Primary productivity and basin redox conditions within the Mesoproterozoic Hongshuizhuang Formation from Chaoyang area, Liaoxi sag

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Abstract. The Mesoproterozoic Hongshuizhuang Formation in Liaoxi sag, northern China, is an important hydrocarbon source unit having good potentials to generate oil and gas. The total organic carbon (TOC) content ranges from 0.54% to 4.07% in the Chaoyang area. Trace element geochemistry was utilized to study the primary productivity and basin redox conditions during the deposition of Hongshuizhuang Formation black shales. The results suggest that primary productivity during the deposition of the Hongshuizhuang Formation was relatively high. The redox-sensitive elements results indicate that the Hongshuizhuang Formation was deposited under euxinic or anoxic bottom water conditions. The degree of environment restriction, diagenesis, reoxygenation, and the presence of free H₂S can make some of the redox-sensitive elements proxies and primary productivity proxies not applicable. The high TOC content of the Hongshuizhuang Formation is contributed by high primary productivity in the surface water combined with euxinic/anoxic in the bottom water.

1. Introduction

Yanshan is one of the areas with most Mesoproterozoic strata in China. Mesoproterozoic hydrocarbon source rocks are widely spread in the Yanshan area and abundant oil seepages have been found. The Hongshuizhuang Formation of the Jixian Group in the Yanshan area has drawn petroleum geologists’ attention for many years. The Hongshuizhuang Formation is the primary target for hydrocarbons because of its potential to be an excellent source rock unit [1]. Compared with the large numbers of studies focused on the Xiamaling Formation in this area, only a few studies have been undertaken to study its organic geochemistry as well as the redox state of the Mesoproterozoic ocean and atmosphere during the Hongshuizhuang period [2-3].

Multi-proxy geochemical studies have illustrated that the Mesoproterozoic was characterized by geological, climatic, and by-and-large evolutionary stasis, and termed as “middle ages” of the earth [4-7]. The ocean in Mesoproterozoic was mostly ferruginous with euxinic wedges on shelf margins and perhaps several pulses of increased oxygen in some areas [8-10]. These pulses of increased oxygen are frequently accompanied by the sediment of black shales, and the Hongshuizhuang Formation is one of them. The Hongshuizhuang Formation contains perhaps the oldest organic-rich sediments with potential oil and gas resources in North China. These marine shales have not only been proposed to be
important for conventional oil and gas explorations but also shale gas explorations. To our best knowledge, there were no higher living organisms in the Mesoproterozoic Eon and organic matter in sediments was primarily derived from prokaryotes. The productivity in the Mesoproterozoic ocean was much lower than that in modern oceans [11]. The primary productivity and basin redox condition play a key role in the preservation of organic matter in the black shales. The primary productivity and basin redox condition during deposition of the Hongshuizhuang Formation are still not well defined. In this study, total organic carbon data is coupled with major and trace element geochemistry to understand key environmental controls on organic matter production and preservation, which can provide useful references for assessing Precambrian petroleum systems.

2. Geological settings
The Liaoxi Sag is one of the five sags in the Yanshan Basin, North China (Fig. 1). The Yanliao Basin has a nearly complete record of Mesoproterozoic sedimentation. The Hongshuizhuang Formation is primarily composed of thin black calcareous shales and argillaceous dolomites deposited in a subtidal zone. The age of Hongshuizhuang Formation was reported to be 1437 ± 21 Ma [12], placing this unit in the middle Mesoproterozoic. The thickness of the Hongshuizhuang Formation in the Chaoyang area, Liaoxi Sag is about 30 to 100m, much thinner than that in its depocenter in the Jixian and Kuancheng areas, where the thickness can reach up to 170m.

Black shales and mudstones make up the majority of the Hongshuizhuang Formation in the Chaoyang area, Liaoxi Sag. In most areas, the Hongshuizhuang Formation can be subdivided into two members based on lithology [3]. The lower Hongshuizhuang Formation consists of thin layers of black shale and mudstone, and the upper Hongshuizhuang Formation consists mainly of silty, argillaceous dolomite. In the Liaoxi area, the Upper member is not well developed, most of Hongshuizhuang Formation is composed of black shales and calcareous yellow and green shales interbedded with dolomites.

![Figure 1. Tectonic subdivisions of the Yanliao Basin and the location of the sampling point](image)

3. Samples and methods
Samples analyzed were from two sections in the Chaoyang area, Liaoning province. A total of 11 fresh rock samples of black shales were collected (Fig. 2). After removing the weathering rind, all samples were pulverized to 200 mesh. Following a standard experimental program, total organic carbon (TOC)
contents, trace elements were analyzed for all samples. Total organic carbon content is measured by LECO CS230 Carbon/Sulfur analytical instrument at Guangzhou Institute of Geochemistry (CAS) based on a standard program. The Rigaku X-ray Fluorescence (XRF) Spectrometer (model 3080E3) was used to analyze selected trace elements based on the Chinese national standard (GB/T14506.28-1993).

4. Results and discussions

4.1. Primary productivity
The TOC content of the black shales varies from 0.54% to 4.07%, with an average of 1.42%, suggesting fair to good organic source rocks. High TOC content in sediments has been attributed to high primary productivity in many areas [13-15], but this is not always the case, especially in the Mesoproterozoic sediments [6]. The marine primary productivity is mainly affected by the availability of key dissolved nutrients such as Phosphorous (P) and Nitrogen (N). Besides, the species of organisms in the ecosystem are also an important factor to affect primary productivity, since most organisms in Mesoproterozoic are prokaryotes.

Since some marine organisms can fix nitrogen from the atmospheric, only P is considered the ultimate limiting element controlling primary productivity in the marine environment. Besides, P is also an important component of the marine organisms’ skeleton and plays an important role in metabolic processes, and has therefore been widely used to study paleo-productivity in geological time [14-16]. Instead of concentrations of P, ratios of P/Ti and P/Al are widely used for its advantages to exclude the effect of dilution from sedimentary organic matter or authigenic minerals. The P/Ti values of the Hongshuizhuang Formation in the study area vary from 0.06 to 0.65 with an average of 0.25. These results are considered to indicate a moderate level of primary productivity [14]. The cross plot of TOC and P/Ti showing a strong positive correlation. The degree of organic matter enrichment was strongly controlled by primary productivity. This result is consistent with previous studies that high primary productivity can contribute to high TOC values in the sediments.

Barium (Ba) is also known to be a reliable productivity proxy. The sedimentary rate of baritite (BaSO₄) in marine sediments shows a positive correlation with primary productivity [14]. Similar to the P proxy, Ba/Al or Ba/Ti is commonly used instead of Ba concentrations. The Ba/Al values of the Hongshuizhuang Formation range from 49.5 to 89.7, with an average of 65.8 (Fig 2). Although the mean values of Ba/Al in Hongshuizhuang Formation are low, this might attribute to the extremely low sulfate concentrations of seawater [17]. In the anoxic environment, bacterial sulfate reduction occurs, resulting in the reduction of sulfate, and the dissolved Ba²⁺ cannot be preserved in situ, but migrates to the sulfate-rich area for precipitation. The Hongshuizhuang Formation is possibly deposited in an environment where H₂S was abundant and sulfate reduction occurred, indicating that the black shales might have lost a large part of Ba. The hypothesis is confirmed by the Ba/Al and TOC cross plot.
The TOC content shows a weak negative correlation with the Ba/Al value, which indicates that most of the sulfate was exhausted.

![Figure 3](image_url)

**Figure 3.** Cross plots of TOC and redox-sensitive trace element ratios

### 4.2. Basin redox conditions

Trace elemental ratios (e.g. V/(V+Ni), U/Th, V/Cr, Ni/Co) are sensitive to redox conditions of water column and are frequently used to interpret the depositional conditions. The V/(V + Ni) ratio is particularly useful to discriminate euxinic, anoxic and dysoxic conditions, where the ratio range is >0.84, 0.60 to 0.84 and 0.4 to 0.6, respectively[18-19]. The V/(V+Ni) ratio of Hongshuizhuang Formation ranges in a very narrow area from 0.76 to 0.89 with an average of 0.84 (Fig.3). This result suggested that the euxinic and anoxic depositional conditions were widespread when the Hongshuizhuang Formations shale deposited. The presence of free H$_2$S can also explain the relatively low Ba/Al ratio discussed above.

However, many other elemental ratios are not consistent with this result, with some of the ratios even indicate oxic conditions (Fig.3). For example, the Ni/Co ratio ranged from 1.5 to 15.9, with only one sample have a value higher than 7.0, indicating oxic conditions in common[20]. This is contradicting with the fact that most of the Hongshuizhuang shales were deposited under euxinic and anoxic conditions. It should be noted that environment restriction, diagenesis, and post-depositional reoxyg enation can profoundly affect the concentrations of redox-sensitive elements. For example, oxygen penetrates to a depth where the authigenic U has accumulated can cause relatively low U/Th ratios. The distribution Co in sediments is strongly affected by the concentrations of provenance area of sediments, which limits its use as a reliable redox proxy [16]. Finally, the presence of free H$_2$S during the deposition of the Hongshuizhuang Formation can inhibitions such as Ni from binding with organic complexes. Even some of the elemental ratios are not well applied in the Hongshuizhuang Formation, they show a relatively strong positive relation to the TOC content (Figure 3). This might indicate a relatively restricted depositional environment. This trend also supports that anoxic water column is a good condition for the accumulation and preservation of organic matters.

### 5. Conclusions
Based on the results discussed above, the main conclusions are listed as follows:

1. The trace element characteristics of the Mesoproterozoic Hongshuizhuang Formation suggest that the primary productivity was relatively high during the deposition of the Hongshuizhuang Formation. The Hongshuizhuang Formation was mainly deposited under euxinic or anoxic bottom water.

2. High degree of organic matter enrichment was closely related to primary productivity and water column redox conditions. Relatively high surface primary productivity combined with euxinic or anoxic bottom water conditions can promote the deposition and preservation of organic matters.

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