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Research paper

Stable carbon isotope ratios of CH_4-rich gas inclusions in shale-hosted fracture-fill mineralization: A tool for tracing hydrocarbon generation and migration in shale plays for oil and gas

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ABSTRACT

Fluid inclusion gases in minerals from shale hosted fracture-fill mineralization have been analyzed for stable carbon isotopic ratios of CH_4 using a crushing device interfaced to an isotope ratio mass spectrometer (IRMS). The samples of Paleozoic strata under study originate from outcrops and wells in the Rhenish Massif and Campine Basin, Harz Mountains, and the upper slope of the Southern Permian Basin. Fracture-fill mineralization hosted by Mesozoic strata was sampled from drill cores in the Lower Saxony Basin. Some studied sites are candidates for shale gas exploration in Germany. Samples of Mesozoic strata are characterized by abundant calcite-filled horizontal fractures which preferentially occur in TOC-rich sections of the drilled sediments. Only rarely are vertical fractures filled with carbonates and/or quartz in drill cores from Mesozoic strata but in Paleozoic shale they occur frequently. The $\delta^{13}C(CH_4)$ values of fluid inclusions in calcite from horizontal fractures hosted by Mesozoic strata suggest that gaseous hydrocarbons were generated during the oil/early gas window and that the formation of horizontal fractures seems to be related to hydraulic expulsion fracturing. The calculated maturity of the source rocks at the time of gas generation lies below the maturity derived from measured vitrinite reflectance. Thus, the formation of horizontal fractures and trapping of gas that was generated in the oil and/or early gas window obviously occurred prior to maximal burial. Rapidly increasing vitrinite reflectance data seen locally can be explained by hydrothermal alteration, as indicated by increasing $\delta^{13}C$ (CH_4–CO_2) values in fluid inclusions. The formation of vertical fractures in studied Mesozoic sediments is related to stages of post-burial inversion; gas-rich inclusions in fracture filling minerals recorded the migration of gas that had probably been generated instantaneously, rather than cumulatively, from high to overmature source rocks. Since no evidence is given for the presence of early generated gas in studied Paleozoic shale, it appears likely that major gas loss from shales occurred due to deformation and uplift of these sediments in response to the Variscan Orogeny.

1. Introduction

Fracture fill-mineralization in any kind of rock is the product of episodic fluid flow in fault-related, stress-controlled fracture systems (e.g. Atkinson, 1987; Sibson, 1994; Bons et al., 2012). Fracture formation enables fluid flow from different sources, e.g. pore waters, hydrothermal fluids and/or meteoric water and precipitation of fracture-fill mineralization. Fracture formation is related to various parameters such as stress, fluid pressure, etc. (e.g. Bons et al., 2012). For example, fluid pressure plays an important role in the formation of horizontal fibrous calcite-filled veins and fractures which are abundant in mature TOC-rich shale. The formation of such bedding-parallel fractures especially in kerogen-rich rocks has been related to hydrocarbon generation from kerogen and/or the cracking of oil which caused overpressured compartments (e.g. Rodriguez et al., 2009; Sturm, 2011), or fluctuation in the pore fluid pressure (Jessel et al., 1994). The $\delta^{13}C$ values of fracture-fill calcites from horizontal veins can be highly variable suggesting either microbial methanogenesis or organic/inorganic origin of the calcite-forming fluids (Budai et al., 2002). However, bedding parallel fractures may also be the product of tectonic stress such as bedding-parallel shearing or fluid flow (Jessel et al., 1994).

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Another commonly occurring type of fault-related fracture system is that of vertical veins and fractures which are related to tectonic stress and tectonic movements, such as thrusting or shearing, etc. Vertical veins often crosscut parallel bedding veins and may penetrate through different stratigraphic units. Mineral replacements in the fracture fillings of vertical veins are widespread and indicate multiple episodes of fracture activation and fluid flow. Fluid inclusions hosted in fracture filling minerals can provide information on fluid composition as well as the temperatures and pressures of fluid entrapment, thus allowing conclusions to be drawn on the evolution of the minerals themselves and their host rocks.

Fluid inclusions studies have been performed in many fields of geological research (e.g., Roedder, 1984; De Vito and Frezzotti, 1994; Goldstein and Reynolds, 1994; Anderson et al., 2001; Samson et al., 2003) and development of new analytical tools for analyzing specific compounds in fluid inclusions still continues. Fluid inclusion studies in hydrocarbon research often focus on fluid and oil/gas migration in reservoir rocks (e.g. Goldstein and Reynolds, 1994) or the compositions of hydrocarbons in oil and/or gas inclusions (e.g. Horsfield and McLimans, 1984; Karlsen et al., 1993; Munz, 2001; George et al., 2007; Burruss et al., 2012).

In an earlier paper (Lüders et al., 2012) we reported stable isotope ratios of CH_4—CO_2-rich inclusions in fracture-fill mineralization hosted by Carboniferous and Triassic-Jurassic rocks from the southern part of the Lower Saxony Basin (Germany) and concluded that the data can be used to discriminate methane generated from each of these source rocks and to estimate the maturity of the source rocks at the time when CH_4 was generated.

The present study provides a data set of stable carbon isotope ratios of CH_4-(CO_2)-rich gas inclusions from fracture-fill mineralization hosted by Paleozoic and Mesozoic shale and attempts to evaluate the probable shale gas potential of the studied rocks.

2. Sample description and fluid inclusion inventory of fracture filling minerals

For this study, 109 samples from outcrops and drill cores in Lower Saxony Basin (LSB), the Rhenish Massif and adjacent Campine Basin, Harz Mts., and the southern slope of the Southern Permian Basin (SPB) were collected and analyzed (Fig. 1). The stratigraphic sequence covers Upper Cambrian to Viséan strata in the Central Ardennes and at the Faille du Midi (Belgium), Lower Carboniferous cherts in the Harz Mts., Lower and Upper Carboniferous strata in the Rhenish Block, uppermost Carboniferous shale and coal seams-bearing sandstone at the southern slope of the SPB, as well as Mesozoic shales of Lower Jurassic (Posidonia Shale) and Lower Cretaceous (Wealden) age in the LSB. The maturity of fracture-hosting shales is highly variable and ranges between ca. 0.9 and 4.5% vitrinite reflectance (Ro). The sample suite comprises mineral filled horizontal fractures as well as vertical fractures. Fracture fillings consist of calcite and/or quartz. The latter is mostly restricted to fracture-fill mineralization hosted by Paleozoic shale. The thickness of the sampled fracture fillings varies between some mm up to ca. 20 cm.

Fluid inclusions in calcite from horizontal fractures hosted in shale showing Ro $< 0.8\%$ often exhibit bluish-white fluorescence indicating the presence of oil. The size of oil inclusions is small and seldom exceeds 5 μm. Calcite from fracture fillings hosted by higher maturity shale contains either gaseous inclusions showing no UV fluorescence or no gas inclusions probably due to leakage and/or decrepitation. Quartz from vertical fracture fillings often contains gas-rich inclusions showing highly variable molar volumes indicating variable pressure conditions (i.e., hydrostatic or overhydrostatic) during gas entrapment. Gas-rich inclusions in quartz are often of primary origin (growth zones, clusters) and more or less associated with co-genetically formed aqueous 2-phase fluid

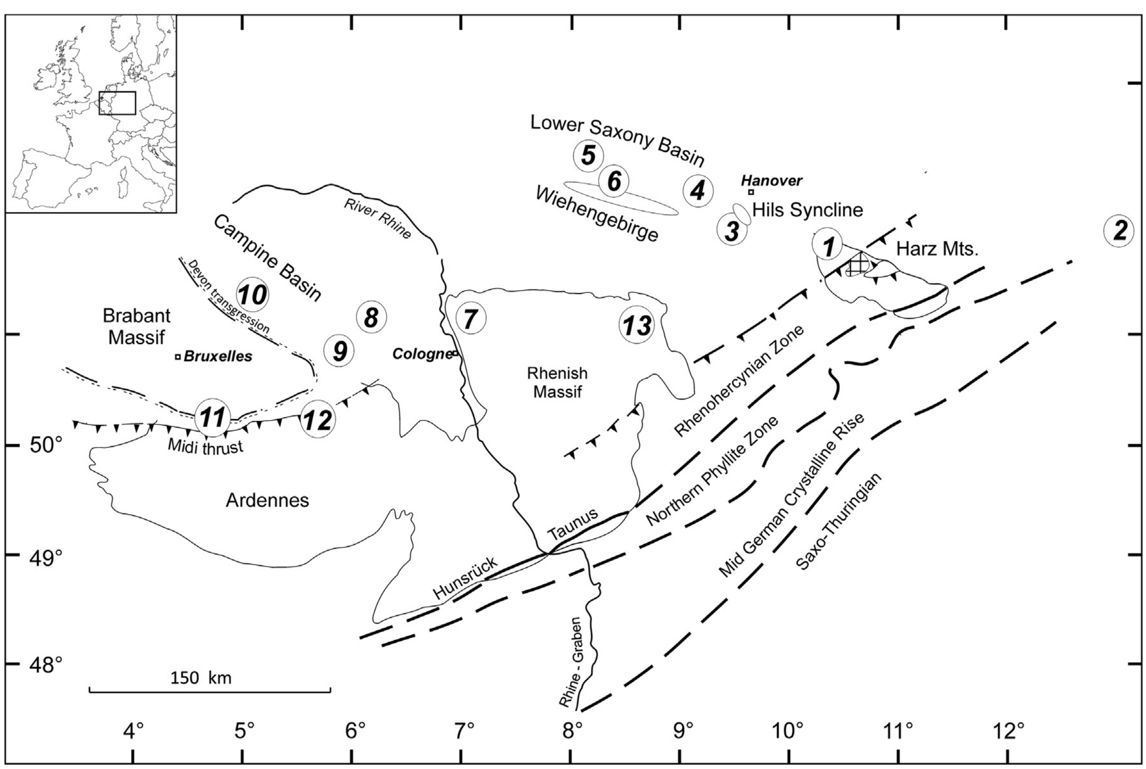

Figure 1. Structural classification of the Rhenohercynian Zone in Central Europe. Sampling sites are shown by numbers. 1: NW Harz Mts., 2: Well D, 3: Hils Syncline, 4: Ex-B, 5: Ex-C, 6: Lübbecke, 7: Velbert area, 8: Well A, 9: Well B, 10: Well C, 11: Namur, Floreffe, 12: Tier dol Preu, Grand Halleux, 13: Kellerwald.