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Research paper

Geochemical characteristics, redox conditions, and organic matter accumulation of marine oil shale from the Changliang Mountain area, northern Tibet, China

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ABSTRACT

The organic-rich Changliang Mountain oil shale, located in the North Qiangtang depression, northern Tibet, is considered to be excellent mineral resource in China. The Changliang Mountain oil shale reported here was deposited in a tidal flat-lagoon environment and is characterized by black thin-layered oil shales intercalated with dark-gray marls. Here, we present geochemical data from the Changliang Mountain oil shale profile, in order to investigate the mechanism of organic matter (OM) accumulation and to establish the formation model for the marine oil shale deposition. Total organic carbon (TOC) values range from 2.96 to 23.47% in the oil shale samples, while the marl samples contains low TOC contents, ranging from 0.06 to 0.21%. In the organic-rich oil shale sediments, many redox indicators, including Mo/Al ratios, V/Cr ratios, Th/U ratios, Ni/Co ratios, and the relationship of Mo to TOC suggest a deposition under dysoxic to anoxic environments. Subsequently, the bottom water evolved into an oxic water body when the organic-poor marls were deposited. However, the negative and/or weak relationship between TOC and productivity indices P/Ti and Ba/Al indicates that OM accumulation was not controlled mainly by primary productivity, but dysoxic/anoxic bottom water environment. A stratified water column may be initiated by the supply of fresh water from the continent nearby, combining with warm and humid climate, which is beneficial to the reproduction of marine organisms. The death and bury of these organisms could lead to the formation of dysoxic/anoxic bottom waters and enhance the preservation of OM. In this study, a preservation model of the Changliang Mountain oil shale was established. The model implies that excellent preservation is the major controlling factor for OM enrichment in the oil shale layer. In addition, factors such as mixed deposition with clay minerals, and detrital matter input cannot be ignored for their influence on OM enrichment.

1. Introduction

Oil shale, as an alternative resource, has received much attention for many years (Dyni, 2006; Kök, 2006; Liu et al., 2009a). In China, oil shale was formed mainly in lacustrine environments, such as the Tertiary oil shale in Maoming, Huadian and Fushun areas (Liu et al., 2009b), and the Cretaceous oil shale in Songliao (Wang et al., 1996) and Minhe basins (Liu et al., 2009b). Marine oil shale was mainly found in the Qiangtang basin, northern Tibet, China (Wang and Zhang, 1987; Fu et al., 2008, 2009a, 2009b), including the Bilong Co oil shale and the Shengli River-Changshe Mountain oil shale, representing another large mineral resource in China (Wang et al., 2009a).

The abundance of organic carbon preserved in modern and ancient sedimentary deposits reflects the interplay of various oceanographic and sedimentological conditions, including primary productivity, bottom-water oxygen supply, nutrient availability, the flux of clastic sediment, and the activity of such degradation processes as bacterial sulfate reduction (e.g. Demaison and Moore,

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1980; Calvert, 1987; Pedersen and Calvert, 1990; Arthur and Sageman, 1994; Wignall, 1994; Murphy et al., 2000; Wei et al., 2012; Fu et al., 2014; Lash and Blood, 2014; Yan et al., 2015), but by far the main control factor is still controversial. The controversies focus on whether the enrichment of OM is mainly controlled by water column condition (i.e. dysoxia/anoxia condition in the water column and the sedimentation rate) (Canfield, 1989; Ingall et al., 1993; Arthur and Sageman, 1994; Arthur et al., 1998; Mort et al., 2007; Huang et al., 2013), or by primary productivity (Pedersen and Calvert, 1990; Caplan and Bustin, 1998; Sageman et al., 2003; Gallego-Torres et al., 2007; Fu et al., 2014). The preservation model emphasises the importance of dysoxia/anoxia in the water column as the cause of enhanced organic accumulation (Demaison and Moore, 1980). However, the productivity model favors a higher settling flux of organic carbon as the main control on organic accumulation (Wignall and Newton, 2001). Variations in the amount of fine-grained clastic sediment delivered to the basin was shown to influence the concentration of organic matter either by accelerating the rate of passage of organic matter through geochemical zones of intense organic degradation or by diluting the organic matter flux (Ibach, 1982; Sageman et al., 2003; Lash and Blood, 2014). However, it seems that no single control can explain organic accumulation in all sediments, and that each sedimentary setting may have specific factors that contribute to the accumulation of organic-rich sediments (Arthur and Sageman, 1994; Canfield, 1994; Rimmer, 2004; Lash and Blood, 2014; Yan et al., 2015).

The Cretaceous oil shales take place in many areas of the Qiangtang Basin, were generally deposited in a tidal flat-lagoon environment (Fu et al., 2009b; Wang et al., 2010a) and characterized by black thin-layered oil shales intercalated with dark-gray marls (or limestones) (Wang et al., 2009, 2010a; Zeng et al., 2014). Stratigraphy, paleontology, paleoenvironment, paleoclimate and source region of these organic rich oil shales have been well documented (Fu et al., 2009a, 2010a, 2011; Zeng et al., 2012; Wang et al., 2010a). Fu et al. (2007) proposed that the deposition of oil shale was not only associated with sea-level fluctuation but also influenced by paleoclimate, which was the essential reason for formation and disappearance of the oil shale. Wang et al. (2010a) considered the injection recharge of plentiful fresh water and high productivity as the controlling factors for the formation of the oil shales. Although there are some publications about the Early Cretaceous marine oil shales, the factors controlling the enrichment of organic matter have not been well understood.

Trace elements Mo, U, V, Cr, Ni, and Co are enriched in reducing sediments and are highly sensitive to redox changes, making them and their ratios as important proxies for paleoredox reconstruction (Holland, 1978; Piper, 1994; Algeo and Maynard, 2004; Rimmer, 2004; Tribovillard et al., 2006). The oceanic redox changes play an important role in organic matter accumulation (Yan et al., 2015). Under oxic conditions, adsorption to insoluble oxyhydroxides is important, and some dissolved trace elements can become enriched along redox gradients from the oxic water column across the sedimentwater interface to sediments. Such processes are particularly efficient under euxinic condition, where trace element may be precipitated as sulfides or become adsorbed onto OM and insoluble oxyhydroxides (Tribovillard et al., 2006). On the other hand, the contents of barium (Ba), phosphorus (P), and the Ba/Al and P/Ti ratios are used as proxies for paleoproductivity (Dymond et al., 1992, 1996; Ingall et al., 1993; Filippelli and Delaney, 1994; Murray et al., 1993, 1996; Paytan et al., 2007; Algeo et al., 2011; Luo et al., 2012). Dean et al. (1997) proposed Ba/Al to evaluate the paleoproductivity of the laminated sediments in the continental margins of Central California (CCAL) during the last interstadial and Algeo et al. (2011) used excess Ba and P/Ti as paleoproductivity proxies in two Permian/Triassic boundary sections in central Japan.

Large-scale regressions took place in the Qiangtang basin during the Cretaceous time. As a result, a barrier-lagoon system was formed in the Changliang Mountain area when the relative sea level was low. So, the Changliang Mountain area was isolated from the sea by a palaeotopographic high (Marguo Chaka uplift) and then a wide lagoonal area developed behind the protecting barriers (Fu et al., 2009b), where environmental changes were more frequent than normal marine systems and organic-rich oil shales may show strong vertical and horizontal variations in hydrocarbon potentials and geochemical characteristics. The organic-rich oil shale of the Changliang Mountain in the North Qiangtang depression provides a useful example for understanding the redox conditions, paleo-productivity, and the mechanisms of organic matter accumulation. The aim of this paper is to discuss the geochemical characteristics of the oil shale from the Changliang Mountain in the North Qiangtang depression and their implications to organic matter accumulation, and to differentiate the two potential driving mechanisms (i) preservation conditions, (ii) primary productivity for different stata (oil shales or marls) and discuss the formation model of the Cretaceous marine oil shale in the North Qiangtang depression.

2. Geological settings

On a large scale, the Tibetan Plateau constitutes a tectonic collage of continental blocks. From north to south, Tibet is comprised of the Kunlun-Qaidam, Songpan-Ganzi flysch complex, Qiangtang, and Lhasa terranes, which are separated by the east striking Anyimaqen-Kunlun-Muztagh, Hoh Xil- Jinsha River and Bangong Lake-Nujiang River suture zones, respectively (Fu et al., 2014) (Fig. 1A). It is generally accepted that the paleo-Tethys represented by the present Jinsha River suture opened possibly in Early Carboniferous time (Yin and Harrison, 2000) and closed by Permian to latest Triassic time (Kapp et al., 2003). The mid-Tethys branch between the Lhasa and Qiangtang terranes was open by Early Jurassic time (Kapp et al., 2003) and closed along the Bangong Lake-Nujiang River suture during the Late Jurassic time (Yin and Harrison, 2000).

The Qiangtang Basin, bounded by Hoh Xil-Jinsha River suture zone to the north and Bangong Lake-Nujiang River suture zone to the south, respectively, consists of the South Qiangtang depression, the central uplift and the North Qiangtang depression (Fig. 1B), which is a Mesozoic marine sedimentary basin overlying folded Paleozoic basement rocks (Wang et al., 2010b) (Fig. 1B). The basin initiated as a foreland basin in the Early Triassic and evolved into a rift basin in the Late Triassic (Fu et al., 2010b; Wang et al., 2010b). At the beginning of the Cretaceous period, the Banggong ocean was closed by the northward subduction beneath the Qiangtang terrane (Kapp et al., 2003), resulting in a large-scale regression in the Qiangtang Basin (Wang et al., 2009b). During this interval, the South Qiangtang depression was uplifted entirely, while the North Qiangtang depression was still a depositional region (Fu et al., 2009b).

The Changliang Mountain oil shale is located in the southern part of the North Qiangtang depression (Fig. 1C), where Lower Cretaceous marine deposits are widespread (Fu et al., 2008), including the upper part of the Suowa Formation, the Xueshan Formation and the Bailong Binghe Formation. On the basis of sedimentary structures, lithology and fossils, three facies associations were recognized: fluvial-delta, tidal flat-lagoon and shallow marine. The Changliang Mountain oil shale was deposited in the tidal flat-lagoon environment.

3. Samples and analytical methods

3.1. Samples

The studied profile is located in the Changliang Mountain area, the western part of the Shengli River-Changshe Mountain oil shale