Chemical Geology 345 (2013) 62–76

Contents lists available at SciVerse ScienceDirect

Chemical Geology

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

Sources of natural gases in Middle Cambrian reservoirs in Polish and Lithuanian Baltic Basin as determined by stable isotopes and hydrous pyrolysis of Lower Palaeozoic source rocks

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ARTICLE INFO

Article history:
Received 5 December 2012
Received in revised form 9 February 2013
Accepted 11 February 2013
Available online 6 March 2013

Editor: David R. Hilton

Keywords:
Gas origin
Hydrous pyrolysis
Stable isotopes
Upper Palaeozoic
Source rocks
Polish and Lithuanian Baltic Basin

ABSTRACT

Origin of natural gases associated with oil and condensate accumulations within the Middle Cambrian sandstone reservoir of the Polish and Lithuanian Baltic Basin was characterised by means of molecular composition, stable carbon isotopes of methane, ethane, propane, butanes, pentanes and carbon dioxide, stable hydrogen isotopes of methane and stable nitrogen isotopes of gaseous nitrogen. Generated gas from potential Upper Cambrian, Tremadocian, and Llandovery source rocks by hydrous pyrolysis at 330 °C and 355 °C for 72 h was used to characterise thermogenic gas to evaluate correlation parameters based on molecular composition and stable isotopes. The pyrolysis conditions represent gas generation during oil generation, which appears to be the conditions represented by the natural gas accumulations and their low GORs (gas:oil ratios). The dryness of the pyrolysis and natural hydrocarbon compositions compare well, but do not provide a means of distinguishing the contributions of each source rock to the natural gas accumulations. The average $\delta^{13}C$ value of the natural methane is 6.9‰ depleted in ^{13}C compared to methane generated in the hydrous pyrolysis experiments. This difference is less for ethane and essentially nonexistent for propane, butanes, and pentanes. Tentatively, this diminishing difference with increasing carbon number is attributed to kinetic effects resulting from higher experimental temperatures. Although the $\delta^{13}C$ values of methane and ethane from the hydrous pyrolysis experiments are not useful in direct correlations with natural gas accumulations, $\delta^{13}C$ of propane, butanes, and pentanes is useful, and indicates that the Upper Cambrian and Tremadocian source rocks are the main contributors and that the Llandovery source rocks are not significant contributors to the Polish and Lithuanian Baltic natural gases. Polish natural gases with relatively higher methane and ethane are attributed to the mixing of drier, more mature gases from deeper parts of the basin to the west. Carbon dioxide of natural gases was generated during thermogenic processes and gaseous nitrogen was generated from NH_4-rich illites of the clayey facies and from thermal transformation of organic matter of the Lower Palaeozoic strata. Hydrous pyrolysis gases have higher concentrations of CO_2, H_2S and H_2 than the natural gases. This difference is attributed to reduction or loss of these highly reactive and soluble gases during migration and entrapment of the natural gases. Although CO_2 concentrations between pyrolysis and natural gases are different, the $\delta^{13}C$ values of the former fall within the range of the latter.

1. Introduction

Kotarba (2010) made a preliminary study of the natural hydrocarbon gases that accumulated in the Middle Cambrian reservoir of the Polish part of the Baltic Basin using gases generated from three potential Lower Palaeozoic source rocks by hydrous pyrolysis at 330 °C for 72 h. He concluded that the Polish Baltic natural gases were primarily thermogenic in origin and sourced by Upper Cambrian and Tremadocian (Ordovician) source rocks. The results also demonstrated that some of the natural gas accumulations contained a component of microbial methane. The objective of this study is to extend this work to include natural gases from the Lithuanian Baltic Basin with two additional source rock samples of Llandovery (Silurian) age. In addition to subjecting these samples to hydrous pyrolysis at 330 °C for 72 h, aliquots of all five samples were subjected to hydrous pyrolysis at 355 °C for 72 h to attain gas molecular- and isotopic-data at higher thermal maturities for comparison. The hydrous pyrolysis conditions of 330 and 355 °C for 72 h are representative of the entire oil window for source rocks with type-II kerogen according to previous hydrous pyrolysis results (Lewan, 1985; Lewan and Ruble, 2002). Simulating the entire oil window for this study is particularly appropriate considering the gas:oil ratios (GORs) of the Baltic petroleum accumulations which are typically

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http://dx.doi.org/10.1016/j.chemgeo.2013.02.023

less than 696 m^3STP/t (3200 scf/bbl) (Ulmishek, 1990; PGI-NRI, 2012 and Sergej Kavev, personal communication), which Danesh (1998) classifies as predominantly oil (black and volatile) reservoirs. This is in general agreement with modelling of the Palaeozoic sequence in the southern offshore Baltic to be in the oil window (Karnkowski et al., 2010). Lewan and Henry (2001) report that GORs range from 238 to 167 m^3STP/t (978 to 768 scf/bbl) for hydrous pyrolysis yields from a source rock with Type-II kerogen between 330 and 355 °C for 72 h, respectively. In addition, hydrous pyrolysis at the higher thermal maturity (355 °C for 72 h) can provide a thermogenic $\delta^{13}C$ signature for methane to determine microbial methane input in a natural gas accumulation (Kotarba et al., 2009).

2. Geological setting and petroleum and source rock occurrence

The Baltic Basin (also called Peribaltic Syneclise) is a large, roughly NE–SW trending depression on NW margin of the Precambrian East European Craton formed by pericratonic subsidence during the Caledonian diastrofic-sedimentation cycle (Witkowski, 1989; Ulmishek, 1990; Brangulis et al., 1992; Zdanaviciute and Bojesen-Koefoed, 1997; Poprawa et al., 1999). The total area of the Baltic Basin is approximately 190,000 km^3 with about 60% covered by the Baltic Sea (Fig. 1). The Baltic Basin was affected by Proterozoic tectonism (early Ediacaran rifting) as well as by Caledonian collision, Permo–Triassic rifting, late Jurassic, and late Cretaceous uplifts (Ulmishek, 1990; Poprawa et al., 1999, 2006; Poprawa, 2006). In southern part of Baltic Basin, Lower Palaeozoic sedimentary sequence prevails with Silurian strata thicknesses up to 3000 m (Modliński and Podhalańska, 2010). The Upper Cambrian strata are represented by black bituminous shales with thin interbeds and lenses of dark, often bioclastic limestones (Modliński and Podhalańska, 2010). Upper Cambrian–Tremadocian Alum Shales are mainly black organic-rich mudstones (Andérsson et al., 1985; Buchardt and Lewan, 1990; Dyni, 2006). Lowermost part of Silurian sequence contains Llandovery claystones and mudstones. Their thickness in the Polish part of Baltic region varies from 10 to 100 m (Modliński and Podhalańska, 2010).

Petroleum onshore and offshore exploration in the Polish Baltic Basin began in 1955 and 1975, respectively (Karnkowski, 1999; Domżalski and Mazurek, 2003). In the onshore part of the Polish Baltic Basin, a small Żarnowiec oil deposit was first discovered in 1970. Later, in this area three small accumulations of oil were discovered at Dębki in 1971 and Białogóra in 1991, and gas-condensate at Żarnowiec-West in 1987 (Karnkowski, 1999; Domżalski et al., 2004; Karnkowski et al., 2010). In the offshore part of the Polish Baltic Basin, three oil accumulations in the Middle Cambrian sandstone reservoirs were discovered at structures B3 in 1981, B8 in 1983, and B24 in 1996. Four gas-condensate accumulations were discovered in the Middle Cambrian sandstone reservoirs at structures B4 in 1991, B6 in 1982, B16 in 1985, and B21 in 1996 (Domżalski et al., 2004; Karnkowski et al., 2010).

More than 40 oil deposits and shows were discovered in the Lower Palaeozoic (Middle Cambrian, Ordovician and Silurian) reservoirs in Latvia, Lithuania and Kaliningrad Region of Russian Federation (Brangulis et al., 1992, 1993; Kanev et al., 1994; Kattai et al., 1997).

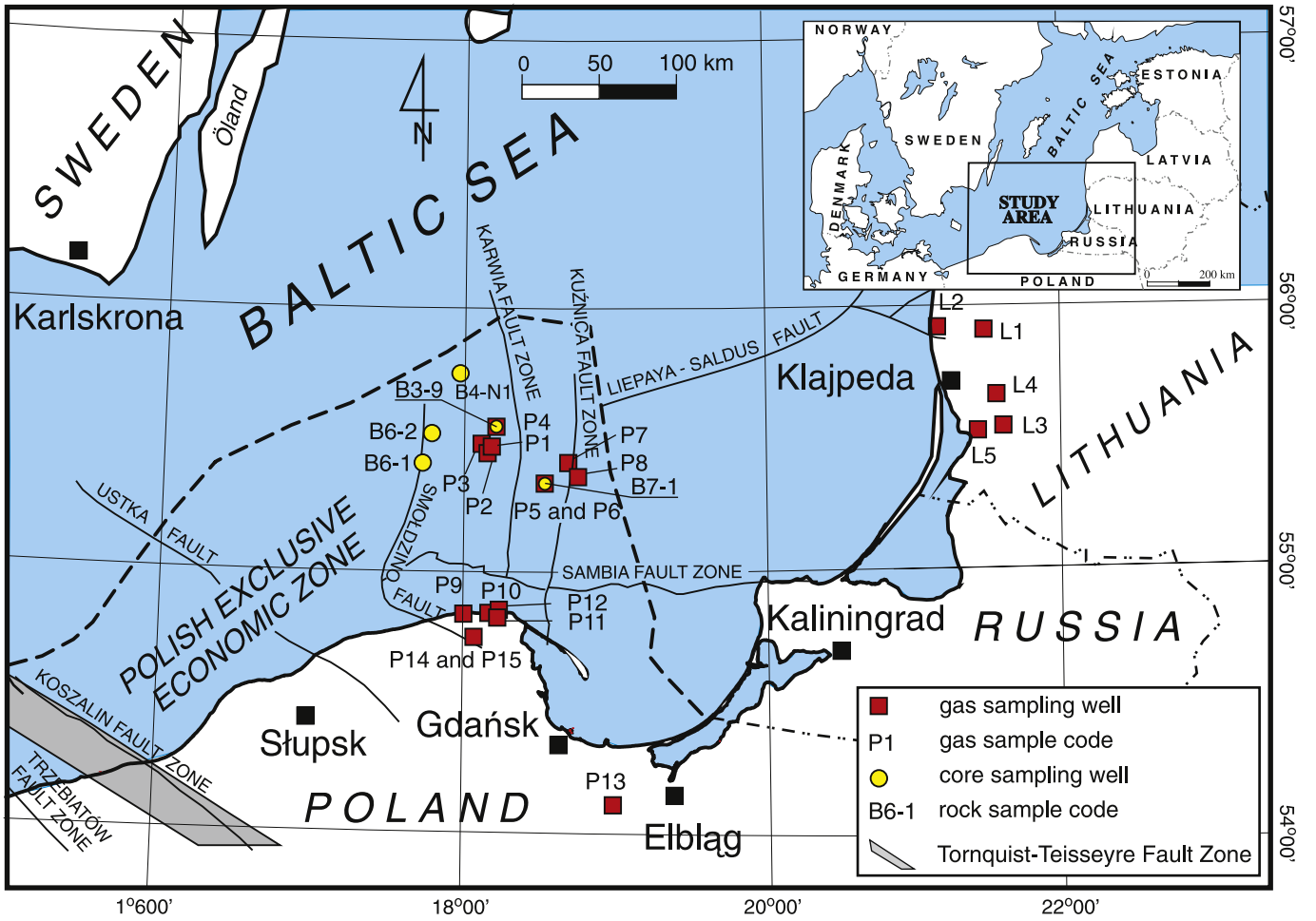

Fig. 1. Sketch map of southern part of the Baltic region showing the location of sampled gas wells and rock boreholes. Geology modified after Pokorski (2010) and Brangulis et al. (1993).