International Journal of Coal Geology 136 (2014) 59–74

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

The biogenic methane potential of European gas shale analogues: Results from incubation experiments and thermodynamic modelling

Martin Krüger [a,*], Wolfgang van Berk [b], Esther T. Arning [c], Núria Jiménez [a], Niels H. Schovsbo [d], Nontje Straaten [a], Hans-Martin Schulz [c]

[a] Federal Institute for Geosciences and Natural Resources (BGR), Department of Microbiology, Stilleweg 2, D-30655 Hannover, Germany
[b] Clausthal University of Technology, Department of Hydrogeology, Leibnizstraße 10, D-38678 Clausthal-Zellerfeld, Germany
[c] Helmholtz Centre Potsdam - GFZ German Research Centre for Geosciences, Sec. 4.3, Organic Geochemistry, D-14473 Potsdam, Germany
[d] Geological Survey of Denmark and Greenland (GEUS), Department of Reservoir Geology, Øster Voldgade 10, Dk-1350 Copenhagen, Denmark

ARTICLE INFO

Article history:
Received 5 March 2014
Received in revised form 10 September 2014
Accepted 20 September 2014
Available online 30 September 2014

Keywords:
Methane
Black shale
Incubation
Carbon dioxide
Stable carbon isotope

ABSTRACT

Core samples from the Lower Jurassic Posidonia Shale (Lower Toarcian), Wealden black shales (both from the Lower Saxony Basin, northern Germany), and from the Cambrian–Ordovician Alum Shale (southern Sweden) have been investigated for their biogenic gas potential in incubation experiments. The sample set represents all stages of thermal maturity (from immature to overmature). Methane and to a higher degree carbon dioxide are generated from all samples by added microorganisms. In general, overmature samples ($Rr > 1.5\%$) show lowest gas generation rates. The highest generation rates for produced methane (up to 89 μmol g^{-1} day^{-1}) and carbon dioxide (139 μmol g^{-1} day^{-1}) were detected in immature Alum Shale samples, when different hydrocarbon-degrading inocula where added; whereas the lowest methane production rates were detected in Wealden sediments. The lightest $\delta^{13}C$ values for produced methane and carbon dioxide have been detected in Posidonia Shale samples of oil window maturity. Such samples are some of the most sensitive for gas generation and exhibit the strongest decreases of hydrogen indices after incubation.

Hydrogeochemical modelling of methane generation, fate and behaviour showed that methane formed during the early diagenesis got lost from Posidonia Shale, the mainly investigated shale in this study. As the mature Posidonia Shale is according to the incubation experiments still sensitive for gas generation, a production scenario of genetically generated methane due to oil degradation is simulated. The basic conditions resemble the conditions in the Antrim Shale in the Michigan Basin. Gas production due to dewatering and pressure decrease results in an increase of the gas volumes coupled to a progressive enrichment of carbon dioxide in the produced gas. Moreover, calcite scaling may be the consequence during progressive production similar to the Antrim Shale in the Michigan Basin. Such calcite precipitation has been demonstrated to predominantly occur in natural samples at oil window maturity.

1. Introduction

Today most shale gas is being produced from thermogenic shale gas plays, perhaps the most famous of which is the Lower Carboniferous Barnett Shale in the Fort Worth Basin, Texas. The gas is mainly generated and stored in black shales with thermal maturities higher than 1.2% vitrinite reflectance (Rr, %). Nevertheless, it is important to note that biogenic methane is being produced from shallow systems (Shurr and Ridgley, 2002), e.g., from the New Albany Shale and the Upper Devonian Antrim Shale in the Michigan Basin, which was the most successfully exploited shale gas system during the 1990–2000 decade in the USA (Curtis, 2002).

The Antrim Shale is an economically significant source of microbially produced methane along the northern margins of the Michigan Basin where meteoric recharge has been focused. The hypothesis suggests that fresh waters, recharged from Pleistocene glaciation and modern precipitation, suppressed basinal brine salinity to great depths and enhanced methanogenesis (Formolo et al., 2008; Golding et al., 2013 and references therein; Martini et al., 1998; McIntosh et al., 2002). This regional geological phenomenon is based on the fact that microorganisms with the potential to form biogenic methane favourably grow in aqueous environments with low contents of dissolved total dissolved solids.

Similar systems may have also developed in Europe as northern Germany was covered by Pleistocene glaciers. To test the biogenic methane potential of black shales in Europe, several prominent black shales, which are known conventional source rocks, have been selected in the framework of the "Gas Shales in Europe" project (GASH) which ran from 2009 to 2012: the Toarcian Posidonia Shale from the Hils half-graben (Lower Saxony Basin, northern Germany), the Cambro-Ordovician Alum Shale in Denmark and Sweden, and Wealden black shales also from the Lower Saxony Basin; core material for investigation

---

[*] Corresponding author. Tel.: +49 511 6433102; fax: +49 511 6432304.
E-mail address: Martin.Krueger@bgr.de (M. Krüger).

http://dx.doi.org/10.1016/j.coal.2014.09.012
0166-5162/

from all of which was accessible in the form of stored, and/or fresh core material. Importantly, samples of Posidonia Shale with a range of thermal maturities (from low maturity to overmaturity) were accessible.

The GASH project (gas-shales.org), coordinated by Helmholtz-Centre Potsdam - GFZ German Research Centre for Geosciences was the first major scientific initiative in Europe that was focussed on shale gas; it was broad ranging in scientific scope and unites leading European research groups and geological surveys with industry. It comprises two main elements: the compiling of a European Black Shale Database (EBSD) and conducting research on the interplaying factors governing shale gas formation and occurrence.

One motivation of the GASH project thus was to investigate the biogenic methane potential of these black shales in the framework of a feasibility study, which aimed to answer several questions:

> First, do these sediments still today form a subsurface environment and a matrix so that biogenic methane can be generated? Secondly, which of these black shales is the most favourable for biogenic methane production in incubation experiments? Furthermore, what are the controlling factors for such a biogenic methane potential? And finally, do microorganisms produce biogenic methane preferentially at a specific range of thermal maturities?

To answer these questions, a series of anaerobic incubations with core materials with different maturities and microbial enrichments were set up.

In addition, the Lower Toarcian Posidonia Shale was selected as the key black shale for further questions such as (1) when in the geological past was the "early" biogenic methane formed, and what was the fate and behaviour of such early formed methane, (2) can the conceptual model to explain the biogenic methane in the Antrim Shale be transferred to Posidonia Shale, and can the generation processes be generically retraced, and (3) which processes occur if such gas in the shale would be produced? These questions were investigated, in contrast to the previous ones, by hydrogeochemical modelling using chemical thermodynamics.

2. Geology of the investigated black shales

2.1. Black shale 1 (key shale): Posidonia Shale (Lower Toarcian) in the Hils half-graben, Lower Saxony Basin, northern Germany

The samples of the Lower Toarcian shale studied here were obtained from boreholes drilled in the Hils half-graben located in the SE part of the Lower Saxony Basin (LSB) during the 1980s. They consist of fine-grained, laminated, carbonate-rich, bituminous shale, and contain abundant type II kerogens (Littke et al., 1991). In wide areas of northern Germany Posidonia Shale is the most important source rock for oil (and gas; Betz et al., 1987), but also in Western Europe (Bodenhausen and Ott, 1981; Hancock and Mithern, 1987; Lott et al., 2010; Wong, 1991). The sediments were deposited at moderate sea level under anoxic or at least oxygen depleted conditions on the seafloor (Rullkötter et al., 1988). Six shallow boreholes were drilled along the western flank of the Hils syncline (Fig. 1) for scientific purposes. The drilled Toarcian shale profiles show increasing maturity from 0.48% Rr (Weenzen borehole) in the SW to 1.45% Rr (Haddessen borehole) in the NW (Littke et al., 1988). Our investigation focuses on samples from three boreholes, namely Wickensen (0.53% Rr), Harderode (0.88% Rr), and Haddessen (1.45% Rr). The latter two occurrences have experienced considerable hydrocarbon generation and expulsion (Rullkötter et al., 1988). In all three shale profiles numerous horizontal calcite and/or bitumen-filled fractures are present. These fractures occur as near vertical planes and are most likely related to hydraulic expulsion as response to burial. Vertical fractures which are most likely related to later stages of inversion were mainly observed in the profiles of the Harderode and Haddessen boreholes. The fillings of vertical fractures mostly consist of carbonates but locally quartz and pyrite can also be present (Jochum, 1988).

The lower part of the Posidonia Shale in the studied boreholes consists of fine-grained carbonaceous marlstone of varying thickness between 4.9 and 7.0 m which is overlain by calcareous clay–shale units (e.g., Littke et al., 1991; Rullkötter et al., 1988). Marlstone from the lower unit shows average carbonate (mostly calcite) content of about 50%, 35% clay minerals, 11% quartz and feldspar, and 4% pyrite (Berner et al., 2012; Mann, 1987). The upper calcareous clay–shale units are made up on average by 43% clay minerals, 37% carbonate (mostly calcite), 15% quartz and feldspar, and 5% pyrite. The clay minerals mainly consist of illite, but also considerable amounts of kaolinite, illite/smectite mixed layer clay minerals, free smectite, and chlorite are present (Mann, 1987). Although the sediments from different boreholes have experienced different maturation, neither bulk mineralogy nor clay mineralogy differ significantly (Mann, 1987).

The southern part of the LSB is locally characterized by extremely high levels of thermal maturity of coaly organic matter within Palaeozoic and Mesozoic strata (e.g., Deutloff et al., 1980; Drozdzewski et al., 2009; Petmecky et al., 1999; Teichmüller, 1986), and by magnetic and positive gravimetric anomalies (e.g., Bachmann and Grosse, 1989). These findings have led to a model assuming intrusions of several small magmatic bodies such as the "Bramsche Massif", and "Vlotho Massif". in Lower Cretaceous times in the southern part of the LSB (e.g. Giebeler-Degro, 1986; Stadler and Teichmüller, 1971). The model of magmatic activity during the Lower Cretaceous was widely accepted until Petmecky et al. (1999) and Brink (2002) proposed that rapidly increasing maturity trends of organic matter with depth found in the boreholes are better explained by a model that invokes a combination of deep burial of individual blocks in the LSB, high heat-flux during Upper Jurassic–Lower Cretaceous subsidence, and subsequent uplift and erosion during the Upper Cretaceous. Both models present strengths and weaknesses and at present there is a still controversy about which one is more appropriate. In addition, the thermal history in the southern part of the LSB is still unclear. Nevertheless, elevated maximum present-day heat flows and hot springs are still observed in this part of the LSB.

Rullkötter et al. (1988) quantitatively determined the amount of hydrocarbons which were generated and expelled during maturation of the type II kerogen in Posidonia Shale. The authors found that about 50% of the initial kerogen was transformed into oil, gas and inorganic compounds during the maturation increase from 0.48 Rr to 0.88% Rr. At thermal maturities from 0.88% Rr to 1.45% Rr the transformation efficiency ceased. Only a small portion of the generated material remained in the source rock even at a relatively early stage of generation (0.68% Rr). Expulsion efficiency of oil plus gas reached a value of 86% at the end of the main generation stage (0.88% Rr). According to these data, the Posidonia Shale appears to be an efficient expeller of liquid hydrocarbons. These findings are supported by Klaver et al. (2012), who showed that Posidonia Shale samples with a thermal maturity of 0.6% Rr still contain large pores which are connected via a low-porous (and low-permeable) clay-rich matrix with pore throats below 10 nm. Having referred to this, it becomes clear why the type II oil-prone Posidonia source rock is also a shale gas system, but not as efficient as the Barnett Shale in the Fort Worth Basin (Texas; Jarvie et al., 2007). Details about maturity, TOC contents and Rock Eval data of the investigated samples from the three boreholes are given in Table 1.

2.2. Black shale 2, for comparison: Alum Shale (Upper Cambrian to Lower Ordovician) from Bornholm Island, Danish Baltic Sea

One of the other black shales investigated in the frame of the GASH project is a prominent black shale with potential for both thermogenic and biogenic shale gas, the Cambro-Ordovician Alum Shale in northern Europe (Pedersen et al., 2006, 2007; Pool et al., 2012; Schulz et al., 2013). This shale is immature in central southern Sweden, the central Baltic Sea basin and the Baltic States Latvia and Estonia (Buchardt, 1999; Petersen et al., 2013; Veski and Palu, 2003). Oil window maturities occur towards Norway and Denmark in a narrow ribbon and