# Conventional and Unconventional Petroleum Systems in the Dniepr-Donets Basin, Ukraine

**PhD thesis**

Dipl.-Ing. David Misch, BSc

Supervisor:

Univ.-Prof. Dr. Reinhard F. Sachsenhofer

Department of Applied Geosciences and Geophysics

Chair of Petroleum Geology

Montanuniversitaet Leoben

Leoben, 2016

**Affidavit**

I declare in lieu of oath, that I wrote this thesis and performed the associated research myself, using only literature cited in this volume.

(Dipl.-Ing. David Misch, BSc)

## DANKSAGUNG

Ich bin unzähligen Menschen zu Dank verpflichtet, welche mich im Rahmen dieser Arbeit wissenschaftlich unterstützt haben. Ich möchte mich daher an dieser Stelle bei allen Mitarbeitern des Departments Angewandte Geowissenschaften an der Montanuniversität Leoben bedanken, mit denen ich in den letzten Jahren zusammenarbeiten durfte. Weiters bedanke ich mich bei allen Ko-Autoren der in dieser Studie aufgeführten Publikationen für die gute wissenschaftliche Zusammenarbeit und die Hilfe beim Erreichen meines Ziels.

Zwei Personen haben mich als Geowissenschaftler wohl am meisten geprägt. Zu großem Dank bin ich zum einen Dr. Heinrich Mali verpflichtet, der mir mit seiner enthusiastischen Einstellung zu vielen geowissenschaftlichen Fragen während meines Grundstudiums das Rüstzeug zum feldtauglichen Geologen mitgegeben und mich, vor allem in meiner Zeit am Lehrstuhl für Geologie und Lagerstättenlehre, stets tatkräftig unterstützt hat. Ganz besonders danken möchte ich meinem Doktorvater, Prof. Reinhard Sachsenhofer, für die großartige Betreuung meiner Dissertation am Lehrstuhl für Erdölgeologie. Einen intensiveren wissenschaftlichen Diskurs, stets geprägt durch ermutigende Worte, kann man sich als Doktorand wohl nicht wünschen. Aber auch in Fragen abseits der Wissenschaft konnte ich immer auf einen guten Rat zählen.

Als „Quereinsteiger“ war ich gerade am Beginn meiner Dissertation häufig auf Hilfe in analytischen Belangen angewiesen. Daher möchte ich Dr. Doris Groß danken, die einen nicht unbeträchtlichen Teil ihrer Arbeitszeit damit verbracht hat, mir helfend zur Seite zu stehen. Danke Doris außerdem für die netten und motivierenden Gespräche im Büro und für die Freundschaft, die sich in den letzten Jahren entwickelt hat.

Eine große menschliche Stütze war mir außerdem Sabine Feuchter, vor allem zu Zeiten in denen mir die Arbeit über den Kopf zu wachsen drohte.

Danke Joel und Anung Samsu, für die gefühlten 100.000 Höhenmeter auf Laufstrecken rund um Leoben. Dieser Ausgleich und die guten Gespräche auf dem Weg waren wesentliche

Erfolgsfaktoren meiner Arbeit in den letzten Jahren. Danke aber auch an alle anderen Freunde, die mich während dieser intensiven Zeit aufgemuntert und unterstützt haben.

Meiner Familie, allen voran meinen Eltern Gabriele und Peter, möchte ich für die stetige Unterstützung während der (langen) Jahre des Studiums danken. Noch mehr muss ich euch jedoch dafür danken, dass ihr bei mir eine lebenslange Begeisterung für die Natur und die Prozesse, die auf sie Einfluss nehmen, sowie für den Erwerb von neuem Wissen geweckt habt.

Zu guter Letzt möchte ich der wichtigsten Person in meinem Leben danken. Danke Claudia, dass du mir in allen Belangen des Lebens zur Seite stehst und jedes noch so verrückte Abenteuer mitmachst. Du bist mein größter Rückhalt und unsere kleine Jana ist der Beweis dafür.

## ABSTRACT

Within the frame of this study, a characterization of the conventional and unconventional petroleum system of the Ukrainian Dniepr-Donets Basin (DDB) was performed based on detailed bulk geochemical data, biomarker and stable isotope geochemistry, organic petrology and high-resolution electron beam techniques.

Oil-source rock correlation was performed to reveal the contribution of several potential source rock horizons to the charging of mainly Visean – Permian conventional hydrocarbon reservoirs. HI values of the least mature Rudov Beds (<300 mgHC/gTOC) agree with the presence of a mixed type III/II kerogen. However, a potential to generate low-wax Parafinic-Naphthenic-Aromatic oils was determined for Upper Visean Rudov Beds from the basin center, based on pyrolysis experiments. Furthermore, it could be proven by combined isotopic and biomarker data, that Upper Visean intervals, particularly the most prolific "Rudov Facies", are likely the most important source for hydrocarbons in the region, whereas Devonian mudstones, formerly suggested to be an important source rock in the northwestern DDB, were ruled out as a main hydrocarbon source based on bulk geochemical and biomarker data. Apart from that, a main contribution is also suggested for highly oil-prone Serpukhovian black shales, whereas Tournaisian rocks might be a local source in some areas. Study results revealed a correlation between $\delta^{13}C$ of the aliphatic fraction of crude oils and the $\delta^{13}C$ of methane in gas samples, arguing for a common (Upper Visean) source. In general, this study highlights that the multi-source, multi-reservoir petroleum system of the DDB needs a field-scale approach for characterization of migration distance, mixed charging from different source horizons, etc.

Following the general proof that Upper Visean black shales in the northwestern DDB are partly prone to the generation of liquid hydrocarbons, a laterally well-resolved evaluation of their shale oil/gas potential was performed focusing on the key parameters (i) shale thickness, (ii) thermal maturity, (iii) mineralogy, as well as (iv) generation potential based on pyrolysis experiments.

Average TOC contents of Rudov Beds within the Srebnen Bay, up to 100 meters thick, are very high (>4 %). Average TOC contents of wells north and northwest of the Srebnen Bay are significantly lower (<4 %), but still in the range of 2-4 %TOC over a relatively wide lateral extend. The thickness of these rocks is generally lower (20-40 m) compared to wells within the Srebnen Bay, although thickness might reach 60 m in some areas. In contrast, TOC contents <2 % in wells located along the northeastern basin margin indicate that these rocks do not hold a shale gas/oil potential. Apart from an obvious maturity trend, pyrolysis experiments indicate a higher amount of oil-prone type II kerogen in the basinal Rudov Facies, whereas marginal samples dominated by vitrinite macerals are predominantly gas-prone. High TOC contents (up to 10 %) along the southeastern basin margin are partly caused by a higher amount of inertinite macerals in these samples, a result of syn-depositional wildfires in the Carboniferous.

However, the cut-off maturity for shale oil (liquids) production (0.8 %Rr) is reached only at considerable depths > 4.0-4.5 km within the Srebnen Bay, whereas the shale gas cut-off (1.2

%Rr) is not reached within the northwestern DDB at all. Sufficient thermal maturity is reached only in great depths (> 5.5 km) along the basin axis within the central DDB and at even greater depths in southeastern positions. Apart from that, kinetic experiments suggest that earlier hydrocarbon generation, e.g. due to present type IIS kerogen, cannot be assumed.

The mineralogy of Rudov Beds varies strongly in lateral and vertical directions, limiting the predictability of shale brittleness. The desired amount of 60 wt.% brittle minerals (quartz, feldspar, carbonates, pyrite, apatite, etc.) is reached only partly by samples from the siliceous (basinal), and rarely by samples from the transitional and lagoonal (clayey & calcareous) facies. The clay mineral fraction within most investigated Rudov samples is dominated by kaolinite, which is suggested to diminish the fraccability of shales. Apart from that, expandable clay minerals (ECM) are present in samples from more than 5 km depth, a result of low Mesozoic heat flow.

In summary, findings of this study arouse the question if the Upper Visean succession in the DDB, despite a considerable amount of oil/gas-in-place, will be an economic unconventional play in the future.

An innovative part of this study focused on the pore space-generation within organic matter during thermal maturation. According to SEM and FIB/BIB-SEM data, nanopores are not abundant in primary macerals (e.g. vitrinite) even in overmature rocks, whereas they develop within secondary organic matter (bitumen) formed mainly at gas window maturity. Frequently occurring sub-micrometer porosity, probably related to gas generation from bituminous organic matter, was detected within mudstones at a vitrinite reflectance >2.0 %Rr. However, such pores have also been detected in solid bitumen of oil-prone samples at oil window maturity (0.65-0.8 %Rr), arguing for the necessity to combine organic geochemical analysis with high resolution-imaging, for a better characterization of pore growth in organic matter. Apart from that, authigenic, nanoscale clay minerals and calcite occur within pyrobitumen at gas window maturity, suggesting a strong interdependency of organic matter-transformation and mineral growth. However, although organic matter-hosted nanopores might contribute to some extent to gas storage and release from Rudov Beds, the main fraction of total pore volume is formed by intra-clay mineral porosity, mostly in the sub-micrometer range. Compared to younger gas shales studied throughout Europe (e.g. Posidonia Shale), more severe compaction might have to be taken into account for the evaluation of mechanical properties as well as gas storage and release behavior.

**KURZFASSUNG**

Die vorliegende Arbeit befasst sich mit der Charakterisierung des konventionellen sowie unkonventionellen Kohlenwasserstoffsystems im Dniepr-Donets Becken (DDB; Ukraine) anhand geochemischer (Biomarker, Isotopie), mineralogischer und petrographischer Untersuchungen, sowie hochauflösender Elektronenmikroskopie.

Zur Evaluierung des Beitrags verschiedener potentieller Muttergesteine zu den zahlreichen Öllagerstätten im nordwestlichen und zentralen DDB wurde eine Korrelation von Ölen/Kondensaten und Muttergesteinsproben anhand von Biomarkern und der Kohlenstoffisotopie einzelner Komponenten oder Komponentengruppen durchgeführt. Dabei wurde festgestellt, dass organisch-reiche Schichten aus dem Oberen Visé (inklusive „Rudov Facies“) das Hauptmuttergestein darstellen, während die Bedeutung von Tonsteinen aus dem Devon im Rahmen der Lagerstättengenese gering zu bewerten ist. Ein beträchtlicher Anteil speziell im zentralen DDB kann ölbildenden serpukhovischen Tonschiefern zugerechnet werden, wobei generell im Serpukhovium zwei verschiedene Faziesbereiche unterschieden wurden und die Verbreitung der ölbildenden Fazies bislang unklar ist. Ein gewisse, wenngleich lokale, Bedeutung kommt außerdem organisch-reichen Sedimenten aus dem Tournaisium zu. Insgesamt wurde im Rahmen dieser Studie festgestellt, dass eine detaillierte Korrelation zwischen Lagerstätten und Muttergesteinen im DDB nur unter Berücksichtigung strukturgeologischer Daten im Feldmaßstab machbar ist.

Aus ihrer Bedeutung als Muttergestein für konventionelle Lagerstätten im DDB ist ein mögliches Potential organisch-reicher Tonsteine aus dem Oberen Visé für die Produktion von Schieferöl/-gas abzuleiten. Daher wurde deren Eignung anhand international üblicher Kriterien wie (i) effektive Mächtigkeit, (ii) thermische Reife, (iii) Mineralogie und (iv) Kohlenwasserstoff-Bildungspotential evaluiert.

Die durchschnittlichen TOC-Gehalte der Rudov Fazies (Horizont V-23) im Bereich der Srebnen Bucht im nordwestlichen DDB sind sehr hoch (>4 %), außerdem werden hier die größten Mächtigkeiten (bis 100 m) erreicht. Am nördlichen und nordwestlichen Rand der Srebnen Bucht liegen deutlich geringere TOC-Gehalte vor (2-4 %), außerdem verringert sich die Mächtigkeit auf 20-40 m (maximal 60 m). Entlang des nordöstlichen Beckenrands kann aufgrund von durchschnittlichen TOC-Gehalten von <2 % nicht von einem Schiefergaspotential ausgegangen werden. Zur Charakterisierung des Kohlenwasserstoffbildungspotentials wurden Pyrolyseexperimente an ausgewählten Proben aus der Srebnen Bucht und randlicheren Positionen durchgeführt. Neben einem augenscheinlichen, beckenwärtigen Reifetrend sprechen die Ergebnisse auch für eine höhere Menge ölbildenden Typ II Kerogens in Proben aus der Beckenmitte, während terrestrisches Typ III Kerogen in randlichen Bereichen stärker dominiert. Hohe TOC-Gehalte in diesen Bereichen sind häufig auf Typ IV Kerogen (Inertinit) zurückzuführen, welcher kein Kohlenwasserstoffbildungspotential besitzt.

Ausreichende thermische Reife ist eine Grundvoraussetzung für die Produktion von Schieferöl/-gas. Die üblicherweise als Grenzwert für Schieferöllagerstätten angegebene Reife von 0.8 %Rr wird innerhalb der Srebnen Bucht nur in großer Tiefe (> 4-4.5 km) erreicht,

während der Grenzwert für Schiefergasproduktion (1.2 %Rr) im nordwestlichen DDB praktisch nicht erreicht wird. Dieser Wert wird nur in großer Tiefe (>5.5 km) entlang der Beckenachse im zentralen DDB und noch tiefer im südöstlichen Teil des Beckens erreicht. Die Pyrolysedatensprechen weiters nicht für das Vorhandensein von Typ IIS Kerogen, daher kann von einer frühzeitigen Kohlenwasserstoffgenese nicht ausgegangen werden.
Die Mineralogie der Rudov Fazies variiert stark in vertikaler und lateraler Ausbreitung, daher kann nur beschränkt eine Aussage über das Bruchverhalten (spröd/duktil) getroffen werden. Der für Schieferöl/-gasproduktion angestrebte Wert von 60 Gew.% spröden Mineralphasen (Quarz, Feldspat, Karbonate, Pyrit, Apatit, etc.) wird nur teilweise von Proben aus der beckenwärtigen Fazies erreicht, während Proben aus randlichen Bereichen kaum über 50 Gew.% kumulierten Anteil an spröden Phasen aufweisen. Die Tonmineralfraktion ist meist dominiert von Kaolinit, welcher das spröde Bruchverhalten während der Bohrlochstimulation weiter herabsetzt. Das Vorhandensein von quellfähigen Tonmineralen in großer Tiefe (bis 5 km) bestätigt den geringen Reifegradienten und spricht für einen geringen Wärmefluss während des Mesozoikums. Anhand der vorliegenden Ergebnisse muss eine Eignung der Rudov Fazies für wirtschaftliche Schieferöl/-gasproduktion nach momentanen Gesichtspunkten in Zweifel gezogen werden, obwohl ein beträchtliches inhärentes Kohlenwasserstoffpotential festgestellt wurde.
Die Evaluierung der Porenraumentwicklung in organischem Material mit zunehmender Reife stellt einen innovativen Teil dieser Arbeit dar. Anhand von Ergebnissen aus REM (Rasterelektronenmikroskopie) und FIB/BIB-REM („focused ion beam/broad ion beam“-Rasterelektronenmikroskopie) Untersuchungen konnte festgestellt werden, dass primäre Mazerale (z.B. Vitrinit) in unreifen bis überreifen Proben keine interne Porosität aufweisen. In Kontrast dazu bilden sich Poren in sekundär gebildetem Festbitumen, hauptsächlich ab einer thermischen Reife >1.35 %Rr (Gasfenster). Diese Poren kommen in hochreifen Proben (>2 %Rr) häufig vor, wurden jedoch in Proben aus der ölbildenden Beckenfazies auch schon im Ölfenster (0.65-0.8 %Rr) nachgewiesen. Ein beträchtlicher „Kerogeneffekt“ auf die Porenraumentwicklung kann dementsprechend zugrunde gelegt werden. Authigene Tonminerale und, in geringerem Ausmaß, Calcit, wurden in Festbitumen >1.35 %Rr nachgewiesen. Daher kann von einer starken Wechselwirkung zwischen Kohlenwasserstoffgenese und Mineralbildung ausgegangen werden. Obwohl Poren in organischem Material wichtige Indikatoren für das Stadium der Kohlenwasserstoffgenese darstellen und einen beträchtlichen Anteil an der Kohlenwasserstoffspeicherung von Gasschiefern haben können, wurde für die untersuchten Proben aus dem Obervisé eine eindeutige Dominanz von Intra-Tonmineral-Poren im Sub-Mikrometer Bereich festgestellt, deren Speichervermögen stark von der Benetzbarkeit des jeweiligen Tonminerals abhängt. Weiters wurde im Vergleich zu hochauflösenden Untersuchungen an stratigraphisch jüngeren Gasschiefern ähnlicher Maturität festgestellt, dass von einer stärkeren Kompaktion und dementsprechend reduzierten Permeabilität der untersuchten Proben aus dem Karbon ausgegangen werden muss.

# CONTENT

**1. Introduction** .......... **11**

*1.1 State of the art and study aims* .......... *11*

*1.2 Conventional and unconventional hydrocarbon production* .......... *12*
1.2.1 Oil/source correlation for conventional plays .......... 13
1.2.2 Evaluation of the shale oil/gas potential .......... 14

*1.3 Shale gas in Europe* .......... *16*
1.3.1 Lower Paleozoic sediments of Northern Europe .......... 17
1.3.2 Silurian black shales in Poland (e.g. Baltic-Podlasie-Lublin Basin, PBLB) .......... 18
1.3.3 Carboniferous shales at the northern margin of the Variscides (e.g. Germany, Belgium) .......... 19
1.3.4 Lower & Upper Jurassic shale gas (e.g. Posidonia Shale; Mikulov Marl) .......... 21

**2. Geology of the Dniepr-Donets Basin** .......... **22**

*2.1 Geological setting* .......... *22*

*2.2 Petroleum Habitat* .......... *24*

**3. Samples and Methods** .......... **28**

**4. Summary of publications and innovative aspects of the presented results** .......... **35**

*4.1 Publication I: Oil/Gas-Source Rock Correlations in the Dniepr-Donets Basin (Ukraine): New insights into the Petroleum System* .......... *35*

*4.2 Publication II: Shale Gas / Shale Oil Potential of Upper Visean Black Shales in the Dniepr-Donets Basin (Ukraine)* .......... *37*

*4.3 Publication III: SEM and FIB-SEM investigations on potential gas shales in the Dniepr-Donets Basin (Ukraine): Pore space evolution in organic matter during thermal maturation* .......... *39*

*4.4 List of conference contributions related to this thesis* .......... *41*

**5. General conclusions and outlook** .......... **42**

**6. References** .......... **45**

**7. Oil/Gas-Source Rock Correlations in the Dniepr-Donets Basin (Ukraine): New insights into the Petroleum System (Publication I)** .......... **57**

**8. Shale Gas / Shale Oil Potential of Upper Visean Black Shales in the Dniepr-Donets Basin (Ukraine)** **121**

**9. SEM and FIB-SEM investigations on potential gas shales in the Dniepr-Donets Basin (Ukraine): Pore space evolution in organic matter during thermal maturation (Publication III)** .......... **178**

**10. Appendix** .......... **201**

# General part of the PhD thesis

# 1. Introduction

## 1.1 State of the art and study aims

The Ukraine has a long-lasting history in oil and gas production. In particular, the Dniepr-Donets Basin (DDB) is a mature oil and gas province with more than 220 discovered fields and, therefore, holds a strong history in hydrocarbon exploration (e.g. Tari, 2010). However, most of the past studies focused on the thermal history of the basin (e.g. Shymanovskyy et al., 2004), the identification of hydrocarbon reservoirs from seismic data and a general characterization of potential source rocks in basin scale, whereas a detailed oil-source correlation based on geochemical parameters and a laterally well-resolved source rock study on the most promising (Upper Visean) intervals is lacking so far (Sachsenhofer et al., 2010; Ruble, 1996).

Apart from that, it has to be noted that, although Ukraine produces significant amounts of oil and gas from so-called conventional deposits, it is still highly dependent on oil and gas imports. Therefore, in the process of becoming a largely energy independent country, the Ukrainian society puts great expectations on “unconventional” hydrocarbon deposits including shale gas and shale oil accumulations, as well as possibly coal bed methane in the southeastern parts of the DDB as well as in the Donbas Foldbelt (Sachsenhofer et al., 2010; 2012). However, shale gas exploration in Ordovician-Silurian rocks in Poland, partly in the vicinity of the Ukrainian border, yielded disappointing results. While these findings led to a decline in exploration interest in western Ukraine, the remaining hopes now focus on shale oil/gas exploration in the DDB (Sachsenhofer & Koltun, 2012). Nevertheless, although prolific hydrocarbon source rocks obviously exist in the basin setting, their suitability for unconventional production is not yet evaluated. Therefore, by now, a realistic assessment of the shale oil and shale gas potential of the DDB is lacking (Schulz et al., 2010).

This study focuses on the conventional and unconventional petroleum systems of the Ukrainian Dniepr-Donets Basin, aiming to characterize (1) the likely source of oil and gas trapped in conventional reservoirs and (2) the shale oil/gas potential of Upper Visean black shales ("Rudov Beds"), abundant throughout main parts of the basin. Both aspects need a different analytical approach, as explained in the following.

## 1.2 Conventional and unconventional hydrocarbon production

In the past decades, the hydrocarbon producing industry focused on gas and oil trapped in sedimentary rocks with reasonable porosity and permeability. Within those rocks, mostly sandstones and carbonate rocks, hydrocarbons are trapped in structures formed either by primary sedimentary deposition or later tectonic processes. Production was limited to targets that fulfilled certain quality parameters in terms of reservoir quality – nowadays referred to as "conventional" hydrocarbon deposits. However, as a result of the globally increasing demand for fossil fuels and the progressing consumption of the conventional resources, advanced production techniques were developed to achieve enhanced oil recovery from already produced targets and decrease the porosity/permeability cut-offs for new – then called unconventional – deposits (e.g. Andruleit et al., 2010; see Fig. 1). Following this trend, many different branches of unconventional production arose or got well established during the last ten years, including:

(i) Tight oil/gas – production from sandstone reservoirs that are termed "tight" because of their extremely low porosity/permeability

(ii) Coal bed methane – production of methane from coal beds

(iii) Oil shales – artificial (pyrolytic) generation of oil from shallow, thermally immature organic-rich shales

(iv) Oil/tar sands – artificial cracking and recovery of (bio-)degraded hydrocarbons from shallow, often unconsolidated sand bodies

(v) Shale oil/gas – production of oil and gas directly from their source rock, usually very tight, fine-grained and organic-rich mudstones

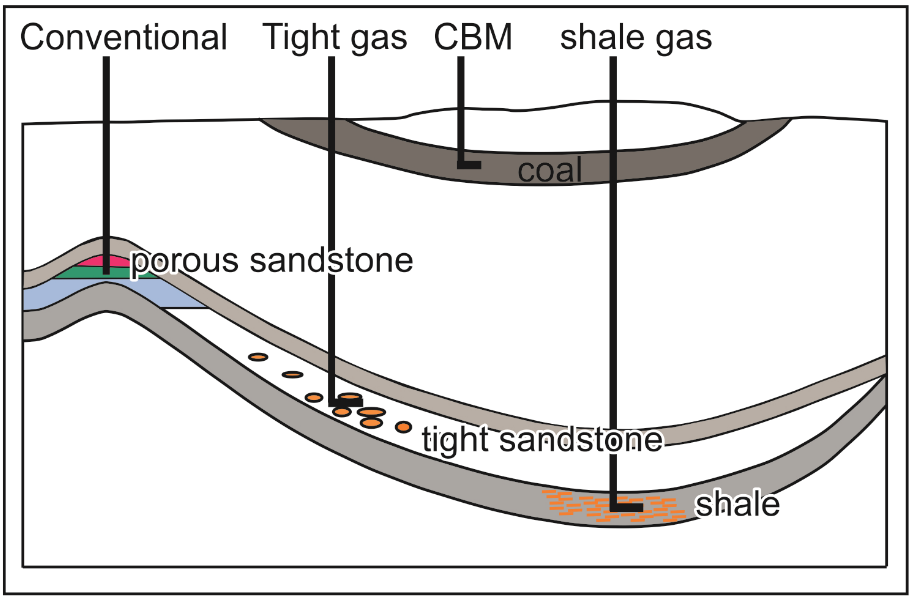


**Fig. 1:** Schematic sketch of different conventional and unconventional hydrocarbon deposits (modified after Andruleit et al., 2010). Red: gas; green: oil; blue: formation water; CBM – coal bed methane;

### 1.2.1 **Oil/source correlation for conventional plays**

Thermogenic hydrocarbon generation usually takes place in so-called source rocks, fine-grained sedimentary rocks (shales), rich in (depositional) organic matter. These rocks, deposited under conditions favourable for organic matter-preservation, are exposed to increasing thermal stress during burial in a sedimentary basin, resulting in a progressive transformation of organic matter. At a certain thermal maturity, the source rocks start to generate liquid and later gaseous hydrocarbons from the solid, primary organic matter (kerogen; e.g. Horsfield, 1989). Furthermore, as the transformation progresses (Fig. 2), the hydrocarbons are expulsed from the source rock horizon and migrate into adjacent formations. Assuming a favourable setting of migration pathways, reservoir lithology, trap and seal, a conventional deposit, often with significant lateral and vertical offset from the hydrocarbon source rock, can form. To correlate the trapped hydrocarbons with their likely source, the hydrocarbons recovered from actually producing wells have to be compared with their counterparts extracted from potential source rock samples. Differences in the molecular and isotopic composition of both are compared and the relative abundance of distinct compounds ("biomarkers") is used for fingerprinting (e.g. Alexander et al., 1992). Apparently, insights drawn from such investigations might potentially also influence the ongoing hydrocarbon exploration in a specific region or even result in new exploration targets.

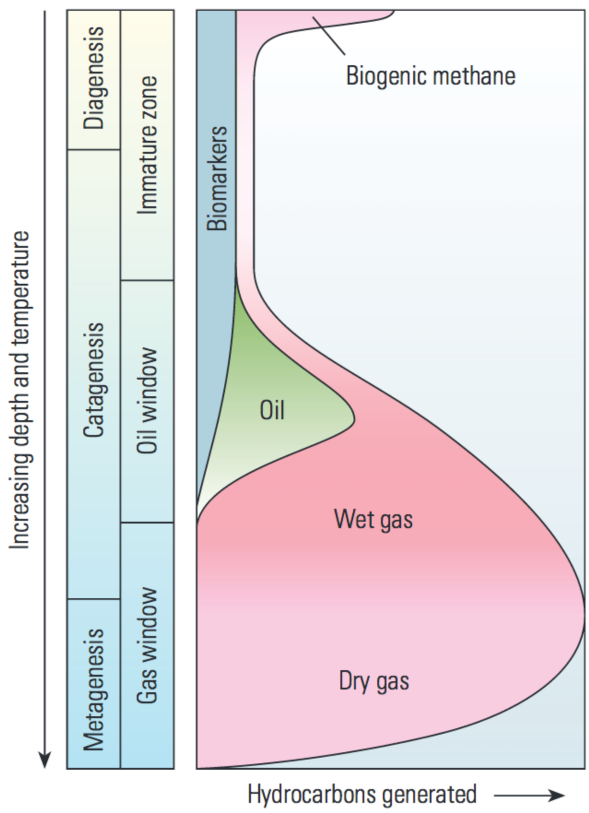


**Fig. 2:** Transformation of kerogen with increasing burial depth and temperature (after Tissot et al., 1974; figure from McCarthy et al., 2011). Differences in generation behaviour can be observed for different types of kerogen.

### 1.2.2 **Evaluation of the shale oil/gas potential**

As explained above, shale oil/gas is produced directly from the hydrocarbon source rocks, instead of secondary reservoir lithologies. This fact results in completely different production behaviour of such targets, and, therefore, different parameters for their evaluation. Most shales are exceptionally tight, therefore, mineralogy plays a major role for producability, as a high content of brittle minerals enhances the effectiveness of well stimulation (Hester & Harrison, 2015; Rybacki et al., 2014). Apart from that, obviously, high organic matter content and a certain hydrocarbon generation potential, as well as a sufficient thermal maturity reached at preferably shallow depths, are key requirements for a successful shale target (Jarvie et al., 2007; Jarvie, 2012). Finally, a certain cut-off thickness over a considerably wide lateral extent, as well as a preferably „stable" tectonic environment, represent important quality parameters (Jarvie et al., 2007; Charpentier & Cook, 2011). In fact, shale gas targets host finely dispersed hydrocarbons over a relatively wide lateral extent, compared to conventional reservoirs. Nevertheless, because of their frequent abundance, gas shales represent an enormous global resource potential that is not yet fully discovered (Schulz et al, 2010; Jarvie, 2012). Exploration studies on potential economic shale gas plays have to take all these aspects into account, which requires a wide range of techniques for geochemical analysis, as well as a sufficient amount of source rock samples from a representatively large area. Because, in contrast to sandstone reservoirs, petrophysical data cannot be as easily acquired in lab experiments, high resolution electron microscopy as well as new, non-invasive preparation techniques based on ion beam polishing are increasingly used on such geological samples, e.g. to visualize pore space in the sub-micrometer range (Bernard et al, 2012a,b; Curtis et al., 2012a,b). Shale oil/gas exploration opened up a distinct field in petroleum geosciences, representing a complex but at the same time promising future energy resource. In recent years, apart from the US, shale gas exploration was increasingly promoted in Europe by the hydrocarbon producing industry, the reason for this being both the advancing exploitation of conventional resources as well as rapid progress in drilling and development techniques (Schulz et al., 2010; Horsfield et al., 2012). Although well stimulation (hydraulic fracturing) aroused concerns regarding its environmental impact, research on gas shales is still growing and unconventional production is considered a main cornerstone of Central Europe's energy policy within the upcoming decades (Boyer et al., 2011).

## 1.3 Shale gas in Europe

Many formations with significant shale gas potential occur throughout the world. Following the shale gas-boom of the last decade, the USA emerged as the world's most important producer of natural gas. There, gas is mainly produced from the (i) Barnett, (ii) Haynesville, (iii) Woodford, (iv) Marcellus and (v) Fayetteville shales (Jarvie et al., 2007; Jarvie, 2012; Bustin et al., 2009), to name the most prominent plays developed in the last years, now setting the benchmark for most globally important exploration studies (e.g. Uffmann et al., 2012; Horsfield et al., 2012). However, major discoveries were also made outside the USA, for example the Canadian part of the Utica shale (Bustin et al., 2009). In Central Europe, promising targets include Silurian mudstones in Poland, Cambrian to Ordovician rocks in Sweden, Oligo/Miocene shales of the Paratethys, and finally, Lower Carboniferous black shales in the Ukraine, to name just a few (Schulz et al., 2010). However, although shale gas exploration already began in 1821 in the USA, it became widely significant in Central Europe only within the last few years (Schulz et al., 2010). Therefore, shale gas exploration is still in its infancy or at least in an early stage in most European sedimentary basins (Schulz et al., 2010). In the following, the most important gas shales of Central Europe are briefly described. However, it has to be mentioned that because of extensive ongoing research in new areas throughout Europe, this summary does not represent an exhaustive description of all potentially economic future shale gas plays. It is important to note, that Carboniferous black shales of the DDB are not listed here, although they are considered a main exploration target for shale gas. A detailed geological setting for the DDB is presented later in the text. Areas with ongoing research on shale gas are shown in an overview in Fig. 3.

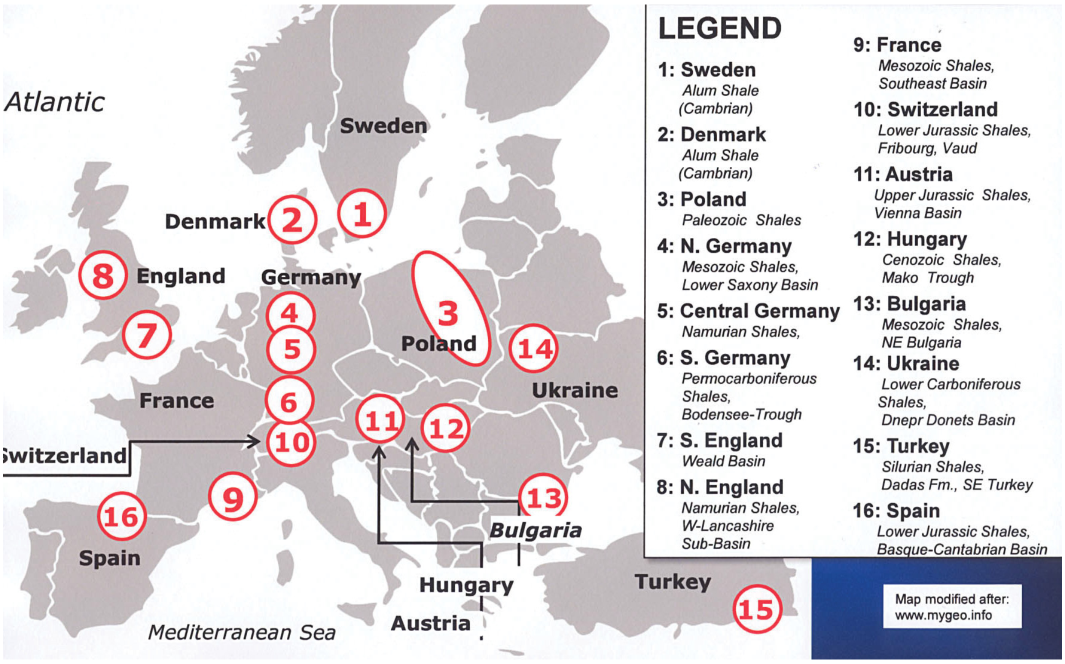


**Fig. 3:** Overview map highlighting European areas with ongoing shale gas exploration (after Horsfield et al., 2012).

### 1.3.1 Lower Paleozoic sediments of Northern Europe

Along the German-Polish and Norwegian-Swedish Caledonides, Lower Paleozoic sediments are preserved in a broad belt (Schovsbo, 2003). At the margin of the Baltic Shield, organic-rich mudstones with relatively uniform composition over a wide lateral extent were deposited mainly in the Middle Cambrian to Lower Ordovician (Tremadoc; Schovsbo, 2003). These shales vary in thickness from up to 100 m in southern Sweden to less than 1 m in Estonia and along the Russian border (Artyushkov et al., 2000). As a result of Proterozoic denudation of large parts of the craton, the influx of coarse siliciclastics was low due to a relatively smooth terrain (Schovsbo, 2003). Therefore, major sand- and siltstone sequences are lacking in the Middle Cambrian – Lower Ordovician shales. Later in the Ordovician, two distinct facies zones with cold-water carbonate platform sediments, developing at the craton interior, and deeper-water shales along the margins of Baltica, formed (Nielsen, 1995).

In terms of shale gas potential, the Alum shale marks the most important organic-rich shale interval deposited during these times along the margins of the Caledonides in Scandinavia. TOC contents might exceed 20 % in some areas (Nielsen & Schovsbo, 2007), with a predominantly marine kerogen (Schulz et al., 2010). Using pyrolysis experiments, Horsfield et al. (1992) and Buchardt (1999) proved that the Alum shale hosts a high intrinsic potential to produce and store gaseous hydrocarbons. Relevant parameters like thickness, average TOC, kerogen type and maturity are comparable to other, successfully producing global shale gas plays (Dyni, 2006). Therefore, extensive exploration takes place e.g. in southern Sweden, where the Alum shale reaches a thickness of up to 100 m (Schulz et al., 2010).

### 1.3.2 **Silurian black shales in Poland (e.g. Baltic-Podlasie-Lublin Basin, PBLB)**

Organic-rich Silurian black shales are widespread throughout Central Europe, often hosting considerably high TOC contents (up to 20 %; Schulz et al., 2010). The Silurian sediments deposited in the Danish-Polish Trough, up to 200 m thick, were proven as a source charging conventional deposits in the Baltic region (Schulz et al., 2010). Nevertheless, although they might hold a significant potential, economic shale gas plays are neither proven in the above-mentioned Silurian succession, nor in other Central European Silurian formations outside of Poland (e.g. Llandoverian – Lodlowian shales in the Czech Republic; Schulz et al., 2010; Volk et al., 2002), yet. However, within the last years, huge effort was put into the evaluation of the Lower Paleozoic Balic-Podlasie-Lublin Basin at the western slope of the Eastern European Craton in Poland (Poprawa, 2006). A shale oil potential was suggested by Poprawa (2010a), although a high uncertainty remains, which is not yet clarified, as an extensive drilling campaign was only set up in 2010 (PGI, 2012). Shales in the PBLB predominantly host type II kerogen, making them favourable for shale oil production in terms of their reasonable generation potential for liquid hydrocarbons (Kanev et al., 1994; Poprawa, 2010b). During the Late Ordovician – Silurian, the PBLB represented the foredeep of the Caledonian collision zone, where organic-rich shales with a low amount of coarser siliciclastics were deposited under anoxic conditions in a marine environment (Poprawa et al., 1999). The detrital influx from the hinterland increased later in the Silurian, leading to progressive dilution of the organic-rich marine sediments. Therefore, the Lower Silurian black shales are considered as the most promising target for unconventional production in the PBLB (PGI, 2012).

### 1.3.3 Carboniferous shales at the northern margin of the Variscides (e.g. Germany, Belgium)

Carboniferous sediments were deposited along the northern foreland of the Variscides from Ireland to Poland. Previous investigations identified a northern calcareous shelf facies, grading into a deeper basinal facies north of the Variscian orogen (Schulz et al., 2010). In an early stage, the Variscian Mountains were the main source of sediment charge of the northern foreland deeps, while organic-rich mudstones of the so-called Culm facies were deposited in times of high bioproduction (Schulz, et al., 2010). The most prominent black shale horizon is the Tournaisian Lower Alum shale, hosting TOC contents of up to 10 % (Siegmund et al., 2002). Later on during Upper Visean and Serpukhovian times, the Upper Alum shale was deposited under conditions similar to the Tournaisian (Schulz et al., 2010). The Serpukhovian Upper Alum shale of Germany is fairly rich in TOC, with contents up to 3 % in some areas (Zimmerle & Stribrny, 1992).

Although previous studies proved a reasonable hydrocarbon potential of the Carboniferous successions, detailed investigations on shale gas potential are mostly lacking. However, especially along the northeastern margin of the North German Basin, calcareous Lower Carboniferous and siliciclastic Upper Carboniferous successions have been studied for their suitability for unconventional production by many authors (Hoth, 1997; Friberg, 2001; Schretzenmayr, 2004; Rempel et al., 2009; Hartwig et al., 2010). The Lower Carboniferous (Tournaisian – Visean) mudstones drilled in the Mecklenburg-Vorpomerania area exhibit an extraordinary thickness of up to 2000 m, with average TOC contents >0.8 % over a cumulated interval of 1000 m (Schretzenmayr, 2004). The Upper Carboniferous strata in the same region, drilled in exploration wells mainly located on the island of Rügen or offshore eastern

Rügen, reaches a total sediment thickness of up to 2500 m, down to burial depths of up to 6900 m (Hartwig et al., 2010). The earliest Upper Carboniferous sediments belong to the Late Namurian, consisting of coastal siliciclastics, overlain by shallow shelf sediments (Hartwig et al., 2010). Younger Westphalian sediments are mainly found in the Strelasund depression in northern Mecklenburg-Vorpomerania (Hartwig et al., 2010). However, Hartwig et al. (2010) reported that despite considerable shale thickness, shale gas potential is generally limited by relatively low TOC contents (mostly <1.0 %TOC on average). According to their investigations, the kerogen is generally of type III, generating gaseous hydrocarbons during pyrolysis. Maturity in some areas with drilled exploration wells is favourable for shale gas production (>1.5 %Rr), whereas in other areas it only reaches the early oil window (0.5 %Rr), due to diverging thermal history, consequently ruling out shale gas production e.g. from Tournaisian and Visean organic-rich intervals in the northern part of Rügen (Hartwig et al., 2010). Deep burial also limits the economic potential in areas where the Lower and Upper Carboniferous rocks reach a reasonable thermal maturity. Therefore, although considerable amounts of gas-in-place can be expected, it is yet unclear if the Carboniferous succession in northeast Germany will have a future in terms of shale gas production. However, some authors argue for a more promising shale facies south and southwest of the areas that were in the focus of previous exploration campaigns (e.g. Friberg, 2001; Gaupp et al., 2008). Especially north of the Renish Massif (e.g. Aachen Basin), Mississippian to Pennsylvanian marine black shales might hold a shale gas potential (Uffmann et al., 2012). The Upper Alum shale (Chokier Fm. in Belgium) is considered particularly promising in terms of shale gas, being comparable to the successful Barnett shale in terms of mineralogy, TOC content, organic matter type and thickness (Uffmann et al., 2012).

Apart from that, the Bowland/Hodder unit in central Britain is also considered a shale gas target of similar quality compared to the successful US plays, often even outplaying its US equivalents in terms of total shale thickness, which reaches up to several thousands of meters in some areas (Andrews, 2013).

### 1.3.4 **Lower & Upper Jurassic shale gas (e.g. Posidonia Shale; Mikulov Marl)**

Early Toarcian black shales, widespread in Europe (Farrimond et al., 1989), often are rich in marine organic matter (Schouten et al., 2000) and occasionally host TOC contents up to 19 % (Schulz et al., 2010). Their hydrocarbon generation potential is proven, as they have been identified as the source of conventional deposits in many basins with active production (e.g. Lower Saxony Basin; Dill et al., 2008). The TOC-rich and several tens of metres thick Posidonia Shale of the Lower Saxony Basin, largely varying in maturity, is one of the most prominent and well-investigated black shale intervals of the Early Toarcian.

In the Upper Jurassic, the Mikulov Formation („Mikulov Marl“) and its equivalents are proven source rocks for conventional hydrocarbon deposits e.g. in the Vienna Basin (Ladwein, 1988; Picha & Peters, 1998). Apart from that, a large potential for shale gas in the Vienna Basin is suggested by Langanger (2008). TOC contents of the interval with a maximum thickness in excess of 1500 m are occasionally as high as 10 %, with a type III-II kerogen composition (Ladwein et al., 1991). However, shale gas maturity is reached at considerable depths of >5000 m (Fisher, 2008). Gas kicks from Mikulov Marls have been reported from deep wells >7000 m (Wessely, 1990), probably a result of natural fracturing due to pressure increase during advanced gas generation (Schulz et al., 2010).

In general, younger gas shales, e.g. the Lower Cretaceous Wealden Shale abundant in the Lower Saxony Basin (Rippen et al., 2013) often are lacking the necessary thermal maturity over a sufficiently wide lateral extent, diminishing suitability for unconventional production (Boyer et al., 2011) despite of a considerable inherent hydrocarbon potential (Rippen et al., 2013).

# 2. Geology of the Dniepr-Donets Basin

## 2.1 Geological setting

The Dniepr-Donets Basin (DDB) is a Late Devonian rift-basin, located within the East-European Craton (Fig. 4a,b) mainly in the Ukraine. It is approximately 650 km long, surrounded by the Pripyat Trough to the northwest and the Donbas Foldbelt to the southeast. The southwestern and northeastern borders are formed by the Ukrainian Shield, as well as the Voronezh Massif in Russia, respectively. Three cross-sections illustrated in Fig. 5 show the southeastward deepening of the basin. Chrono- and lithostratigraphy of the DDB are shown in Fig. 6.

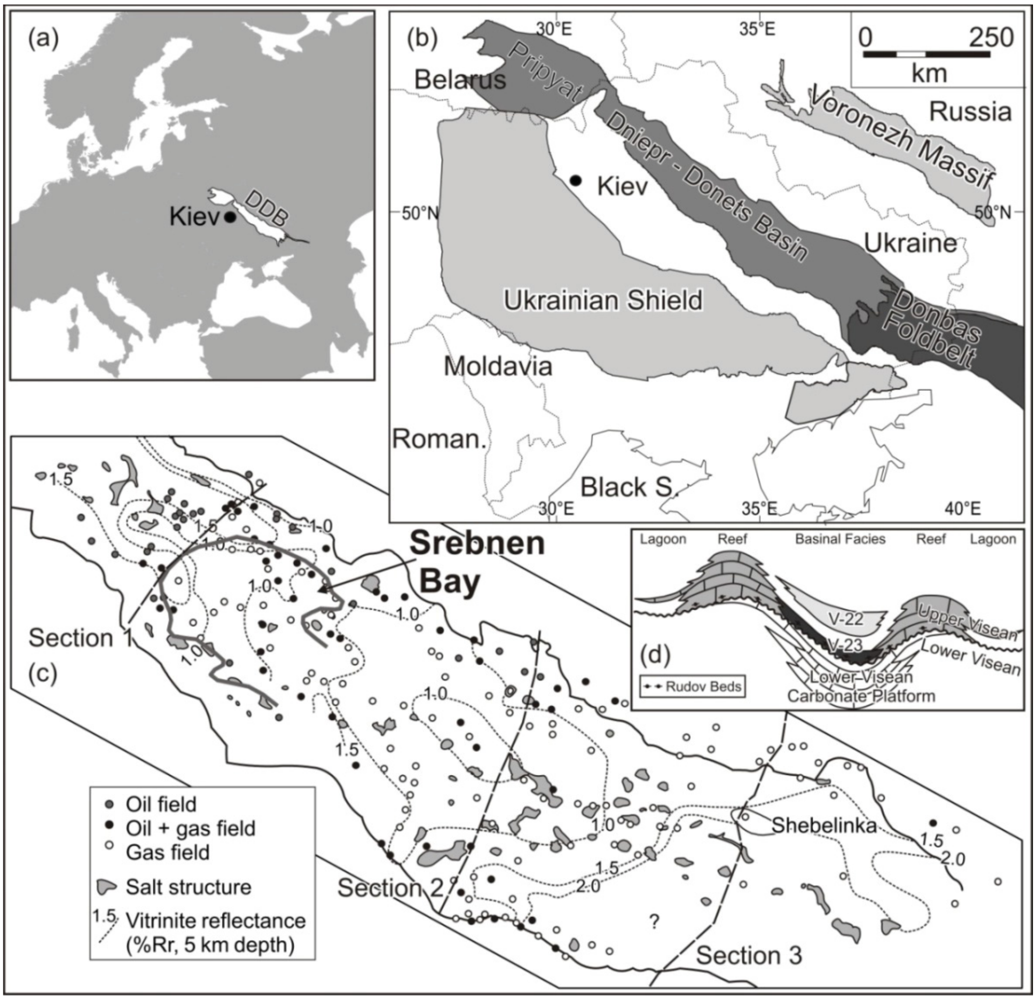


**Fig. 4:** (a), (b) Regional setting of the Dniepr-Donets-Basin (DDB) in Eastern Europe. (c) Location of salt structures and oil and gas fields in the northeastern and central DDB. Contour lines indicate vitrinite reflectance (%Rr) at 5000 m below sea-level (after Shpak, 1989 and Shymanovskyy et al., 2004). Dashed lines indicate position of cross sections 1-3 (d) Schematic cross section of the Srebnen Depression with position of Rudov Beds (V-23) overlying a Lower Visean carbonate platform in the depression center (after Babko et al., 2003).

Middle Devonian terrestrial and shallow-marine pre-rift deposits represent the oldest strata in the DDB (Fig. 6). These successions are about 300 to 400 m thick, comprising clastic and carbonate rocks deposited under terrestrial and shallow-marine conditions (Sachsenhofer et al., 2010). Late Devonian (Late Frasnian – Famennian) syn-rift sediments, up to 4 km thick, include clastic deposits, carbonate rocks and extensive salt (Kabyshev et al., 1998). Devonian salt is deformed to salt domes and plugs (Stovba & Stephenson 2003). Syn-rift volcanic and associated pyroclastic rocks attain a thickness of 2 km (Wilson & Lyashkevich 1996).

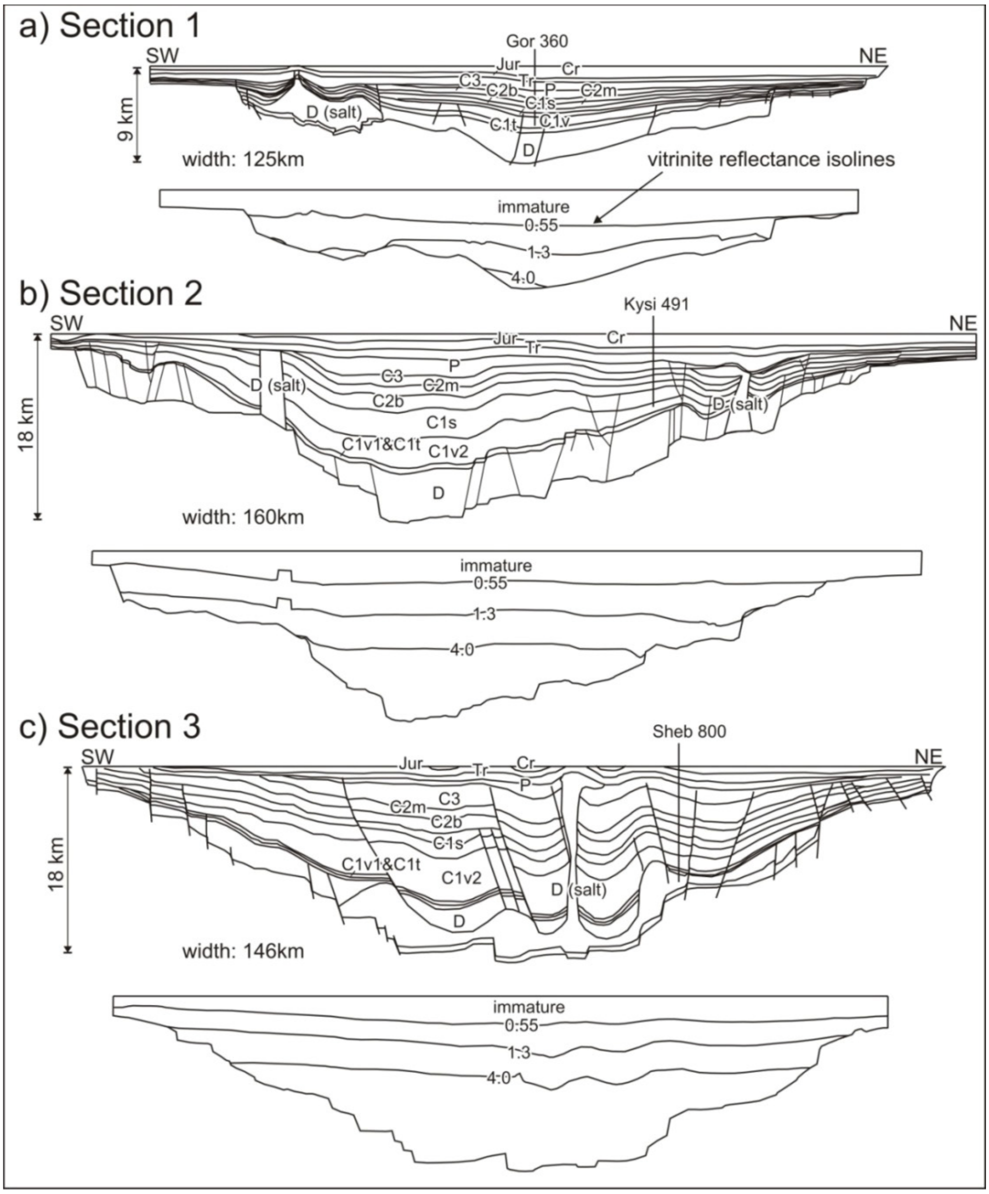


**Fig. 5:** Cross-sections through the Dniepr-Donets Basin (after Kivshik et al., 1993; Stovba & Stephenson, 2003; Ivanyuta et al., 1998). Locations of sections 1 to 3 are shown in Fig. 1c. Position of iso-reflectivity lines follows Mohsenian (2013).

The Carboniferous post-rift succession with a maximum thickness in excess of 10 km is represented by continental deposits in the northwestern DDB and by cyclic successions of siliciclastic and minor carbonate rocks deposited in fluvial, shallow-marine and lagoonal environments elsewhere. Water depth was typically low and exceeded 200 m only in the axial part of the basin. The architecture of the Carboniferous succession reflects short-term transgressive-regressive cycles controlled by tectonics and eustatic sea-level fluctuations (Dvorjanin et al., 1996). These cycles, up to 50 m in thickness, usually include a sand interval ("productive unit") and a shallow marine, organic-rich shale interval. The "Rudov Beds" (up to 70 m thick), form the base of the Upper Visean section and mark the most prominent black shale horizon. Basin-wide Lower Visean and Bashkirian carbonate platforms were the result of major transgressions from the southeast (Dvorjanin et al., 1996; Fig. 6). The Lower Serpukhovian succession is dominated by fine-grained lithologies. The percentage of fluvial and deltaic sands increases in the Upper Serpukhovian succession. Lacustrine environments prevailed in the northwestern DDB during Serpukhovian time, whereas marine environments existed in its southeastern part (Dvorjanin et al., 1996). Serpukhovian to Moscovian coal seams are extensively mined in the Donbas Foldbelt, but extend also into the DDB. Clastic deposits, carbonate rocks and evaporite rocks prevail in the Permian section. The Mesozoic section, comprising terrestrial and marine deposits, unconformably overlies the Paleozoic series. Another unconformity separates Mesozoic from up to 500 m thick Cenozoic rocks.

## 2.2 Petroleum Habitat

With more than 220 explored fields and known reserves of slightly more than 11.5 x $10^9$ barrels of oil equivalent, of which 86% is gas (Petroconsultants, 1996 in Ulmishek, 2001), the DDB is a major petroleum province of Eastern Europe. The shallow northwestern part is dominantly hosting oil deposits, whereas gas deposits prevail in the deeper central and southeastern part of the basin. The largest producing field so far is the giant Shebelinka gas-condensate field, located in the central part of the basin.

**Source rocks** occur in different stratigraphic intervals within the Paleozoic section and have been described by Kabyshev et al. (1999) and Sachsenhofer et al. (2010). The following review is based on the latter paper.

In analogy to the Pripyat Trough, Devonian rocks have been considered a major source rock in the DDB (Ulmishek, 2001). Rare available information shows that TOC contents may reach 2.4 %, but are typically low. Moreover, HI of immature, organic matter-rich rocks in the northeastern part of the DDB is only about 200 mgHC/gTOC (Kabyshev et al., 1999). Nevertheless, the presence of hydrocarbon shows in rocks beneath Devonian salt may be an additional hint to a Devonian source (S. Kitchka, pers. comm.).

Coal occurs in the northeastern part of the DDB in Tournaisian and Lower Visean horizons, but mudstones with high TOC contents occur as well.

The Upper Visean section comprises black shales containing kerogen type III-II in several horizons (Kabyshev et al., 1999; Sachsenhofer et al., 2010). Although their precise stratigraphic definition is still under discussion, the "Rudov Beds" (V-23), overlying the Lower Visean carbonate platform with an unconformity (Kitchka et al., 2013), are considered as the main source rock (e.g. Gavrish et al., 1994; Ulmishek, 2001; Machulina & Babko, 2004; Sachsenhofer et al., 2010). Rudov Beds are several tens of metres thick and show remarkably high TOC contents (~5.0 %). However, according to the HI values below 300 mgHC/gTOC (Kabyshev et al., 1999), these rocks are rather gas- than oil-prone.

The Rudov facies occurs within the Srebnen Depression in a low-energy basin surrounded by a reef belt. This structure was termed "Srebnen Mega-Atoll" (Fig. 4c,d) by Lukin et al. (1994). Because this structure is not related to any volcanic seamount, the term "Srebnen Bay" instead of Mega-Atoll seems to be more appropriate.

The Rudov facies occurs within the Srebnen Bay, a low-energy basin surrounded by a reef belt (Fig. 4c,d; Lukin et al., 1994), which was formed during early Late Visean time. The Srebnen Bay is located within the Srebnen Depression. Information on the source rock facies of the V-23 horizon outside of the Srebnen Bay is rare, partly due to its considerable depths exceeding 6000 m in the central and southeastern DDB.

The Serpukhovian section includes potential source rocks with different facies. Serpukhovian rocks with TOC contents ranging from 1 % to 4 % and HI values up to 300 mgHC/gTOC occur in several wells. Highly oil-prone source rocks with high TOC contents (up to 16 %) and HI values (up to 550 mgHC/gTOC) are so far known only from the northwestern part of the basin. Intercalated oil-prone coal layers occur in the same area, but Serpukhovian coal is widespread along the south(eastern) basin margin, where it is mined west and south of the city of Donetsk (Sachsenhofer et al., 2012).

Pelitic rocks in Bashkirian and Moscovian horizons typically have TOC contents up to 1.5 %, although higher values occur as well. Coal seams are widespread in the southeastern part of the DDB and are extensively mined there (Sachsenhofer et al., 2003).

Oil window maturity (~0.65 %Rr) is reached at around 3500 m depth (Fig. 5). A general vitrinite reflectance map for 5000 m depth is shown in Fig. 4c. Whereas vitrinite reflectance at that depth is typically low (partly <1.0 %Rr), higher values occur in the inverted SE part of the DDB (Shymanovskyy et al., 2004; Sachsenhofer et al., 2012). Hydrocarbon generation occurred predominantly during Permian deep burial, according to basin modeling studies carried out by Shymanovskyy et al. (2004). Additionally, a potential generation of hydrocarbons is suggested for Mesozoic to Cenozoic burial stages.

**Hydrocarbon reservoirs** are termed “productive horizons” and labelled according to a code reflecting their stratigraphic position (Fig. 6). Carboniferous and Permian clastic rocks are the dominant reservoir lithology (Ulmishek, 2001). Small quantities of hydrocarbons occur in Lower Carboniferous and Lower Permian carbonates. Oil fields prevail in the northwestern part of the basin as well as along the basin flanks, filled mostly due to vertical petroleum migration. Devonian salt domes often produced faulted uplifts, hosting Carboniferous to Lower Permian reservoirs (Sachsenhofer et al., 2010), which are often sealed by Permian salt. The oils are commonly light in grade (35-45° API) and low in sulfur (<0.5 %). Gas deposits prevail along the basin axis. The gases are usually wet, free of $H_2S$ and contain minor amounts of nitrogen (~2 %) and $CO_2$ (~1 %; Ivanyuta et al., 1998).

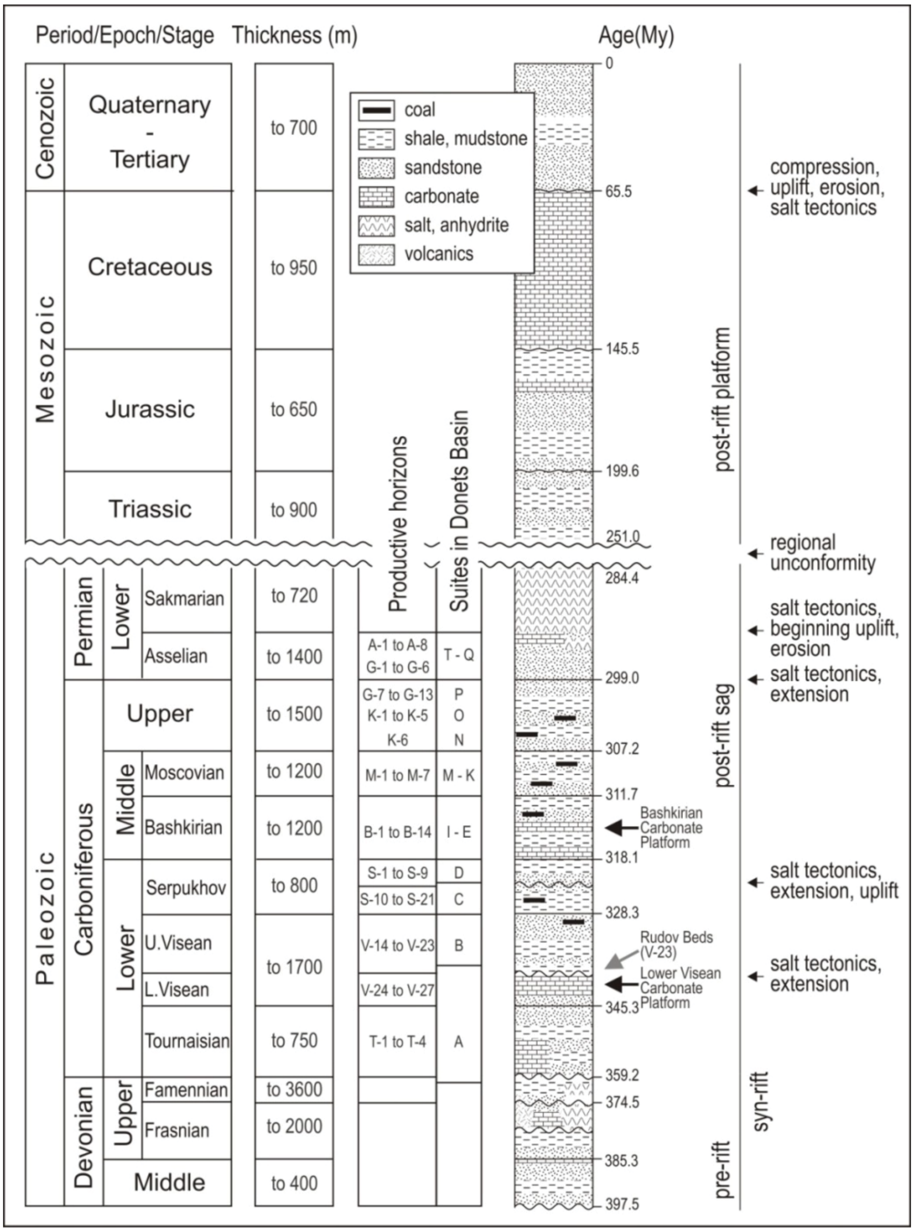


**Fig. 6:** Chrono- and lithostratigraphy of the Paleozoic succession of the Dniepr-Donets Basin (Sachsenhofer et al., 2010). Age data follow Gradstein et al. (2004). Information on "productive horizons" is shown according to Lukin in Ivanyuta et al. (1988).

# 3. Samples and Methods

The study is mainly based on core samples from wells of the DDB were Upper Visean intervals have been drilled. Because of limited access to local core stores, the study is based on two different sample sets representing the V-23 interval (Rudov Beds). In the Chernigiv core store, 206 black shale samples were collected from 10 wells drilled in the northwestern DDB. These samples have been taken at 1 to 2 m intervals. Because the stratigraphic assignment is ambiguous, bottom and top of “Rudov Beds” have been picked differently in well logs. Therefore some samples from the upper and lower parts of productive horizons V-24 and V-22, respectively, have been added to the sample set. In addition, Lower Visean samples from well Moshkovska-1 have been investigated. Apart from that, 109 core samples from 43 wells with Rudov Beds were provided by the Ukrainian State Geological Institute (UkrSGI) for analysis in the Leoben lab. Those samples represent a larger part of the DDB although they do not provide the same vertical resolution as the above-mentioned sample set from key wells. For oil-source correlation, 24 additional core samples were chosen from a previous sampling campaign, partly representing other potentially important hydrocarbon source rocks in the DDB. These samples have been re-investigated within the frame of this study. Apart from that, 13 oil/condensate samples from 12 producing fields with Lower Visean to Moscovian reservoir horizons have been investigated. As access to oil samples is limited due to the political situation in the Ukraine, these data have been supplemented by datasets from the USGS Energy Geochemistry Data Base (USGS, 2009), including molecular and carbon stable isotopic composition of 14 oil samples, exclusive carbon stable isotope composition of another 29 oil samples, as well as molecular and isotopic composition of 18 gas samples.

In the following, all analytical methods, used for a detailed characterization of the investigated rocks and oil/condensate samples, are described. Obviously, not all methods have been applied to the whole set of rock samples, as they are often very expensive and time consuming. Therefore, it is important to note that a more detailed description of the analytical procedures can be found in the samples & methods sections of the journal publications related to this thesis.

**<u>Carbon and sulphur analyses</u>**

All rock samples were analysed in duplicate for total sulphur (S), total carbon (C), and total organic carbon (TOC, after acidification of samples to remove carbonate) using an Eltra Helios analyzer to analyze roughly 100 mg of analytical powder per measurement run. The difference between C and TOC is the total inorganic carbon (TIC). TIC contents were used to calculate calcite equivalent (calcite equ.) percentages using the formula TIC*8.34.

**<u>Rock Eval pyrolysis</u>**

For a first estimation of the hydrocarbon generation potential, Rock Eval pyrolysis was performed on all investigated rock samples, using a Vinci Rock Eval 2+ pyrolyzer. Roughly 70-90 mg of analytical powder were used for a single measurement run, all samples were measured in duplicate and mean values of these measurements were used for interpretation. The S1 and S2 peaks [mg HC/g rock] were recorded and used to calculate the Hydrogen-Index (HI = S2*100/TOC [mg HC/g TOC]) and the Production-Index (PI = S1/(S1+S2); Espitalié et al., 1977). As a maturation indicator, the temperature of maximum hydrocarbon generation (Tmax) was measured.

**<u>X-ray diffraction analyses (XRD)</u>**

X-ray diffraction (XRD) measurements of texture-free and textured powder mounts were done following established procedures (Brunton, 1955). Measurement parameters were set at a goniometer speed rate of 0.5 °2θ/minute and a registration range from 2 to 66 °2θ. Particularly for the analyses of clay minerals, textured mounts were measured four times at a goniometer speed rate of 0.5°θ/minute with a registration range from 2 to 42 °2θ in the following order: (1) in untreated condition, (2) after solvation with ethylene glycol (12 h, 60°C), after thermal treatment (2 h) at (3) 350°C and (4) at 550°C. The quantification followed the method of Schultz (Schultz, 1964). The results were cross-checked using the ADM software (Version 6.22) of Wassermann Röntgenanalytik (Germany) which is based on the Rietveld method. To verify the quantitative analysis, a comparison between the percentage-composition based on XRD-data of the shale samples, XRD-data of quartz standards and data of calcimeter measurements in accordance with the method of Scheibler (ON L 1084-99) took place.

**Organic petrography**

For maturity assessment, vitrinite reflectance was determined in non-polarized light at a wavelength of 546 nm on samples prepared as polished blocks, using a Leitz DM optical microscope equipped with an 100x oil objective and following established procedures (Taylor et al., 1998). To maximize the representativeness of investigations, samples were cut perpendicular to the bedding planes and embedded into epoxy resin, so that a cross-section through the bedding is visible. In addition to vitrinite reflectance, the maceral composition (liptinite, vitrinite, inertinite, solid bitumen) was determined using the “single-scan” method on 300 randomly distributed points in conventional white and UV light (Taylor et al., 1998).

**Biomarker analyses**

Representative portions of the selected rock samples were extracted for approximately 1 h using dichloromethane in a Dionex ASE 200 accelerated solvent extractor at 75°C and 75 bar. After evaporation of the solvent to 0.5 ml total solution in a Zymark TurboVap 500 closed cell concentrator, asphaltenes were precipitated from a hexane-dichlormethane solution (80:1) and separated using centrifugation. The hexane-soluble fractions were separated into NSO compounds and saturated plus aromatic hydrocarbons, which were separated again, using medium-pressure liquid chromatography (MPLC) with a Köhnen-Willsch instrument (Radke et al., 1984). Oil samples (ca. 60 mg) were diluted with a hexane-dichloromethane (80:1) mixture and the insoluble asphaltenes were separated by centrifugation. The fractions of the hexane-soluble organic matter were separated into polar compounds, saturated hydrocarbons, and aromatic hydrocarbons by medium-pressure liquid chromatography using a Köhnen-Willsch MPLC instrument (Radke et al., 1984). Condensates were diluted in *n*-pentane and subjected to the gas-chromatographic analyses (GC-MS) without further pre-treatment.

The total hydrocarbons of condensate samples, as well as the saturated and aromatic hydrocarbon fractions of oils and source rock extracts were analyzed with a gas chromatograph equipped with a 30 m DB-5 MS fused silica capillary column (i.e. 0.25 mm; 0.25 µm film thickness) and coupled to a ThermoFisher ISQ quadrupol mass spectrometer. The oven temperature was programmed from 70° to 300°C at 4°C $min^{-1}$, followed by an isothermal period of 15 min. Helium was used as carrier gas. The sample was injected splitless, with the injector temperature at 275°C. The spectrometer was operated in the EI (electron ionisation) mode over a scan range from m/z 50 to m/z 650 (0.7 s total scan time). Data were processed with an Xcalibur data system. Individual compounds were identified on the basis of retention time in the total ion current (TIC) chromatogram and comparison of the mass spectra with published data. Relative percentages and absolute concentrations of different compound groups in the saturated and aromatic hydrocarbon fractions were calculated using peak areas in the TIC chromatograms in relation to those of internal standards (deuteriated *n*-tetracosane and 1,1´-binaphthyl, respectively), or by integration of peak areas in appropriate mass chromatograms using response factors to correct for the intensities of the fragment ion used for quantification of the total ion abundance.

**Pyrolysis gas chromatography (Py-GC)**

Pyrolysis gas chromatography was carried out on immature to mature samples in order to infer bulk petroleum quality. The analyses were performed in the geochemical lab of GFZ Potsdam, using the Quantum MSSV-2 Thermal Analysis System©. Thermally extracted (300°C; 10 minutes) whole rock samples were heated in a flow of helium, and products released over the temperature range of 300-600°C (40 K/min) were focussed using a cryogenic trap, and then analysed using a 50 m x 0.32 mm capillary column (J&W Scientific

HP-Ultra 1 [Dimethylpolysiloxan-phase], 0.52 µm film thickness) heated from 30 to 320°C at 5°C/min and a flame ionisation detector. The GC oven temperature was programmed from 40°C to 320°C at 8°C/minute. Boiling ranges ($C_1$, $C_2$-$C_5$, $C_6$-$C_{14}$, $C_{15+}$) and individual compounds (*n*-alkenes, *n*-alkanes, alkylaromatic hydrocarbons and alkylthiophenes) were quantified by external standardisation using *n*-butane. Response factors for all compounds were assumed the same, except for methane whose response factor was 1.1.

**Bulk kinetic experiments**

Bulk kinetic parameters of rock samples were determined by non-isothermal open system pyrolysis at four different laboratory heating rates (0.7, 2.0, 5.0 and 15 K/min) using a Source Rock Analyzer©. The generated bulk petroleum formation curves serve as input for the bulk kinetic model consisting of an activation energy distribution and a single frequency factor.

**Bulk and compound specific stable isotope geochemistry**

Carbon isotope determination of *n*-alkanes and acyclic isoprenoids was performed using a Trace GC instrument attached to a ThermoFisher DELTA-V isotope ratio mass spectrometer via a combustion interface (GC isolink, ThermoFisher). For calibration, $CO_2$ was injected at the beginning and end of each analysis. The GC column and temperature programmes are the same as for GC-MS. Stable isotope ratios are reported in delta notation ($\delta^{13}C$) relative to the Vienna-Pee Dee Belemnite (V-PDB) standard ($\delta^{13}C=[(^{13}C/^{12}C)sample/(^{13}C/^{12}C)standard-1]$). Delta notation is expressed in parts per thousand or per mil (‰). For bulk carbon isotope analyses of the saturated and aromatic hydrocarbon fractions, the samples were placed into tin foil boats and combusted using an elemental analyzer (Flash EA 1112) at 1020°C in an excess of oxygen. The resulting $CO_2$, separated by column chromatography, was analyzed online by the DELTA V ir-MS, mentioned above. The $^{13}C/^{12}C$ isotope ratios of the $CO_2$ were compared with the corresponding ratio in a monitoring gas, calibrated against the V-PDB standard by the NBS-19 reference material. The reproducibility of the total analytical procedure is in the range of 0.1 – 0.2 ‰.

**Conventional scanning electron microscopy (SEM)**

For conventional SEM investigations, freshly broken surfaces of rock samples have been coated with an Au layer to enhance conductivity. To prevent charging effects, relatively even surfaces were chosen for investigation. Investigations were conducted with a Zeiss Evo MA 10 SEM, equipped with a secondary electron (SE) and a backscattered electron (BSE) detector, as well as a Bruker Nano XFlash 430M energy-dispersive X-ray (EDX) detector.

**Broad ion beam/focused ion beam - scanning electron microscopy (BIB/FIB-SEM)**

For high resolution-SEM on largely artefact-free surfaces, specimen surfaces were prepared using a Jeol IB-09010 broad ion beam (BIB) cross-section polisher with an Ar ion beam (5kV; 6h), followed by a tungsten coating to make the specimen conductive for high resolution imaging. BIB-SEM allows the investigation of damage-free microstructures over comparably large areas (>1 $mm^2$). For FIB-SEM investigations, regions of interest were selected from the BIB cross-sections. Afterwards, a FEI Versa 3D Dual Focused Ion Beam microscope was used for a manual 3D tomography of selected volumes. The particular area of interest was polished serially with a Ga ion beam at 30 kV for 30 s at low current (10 pA or less), to create an image stack. With the electron beam of the microscope, the image surface was investigated at 5 kV and 10 kV using SE and BSE detectors. The gradient distribution of pores to depth within the organic matter can be obtained by progressive ion polishing and image capturing. EDX analysis on OM-hosted mineral phases was done with an Octane Silicon Drift detector (SDD) from EDAX and a Genesis software package. In order to decrease the interacting volume, measurements were performed with 6 kV.

**1D Thermal Modelling**

1D modelling of thermal histories was performed using the PetroMod 1D software of Schlumberger. Input data for the thermal models include the thickness of stratigraphic units, the physical properties of their lithologies and the temporal evolution of the heat flow at the base of the sedimentary sequence, as well as the temperature at the sediment-water interface.

Physical parameters for different lithologies pre-defined in the software were used, the pressure outflow factor for lithotypes including evaporitic rocks was set at 100%. The applied timescale follows Gradstein et al. (2004). The above-mentioned information was used to reconstruct decompacted subsidence histories and the temperature field through time. The models were calibrated by modifying the heat flow until a satisfactory fit between measured and calculated formation temperatures, vitrinite reflectance and biomarker ratios (sterane and hopane isomerisation; steroid aromatization; calibration data from Sachsenhofer et al., 2010 and own data) was reached. Vitrinite reflectance was calculated using the kinetic EASY%Ro approach (Sweeney & Burnham, 1990). Biomarker ratios were calculated using kinetic data from Rullkötter & Marzi (1988).

# 4. Summary of publications and innovative aspects of the presented results

Note: Detailed information on author contributions to the publications mentioned below is given in appendix I.

### 4.1 Publication I: Oil/Gas-Source Rock Correlations in the Dniepr-Donets Basin (Ukraine): New insights into the Petroleum System

This publication targets an oil-source rock correlation particularly in the northwestern part of the DDB, where the TOC-rich Rudov facies is abundant in the so-called Srebnen Bay, a vast syncline surrounded by a reef belt. Although the most promising source rocks of the DDB have been generally described in the past (e.g. Sachsenhofer et al., 2010), a laterally well resolved biomarker study is lacking. By now, only Ruble (1996) and Ruble et al. (1997) attempted a correlation between liquid hydrocarbons and source rock extracts, within the frame of an US Geological Survey exploration study. In his study, Ruble stated that a Devonian source is responsible for oils with light bulk carbon isotopic composition and low pristane/phytane (Pr/Ph), whereas Carboniferous rocks yield oils with comparably heavy isotopic composition and higher Pr/Ph ratios.

Within the frame of this study, molecular and isotopic compositions determined for oil/condensate samples and source rock extracts were used together with USGS data for a detailed oil-source correlation. A major contribution of a Devonian source could be ruled out for the northwestern DDB, mainly because TOC-rich samples are lacking in wells were Devonian mudstones were drilled. In contrast, it could be proven by biomarker ratios and stable isotope geochemistry performed on source rock extracts and oil/condensate samples, that Upper Visean black shales partly yield liquid hydrocarbons with comparably light carbon stable isotopic composition and low Pr/Ph, as stated for Devonian rocks and oils by Ruble (1996). Taking into account the significantly higher average TOC of the Upper Visean succession, the oil window maturity as well as the lateral and vertical extent of these layers in the Srebnen Bay and the central DDB, it is reasonable to assume that the Upper Visean represents the main source rock in the region. Apart from that, a correlation was found between the isotopic composition of aliphatic compounds in oils and methane in gas samples investigated within the frame of the USGS study. It is therefore suggested that both might originate from a similar (Upper Visean) source. Furthermore, two distinct oil families with overlapping molecular and isotopic composition could be proven. Biomarkers and stable carbon isotopic composition of aliphatic and aromatic compounds, as well as the fact that both Visean and oil-prone Serpukhovian rocks hold a potential to generate low-sulphur, low-wax paraffinic-aromatic-naphtenic oil according to open pyrolysis experiments, argue for a mixed contribution of these intervals, with minor contribution of isotopically heavier oils from the Tournaisian. Important to note, that Visean source rock extracts at comparable maturity gradually vary in $\delta^{13}C$ and Pr/Ph, whereas two distinct organic facies are indicated in the Serpukhovian by light and heavy clusters of $\delta^{13}C$. Therefore, both Visean and Serpukhovian intervals might contribute to both oil families, requiring field-scale interpretation for a reliable oil-source correlation. Therefore, geochemical data was combined with detailed structural information on producing oil and gas fields, for an estimation of migration distances. While data on oil maturity and oil-source correlation suggest that fields in the northwestern DDB typically have been charged from local sources and that lateral and vertical hydrocarbon migration distances are short, results point to significant vertical migration distances up to >4000 m in many fields especially in the central DDB, although locally sourced hydrocarbons also exist there.

1-D thermal models indicate hydrocarbon generation during Permo-Carboniferous time, although Mesozoic generation might have occurred in coal-bearing Middle Carboniferous horizons in the SE part of the basin.

<u>Note:</u> Gas chromatograms of total hydrocarbons of condensate samples and of saturated and aromatic hydrocarbon fractions of oils are shown in appendix II, whereas chromatograms of saturated and aromatic hydrocarbon fractions of extracts from selected Rudov samples are shown in appendix III.

## 4.2 Publication II: Shale Gas / Shale Oil Potential of Upper Visean Black Shales in the Dniepr-Donets Basin (Ukraine)

In contrast to the publication described above, this paper focuses on the suitability of the Upper Visean for shale oil/gas production. Unconventional production requires certain thresholds for formation thickness, TOC content, amount of brittle minerals and thermal maturity. Therefore, a laterally well-resolved sample set is necessary for an accurate quality prediction of a shale gas target. Within the frame of this study, more than 300 source rock samples have been investigated for bulk geochemical parameters, whereas sufficient subsets of samples have been chosen for additional geochemical (open pyrolysis, kinetics), mineralogical (XRD, SEM) and petrographical (maceral percentages, vitrinite reflectance) investigations.

The most prolific Upper Visean sections occur within the Srebnen Bay, with >4 %TOC on average over considerable thickness up to 100 m. Average TOC contents of wells north and northwest of the Srebnen Bay are significantly lower (<4 %), but still in the range of 2-4 %TOC over a relatively wide lateral extend. Although the shale thickness is generally lower in this part of the basin (usually 20-40 m), it still reaches up to 60 m in some areas. In contrast, well from the northeastern basin margin do not hold a shale oil/gas potential in terms of organic matter richness. Regarding oil generation potential, pyrolysis experiments revealed an oil potential for basinal Upper Visean samples from the Srebnen Bay, although hydrogen indices of the least mature samples do not exceed 300 mgHC/gTOC, arguing for predominating type III(/II) kerogen. However, although a clear maturity trend is visible in pyrolysis measurements, facies zones with different organic matter composition could still be distinguished. Whereas the basinal facies is richer in type II kerogen, the marginal samples host predominant terrestrial (type III) kerogen, generating mainly short-chained compounds during pyrolysis. Organic petrography revealed that marginal samples are sometimes rich in inertinite, probably a result of syn-depositional wildfires in the Carboniferous.

The cut-off maturity for shale oil production (usually about 0.8 %Rr) is reached only in considerable depths along the basin axis (> 4-4.5 km), arguing for a relatively low heat flow during burial. This agrees with the presence of expandable clay minerals down to depths of 5000 m. Gas window maturity, necessary for shale gas production, is not reached in Upper Visean mudstones of the northwestern DDB at all, and only reached along the basin axis in the central part of the basin as well as in the southeastern part. The presence of type IIs kerogen, potentially triggering earlier hydrocarbon generation, cannot be assumed considering results of bulk kinetic experiments.

Laterally and vertically well-resolved data on bulk mineralogy (> 100 samples) was acquired within the frame of this study and revealed a strongly heterogeneous composition of Rudov Beds in both lateral and vertical directions. Therefore, the concept of clear facies zones throughout the basin (Gavrish et al., 1994; Machulina & Babko, 2004) is questionable. As shale brittleness is a key quality parameter for unconventional production, the finding that basinal Rudov Beds, termed as siliceous according to the facies zone model (Machulina & Babko, 2004), might be as well clay-dominated, has important implications for further exploration. Nevertheless, the bulk amount of brittle minerals is usually higher in basinal compared to marginal samples, and SEM investigations revealed a more layered fabric for marginal shales while basinal samples seem to host a higher amount of microcrystalline quartz, probably a result of a higher contribution of deeper-water radiolaria. However, the desired value of 60 wt.% brittle minerals is reached only partly by samples from the siliceous (basinal) facies, while it is almost not reached by samples from the transitional and lagoonal (clayey & calcareous) facies. Furthermore, the clay mineral fraction within most investigated Rudov samples is dominated by kaolinite, which is suggested to diminish the fraccability of shales. In summary, the assessment of all quality parameters leave it questionable if Rudov Beds and adjacent Upper Visean intervals are an economic target for unconventional production, although they clearly hold a potential for shale oil/gas to some extent.

Note: X-ray diffractograms of selected Rudov samples investigated during this study are shown in appendix IV.

### 4.3 Publication III: SEM and FIB-SEM investigations on potential gas shales in the Dniepr-Donets Basin (Ukraine): Pore space evolution in organic matter during thermal maturation

This publication targets a characterization of organic matter-hosted pore space in Upper Visean black shales and its evolution with thermal maturity. Despite major achievements in the investigation of OM-hosted pores in the nanometer scale (e.g. Curtis et al, 2012a,b; Bernard et al., 2012a,b; Klaver et al., 2012, 2015a), storage capacity and production behaviour of gas shales are still poorly understood. Visualization of nanopores from conventionally (mechanically) polished surfaces is impossible, whereas FIB-SEM techniques as well as sample preparation with a BIB ion-milling device generate undisturbed surfaces without preparation-induced artefacts, allowing imaging of nanopores in the range of >5-10 nm in equivalent diameter. Such pores might contribute largely to hydrocarbon storage capacity and release behaviour. Many authors suggest the generation of OM-hosted porosity to be related primarily to thermal maturation of kerogen (e.g. Loucks et al., 2009), causing the formation of nanoporous (pyro)bitumen (Curtis et al., 2012a,b; Bernard et al., 2012a,b), whereas several studies take into consideration that even primary kerogen might host nanoscale pores (Reed et al., 2014). The influence of kerogen type (Lu et al., 2015) as well as TOC content (Milliken et al., 2013) is controversially discussed.

Most recent studies focus on well investigated shale gas targets (e.g. Barnett Shale), hosting mainly type II or even mixed type II/I kerogen. However, apart from that, enormous potential might also be related to considerably more widespread targets hosting a vitrinite-dominated (mixed type III-II) kerogen, comparable to the Upper Visean succession in the DDB. If, at which maturity, and to which amount, nanopores form within primary or secondary organic matter especially in mixed type III/II kerogen with terrestrially dominated organofacies is by now understudied. Taking into account the high TOC contents (average 5.5 %) and original hydrogen index values of 270 mgHC/gTOC, the Upper Visean “Rudov Beds” (V-23) in the DDB offer a unique possibility to study organic-rich rocks with a kerogen type III-II at different maturities. Therefore, this contribution focused on the investigation of organic matter-porosity in these black shales with increasing thermal maturity and varying amount of oil-prone type II kerogen. Results suggest that OM-hosted nanopores are restricted to secondary (pyro)bitumen, formed during generation and release of hydrocarbons. Interestingly, OM-pores form already at oil-window maturity (0.65 – 0.8 %Rr), which contradicts findings from many other publications in the field. This implies that kerogen composition has a strong influence on the timing of pore generation in organic matter. However, the main generation of nanopores starts at advanced maturity (>1.4-1.6 %Rr). Pore sizes increase drastically within the dry gas window, as isolated, bubble-shaped nanopores merge to form connected, irregular pores in the µm-range. An interdependence between TOC and OM-porosity, as suggested by Milliken et al. (2013), was not found for the investigated sample set. 2D high resolution mapping (SEI, BSE, EDX), performed on BIB-milled samples using a FE-SEM, revealed that although organic matter-porosity might be an important indicator for the present amount of gas and also contributing to the storage capacity to some extent, the main pore space in most of the Upper Visean shales from the DDB is likely intra-clay mineral porosity. Compared to younger, well-studied shale gas targets (e.g. Posidonia Shale), advanced compaction seems to be more critical in case of Rudov Beds, drastically reducing mineral matrix porosity and, likely, also permeability.

During FIB-SEM analysis, authigenic mineral phases grown in secondary bitumen have been detected for the first time. EDX measurements enabled the identification of platy phases as clay minerals (Si, Al, K, Mg, Ti), whereas nodules (Ca, C, O) where interpreted as authigenic calcite. Such phases are useful for the understanding of OM-mineral interactions during diagenesis, as they can provide information about changes in pore fluid geochemistry during bitumen formation and will also help to distinguish between different types of bitumen.

### 4.4 List of conference contributions related to this thesis

Misch, D., Bechtel, A., Gratzer, R., Makogon, V., Prigarina, T., Sachsenhofer, R.F. (2014) Oil-source rock and gas-source rock correlations in the Dniepr Donets Basin (Ukraine): Preliminary results. AAPG International Conference and Exhibition (Poster Presentation), Istanbul, Turkey.

Misch, D., Wegerer, E., Makogon, V., Prigarina, T., Sachsenhofer, R.F., Scheucher, L. (2014) Mineralogical composition of Late Devonian to Carboniferous rocks of the Srebnen Depression – Dniepr Donets Basin, Ukraine (Poster Presentation). 19th International Sedimentological Congress, Geneva, Switzerland.

Misch, D., Wegerer, E., Scheucher, L. (2014) Clay-mineral composition of black shales from the Dniepr-Donets Basin, Ukraine (Poster Presentation).7th Mid-European Clay Conference, Dresden, Germany.

Misch, D., Gross, D., Mendez Martin, F., Onuk, P., Sachsenhofer, R.F. (2015) Micro- and Nanoscale Investigations on Gas Shales from the Dniepr Donets Basin (Ukraine): Implications for Shale Gas Potential (Poster & Oral Presentation).14th EMAS European Workshop, Portoroz, Slovenia.

Misch, D., Mendez-Martin, F., Klaver, J., Gross, D., Hawranek, G., Schmatz, J., Sachsenhofer, R.F. (2015) EPMA, BIB-SEM and FIB-SEM Investigations on Gas Shales from the Dniepr Donets Basin (Ukraine): Evolution of Micro- and Nanoscale Porosity during Thermal Maturation (Oral Presentation). 4th ACA Conference of the Serbian Ceramic Society – New Frontiers in Multifunctional Material Science and Processing, Belgrade, Serbia.

Misch, D., Sachsenhofer, R.F., Gross, D., Mahlstedt, N., Bechtel, A. (2016) Conventional and Unconventional Petroleum System in the Dniepr-Donets Basin, Ukraine (Extended Abstract & Oral Presentation). 78th EAGE Conference & Exhibition 2016, Vienna, Austria.

Misch, D., Klaver, J., Gross, D., Schmatz, J., Sachsenhofer, R.F., Mendez-Martin, F. (2016) Nanostructural Investigations on Potential Gas Shales of the Dniepr-Donets Basin, Ukraine (Extended Abstract & Oral Presentation).78th EAGE Conference & Exhibition 2016, Vienna, Austria.

Selected posters related to this thesis are shown in appendix V.

# 5. General conclusions and outlook

In this section, the research highlights related to this thesis are summarized. The thesis contributes to a better understanding of both conventional and unconventional (shale oil/gas) hydrocarbon plays in the DDB.

**Implications for conventional oil and gas deposits**

As described above, oil-source rock correlation has been successfully carried out for numerous fields in the northwestern and central DDB. The study confirmed the importance of Upper Visean as well as highly oil-prone Serpukhovian shales as a hydrocarbon source, whereas a major contribution from the Devonian could be ruled out. The suitability of combined biomarker and stable isotope geochemistry for oil source correlation could be proven. Apart from that, likely migration pathways as well as timing of hydrocarbon generation could be determined. In summary, this study contributed to a better understanding of the conventional petroleum system present in the DDB, with a special focus on source rock geochemistry as well as molecular and isotopic composition of yielded hydrocarbons.

**Implications for unconventional (shale oil/gas) hydrocarbon production**

Within the frame of this study, important insights could be drawn for future shale oil/gas exploration especially in the northwestern DDB. Although it could be proven by pyrolysis experiments that Upper Visean black shales from the basin center (Srebnen Bay) tend to generate low-wax P-N-A oils, TOC contents are high (>4 %TOC on average) and thickness often exceeds 60-80 m, the shale oil/gas potential has to be rated questionable, the main reason for this being partly disadvantageous mineralogy and a comparably low maturity gradient to depth. Therefore, drilling costs and difficulties in terms of well stimulation might impede future economic shale oil/gas production in the DDB. Nevertheless, a certain potential could be proven, which argues for further studies to enhance the lateral resolution throughout the basin. This particularly includes a better characterization of the basinal facies that is obviously more rich in oil-prone type II kerogen, compared to the more terrestrially influenced marginal counterparts. A difference in organic facies also could be shown by high-resolution BIB/FIB-SEM, showing that oil-prone endmembers tend to show organic matter-hosted nanoporosity in an earlier maturity stage (0.65 – 0.8 %Rr) compared to predominantly gas-prone samples (1.3-1.5 %Rr). Interestingly, transformation of primary kerogen to secondary solid bitumen triggered the formation of bitumen-hosted mineral phases, which have not been described so far.

Many open questions have been resolved within the frame of this thesis. However, as research in the field of applied geosciences is always an iterative process, suggestions for future work on the multi-source, multi-reservoir petroleum systems of the DDB are intended to bring the general part of this thesis to a close.

Clearly, future work on oil-source correlation should include a higher amount of oil/condensate samples, as the political situation in the Ukraine decreased the availability of samples from active production during the time when the work for this thesis was performed. Apart from that, additional sampling would have been beneficial for a better characterization of highly oil-prone Serpukhovian rocks, to better define their lateral distribution in the central part of the basin. However, it is questionable if additional core information on these intervals actually exists so far.

Modelling of the thermal basin history should be extended from 1 and 2D to a more accurate 3D model, to better characterize the local influence of Devonian salt structures on thermal fields and source rock maturity.

Work on the micro-/nanostructure of Upper Visean black shales hosting a mixed type III/II kerogen should be extended, as this touches fundamental aspects of shale geology and likely provides important insights for the understanding of the production behaviour of shale oil/gas targets. In particular, the gas storage capacity of intra-clay porosity in the sub-micrometer range should be investigated by adsorption measurements. As these are very time consuming and cost-intensive, they could not be performed within the frame of this study. However, a correlation between (clay) mineralogy, p-T-conditions, fluid saturation and adsorption behaviour would be highly interesting. Apart from that, a better definition of pore/mineral growth in secondary bitumen, related to (1) the primary kerogen type and (2) the compositional evolution of solid bitumen would be desirable. Additional methods like high lateral resolution secondary ion mass spectrometry (Nano-SIMS) could be used complementary to high resolution-imaging techniques like FIB-SEM or transmission electron microscopy (TEM). First in-situ geochemical investigations on organic matter yielded promising results, showing that light element (C, O, S) and trace element concentrations might vary considerably within a single maceral group of one sample. Apart from that, according to these experiments, maceral compositions might be more sensitive to changes in the depositional environment (e.g. high-sulphur environments) than previously thought, causing differences in bitumen composition during thermal transformation of organic matter in a later stage.

New methods are currently developed to better characterize the permeability of shales (e.g. Woods-Metal-Injection; Klaver et al., 2015b) as well as their mechanical properties in relation to bulk mineralogy, porosity, etc. (e.g. use of nano indenters). Future research should include a more intense cooperation of materials sciences (e.g. functional ceramics) and applied geosciences, as entering the nanoscale brings up many parallels between both fields.

## 6. References

Alexander, R., Larcher, A.V., Kagi, R.I., Price, P.L., 1992. An oil-source correlation study using age specific plant-derived aromatic biomarkers. In: Moldowan, M.J., Albrecht, P., Philip, P.R. (Eds.), Biological Markers in Sediments and Petroleum. Prentice-Hall, Englewood Cliffs, N.J., pp. 201–221.

Andrews, I.J., 2013. The Carboniferous Bowland Shale gas study: geology and resource estimation. British Geological Survey Report for the Department of Energy and Climate Change, London, UK.

Andruleit, H., Babies, H.G., Cramer ,B., Messner, J., Rempel, H., Schlömer, S., Schmidt, S., 2010. Nicht-konventionelles Erdgas: Weltweite Ressourcen und Entwicklungen eines „Hoffnungsträgers“ unter den fossilen Energierohstoffen. Erdöl, Erdgas, Kohle, 126 (7/8), 277-282.

Artyushkov, E.V., Lindström, M., Popov, L.E., 2000. Relative sea-level changes in Baltoscandia in the Cambrian and early Ordovician: the predominance of tectonic factors and the absence of large scale eustatic fluctuations. Tectonophysics, 320, 375-407.

Babko, I.M., Gontcharov, V.E., Kononenko, L.P., 2003. Modern view on carbonate deposits near the base of the Visean stage in the Dniepr–Donets Basin [in Ukrainian]. Mineral Resources of Ukraine, 2003, 20–25.

Bernard, S., Wirth, R., Schreiber, A., Schulz, H.M., Horsfield, B., 2012a. Formation of nanoporous pyrobitumen residues during maturation of the Barnett Shale (Forth Worth Basin). International Journal of Coal Geology, 103, 3-11.

Bernard, S., Horsfield, B., Schulz, H.-M., Wirth, R., Schreiber, A., Sherwood, N., 2012b. Geochemical evolution of organic-rich shales with increasing maturity: A STXM and TEM study of the Posidonia Shale (Lower Toarcian, northern Germany). Marine and Petroleum Geology, 31, 70-89.

Boyer, C., Clark, B., Jochen, V., Lewis, R., Miller, C.K., 2011. Shale Gas: A Global Resource. Schlumberger Oilfield Review, 23 (3), 28-39.

Brunton, G., 1955. Vapor pressure glycolation of oriented clay minerals. American Mineralogist, 40, 124-126.

Buchardt, B., 1999. Gas Potential of the Cambro-Ordovician Alum Shale in Southern Scandinavia and the Baltic Region. In: Whiticar, M.J., Faber, E. (Eds.), The Search for Deep Gas Selected. Papers presented at the I.E.A./BMFT International Deep Gas Workshop, Hannover. Geologisches Jahrbuch, Reihe D, 107, 9-24.

Bustin, R.M., Bustin, A., Ross, D., Chalmers, G., Murthy, V., Laxmi, C., Cui, X., 2009. Shale Gas Opportunities and Challenges. American Association of Petroleum Geologists - Search and Discovery Article #40382 (2009).

Carpentier, R.R., Cook, T.A., 2011. USGS Methodology for Assessing Continuous Petroleum Resources. U.S. Geological Survey Open-File Report 2011-1167.

Curtis, M.E., Sondergeld, C.H., Ambrose, R.J., Rai, C.S., 2012a. Microstructural investigation of gas shales in two and three dimensions using nanometer-scale resolution imaging. AAPG Bulletin, 96 (4), 665-677.

Curtis, M.E., Cardott, B.J., Sondergeld, C.H., Rai, C.S., 2012b. Development of organic porosity in the Woodford Shale with increasing thermal maturity. International Journal of Coal Geology, 103, 26-31.

Dill, H. G., Sachsenhofer, R. et al., 2008. The origin of mineral and energy resources of Central Europe II. In: McCann, T. (ed.) Geology of Central Europe. Geological Society, London, Special Publications, 1341-1449.

Dvorjanin, E.S., Samoilyuk, A.P., Egurnova, M.G., Zaykovsky, N.Y., Podladchikov, Y.Y., van den Belt, F.J.G., de Boer, P.L., 1996. Sedimentary cycles and paleogeography of the Dnieper Donets Basin during the late Visean-Serpukhovian based on multiscale analysis of well logs. Tectonophysics 268, 169-187.

Dyni, J.R., 2006. Geology and resources of some world oil-shale deposits. US Geological Survey Scientific Investigations Report 2005-5294. http://pubs.usgs.gov/sir/2005/5294/pdf/sir5294_508.pdf.

Espitalié, J., LaPorte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Méthode rapide de characterisation des roches mères de leur potential pétrolier et de leur degree d'evolution. Revue de l'Institut Francais du Pétrole, 32, 23–42.

Farrimond, P., Eglinton, G., Brassell, S. C., 1989. Toarcian anoxic event in Europe: an organic geochemical study. Marine and Petroleum Geology, 6, 136-147.

Fisher, T., 2008. Austria turns to unconventional, shale gas. International Gas Report, 596, 7-8.

Friberg, L.J., 2001. Untersuchungen zur Temperatur- und Absenkungsgeschichte sowie zur Bildung und Migration von Methan und molekularem Stickstoff im Nordostdeutschen Becken. Berichte des Forschungszentrums Jülich, 3914. Forschungszentrum Jülich GmbH-Zentralbibliothek, Jülich.

Gaupp, R., Möller, P., Lüders, V., di Primio, R., Littke, R., 2008. Fluids in sedimentary basins: an overview. In: Littke, R., Bayer, U., Gajewski, D., Nelskamp, S. (Eds.), Dynamics of Complex Intracontinental Basins-The Central European Basin System. Springer-Verlag, Berlin-Heidelberg, 345-365.

Gavrish, V.K., Machulina, S.A., Kurilenko, V.S., 1994. Visean oil-source formation of the Dnieper-Donets basin. Doklady Akademii Nauk Ukrainy 7, 92-95.

Gradstein, F., Ogg, J., Smith, A., 2004. A Geological Time Scale 2004. Cambridge University Press, Cambridge.

Hartwig, A., Könitzer, S., Boucsein, B., Horsfield, B., Schulz, H.-M., 2010. Applying classical shale gas evaluation concepts to Germany-Part II: Carboniferous in Northeast Germany. Chemie der Erde, 70 (S3), 93-106.

Hester, R.E, Harrison, R.M. (eds.), 2015. Issues in Environmental Science and Technology Vol. 39 – Fracking. Royal Society of Chemistry, Cambridge, 228pp.

Horsfield, B., Bharati, S., Larter, S. R., Leistner, F., Littke, R., Schenk, H. J., Dypvik, H., 1992. On the atypical petroleum-generating characteristics of alginite in the Cambrian Alum Shale. In: Schidlowski, M. et al. (eds) Early Organic Evolution: Implications for Mineral and Energy Resources. Springer, Berlin, 257-266.

Horsfield, B., Schulz, H.-M., Kapp, I., 2012. Shale Gas in Europe. American Association of Petroleum Geologists - Search and Discovery Article #10380 (2012).

Horsfield, B., 1989. Practical criteria for classifying kerogens: some observations from pyrolysis-gas chromatography. Geochim. Cosmochim. Acta 53, 891-901.

Hoth, P., 1997. Fazies und Diagenese von Präperm-Sedimenten der Geotraverse Harz-Rügen. Verlag der Gesellschaft für Geowissenschaften e.V., Berlin.

Ivanyuta, M.M., Fedyshyn, V.O., Denega, B.I., Arsiriy, Y.O., Lazaruk, Y.G., 1998. Atlas of oil and gas fields of Ukraine. Six volumes. Ukrainian Oil and Gas Academy, Lviv.

Jarvie, D.M., 2012. Shale resource systems for oil and gas: Part 1 - Shale-gas resource systems, in J. A. Breyer (ed.). Shale reservoirs - Giant resources for the 21st century. AAPG Memoir, 97, 69-87.

Jarvie, D.M., Hill, R.J., Ruble, T.E., Pollastro, R.M., 2007. Unconventional shale-gas systems: the Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment. AAPG Bulletin, 91 (4), 475-499.

Kabyshev, B., Krivchenkov, B., Stovba, S., Ziegler, P.A., 1998. Hydrocarbon habitat of the Dniepr–Donets Depression. Marine and Petroleum Geology, 15, 177–190.

Kabyshev, B.P., Kabyshev, Y.B., Krivosheev, V.T., Prigarina, T.M., Ulmishek, G.F., 1999. Oil-gas-generating characteristics of Paleozoic rocks of the Dniepr-Donets Basin based on Rock-Eval pyrolysis [Russian]. Reports of the National Academy of Sciences of Ukraine 12, 112-117.

Kanev, S., Margulis, L., Bojesen-Koefoed, J.A., Weil, W.A., Merta, H., Zdanavičiūtė, O., 1994.Oils and hydrocarbon source rocks of the Baltic syneclise. Oil and Gas Journal, 92, 69-73.

Kitchka, A.A., Vakarchuk, S.G., Dovzhok, T.E., Prykhodchenko. O.E., 2013. Hydrothermal Reservoirs - New Exploration Life for the Mississippian Carbonate Platform, the Dnieper-Donets Basin. Proceedings of the 75th EAGE Conference & Exhibition, paper Tu 09 10, London, UK, 10-13 June 2013.

Kivshik, M. K., Stovba, S. M., Turchanenko, M. T., and Redkolis, V. A., 1993. The Regional Seismostratigraphic Investigations in the Dniepr-Donets Depression (in Russian). Ukrgeofisika, Kiev, 84 p.

Klaver, J., Desbois, G., Urai, J.L., Littke, R., 2012. BIB-SEM study of the pore space morphology in early mature Posidonia Shale from the Hils area, Germany. International Journal of Coal Geology, 103, 12-25.

Klaver, J., Desbois, G., Littke, R., Urai, J.L., 2015a. BIB-SEM characterization of pore morphology and distribution in postmature to overmature samples from the Haynesville and Bossier Shales. Marine and Petroleum Geology, 59, 451-466.

Klaver, J., Hemes, S., Houben, M., Desbois, G., Radi, Z., Urai, J.L., 2015b. The connectivity of pore space in mudstones: insights from high-pressure Wood's metal injection, BIB-SEM imaging, and mercury intrusion porosimetry. Geofluids, doi: 10.1111/gfl.12128.

Ladwein, W. 1988. Organic geochemistry of Vienna Basin: model for hydrocarbon generation in overthrust belts. American Association of Petroleum Geologists Bulletin, 72, 586–599.

Ladwein, W., Schmidt, F., Seifert, P. & Wessely, G. 1991. Geodynamics and generation of hydrocarbons in the region of the Vienna basin, Austria. In: Spencer, A. M. (ed.) Generation, Accumulation, and Production of Europe's Hydrocarbons. Oxford University Press, Oxford, 289–305.

Langanger, H. 2008. Exploration and Production. OMV Capital Markets Day 2008, London. http://www.omv.com/SecurityServlet/secure?cid=1225986876259&lang= de&swa_site=wps.vp.com&swa_nav=OMV+Holding%7C%7CInvestor +Relations%7C%7CEvents%7C%7CCapital+Markets+ Day+ 2008%7C%7C&swa_pid= 6_B_QFO þ %5BCONTENT_NODE%3A3096224743844344%5D&swa_lang=de.

Loucks, R.G., Reed, R.M., Ruppel, S.C., Jarvie, D.M., 2009. Morphology, genesis, and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett Shale. J. Sediment. Res., 79, 848-861.

Lukin, A.E., Shpak, P.F., Chepil, P.M., Machulina, S.A., 1994. Visean Srebnin megaatoll of the Dnieper-Donets basin and its petroleum potential. Doklady Akademii Nauk Ukrainy, 8, 101-104.

Lu, J., Ruppel, S.C., Rowe, H.D., 2015. Organic matter pores and oil generation in the Tuscaloosa marine shale. AAPG Bulletin, 99 (2), 333-357.

Machulina, S.A., Babko, I.M., 2004. On the geology of Visean Domanik-type rocks in the Dniepr-Donetsk Depression (in Ukrainian). Naft.i gasova prom-st. 5, 3-8.

McCarthy, K., Rojas, K., Niemann, M., Palmowski, D., Peters, K., Stankiewicz, A., 2011. Basic Petroleum Geochemistry for Source Rock Evaluation. Schlumberger Oilfield Review, 23 (2), 32-43.

Milliken, K.L., Rudnicki, M., Awwiller, D.N., Zhang, T., 2013. Organic matter-hosted pore system, Marcellus Formation (Devonian), Pennsylvania. AAPG Bulletin, 97 (2), 177-200.

Mohsenian, E., 2013. Multidimensional Basin Modeling in the Central Persian Gulf basin (offshore Iran) and the Dniepr-Donets basin (Ukraine), PhD thesis Montanuniversitaet Leoben, 200 pp.

Nielsen, A.T., 1995. Trilobite systematics, biostratigraphy and palaeoecology of the Lower Ordovician Komstad Limestone and Huk Formations, southern Scandinavia. Fossils and Strata 38, 1–374.

Nielsen, A. T., Schovsbo, N.H., 2007. Cambrian to basal Ordovician lithostratigraphy in southern Scandinavia. Bulletin of the Geological Society of Denmark, 53, 47-92.

Petroconsultants, 1996. Petroleum exploration and production database. Petroconsultants, Inc., PO Box 740619, 6600 Sands Point Drive, Houston TX 77274-0619, USA or Petroconsultants, Inc., PO Box 152, 24 Chemin de la Mairie, 1258 Perly, Geneva.

PGI, 2012.Assessment of Shale Gas and Shale Oil Resources of the Lower Paleozoic Baltic-Podlasie-Lublin Basin in Poland-First Report. Published Exploration Report of the Polish Geological Institute, 29p.

Picha, F.J., Peters, K.E., 1998. Biomarker oil-to-source rock correlation in the Western Carpathians and their foreland, Czech Republic. Petroleum Geoscience, 4, 289-302.

Poprawa, P., 2006. Unconventional gas fields - the outline of exploration potential in Poland. Unpublished Report of the Polish Geological Institute for the Department of Geology and Geological Concessions at Ministry of Environment, 1-13.

Poprawa, P., 2010a. Preliminary evaluation of potential for shale oil exploration in the Lower Paleozoic and other shale source rocks in Poland. Unpublished Report of the Polish Geological Institute for the Department of Geology and Geological Concessions at Ministry of Environment, 1-21.

Poprawa, P., 2010b. Potencjał występowania złóż gazu ziemnego w łupkach dolnego paleozoiku w basenie bałtyckim i lubelsko-podlaskim. Przegląd Geologiczny, 58(3), 226-249.

Poprawa, P., Šliaupa, S., Stephenson, R.A., Lazauskienė, J., 1999. Late Vendian-Early Palaeozoic tectonic evolution of the Baltic Basin: regional implications from subsidence analysis. Tectonophysics, 314, 219-239.

Radke, M., Leythaeuser, D., Teichmüller, M., 1984. Relationship between rank and composition of aromatic hydrocarbons for coal of different origins. Organic Geochemistry 6, 423-430.

Reed, R.M., Loucks, R.G., Ruppel, S.C., 2012. Comment on „Formation of nanoporous pyrobitumen residues during maturation of the Barnett Shale (Fort Worth Basin)“ by Bernard et al. (2012). International Journal of Coal Geology, 127, 111-113.

Rempel, H., Schlömer, S., Schmidt, S., Andruleit, H., 2009. Erdgas. In: Cramer, B., Andruleit, H. (Eds.), Energierohstoffe 2009 Reserven, Ressourcen,Verfügbarkeit. Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover, pp. 284.

Rippen, D., Littke, R., Bruns, B., Mahlstedt, N., 2013. Organic geochemistry and petrography of Lower Cretaceous Wealden black shales of the Lower Saxony Basin: The transition from lacustrine oil shales to gas shales. Organic Geochemistry, 63, 18-36.

Ruble, T.E., 1996.Attachment III: Petroleum Geochemistry of the Dniepr-Donets Basin, Ukraine. Unpublished USGS report, 7 pp.

Ruble, T.E., Clayton, J.L., Warden, A., Daws, G.F., Ulmishek, B.P., Kabyshev, 1997.Petroleum Geochemistry of the Dnieper-Donets Basin, Ukraine. 1997 AAPG Annual Convention, Dallas, Texas, AAPG Search and Discovery Article #91021©

Rullkötter, J., Marzi, R., 1988. Natural and artificial maturation of biological markers in a Toarcian shale from northern Germany. Org. Geochem. 13, 639-645.

Rybacki, E., Reinicke, A., Meier, T., Makasi, M., Dresen, G., 2014. What controls the strength and brittleness of shale rocks? Geophysical Research Abstracts, 16, EGU 2014-1877.

Sachsenhofer, R.F., Privalov, V.A., Izart, A., Elie, M., Kortensky, J., Panova, E.A., Sotirov, A., Zhykalyak, M.V., 2003. Petrography and geochemistry of Carboniferous coal seams in the Donets Basin (Ukraine): implications for paleoecology. International Journal of Coal Geology, 55, 225-259.

Sachsenhofer, R.F., Shymanovskyy, V.A., Bechtel, A., Gratzer, R., Horsfield, B., Reischenbacher, D., 2010. Paleozoic Source Rocks in the Dniepr-Donets Basin (Ukraine). Petroleum Geoscience, 16, 377-399.

Sachsenhofer, R.F., Koltun, Y.V., 2012. Black shales in Ukraine – A review. Marine and Petroleum Geology, 31, 125-136.

Sachsenhofer, R.F., Privalov, V.A., Panova, E.A., 2012. Basin evolution and coal geology of the Donets Basin (Ukraine, Russia): An overview. International Journal of Coal Geology, 89, 26-40.

Schouten, S., van Kaam-Peters, H.M.E., Rijpstra, W.I.C., Schoell, M., Sinninghe Damste, J. S., 2000. Effects of an oceanic anoxic event on the stable carbon isotopic composition of early Toarcian carbon. American Journal of Science, 300, 1-22.

Schretzenmayr, S., 2004. Erdöl und Erdgas. In: Katzung, G. (Ed.), Geologie von Mecklenburg-Vorpommern. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

Schultz, L.G., 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre shale. US Geol. Surv. Prof. Pap. 391-C, 1–31.

Schovsbo, N.H., 2003. The geochemistry of Lower Palaeozoic sediments deposited on the margins of Baltica. Bulletin of the Geological Society of Denmark, 50, 11–27.

Schulz, H.-M., Horsfield, B., Sachsenhofer, R.F., 2010. Shale gas in Europe: a regional overview and current research activities. In: Vining, B.A., Pickering, S.C. (Eds.), Petroleum Geology: From Mature Basins to New Frontiers-Proceedings of the 7th Petroleum Geology Conference. Geological Society, London, 1079-1085.

Shpak, P.F. (ed.), 1989. Geology and petroleum productivity of the Dniepr-Donetsk depression - petroleum productivity [Russian]. Naukova Dumka, Kiev.

Shymanovskyy, V.A., Sachsenhofer, R.F., Izart, A., Li, Y., 2004. Modelling of the thermal evolution of the northwestern Dniepr-Donets Basin (Ukraine). Tectonophysics 381, 61-79.

Siegmund, H., Trappe, J., Oschmann, W., 2002. Sequence stratigraphic and genetic aspects of the Tournaisian 'Liegender Alaunschiefer' and adjacent beds. International Journal of Earth Sciences, 91, 934-949.

Stovba, S.M., Stephenson, R.A., 2003. Style and timing of salt tectonics in the Dniepr-Donets Basin (Ukraine): implications for triggering and driving mechanisms of salt movement in sedimentary basins. Marine and Petroleum Geology, 19, 1169-1189.

Sweeney, J.J., Burnham, A.K., 1990. Evaluation of a simple model of vitrinite reflectance based on chemical kinetics. Am. Assoc. Pet. Geol. Bull. 74, 1559-1570.

Tari, G., 2010. Exploration Country Focus: Ukraine. In: AAPG European Region Newsletter, 5, 4-6. http://www.aapg.org/europe/newsletters/index.cfm.

Taylor, G.H., Teichmüller, M., Davis, A., Diessel, C.F.K., Littke, R., Robert, P., 1998. Organic Petrology. Gebrüder Borntraeger, Berlin.

Tissot, B., Durand, B., Espitalie, J., Combaz, A., 1974. Influence of Nature and Diagenesis of Organic Matter in Formation of Petroleum. AAPG Bulletin, 58 (3), 499-506.

Uffmann, A.K., Littke, R., Rippen, D., 2012. Mineralogy and geochemistry of Mississippian and Lower Pennsylvanian Black Shales at the Northern Margin of the Variscan Mountain Belt (Germany, Belgium). International Journal of Coal Geology, 103, 92-108.

Ulmishek, G.F., 2001. Petroleum Geology and Resources of the Dnieper-Donets Basin, Ukraine and Russia. US Geological Survey Bulletin 2201-E.

USGS, 2009. Energy Geochemistry Data Base. http://energy.cr.usgs.gov/prov/og/index.htm.

Volk, H., Horsfield, B., Mann, U., Suchy, V., 2002. Variability of petroleum inclusions in vein, fossil and vug cements – a geochemical study in the Barrandian Basin (Lower Palaeozoic, Czech Republic). Organic Geochemistry, 33, 1319-1341.

Wessely, G. 1990. Geological results of deep exploration in the Vienna basin. Geologische Rundschau, 79, 513-520.

Wilson, M. & Lyashkevich, Z.M. 1996. Magmatic evolution and the geodynamics of rifting in the Pripyat-Dniepr-Donets rift. Tectonophysics, 268, 65-81.

Zimmerle, W., Stribrny, B., 1992. Organic carbon rich pelitic sediments in the Federal Republic of Germany. Courier Senckenbergsche Naturforschende Gesellschaft, 152, 1-142.

# Journal Publications

# 7. Oil/Gas-Source Rock Correlations in the Dniepr-Donets Basin (Ukraine): New insights into the Petroleum System (Publication I)

Misch, D.[a*], Sachsenhofer, R.F. [a], Bechtel, A. [a], Gratzer, R. [a], Gross, D. [a], Makogon, V. [b]

[a)] Department of Applied Geosciences and Geophysics, Montanuniversitaet Leoben, A-8700

[b)] Ukrainian State Geological Institute (UkrSGI), Chernigiv, Ukraine

Published in:

*Marine and Petroleum Geology 67 (2015), 720 – 742*

*doi:10.1016/j.marpetgeo.2015.07.002*

*Corresponding Author: David.Misch@unileoben.ac.at

Address: Department of Applied Geosciences and Geophysics - Chair of Petroleum Geology, Montanuniversitaet Leoben, Peter-Tunner-Straße 5, A-8700 Leoben

**Key words**: Source Rocks, Hydrocarbons, Biomarkers, Stable Carbon Isotopy, Rudov Beds, Paleozoic, Shebelinka

**Research Highlights**:

- Upper Visean rocks host potential to generate liquid hydrocarbons
- Presence of at least two oil families revealed
- Biomarker data prove multi-source petroleum system
- Main hydrocarbon generation occurred during Permo-Carboniferous time
- Vertical migration distances up to more than 4000 m
- Isotope data from liquid and gaseous hydrocarbons in the northwestern DDB suggests a common source

**ABSTRACT**

The Dniepr Donets Basin (DDB) hosts a multi-source petroleum system with more than 200 oil and gas fields, mainly in Carboniferous clastic rocks. Main aim of the present study was to correlate accumulated hydrocarbons with the most important source rocks and to verify their potential to generate oil and gas. Therefore, molecular and isotopic composition as well as biomarker data obtained from 12 oil and condensate samples and 48 source rock extracts was used together with USGS data for a geological interpretation of hydrocarbon charging history. Within the central DDB, results point to a significant contribution from (Upper) Visean black shales, highly oil-prone as well as mixed oil- and gas-prone Serpukhovian rocks and minor contribution from an additional Tournaisian source. Devonian rocks, an important hydrocarbon source within the Pripyat Trough, have not been identified as a major source within the central DDB. Additional input from Bashkirian to Moscovian (?) (Shebelinka Field) as well as Tournaisian to Lower Visean rocks (e.g. Dovgal Field) with higher contents of terrestrial organic matter is indicated in the SE and NW part, respectively.

Whereas oil-source correlation contradicts major hydrocarbon migration in many cases for Tournaisian to Middle Carboniferous reservoir horizons, accumulations within Upper Carboniferous to Permian reservoirs require vertical migration up to 4000 m along faults related to Devonian salt domes.

1-D thermal models indicate hydrocarbon generation during Permo-Carboniferous time. However, generation in coal-bearing Middle Carboniferous horizons in the SE part of the basin may have occurred during the Mesozoic.

# CONTENT

**1. Introduction** ........ **60**

**2. Geological Setting** ........ **63**

**3. Samples and Methods** ........ **68**

**4. Results** ........ **73**

*4.1 Source rocks* ........ *73*
4.1.1 Bulk Geochemical Parameters ........ 73
4.1.2 Pyrolysis-gas chromatography ........ 78
4.1.3 Molecular composition and biomarkers ........ 79
4.1.4 Isotopic composition of molecular fractions ........ 85

*4.2 Oil and condensate samples* ........ *87*
4.2.1 Molecular composition and biomarkers ........ 87
4.2.2 Isotopic composition of molecular fractions, n-alkanes and isoprenoids ........ 89

*4.3 Thermal history and timing of hydrocarbon generation* ........ *93*

**5. Discussion** ........ **95**

*5.1 Facies related biomarker and isotope ratios of source rock extracts* ........ *95*

*5.2 Oil families and oil-source correlation* ........ *97*

*5.3 Gas formation and alteration* ........ *100*

*5.4 Hydrocarbon generation, migration and accumulation in different parts of the DDB* ........ *103*
5.4.1 Fields in the NW DDB ........ 103
5.4.2 Fields in the central DDB ........ 107
5.4.3 Shebelinka Field ........ 111

**6. Conclusions** ........ **112**

**7. References** ........ **114**

# 1. Introduction

The Dniepr–Donets Basin (DDB) is a Devonian rift-structure, about 650 km long (Fig. 1). With more than 200 explored fields and known reserves of slightly more than 11.5 x $10^9$ barrels of oil equivalent, of which 86% is gas (Petroconsultants 1996 in Ulmishek 2001), the DDB is a major petroleum province in Eastern Europe. The shallow northwestern part is dominantly hosting oil deposits, whereas gas deposits prevail in the deeper central and southeastern part of the basin (Fig. 1c). The largest producing field is the giant Shebelinka gas-condensate field, located in the central part of the basin.

Hydrocarbon fields typically contain multiple reservoirs and are found in Tournaisian to Lower Permian horizons. Upper Carboniferous and Lower Permian levels, often sealed by Lower Permian salt, contain the highest percentage of reserves (57% of gas and 39% of oil), but the highest number of hydrocarbon fields (119) are found in Upper Visean clastic rocks (Ivanyuta et al., 1998). Some fields are also found in the crystalline basement, Devonian, and Mesozoic horizons (Ulmishek 2001).

Sachsenhofer et al. (2010) showed that several horizons host a hydrocarbon source potential. The Upper Visean Rudov Beds contain very high total organic carbon (TOC) contents (average 5.5 %), but only a type III-II kerogen. This classification is supported by high percentages of vitrinite and inertinite macerals. Thus, it is unclear, whether Rudov Beds are prolific sources for liquid hydrocarbons. In contrast, Serpukhovian horizons contain highly oil-prone black shales with up to 16 % TOC, hydrogen index (HI) values up to 550 mgHC/gTOC and high liptinite percentages (Sachsenhofer et al., 2010). In addition, oil-prone Lower Serpukhovian and gas condensate-prone Middle Carboniferous coal is widespread in the southern and southeastern part of the basin. Devonian rocks are the most important source rocks in the Pripyat Trough (Ulmishek et al., 1994). Although no prolific Devonian source intervals have been detected by Sachsenhofer et al. (2010), their presence cannot be excluded.

Considering the huge lateral extension of the basin, the high number of potential source rock and reservoir rock horizons, oil/gas to source rocks correlation is challenging. According to our knowledge, Ruble (U.S. Geological Survey) was the only one who tried to correlate oil and source rocks in the DDB. However, his results are summarized only in an unpublished report (Ruble, 1996) and in a conference abstract (Ruble et al., 1997).

Thus the main deficit in the understanding of the multi-source, multi-reservoir petroleum system in the DDB is oil/gas-source correlation. Most authors (Kabyshev et al., 1998; Ulmishek, 2001, Shymanovskyy et al., 2004) assume that hydrocarbons were generated during Permo-Carboniferous time, however this assumption needs reassurance.

The main aim of this paper is to enhance oil-source correlation in the DDB. Therefore, the potential of relevant source rocks (including Rudov Beds) to generate liquid hydrocarbons was checked and the biomarker and stable carbon isotope compositions of their extracts were determined. In addition, 13 oil/condensate samples from Lower Visean to Moscovian reservoir horizons (5300 - 2400 m depth) were investigated. For the interpretation, source rock data from Sachsenhofer et al. (2010), oil data from Ruble (1996), which are (partly) stored in the USGS Energy Geochemistry Data Base (USGS, 2009), as well as gas data available in the same data base, have also been taken into consideration. 1D models of selected wells have been established to verify the general assumption of Permo-Carboniferous hydrocarbon generation (see Kabyshev et al., 1998; Ulmishek, 2001; Shymanovskyy et al., 2004).

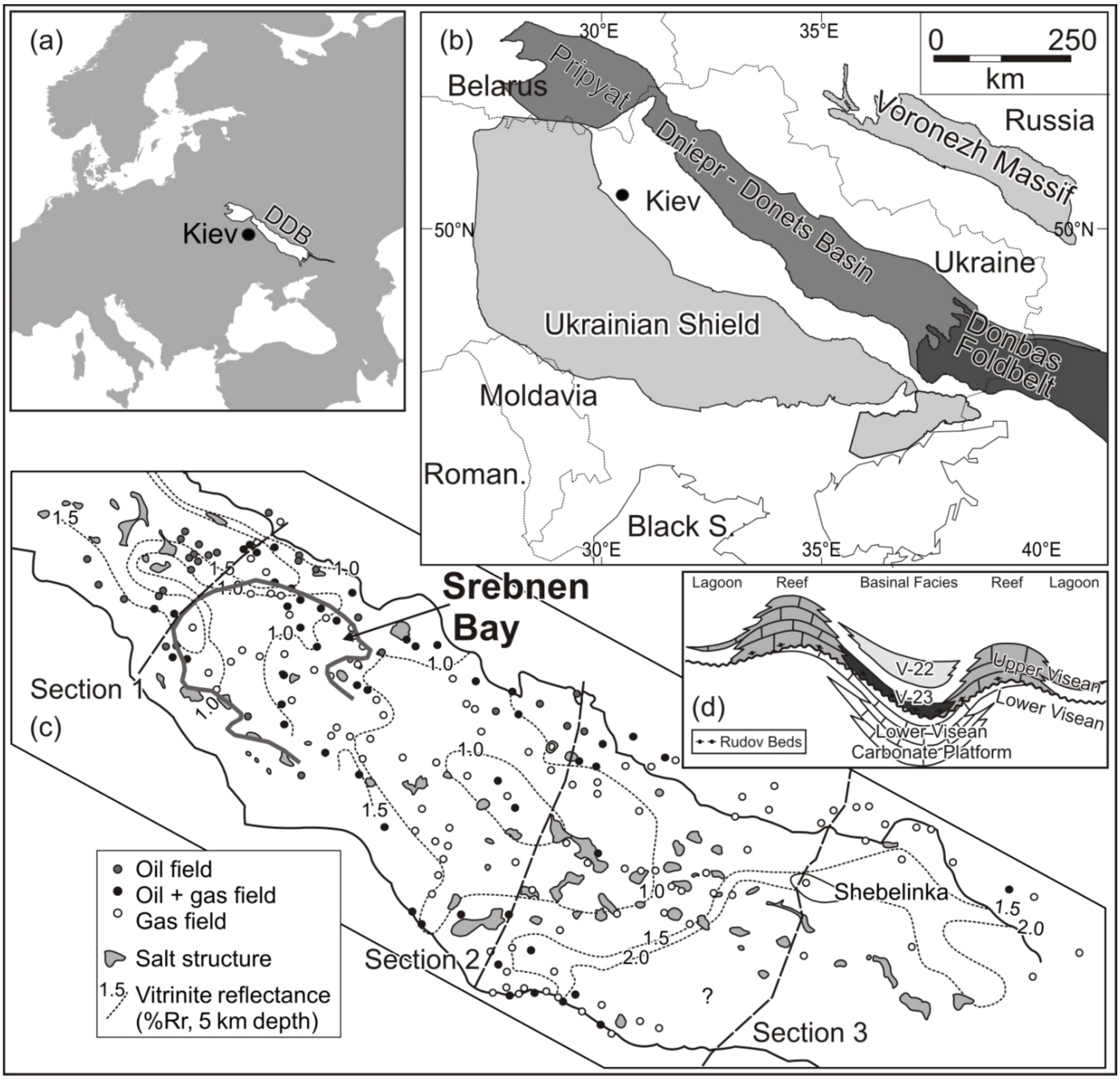


**Fig. 1:** (a), (b) Regional setting of the Dniepr-Donets-Basin (DDB) in Eastern Europe. (c) Location of salt structures and oil and gas fields in the northeastern and central DDB. Contour lines indicate vitrinite reflectance (%Rr) at 5000 m below sea-level (after Shpak, 1989 and Shymanovskyy et al., 2004). Dashed lines indicate position of cross sections 1-3 (d) Schematic cross section of the Srebnen Depression with position of Rudov Beds (V-23) overlying a Lower Visean carbonate platform in the depression center (after Babko et al., 2003).

## 2. Geological Setting

The DDB is a Late Devonian rift-basin, located within the East-European Craton (Fig. 1a,b). Three cross-sections illustrated in Fig. 2 show the southeastward deepening of the basin. Chrono- and lithostratigraphy of the DDB are shown in Fig. 3.

Middle Devonian terrestrial and shallow-marine pre-rift deposits represent the oldest strata in the DDB (Fig. 3). Late Devonian syn-rift sediments, up to 4 km thick, include clastic deposits, carbonate rocks and extensive salt (Kabyshev et al., 1998). Devonian salt is deformed to salt domes and plugs (Stovba & Stephenson 2003). Syn-rift volcanic and associated pyroclastic rocks attain a thickness of 2 km (Wilson & Lyashkevich 1996).

The Carboniferous post-rift succession with a maximum thickness in excess of 10 km is represented by continental deposits in the northwestern DDB and by cyclic successions of siliciclastic and minor carbonate rocks deposited in fluvial, shallow-marine and lagoonal environments elsewhere. Water depth was typically low and exceeded 200 m only in the axial part of the basin. The architecture of the Carboniferous succession reflects short-term transgressive-regressive cycles controlled by tectonics and eustatic sea-level fluctuations (Dvorjanin et al., 1996). Typically each cycle, up to 50 m in thickness, includes a sand interval ("productive unit") and a shallow marine, organic-rich shale interval. The “Rudov Beds” (up to 70 m thick), form the base of the Upper Visean section and mark the most prominent black shale horizon. Basin-wide Lower Visean and Bashkirian carbonate platforms were the result of major transgressions from the southeast (Dvorjanin et al., 1996; Fig. 3). The Lower Serpukhovian succession is dominated by fine-grained lithologies. The percentage of fluvial and deltaic sands increases in the Upper Serpukhovian succession. Lacustrine environments prevailed in the northwestern DDB during Serpukhovian time, whereas marine environments existed in its southeastern part (Dvorjanin et al., 1996). Serpukhovian to Moscovian coal seams are extensively mined in the Donbas Foldbelt, but extend also into the DDB. Clastic deposits, carbonate rocks and evaporite rocks prevail in the Permian section.

The Mesozoic section, comprising terrestrial and marine deposits, unconformably overlies the Paleozoic series. Another unconformity separates Mesozoic from up to 500 m thick Cenozoic rocks.

**Source rocks** occur in different stratigraphic intervals within the Paleozoic section and have been described by Kabyshev et al. (1999) and Sachsenhofer et al. (2010). The following review is based on the latter paper.

In analogy to the Pripyat Trough, Devonian rocks have been considered a major source rock in the DDB (Ulmishek, 2001). Rare available information shows that TOC contents may reach 2.4 %, but are typically low. Moreover, HI of immature, organic matter-rich rocks in the northeastern part of the DDB is only about 200 mgHC/gTOC (Kabyshev et al., 1999). Nevertheless, the presence of hydrocarbon shows in rocks beneath Devonian salt may may be an additional hint to a Devonian source (S. Kitchka, pers. comm.).

Coal occurs in the northeastern part of DDB in Tournaisian and Lower Visean horizons, but mudstones with high TOC contents occur as well.

The Upper Visean section comprises black shales containing kerogen type III-II in several horizons (Kabyshev et al., 1999; Sachsenhofer et al., 2010). Although their precise stratigraphic definition is still under discussion, the “Rudov Beds” (V-23), overlying the Lower Visean carbonate platform with an unconformity (Kitchka et al., 2013), are considered as the main source rock (e.g. Gavrish et al., 1994; Ulmishek, 2001; Machulina & Babko, 2004; Sachsenhofer et al., 2010). Rudov Beds are several tens of metres thick and show remarkably high TOC contents (~5.0 %). However, according to the HI values below 300 mgHC/gTOC (Kabyshev et al., 1999), these rocks are rather gas- than oil-prone.

The Rudov facies occurs within the Srebnen Depression in a low-energy basin surrounded by a reef belt. This structure was termed “Srebnen Mega-Atoll” (Fig. 1c,d) by Lukin et al. (1994). Because this structure is not related to any volcanic seamount, we use the term “Srebnen Bay” instead of Mega-Atoll in the present paper.

The Rudov facies occurs within the Srebnen Bay, a low-energy basin surrounded by a reef belt (Fig. 1c,d; Lukin et al., 1994), which was formed during early Late Visean time. The Srebnen Bay is located within the Srebnen Depression. Information on the source rock facies of the V-23 horizon outside of the Srebnen Bay is rare, partly due to its considerable depths exceeding 6000 m in the central and southeastern DDB.

The Serpukhovian section includes potential source rocks with different facies. Serpukhovian rocks with TOC contents ranging from 1 % to 4 % and HI values up to 300 mgHC/gTOC occur in several wells. Highly oil-prone source rocks with high TOC contents (up to 16%) and HI values (up to 550 mgHC/gTOC) are so far known only from the northwestern part of the basin. Intercalated oil-prone coal layers occur in the same area, but Serpukhovian coal is widespread along the south(eastern) basin margin, where it is mined west and south of the city of Donetsk (Sachsenhofer et al., 2012).

Pelitic rocks in Baskririan and Moscovian horizons typically have TOC contents up to 1.5 %, although higher TOC contents occur as well. Coal seams are widespread in the southeastern part of the DDB.

Oil window maturity (~0.65 %Rr) is reached at around 3500 m depth (Fig. 2). A vitrinite reflectance map for 5000 m depth is shown in Fig. 1c. Whereas, vitrinite reflectance at that depth is typically low (partly <1.0 %Rr), higher values occur in the inverted SE part of the DDB (Shymanovskyy et al., 2004; Sachsenhofer et al., 2012). Hydrocarbon generation occurred predominantly during Permian deep burial, according to basin modeling studies carried out by Shymanovskyy et al. (2004). Additionally, a potential generation of hydrocarbons is suggested for Mesozoic to Cenozoic burial stages.

**Hydrocarbon reservoirs** are termed “productive horizons” and labelled according to code reflecting its stratigraphic position (Fig. 3). Carboniferous and Permian clastic rocks are the dominant reservoir lithology (Ulmishek, 2001). Small quantities of hydrocarbons occur in Lower Carboniferous and Lower Permian carbonates. Oil fields prevail in the northwestern part of the basin as well as along the basin flanks, filled mostly due to vertical petroleum migration. Devonian salt domes often produced faulted uplifts, hosting Carboniferous to Lower Permian reservoirs (Sachsenhofer et al., 2010), which are often sealed by Permian salt. The oils are commonly light in grade (35-45° API) and low in sulfur (<0.5 %). Gas deposits prevail along the basin axis. The gases are usually wet, free of $H_2S$ and contain minor amounts of nitrogen (~2 %) and $CO_2$ (~1 %; Ivanyuta et al., 1998).

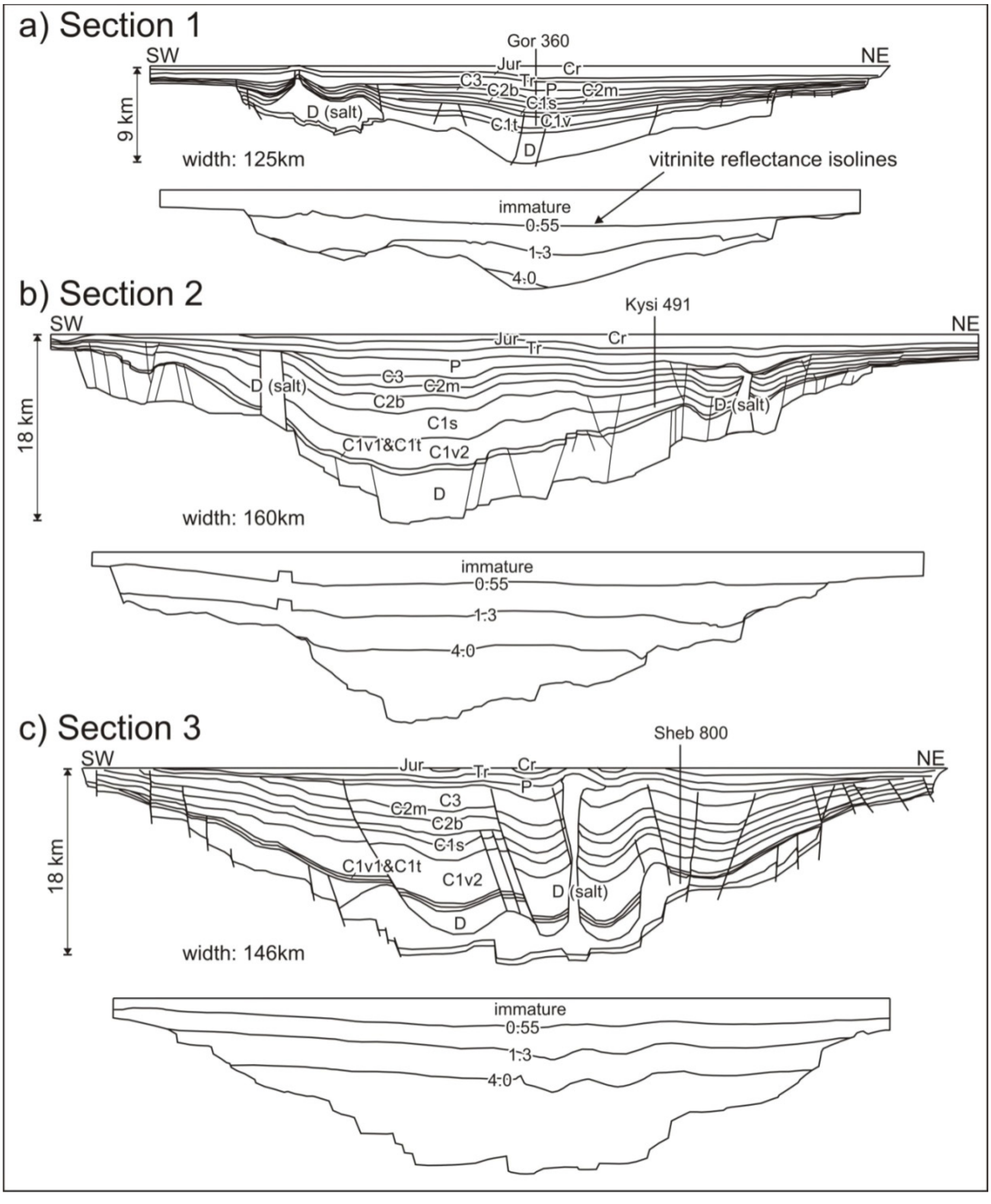


**Fig. 2:** Cross-sections through the Dniepr-Donets Basin (after Kivshik et al., 1993; Stovba and Stephenson, 2003; Ivanyuta et al., 1998). Locations of sections 1 to 3 are shown in Fig. 1c. Position of iso-reflectivity lines follows Mohsenian (2013).

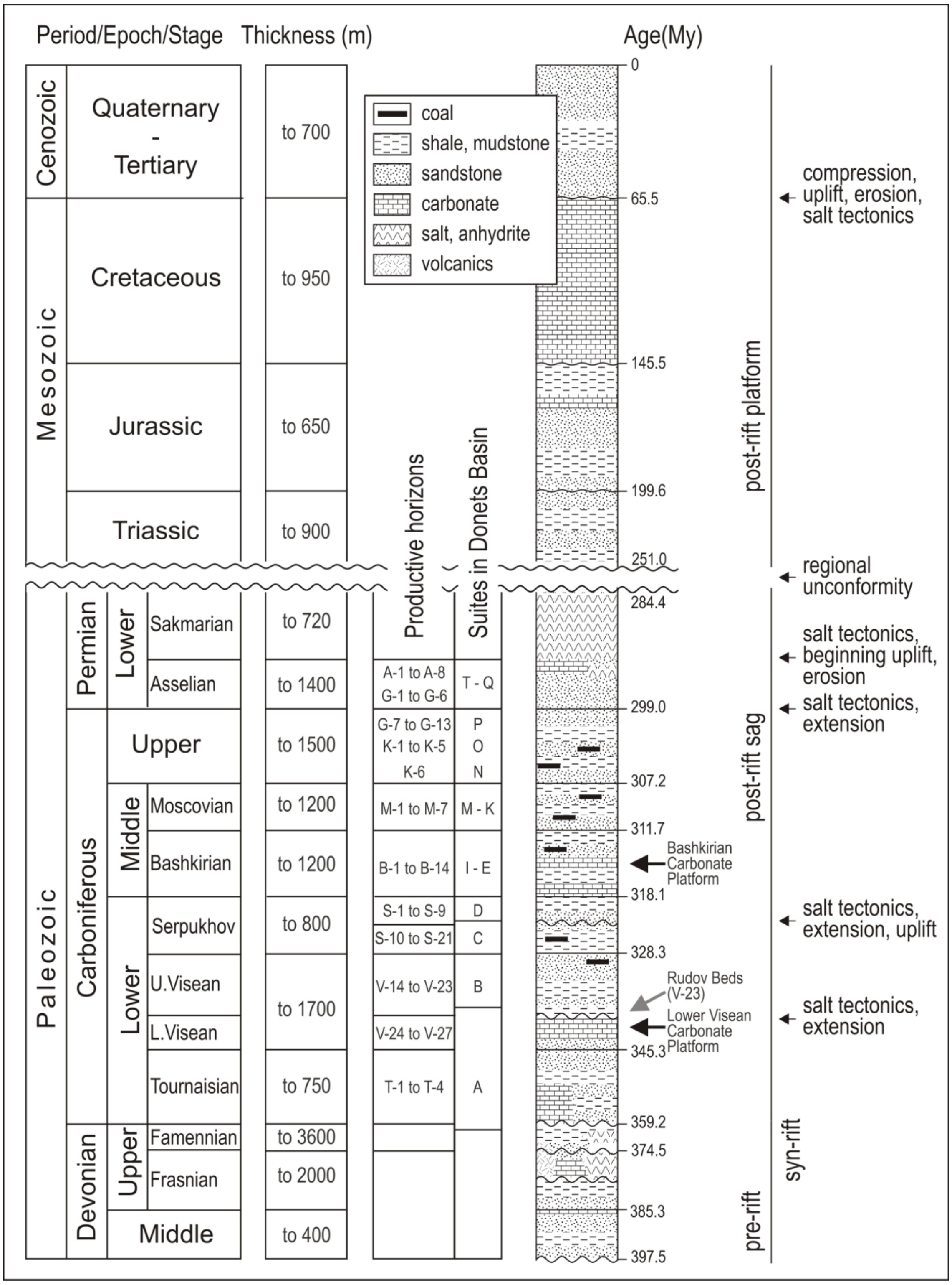


**Fig. 3:** Chrono- and lithostratigraphy of the Paleozoic succession of the Dniepr-Donets Basin (Sachsenhofer et al., 2010). Age data follow Gradstein et al. (2004). Information on “productive horizons” is shown according to Lukin in Ivanyuta et al. (1988).

## 3. Samples and Methods

52 rock samples from 17 wells ranging in age from Devonian to Bashkirian and 13 oil/condensate samples from 12 fields with Lower Visean to Moscovian reservoir horizons have been investigated within the frame of this study. Maturity and bulk parameters of about half of the rock samples have already been described by Sachsenhofer et al. (2010).

Data from these samples have been supplemented with datasets from the USGS Energy Geochemistry Data Base (USGS, 2009) including Pr/Ph and stable carbon isotope ratios of 14 oil samples, additional stable carbon isotope ratios for another 29 oil samples, and molecular and isotope composition of 18 gas samples. The locations of studied rock, oil and gas samples are shown in Fig. 4.

Powdered rock samples were analysed in duplicate for total sulphur (S), total carbon (C), and total organic carbon (TOC, after acidification of samples to remove carbonate) using an Eltra Helios analyzer. The difference between C and TOC is the total inorganic carbon (TIC). TIC contents were used to calculate calcite equivalent (calcite equ.) percentages using the formula TIC*8.34.

Pyrolysis measurements were performed in duplicate using a "Rock-Eval 2+" instrument (Vinci Technologies). The S1 and S2 peaks [mg HC/g rock] were recorded and used to calculate the Hydrogen-Index (HI = S2*100/TOC [mg HC/g TOC]) and the Production-Index (PI = S1/(S1+S2); Espitalié et al., 1977). As a maturation indicator, the temperature of maximum hydrocarbon generation (Tmax) was measured.

Vitrinite reflectance was determined following established procedures (Taylor et al., 1998).

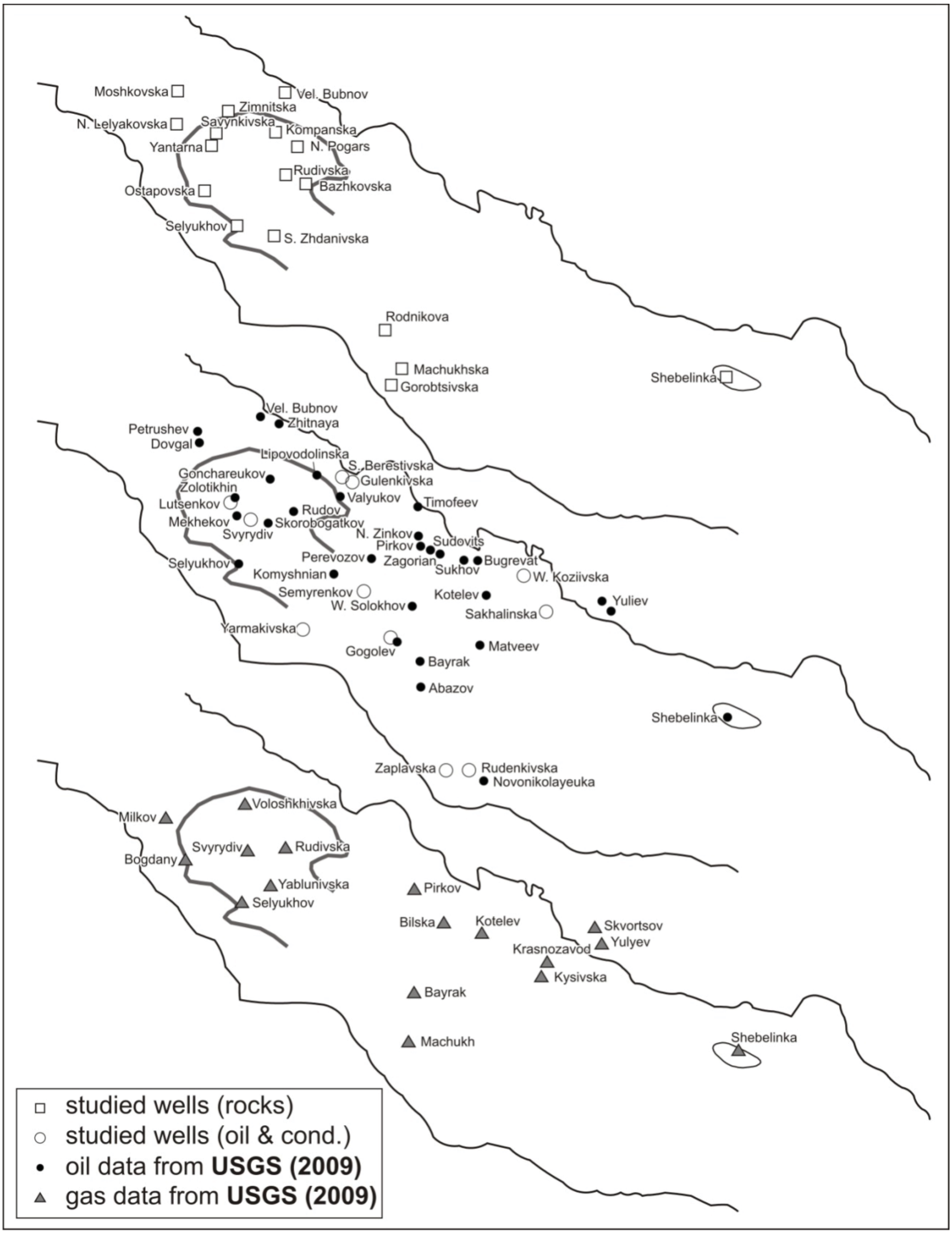


**Fig. 4**: Well locations within the study area. Rock, oil and gas samples are highlighted separately.

Pyrolysis gas chromatography was carried out by GeoS4 GmbH (Potsdam) on immature to marginally mature samples using the Quantum MSSV-2 Thermal Analysis System©. Thermally extracted (300°C/10 minutes) whole rock samples were heated in a flow of helium, and products released over the temperature range 300-600°C (40K $min^{-1}$) were focussed using a cryogenic trap, and then analysed using a 50 m x 0.32 mm BP-1 capillary column equipped with a flame ionisation detector. The GC oven temperature was programmed from 40°C to 320°C at 8°C $min^{-1}$. Boiling ranges (C1, C2-C5, C6-C14, C15+) and individual compounds (n-alkenes, n-alkanes, alkylaromatic hydrocarbons and alkylthiophenes) were quantified by external standardisation using n-butane. Response factors for all compounds were assumed as equal, except for methane whose response factor was 1.1.

Representative portions of the rock samples were extracted for approximately 1 h using dichloromethane in a Dionex ASE 200 accelerated solvent extractor at 75°C and 75 bar. After evaporation of the solvent to 0.5 ml total solution in a Zymark TurboVap 500 closed cell concentrator, asphaltenes were precipitated from a hexane-dichlormethane solution (80:1) and separated using centrifugation. The hexane-soluble fractions were separated into NSO compounds and saturated plus aromatic hydrocarbons, which were separated again, using medium-pressure liquid chromatography (MPLC) with a Köhnen-Willsch instrument (Radke et al., 1984). Oil samples (ca. 60 mg) were diluted with a hexane-dichloromethane (80:1) mixture and the insoluble asphaltenes were separated by centrifugation. The fractions of the hexane-soluble organic matter were separated into polar compounds, saturated hydrocarbons, and aromatic hydrocarbons by medium-pressure liquid chromatography using a Köhnen-Willsch MPLC instrument (Radke et al., 1984). Condensates were diluted in *n*-pentane and subjected to the gas-chromatographic analyses (GC-MS) without further pre-treatment.

The total hydrocarbons of condensate samples, as well as the saturated and aromatic hydrocarbon fractions of oils and source rock extracts were analysed with a gas chromatograph equipped with a 30 m DB-5MS fused silica capillary column (i.e. 0.25 mm; 0.25 µm film thickness) and coupled to a ThermoFisher ISQ quadrupol mass spectrometer. The oven temperature was programmed from 70° to 300°C at 4°C $min^{-1}$, followed by an isothermal period of 15 min. Helium was used as carrier gas. The sample was injected splitless, with the injector temperature at 275°C. The spectrometer was operated in the EI (electron ionisation) mode over a scan range from m/z 50 to m/z 650 (0.7 s total scan time).

Data were processed with an Xcalibur data system. Individual compounds were identified on the basis of retention time in the total ion current (TIC) chromatogram and comparison of the mass spectra with published data. Relative percentages and absolute concentrations of different compound groups in the saturated and aromatic hydrocarbon fractions were calculated using peak areas in the TIC chromatograms in relation to those of internal standards (deuteriated *n*-tetracosane and 1,1′-binaphthyl, respectively), or by integration of peak areas in appropriate mass chromatograms using response factors to correct for the intensities of the fragment ion used for quantification of the total ion abundance.

Carbon isotope determination of n-alkanes and acyclic isoprenoids was performed using a Trace GC instrument attached to a ThermoFisher DELTA-V isotope ratio mass spectrometer via a combustion interface (GC isolink, ThermoFisher). For calibration, $CO_2$ was injected at the beginning and end of each analysis. The GC column and temperature programmes are the same as for GC-MS. Stable isotope ratios are reported in delta notation ($\delta^{13}C$) relative to the Vienna-Pee Dee Belemnite (V-PDB) standard ($\delta^{13}C=[(^{13}C/^{12}C)sample/(^{13}C/^{12}C)standard-1]$). Delta notation is expressed in parts per thousand or per mil (‰). For bulk carbon isotope analyses of the saturated and aromatic hydrocarbon fractions, the samples were placed into tin foil boats and combusted using an elemental analyzer (Flash EA 1112) at 1020°C in an excess of oxygen. The resulting $CO_2$, separated by column chromatography, was analyzed online by the DELTA V ir-MS, mentioned above. The $^{13}C/^{12}C$ isotope ratios of the $CO_2$ were compared with the corresponding ratio in a monitoring gas, calibrated against the V-PDB standard by the NBS-19 reference material. The reproducibility of the total analytical procedure is in the range of 0.1 – 0.2 ‰.

1D modelling of thermal histories was performed using the PetroMod 1D software of Schlumberger. Input data for the thermal models include the thickness of stratigraphic units, the physical properties of their lithologies and the temporal evolution of the heat flow at the base of the sedimentary sequence, as well as the temperature at the sediment-water interface.

Physical parameters for different lithologies pre-defined in the software were used, the pressure outflow factor for lithotypes including evaporitic rocks was set at 100%. The applied timescale follows Gradstein et al. (2004).

The above information was used to reconstruct decompacted subsidence histories and the temperature field through time. The models were calibrated by modifying the heat flow until a satisfactory fit between measured and calculated formation temperatures, vitrinite reflectance and biomarker ratios (sterane and hopane isomerisation; steroid aromatization; calibration data from Sachsenhofer et al., 2010 and own data) was reached.

Vitrinite reflectance was calculated using the kinetic EASY%Ro approach (Sweeney & Burnham, 1990). Biomarker ratios were calculated using kinetic data from Rullkötter & Marzi (1988).

# 4. Results

Results from 52 rock samples, representing most of the relevant source rock horizons, are discussed in the first part of this section. Data obtained on oil/condensate samples are presented in the second part. Bulk geochemical parameters of investigated source rock samples are shown in table 1.

## 4.1 Source rocks

### 4.1.1 **Bulk Geochemical Parameters**

Devonian (Dev) and Tournaisian (C1t) horizons have been sampled in well Rudivska 2 at depths exceeding 5500 m (see also Sachsenhofer et al., 2010). TOC contents are 1.55 % and 1.73 % for Devonian and 3.4 % and 5.9 % for Tournaisian samples. Tmax values above 485 °C (Fig. 5) and a vitrinite reflectance (VR) exceeding 1.3 %Rr indicate gas window maturity and show that HI values are reduced due to advanced maturity.

Samples from Upper Visean horizon V-23 (Rudov Beds) and adjacent shales have been collected from 13 wells between depths of 3100 and 5600 m. Wells within the central Srebnen Bay (Yantarna, Ostapovska, Kompanska, Northern Pogarshchinska) exhibit an average TOC content of 5.5 % (7 samples), with a minimum of 4.6 %. Wells in the transition zone between the basinal and reef facies and outside of the Srebnen Bay (Moshkovska, Northern Lelyakovska, Selyukhovska, South Zhdanivska, Veliky Bubnovska) are less prolific with an average TOC of 2.5 % (11 samples) and a minimum TOC of 0.8 %.

Table 1: Bulk geochemical parameters of investigated source rock samples.

| Sample | Depth | Strat. | TIC | TOC | S | TOC/S | S1 | S2 | HI | PI | $T_{max}$ | EOM | Sat. | Aro. | NSO | Asph. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | mgHC | mgHC | mgHC | | | mg | HC | HC | | |
| | m | | wt.% | wt.% | wt.% | | /g | /g | /gTOC | | °C | /gTOC | % | % | % | % |
| **Bashk.** | | | | | | | | | | | | | | | | |
| Yz 13 | 3893.0 | C2b | 2.0 | 29.3 | 8.2 | 3.6 | 3.5 | 64.6 | 220 | 0.05 | 423 | 24 | 4 | 13 | 41 | 42 |
| Yz 20 | 3947.0 | C2b | 0.1 | 0.8 | 0.2 | 4.8 | | | | | | 16 | | | | |
| | | | | | | | | | | | | | | | | |
| **Serpukh.** | | | | | | | | | | | | | | | | |
| Bazh 1 | 3492.0 | C1s2 | 6.5 | 4.3 | 0.8 | 5.3 | 1.3 | 21.4 | 503 | 0.06 | 429 | 22 | 44 | 19 | 33 | 4 |
| Bazh 3 | 3494.0 | C1s2 | 3.5 | 4.0 | 0.6 | 6.4 | 1.3 | 20.3 | 511 | 0.06 | 427 | 49 | 44 | 6 | 40 | 10 |
| Bazh 4 | 3495.0 | C1s2 | 2.6 | 6.8 | 0.7 | 9.1 | 2.9 | 36.3 | 534 | 0.07 | 429 | 24 | 38 | 14 | 40 | 8 |
| Bazh 5 | 3495.0 | C1s2 | 3.7 | 8.4 | 0.9 | 9.4 | 3.0 | 44.2 | 525 | 0.06 | 429 | 43 | 37 | 9 | 41 | 12 |
| | | | | | | | | | | | | | | | | |
| Sav 03 | 4703.0 | C1s2 | 3.1 | 5.4 | 1.0 | 5.5 | 3.7 | 25.4 | 469 | 0.13 | 438 | 52 | 32 | 16 | 45 | 8 |
| Sav 06 | 4706.0 | C1s2 | 0.0 | 1.9 | 2.9 | 0.6 | 0.4 | 1.4 | 74 | 0.21 | 433 | 16 | 23 | 46 | 18 | 14 |
| Sav 13 | 4806.0 | C1s1 | 0.5 | 2.7 | 0.2 | 11.1 | 0.2 | 2.8 | 103 | 0.07 | 436 | 10 | 31 | 19 | 41 | 9 |
| Sav 18 | 4810.0 | C1s1 | 0.0 | 66.8 | 6.0 | 11.0 | 14.7 | 178.1 | 267 | 0.08 | 433 | 31 | 33 | 8 | 38 | 21 |
| | | | | | | | | | | | | | | | | |
| Yz 61 | 4258.0 | C1s2 | 0.4 | 2.5 | 0.1 | 25.4 | 0.3 | 4.7 | 186 | 0.07 | 428 | 23 | 31 | 16 | 37 | 17 |
| Yz 78 | 4426.0 | C1s1 | 1.7 | 4.4 | 0.6 | 7.9 | 0.7 | 8.5 | 195 | 0.07 | 430 | 15 | 12 | 21 | 54 | 13 |
| Yz 84 | 4431.0 | C1s1 | 1.0 | 3.5 | 0.7 | 5.1 | 0.5 | 6.2 | 179 | 0.08 | 430 | 20 | 8 | 37 | 41 | 13 |
| | | | | | | | | | | | | | | | | |
| **Visean** | | | | | | | | | | | | | | | | |
| Rud 07 | 4252.0 | V-16 | 0.0 | 3.5 | 0.5 | 7.5 | 0.6 | 6.7 | 194 | 0.08 | 440 | 17 | 29 | 17 | 38 | 16 |
| Rud 13 | 4416.0 | V-17 | 0.6 | 2.1 | 0.1 | 30.3 | 0.2 | 1.6 | 75 | 0.11 | 442 | 19 | 22 | 19 | 42 | 18 |
| Rud 26 | 4604.0 | V-19 | 0.0 | 2.7 | 0.0 | 57.8 | 0.3 | 3.3 | 122 | 0.09 | 449 | 14 | 10 | 12 | 51 | 27 |
| Rud 38 | 4765.0 | V-21 | 0.2 | 3.8 | 0.7 | 5.5 | 0.5 | 2.8 | 72 | 0.14 | 449 | 16 | 11 | 11 | 43 | 35 |
| Rud 50 | 4966.0 | V-22 | 0.5 | 3.3 | 0.7 | 4.7 | 0.4 | 2.7 | 81 | 0.14 | 456 | 14 | 17 | 13 | 42 | 28 |
| | | | | | | | | | | | | | | | | |
| N.Lelya 163 | 3793.8 | V-23 | 0.1 | 0.8 | | | 0.1 | 0.3 | 30 | 0.19 | 429 | 53 | 18 | 48 | 16 | 18 |
| | | | | | | | | | | | | | | | | |
| Mosh 30 | 4477.8 | V-23 | 0.6 | 3.2 | 3.9 | 0.8 | 1.6 | 7.0 | 214 | 0.18 | 439 | 49 | 22 | 20 | 44 | 14 |
| Mosh 40 | 4601.7 | V-24 | 0.4 | 3.3 | 2.3 | 1.5 | 0.3 | 3.7 | 106 | 0.07 | 440 | 19 | 4 | 7 | 29 | 60 |
| | | | | | | | | | | | | | | | | |
| Zim 87 | 5021.3 | V-22 | 1.5 | 5.3 | 2.0 | 2.6 | 2.2 | 7.9 | 142 | 0.22 | 442 | 35 | 28 | 17 | 46 | 9 |
| Zim 112 | 5103.8 | ? | 1.7 | 3.5 | 2.3 | 1.6 | 0.6 | 2.4 | 59 | 0.19 | 448 | 15 | 18 | 7 | 62 | 12 |
| | | | | | | | | | | | | | | | | |
| Vel Bub 54 | 3313.5 | ? | 0.1 | 1.2 | 0.1 | 18.8 | 0.2 | 1.1 | 63 | 0.14 | 440 | 32 | 18 | 13 | 35 | 35 |
| Vel Bub 58 | 3340.5 | ? | 0.4 | 0.7 | 2.3 | 0.3 | 0.2 | 1.2 | 129 | 0.15 | 434 | 64 | 32 | 18 | 38 | 12 |
| | | | | | | | | | | | | | | | | |
| Komp 130 | 4989.0 | V-23 | 1.1 | 7.2 | 3.1 | 2.3 | 1.9 | 6.1 | 85 | 0.23 | 453 | 30 | 31 | 12 | 53 | 4 |
| | | | | | | | | | | | | | | | | |
| Npog 67 | 5085.0 | V-24 | 3.4 | 6.0 | 1.8 | 3.3 | 2.1 | 6.2 | 97 | 0.25 | 456 | 24 | 30 | 13 | 52 | 5 |
| Npog 79 | 5096.5 | V-24 | 0.8 | 4.3 | 3.8 | 1.1 | 2.0 | 3.5 | 74 | 0.36 | 452 | 31 | 28 | 7 | 54 | 11 |
| | | | | | | | | | | | | | | | | |
| Yan 200 | 5195.0 | V-23 | 1.4 | 4.8 | 3.3 | 1.4 | 1.5 | 4.1 | 83 | 0.26 | 457 | 32 | 28 | 12 | 56 | 4 |
| | | | | | | | | | | | | | | | | |
| Yz 131 | 5080.8 | V-23 | 5.6 | 3.7 | 0.8 | 4.5 | 3.1 | 5.3 | 142 | 0.37 | 448 | 125 | 57 | 6 | 31 | 6 |
| Yz 137 | 5091.0 | V-23 | 3.3 | 3.6 | 1.1 | 3.3 | 2.2 | 4.7 | 131 | 0.32 | 455 | 76 | 51 | 8 | 35 | 5 |
| | | | | | | | | | | | | | | | | |
| Ost 49 | 3845.7 | V-23 | 1.6 | 5.4 | 2.4 | 2.3 | 7.4 | 9.0 | 168 | 0.45 | 440 | 147 | 37 | 12 | 39 | 11 |
| Ost 51 | 3847.5 | V-23 | 1.9 | 6.2 | 2.8 | 2.2 | 3.1 | 14.9 | 242 | 0.17 | 444 | 92 | 32 | 12 | 43 | 13 |
| Ost 53 | 3848.9 | V-23 | 1.0 | 4.6 | 3.3 | 1.4 | 2.7 | 11.7 | 256 | 0.18 | 442 | 149 | 38 | 12 | 42 | 8 |
| | | | | | | | | | | | | | | | | |
| Selyu 41 | 3119.6 | V-23 | 0.1 | 1.8 | 1.0 | 1.9 | 0.1 | 0.7 | 37 | 0.08 | 430 | 21 | 8 | 12 | 43 | 38 |
| Selyu 45 | 3123.0 | V-23 | 0.1 | 1.1 | 0.7 | 1.6 | 0.1 | 0.4 | 33 | 0.13 | 431 | 13 | 10 | 9 | 52 | 28 |
| Selyu 47 | 3125.0 | V-23 | 0.0 | 1.2 | 0.4 | 3.5 | 0.0 | 0.5 | 42 | 0.07 | 442 | 28 | 3 | 5 | 29 | 63 |
| Selyu 48 | 3126.0 | V-23 | 0.1 | 2.3 | 0.1 | 40.1 | 0.1 | 2.1 | 85 | 0.06 | 435 | 21 | 4 | 6 | 20 | 70 |

| Sample | Depth | Strat. | TIC | TOC | S | TOC/S | S1 | S2 | HI | PI | $T_{max}$ | EOM | Sat. | Aro. | NSO | Asph. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | mgHC | mgHC | mgHC | | | mg | HC | HC | | |
| | m | | wt.% | wt.% | wt.% | | /g | /g | /gTOC | | °C | /gTOC | % | % | % | % |
| **Vis. cont'd** | | | | | | | | | | | | | | | | |
| Rodni 5595m | 5595.0 | V-23 | 1.1 | 9.9 | 2.5 | 4.0 | 0.3 | 3.0 | 27 | 0.09 | 517 | 5 | 8 | 15 | 65 | 12 |
| Rodni 5595b | 5595.0 | V-23 | 0.4 | 5.0 | 2.9 | 1.7 | 0.1 | 1.2 | 17 | 0.10 | | 5 | 36 | 11 | 41 | 13 |
| | | | | | | | | | | | | | | | | |
| Machuk 5050 | 5050.0 | V-23 | 0.6 | 2.2 | 0.2 | 11.3 | 0.1 | 0.9 | 25 | 0.12 | 519 | 4 | 11 | 42 | 24 | 22 |
| | | | | | | | | | | | | | | | | |
| Goro 4432 | 4432.0 | V-23 | 0.2 | 4.3 | 4.0 | 1.1 | | | | | | 4 | 30 | 6 | 34 | 30 |
| Goro 4447 | 4447.0 | V-23 | 0.7 | 1.7 | 0.4 | 4.6 | | | | | | 7 | 15 | 8 | 54 | 23 |
| Goro 4476 | 4476.0 | V-23 | 0.5 | 1.5 | 0.1 | 11.3 | | | | | | 6 | 15 | 24 | 44 | 17 |
| | | | | | | | | | | | | | | | | |
| **Tournais.** | | | | | | | | | | | | | | | | |
| Rud 88 | 5585.0 | C1t | 0.3 | 5.9 | 3.4 | 1.8 | 0.1 | 2.2 | 38 | 0.06 | 488 | 9 | 6 | 11 | 35 | 48 |
| Rud 91 | 5587.0 | C1t | 0.1 | 3.4 | 4.7 | 0.7 | 0.1 | 0.6 | 18 | 0.08 | 491 | 5 | 8 | 13 | 61 | 18 |
| | | | | | | | | | | | | | | | | |
| **Devonian** | | | | | | | | | | | | | | | | |
| Rud 103 | 5754.0 | Dev | 0.6 | 1.7 | 0.3 | 5.9 | 0.0 | 0.3 | 19 | 0.12 | 513 | 12 | 6 | 22 | 47 | 24 |
| Rud 109 | 5772.0 | Dev | 0.0 | 1.6 | 0.1 | 29.5 | 0.0 | 0.3 | 16 | 0.07 | | 12 | 17 | 12 | 59 | 11 |

Depth: sampling depth; Strat.: stratigraphic position of source rock interval; TIC: total inorganic carbon; TOC: total organic carbon; S: sulfur content; TOC/S: ratio of total organic carbon against sulfur content; S1: free hydrocarbons; S2: hydrocarbons generated during Rock Eval pyrolysis; HI: Hydrogen Index; PI: Production Index; Tmax: temperature with maximum hydrocarbon generation; EOM: extractable organic matter; Sat: saturated hydrocarbons; Aro: aromatic hydrocarbons; NSO: polar compounds; Asph: asphaltenes

Rudov Beds drilled in three wells SE of the Srebnen Bay (Rodnikova, Machukhska, Gorobtsivska; Fig. 4) exhibit TOC values varying largely between 1.5 % and 9.9 % (average TOC of 6 samples: 4.1 %). Even the least thermally mature Rudov Beds from shallow depths (Tmax: 430-440 °C; VR: 0.7 %Rr) exhibit HI values below 260 mgHC/gTOC, suggesting a transitional type II/III kerogen (Fig. 5).

Upper Visean rocks from higher stratigraphic levels (V-22 to V-16) have been sampled in well Rudivska 2. Their TOC contents and HI values vary between 2.1 % and 3.8 % and 75 and 195 mgHC/gTOC, respectively.

Studied Serpukhovian (C1s) and Bashkirian (C2b) rocks from the northwestern DDB are immature (to marginally mature). Serpukhovian rocks from well South Zhdanivska 313 are characterized by TOC contents between 2.5 % and 4.4 % and HI values in the order of 180 to 200 mgHC/gTOC. In contrast, TOC contents (4.0-8.4 %) and HI values (500-535 mgHC/gTOC) in samples from well Bazhkovska 1 and a single sample from well Savynkivska 361 are significantly higher indicating the presence of oil-prone kerogen type II. The uppermost sample from well Savynkivska 361 represents the oil-prone facies, whereas other samples are lower in TOC (1.9-2.7 %) and contain a type III kerogen (~100 mgHC/gTOC). The TOC content of a Serpukhovian coal with relatively high HI (267 mgHC/gTOC) is 66.8 %. Bashkirian rocks sampled in well South Zhdanivska 313 include a clastic rock (0.8 %TOC) and a coaly sample (29.3 %TOC; 220 mgHC/gTOC).

Serpukhovian to Moscovian mudstones from a well in the Shebelinka area are mature to overmature (0.88-1.54 %Rr) and high in TOC (1.7-3.8 %). Because of high maturity HI values are low (9-70 mgHC/gTOC).

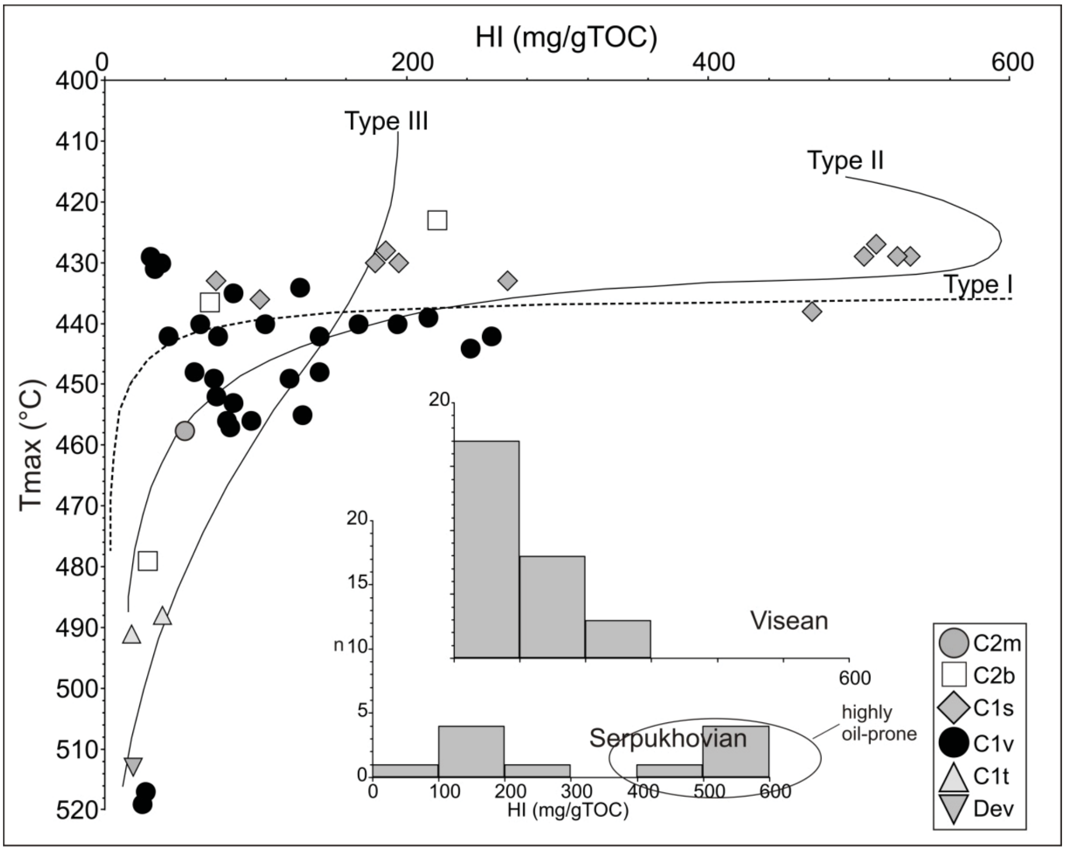


**Fig. 5:** Plot of HI versus Tmax. Histograms show distribution of HI values of Visean and Serpukhovian rocks. Dev – Devonian; C1t – Tournaisian; C1v – Visean; C1s – Serpukhovian; C2b – Bashkirian.

### 4.1.2 **Pyrolysis-gas chromatography**

Pyrolysis-gas chromatography (Py-GC) measurements were performed on three samples representing horizon V-23 in wells Ostapovska and Northern Lelyakovska. Results from additional Visean, Serpukhovian, and Moscovian samples from a former study (Sachsenhofer et al., 2010) are also presented.

Fig. 6 provides classifications of petroleum potential based on chain length distribution. Most samples have black oil potential and fall in the Paraffinic-Naphthenic-Aromatic (PNA) facies. These include Rudov Beds (V-23), the Lower Visean sample (V-24), Serpukhovian samples with high HI values, and Serpukhovian coal. Only a Moscovian coal, a sapropelite overlying the Serpukhovian coal and an Upper Visean sample (V-16) are gas condensate-prone. All samples yield hydrocarbons with low sulphur contents.

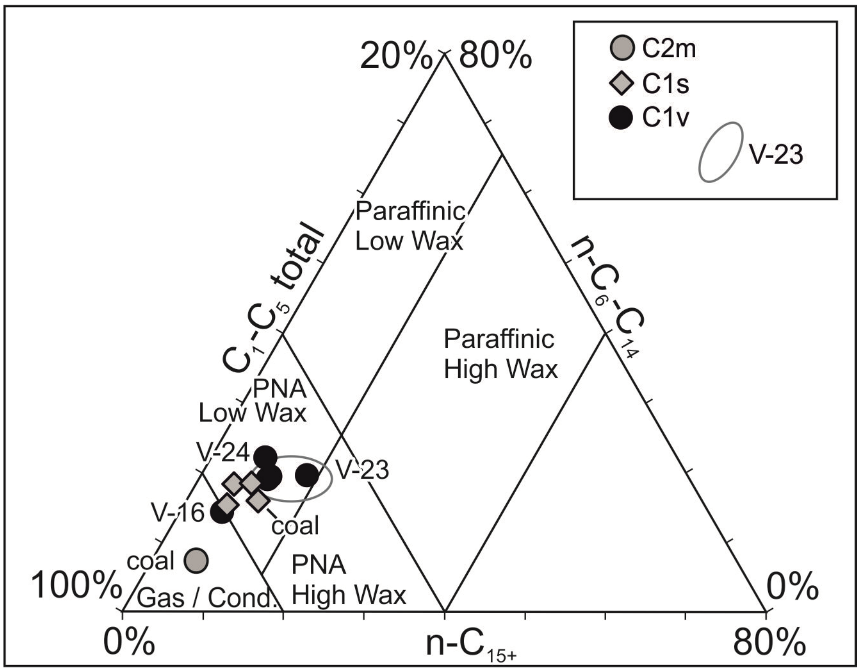


**Fig. 6:** Petroleum type organofacies obtained from pyrolysis gas chromatography after Horsfield (1989). The figure considers samples investigated within the frame of this study and immature samples from Sachsenhofer et al. (2010).

### 4.1.3 **Molecular composition and biomarkers**

The amount of the extractable organic matter (EOM) varies between 4 and 149 mg/g TOC. The proportion of hydrocarbons varies between 8 and 69 % of the EOM. The alkane distribution patterns vary considerably due to facies and maturity effects. Rocks from the Upper Visean horizon (V-23) recovered from the basin axis are characterized by the highest contents (>50%) of short-chain *n*-alkanes (*n*-$C_{15-19}$) and the lowest contents in long-chain n-alkanes (<10%). In contrast, rocks with a similar age in the southeastern part of the basin and Tournaisian rocks contain the lowest amounts (<28%) of *n*-$C_{15-19}$. Highly oil-prone Serpukhovian rocks contain higher amounts (43 - 51%) of *n*-$C_{15-19}$ than the rest of the Serpukhovian sample set (27 – 38%). Samples from shallow depth are partly characterized by the presence of a noticeable odd-over-even carbon number predominance reflected by carbon preference index (CPI) values up to 2.0 (Bray and Evans, 1961).

The aromatic hydrocarbon fractions of rock samples are dominated by alkylated naphthalenes, phenanthrene, and methylphenanthrenes. Sulfur-aromatic compounds (i.e. dibenzothiophene (DBT)) are present in very low contents. In several V-23 samples from different wells in marginal positions of the Srebnen Bay, PAHs with 4-5 rings ranging from fluoranthene to benz-(ghi)-perylene as well as oxygen-bearing PAHs (e.g. dibenzofuran, dibenzopyrane, dimethyl-xanthene) are present in considerable amounts. PAHs show low abundance in most Serpukhovian and Bashkirian rocks, similar to basinal Rudov (V-23) facies. Generally, Serpukhovian and Bashkirian extracts show similar compositional trends as V-23 extracts, with varying contents of aromatic compounds. Oil-prone Upper Serpukhovian shales revealed hydrocarbon extracts with remarkably red coloration, suggesting the presence of carotenoid pigments. This was observed exclusively for Serpukhovian samples with high HI values (~500 mgHC/gTOC). Aryl-isoprenoids, which are carotenoid derivatives, were detected in those rocks.

Pr/Ph ratios of Devonian rock samples are < 1.0 (Fig. 7), as suggested also by Ruble (1996). Pr/Ph ratios of Tournaisian rocks are slightly higher (1.0-1.2), whereas values range between 0.4 and 1.7 for Visean and between 0.8 and 3.2 for Serpukhovian rock extracts. Highly oil-prone Upper Serpukhovian source rocks are characterized by Pr/Ph ratios in the range of 1.4 to 2.4. Bashkirian rocks display diverging ratios of 0.6 to 1.5 (shales) and 3.9 (coaly sample), respectively. A Moscovian mudstone sample from the Shebelinka area yields an extract with a Pr/Ph ratio of 1.1.

Dibenzothiophene/Phenantrene (DBT/P) ratios are generally low for Devonian to Moscovian rocks, ranging between 0.02 and 0.35, except for one carbonate rich V-23 sample (28 % calc. equ.) from well South Zhdanivska 313 (see Fig.7; YZ 313), which exhibits a DBT/P ratio of 0.81. An even higher DBT/P ratio (2.5) has been observed in a Lower Visean (V-24) sample from well Selyukhovska 1 by Sachsenhofer et al. (2010). This sample is included in Fig. 7, which shows a cross-plot of the DBT/P versus the Pr/Ph ratio.

Results from biomarker studies on source rock extracts and oils/condensates in table 2.