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Mineralogical changes in organic-rich Posidonia Shale during natural and experimental maturation

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ABSTRACT

The diagenesis of clay minerals and organic matter in Posidonia Shale has been typically studied independently of each other. Here, the results of an experimental investigation focused on the mineralogical changes of organic-rich shales are presented to understand the dissolution and precipitation processes of minerals as a function of thermal maturity. Three core samples of Posidonia Shale (Hils Syncline, Germany) with increasing natural thermal maturity (Wickensen (WIC) 0.53% $R_{0,}$ Dohnsen (DOH) 0.73% R_0, Haddessen (HAD) 1.45% R_0) were reacted in experimental aliquots of 0.3 M KCl solution (rock/fluid ratio 1:5) sealed in gold capsules at 300 °C and 120 bars for 27 days. Following treatment, the calculated maturities (Easy-R_0 values) of the two samples with the lowest vitrinite reflectance values indicates thermal enhancement (WIC 1.14% R_0, DOH 1.15% R_0), whereas the most mature sample remained unchanged (HAD 1.45% R_0). The educts and products were analysed by transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). In all experiments kaolinite and carbonates were extensively dissolved whereas quartz underwent partial dissolution. Reaction products consisted of lath shaped Mg^{2+} rich $1M_d$ illite together with K-feldspar in the form of sanidine. Trioctahedral saponite precipitated only in the oil producing sample (WIC), along with less sanidine and $1M_d$ illite. The unexpected formation of metastable $1M_d$ illite at 300 °C instead of stable $2M_1$ illite is attributed to low K^+ reactivity due to either depletion of this element by the early formation of sanidine and/or the chemical effects of organic acids that shift the stable phase into the K-poor stability field. The precipitation of saponite and the limited sanidine and $1M_d$ illite formation in sample DOH is attributed to high dolomite content and hence Mg^{2+} availability, along with the more extensive release of hydrocarbon compounds and further reduction of K^+ reactivity in this sample. It is concluded that the neoformation of metastable phases ($1M_d$ illite and trioctahedral smectite) observed in short-term, higher-temperature experiments may differ significantly from prolonged mineral transformations occurring under natural conditions.

1. Introduction

Over the last decade, gas production from unconventional shale gas resources has seen a significant increase, particularly in the United States, which has stimulated new interest in investigating potential resources around the world (McGlade et al., 2013; Wang et al., 2014). In Central and Western Europe, the lower Toarcian Posidonia Shale of northern Germany represents an important petroleum source rock and a possible future gas shale resource (Schulz et al., 2010). Many investigations have studied these shales regarding their mineralogy, microstructure (Kanitpanyacharoen et al., 2012), petrology and geochemistry (Leythaeuser et al., 1988; Littke and Rullkötter, 1987; Littke et al., 1988, 1991; Mann, 1987; Mann and Müller, 1988; Radke et al., 2001; Rullkötter and Marzi, 1988; Rullkötter et al., 1988; Vandenbroucke et al., 1993; Wilkes et al., 1998), as well as their pore space morphology and fluid transport properties (Bernard et al., 2012; Ghanizadeh et al., 2014; Klaver et al., 2012). However, the clay–organic interactions of these shales remains poorly understood. Therefore, the present study aimed at experimentally investigating the mineralogical changes with increasing degree of organic maturation. Three representative Posidonia Shale core samples from the Hils Syncline of different thermal maturities were analysed before (educts) and after (products) thermal treatment in closed hydrous pyrolysis experiments. The educts were selected to represent the maturation states of the immature state to early oil window (0.54% R_0), the oil window (0.73% R_0) and the gas generating zone (1.45% R_0) based on the classification of Vassoyevich et al. (1969).

As clay minerals are abundant in most shales they are generally considered to be of importance when considering the physical and chemical properties of these rocks. As a result, processes of transformation and neoformation of clay minerals during diagenesis are likely to affect organic maturation and vice versa (e.g. Taylor et al., 1998). Many investigations have studied the illitisation of smectite, which is

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volumetrically the most important diagenetic reaction during a shale's burial history (e.g. Altaner and Ylagan, 1997; Hower et al., 1976; Huang et al., 1993; Nadeau and Bain, 1986; Perry and Hower, 1970), but only a few have considered the migration or retention of hydrocarbons in diagenetic clay mineral reactions (e.g. Freed and Peacor, 1989). In general, the interaction of organic matter and its maturation products with clay minerals remains insufficiently studied. It has been proposed, for example, that organic acids in oil-bearing clastic rocks may act as complexing agents for dissolved cations and therefore influence clay mineral reactions (Fein, 1994; Surdam et al., 1984, 1989). Conversely, clay mineral reactions may also catalyse the transformation of the organic matter into hydrocarbons (Zimmerle, 1995), or in the case of smectite may inhibit or alter petroleum generation (Clauer et al., 2014).

In order to further investigate the relationship between clay mineral diagenesis and the state of organic maturation, we conducted a set of hydrous pyrolysis experiments to establish, i) how the initial natural maturation state influences the clay mineral reactions of Posidonia Shale, and ii) if the mineral assemblages formed during experimental thermal maturation reflect natural diagenetic trends observed in organic-rich rocks.

2. Material and methods

2.1. Sample description

The investigated samples were collected from the Middle Jurassic Posidonia shale formation of the Hils Syncline of Northwestern Germany, southwest of the city of Hannover (Lower Saxony) (Fig. 1). The northern part of Lower Saxony is characterised by Quaternary deposits which overlie Mesozoic and Paleozoic sedimentary rocks that are exposed in the hilly countryside of southern Lower Saxony. The Hils Syncline consists of Jurassic argillites, limestones and Cretaceous marlstones. The investigated shales from this syncline were deposited in a low-energy, anoxic environment (compared to the underlying and overlying Pliensbachian and Aalenian shales), with lateral variations and large fluctuations in total organic content (TOC) and hydrogen index (HI) values (Rullkötter et al., 1988; Sundararaman et al., 1993). An increase in thermal maturity occurs towards the northwest across the Hils Syncline, which changes from 0.48% R_0 to 1.45% R_0 (Littke et al., 1988) (Fig. 1). This increase in maturity has been attributed either to a nearby underlying magma pluton of Cretaceous age, known as the Bramsche Massif (Henningsen and Katzung, 2002), or due to a combination of rapid pre-Turonian subsidence and deep burial, followed by uplift related to late Cretaceous inversion, with organic maturation continuing into the Cenozoic (Adriasola-Munoz et al., 2007; Doornenbal and Stevenson, 2010; Petmecky et al., 1999).

The investigated samples were selected from three shallow boreholes Wickensen (WIC), Dohnsen (DOH) and Haddessen (HAD). WIC with the lowest vitrinite reflectance (R_0) of 0.53% represents the start of oil generation, DOH with R_0 0.73% corresponds to the termination of oil production and HAD with a vitrinite reflectance of 1.45% comes from the gas window (Bernard et al., 2012; Horsfield et al., 2010; Littke and Rullkötter, 1987; Littke et al., 1988). All samples are composed of Type II kerogen of petroleum type organofacies Low Wax P-N-A (Horsfield et al., 2010). Teichmüller and Ottenjann (1977) determined the bulk of the organic matter as alginites (derived from green algae phytoplankton) and bituminites. The total organic content of the three Hils Syncline samples ranges between 5.2 and 8.5 wt.% (Table 1) and the different thermal maturities are characterised by similar mineral assemblages but with some variation in mineral abundance. The

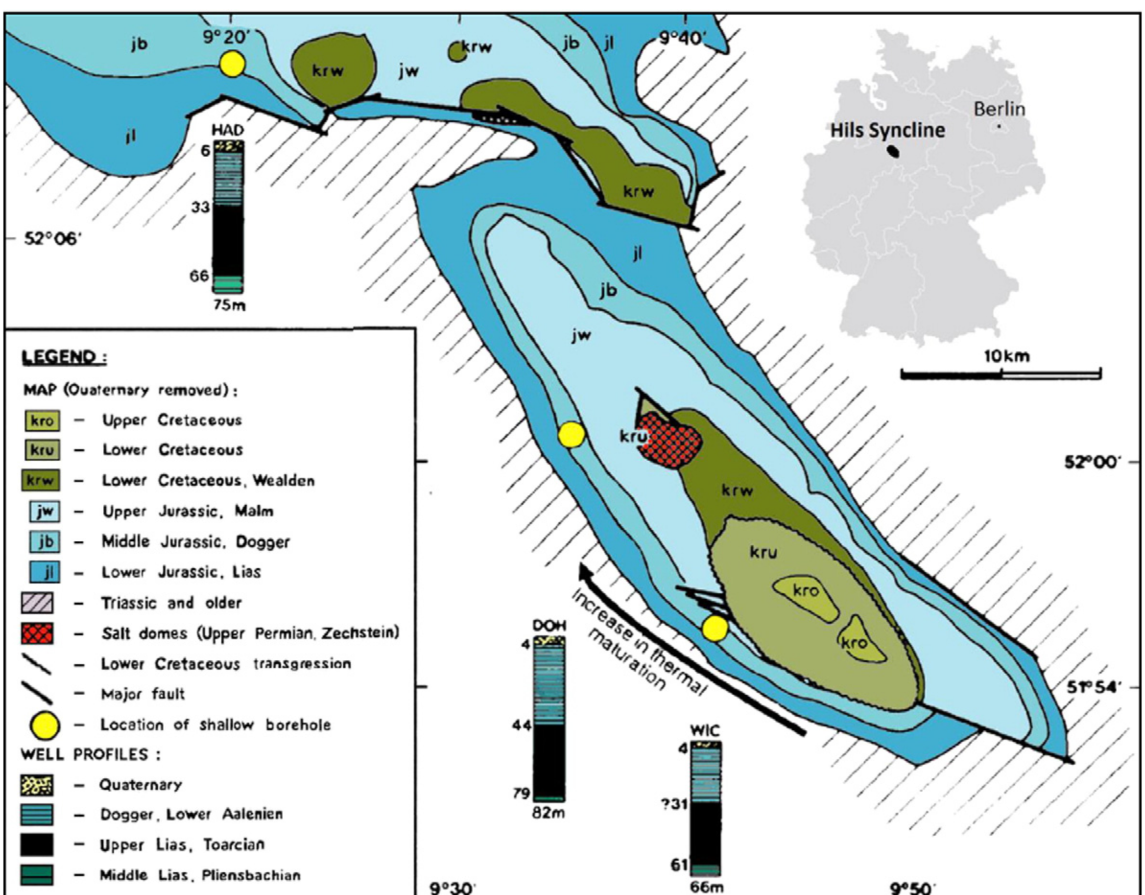

Fig. 1. Geological map of the Posidonia Shale in the Hils Syncline with the marked bore hole locations Wickensen, Dohnsen and Haddessen. Modified from Jochum et al., 1995.