



# Sedimentary geochemical investigation for paleoenvironment of the Lower Cambrian Niutitang Formation shales in the Yangtze Platform



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## ABSTRACT

The geochemical data and geochemical proxies of the Niutitang Formation shales in the Yangtze Platform were investigated for deciphering paleodepositional environment and elucidating paleoenvironment conditions responsible for organic carbon accumulation. Ce anomalies, Eu anomalies and Y anomalies of the Niutitang Formation shales is between 0.39 and 0.92, between 0.65 and 1.03, between 0.97 and 1.71, respectively. The REE patterns of the Niutitang Formation shales show enrichment in HREE relative to LREE with negative Ce anomalies, positive Y anomalies and negative Eu anomalies, indicating of a greater influence of seawater compared to hydrothermal fluids. U, V and Mo are enriched in the shales, and Mo/Al exhibits strong covariation with TOC contents, whereas U/Al and V/Al show weak covariation with TOC contents, indicating that H<sub>2</sub>S associated with hydrothermal vents is present. Compare with upper Niutitang Formation shales, higher V/(V + Ni), Ni/Co and V/Cr ratios in lower Niutitang Formation shales imply that the lower Niutitang Formation shales are deposited in anoxic conditions. Higher Mo/Al and Ni/Al ratios exist in the lower Niutitang Formation shales relative to the upper Niutitang Formation shales, indicating higher primary productivity during deposition of the lower Niutitang Formation shales. Thus, the variations of primary productivity and preservation of organic matter associated with redox conditions of bottom water lead to greater TOC contents in lower Niutitang Formation shales relative to upper Niutitang Formation shales.

## 1. Introduction

Sedimentary environment had a significant influence on genesis and richness of organic matter, and inorganic geochemical variations in shales (Calvert et al., 1996; Morford et al., 2001; Tyson, 2001; Meyers et al., 2006; Loucks and Ruppel, 2007). The three conventional methods used to characterize sedimentary environment are biostratigraphic analysis, petrographical method and geochemistry analysis. The biostratigraphic analysis has been applicable for elucidating paleoecology, but is limited to barren strata. Sedimentary facies is characterized using the petrographical method, which cannot provide information on paleoenvironmental redox conditions.

Major and trace element geochemistry of shales have been applied to decipher paleoenvironment, attributable to use of modern sedimentary environment as a reference for ancient strata (Demaison and Moore, 1980; Wignall and Newton, 2001; Piper and Perkins, 2004). The large variations in major elements and trace elements were associated with tectonic setting, lithology constituents, diagenetic constraints, detrital

input and hydrothermal activity (Bhatia and Crook, 1986; Plank and Langmuir, 1998; Shields and Stille, 2001; Clark et al., 2004; Brumsack, 1980; Ross and Bustin, 2009), used as proxies for elucidating different paleoenvironment.

In this study, we presented the results of organic and inorganic geochemistry for the Lower Cambrian Niutitang Formation shales from the Yangtze Platform in South China (Fig. 1). The paper has two purposes:

- 1) to discuss the variation of the geochemical data of the Niutitang Formation shales and geochemical proxies for deciphering paleodepositional environment.
- 2) to elucidate paleoenvironment conditions responsible for organic carbon accumulation, favoring for the generation of shale gas reservoir.

## 2. Geological setting and samples

During the Ediacaran-Cambrian transition, the Yangtze Block, located between the North China Block and the Cathaysia Block (Fig. 1), was

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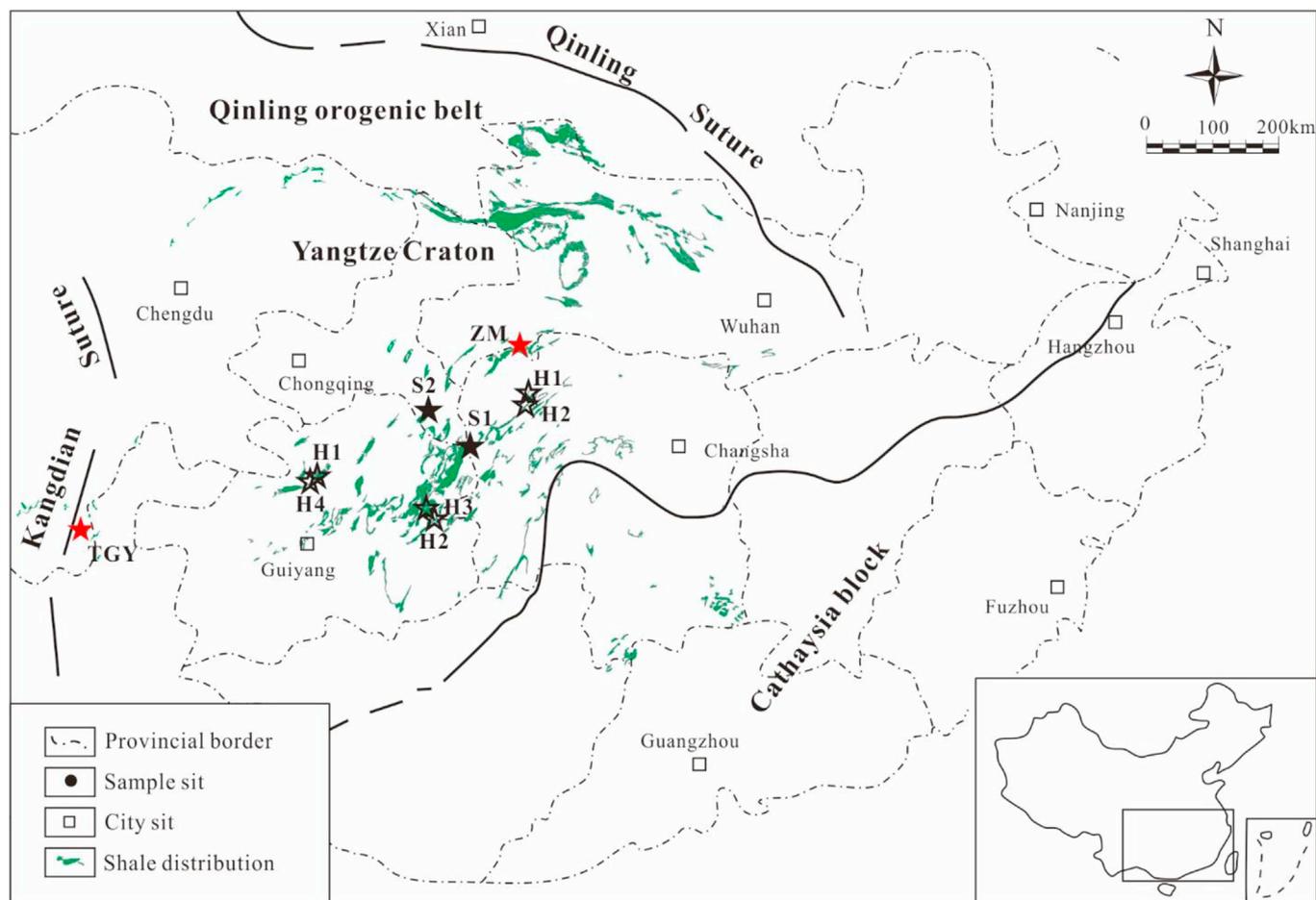


Fig. 1. Distribution of Lower Cambrian Niutitang Formation shales in Yangtze Platform, South China (modified from Mao et al., 2002). Red cross-star locates the outcrops in this study, black cross-stars are outcrops studied previously (Xu et al., 2013; Li et al., 2015), and hollow stars are outcrops studied previously (Steiner et al., 2001; Jiang et al., 2007; Chen et al., 2009; Han et al., 2015). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

covered by carbonate platform with two narrow margin-slope zones (Chen et al., 2009; Wang et al., 2012). The Yangtze Platform contained a sedimentary succession, including the Dengying Formation (DY Fm.), the Niutitang Formation (NTT Fm.) and the Canglangpu Formation (CLP Fm.). The Niutitang Formation shales were defined as the transgressive sequence, lying between the Dengying Formation dolomite and limestone and the Canglangpu Formation limestone and sandstone (Fig. 2). The chronological constrains of the Niutitang Formation were determined through Re-Os method and SHRIMP U-Pb zircon dating from sulfide ore layer at the bottom of the Niutitang Formation and defined an age range of 521–542 Ma (Mao et al., 2002; Jiang et al., 2007, 2009; Xu et al., 2012), consistent with biostratigraphic Tommotian age.

The Lower Cambrian Niutitang Formation shales in the Middle Yangtze Platform, Southwest China, was a potentially promising shale play for natural gas extraction, due to its high organic matter richness, high thermal maturity, large hydrocarbon generative potential and high brittleness (Zhou and Kang, 2016). Twenty-three samples were collected from the Lower Cambrian Niutitang Formation, 14 from Zouma (ZM) outcrop and 9 from Tanguanyao (TGY) outcrop (Fig. 2). Shale samples were collected from a half meter underground in order to avoid the influence of weathering on outcrop samples.

### 3. Methods

Shale samples were ground to a powder, treated with hydrochloric acid to eliminate the interference of carbonates. Total organic carbon (TOC) contents and sulfur contents were measured using a Leco CS-200 carbon/sulfur analyzer. The concentrations of major elements were

analyzed using the AxiosMAX X-ray fluorescence spectrometer at Analytical Laboratory of Beijing Research Institute of Uranium Geology. Precision of the major elements was  $\pm 3\%$ . Trace elements were determined using the ELEMENT XR plasma mass spectrometer, and the detailed procedures followed the methods of Balaram et al. (1995) and Wu et al. (1996). The analytical precision for trace elements was about  $\pm 4\%$ . Element enrichment factors ( $EF_{\text{element}}$ ) were calculated using the published method below,  $EF_{\text{element}} = (\text{element}/\text{Al})_{\text{sample}} / (\text{element}/\text{Al})_{\text{average shale}}$ , where  $(\text{element}/\text{Al})_{\text{average shale}}$  refers to the data from Wedepohl (1971). Dulski (1994) proposed a method to prevent interference on calculations of Europium anomalies ( $\delta\text{Eu}$ ) from Ba concentrations, and could be summarized as follows:  $\delta\text{Eu} = (3 \times \text{Eu}_n) / (2 \times \text{Sm}_n + \text{Tb}_n)$ . Cerium anomalies ( $\delta\text{Ce}$ ), Praseodymium anomalies ( $\delta\text{Pr}$ ) and Yttrium anomalies ( $\delta\text{Y}$ ) were calculated using the method of Bau and Dulski (1996):  $\delta\text{Ce} = \text{Ce}_n / (0.5\text{La}_n + 0.5\text{Pr}_n)$ ,  $\delta\text{Pr} = \text{Pr}_n / (0.5\text{Ce}_n + 0.5\text{Nd}_n)$ ,  $\delta\text{Y} = \text{Y}_n / (0.5\text{Dy}_n + 0.5\text{Ho}_n)$ , where “n” refers to normalized concentrations against PAAS (McLennan, 1989; Taylor and McLennan, 1985). The geochemical results of twenty-three selected the Niutitang Formation samples were present in Tables 1–3.

### 4. Results

Total organic carbon contents and total sulfur contents were present in Table 1. The TOC contents of the Niutitang Formation shales varied from 0.5% to 9.5%, whereas total sulfur contents were between 0.20% and 0.91%.

$\text{SiO}_2$  contents ranged from 51.62% to 78.33%, whereas  $\text{Al}_2\text{O}_3$  and CaO varied from 3.53% to 19.53%, from 0.58% to 11.41%, respectively

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