Application of SEM and EDS for mineral composition of shale gas reservoir

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Abstract: In recent years, great progress has been made in the exploration and exploitation of shale gas, making it the main driving force for the growth of world natural gas production. Mineral composition restricts the pore size, distribution, geometry and connectivity of shale reservoirs, and also affects the brittleness and fracturing ability of shale reservoirs. Therefore, mineral composition is of great significance to the evaluation and exploration and development of shale gas reservoirs. Taking the Paleogene shale reservoir in Liaozhong Sag as an example, this study explored the application of argon ion polishing technology, Field Emission Scanning Electron Microscope (FE-SEM) and X-ray Energy Dispersive Spectrometer (EDS) analysis in mineral identification.

1. Introduction
Shale gas is a kind of clean and efficient unconventional natural gas, which occurs in dark shale in the state of free, adsorption and dissolution, and has the characteristics of self-generation, self-storage and in-situ saturation accumulation [1, 2]. In recent years, shale gas exploration and exploitation has made great progress, and has become the main driving force for the growth of world natural gas production [3]. Shale gas resources in China are at the forefront of the world. After cooperation and reference, exploration and evaluation and the development of large-scale production stage, China has become the third-largest shale gas producer in the world after the United States and Canada [3, 4]. Shale is composed of fine elastic, clay and organic matter with particle size less than 0.0039mm [3]. Its composition and structure are complex, permeability is ultra-low, anisotropy is significant, and has multi-scale pores from nanometre to micron [5]. These characteristics of shale are the key factors affecting the occurrence state of shale gas, reservoir performance and gas reservoir production [6]. The mineral composition not only restricts the pore size, distribution, geometry and connectivity of shale reservoir [7], but also affects the brittleness and fracturability of shale reservoir [8]. Therefore, the mineral composition is of great significance to the reservoir evaluation, exploration and development of shale gas.

Scanning Electron Microscope ((SEM)) breaks through the limit of traditional optical microscope, and its ultra-high resolution makes it a powerful tool to explore the micro world. Scanning electron microscope can be used to observe the surface morphology and mineral composition of the sample [9]. Combined with its matching X-ray Energy Dispersive Spectrometer (EDS), the composition can be analysed quantitatively or semi-quantitatively [10]. In this paper, the mineral composition of
Paleogene shale reservoir in Liaozhong sag is studied by using argon ion polishing technique, Field Emission Scanning Electron Microscope and X-ray Energy Dispersive Spectrometer analysis.

2. Samples and experiments

2.1. Samples and instruments
The samples were taken from the 2nd member of the Dongying Formation (E3d2, well JZ16-4-1), the 3rd member of the Dongying Formation (E3d3, well JX1-1-1 and LD32-2N-1), the 1st member of the Shahejie Formation (E3s1, well JX1-1E-2 and JX1-1-1) and the 3rd member of the Shahejie Formation (E2s3, well JX1-1-3) in Liaozhong area. The instruments used in this experiment include PECS II 685 type precision etch coating system (GATAN, USA), Quanta 250 FEG type Field Emission Environmental Scanning Electron Microscope (FEI, USA) and Quantax200 Xflash type X-Ray Energy Dispersive Spectrometer (Bruker, Germany).

2.2. Experimental Process
Firstly, fresh rock samples with smooth surface were selected, and then argon ion polishing was carried out in PECS II 685 precision etch coating system. The high-speed ion beam bombardment can eliminate the roughness of shale sample surface and obtain high-quality surface. Finally, Quanta250 FEG field emission environment Scanning Electron Microscope was used to observe high-quality samples. The accelerated voltage of SEM is 10.00kv, and the detector is Backscattered Electron (BE), which is used for image of morphology and composition contrast. The analysis of element composition of points, lines and planes was carried out by Energy Dispersive Spectrometer, and then the mineral components in the samples were identified.

3. Result and discussion

3.1. SEM Analysis
Minerals with similar average atomic numbers, such as quartz, feldspar and illite, have little gray difference and are difficult to identify directly (figure 1a). The composition and distribution of elements shown by further X-ray Energy Dispersive Spectrometer analysis are shown in figure 2. Pyrite is one of the common minerals in shale, generally in the form of strawberry, formed by the close accumulation of equal size sub micron pyrite crystals or microminerals. Because of its large average atomic number and high brightness, pyrite is easy to identify in backscattered electron images (figure 1b). Siderite is a common mineral in continental fine-grained sedimentary rocks, which is generally irregular in shape, and the particle size ranges from several to tens of microns. Under the backscattered electron image, siderite has high brightness, remarkable characteristics and is easy to identify (figure 1c). Calcite is generally rhombic or irregular, the particle size changes greatly, and the internal dissolution phenomenon is very developed. Calcite is easy to identify because of its low average atomic number and lower brightness in backscattered electron images, but higher brightness than minerals such as quartz, feldspar and illite (figure 1d). Illite is long strip or plate, tens of microns long, several microns wide, flaky pores developed in the middle, and the brightness of illite is close to that of quartz and feldspar under the backscattered electron image. Because of its special shape, it is relatively easy to identify (figure 1e). The morphology of organic matter is irregular, and its internal organic matter pores are easy to develop. Because of its low average atomic number, the brightness of organic matter is the lowest in the backscattered electron image (figure 1a, f).
Figure 1. Backscattered electron images of common minerals in shale

a. ① = Rutile, ② = quartz, ③ = albite, ④ = illite, ⑤ = organic matter, well JX1-1-1; b. ⑥ = pyrite, well JX1-1-1; c. ⑦ = siderite, well LD32-2N-1; d. ⑧ = calcite, JZ16-4-1; e. ④ = illite, well JX1-1E-2; f. ⑤ = organic, well JX1-1-1.

3.2. EDS Analysis
In the middle of figure 1a, the brightness is high, and the minerals distributed as flaky aggregates are difficult to identify, while the grayscale of quartz, feldspar and Illite are close and difficult to distinguish. Therefore, the composition and distribution of the elements were obtained by X-ray energy spectrum scanning (figure 2). Among them, the mineral in the middle of figure 1a is bright, and the mineral with flaky aggregate contains a lot of O (figure 2a) and Ti (figure 2d, i) elements, so it is speculated that it is rutile. X-ray energy spectrum scanning shows that the black organic matter in the upper part of figure 1a contains a large amount of C element (figure 2h, i), which is consistent with the previous understanding. The brightness of quartz, feldspar and illite is close and difficult to distinguish. According to the X-ray energy spectrum scan, the mineral in the lower right of figure 1a contains a lot of O (figure 2a) and Si (figure 2b, i) elements, so it is speculated that it is quartz. The minerals in the lower left and middle part of figure 1A contain a large amount of O (figure 2a), Si (figure 2b, i), Al (figure 2e, i) and Na (figure 2g), which is presumed to be albite. Illite is distinguished according to its special morphological characteristics, and contains K (figure 2f) element distribution, which is consistent with the previous understanding.
Figure 2. X-ray Energy Dispersive Spectrometer analysis of figure 1a

a. Distribution of oxygen (O); b. Distribution of silicon (Si); c. Distribution of strontium (Sr); d. Distribution of titanium (Ti); e. Distribution of aluminum (Al); f. Distribution of potassium (K); g. Distribution of sodium (Na); h. Distribution of carbon (C); i. The composition and distribution of the main elements.

Quartz, potassium feldspar and albite are similar in morphology, similar in brightness under backscattered electron images (figure 3a, c, e), and all contain large amounts of O and Si elements, which are difficult to distinguish according to SEM images and element distribution characteristics. These minerals need to be judged by the proportion of quantitative atoms obtained by X-ray energy spectra. The X-ray spectra of quartz show that the main elements are O and Si, and the atomic ratio of O to Si is close to 2:1 (figure 3b). The X-ray energy spectrum of potash feldspar shows that it mainly contains O, Si, K and Al (figure 3d). The X-ray spectra of albite show that O, Si, Al and Na are the main ones (figure 3f).
Figure 3. X-ray Energy Dispersive Spectrometer analysis of minerals with similar gray scales in the SEM image

a. Backscatter Electron image and analysis point of quartz, JZ16-4-1 well; b. X-ray Energy Dispersive Spectrometer analysis of the analysis point in Figure 3a; c. Backscatter Electron image and analysis point of potash feldspar, well LD32-2N-1; d. X-ray Energy Dispersive Spectrometer analysis of the analysis point in Figure 3c; e. Backscatter Electron image and analysis point of albite, JX1-1-1 well; f X-ray Energy Dispersive Spectrometer analysis of the analysis point in Figure 3e.

4. conclusion
When the shale reservoir minerals are studied by scanning electron microscope, the backscattered electrons are not as good as the secondary electrons in reflecting the morphological details of the sample surface, but they can show the difference of chemical composition or atomic number in the micro-region. The mineral can be preliminarily identified by grayscale differences and mineral morphological characteristics.

The minerals with similar morphology and small grayscale differences of backscattered electron images can be distinguished according to the element composition, distribution and atomic ratio of X-ray Energy Dispersive Spectrometer analysis.
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