are usually observed on the surface of organic particles, indicating the location of the absorbed movable oil. For shale samples with high maturity, the charging effects usually originate from residual oil retained in microcracks and nanopores.

The novel 2D/3D visualization method offers several merits for better

understanding shale oil occurrence characteristics, favorable reservoir prediction, and development plan-making. Firstly, the 3D oil distribution indicates that the retained oil clusters are mostly scattered, isolated, and associated with organic particles, and the development of shale oil must involve the use of the entire organic particle network and the matrix pore-throat system. Secondly, based on the 2D and 3D analyses of movable hydrocarbons in the shale rock combined with simulation methods at a larger scale, sweet spots and more favorable locations in the reservoir can be predicted, particularly in thin-bed tight formations. Thirdly, 2D and 3D analyses of pore structures, organic particle distribution, and movable hydrocarbon distribution combined with reservoir parameters, such as reservoir temperature and pressure, wettability, and oil composition,⁴⁴ can guide shale oil engineers to implement a reasonable and effective development plan, which will not be limited to combinations of water injection, hydraulic fracturing, in situ heat conversion process, steam-assisted gravity drainage, lean gas and CO₂ flooding, and other possibilities.⁴⁵⁻⁴⁹

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AUTHOR CONTRIBUTIONS

X.W. proposed the idea and wrote the original draft. B. L. and X.J. supervised the research. S.M., X.L., and J. T. collected the samples and the experimental data. X. L., C. Z., and M. S. performed the 2D and 3D visualization experiment. H. X contributed in data analysis. S.B., M. O., and W. Z. revised the paper.

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

Data are available from the corresponding author upon reasonable request.

SUPPLEMENTAL INFORMATION

It can be found online at <https://doi.org/10.59717/j.xinn-ener.2024.100011>