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Research paper

Chemistry and isotopic composition of Rotliegend and Upper Carboniferous formation waters from the North German Basin

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ABSTRACT

Element concentrations and isotopic composition (δD, $\delta^{18}O$, $\delta^{15}N$ of ammonium, $^{87}Sr/^{86}Sr$) have been determined in highly-saline formation waters from the Rotliegend Altmark gasfield and the Upper Carboniferous Husum–Schneeren gasfield in the North German Basin. Both reservoirs have been covered by huge Zechstein evaporite caps since the Late Permian. Formation waters from the Altmark gasfield are characterized by high total dissolved solids and are enriched in $\delta^{18}O$ relative to meteoric waters and either show positive or negative δD values which typically follow the proposed δD vs. $\delta^{18}O$ paths for seawater evaporation. Formation waters stored in Upper Carboniferous sandstones show much more variable element concentrations and $\delta^{18}O$ and δD values than the Rotliegend Formation waters. The Br vs. Cl concentrations of the brines suggest seawater evaporation being the principal source of salinity at both sites. The ammonium concentrations in the analyzed brines are highly variable and the $\delta^{15}N$ isotopic composition of dissolved ammonium is controlled either by the isotopic composition of the gas in the reservoir (Rotliegend) or that of the host rocks (Upper Carboniferous). At both sites, early formation waters interacted with the sedimentary host rocks after deposition. $^{87}Sr/^{86}Sr$ ratios suggest that re-equilibration between fluids and their host rocks occurred in pre-Triassic times. There is no chemical or isotopic evidence that original formation waters which occur in sandstone below the overlying Zechstein evaporites were flushed out or mixed by later meteoric water as has been documented in deep-seated Mesozoic and other Paleozoic aquifers of the North German Basin.

1. Introduction

Fluids in sedimentary basins play a fundamental role as media for the transport and/or redistribution of mass and heat. Depending on the sedimentation and burial history, regional thermal events, and migration history, fluids in porous sediments of different stratigraphic units may be very different from each other with regard to their chemical composition and/or temperature. Most fluids stored in the deeper parts of sedimentary basins are highly-saline brines that could be different in origin (e.g., Clayton et al., 1966; Kharaka et al., 1974; Carpenter, 1978; Eugster and Jones, 1979; Kharaka and Thordsen, 1992; Hanor, 1994; Kloppmann et al., 2001; Möller et al., 2008). Many of these brines are fluids of meteoric origin that displaced connate waters that were entrapped in the interstices of sediments at the time of deposition (e.g., Clayton et al., 1966; Taylor, 1974; Knauth and Beeunas, 1986). Recharging meteoric water may have interacted with halite from evaporites or mixed with saline brines ascending from depth on a regional scale over long periods of time.

Flow of fluids at depth depends, among others, on topographic relief, physical compaction, and/or gravity-driven reflux. Water–rock interaction (WRI), metamorphism, and/or devolatilization reactions can modify the chemical signature of the original fluid. Upward percolation of fluids through pores and networks of microfractures driven by subsidence (Bjørlykke, 1994) or channelized rapid fluid flow along fractures and faults during tectonic events (Sibson, 1994; Stephenson et al., 1994; Muchez and Sintubin, 1998) may lead to the mixing of saline sedimentary brines with connate and/or even meteoric waters from shallower groundwater systems resulting in the dilution of the ascending brines. Formation waters may show differences in salinity, element content and/or isotopic composition on a local scale of hundreds of meters or even kilometers, when compared with water stored in the same strata but from other areas of

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the basin (e.g., Hanor et al., 1986). Therefore, using geochemical information obtained from one regional part of the basin for the reconstruction or modeling of the fluid evolution in the entire sedimentary basin may be highly problematic.

Formation waters of the North German Basin (NGB), which is filled with sedimentary sequences up to 12 km, have been studied so far from aquifers above the Zechstein salt (e.g., Lehmann, 1974a,b; Carlé, 1975; Müller and Papendieck, 1975; Hoth et al., 1997; Kloppmann et al., 2001; Tesmer et al., 2007; Möller et al., 2008). In contrast, sedimentary brines stored at depth below the Zechstein, for example, Rotliegend and Carboniferous strata in the Central European Basin (CEB) can only be studied at a few localities where such fluids mainly are produced along with gases from deep-seated reservoirs. Therefore, reliable chemical data of Paleozoic deep basinal brines from the NGB have not been reported so far, except for few fluid inclusion data from wells penetrating Paleozoic units (e.g., Rieken, 1988; Reutel and Lüders, 1998; Schmidt Mumm and Wolfgramm, 2004; Lüders et al., 2005).

Here we present chemical analyses and stable isotope composition of formation waters stored in Lower Permian (Rotliegend) sandstones from various subreservoirs of the Altmark gasfield in the central part of the NGB and Upper Carboniferous sandstones from the Husum–Schneeren gasfield which is situated in the western part of the NGB within the Lower Saxony Basin (Fig. 1). At both sites the reservoirs have been overlain by thick Zechstein evaporites since the Late Permian. Fifteen water samples studied here were collected from separators of producing gas reservoirs. Additionally, three water samples from the Rotliegend Altmark gasfield were directly collected at depth (*c*. 3500 m) in the water column close below the gas–water contact for comparison by using a special sampling device which is regularly used for fluid sampling during gasfield observation. It consists of small stainless steel tubes with sample volumes between 1 and 3 l and can be connected with temperature and resistivity sensors as additional tools to detect gas–water boundaries. Formation water flows through the tubes below the gas–water contact and the sampler can be closed with check valves at specific depth positions.

This study aims to provide insights into the origin and fate of Paleozoic waters in the NGB, in particular into the sources of salinity and the history of water–rock interaction.

2. Geological setting

2.1. General overview

The NGB forms part of the Central European Basin (CEB) which extends from Poland through Germany, Denmark, The Netherlands, the Southern North Sea to eastern England and the Atlantic Shelf. The CEB is situated between the Precambrian Baltic Shield to the north, the Russian platform to the east and blocks of crystalline basement, of Cadomian through Variscan age, to the south. To the west it is flanked by the Caledonides of Scotland. The NGB developed on crystalline rocks of Cadomian and Variscan age and is filled with Paleozoic–Cenozoic sediments with up to 12 km thickness in its central part (Schwab, 1985). Basin evolution started in the Upper Carboniferous after the Variscan Orogeny with the sedimentary fill in a foreland basin and extensional bimodal volcanism due to rifting processes (Ziegler, 1990; Brink et al., 1992; Benek et al., 1996; Geissler et al., 2008). Above marine carbonate-dominated Lower Carboniferous sediments, clastic–turbiditic, organic-rich Namurian were sediments deposited, reflecting deep marine to paralic sedimentary conditions. Especially in the western part of the NGB the continental development during the Upper Carboniferous is dominated by thick Westphalian coal measures. At the beginning of the Permian, the climatic conditions changed from humid to arid, and the

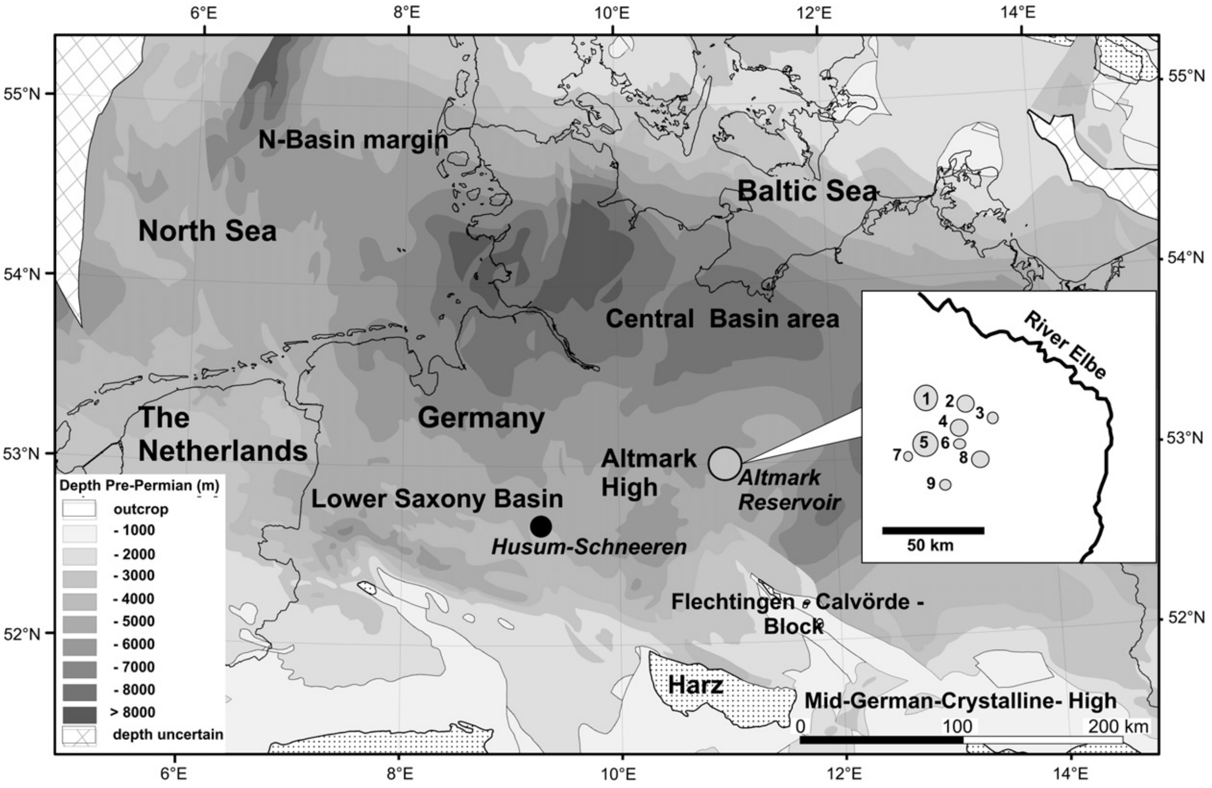

Fig. 1. Locations of the Altmark gasfield and the Husum–Schneeren gasfield in the North German Basin (depth of the Pre-Permian according to Gerling et al., 1999; Lokhorst et al., 1998, and Hoth, 1997). The insert map shows the nine gas subreservoirs of the Altmark as numbered in the diagram: 1 Salzwedel–Peckensen, 2 Riebau, 3 Sanne, 4 Altensalzwedel, 5 Heidberg–Mellin, 6 Zehtlingen, 7 Mellin–Süd, 8 Winkelstedt, 9 Wenze (numbers refer to Table 1).