



# Occurrence of stable and mobile organic matter in the clay-sized fraction of shale: Significance for petroleum geology and carbon cycle



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## ABSTRACT

Stability and mobility of organic matter (OM) in shale is of great significance for the carbon cycle and petroleum exploration and exploitation. To examine the stability and mobility of OM occurrence in shales, clay-sized fractions (<2 μm) were separated from shales physically and chemically treated with different reagents. These fractions were followed by pyrolysis and measurements of specific surface area (SSA) and Fourier transform infrared spectrophotometry (FTIR). It is revealed that after wet chemical oxidation and organic solvent extraction, there exist: a) changes in total organic carbon (TOC), hydrogen index (HI) and oxygen index (OI); b) appreciable decrease in absorption intensity of –CH<sub>2</sub>– stretching vibration bands at 2924 and 2853 cm<sup>-1</sup>; and c) dramatic increase of SSAs after wet chemical oxidation. These characteristics suggest that the TOC in the clay-sized fraction can be categorized into physical mobile-OC (PmOC), chemical mobile-OC (CmOC) and stable-OC (SOC), which account for 43.3%, 17.1% and 39.6% of TOC on average in the studied samples, respectively. The OM in the clay-sized fraction mainly occurs on mineral internal surface, and the occurrence of OM determines the stability and mobility of OC. The PmOC mainly accumulates in the pores and at the mouth and/or edge of the interlayer spaces of clay minerals, the CmOC chiefly adsorbs on the mineral external surface, and the SOC mainly occurs on the mineral internal surface. These occurrence characteristics of different OCs indicate that the mobility and stability of OM occurrence in a sample have different levels. The occurrence of stable and mobile OM in the clay-sized fraction of shale as investigated can improve the understanding of the occurrence of OM in shales, and provide a new insight for carbon cycle research and petroleum exploration and exploitation.

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## 1. Introduction

Shale is composed of organic matter (OM) and minerals, both of which have different components and types, and interact with each other. OM occurrences have been broadly investigated for a variety of reasons (e.g., carbon sequestration, carbon cycle and carbon distribution) in soils, marine sediments and shales (Arndt et al., 2013; Kennedy and Wagner, 2011; Mikutta et al., 2006; Solomon et al., 2012; Torn et al., 1997). As sedimentary OM and minerals are heterogeneous materials, OM occurs in many different forms in sediments and sedimentary rocks (Durand, 1980; Sebag et al., 2006; Tissot and Welte, 1984; Tyson, 1995; Zhu et al., 2014), which can be divided into free and mineral-combined states. The free OM constitutes no more than 10% of the total organic carbon content (TOC) (Ertel and Hedges, 1985; Fan et al., 2011a; Keil et al., 1994a, 1994b; Mayer, 1994), is not bounded to the minerals (Cai et al., 2007; Fan et al., 2011b; Ransom et al., 1997, 1998), and occurs in the pores and is vulnerable to decomposition by bacteria and through oxidation (Baldock and Skjemstad, 2000; Six

et al., 2002). The mineral-combined OM is the main form of occurrence of sedimentary OM, especially among clay-sized minerals (Bergamaschi et al., 1997; Dexter et al., 2008; Mayer, 1999; Suess, 1973; Tanoue and Handa, 1979) where the OM can be adsorbed on the mineral surface, intercalated in the clay mineral domain and occluded in the carbonates (Cai et al., 2007; Hedges and Keil, 1995; Ingalls et al., 2004; Lopez-Sangil and Rovira, 2013; Mayer, 2004; Ramseyer et al., 1997). These different forms of OM occurrences can lead to the variation in stability and persistence of OM occurrences in shales.

Based on the variation of OM occurrences, many laboratory methods have been proposed for OM separation, including physical and chemical methods, with each method obtaining a specific organic component. For example, density fractionation can obtain the particulate OM and mineral-combined OM (Arnason and Keil, 2001; Yu et al., 2009), organic solvent extraction can acquire the soluble OM that occurs in the pores and on the mineral surface (Cai et al., 2007; Ding et al., 2013; Löhr et al., 2015), and wet chemical oxidation can differentiate the young and old OM (Kleber et al., 2005; Mikutta et al., 2006; Zimmermann et al., 2007). These different organic components (or types of OM) have distinct contributions to petroleum generation in source rocks (Cai et al., 2007; Ding et al., 2013; El Atfy et al., 2014; Fan et al., 2011a, 2011b;

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Thompson and Dembicki, 1986). Separation of different organic components based on physical and chemical methods reveals the variation of stability, mobility and persistence of the OM occurrence (Duce et al., 2015; Mikutta et al., 2006; Schmidt et al., 2011; Zhang et al., 2014), which triggers the differences in hydrocarbon generation and migration as well as the fate of OC in shales. Therefore, the mobility of OM occurrence is of great influence to petroleum preservation in shale and its exploitation, and its study can facilitate the full understanding of the variation in stability of OM occurrence in shales.

As mineral surfaces are the principal places for organic–inorganic interaction, they are of critical importance for OM occurrence. Many studies on the influence of OM occurrence from mineral surfaces have been conducted, and it is revealed that the adsorption of OM on mineral surfaces favours OM preservation (Hedges and Keil, 1995; Keil et al., 1994a, 1994b; Kennedy et al., 2002, 2014; Mayer, 1994), but the occurrence of OM varies on different types of mineral surfaces (Ding et al., 2013; Kennedy et al., 2002; Kuila et al., 2012; Mayer, 1994; Zhu et al., 2014). Clay-sized minerals, which have remarkable control over OM enrichment, are the main carriers of OM occurrence (Bergamaschi et al., 1997; Cai et al., 2010; Keil et al., 1998; Fan et al., 2011a; Mayer, 1999) and the major contributor to specific surface areas (SSAs) in sediments (or sedimentary rocks) (Keil et al., 1994b; Kennedy and Wagner, 2011; Mayer, 1994; Zhu et al., 2014, 2015). Thus, the clay-sized fraction can be the object for investigation of OM occurrence in shales. This study isolated the clay-sized fractions (<2  $\mu\text{m}$ ) from shales which were physically and chemically treated with different reagents. With the aid of pyrolysis, measurements of specific surface area (SSA) and Fourier transform infrared spectrophotometry (FTIR), the OM in different forms of occurrence were obtained, and the relationships between those different OM and SSAs were established. The variety of stability and mobility of OM occurrence is further discussed.

## 2. Materials and methods

A total of 27 coring shales were selected for clay-sized fraction separation, which were from the Oligocene Member Es<sub>3</sub><sup>lower</sup> of Well L in the Zhanhua Sag with a burial depth of 2960–3115 m. The Zhanhua Sag, located in the Jiyang Depression of the Bohai Bay Basin of eastern China (Fig. 1), was formed in the Meso-Cenozoic and is one of the secondary tectonic units of the Jiyang Depression, where shales were extensively developed in the strata of the Paleogene Member Es<sub>4</sub><sup>upper</sup>

and Member Es<sub>3</sub> (Wang and Qian, 1992; Zhu et al., 2004). The Member Es<sub>3</sub><sup>lower</sup> is a suite of fine grained sediments deposited in a half-deep lake facies, with the largest thickness and the widest distribution as well as an elevated content of organic matter in Members Es<sub>4</sub><sup>upper</sup> and Es<sub>3</sub> (Deng and Liang, 2012; Wang et al., 2013). The lithology is dominated by dark shale and argillaceous limestone. This member is one of the most important source rocks in the Jiyang Depression and is regarded as an important stratum for its capacity for self-generation and self-accumulation (Chen, 2012).

### 2.1. Sample processing

The bulk shale was ground and milled to less than 1 mm in an agate mortar and pestle until there were no individual particles that could be seen with the naked eye, then placed into a 3000 mL beaker, fully immersed with deionized water, and treated in an ultrasonic bath to accelerate dispersing. Ultrasonic treatment conducted until the colloids appeared, the clay-sized fraction (<2  $\mu\text{m}$ ) was then separated from the shale using natural sedimentation. The sample of the clay-sized fraction was concentrated and dried in an oven at 60 °C. X-ray diffraction (XRD) patterns were measured following Zhu et al. (2015) and showed that the clay-sized fractions were dominated by calcite and clay minerals, as well as quartz; the clay minerals mainly consisted of interstratified illite/smectite, followed by the illite and kaolinite, with a small amount of chlorite (Fig. 2).

The raw clay-sized fractions underwent two treatments: wet chemical oxidation and organic solvent extraction. All of the samples were treated by wet chemical oxidation, and ten samples were also treated by organic solvent extraction; both treatments were performed independently. Wet chemical oxidation was conducted by means of sodium hypochlorite (NaClO) treatment following a method modified after Siregar et al. (2005). The 6 wt.% NaClO solution was adjusted to pH 8 with concentrated hydrochloric acid. At room temperature, the treatment was performed in a flask with a solid-to-solution ratio of 1:50 (vol:vol). After 24 h, the supernatant was removed by injector and the fresh adjusted solution was simultaneously added into the flask. These steps were repeated seven times until the sample colour changed to off-white and no bubbles occurred when the flask was shaken. Then, the sample was collected and dried in an oven at 60 °C. Organic solvent extraction was performed on the oven-dried sample (1–2 mm) that was wrapped with a filter paper (with maximum pore size of 10–15  $\mu\text{m}$ )

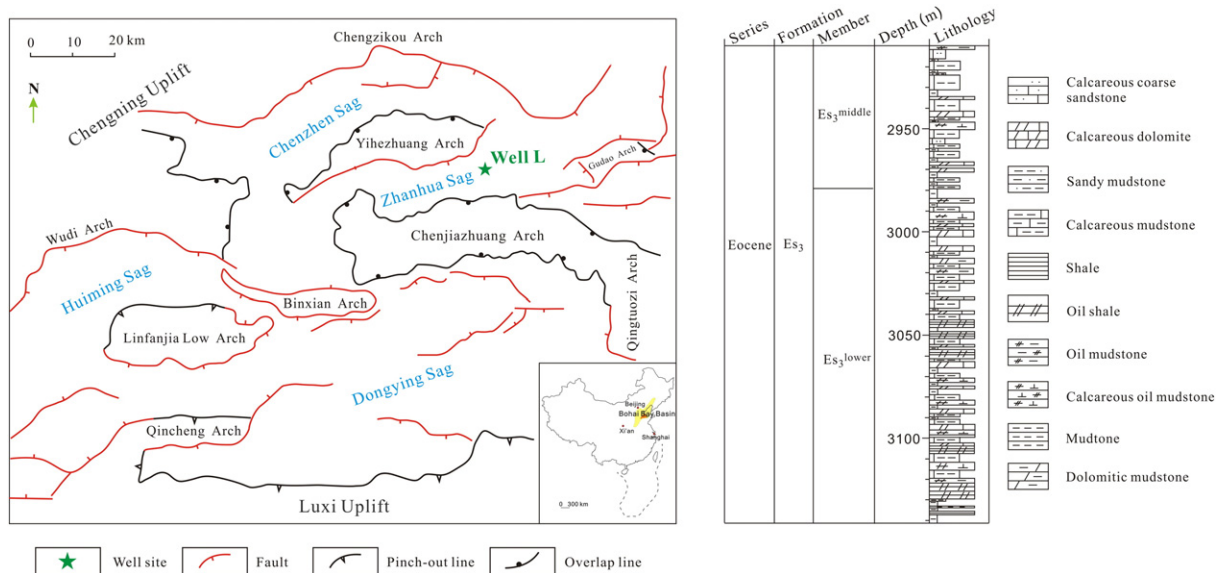


Fig. 1. Tectonic unit division of the Jiyang Depression with sampling sites and lithology profile of Well L.

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