[PS]Magnetic Mineral Composition as a Potential Indicator of Depositional Conditions in Gas-Bearing Silurian Shale Rocks from Northern Poland*

Dominika Niezabitowska[1], Rafał Szaniawski[1] and Michael Jackson[2]

Search and Discovery Article #51574 (2019)**
Posted June 10, 2019

*Adapted from poster presentation given at 2018 International Conference and Exhibition, Cape Town, South Africa, November 4-7, 2018
 DOI:10.1306/51574Niezabitowska2019

[1]Magnetism, Institute of Geophysics Polish Academy of Sciences, Warsaw, Poland (dniezabitowska@igf.edu.pl)
[2]Institute for Rock Magnetism, Minneapolis, Minnesota, United States

Abstract

In our studies we focus on the rock magnetic properties of two types of Silurian gas-bearing shales from Northern Poland: the Pelplin Formation and the Jantar Member, which both represent a potential source of unconventional hydrocarbons. The analyzed rocks have similar burial evolution, but different amounts of organic matter (in the Pelplin samples the TOC content does not exceed 1.5 percent, while in the Jantar it reaches up to 7 percent). Additionally, spherical carbonate concretions in the Pelplin Formation were investigated. The differences in magnetic mineral assemblage may help in better understanding the determinants, which influence water chemistry at the bottom of the sedimentary basin and thus the preservation of organic matter.

In order to recognize nano-particles not detectible in basic rock magnetic studies, low temperature SIRM measurements in the 10-300 K range were performed. The results show the presence of MD and SP magnetite, which we associate with detrital and chemical origin (smectite illitization or organic maturation), respectively. Furthermore, the most interesting observation is the appearance of hematite in the Pelplin Fm. (mostly SD grains), while in the organic-rich Jantar Member this mineral is absent. We suggest that hematite in mudstones and concretions is a product of magnetite reaction in oxic conditions (with probable activity of bacteria). This hypothesis is consistent with the presence of early diagenetic carbonate concretions and also with lower values of organic matter in the Pelplin Formation. Moreover, the hematite preserved in both mudstones and concretions in the Pelplin Formation suggests that stable oxic conditions were present during sedimentation and the early compaction process.

As a main conclusion, we propose a correlation between hematite and organic matter content in shale rocks, which may be a useful factor in understanding the preservation of organic matter. However, further investigation is necessary to fully recognize this complex problem.

Magnetic mineral assemblage as a potential indicator of depositional environment in gas-bearing Silurian shale rocks from Northern Poland

Dominika Niezabitowska[1], Rafał Szaniawski[1], and Michael Jackson[2]
1) Institute of Geophysics Polish Academy of Sciences, Department of Magnetism, Warsaw, Poland
2) Institute for Rock Magnetism, University of Minnesota, Minneapolis, the USA

CONTACT:
dniezabitowska@igf.edu.pl

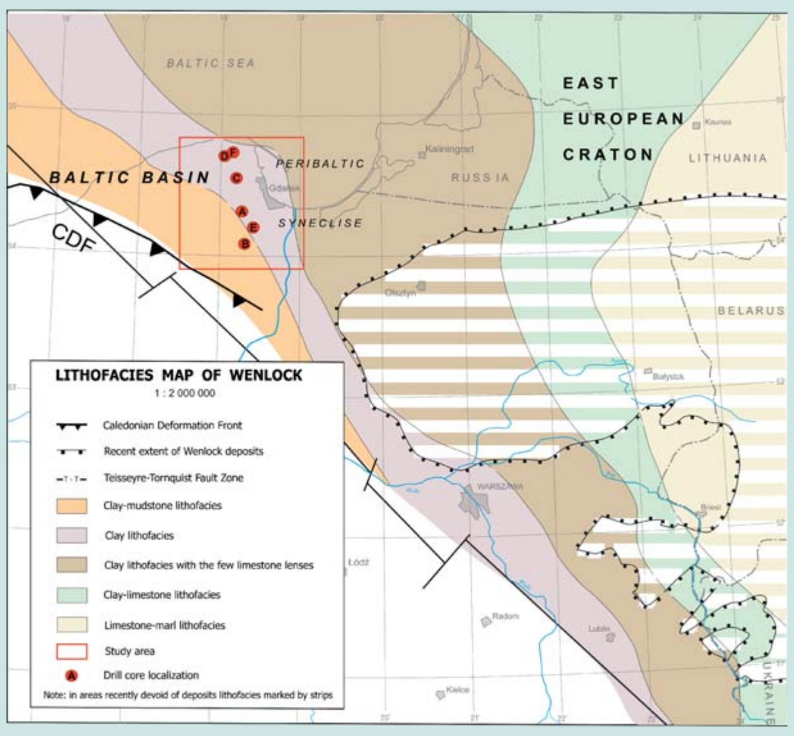
GOALS

Depositional environments and processes to which rocks are subjected to during burial, and subsequent diagenesis, compaction, heating, etc. are very complex. Therefore, in order to understand the mechanism of preservation of organic matter and the occurrence of oil and gas in shale, several different methodologies and proxies have to be applied. These include several indicators of deposition and diagenesis: the degree of oxygenation (redox conditions), the degree of bioturbation, the presence of benthic fauna, salinity (...). In addition, the magnetic properties of gas-bearing shales were also investigated, to obtain additional information on thermal maturation of rocks (e.g., Kars et al., 2015; Manning & Elmore, 2015).

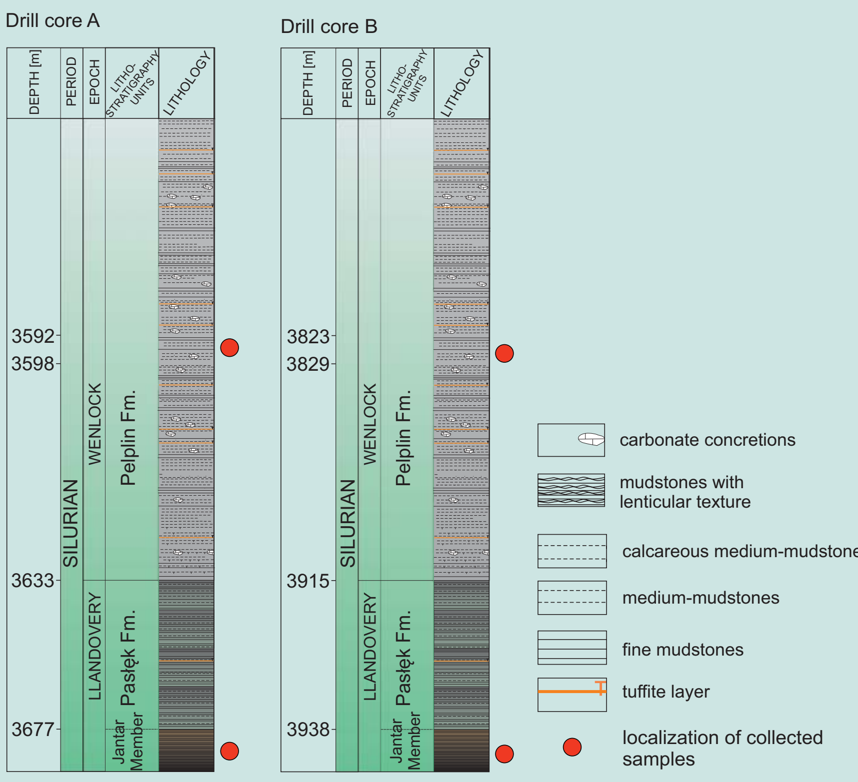
Our goal was to determine the composition and the **properties of magnetic minerals** in two shale rock facies characterized by similar thermal evolution, but **different amounts of organic matter**, and also to define the rock-magnetic **differences between them**, if any. Next, we intend to check the potential of this differentiation as a factor to better understand the processes which influence water chemistry at the bottom of sedimentary basins, and thus to better understand **factors controlling the preservation of organic matter**.

GEOLOGICAL FRAMEWORK

- The samples represent the **organic-rich**, **Silurian - lower Wenlockian** rocks; the sediments lie almost horizontally and do not show significant signs of tectonic deformations
- Mudstones were deposited in the Baltic Basin (BB), situated along the western margin of Baltica; the eastern part of the basin was dominated by **carbonate** sedimentation, which was replaced by more siliciclastic deposition westward
- During the Silurian times the BB became a distal part of the **Caledonian foredeep basin** with the subsidence controlled by flexural bending of Baltica (after Poprawa, 2010)
- The rocks were derived from **two shale gas exploration wells** drilled by **Polish Gas and Oil Company**
- the depth of analyzed rocks samples ranges from 3500 to 3700 m - the middle part of Wenlockian succession
- In depth interval (2400 – 4300 m) values of the Ro (vitrinite reflectance) do not exceed 1.42% (Karcz et al., 2013), which corresponds to **early dry gas** up to **wet gas** diagenetic/catagenetic stage (Mastalerz et al., 2013)
- Analyzed rocks were heated maximally to **150°C** before the end of Devonian (Środoń & Clauer, 2001).
- In the individual boreholes the Silurian strata is locally enriched in organic matter (TOC content reaches locally 10 wt.% (usually 1–2 wt.%) (Kowalski et al., 2010).



SAMPLING



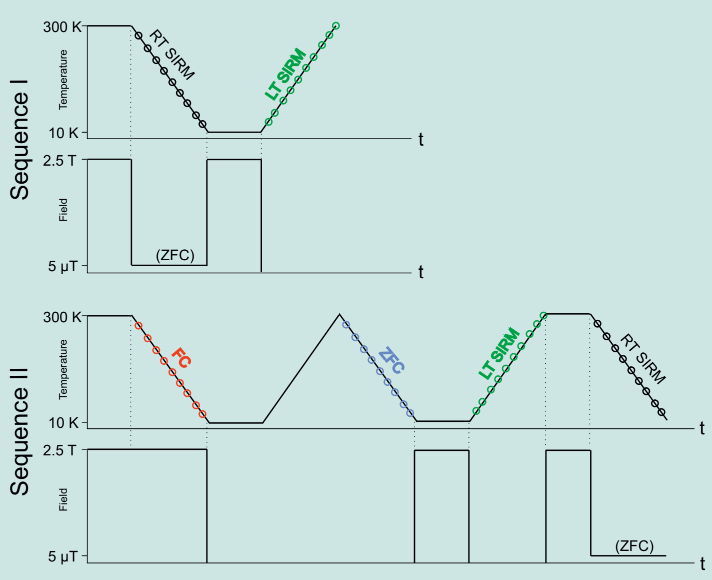
The samples come from two homogenous lithofacies from two shale gas exploration wells (labelled A and B) located in **Northern Poland**, which were derived by the Polish Oil and Gas Company.

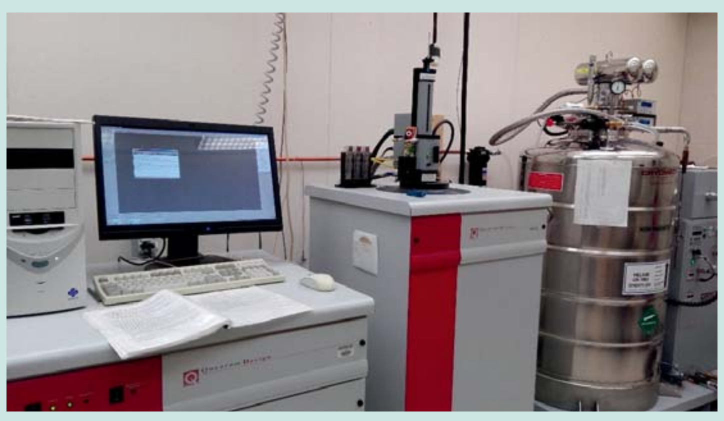
- The samples JAN1 - 3 represent **the most prospective** (in context of gas exploration) **shale layer**, called the Jantar Member, where TOC achieved 5% (Karcz et al., 2013).
- The second type of samples (PEL1 - 3) represent **typical mudstones** from the middle part of the Pelplin formation, which contain **smaller amounts of TOC** (not exceeding 1.5 %) and are characterized by the presence of calcareous concretions.
- The samples were collected also from the early diagenetic calcareous concretions, which occur in the Pelplin shale rocks, from the same depth intervals as mudstone samples (Fig.2).

METHODS

- Detailed magnetic measurements were performed in temperatures ranging from **300–10 K**, including changes in **SIRM** (Saturated Isothermal Remnant Magnetization), and **hysteresis loops** with temperature.
- The measurements at low temperatures were carried out at the **Institute for Rock Magnetism, University of Minnesota, the USA**. The measurements were conducted using Magnetic Properties Measurement System instruments (MPMSs, built by Quantum Design INC., San Diego).
- Samples (not exceeding 400 mg) were enclosed in gel capsules.
- The measurements (**sequence I**) start with applying a 2.5 T field at room temperature to reach SIRM. The next step is to cool down the sample from 300 to 10 K in a weak magnetic field (5 μT), in 5 K steps. This part is called **Room Temperature SIRM (RT-SIRM) cooling.**
- The RT-SIRM cooling experiments in a small (5 μT) magnetic field (based on Kars and Aubourg (2014; 2015)), represent a **combination of remanent and induced magnetization.**
- The next step is to apply a 2.5 T field at 10 K to reach **LT-SIRM (Low Temperature SIRM)**. After switching off the magnetic field, the sample is heated up to 300 K in the Zero Field (ZF), in 10 K steps.
- A more comprehensive measurement **sequence (II)** comprise the two proceeding steps, and also **Field Cooling (FC)**, which is a measurement of magnetization while cooling in a continuous 2.5 T field, and **Zero Field Cooling (ZFC)**, which is a measurement of magnetization during cooling in zero magnetic field.

Sequences precedure





RESULTS

The Pelplin Formation (with modest amount of organic matter)

MUDSTONES

- The samples display well defined **Verwey transitions**, indicative of **magnetite**, on the RT-SIRM curves. The transition occurs at 110 - 115 K.
- In both ZFC and FC curves the transition is hardly visible, which may suggest titanium substitution or a grain-size effect.
- The **Morin transition** of **hematite** is also well marked and occurs at 220 – 240 K on the RT-SIRM curves.
- Higher values of ZFC than FC remanence inform about occurrence of **multidomains (MD)** ferromagnetic grains, which is confirmed by substantially lower recovery of magnetization on RT remanence curve during heating (Carter-Stiglitz et al., 2006).

CARBONATE CONCRETIONS

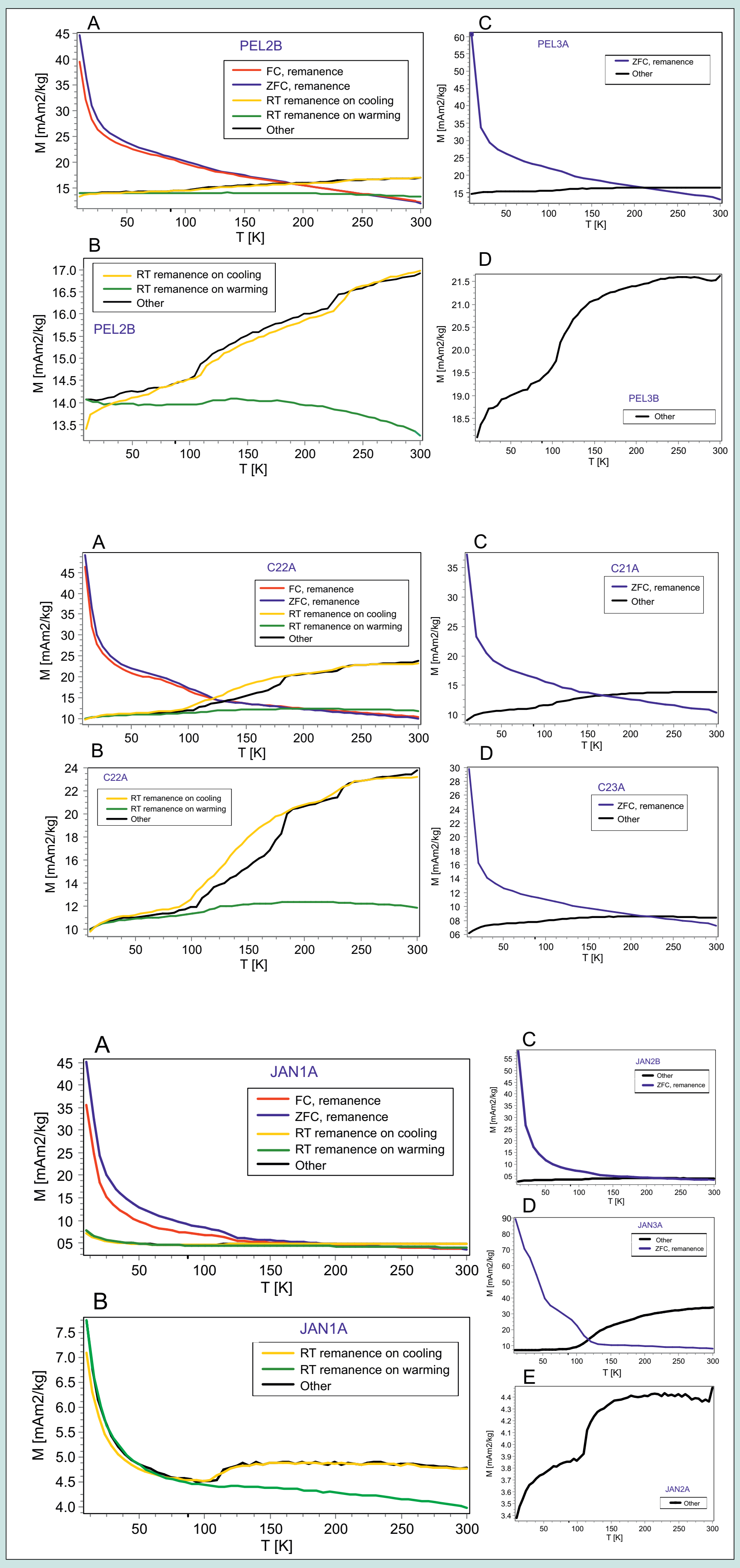
Similar results were obtained for calcareous concretions:

- The **Verwey transition** is well developed on RT-SIRM curves. In contrast to the mudstones, the transition is also clearly visible in both the ZFC and FC curves.
- For these rocks the **Morin transition of hematite** is also well marked and occurs at 230 – 240 K on the RT-SIRM curves.
- Similarly, like in the mudstones, higher values of ZFC than FC remanence are visible, suggesting the presence of **MD grains** (after Jackson et al., 2011). This is corresponding also with significantly lower recovery of magnetization on RT remanence curve during heating (Carter-Stiglitz et al., 2006).

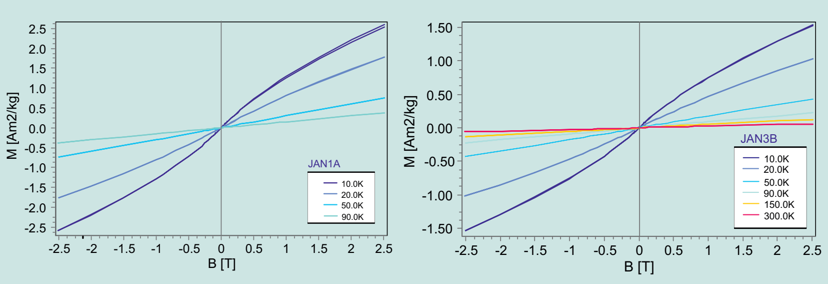
The Jantar Member (sweet spot)

- The samples display very well developed Verwey transitions on the RT-SIRM cooling curves, which is also well visible in both the ZFC and FC warming curves.
- In all specimens the transitions occur at ~120 K, suggesting fairly pure magnetite, and the grain size is probably pseudo-single domain (**PSD**) or **MD magnetite**, due to the small recovery of remanence upon rewarming of the RT-SIRM (Bilardello and Jackson, 2013).
- Higher values of ZFC than FC remanence are also indicative of **MD** grains.

Generally, in both Formations, circa 60 % losses of a magnetization on FC and ZFC curves imparted at 10 K and lost upon warming to 35 K suggests most likely occurrence of very small, probably **superparamagnetic (SP) or SD particles** (e.g., Banerjee et al., 1993; Passier and Dekkers, 2002).



Hysteresis loops performed in LT



Summarized results of magnetic minerals composition

[illegible]	Lithology	Transition temperature [K]	Magnetic mineral	Particles		
				MD/PSD	SD	SP
Pelplin	mudstones	110 - 115	magnetite	×		×?
		220 - 240	hematite	×?	×	×?
	calcareous concretions	110	magnetite	×		×?
		230 - 240	hematite	×?	×	×?
Jantar	mudstones	120	magnetite	×		×?

- Generally, the circumstances to preserve **hematite** in that depth during sedimentation favor **oxic to suboxic conditions** (Liu et al., 2004; Roberts & Weaver, 2005), and also low sedimentation rate (e.g., Kiipli, 2004), which is linked with occurring aerobic and anaerobic **degradation of organic matter** (Tromp et al., 1995). In the Pelplin Formation we observed **higher sedimentation rate** than in the lower Jantar Member, which occurred due to the approaching CDF. Despite this fact, more oxygen-rich conditions appeared, which led to a reduction of organic matter in this facies and at the same time to preserve hematite. In turn, an absence of hematite in the organic-rich Jantar Member can be linked with **rather anoxic conditions** at the bottom and very **low sedimentation rate** (see Karlin & Levi, 1983; Karlin and Levi, 1985 for discussion).
- The presence of hematite in early diagenetic carbonate concretions suggests that chemical conditions during deposition and compaction of detrital material of the Pelplin Formation, and continuously during precipitation of the carbonate concretions, were **relatively stable and oxic**, and also that the hematite appeared in the very early stage of diagenesis.

CONCLUSIONS

- Both Formations exhibit the presence of MD or PSD magnetite. The occurrence of MD/PSD magnetite we interpret as a **detrital in origin**. The presence of SD-SP grains may suggest crystallization of magnetite during **chemical processes like illitization of smectite** and/or **organic maturation**.
- The absence of pyrrhotite suggests that rocks were heated to less than 200 °C, which agrees with paleotemperatures - maximal temperature of approximately 150 °C.
- The Pelplin Fm. (with lower values of TOC) has a slightly **different magnetic mineral composition** than the Jantar Member (the sweet spot layer), as the appearance of hematite is interesting.
- **Hematite** (mostly SD grains), most likely detrital in origin. This is in agreement with precipitation of calcareous concretions and lower values of organic matter.
- **Hematite** preserved in the **Peplin Fm.** suggests that **stable oxic conditions** were present at the bottom of sedimentary basin continuously during deposition of clastic material, concretion cementation and compaction.
- The **absence of hematite** in the **Jantar Mb.** suggests that during sedimentation and early diagenesis more **anoxic conditions** appeared at the bottom.

As a main conclusion we suggest that the magnetic mineral assemblages in studied Silurian shales is related to the amount of organic matter. The presence of hematite correlates with the significantly lower amount of organic matter in sedimentary rocks, which may be a useful factor in case of the organic matter preservation. However, further investigation is necessary to fully recognize this complex problem.

KEY POINTS

- **All analyzed rocks exhibit the presence of MD or PSD magnetite, which we interpret as detrital in origin.**
- **We observed hematite in rocks with modest amounts of organic matter, while in organic-rich layers hematite was absent.**
- **We suggest that occurrence of hematite is related to oxic-anoxic conditions in the bottom of sedimentary basins.**

ACKNOWLEDGEMENTS

This project was helped by a Visiting Fellowship at the Institute for Rock Magnetism, which is funded by the US National Science Foundation and the University of Minnesota. The visit has been partially financed from the funds of the Leading National Research Centre (KNOW) received by the Centre for Polar Studies for the period 2014-2018. This work has been also funded by the Polish National Centre for Research and Development within the Blue Gas project (No BG2/SHALEMECH/14). Samples were provided by the PGNiG SA.
The presentation has been partially financed from the funds of the Leading National Research Centre (KNOW) received by the Centre for Polar Studies for the period 2014-2018

AAPG International Conference and Exhibition 2018, Cape Town, South Africa, 4-7 November 2018

Institute of Geophysics PAS
64 Księcia Janusza St.
01-452 Warsaw
www.igf.edu.pl