



Multiple geochemical proxies controlling the organic matter accumulation of the marine-continental transitional shale: A case study of the Upper Permian Longtan Formation, western Guizhou, China

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ABSTRACT

The organic-rich shale of the Longtan Formation of the Upper Permian in western Guizhou formed during the marine-continental transitional facies depositional environment. With a high total organic carbon (TOC) content and a large cumulative thickness, it is thought to be the superior source rock for shale gas development. The depositional environment of marine-continental transitional shale is significantly different from marine shale, which leads to the various accumulation characteristics of the organic matter. In this paper, shale samples were collected from the Longtan Formation of the Upper Permian, which is typical marine-continental transitional shale. The TOC, major elements and trace elements were measured, and the formation and preservation conditions were investigated using multiple geochemical proxies, including paleoclimate, detrital influx, redox parameters, paleoproductivity and sedimentation rate. The TOC decreases first and then increases from the bottom to the top of the Longtan Formation shale, and the TOC for the lower Longtan Formation is higher than the upper Longtan Formation. For the lower Longtan Formation, the positive correlations between TOC and redox indicators (V, U and V/Cr) demonstrate that the dysoxic bottom water environment was the key factor that controlled the accumulation of organic matter. For the upper Longtan Formation, there are positive correlations between the TOC and the paleoclimate and sedimentation rate, which suggests that the enrichment of the organic matter was influenced by both a warm and humid paleoclimate and the high sedimentation rate of an oxic environment. However, the high detrital influx (aluminosilicate) occurred as the diluent decreased the concentration of organic matter. The paleoproductivity has a poor correlation with TOC for the Longtan Formation, suggesting that it was inferior to the gathering of organic matter. The sedimentary models built for the upper and lower Longtan Formation shale can reproduce the enrichment of organic matter.

1. Introduction

The marine-continental transitional organic-rich shale is mainly dark coal-measured shale, with a high total organic carbon (TOC) content and large cumulative thickness, which are the best features and qualities for exploiting shale gas (Zou et al., 2010). The Carboniferous-Permian is the key period for the change of sedimentary environment from marine facies to continental facies in China, and the marine-continental transitional organic-rich shale is widely deposited, including Northern China, the Tarim Basin and the Junggar Basin of the Carboniferous-Permian, the Upper Carboniferous Benxi Formation, the

Lower Permian Taiyuan Formation- Shanxi Formation in the Ordos Basin (Zou et al., 2011; Song et al., 2016). The Upper Permian Longtan Formation shale is deposited in the environment of a lagoon-tidal flat and delta at the Yangtze Platform in Southern China, which consists of carbon mudstone, silty mudstone and pelitic siltstone. Due to the abundance of organic matter, this area has prime geological conditions for the development of shale gas (Luo et al., 2017; Zhang et al., 2017).

The accumulation of organic matter is a complex physical and chemical process. According to detailed research studies of dark organic-rich shale in the marine strata, the influence of organic matter accumulation is multi-faceted. However, there are still several

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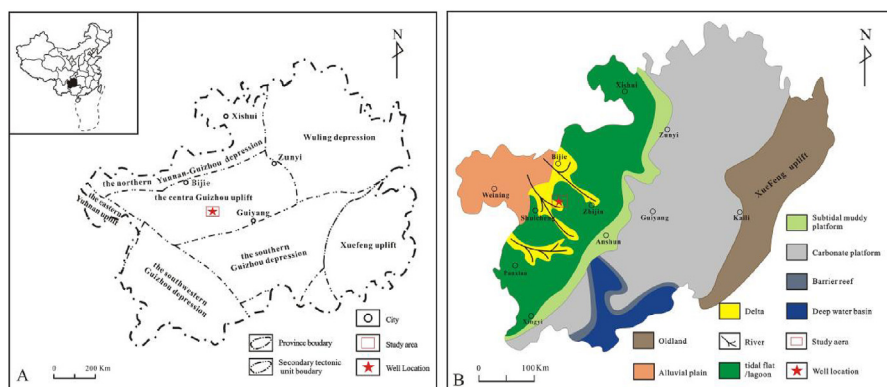


Fig. 1. (A) Tectonic location of study area and division of regional tectonic units (modified from Luo et al., 2017); (B) Paleogeographic map of late Permian sediment in the study area (modified from Xu and He, 2003).

controversies, including the factors controlling the accumulation of organic matter during shale formation (Murphy et al., 2000); the two main schools of thought are the preservation model and productivity model (Talbot, 1988; Carroll and Bohacs, 1999). The preservation model emphasizes that redox conditions, sedimentation rate, and water depth variation are the key factors that influence organic matter accumulation, especially the bottom water dysoxia/anoxia plays a decisive role (Demaison and Moore, 1980; Arthur and Sageman, 1994; Arthur et al., 1998). For example, the diminution of aerobic decomposition of the Black Sea contributes to organic matter preservation (Yan et al., 2015). The productivity model favors the organic carbon flux influenced by paleoclimate, paleoproductivity and detrital influx (Wignall and Newton, 2001). This model claims that marine surficial primary productivity is the key factor (Pedersen and Calvert, 1990; Sageman et al., 2003; Gallego-Torres et al., 2007; Lash and Blood, 2014). The deposition of shale is influenced by the paleoenvironment and contributes to the differences in the controlling factors at various depositional environments (Arthur and Sageman, 1994; Ganeshram et al., 1999; Lash and Blood, 2014), and no single factor can clarify the mechanisms of organic matter accumulation (Rimmer, 2004). Marine shale is usually deposited in deep water with large quantity of microplankton, the anoxic preservation condition and high paleoproductivity contribute to the enrichment of organic matter, such as the Barnett shale and Antrim shale in North America and the Longmaxi Formation shale in South China (Martini et al., 2003; Loucks and Ruppel, 2007; Ma et al., 2016). The marine-continental transitional organic-rich shale is usually deposited in the shallow water environment (dysoxic-oxic depositional environment and mixed organic source), which is influenced by both the ocean and river, and that is really different from that for marine shale (Adegoke et al., 2014; Hou et al., 2015). Then, the key factors that influence the enrichment of organic in the marine-continental transitional shale would be the primary coverage in this paper.

Geochemistry is used extensively to elucidate the evolution and reconstruction of the paleoenvironment (Böning et al., 2004; Tribouillard et al., 2006). Nesbitt and Young (1982) first presented the chemical index of alteration (CIA) to investigate the weathering degree of feldspar from the Paleoproterozoic period in Canada. The CIA, which can reflect the degree of chemical weathering of the source rock and rebuild the paleoclimate, has been utilized widely (McLennan, 1993; Ahmad et al., 1998; Vital and Statterger, 2000; Roddaz et al., 2006; Li and Yang, 2010). The elements Al and Ti are considered detrital influx indicators with stable chemical properties. Combined with the Si, the source and component of the clastics can be acquired (Yan et al., 2015; Zeng et al., 2015; Chen et al., 2016; Zhao et al., 2016). The trace elements U, V, Cr and Ni collected from sediment are insoluble under reduced conditions. These elements and their ratios can be used to identify the redox environment of the water column (Riboulleau et al., 2003; Algeo and Maynard, 2004; Rimmer, 2004). For plankton, there is

a positive correlation between the nutrient element P and paleoproductivity. This is similar to the Ba accumulation rate therefore, they are considered indicators of marine paleoproductivity (Dymond et al., 1992; Filippelli and Delaney, 1994; Zeng et al., 2015). To avoid the dilution effects of other components, the ratios of Ba/Al and P/Ti are replaced (Algeo et al., 2011). Recently, the geochemical analysis methods have been used to investigate the organic enrichment law of marine-continental transitional organic-rich shale. Adegoke et al. (2015) found that the suboxic to relatively anoxic bottom water conditions contribute to the enrichment of organic matter for Gongila shales from northeastern Nigeria, these shales are mainly influenced by the marine environment. Wang et al. (2017) studied the enrichment of organic matter for the Tumengela Formation shale from the north Qiangtang Depression under delta environment, they presented that the high paleoproductivity and fast sedimentation rates favor the enrichment of organic matter under the oxidizing environment.

Previous studies on the enrichment of organic matter with geochemical analysis methods mainly focus on the marine shale. Although there are a spot of relevant research on that for the marine-continental transitional organic-rich shale, they paid attention to the part of the marine-continental transitional deposition environment (Adegoke et al., 2015; Wang et al., 2017). Then, it is lack of the scientific study on the enrichment of organic matter in the marine-continental transitional organic-rich shale completely. In this paper, the major elements, trace elements and TOC of the Upper Permian Longtan Formation organic-rich shale in western Guizhou, China are tested. The dynamic response relationships between the enrichment of organic matter and paleoclimate, redox conditions, paleoproductivity, and detrital influx are built. Finally, the key factors that influence the enrichment of marine-continental transitional organic-rich shale are discussed.

2. Geological setting

Guizhou Province is in the south of the Upper Yangtze plate with 7 secondary tectonic units, including the northern Yunnan-Guizhou depression, the eastern Yunnan uplift, the central Guizhou uplift, Wuling depression, the southwestern Guizhou depression, the southern Guizhou depression and the Xuefeng uplift (Luo et al., 2017) (Fig. 1A). From the Middle Permian to the Late Permian period, the Dongwu Movement elevated the West Sichuan Central Yunnan oldland. The fierce rifting led to the extensive eruption of basalt, which created a gentle slope with a trend from northwest to southeast, and the seawater retreated eastward. During the Late Permian period, seawater intruded from the southeast with frequent transgression and regression. Finally, the paleogeographic pattern of the continental facies, transitional facies and marine facies from northwest to southeast were formed (Fig. 1B).

The study area is located in the western part of Guizhou (Fig. 1). The Upper Permian Longtan Formation is influenced by both the river from

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