



Role of organo-clay composites in hydrocarbon generation of shale

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ABSTRACT

Organic-mineral interactions are universal in natural environments. They cause the majority of the total organic carbon (TOC) in sediments and sedimentary rocks to combine with clay minerals to form organo-clay composites. However, the role of organo-clay composites in hydrocarbon generation is not clear. In this study, we select a suite of successively deposited shales to examine the association between organic matter (OM) and minerals, and to analyze the correlations of TOC with different mineral surface areas (MSAs) and the Rock-Eval pyrolysis in both bulk shales and their organo-clay composites. We find that OM in shale is dominantly incorporated with clay minerals by the main way of adsorbing on internal mineral surfaces rather than external mineral surfaces, which forms organo-clay composites. Further analyses on TOC-MSA correlations demonstrate the great heterogeneity of OM occurrence within shale. Also, the OM quality of organo-clay composites is poorer for hydrocarbon generation than that of bulk shales. We conclude that the variations in organic geochemistry between bulk shales and organo-clay composites are caused by hydrocarbon generation, which reduces the OM quality for further generation. Taken together, organo-clay composites dominate OM occurrence and have been generating hydrocarbons, which highlight the main control of organo-clay composites on hydrocarbon generation in natural samples. In comparison with the long-standing theory of hydrocarbon generated from kerogen, we propose the organo-clay composites to be the in situ and main source for hydrocarbon generation. This new hypothesis improves the existing knowledge of the organic origin of hydrocarbons in natural systems.

1. Introduction

Hydrocarbons (HCs) are widely considered to be originated from sedimentary organic matter (OM), which has been called as “kerogen” (complex sedimentary OM) in the past. In natural environments, sedimentary OM has different preservation mechanisms, such as polycondensation, natural sulfurization, selective preservation and sorptive protection (e.g., Tissot and Welte, 1984; Burdige, 2007; Vandenbroucke and Largeau, 2007; Salmon et al., 2000; Kennedy et al., 2002; Keil and Mayer, 2014), which exhibit various forms of OM preservation and result in that OM can be occurred in free and mineral-combined states (Ransom et al., 1997, 1998; Kennedy et al., 2002, 2014; Zhu et al., 2016). Studies of sedimentary OM have revealed that > 90% of total organic carbon (TOC) in marine sediments and mudstones is combined with minerals (particularly clay minerals), which cannot be separated from mineral matrix by either size or density fractionation (Keil et al., 1994; Hedges and Keil, 1995; Fan et al., 2011). The intimate association between OM and clay minerals in sediments and sedimentary rocks is evidenced by the studies on the correlation between TOC and mineral

surface area (MSA) (Mayer, 1994; Hedges and Keil, 1995; Kennedy et al., 2002; Kennedy and Wagner, 2011; Keil and Mayer, 2014; Zhu et al., 2016) and further supported by optical/electron microscopy (Macquaker et al., 2010; Kennedy et al., 2014; Milliken et al., 2014; Pommer and Milliken, 2015; Berthonneau et al., 2016) and spectroscopy (Solomon et al., 2012; Löhr and Kennedy, 2014). These suggest that the OM is dominantly adsorbed on clay mineral surfaces. As compared to the free OM, those OM adsorbed on clay mineral surfaces has intrinsic variations in molecular and/or chemical compositions (Bergamaschi et al., 1997; Keil et al., 1998; Zhu et al., 2016). Thus, the adsorption of OM onto clay mineral surfaces makes the OM and clay minerals aggregate as a whole and is called organo-clay composites in this study, which have been identified such as “organomineralic aggregates” or “clay-organic nanocomposites” (Macquaker et al., 2010; Kennedy et al., 2014; Milliken et al., 2014; Pommer and Milliken, 2015) and are concentrated in clay-sized fractions in natural environments (Bergamaschi et al., 1997; Cai et al., 2010; Keil and Mayer, 2014). In comparison with the traditional knowledge that sedimentary OM is discretely distributed in sedimentary rocks (Hunt, 1979; Tissot and

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Welte, 1984), these findings suggest that the OM incorporated with clay minerals (i.e., organo-clay composites) accounts for the primary fraction of the sedimentary OM in both surface sediments and sedimentary rocks.

To date, the long-standing theory of HC generation from kerogen is very popular in organic geochemistry and petroleum geology. However, kerogen is used to describe the insoluble (i.e., non-extractable in organic solvents) OM and is concentrated after removing minerals by hydrochloric and hydrofluoric acid attack for experimental usages (Tissot and Welte, 1984; Vandenbroucke and Largeau, 2007), and the kerogen-generating HCs is only focused on the properties of OM itself. Moreover, HC generation can be catalyzed by minerals, which has been proposed since 1940s (Kuhl, 1942; Grim, 1947). After that, a large number of studies have found that the generated HC compositions and yields from OM (either kerogen isolates or synthetic organic compounds) can be modified by the interactions between OM and clay minerals (Shimoyama and Johns, 1971; Galwey, 1972; Johns, 1979; Tannenbaum and Kaplan, 1985; Hetényi, 1995; Lewan, 1997; Yuan et al., 2013; Bu et al., 2017). Recent study of pyrolysis experiments by Yang and Horsfield (2016) indicated that the effect of clay mineral catalysis on HC generation is largely dependent on heating rate. They also speculated that the catalyzed effect only occurs in a laboratory environment and is not significant in natural geological environments. However, the extrapolated conclusion is only confined in their three source rock samples and does not fully consider the association between OM and minerals. Studies have shown that the degree of surface contact of OM on clay mineral surfaces can influence the HC yield and generation temperature (Rahman et al., 2017, 2018), suggesting that the extent of organic-clay interactions is a function of HC generation. Therefore, it can be found that the role of clay minerals in HC generation should not be neglected, and that HC generation of sedimentary OM is not only ascribed to the properties of OM itself but also the organic-mineral interactions. Thus, although kerogen can account for 90–95% of TOC in sedimentary OM (Durand, 1980; Tissot and Welte, 1984), there may exist mistakes to separate kerogen alone to experimentally investigate HC generation for source rock assessment, which will profoundly affect the resource assessment and strategic decision in petroleum exploration and exploitation. Consequently, to fully understand the fundamental source of HC generation in geological environments, it is crucial to consider the organic-mineral interactions (not only the properties of OM itself) and pay attention to the in situ occurrence of sedimentary OM in source rocks.

Shales record OC preservation in geological strata and are important HC sources (Potter et al., 2005). In this study, we select a suite of successively deposited shales from the Jiyang Depression (eastern China). These shales are hydrocarbon source rocks in oil-generation window (detailed below), which can directly reflect the information of hydrocarbon generation in natural geological evolution. Also, we separate their clay-sized fractions (< 2 μm) for comparison. With the aid of thin-section observation, N_2 adsorption (BET), ethylene glycol monoethyl ether (EGME) adsorption and Rock-Eval pyrolysis, we examined the association between OM and minerals in shale, and analyzed the MSA and organic geochemical characteristics of both bulk shales and clay-sized fractions. By discussing the correlations between the MSA and TOC and comparing the organic geochemistry of bulk shales with clay-sized fractions, we firstly reveal the dominant control of OM occurrence, and then investigate the role of organo-clay composites in HC generation.

2. Materials and methods

Coring shale samples buried at 2960–3115 m were collected from the Eocene $\text{Es}_3^{\text{lower}}$ of well L in the Zhanhua Sag of the Jiyang Depression, Bohai Bay Basin of eastern China (Fig. 1). The geological setting of the Zhanhua Sag is well described in Wang et al. (2015). Formed in the Meso-Cenozoic, the sag is located on the southern slope

of the Bonan Sub-depression and is one of the sub-tectonic units in the Jiyang Depression. Shale was extensively developed in this area and is concentrated in the strata of $\text{Es}_4^{\text{upper}}$ and $\text{Es}_3^{\text{lower}}$, which have been regarded as important source rocks in the Jiyang Depression (Wang et al., 2013, 2015). $\text{Es}_3^{\text{lower}}$ is a suite of fine-grained deposition with a large thickness and a broad distribution range. The selected shales in well L were successively deposited and were mainly buried in an oxygen-deficient environment, thus have an elevated TOC content (He et al., 2017). Mineralogy of these shales is dominated by calcite (52%), followed by clay minerals (19%) and quartz (18%); and the clay minerals are identified by mixed-layer illite/smectite (61%), illite (30%), kaolinite (6%), and chlorite (3%) (Wang et al., 2015). The OM of these shales has been reported as oil prone Type I with over 90 vol% of sapropelinite (Wang et al., 2015), and the maturity of these studied shales has been indicated to be in oil-generation window (Li et al., 2015; Wang et al., 2015).

Twenty-seven shale samples were selected for clay-sized fraction (< 2 μm) separation, and adjacent shales were selected for thin-section observation. The separation of clay-sized fractions was performed using the ground shales (< 1 mm) by natural sedimentation in deionized water, with no OM removal. The separated clay-sized fraction was concentrated and dried in an oven at 60 °C. Mineralogy of these clay-sized fractions is mainly calcite (43%), clay minerals (37%) and quartz (16%). Both the ground shale samples and their clay-sized fractions were treated using wet chemical oxidation (6 wt% NaClO , pH 8) to remove OM following Zhu et al. (2016) prior to MSA determination. Each sample was repetitively treated with a solid-to-solution ratio of 1:50 (vol:vol) in a flask at room temperature for approximately 24 h. Over seven treatments were needed to oxidize OM. By then, the sample colour changed from black/gray to brick-red/off-white and no bubbles occurred in the flask after gentle shake. Finally, the treated sample was washed with deionized water to remove the halide ions, and then dried in an oven at 60 °C for MSA measurement.

Thin-section of coring shale was made based on the core cutting in half vertically along the length of the cylinder. The observation of thin-section was conducted under transmitted light and fluorescence using a ZEISS microscope. The MSA of bulk shale and clay-sized fraction was measured using adsorption method. The total MSA was examined by ethylene glycol monoethyl ether (EGME) adsorption and was converted by a factor of $2.86 \times 10^{-4} \text{ g/m}^2$ based on the absorbed quantity of EGME molecules (Carter et al., 1986). The exposed surface area of minerals (i.e., external MSA) was probed by multipoint N_2 adsorption and was calculated based on BET equation. The procedures of these two adsorption methods have been detailed in previous studies (Zhu et al., 2015). These two adsorption methods are used extensively for MSA determination. The difference between the total MSA and external MSA yields the internal MSA (Kennedy et al., 2014; Zhu et al., 2015). A Rock Eval-VI apparatus for pyrolysis was employed to determine organic geochemistry of bulk shales and clay-sized fractions. The sample was milled to $\sim 0.1 \text{ mm}$, and the pyrolysis procedure has been described in Behar et al. (2001). From pyrolysis measurement, data of thermally cracking hydrocarbon (S_2 , mg/g), total organic carbon (TOC, wt%), hydrogen index (HI, mgHC/gTOC), oxygen index (OI, mg CO_2 /gTOC) and temperature maximum (T_{max} , °C) were collected. Many studies have found that TOC measured by pyrolysis is very similar to the TOC output from elemental analyses ($R^2 > 0.9$) (Behar et al., 2001; Carvajal-Ortiz and Gentzis, 2015), which indicates the credibility and validity of the TOC measurements.

3. Results

3.1. Thin-section observation

Thin-section observation of studied shales (Fig. 2) shows that the sedimentary texture is mainly oriented and bedding-parallel and the OM is worm-like dispersed along the orientation and enriched along the

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