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Mineralogy and geochemistry of Mississippian and Lower Pennsylvanian Black Shales at the Northern Margin of the Variscan Mountain Belt (Germany and Belgium)

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A B S T R A C T

Exploration of unconventional gas resources from Paleozoic formations in northwestern Germany is just getting started. Large, potential gas reservoirs are presumed to be present north of the Rhenish Massif, where Mississippian and Pennsylvanian marine black shales occur. This paper comprises geochemical and mineralogical data and other important aspects of potentially economic black shale formations of the Carboniferous. Additionally, the burial and thermal history was reconstructed using 1D modeling software (Schlumberger). These 1D models were calibrated with vitrinite reflectance data from outcrops and shallow wells. In general, all Paleozoic black shales are at present highly mature, between about 1.5 and >3% vitrinite reflectance. The shales of the uppermost Mississippian (Upper Alum Shale/Chokier Formation) have high contents of organic carbon, are tens of meters thick and can be regarded as potential gas shale targets. Most other Mississippian and Pennsylvanian black shales are relatively thin. Adjacent carbonates are often stained black and rich in solid bitumen, indicating former oil impregnation of these reservoirs.

1. Introduction

Carboniferous sediments are widespread throughout central Europe, extending from Great Britain to northern France, Belgium, Germany, Poland, and Ukraine. These thick sedimentary units have been intensely studied due to the presence of numerous coal seams in the Pennsylvanian which were mined in the past. Mining is still active in some parts of Europe, but overall activity has been declining over the last few decades, mainly due to complex geological conditions, great depth of the coals and high population density. Little is known about the black shales occurring in the Carboniferous, which have not been considered economically interesting targets due to their high thermal maturity. The high maturity has exhausted all oil potential, but some of these shales are still well within the gas window. As interest turns more and more towards such gas shales, we investigated the geochemistry and mineralogy, as well as thermal maturity of these rocks. A large shale gas potential is expected in Pre-Permian black shales; in particular, the Mississippian contains abundant marine, organic matter-rich shales (Kombrink, 2008; Korn, 2010; Littke et al., 2011). Our study mainly focuses on the Mississippian units, especially on the Upper Alum Shale ("Hangende Alaunschiefer") of Late Mississippian age and its Belgian equivalent, the "Chokier Formation", but also includes some information on other Mississippian (Tournaisian and Viséan) and Lower Pennsylvanian shales located within the study area.

Many of these Paleozoic black shales are rich in carbonate or quartz, i.e. they can be regarded as marlstones or siliceous shales. Shale systems differ considerably in mineralogy, thermal maturity, (original) kerogen type, and occurrence of natural fractures. Permeabilities of unfractured shales are usually in the nanodarcy range (Aplin and Macquaker, 2011; Eseme et al., 2012; Hildenbrand, 2003) and porosity is generally low and strongly controlled by clay content and maximum burial depth.

Key characteristics of gas shales are organic richness and a high gas generation and storage potential. Most gas shales were primarily oil source rocks, which retained a large part of their oil, either adsorbed to the kerogen matrix or within the pore space. Thus, secondary cracking of oil to gas (and solid bitumen) is an important process in these rocks. Secondary porosity in organic matter-rich shales partly results from primary and secondary cracking of kerogen and retained oil as well as brittle deformation of these rocks (Jarvie et al., 2007).

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Black shales in general are organic-rich shales, in which organic carbon contents usually exceed 1% and mostly vary between 2% and 10% (Tourtelot, 1979). They generate hydrocarbons during ongoing burial and heating. Kerogen in marine immature black shales is most often classified as Type II with an excellent petroleum generation potential.

Black shales do not differ significantly in terms of mineralogical composition compared to ordinary shales. Nevertheless, the deposition in anoxic or oxygen-depleted environments has some effect on the relative amount of minerals. Pyrite content especially varies largely across black shale successions and is commonly high in marine shales. Berner (1984) states that sulfur availability for pyrite formation is provided by the HS^- production from sulfate reducing bacteria and additional intra-sedimentary processes. The amount of pyrite in marine black shales is strongly controlled by the availability of iron, which directly correlates with the amount of iron-bearing minerals.

In particular, Alum shales are relatively enriched in pyrite. Weathering of the dispersed pyrite results in sulfuric acid reacting with potassium and aluminium to form a mineral called alunite, which is part of the alum-mineral group. Alunite provides the name for this lithology. In the past, alunite was used in the leather tanning industry. The most prominent Alum Shale examples are the Swedish Cambrian and Lower Ordovician Alum Shale formations, which were mined for several reasons for over a total of 350 years. The Swedish Alum Shale has an average thickness of 40 m (max. >100 m) and total organic carbon (TOC) contents ranging from 2% to 20% (Buchardt et al., 1997). In addition to being a source for alunite, it also supplied crude oil and was later used for its metal ores. For example, the Swedish Alum shales are enriched in uranium and vanadium (Dyni, 2005).

The goal of this work is to provide detailed information on organic carbon content, thickness, mineralogy, geochemistry and thermal maturity of Mississippian and Pennsylvanian black shales, occurring in outcrops at the northern margin of the Rhenohercynian zone of the western European Variscides, with special emphasis on the Late Mississippian Upper Alum Shale and its Belgian time-equivalent, the Chokier Formation. This same (outcropping) sequence of rocks also underlies Pennsylvanian, Mesozoic, and Tertiary sediments in the Münsterland Basin, the Lower Saxony Basin, the Lower Rhine Valley Basin, and the Campine Basin at depths where they could become a shale gas target in the future.

2. Geological setting

The results presented in this paper are based on samples from the northern rim of the Ardennes in Belgium and the Rhenish Massif in western Germany (Fig. 1), which are low mountain ranges. The study area extends from the Hochsauerland in the east to the Belgian city of Namur in the west. East of the river Rhine the Paleozoic rocks of the Rhenish Massif descend in the Ruhr Basin below Cretaceous rocks, dipping towards the north. Further to the west, they are covered by the Tertiary units of the Lower Rhine Valley Basin, and the Mesozoic units of the Campine Basin, Belgium (Fig. 1).

Five sampling areas are marked in Fig. 1, from which outcrop and well samples are derived. In the west, area 1 is part of the northernmost Ardennes mountains in Belgium, where Namurian, Tournaisian and Viséan samples were taken from outcrops and from one well. The same stratigraphic range was studied in the Aachen area (area 2) at the border between Germany, Belgium, and The Netherlands. Sampling area 3 is located in the westernmost part of the Rhenish Massif, close to the city of Wuppertal, while sampling area 4 is further to the east (see Fig. 1). In these three areas, only samples from outcrops were investigated. The easternmost sampling area (area 5) was considered because of the occurrence of Lower Alum Shale in outcrops, but only a few samples were studied from that area.

The Rhenohercynian Zone (RHZ) was positioned at the southern part of the Avalonian microcontinent from the Late Proterozoic until the Variscan Orogeny in the Late Paleozoic (Franke, 2000). It is assumed that the formation of the RHZ began during the Cadomian Orogeny. Relics of these Cambrian rock units can be found in the Rocroi and Stavelot-Venn Massifs of the Ardennes represented by metamorphic rock units of mainly siliciclastic protoliths. During the Lower and Middle Devonian, sedimentation changed from siliciclastic to shallow marine carbonates. Clastic input from the London-Brabant Massif (Fig. 1) declined and extensive reef and shelf carbonates precipitated during the Eifelian and Frasnian. The Upper Devonian was predominately a mostly marine environment, leading to pelagic black shale but also sandstone deposition. Around local ridges, carbonate sedimentation was still ongoing.

Carboniferous times were characterized by diversified marine, fluvial, deltaic and continental sedimentation and the northward drift of Laurasia from an arid to a more humid, tropical latitude (Ziegler, 1990). A northward trending transgression affected large parts of Central Europe in the lower Carboniferous, leading to the regionally extensive formation known as the “Kohlenkalk Platform”, representing shallow marine carbonates. In the east, the “Kulm”-succession is much more shaly with abundant dark organic matter-rich shales, represented by a starved basin facies with thicknesses of less than 50 to more than 150 m in the northern Rhenish Massif. Towards the north, the thickness of Viséan and Namurian black shales seems to decrease (Ricken et al., 2000), but only a few wells penetrate these units.

Under starved basin conditions, bituminous black shales and siliceous shales were deposited in most regions of the Netherlands and northwest Germany. In some areas, stagnant conditions must have prevailed during the Mississippian (Kombrink et al., 2010). The deposition of thick Upper Viséan Kulm greywackes along the eastern margin of the Rhenish Massif marked the Variscan Uplift and initial erosion of the southern Rhenish Massif.

The Mississippian/Pennsylvanian border marks an important change of depositional environment. Instead of marine sedimentation, terrestrial conditions started to prevail, with the deposition of abundant tropical peat mires (Jasper et al., 2010; Littke and ten Haven, 1989). Nevertheless, marine ingressions led to several black shale depositional cycles typically occurring above coal seams.

Just before the Variscan orogeny, the maximum burial depth of all sedimentary units was reached as well as highest temperatures (Karg et al., 2005; Littke et al., 1994). A few Permian sediments in the study area are thermally much less mature than the underlying Paleozoic, evidence of strong uplift during the latest Carboniferous or Early Permian.

The Lower Alum Shale (“Liegende Alaunschiefer”, Fig. 2) can be traced along outcrops at the Variscan Deformation Front from the Rhenish Massif in the west (roughly time equivalent to the base of the Pont d`Arcole Shale in the Dinant Synclinorium) to the Harz Mountains in the east where it is an important reference horizon in the local stratigraphy. Thicknesses are reported to be 10–50 m in the northeast of the Rhenish Massif (Stoppel et al., 2006). We identified a 20 m thick sequence in the East-Sauerland Anticline (“Ostsauerländer Hauptsattel”) which is one of the major anticlines in the eastern Rhenish Massif. Lower Alum Shale horizons of the Dill Syncline in the southeast of the Rhenish Massif have thicknesses of up to 15 m (Bender and Stoppel, 2006). To the north, thickness decreases to just a few meters as proven by the Münsterland 1 and Vingerhoets wells with thicknesses of just 3–4 m for the Lower Alum Shale (Wolburg, 1963).

Thicknesses of the Upper Alum Shale Formation deviate largely throughout the area. Stoppel et al. (2006) identified a 110 m succession at the NE margin of the Rhenish Massif. In contrast, in the East-Sauerland Anticline successions of just 4 to 10 m exist. Between Aachen and Wuppertal, thicknesses vary from 50 to 70 m at outcrops in the Wuppertal area and in the Schwalmtal 1001 well (Amler and Herbig, 2006). A slight thinning towards the north is observed in