

# GEOCHEMICAL CHARACTERISTICS OF ILLITE CLAY ROCKS IN ZHANGCUN COAL MINE

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## Introduction

Some characteristic elements can indicate the water medium conditions of sedimentary rocks (Institute of Geochemistry Chinese Academy of Sciences, 2000) and be as evidence for confirming sedimentary source and sedimentary environment (Zhao Hong-ge et al., 2003). In recent years, many researchers have done a lot of studies on geochemistry characteristics of coal measure strata ( Yang Lei et al., 2008; Liu Guijian et al., 2001; Dai Shifeng et al., 2003; Wu Zi-yu et al., 2004; Yang Pinyue et al., 2004), but the most focused on the geochemistry characteristics of coal seams ( Dai Shifeng et al., 2002), in contrast, the geochemistry characteristics of associated clay minerals including kaolinite, smectite and illite were not paid much attention, especially geochemistry characteristics of illite clay rocks were few reported ( Zhu Rukai et al., 1997; Liu Qinfu et al., 1997, 1998;). The purpose of this paper is to study geochemical characteristics of illite clay rocks and its significance, from Shihezi Formation of Late Permian in Zhangcun coal mine, and to analyze sedimentary environment through characteristic element ratio method.

## Materials and methods

### Materials

22 clay rocks samples which include 7 samples from lower Shihezi formation and 15 samples from upper Shihezi formation, were collected from three wells drilled in Zhangcun coal mine from the Permian strata. Clay rock samples with compact structure, which are not weathering obviously and appear to be gray, celadon and graniphyric partly.

### Methods

The analysis of major chemical constituents were performed using sequential X-ray fluorescence spectrometer to estimate the major elements wt.% in the illite samples. Sequential X-ray fluorescence spectrometer with Rh-filtered using 3kW. The elements including F-U were X-rayed with measuring accuracy from major(%) to trace (ppm).The clay fraction (<2 μm) was separated by disaggregating and dispersing the sample in distilled water and immediately washed by centrifugation. The fraction of <2 μm was isolated by centrifugation and suspension was dried on glass slides. The trace elements of 22 samples were analyzed by using inductively coupled plasma mass spectrometry (ICP-MS). The HR-ICP-MS ( Element I ) made by Finnigan MAT is equipped with atomization chamber made up by quartz and Piltier semiconductor for controlling temperature 20.1°C and quartz intergrated torch tube with 2.5 mm central passage. The parameters of HR-ICP-MS( Element I ) are that the power is 1350 W and the velocity of carrier gas is 1.08 L·min<sup>-1</sup>. The internal standard is mixed by many elements including Ge, In and Ni, *et al.*

## Results and Discussion

### Results

Major elements: The contents of major elements of 9 representative samples in study area were analyzed (Table 1). The results show that the SiO<sub>2</sub> content is 53.37-61.58 wt.% and the Al<sub>2</sub>O<sub>3</sub> content the is 22.40-31.31 wt.%, the ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is

1.71-2.75, which are closed to their theoretical values in illite clay rock.; The contents of Fe and Ti are higher than their theoretical values in illite clay rock. The contents of range Fe<sub>2</sub>O<sub>3</sub> from 3.67 wt.% to 11.22 wt.% and the average value is 7.85 wt.%; the contents of range TiO<sub>2</sub> from 0.77 wt.% to 1.05 wt.%.

Trace elements: The trace elements of 22 illite samples are shown in Table 2. The results show that the most of trace elements don't enrich obviously and are close to their abundance values in lithosphere(Han Yinwen, 2003). Some trace elements including Ga, As, Ba, Cu, Th and U are higher than their Clark values and the other 23 trace elements detected are closed to their Clark values. The analysis results of REE are shown in Table 3. The REE contents range from 22.59 to 570.54  $\mu\text{g} \cdot \text{g}^{-1}$  and the average content is 163.23  $\mu\text{g} \cdot \text{g}^{-1}$ , which are closed to the REE average values of shale rock in north America ( 173.2 $\mu\text{g} \cdot \text{g}^{-1}$  ) ( Henderson P, 1998). The ratios of LREE/HREE range from 5.41 to 21.82, and the average value is 8.87. These characteristics show that LREE are much richer than HREE. The REE distribution patterns of samples are characterized by obvious negative Ce anomaly and negative Eu anomaly.

### Discussions

Mn/Fe: Iron compounds enrich easily in coastal area because Fe is oxidated easily to be Fe<sup>3+</sup> and exists in form of Fe(OH)<sub>3</sub> compounds. In contrast, Mn often deposits far from the coast because of its stability in hydronium solution. So that, the ratio value of Mn / Fe in marine shale is higher than freshwater shale(Li Jinlong, 2003). The ratios of Mn/Fe range from 0 to 0.0168, which are lower than Mn/Fe ratio value of marine sedimentary environment. We can conclude that sedimentary environment of Hanxing minning area in Late Permian is mainly continental sedimentary environment.

Sr/Ba: Both Sr and Ba belong to lithophile element and they have similar geochemical properties. But they have different geochemical behavior that Sr deposits directly from seawater, contrastly Ba is adsorbed easily by clay minerals and fine clastic sediments. Many research results show that Ca and Sr are abundant but Ba is low content in marine

sedimentary, which are opposite in freshwaer sedimentary. It is generally believed that the sedimentary environment is marine if the radio value of Sr / Ba is more than 1, or else is continental freshwater condition (Wu Shaobo, 2001). The Sr of all illite rock samples in this study exhibit a wide distribution range from 57.8  $\mu\text{g} \cdot \text{g}^{-1}$  to 316  $\mu\text{g} \cdot \text{g}^{-1}$ , the average value is 148.84  $\mu\text{g} \cdot \text{g}^{-1}$ ; and the contents of Ba are 210-976  $\mu\text{g} \cdot \text{g}^{-1}$  and the average value is 533.36  $\mu\text{g} \cdot \text{g}^{-1}$ . The radio values of Sr / Ba range from 0.20 to 0.41, where the average radio value of Sr / Ba in upper Shihezi formation is 0.35 and in lower Shihezi formation is 0.20. The Sr / Ba value of all samples are less than 1, which indicate that sedimentary environment of Zhangcun coal mine in Late Permian is mainly continental sedimentary environment. This is consist with conclusions above.

### Conclusions

The SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio values of illite clay rocks in Zhangcun coal mine are 1.71-2.75; The contents of Fe and Ti are higher than their theoretical value in illite clay rock. Some trace elements including Ga, As, Ba, Cu, Th and U are higher than their Clark values and the other 23 trace elements detected are closed to their Clark values. The REE contents range from 22.59 to 570.54  $\mu\text{g} \cdot \text{g}^{-1}$  and the average content is 163.23  $\mu\text{g} \cdot \text{g}^{-1}$ . The ratios of LREE/HREE range from 5.41 to 21.82, and the average value is 8.87. These characteristics show that LREE are much richer than HREE. The REE distribution patterns of samples are characterized by obvious negative Ce anomaly and negative Eu anomaly

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