



GeoShale 2012

**Recent Advances
in Geology
of Fine-Grained
Sediments**

Polish Geological Institute
National Research Institute

**14–16 May 2012
Warsaw, Poland**

**Book of Abstracts
Field Trip Guidebook**

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Contents

ORAL PRESENTATIONS

EFFECTS OF UPLIFT AND EROSION ON SHALE COMPACTION AND EXHUMATION ESTIMATES IN THE SW BARENTS SEA Baig I., Faleide J.I., Mondol N.H., Jahren J.	11
THE USE OF FMI IMAGES IN GEOLOGICAL INTERPRETATION OF ORDOVICIAN UNIT AND DEVONIAN THROUGH THE WELLS TAKW-1 AND TAKE-1. ILLIZI BASIN. ALGERIA Baouche R.	13
INTEGRATING CMR, MRF LOG AND CONVENTIONAL LOGS IN DEVONIAN AND ORDOVICIAN Baouche R.	15
FACIES EVOLUTION AND STRATIGRAPHIC CORRELATION IN THE EARLY OLIGOCENE TARD CLAY OF HUNGARY Bechtel A., Hámor-Vidó M., Gratzner R., Sachsenhofer R.F., Püttmann W.	17
ASSESSING GAS SHALES – EXAMPLE FROM THE LOWER CRETACEOUS OF GERMANY Berner U., Marquardt D., Stiller E.	19
SOME OF MY SOURCE ROCKS ARE NOW OIL RESERVOIRS – THE SPECTRUM OF FINE-GRAINED RESERVOIRS FROM ‘SHALE GAS’ TO ‘SHALE OIL’ Bohacs K.M., Passey Q.R., Lazar O.R., Rudnicki M., Esch W.L.	21
CLAY MINERALS RECORD OF CLIMATIC DISASTERS AT THE TRIASSIC-JURASSIC BOUNDARY AND IN EARLY TOARCIAN (EXAMPLES FROM THE FINE-GRAINED DEPOSITS IN POLISH BASIN) Brański P.	23
LITHOLOGIC AND STRATIGRAPHIC VARIATION IN A CONTINUOUS SHALE GAS RESERVOIR: THE BARNETT SHALE (MISSISSIPPIAN), FORT WORTH BASIN, TEXAS Breyer J.A., Bunting P.J., Monroe R.M., Steed M.B.	25
THE MECHANICS AND PHYSICS OF STRENGTH PREDICTION AND PARTIAL SATURATION IN SHALES Dewhurst D., Sarout J., Delle Piane C., Siggins T., Clennell B., Raven M.	27
NEEDS AND CHALLENGES IN COMPREHENSIVE HYDRO-GEO-MICROBIO-CHEMICAL APPROACH TO FORECAST INTERACTIONS IN THE FRACTURING FLUID – RESERVOIR ROCK – PRISTINE GROUNDWATER SYSTEM Dobrzyński D., Wolicka D.	29
MATHEMATICAL OPTIMIZATION OF CLASSIFICATION SYSTEMS OF THE DESCRIPTIVE GRAIN SIZE DISTRIBUTION: A NEW CLASSIFICATION SCHEME BASED ON MATHEMATICAL CRITERIA Essefi E., Yaich C.	31
THE MIDDLE JURASSIC BLACK SHALES FROM THE CENTRAL PART OF POLISH BASIN – SEDIMENTARY ENVIRONMENTS STUDIES Feldman-Olszewska A.	33
HIGH-RESOLUTION STRATIGRAPHIC CORRELATION AND BIODIVERSITY DYNAMICS OF MIDDLE AND LATE ORDOVICIAN MARINE FOSSILS FROM POLAND AND BALTOSCANDIA Goldman D., Podhalańska T., Sheets D.H., Bergström S.M., Nölvak J., Reinhart K.	35
BELOVEŽA FORMATION VERSUS HIEROGLYPHIC BEDS IN THE MAGURA NAPPE, OUTER CARPATHIANS, POLAND Golonka J., Waškowska A.	37
SOURCE ROCK PREDICTION VALUE AS A TOOL FOR EXPLORATION OF UNCONVENTIONAL HYDROCARBONS IN CARPATHIANS Golonka J., Krobicki M., Waškowska A., Słomka T.	39
ANALYSIS AND EVALUATION OF EUROPEAN SHALE GAS PLAYS. CASE STUDY Gunning A., Drop K., Kozłowski M.	41
POLAND SHALE GAS/OIL PLAY: INTEGRATING OLD AND NEW DISCIPLINES TO INTERPRET UNCONVENTIONAL RESOURCE POTENTIAL OF AN EARLY PALEOZOIC SOURCE ROCK Hardy M.J., Davis C., Kaufman J., Molyneux S., Klimentidis R., Ferguson I.	43
BLACK SHALE DEPOSITION ON A CARBONATE PLATFORM (ARAN ISLANDS, IRELAND) – ORGANOFACIES, GEOCHEMISTRY AND SEQUENCE STRATIGRAPHIC INTERPRETATION Jaeger H., Clayton G., Goodhue R.	45
QUARTZ CEMENTATION IN SHALES RELEVANT FOR SHALE GAS RESERVOIRS Jahren J.	47

WELL TEST ANALYSIS OF HORIZONTAL WELLS WITH MULTIPLE HYDRUALIC FRACTURES IN A GAS SHALE RESERVOIR Kabdenov S., Gringarten A., Kostyleva I.	49
RED BED SHALES FROM THE POLISH ROTLIEGEND BASIN AND THEIR SIGNIFICANCE AS GAS TRAP SEALS Kiersnowski H., Buniak A.	51
TIME RESOLVED 3D IMAGING OF ORGANIC-RICH SHALES DURING HEATING Kobchenko M., Panahi H., Renard F., Malthe-Sørenssen A., Scheibert J., Dysthe D. K, Meakin P.	53
ENVIRONMENTAL IMPACT OF HYDRAULIC FRACTURING TREATMENT PERFORMED ON THE ŁEBIEŃ LE-2H WELL Koniecznyńska M., Antolak O., Starzycka A.	55
ORIGIN OF ORGANIC MATTER IN THE EARLY SILURIAN CHERTS AND SILICEOUS SHALES OF POLAND Kremer B.	57
ROLE OF SHALES DURING COMPRESSIONAL TECTONICS: COMPARISON OF THE VARISCAN (L. CARBONIFEROUS) BASIN INVERSION OF THE LUBLIN BASIN AND THE APPALACHIANS Krzywiec P.	59
SOURCE ROCK EVALUATION TECHNIQUE: A PROBABILISTIC APPROACH FOR DETERMINING HYDROCARBON GENERATION POTENTIAL AND IN-PLACE VOLUME FOR SHALE PLAYS Kuchinskiy V., Gentry K., Hill R.	61
MULTISCALE IMAGING OF SHALE CORE SAMPLES Lemmens H.	63
THE INTERPLAY OF SEDIMENTATION, EUSTASY, AND TECTONICS IN CONTROLLING VERTICAL TOC VARIATION IN ORDOVICIAN TO SILURIAN SHALES, EASTERN POLAND Lis P., Kaufman J., Bohacs K.M., Hardy M.J.	65
GAS FROM SHALE. LOCAL COMMUNITIES – COOPERATION OR CONFLICT? Maj T.	67
MICROBIAL VERSUS THERMOGENIC GAS SYSTEM: COMPARISON OF DEVONIAN/MISSISSIPPIAN SHALES WITH PENNSYLVANIAN COALS IN THE ILLINOIS BASIN Mastalerz M., Schimmelmann A., Gao L.	69
SHALE AND COAL BASINS OF NE ENGLAND: OPPORTUNITIES FOR RESEARCH AND INDUSTRY COLLABORATION IN UNCONVENTIONAL HYDROCARBONS McCaffrey K., Gluyas J.G., Davies R.J., Imber J., Armstrong H.A.	71
SUPERGIANT PETRIFIED OIL FIELD IN TWO-BILLION-YEAR TURBIDITIC GREYWACKE-SHALE SUCCESSION IN THE EASTERN FENNOSCANDIAN SHIELD Melezhik V.A., Fallick A. E., Črne A.E., Lepland A.	73
RELATIONSHIPS AMONG POROSITY, PERMEABILITY AND SEISMIC VELOCITY IN MUDSTONES AND SHALES Mondol N.H.	75
FROM BLACK TO GREEN SHALE – ANOXIC SEAS AND GREENHOUSE LANDS IN DISTURBED JURASSIC WORLD Pierńkowski G.	77
LOWER SILURIAN „HOT” SHALES IN POLAND – STRATIGRAPHY AND DEPOSITIONAL ENVIRONMENT Podhalańska T.	79
GAS AND OIL SHALE FORMATIONS IN CENTRAL EUROPE – AN OVERVIEW Poprawa P.	81
ENVIRONMENTAL CONCERNS RELATED TO GAS AND OIL PRODUCTION FROM SHALE RESERVOIRS – IMPACT RELATED TO TECHNOLOGICAL APPROACH VERSUS IMPORTANCE OF LOCAL GEOLOGICAL SETTING Poprawa P.	83
NANO- AND MICROPOROUS STRUCTURE AND ACCESSIBILITY IN SOURCE ROCKS AND TIGHT RESERVOIRS AS DETERMINED BY NEUTRON AND X-RAY SCATTERING Radlinski A.P., Melnichenko Y.B., Blach T.P.	85
MUD MOBILIZATION AND FOLDING HISTORY IN THE SOUTH CASPIAN BASIN Santos Betancor I., Soto J.I., Lonergan L., Sánchez Borrego I., Macellari C.E.	87

CLAY MINERAL AND ORGANIC DIAGENESIS OF MALMIAN MARLSTONES, VIENNA BASIN Schicker A., Gier S.	89
AN OVERVIEW OF EXPERIMENTAL MUDSTONE SEDIMENTOLOGY – RESULTS OF EXPERIMENTS AND APPLICATIONS TO THE ROCK RECORD Schieber J.	91
RADIOLOGICAL SAFETY OF METAMORPHOSED BLACK SHALES OF THE NIEMCZA ZONE (NZ) AND THE NIEMCZA – KAMIENIEC ZĄBKOWICKI METAMORPHIC UNIT (N-KZMU) Solecki A.T., Nowak K.J., Gasz M.R.	93
THIN-SKINNED EXTENSION AND SHALE TECTONICS IN A TILTED BASIN MARGIN: THE CASE OF THE NORTHERN ALBORAN SEA (MEDITERRANEA) Soto J.I., Fernández-Ibáñez F., Betancor Santos I., Talukder A.R., Macellari C.E.	95
IDENTIFICATION, INTEGRATION AND UPSCALING OF MUDROCK TYPES IN POLAND – A PATHWAY TO UNLOCKING SHALE RESOURCES Spaw J.M., Stone R.A., Wilty R.H., Kuchinskiy V.	97
RELATIONSHIP BETWEEN MINERALIZATION AND FABRIC IN THE NONESUCH SHALE: IMPLICATIONS FOR FLUID MIGRATION PATHWAYS IN FINE-GRAINED ROCKS Sutton S.J., King N.	99
CONTROLS ON DISTRIBUTIONS OF METHYLPHENANTHRENES IN SEDIMENTARY ROCK EXTRACTS: CRITICAL EVALUATION OF EXISTING GEOCHEMICAL DATA FROM MOLECULAR MODELING Szczërba M., Rpondek M.	101
TIMING AND THE MAXIMUM PALEOTEMPERATURES OF DIAGENESIS OF THE LOWER PALEOZOIC SHALES ON THE PERI-TORNQUIST MARGIN OF THE EAST EUROPEAN CRATON EVALUATED FROM CLAY MINERAL DATA Środoń J.	103
MINERAL DIAGENESIS IN CLAY- AND SILT-RICH MUDSTONES: THE MANCOS SHALE, BOOK CLIFFS, UTAH Taylor K.G., Macquaker J.H.S.	105
OPAL AS A CARRIER OF URANIUM IN MENILTE SHALES Tchorz-Trzeciakiewicz D.E., Solecki A. T.	107
TECTONIC DECOUPLING ALONG THE SILURIAN SHALE COMPLEX IN THE LUBLIN BASIN, SE POLAND Wróbel G., Walker P., Poprawa P., Tomaszczyk M., Krzywicz P.	109
POSTERS	
GEOMECHANICAL ASSESSMENT OF THE ELASTIC PROPERTIES OF RESERVOIR ROCKS UNDER HIGH PRESSURES AND TEMPERATURES Bobrowska A., Dziedzic A.	113
TWO-STAGES GAS GENERATION IN THE CARBONIFEROUS SHALES OF THE SOUTHERN PART OF THE FORE-SUDETIC MONOCLINE (SW POLAND) Botor D.	115
THE SECONDARY OXIDATION OF COPPER BEARING SHALE IN THE KOZUCHOW AREA Chmielewski A.	117
THE UNCONVENTIONAL GASES RESOURCES OF ROMANIA. CASE STUDY: SILURIAN FROM MEOSIAN PLATFORM Coltoi O.	119
MINERALOGY OF SILURIAN SHALES FROM THE LUBLIN BASIN (EASTERN POLAND) Gąsiński A., Poszytek A., Poprawa P., Wolicka D.	121
PHENYL DERIVATIVES OF PACS IN THE SILURIAN SUCCESSION OF THE BARDZKIE MTS, POLAND Grafka O., Marynowski L.	123
NATURAL FRACTURES IN LOWER JURASSIC BLACK AND GREY SHALE, CLEVELAND BASIN, UK Imber J., Clancy S., Warren C., Armstrong H., McCaffrey K., Davies R., Jones S., Gluyas J., Trevelyan J.	125
INTEGRATED STRATIGRAPHY AND CORRELATION OF THE UPPER SILURIAN PERIPLATFORM SHALE SUCCESSION IN THE MIELNIK IG1 AND GOŁDAP IG1 BOREHOLES (EASTERN POLAND) Kozłowski W., Sobień K.	127
LIPID BIOMARKERS AND D15N AS GEOCHEMICAL TRACERS OF ORGANIC MATTER IN EARLY SILURIAN SILICEOUS SHALES OF POLAND Kremer B., Bauersachs T., Kaźmierczak J.	129

THE KUPFERSCHIEFER IN THE WARKA IG-1 BOREHOLE, MAZOVIA Krzemiński P.	131
PERSPECTIVE OF SHALE GAS EXPLORATION IN THE LOWER PALEOZOIC DEPOSITS OF VOLYNO-PODILLYA, UKRAINE Kurovets I., Chepil P., Gladun V., Mikhailov V., Shevchenko T.G., Koltun Y., Kurovets S.	133
TEMPESTITES FROM MIDDLE JURASSIC ORE-BEARING CLAYS FROM THE SILESIA-CRACOW UPLAND Leonowicz P.	135
TURBIDITIC SHALES VERSUS HEMIPELAGIC SHALES IN THE MAGURA BEDS OF GLAUCONITIC FACIES (UPPER EOCENE–LOWER OLIGOCENE, POLISH OUTER CARPATHIANS) Leszczyński S., Hawryłko S., Schnabel W., Malata E.	137
GEOPHYSICAL PROPERTIES OF SHALE WITH RESPECT TO RESOURCE IDENTIFICATION: A CASE STUDY FROM THE WESTERN KAROO BASIN, SOUTH AFRICA Maré L.P., Hallbauer-Zadorozhnaya V.	139
THE HANGENBERG BLACK SHALE AND OTHER EUXINIC EVENTS THROUGH THE FAMENNIAN SUCCESSION OF THE HOLY CROSS MOUNTAINS, POLAND Marynowski L., Filipak P., Pisarzowska A., Rakociński M., Zatoń M.	141
INFLUENCE OF THE INTERLAYER CATIONS HYDRATION ON SMECTITE ELASTIC PROPERTIES BY FIRST PRINCIPLE CALCULATIONS Muñoz-Santiburcio D., Hernández-Laguna A., Soto J. I.	143
METHODOLOGY AND FIRST RESULTS OF AN ASSESSMENT OF SHALE GAS RESOURCES IN GERMANY Pierau R., Rogalla U., Franke D., Bahr A., Ladage S., Berner U.	145
NEW PERSPECTIVES OF MICROFOSSIL AND HEAVY MINERALS EXTRACTION FROM THE FINE-GRAINED SEDIMENTS WITH THE USE OF THE LIQUID NITROGEN METHOD [LN ₂] Remin Z., Jarochowska E., Wójcik K.	147
LOW-GRADE METAMORPHIC SLATES, A POTENTIAL HOST-ROCK FOR HIGH-LEVEL AND/OR LONG-LIVED RADIOACTIVE WASTE DISPOSAL Sintubin M., Brassinnes S., Depaus Ch., Van Geet M.	149
PERYLENE AS AN INDICATOR OF FOSSIL WOOD DEGRADATION BY WOOD-DEGRADING FUNGI Smolarek J., Marynowski L., Philippe M.	151
COMPARISON OF THERMAL MATURITIES FROM LOWER JURASSIC AND LOWER CRETACEOUS SEDIMENTS FROM THE SOUTHERN MARGIN OF THE LOWER SAXONY BASIN, NORTHWEST GERMANY, USING ORGANIC GEOCHEMICAL AND PETROGRAPHICAL METHODS Stiller E., Berner U., Marquardt D.	153
GLACIO-EUSTATIC AND PALAEOCEANOGRAPHIC IMPLICATIONS OF THE HIRNANTIAN AND RHUDDANIAN SEDIMENTARY RECORD IN THE HOLY CROSS MOUNTAINS (POLAND) Trela W., Podhalańska T.	155
ORGANIC-RICH SHALES OF THE PROTO-SILESIA BASIN IN POLISH-CZECH CARPATHIANS Waškowska A., Golonka J., Krobicki M., Strzeboński Piotr, Vašíček Zdenek., Skupien P.	157
PETROLEUM POTENTIAL OF KIMMERIDGIAN AND TITHONIAN STRATA OF THE POLISH LOWLANDS AS DETERMINED BY HYDROUS PYROLYSIS Więclaw D., Kotarba M., Lewan M.D.	159
COMPARISON OF GEOLOGICAL SETTING OF TWO, SHALE GAS – BEARING, VARISCAN FORELAND BASINS – FORT WORTH BASIN, TEXAS, USA AND SILESIA BASIN, S POLAND Wieczorek A., Kłakowicz A., Sitarz A.	161
FIELD TRIP GUIDEBOOK	
SILURIAN SUCCESSION OF THE HOLY CROSS MOUNTAINS Trela W., Salwa S., Marynowski L., Pieńkowski G., Szrek P., Malec J.	165
THE CARPATHIANS – MENILITE SHALE AS THE MAIN OIL SOURCE IN THE CARPATHIANS Krobicki M., Golonka J., Ślęczka A.	195
CORE WAREHOUSE WORKSHOP – PARASEQUENCE IN MUDSTONES Lis P.	237
SILURIAN SUCCESSION WITHIN THE LOWER PALEOZOIC BASIN OF PODOLIA Wrona R., Lis P.	255

GeoShale 2012  **book of abstracts**
oral presentations

EFFECTS OF UPLIFT AND EROSION ON SHALE COMPACTION AND EXHUMATION ESTIMATES IN THE SW BARENTS SEA



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Key words:

compaction, diagenesis, exhumation, maturation, migration

1

Late Cenozoic exhumation of Barents Sea sedimentary strata has influenced the mechanical and physical properties of the rocks and also migration and trapping of hydrocarbons. This study seeks to quantify the changes in shale rock properties as a function of compaction and exhumation and its influences on hydrocarbon exploration. Based on well logs and geochemical data from more than 20 wells along two SW-NE (~450 km) and NW-SE (~550 km) transects, and seismic refraction velocities from shot data along seven E-W and N-S oriented lines, shale compaction in the uplifted Barents Sea has been estimated. The data used include gamma ray logs, neutron – density logs, sonic logs (P&S-wave), resistivity logs, formation tops, vitrinite reflectance, bottom hole temperatures and P-wave velocity-depth curves from seismic refraction. P&S-waves velocities were calculated from compressional and shear sonic logs where available. Shear wave velocities for the remaining wells were computed by P and S-waves velocity relationships developed from the available shear and compressional sonic logs. The shear moduli (rock resistance to shear movement) were calculated from bulk density and S-wave velocity. The shale volumes were calculated using a combination of gamma ray-deep resistivity and neutron-density porosity logs. These data sets measure different parameters within the sediments but they are all related to depth of burial and temperature, so these have been used to quantify exhumation in the area. Reference velocity-depth trends for P-wave velocity from sonic logs and seismic refraction data were established for the study area at locations where the velocity is lowest, and a relatively thick and complete Cenozoic succession is present (most likely at or close to maximum burial today). The velocity-depth trends from the remaining areas were then calibrated to the reference trend

and any shift from the reference trend is measured as erosion\uplift. Vitrinite reflectance vs. depth was plotted on a semi-logarithmic scale and best fit curves were drawn for each well and extrapolated to a near surface vitrinite reflectance of 0.2% to measure the exhumation. The difference between zero and extrapolated depth at 0.2% was measured as exhumation. The results showed that petrophysical properties are changing both vertically and laterally in all areas of the SW Barents Sea. Significantly higher velocities, densities and thermal maturities of shales have been observed at shallower depths compared to shales from similar depths in normally compacted basins. The probable transition zones between mechanical and chemical compaction zones are identified from well logs, bottom hole temperatures, and rock physics analyses in the two reference wells. In the other wells studied the transition zones are located at much shallower depths with respect to temperature than expected from normal compaction (in some wells it was not possible to differentiate/identify the transition zones due to uplift). Exhumation was estimated from velocity and thermal maturity trends. The exhumation estimates agree quite well (within 70-90% for the individual wells). Combining and averaging the exhumation results suggest minimal or no erosion at the western margin of the SW Barents Sea whereas exhumation increases significantly towards the NNE and increases slightly towards the East. The shale properties in the Barents Sea area are significantly affected by exhumation resulting in higher velocities and densities, and lower porosities at shallow depths than expected for normal compaction. The results from this study are useful input for modeling of maturation, generation, migration and trapping of hydrocarbons in the area.

THE USE OF FMI IMAGES IN GEOLOGICAL INTERPRETATION OF ORDOVICIAN UNIT AND DEVONIAN THROUGH THE WELLS TAKW-1 AND TAKE-1. ILLIZI BASIN. ALGERIA



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Key words:

Devonian, Ordovician, FMI, Illizi Basin, Algeria

2

This study presents the Ordovician unit and Devonian interpretation for the Formation Micro Imager data recorded both in the well Takw-1 and Take-1 in the Illizi basin, Algeria. These vertical wells (2.2° and 2.7° less than hole deviation) in the Ordovician formation and Devonian are located in the Eastern part of Algeria very close to the In-Amenas field. The full FMI image has been acquired in a log up and covers the interval 2475 m – 1658 m (MD). The interested zone (Ordovician unit) stretches actually from the bottom of the section up to 2332 m (MD).

The objectives of both Takw-1 and Take-1 FMI analysis are stratigraphic and structural.

A detailed picking of all the sedimentary and structural events identified on the FMI processed image and classification as either beds boundaries, cross-beddings, erosive surfaces and conductive faults or resistive fracture.

The steps for this interpretation were as follows:

- A statistical analysis of the sedimentary and tectonic fracture.
- Sedimentological description as determination of facies type.
- Implication of the geology on the reservoir dynamic.

In this study, this technology applied to fracture system classification. The figures can be shown with a fracture classification in terms of numbers of fracture imaged, type and orientation that is at least as good as seen in previous conductive, water based devices. It is shown that results provide important data to be taken into a wider dynamic fracture model.

INTEGRATING CMR, MRF LOG AND CONVENTIONAL LOGS IN DEVONIAN AND ORDOVICIAN



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Key words:

Devonian, Ordovician, CMR, MRF, Illizi Basin, Algeria

3

This study an evaluation integrating MRF, CMR logs and conventional logs for the well Take-1, Illizi basin in Algeria. MRF, CMR logs and conventional logs provide formation permeability in different ways though the parameter can be derived in the three kinds of data. Integrating the three kinds of data and comparing the change trends among the data, the rock properties of reservoirs are analyzed in this research. The Nuclear Magnetic Resonance (NMR) tool makes it possible independently to determine parameters such as total and effective porosities, irreducible saturation, permeability, the volume of clay, the volume of water related to clays and the distribution of the size of the grains. In particular, NMR analysis, as demonstrated from the Take-1 well, allowed, in addition to the determination of the petrophysical parameters:

- Analysis of the distribution of dimensions of the pores.
- Improved definition of hydrocarbon zones.
- Measurement of the portion of the S_w within interstitial clays.
- The determination of the irreducible water portion and of an accurate S_w cutoff.

The interpretation of the magnetic resonance data recorded from the Ordovician and Devonian reservoirs made it possible to evaluate irreducible water saturation and to determine the volume of movable water. Moreover, the NMR depth log, provided measurements for the determination of accurate porosity, permeability and irreducible water saturation, which were used for enhanced formation evaluation in these reservoirs.

FACIES EVOLUTION AND STRATIGRAPHIC CORRELATION IN THE EARLY OLIGOCENE TARD CLAY OF HUNGARY

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Key words:

anoxia, biomarkers, central paratethys, planktonic productivity, stratigraphy

4

Hydrocarbon source rocks (i.e. Tard Clay Formation), containing type-II organic matter, were deposited in the Hungarian Paleogene Basin during Lower Oligocene. A major contribution of aquatic organisms (green algae, dinoflagellates, Chrysophyte algae) and minor inputs from macrophytes and land plants to organic matter accumulation is indicated by n-alkane distribution patterns, composition of steroids, and $d^{13}C$ of hydrocarbon biomarkers. Microbial communities included heterotrophic bacteria, cyanobacteria, chemoautotrophic bacteria, as well as green sulfur bacteria. The presence of methanotrophic bacteria is indicated by ^{13}C -depleted hop-17(21)-ene. Higher inputs of terrestrial organic matter occurred during deposition of the lower and uppermost units of the Tard Clay Formation. The terpenoid hydrocarbon composition argues for angiosperm-dominated vegetation in the area of the Hungarian Paleogene Basin. Diterpenoid hydrocarbons, derived from the resins of conifers, are about 2–3‰ enriched in ^{13}C compared to the angiosperm biomarkers.

Environmental conditions changed from marine to brackish, accompanied by oxygen-depletion in the lower parts of the water column. Organic carbon accumulation during this period was a consequence of stagnant bottom water conditions in the Hungarian Paleogene Basin due to salinity stratification. This is indicated by low pristane/phytane ratios (varying from 0.27 to 1.44), enhanced ratios of dimethylated versus trimethylated MTTCs (0.14–0.59), and the presence of aryl isoprenoids (from 0.4 to 14.1 mg/g TOC). A major marine incursion is evidenced by stable isotope ratios of organic matter and carbonates. In the uppermost member of the Tard Clay, a transition from brackish towards normal marine conditions is proposed.

Up to 3 anoxic cycles are recognized in the drill core sections, separated by minima in pristane/phytane ratios and maxima in the depth trends of di-/tri-methylated MTTCs and aryl isoprenoid concentrations. In combination with the position of maxima of $d^{13}C$ of carbonate and organic matter and an abrupt decrease in perylene concentrations, the cycles can be used for intra-formational correlation of the Tard Clay.

ASSESSING GAS SHALES – EXAMPLE FROM THE LOWER CRETACEOUS OF GERMANY



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Key words:

gas shale assessment, mass balance calculation, German Wealden Basin

5

Within the petroleum system of NW Germany the German Wealden has already gained specific interest during early stages of hydrocarbon exploration because of its excellent hydrocarbon potential. The interest in exploring the basin shales of the German Wealden revived recently with the onset of the search for shale gas. Our recent investigations relate to the evaluation of the shale oil and shale gas potential of organic-rich sediments. We present a refined approach to restore the initial hydrocarbon potential, as well as hydrocarbon redistribution through expulsion and migration, as these parameters affect estimates on hydrocarbons in place significantly. In our methodology we com-

bine data from Rock-Eval pyrolysis and solvent extraction in mass balance considerations, which also incorporate thermal maturities and related hydrocarbon transformations ratios. We present two applications related to Lower Cretaceous strata of the Lower Saxony Basin. Data from a research well suggests extensive hydrocarbon redistribution within the sedimentary column and also a hydrocarbon surplus gained through lateral migration. A further application of the methodology to surface prospecting demonstrates how to successfully evaluate the unconventional shale oil and shale gas potential of a basin along a geochemical traverse.

SOME OF MY SOURCE ROCKS ARE NOW OIL RESERVOIRS – THE SPECTRUM OF FINE-GRAINED RESERVOIRS FROM ‘SHALE GAS’ TO ‘SHALE OIL’



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Key words:

shale oil, shale gas, porosity, permeability, matrix

6

Commercial production from mudstones can result from various combinations of rock and hydrocarbon properties, effectively spanning ‘conventional’ tight oil to ‘shale’ reservoir matrix production: ‘Conventional’ tight-non associated, Interbedded/Hybrid, Porous ‘shale’, Fractured ‘shale’. In this presentation, we concentrate on ‘shale’ reservoir types that comprise ‘shale oil’ reservoirs at lower thermal maturities and pressure-temperature (P-T) conditions to ‘shale-gas’ reservoirs at higher maturities and P-T conditions. Both contain a variety of pore types: inter-granular, intra-granular, intra-kerogen, and intra-bitumen – the last two, ‘organic-associated’ types, are better developed and connected at higher maturities. (Note that all plays have some component of inter/intra-granular porosity as well as some fracture permeability, but can be usefully categorized by their dominant or distinctive factor.)

Most currently producing ‘shale’ reservoirs are mature to overmature oil-prone source rocks. Shale oil reservoirs share many attributes with shale gas reservoirs, but also have some distinct differences. Key additional dimensions include fluid properties: over geological time, fluid density and phase control fluid saturation in the matrix, and in the short term, viscosity and phase affect flow and production rates. Hence, two main classes of attributes affect ultimate ‘shale’ reservoir performance: rock properties (mainly per-

meability) and fluid properties (mainly viscosity). Both are influenced by the full geological history of the reservoir. Overall reservoir permeability includes both matrix and fracture characteristics: Matrix permeability is a function of original depositional composition, texture, bedding, and stratal stacking plus burial history (thermal stress, diagenesis). Fracture permeability is a function of the same controls as matrix permeability along with structural history (mechanical stress). Fluid properties are also controlled by the original depositional properties and burial/uplift history, along with present-day reservoir pressure and temperature. The higher thermal maturities of ‘shale-gas’ reservoirs result in some contrasts with ‘shale-oil’ reservoirs: they tend to have less smectite (inter-layer water) due to illitization, but develop significant porosity associated with kerogen and bitumen. SEM images of ion-beam-milled samples reveal development of a distinct separate nanoporosity system contained within the organic matter, in some cases comprising >50% of the total porosity, and these pores tend to be hydrocarbon wet, at least during most of the thermal maturation process.

Appreciation of the similarities and differences between ‘shale-gas’ and ‘shale-oil’ enables more efficient, effective, and economic exploitation of the full range of resource types.

CLAY MINERALS RECORD OF CLIMATIC DISASTERS AT THE TRIASSIC-JURASSIC BOUNDARY AND IN EARLY TOARCIAN (EXAMPLES FROM THE FINE-GRAINED DEPOSITS IN POLISH BASIN)

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Key words:

clay minerals, global warming, Rhaetian-Hettangian transition, Lower Toarcian, Polish Basin

7

Results of mineralogical and geochemical analyses of the Triassic-Jurassic boundary interval (Zagaje Fm.) and Lower Toarcian successions (Ciechocinek Fm.) from the epicontinental Polish Basin are presented. A set of nearly 200 samples of claystones and mudstones from 8 boreholes was analyzed for mineralogy (XRD of bulk samples and clay fractions) and for major-element geochemistry (XRF of bulk samples). SEM observations of some samples were also performed. The end of Triassic and the latest Pliensbachian – Early Toarcian time interval were the periods of violent global environmental changes linked to the Pangea breakup and development of two large igneous provinces. The aim of the current research was to recognize effects of the rapid climatic changes in the hinterland of Polish Basin on the clay mineral composition and compare these data with published so far results of the carbon isotope analyses.

In the uppermost Rhaetian an abrupt increase in detrital kaolinite content was observed. Kaolinite-illite (or kaolinite-smectite) association dominated in studied sections. In the Lower Hettangian and also in Lower Toarcian succession, clay minerals assemblages comprise predominantly detrital kaolinite and illite with subordinate chlorite and only trace amounts of smectite. The burial diagenesis (and also telodiagenesis) altered the clay mineral composition in very local scale. It suggests that clay mineral assemblages were controlled chiefly by chemical weathering in generally warm and humid climate. Reworking and redeposition of the ancient sediments (caused by local tectonic processes and/or by sea-level falls) could modify the clay mineral composition and sometimes could obscure the palaeoclimatic signal. In some cases the original clay minerals assemblage was somewhat altered by early diagenetic processes.

It should be emphasized that some levels of the very high kaolinite/illite ratio just below Triassic-Jurassic boundary and above the base of Hettangian suggest extreme chemical weathering in the humid-subtropical to tropical climate in the aftermath of rapid warming and abundant rainfall. In Early Toarcian, otherwise illite-dominated deposition was again interrupted by the amplified kaolinite input. Levels of the high kaolinite/illite ratio indicate intense continental weathering related to the global warming spanning the late *tenuicostatum*-early *falciferum* biochronozonal transition. Cyclic variations observed in the clay minerals composition were most probably astronomically controlled, mainly due to probably the short orbital eccentricity cycles (~100,000 years). These results of clay minerals and major-elemental analyses are consistent with carbon isotope record in marine and terrestrial materials received from sections in Polish Basin (Hesselbo, Pieńkowski, 2011; Pieńkowski et al., 2012) and different parts of the world. They confirm sudden, catastrophic climate shifts at the Triassic-Jurassic boundary (including super-greenhouse conditions), more extended cyclic variations in generally warm Hettangian times and stepped nature of the super-greenhouse/anoxic event in Early Toarcian.

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LITHOLOGIC AND STRATIGRAPHIC VARIATION IN A CONTINUOUS SHALE GAS RESERVOIR: THE BARNETT SHALE (MISSISSIPPIAN), FORT WORTH BASIN, TEXAS



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8

Shale-gas reservoirs commonly consist of large volumes of rock that are regionally extensive and pervasively charged with gas. Just a few years ago, many workers considered the dark, organic-rich mudrocks that comprise shale-gas reservoirs to be homogeneous, widespread and continuous stratigraphic units. However, more recent work has shown shale-gas systems to have significant intrabasin differences in lithology and reservoir properties.

Dark, siliceous mudstone to claystone with a matrix of clay minerals and cryptocrystalline quartz is the most common facies in the Barnett Shale. The composition of the silt-size fraction changes across the basin. Sponge spicules are conspicuous among the sand- and silt-sized grains in the mudstone, but are much more common in the central portion of the basin than in the northern portion. Two predominantly calcareous facies are next in abundance after the siliceous mudstone: laminated, argillaceous lime mudstone and skeletal, argillaceous lime packstone. Both facies decrease in bed thickness and relative abundance from the northern to the central portions of the basin. Two silty, quartz-rich claystone to mudstone facies are present in the Barnett. One consists of alternating laminae of angular quartz silt and mud. In the second,

the quartz grains are scattered throughout the clay matrix, not concentrated in discrete laminae. The second type is unique in containing measurable amounts of mica and lacking sponge spicules.

All of the major facies recognized in the Barnett have high concentrations of organic matter. Variation in facies is greater than variation in organic matter. The location of "sweet spots" within the Barnett may ultimately be explained by the distribution of facies that respond differently to various completion procedures. Lithofacies stacking patterns have been recognized and mapped in the northern portion of the basin. Work in the central and eastern portion of the basin reported here has related the distribution of facies to the location of the depositional site on advancing shale wedges. As the play matures it is likely that a detailed understanding of the geology, especially the distribution of facies, will become increasingly important in selecting well locations, intervals in which to land laterals, and which fracture stimulation techniques to employ. [Abstract published with permission of AAPG. Full article will appear in AAPG Memoir 97 Shale Reservoirs – Giant Resources for the 21st Century.]

THE MECHANICS AND PHYSICS OF STRENGTH PREDICTION AND PARTIAL SATURATION IN SHALES



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Key words:
shale, strength, saturation, rock properties

9

Knowledge of mechanical, physical and petrophysical properties of shales has slowly increased in recent times partly through investigations of the problems they cause for drillers (wellbore stability, overpressure), further through investigations of top seal capacity and integrity (capillary and mechanical properties) and finally through the advent of shales as reservoirs for prospecting for unconventional sources of gas (flow, diffusion, strength, fracturing). In particular, understanding factors controlling the strength of 'conventional' shales (e.g. overburden shales, top seals etc. which are fully saturated and clay-rich) are important for predicting wellbore stability and trap integrity, issues which if not well understood, can cost billions of dollars a year. In this paper, we look at laboratory methods of measuring the strength of shales and then relate them empirically to other more easily measured physical and petrophysical properties. While

regularly used as a proxy for rock strength, velocity was found to be a poor indicator of absolute shale strength, although useful for determining upper bounds. Porosity and cation exchange capacity give good empirical correlations to strength on a global suite of shales. However, partial saturation complicates this picture as water content affects rock strength in both fully and partially saturated clay-bearing shales. Strength and static mechanical stiffnesses can increase as water saturation decreases in low porosity, low clay, hard, stiff shales, as do dynamic moduli such as Young's and Shear moduli calculated from velocity. This has implications for proper preservation of clay-bearing shales for laboratory testing for mechanical, physical and petrophysical properties, especially those now considered as reservoirs as well as for predicting gas shale properties from seismic data or wireline logs under partially saturated conditions.

NEEDS AND CHALLENGES IN COMPREHENSIVE HYDRO-GEO-MICROBIO-CHEMICAL APPROACH TO FORECAST INTERACTIONS IN THE FRACTURING FLUID – RESERVOIR ROCK – PRISTINE GROUNDWATER SYSTEM



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Key words:

fluid–rock interaction, geomicrobiological processes, hydrogeochemical modelling, reservoir rock mineralogy, shale gas E&P

10

Shale gas exploration and production (SGEP) trigger various technological and environmental issues. The severe lack of sufficient data on geomicrobiological, hydrogeochemical and mineralogical aspects of SGEP was a reason for undertaking the comprehensive studies. The main aims of pilot case studies were: (1) forecasting geochemical effects of hydraulic fracturing, (2) working out methodology of such research. Studies were carried out to identify interactions between fracturing fluid/formation fluid (FF), microbial community (MC), reservoir rocks (RR) and overlying aquifers (AQ).

The studies covered: chemical analyses and microbiological essays of FF, lab experiments on FF-MC-RR interactions at controlled temperature, mineralogical (XRD, DTA, SEM, EDS) tests of RR and minerals formed during lab experiments, hydrogeochemical modelling of FF-RR and FF-AQ interactions.

The studied FF can be characterized as organic-rich, microbial non-free, alkaline, saline fluids of the chemistry much differing from primordial geochemistry of RR. The microorganisms identified in FF change its chemistry. Results show that autochthonous MC can produce different bio-gases, e.g. CO₂, H₂, CH₄, which could increase the reservoir pressure, and sulphate reducing bacteria produce

H₂S, which deteriorate the gas quality. Moreover, minerals of studied RR (plagioclase, illite, calcite/dolomite, chlorite, pyrite) may also quickly and effectively affect the FF chemistry. Lab tests revealed carbonate, sulphate and sulphide minerals neoformed due to the reactions between FF solutes, autochthonous MC in FF, and genuine minerals of RR.

Hydrogeochemical modelling allowed to: quantify saturation of FF with respect to RR minerals; forecast changes of FF chemistry in deposit; identify thermodynamically preferred secondary minerals which might reduce rock permeability; evaluate the risk for the AQ quality.

The presented multidisciplinary applied research were the first one in Poland, and proved severe needs to work on methodology of studies on the geochemical effects of SGEP. Understanding the genuine biogeochemical reactions between rock and fluids has numerous applied aspects, like, for instance, formation of bio-gases, or explaining the role of neoformed minerals in changing properties of newly fractured shale rocks. Forecasting and quantifying of such reactions requires detailed high-quality hydrochemical, geomicrobiological and mineralogical data, and doing thermodynamic and kinetic modelling.

MATHEMATICAL OPTIMIZATION OF CLASSIFICATION SYSTEMS OF THE DESCRIPTIVE GRAIN SIZE DISTRIBUTION: A NEW CLASSIFICATION SCHEME BASED ON MATHEMATICAL CRITERIA



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Key words:

descriptive grain size distribution, ternary diagrams, mathematical optimization, Index of Resolution Capacity, fine sediments

11

The aim of this work is threefold. (1) Proposing a mathematical method to choose the adequate system of classification from the commonly used ternary (clay-silt-sand) systems of classification such as of Shepard (1954), Folk (1968), Folk et al. (1970), Reineck and Siefert (1980), Pejrup (1988), and Flemming (2000). In doing so, it coins the Index of Resolution of Capacity (IRC) as an index measuring the capacity of a ternary classification system to distinguish between two different sediments. (2) Applying this mathematical optimization to maximize the capacity of these systems to distinguish sediments with comparable grain size distributions. (3) Introducing a new system of classification allowing better descriptive classification. Added to its high IRC, this system is able

to generate itself by a number of successive iterations increasing its subdivision and improving its resolution. When the number of subdivision increases and the generation of names becomes next to impossible (e.g., clay, silty clay, clayey sand), the system takes away the use of terminology. Instead, it uses codes to specify samples. To test the efficiency of classification of each system, 400 samples from cores carried out within seven saline environments in Tunisia are plotted. We notice, as it is anticipated by the mathematical method, that systems having high IRCs distinguish more sedimentary populations. Thus, they are more efficient, especially when studying clay pans, where fine sediments are difficult to distinguish.

THE MIDDLE JURASSIC BLACK SHALES FROM THE CENTRAL PART OF POLISH BASIN – SEDIMENTARY ENVIRONMENTS STUDIES



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Key words:

Middle Jurassic, shales, sedimentation, sedimentary environment, Polish Basin

12

Sedimentation of the Middle Jurassic deposits in the Polish Basin took place in a shallow storm-dominated epicontinental sea. The zone of maximum thickness runs along the Mid-Polish Trough with the depocentre in Kujavian Region where profile exceeds 1100 m.

Three complexes of the offshore black shales separated by transition – middle shoreface heteroliths and sandstones are observed there. The oldest complex, Upper Aalenian – Lower Bajocian in age, is about 150-300 m thick. The second one, 100-200 m thick, is of Upper Bajocian age. The youngest, Lower Bathonian complex is 30-60 m thick.

The oldest complex is typified by the predomination of benthic agglutinated foraminifera (75%) over calcareous ones (25%) and mostly by lack of bivalves. Agglutinated foraminifera are dominated by epifaunal morphogroups. It contains marly concretions. Geochemical investigations point that the TOC content ranges from 0.9 to 12.7%. The highest amounts are found within the Aalenian part of black shales with TOC values above 3%. It is mostly terrestrial organic matter (vitrinite) of low maturity. The S/C plot indicates a contribution of a syngenetic pyrite component. DOP index ranges from 0.11 to 0.82 with the most common values falling between 0.45-0.75.

Its suggests that the sedimentation took place mostly in strongly dysoxic to anoxic environment.

In the middle complex a balance between agglutinated and calcareous foraminifera is observed. New genera with an infaunal mode of life appear. Bivalves dominated by *Bositra buchii* occurred only in thin horizons. Both marly and sideritic concretions are observed. Organic matter content is lower than in the first complex and ranges from 0.8 to 4.2% TOC. The S/C plot indicates normal marine environment with very small amounts of syngenetic pyrite. DOP value is between 0.18-0.63 with average 0.4. Strongly to weakly dysoxic bottom environment is suggested.

The youngest complex is characterized by abundance of benthic fauna. Almost only calcareous foraminifera (>95%) with both an epifaunal and infaunal mode of life are observed. Bivalves are very numerous and coquina beds are frequently noted. Sideritic concretions and siderite ore layers are common. TOC content is low, ranging between 0.2-3.3%, mostly < 2%. The S/C plot indicates normal marine environment. DOP ranges between 0.18-0.59. Weakly dysoxic to oxic bottom sedimentary environment is suggested.

HIGH-RESOLUTION STRATIGRAPHIC CORRELATION AND BIODIVERSITY DYNAMICS OF MIDDLE AND LATE ORDOVICIAN MARINE FOSSILS FROM POLAND AND BALTOSCANDIA



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13

The Middle and Upper Ordovician rocks of Baltoscandia have been divided into spatially distinct, composite litho- and biofacies units called confacies belts. A precise regional correlation of outcrops and boreholes in different confacies belts has always been problematic due to the pronounced biogeographical and lithofacies differentiation. Correlation between sections in the graptolite-rich black shales of the Scanian confacies and the carbonate-rich North Estonian confacies belts has been particularly difficult. Additionally, because of sampling inconsistencies, partial preservation of taxon ranges, and missing taxa, the sequence of events (particularly species FAD's and LAD's) is often contradictory among stratigraphic sections.

To overcome these problems we used Constrained Optimization (CONOP9, Sadler et al., 2003) to construct a high resolution correlation model and composite range chart compiled from the stratigraphic range data of 538 chitinozoan, conodont, ostracod, and graptolite species from 22 boreholes and 2 outcrops in Poland and Baltoscandia. One borehole from Latvia and seven from the Łeba Elevation in northern Poland contained numerous biostratigraphically useful graptolites and chitinozoans, and were particularly useful in making precise correlations across the disparate biofacies. CONOP9 can be a useful method for examining the age and relationship of organic-rich source rocks and productive reservoir units.

We also used the CONOP composite as a timescale in which to calculate biodiversity, extinction, and origination rates through the Middle and Late Ordovician. Traditional biodiversity metrics and more recent probabilistic methods based on capture-mark-recapture analysis were

used to estimate biodiversity and fossil recovery patterns. We divided the CONOP composite into 860 kyr intervals spanning the Läsnamagi through Porkuni stages. Our data show that overall biodiversity increases steadily from the base of the Keila to the middle Rakvere, mainly due to an increase in ostracod diversity. Chitinozoan diversity reaches a zenith in the Late Keila, drops through the Oandu Stage, and then gradually declines across the rest of the Ordovician. Chitinozoans exhibit constant origination but variable extinction rates and undergo a dramatic diversity decline associated with the $\delta^{13}\text{C}$ isotope excursion known as the GICE event. Conodonts have diversity peaks in the lower Uhaku and lower Kukruse Stages, and then decline gradually through the Late Ordovician. Conodonts exhibit constant extinction and origination rates and their diversity decline is attributable to higher extinction than origination rates. Graptoloid diversity reaches a peak in the Uhaku (late Darriwilian) and declines thereafter. This pattern is quite different from global graptolite diversity patterns and may be attributable to unsuitable Late Ordovician facies in Baltoscandia.

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BELOVEŽA FORMATION VERSUS HIEROGLYPHIC BEDS IN THE MAGURA NAPPE, OUTER CARPATHIANS, POLAND



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Key words:

flysch, shales, Eocene, Outer Carpathians

14

The Eocene thin-bedded flysch sequence in the Rača Unit of the Magura Nappe is a subject of live discussion and controversies since XIX century. The different names like Hieroglyphic beds, Hieroglyphic Formation, Grzechynia beds, variegated Eocene shales, Beloveža beds, Beloveža Formation were used in the Outer Carpathian literature.

Beloveža beds (Schichten) was first used by Paul (1869) for variegated shales and thin-bedded flysch (Eocene) in locality Beloveža near Bardejov (Rača Unit) in Slovakia (Paul's locality is still available for detail studies). Next Uhlig (1889) distinguish thin-bedded flysch as Beloveža Beds and variegated shales separately. Beloveža Beds are represented by thin-bedded typical flysch with dominant shales. Shales are gray to green, blue and olive in color, usually clay, small amount of carbonates is possible. Shales are intercalated by fine-grained gray to blue-gray, siliceous sandstones with abundant hieroglyphs and lamination. However Uhlig's division was accepted in 50' and 70' for Rača Unit in Beskid Niski, name Beloveža beds was only applied to the Bystrica Unit in Polish flysch Carpathians (Oszczypko, 1991).

Hieroglyphic beds were first distinguished by Paul and Tietze (1879), later Rajchel (1990) formalized the

Hieroglyphic Formation in the Skole Unit. Książkiewicz (1948) used term "Hieroglyphic Beds" for thin-bedded Eocene flysch deposits in the Rača Unit in Beskid Wysoki north of Babia Góra, and his approach is still being used by some Polish authors for this part of Beskid and in 70th was also introduced into Beskid Niski area.

The present authors noted striking resemblance of the Beloveža Beds (Formation) from type locality in Slovakia to the typical "Hieroglyphic Beds" in Beskid Wysoki area and to typical Beloveža beds from Hańczowa Mts. (Beskid Niski area). Similarities includes lithology, development, age, taxonomy and structure of foraminiferal assemblages, stratigraphical position. Present authors indicate need to unify the lithostratigraphical names. They propose to restrict name Hieroglyphic Formation to the Skole Nappe and use consequently name Beloveža Formation to thin-bedded Eocene flysch within both Bystrica and Rača units of the Magura Nappe. The original type locality in Beloveža near Bardejov was selected for *type section* of the Beloveža Formation according to principle of priority. This research has been financially supported by AGH University of Science and Technology in Cracow grant no. 11.11.140.447.

SOURCE ROCK PREDICTION VALUE AS A TOOL FOR EXPLORATION OF UNCONVENTIONAL HYDROCARBONS IN CARPATHIANS



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Key words:

shale-gas, Jurassic, Cretaceous, Carpathians

15

The authors focused on three major processes, which control the organic richness in a specific paleogeographic, climatic and tectonic setting in order to predict the Source Rocks Prediction Value (SRPV). These three processes are biologic productivity, background sedimentation rates with non-dilution of organic richness by clastic sedimentation, and preservation of organic matter. The modeling of the Source Rocks Prediction Value has placed the marginal Tethyan Ocean (Carpathian basin) among the basins, which contain the richest Late Jurassic-Early Cretaceous source rocks in the world. Using the semi-quantitative Delphi method for 36 Late Jurassic regions, which represent tectono-depositional provinces in this time, the evaluation ranked Carpathian basin ninth. The paleogeographic and paleoclimatic settings are indicated as main factors in distribution by basins of known organic-rich rocks. The high organic productivity of the Carpathian proto-Silesian basin was caused by upwelling, as well as restricted conditions. By calibrating SRPV with known, measured values of source rock richness (SPI), the presence and richness of

potential source rocks can be predicted. The source potential index (SPI) is a measure of cumulative petroleum potential. It is defined as the maximum quantity of hydrocarbons (in metric tons) that can be generated within a column of source rock under 1 m² of surface area. This index combines thickness and richness into a single parameter, which does not distinguish between gas or oil or depend on maturity or source rock type. Inis source rock richness or genetic potential, measured from Rock-Eval pyrolysis. The average genetic potential is calculated from systematic sampling of the source rock section. The applied method allowed the calculation of SPI values for the depositional settings for which SRPV's were assessed. The estimated SPI for Carpathians Late Jurassic-Early Cretaceous is 10 tons per 1 m². This value was confirmed by pyrolysis of random samples. The potential shale-gas reserves derived from the SPI potential were estimated (in the most optimistic case) as 3000 million m³, cash value 27000 million PLN.

ANALYSIS AND EVALUATION OF EUROPEAN SHALE GAS PLAYS. CASE STUDY



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Key words:

ShaleGas basins, European Shale Plays, basins evaluation, licenes

16

Halliburton Consulting carried out an analysis and evaluation of shale gas plays for an independent oil and Gas Company during 2009-2010. The objective of the project was to assess the potential for economic production from Shale Plays outside of North America, with as particular focus on European opportunities. The Halliburton Team utilised on the project include geologists and petrophysicists from Poland, USA and UK.

In the first stage of the project a Basin Ranking of the onshore European sedimentary basins with Shale Gas/Oil prospectivity was carried out. This ranking was based on publically available data and using Halliburton background knowledge and expereince in developing shale plays in North America. Information was also provided by *the Client*.

The second stage of the project was the identification of Shale Gas/Oil Prospects in the selected basins and an estimation of the overall resources. This was carried out by:

1. Purchasing the available data from government agencies.

2. Performing an integrated study of the Geological, Geophysical and Petrophysical data for each potential area for the establishment of the shale reservoir properties (GGX, Prizm, ShaleLog).
3. Delineation of the exploration leases in the identified subsurface sweet spots and resource estimation.

As a result of this study the client identified prospects as follows:

- 6 Exploration licences across Spain, Poland and Germany;
- 8 Licence applications to be made in Spain and 10 licence applications in France;

This has resulted in more than 2.4 million gross acres under application in France and >2.0 million gross acres under application in Spain.

The client has also gained an extended database of prospects in a number of other European countries.

This paper is the description of how we deployed Halliburton best practice to the estimation of the potential in European Shale Gas.

POLAND SHALE GAS/OIL PLAY: INTEGRATING OLD AND NEW DISCIPLINES TO INTERPRET UNCONVENTIONAL RESOURCE POTENTIAL OF AN EARLY PALEOZOIC SOURCE ROCK



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17

Poland has recently experienced increased exploration activity associated with an emerging shale gas/oil play developed in thick Upper Ordovician to Lower Silurian shales. The prospective section is part of the southwestern margin of Baltica (East European Platform). ExxonMobil has acquired a large acreage position to test the potential of the play. As part of this evaluation, reservoir and source studies were performed on samples from an extensive collection of conventional core archived in Poland.

Eighty samples were analyzed for palynology, bulk organic and inorganic geochemistry (total organic carbon, Rock Eval pyrolysis, XRD mineralogy, elemental analyses), and GRI porosity / matrix permeability. A subset of samples were selected for advanced biomarkers characterization and nanometre-scale pore imaging using SEM on BIB – (Broad Ion Beam milling) prepared samples.

Relative distance to shore, expressed as paleo-water depths, were interpreted from palynological assemblages. Integrating palynological results with organic geochemistry allowed classification of source facies from restricted shallow marine (excellent oil-prone) to open marine (good gas-prone and poor oil-prone) to deep marine (poor gas-prone). Molecular signatures of sol-

vent extracts and pyrolyzates contribute to interpreting source facies and character of generated hydrocarbons. These were consistent with deposition of primitive marine algae in dysoxic conditions, either as algal bloom or dispersed organic matter.

Shale matrix mineralogy, porosities, and permeabilities have thus far not been linked to source facies or level of thermal maturation. However, SEM imaging revealed nanometer-scale pore architecture comprising voids in select organic matter clasts, as well as intercrystalline and intracrystalline pore networks in the mineral matrix. Ongoing research is examining the relationship between mineral and organic elements.

The integration of palynology with modern rock characterization techniques is a significant advance in the resource evaluation of early Paleozoic source. Despite the paucity of land plants in the Ordovician / Silurian, marine source rocks have the hydrocarbon potential of being both oil-prone, as expected for such rocks, and gas-prone of primary generation. Areal and stratigraphic variations in source rock quality may exert a major control over “sweetspot” development in the play.

BLACK SHALE DEPOSITION ON A CARBONATE PLATFORM (ARAN ISLANDS, IRELAND) – ORGANOFACIES, GEOCHEMISTRY AND SEQUENCE STRATIGRAPHIC INTERPRETATION

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Key words:

black shales, palynology, geochemistry, sequence stratigraphy, hydrocarbon potential

18

The Aran Islands are made of Lower Carboniferous limestones of typical carbonate platform facies, several hundred meters in thickness. This represents a very stable palaeoenvironment, covering several million years (Upper Viséan). Within the limestone succession a thin black shale interval was observed, recording a significant change from an highly productive, oxygenated to an euxinic platform environment. The limited thickness (0.2–1.6 m) and sharp lithological boundaries of the shale suggest a short-lived and rapid change of the depositional system on this platform.

The shale interval can be divided into two lithostratigraphic units. The black shale in the uppermost part is rich in pyrite aggregates, often several cm in size, and rich in C_{org} , showing a lateral constant thickness of 0.2–0.3 m along the whole width of the accessible section. The lower part of the shale interval consists of medium grey mudstones still rich in pyrite nodules, getting darker in the upper part. Its thickness shows strong lateral variation with >1 m in some places and pinching out in other places. The lithological differences suggest a significant change of palaeoenvironmental conditions even during shale deposition. For a better understanding of the palaeo-environmental changes and the factors controlling shale deposition on this platform, a detailed palynological and geochemical study was undertaken. This includes palynology, organofacies analysis, TOC and CNS analysis, clay mineralogy, just as C-isotopes.

Based on miospores in the uppermost part the shale interval is precisely dated for regional just as long distance correlations along the Lower Carboniferous carbonate

shelf. Palynofacies of the shales shows a change from restricted brackish to marine conditions without terrestrial input at the bottom to shallow marine conditions with high terrestrial input at the top. The lower part represents deposition within locally restricted deeps (residual water ponds) on the platform, isolated from both terrestrial and normal marine input. Slightly rising sea-level leads to marginal marine conditions in the lower shales. The black shales at the top represent shallow marine conditions with widespread deposition of mainly terrestrial organic matter on the platform. TOC is very low in the lower part of the shales, increasing strongly in the black shales at the top due to the input of terrestrial organic matter.

Shale deposition and composition is mainly controlled by sea-level. A significant sea-level fall at the base, representing the sequence boundary (SB), led to isolated ponds of sea-water on the platform, cut off from any terrestrial input during the early lowstand system tract (LST). Shale deposition during the LST shows 4 phases, representing the different stages of early sea-level rise and connection to the hinterland. The black shales at the top of the interval are interpreted as transgressive surface (TS), overlain by the thick succession of carbonate platform deposits of the transgressive system tract (TST). Organofacies analysis of the kerogen composition throughout this sequence gives a high-resolution data set on development of hydrocarbon potential within this sequence. This gives a good example for transgressive shale systems on carbonate shelves, often linked to hydrocarbon systems throughout earth history.

QUARTZ CEMENTATION IN SHALES RELEVANT FOR SHALE GAS RESERVOIRS



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Key words:

quartz, cement, shale, diagenesis

19

Scanning Electron Microscopy (SEM) of mudstones and shales from offshore Norway reveal the formation of extensive authigenic sheet-like quartz cement parallel to depositional during burial diagenesis. This incipient quartz schistosity form in mudstones originally rich in reactive clays (containing smectite, kaolinite and a source of potassium) from about 90-100°C. Dissolution-precipitation processes in reactive clay containing mudstones will produce illite, illite/smectite and quartz from smectite and illite and quartz from kaolinite. Some of the mudstones studied also contain recrystallized originally organically formed silica contributing to both the schistosity formation and quartz cementation. The formation of quartz sheets result in alternating quartz cemented layers and uncemented clay rich layers. The orientation of the quartz cemented sheets normal to the overburden will have an anisotropic stiffening effect that likely affect pressure related deformation of the mudstone during petroleum generation. This is seen in SEM as fractures in between the quartz sheets. The fracture systems developed are

normal to the original bedding in two directions and may be filled with quartz cement. The quartz cemented layers parallel to bedding shows much less fracturing than the uncemented layers but some fractures also penetrate the cemented layers. Since the distance between the quartz cemented zones are limited the fractures found normal to bedding are short. The alternation of weak uncemented and stiff quartz cemented mudstone layers likely results in preferential primary petroleum migration within the weak uncemented layers in organic rich shales. The stacking of fracture packets parallel to bedding with stiff cemented layers in between could have profound influence on primary petroleum expulsion distances laterally within source rocks. In addition the findings above could be significant for understanding shale gas reservoirs response to hydraulic fracturing. The self organizing nature of the system (cemented/uncemented stacking of packets) also strongly suggests that mudstones are geochemically closed during burial diagenesis.

WELL TEST ANALYSIS OF HORIZONTAL WELLS WITH MULTIPLE HYDRAULIC FRACTURES IN A GAS SHALE RESERVOIR



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Key words:

shale gas, well test, simulation

20

Shale gas has become a significant unconventional source of energy in recent years, mostly in North America, and is a “global game changer”, with interest growing in many other regions such as Europe, Asia and Australia. The popularity of shale gas is explained by a growing demand for natural gas and a potential shortage of supply from conventional sources in the future. Advances in technology, such as horizontal well completion and multiple hydraulic fracturing, which may reactivate natural fractures, have played a major role in the successful exploitation of shale gas reservoirs. Characterization of such reservoirs, however, is a complex task which requires the integration of a huge amount of data from different sources. This paper illustrates the combined use of well test analysis and reservoir simulation to characterize five horizontal well with multiple perpendicular hydraulic fractures in a shale gas reservoir.

Conventional well test analyses are usually not applicable in unconventional shale gas reservoirs because build ups are too short and noisy, and do not allow calculation of the very low reservoir permeabilities as transient flow in the reservoir is mostly fracture-dominated. Well test deconvolution was therefore used, which converts the variable rate pressure history into an equivalent unit rate initial drawdown with the duration of the entire production. The resulting deconvolved derivative can be analysed with conventional technique to yield all the well and reservoir parameters (permeability, equivalent fracture length, and so on). Well test analysis results were then used as inputs into a numerical simulator to model and history match all five wells, and to forecast gas rates and cumulative gas production.

RED BED SHALES FROM THE POLISH UPPER ROTLIEGEND BASIN AND THEIR SIGNIFICANCE AS GAS TRAP SEALS



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Key words:

Rotliegend, playa-lake fines, clay-mud seals, gas traps

21

Fine-grained sediments form thick units of mudstones and claystones with addition of siltstones in playa and inland sabkha-salt flat settings of the Southern Permian Rotliegend Basin (SPRB). These units interbed with eolian sand and salt beds. Due to vast lateral spread of these units almost across the SPRB, they form, either separately or together with salt beds, good lithological seals for gas accumulations in sandstones. The best, proven seals in the SPRB are Ten Boer Claystone Member (sealing sandstones of Upper Slochteren Sandstone Mb), several clay and salt members of Hannover Formation (sealing sandstones of Wustrow Mb) and in the Polish Rotliegend Basin - Claystone Resko Member (Drawa Fm) (sealing sandstones of Piaski Mb).

In the Polish Upper Rotliegend Basin (PURB), internal lithological seals are poorly recognized and mostly supposed. Predicted gas traps occur in eolian sandstones interbedded with playa-lake deposits, forming a potential seals. This depositional system (called lower playa) is poorly known from the Drawa Fm, where thick claystone units overlapped eolian beds. Claystones and mudstones of lower playa (Resko Mb) are usually highly cemented with carbonate minerals (calcite) and sulphates (anhydrite and barite). Porosity of these deposits does not exceed 3-4%, and permeability is above 0.001 mD.

From the upper Notec Fm such a case is not confirmed yet, however can be expected. The clastic seal quality, playing a role of an impermeable barrier for gas migration depends on prevailing clay occurrences. The present study on the upper playa fines has shown that clay content is smaller in comparison to the lower playa, and therefore the seal quality should be debatable as sufficient for conventional and unconventional gas traps in the PURB. There are fine-grained clayey sandstones and mudstones cemented with calcite and anhydrite in the upper playa. Claystones occur only occasionally. Reservoir properties here are better than in the lower playa. It seems that the upper playa sediments in their maximum southern limit, on the boundary of an eolian system, do not seal potential reservoir traps.

The "shale" seal issue is now considered with reference to Basin Centred Gas System (BCGS) in the PURB. Apart from capillary and diagenetic seals in tight reservoir in the BCGS, the lateral facies changes: from sandstones to mudstones and claystones, are crucial for gas and water migrations and for predicted model of mudstone-claystone seals. This model derives from the US Mesaverde Basin, where vertically stacked reservoir is divided by interbedded mudstones.

TIME RESOLVED 3D IMAGING OF ORGANIC-RICH SHALES DURING HEATING



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Key words:

primary migration, shale, X-ray computed micro-tomography, kerogen, reaction fracturing

22

We study mechanisms of fracture pattern development and fluid escape in low permeability shales. We performed time-resolved *in situ* X-ray tomography imaging to investigate the processes that occur during the slow heating (from 60° to 400°C) of organic-rich Green River shale. At about 350°C cracks nucleated in the sample, and as the temperature continued to increase, these cracks propagated parallel to shale bedding and coalesced, thus cutting across the sample. Thermogravimetry and gas chromatography revealed that the fracturing occurring at ~350°C was associated with significant mass loss and release of light hydrocarbons generated by the decomposition of immature organic matter. Kerogen decomposition is thought to cause an internal pressure build up sufficient to form cracks in the shale, thus providing pathways for the outgoing hydrocarbons. We show that a 2D numeri-

cal model based on this idea qualitatively reproduces the experimentally observed dynamics of crack nucleation, growth and coalescence, as well as the irregular outlines of the cracks. Our results provide a new description of fracture pattern formation due to chemical reaction in low permeability rocks.

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ENVIRONMENTAL IMPACT OF HYDRAULIC FRACTURING TREATMENT PERFORMED ON THE ŁEBIEŃ LE-2H WELL



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Key words:

hydraulic fracturing, environmental impact, gaseous emissions, waste management, flowback fluid

23

The main objectives of research carried out by a consortium led by the PGI-NRI was to assess environmental impact of hydraulic fracturing performed in August, 2011 on the Łebień LE-2H exploratory well operated by the Lane Energy Poland, company of the 3Legs Resources Group. The hydraulic fracture treatment on the Łebień LE-2H well is the first multi-stage hydraulic frac stimulation of a horizontal shale gas well in Poland.

The study was commissioned by the Ministry of the Environment, in cooperation with the operator. It was conducted from 13 June to 13 October 2011. It comprised seismic monitoring, measurements of gaseous emissions and noise, analyses of soil gas, hydraulic fracturing fluid and surface and ground water before, during and after the hydraulic fracturing. The team comprised geologists and hydrogeologists from PGI-NRI as well as specialists from the Institute of Geophysics of the Polish Academy of Sciences, Voivodeship Inspectorate for Environmental Protection in Gdańsk, Biology Division of the Faculty of Environmental Engineering of the Warsaw University of Technology and Oil and Gas Institute in Cracow. Over 30 specialists took part in the field works and about 30 laboratory studies.

The well named Łebień LE-2H is 4,075 m deep, with horizontal section 1,000 m long. It is located near Łebień in Pomerania voivodeship. This is typical agricultural area. It is drained by the Kisewska Struga Creek. The main usable ground water horizon occurs at the depth 10 to 20 m below terrain surface.

The studies carried out on such scale for the first time in Poland did not show any changes in the natural environment which could be linked with the hydraulic fracturing. Neither methane nor radon were found. Seismic stations of the Institute of Geophysics did not record any shakes in the time of fracturing. Also analyses of water from creeks and water wells did not show any changes from chemical composition as found in detailed studies performed before the hydraulic fracturing. Only noise level turned to be arduous from time to time but only in the direct proximity of aggregates. The studies also covered management of waste and flowback fluids. As expected, a part of injected technological fluid came back to the surface. In result of contact with strongly saline water and shales in the zone of hydraulic fracturing the fluids became enriched with chlorides and barium salts.

ORIGIN OF ORGANIC MATTER IN THE EARLY SILURIAN CHERTS AND SILICEOUS SHALES OF POLAND

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Key words:

cyanobacterial mats, acritarchs, radiolarians, organic matter, mineralization

24

The Early Silurian deposits of Poland consist, in part, of dark grey to black siliceous and siliceous clayey shales and black radiolarian cherts (lydites) cropping out in several localities in the Holy Cross Mts and Sudetes (Bardzkie Mts and Kaczawskie Mts). They represent marine sediments deposited probably at depths not exceeding the photic zone (Kremer & Kaźmierczak, 2005). They are rich in organic matter (OM) (TOC 0.4% to 8.1%, Bauersachs et al, 2009). The thermal maturity of OM is different in each of these three areas, with the lowest range in the Holy Cross Mts. and the highest in the Kaczawskie Mts. Morphological preservation of organic remnants is highly dependent on the grade of thermal alteration, therefore cherts from the Kaczawskie Mts do not contain any morphologically recognizable microfossils. Cherts and shales from the Holy Cross Mts (Zalesie Nowe) and the Bardzkie Mts (Łupianka, Żdanów, Podtynie, Wojciechowice) contain morphologically well-preserved microfossils what allows identification of precursor organisms and determination of the depositional environment. Detailed study of the cherts and siliceous shales with optical and scanning microscopy, Raman spectroscopy and geochemical methods revealed that the main part of the organic matter derives from benthic cyanobacterial mats (Kremer & Kaźmierczak, 2005; Kremer, 2006). The cyanobacteria in the studied Early Silurian rocks can be preserved as cells, as remains of mucilaginous cell-enveloping capsules (EPS) forming characteristic web-like texture, and as unidentifiable (amorphous) organic matter, usually arranged in more or less distinct laminae. Two other groups of microfossils that dominate in cherts are acritarchs and radiolarians. Acritarchs occur as usually well-preserved individuals (Kremer, 2001; Masiak et al, 2003; Kaźmierczak & Kremer, 2009), and

as silicified and variously degraded post-bloom macroaggregates (Kremer, 2011). Radiolarians are mostly preserved as molds of variously dissolved skeletons. White spots of silica are often the only left evidence after the dissolved radiolarians. Graptolites are more frequent in grey shales (graptolite shales) than in massive cherts (Porębska, 1982; Masiak et al, 2003). Black radiolarian cherts and siliceous shales were traditionally regarded as products of deep and anoxic environments. The recently documented mass occurrence of benthic coccoidal cyanobacterial mats in these deposits changes radically the hitherto accepted sedimentation model for these deposits and indicates rather moderately deep and at least dysoxic depositional environment located within the photic zone.

The abundance of acritarchs (reinterpreted recently as unicellular green algae – Kaźmierczak & Kremer, 2009; Kremer et al, 2012) and radiolarians suggests that eutrophic conditions prevailed at least temporarily in the Early Silurian marine realm (Kremer, 2011).

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ROLE OF SHALES DURING COMPRESSIONAL TECTONICS: COMPARISON OF THE VARISCAN (L. CARBONIFEROUS) EVOLUTION OF THE LUBLIN BASIN AND THE APPALACHIANS

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25

Role of thick ductile shales in compressional tectonics has been long recognized within the trailing edge of the Appalachians. In this area, presence of thick Cambrian shales together with faulted top of the Precambrian basement led to development of numerous thick-skinned thrust structures (e.g. Thomas & Bayonne, 2005; Thomas, 2010). They form systems of complex fault-bent folds and associated reverse and thrust faults developed within the Ordovician – Carboniferous, generally stiff layer above ductile layer of Cambrian shales that presently form the so-called MUSHWAD (Malleable, Uncutuous SHale, Weak-layer Accretion in a ductile Duplex) zones: giant antiformal stacks of intensely deformed shale, in places more than 2.5 km thick, formed during Late Carboniferous (Variscan) tectonic phase.

Lublin Basin in SE Poland was also formed above faulted cratonic edge and was strongly inverted in Late Carboniferous times during Variscan orogeny. Sedimentary cover in this area includes thick Silurian, not Cambrian shales, deposited within the Caledonide foredeep basin. Earlier thick-skinned models defined the Lublin Basin as a NW-SE striking tectonic graben bounded by very steep, deeply-rooted fault zones: the Kock Fault Zone and the Ursynów-

Kazimierz Fault Zone (Żelichowski & Kozłowski, 1983). Later models neglected role of thick-skinned tectonics and stressed thick-skinned character of the Lublin Basin. Kock Fault Zone and the Ursynów-Kazimierz Fault Zone were interpreted as a triangle zones cored by compressional duplexes made up of Cambrian – Silurian deformed deposits (Antonowicz et al., 2003). Above these triangle zones Devonian – Carboniferous succession was locally uplifted relative to the central part of the Lublin Basin, and this has created “passive syncline”, i.e. syncline created not by active folding of the Devonian – Carboniferous cover but by localized uplift at the flanks of such synclinal form.

Recently completed regional interpretation of seismic data along the Kock Fault Zone allowed to propose a new model that combines thick-skinned and thin-skinned tectonics. In this model, Late Carboniferous (Variscan) thin-skinned thrust / reverse faulting and associated folding was focused above the regional basement step i.e. deeply rooted (thick-skinned) Kock Fault Zone. Stiff Devonian – Carboniferous layer was folded and faulted above strongly deformed thick Silurian shales, forming the „Kock MUSHWAD” structure, similarly to the Appalachians.

SOURCE ROCK EVALUATION TECHNIQUE: A PROBABILISTIC APPROACH FOR DETERMINING HYDROCARBON GENERATION POTENTIAL AND IN-PLACE VOLUME FOR SHALE PLAYS



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26

The hydrocarbon generation potential of a source rock is a calculated volume that utilizes multiple rock properties including gross rock volume, total organic carbon, kerogen type, and pyrolysis parameters. Here we detail a probabilistic workflow to the generation potential calculation, using Monte Carlo simulation of the modified Schmoker, 1994, equation with a distribution of values for each input parameter. This methodology can be an important component in identifying prospective shale plays for oil and gas production, and can be compared against traditionally calculated hydrocarbons-in-place as a screening tool for ranking prospects. Specifically, traditional oil-in-place calculations for shale plays, due to uncertainties in porosity and fluid saturation, may overestimate available resources that can be estimated independently by calculating oil generation potential. The comparison of the two calculations can provide valuable insight into the volume of oil that can be generated and stored within a source rock interval and adjacent reservoirs.

In a test of the probabilistic workflow, we use source rock data from the Upper Cretaceous Niobrara Formation and evaluate the results in comparison to horizontal Niobrara

production at Silo Field, Wyoming, USA. The simulation outputs show that the Niobrara formation in Silo Field has the potential to generate a mean resource of 29 million barrels of oil equivalent (MMBOE) of hydrocarbons per square mile, and store a mean of 21 MMBOE per square mile. A calculated net resource of 140 thousand barrels of oil equivalent per well closely approximates historical production for unstimulated, horizontal Niobrara wells at Silo Field.

We then apply the methodology to Ordovician and Silurian source rocks in Poland to determine source rock quality, and compare calculated generation potential against traditional volumetric in-place calculations. The results indicate the potential for significant resources in shale plays and can be used as screening criteria for ranking various acreage positions.

Determining generation potential provides a first step in understanding resource distribution by validating traditional in-place calculations. An integrated, probabilistic approach is crucial in areas where individual rock properties are inadequate indicators of source rock quality. To be truly robust, this method must incorporate resource preservation, migration, and flow characteristics to determine ultimate recoverability.

MULTISCALE IMAGING OF SHALE CORE SAMPLES



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Key words:

FIBSEM, porosity, shale, SEM

27

Typical for shales is the occurrence of porosity at the nanoscale and very fine features in the clays, requiring high imaging magnifications. FIB/SEM takes this even one step further by providing a 3D dataset composed of hundreds of such high resolution SEM images. A typical FIB/SEM dataset has a spatial resolution of 10 nm for a volume of 10x10x10 micrometer.

A most relevant question is how representative those small volume FIB/SEM datasets are. Industry-standard approaches are to take about 10 SEM images and decide from those images what the relevant and representative features are. For a 1 inch core sample, this still means that less than 1% of the sample surface is actually imaged at a resolution able to resolve the porosity before deciding where to perform a FIB/SEM experiment.

The risk associated with the much higher resolution characterization of shale core sample material with high reso-

lution SEM and FIB/SEM is that the structural association with fabric is lost. Yet fabric heterogeneity is equally important for the characterization of shale samples, and the association of nanoscale pore structures with fabric domains may provide important information to permeability and fluid flow on the scale of the core.

Tiling and stitching SEM images into mosaics enables pore scale resolution over the full core surface in one image. This allows simultaneously retrieving fabric and pore level information without losing correlation. Furthermore, it allows choosing the FIB/SEM locations in a more representative way.

Examples are presented for Eagle Ford and Marcellus shale samples for productive and non productive parts of the reservoir.

THE INTERPLAY OF SEDIMENTATION, EUSTASY, AND TECTONICS IN CONTROLLING VERTICAL TOC VARIATIONS IN ORDOVICIAN TO SILURIAN SHALES, EASTERN POLAND



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Key words:

sedimentation, eustasy, TOC, shales, Ordovician-Silurian

28

The application of sedimentologic analysis to unconventional shale gas/oil plays has been shown to improve prediction of source rock distribution and matrix properties, and highgrade potential “sweetspots” for acreage capture and management. To test the utility of this analysis in an unproven shale gas/oil play in eastern Poland, a joint technical study between the Polish Geological Institute and ExxonMobil was conducted in the Podlasie and Lublin basins utilizing the rich archive of cored wells. The main target of the Poland shale gas/oil play is organic-rich, Ordovician to Silurian shales deposited along the margin of Baltica. Tectonically, this period spans the transition from a passive margin (Ordovician to Llandoveryan) to a foreland basin influenced by an advancing deformation front (Caledonian Orogeny, Wenlockian to Ludlovian). This study illustrates how vertical changes in sedimentology and source rock quality are linked to tectonic history and eustasy.

Five cored wells were described at the cm-scale for the following features: color, lithology, grain-size and types, laminae geometry, sedimentary structures, degree of bioturbation, diagenetic features including cement and fractures, and nature of vertical contacts. Twelve lithofacies were recognized in the Caradocian to Ludlovian succession; these lithofacies were further organized into three lithofacies

associations based on similarity of rock properties. Important sedimentological and organic geochemical changes are recognized in vertical profiles through the Ordovician to Silurian shale succession. The Caradocian to Llandoveryan sediments consist of dark-colored, laminated to bioturbated claystone/mudstone with highly variable TOC (up to 17% present-day TOC). Elevated TOC is found mainly in the laminated claystones of the basal Llandovery, which lies on a major unconformity developed at the close of the Ordovician. The Wenlockian to lower Ludlovian sediments consist of mm-scale, parallel to wavy laminated, mudstone to silty mudstone with generally low TOC; bioturbation is rare to absent.

The stratigraphic change in lithofacies and TOC abundance is interpreted, in part, to reflect the effects of the Caledonian Orogeny. As sedimentation rate increased in the Wenlockian and Ludlovian due to the advancing deformation front, dilution of organic carbon resulted, and well-bedded sediments with generally poor source quality were deposited. The richest source rock (basal Llandoveryan) formed during initial transgression of a karsted, top Ordovician surface, following a eustatic sea-level fall. This initial transgression may have triggered localized algal blooms, contributing to the high TOC and excellent source rock quality seen in this interval.

GAS FROM SHALE. LOCAL COMMUNITIES – COOPERATION OR CONFLICT?



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Key words:

communication, education, information

29

The key to relations between those companies engaged in shale gas exploration and local communities can be summed up in two words: TRANSPARENCY and EDUCATION.

Talisman's primary objective is to ensure that the activities that it undertakes are clearly and fully communicated to the local community – before, during and after any operational phase. Through a series of meetings – both “town-hall” and individual – we endeavor to explain the technology involved, the scale and timing of the operation and the possible inconvenience that it may cause.

Given the genuine concerns of local residents, we explain the process of exploring for and potentially exploiting shale gas. Specific, local cultural sensitivities have to be taken into consideration.

We are aware of an increasing amount of misinformation that is being propagated at the local level, most commonly from the outside the community (or even the country).

Our response is to present fact-based arguments, invoking – as far as is possible – independent sources of information.

To facilitate direct and immediate contact with the community Talisman in North America has a telephone “hot-line” for local residents to ask questions and comment on our activities. In Poland we have appointed “local ambassadors” in the villages where we are active. Their role is to ensure that all local concerns are addressed in the shortest possible time.

Talisman, together with other operators, look to the Polish government to fully participate in the the process of communication and education. There has been some progress in this direction, for example with the formation of a forum for the Marshalls of the 9 voivodships in which shale gas exploration is taking place. This forum allows for the exchange of opinion, experiences, educational materials etc.

MICROBIAL VERSUS THERMOGENIC GAS SYSTEM: COMPARISON OF DEVONIAN/MISSISSIPPIAN SHALES WITH PENNSYLVANIAN COALS IN THE ILLINOIS BASIN

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Key words:

shale gas, isotopes, biomarkers, adsorption capacity, Illinois Basin

30

Shales from Devonian-Mississippian New Albany Shale, along with their associated gases, have been characterized using petrological, geochemical, and isotopic techniques to determine gas origin, timing of gas generation, controls on gas distribution, and biodegradation characteristics of the source organic matter. These characteristics were compared to those of the overlying Pennsylvanian coals. The study used gas and co-produced water samples from commercial shale gas-producing wells and coalbed methane (CBM) in the eastern part of the Illinois Basin in Indiana, in addition to the core samples of shales and coals. Gas from the New Albany Shale from depths of 400 m to 823 m ranges in origin from dominantly microbial [$C_1/(C_2+C_3)$ close to 100 and methane $\delta^{13}C$ of -60‰] to dominantly thermogenic [$C_1/(C_2+C_3)$ less than 10 and methane $\delta^{13}C$ of -52‰]. The origin of gas from the New Albany Shale is controlled by depth, maturity, and salinity of formation water. Deeper, more mature shales that contain higher-salinity pore water are associated with thermogenic gas, whereas shallower, less mature, and lower-salinity shales tend to host microbial gas. Biodegradation of organic matter in

the shales containing dominantly microbial gas is limited almost exclusively to the saturated fraction. Organic carbon content and the micropore volume of the New Albany shales serve as excellent predictors of gas content as long as there is no gas leakage because of the presence of conducting faults or hydrologic continuity. In comparison, gas compositional [$C_1/(C_2+C_3)$ ranges from 900 to 20,000] and isotopic data ($\delta^{13}C$ of methane ranges from -56 to -65‰) indicate that the gas from coals at depths of up to 300 m is almost exclusively of microbial origin. Thermogenic gas is limited to the tectonically complex area of the basin. Coal organic matter shows much more advanced biodegradation of both aliphatic and aromatic compounds compared to that of the organic matter present in New Albany shales. Microbially generated gas volumes are highly variable between and within individual coal seams, and no relationship exists between gas content and coal depth. We suggest that these variations are either related to extent of microbial methanogenesis or to the degree of preservation of the gas.

SHALE AND COAL BASINS OF NE ENGLAND: OPPORTUNITIES FOR RESEARCH AND INDUSTRY COLLABORATION IN UNCONVENTIONAL HYDROCARBONS

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Key words:

shale, unconventional, Durham, gas

31

Unconventional resources such as tight gas, shale gas, coal bed methane have been estimated to be at least equal to conventional gas (World Energy Council 2010). However in order to produce such gas both economically and without environmental damage we need to better understand permeability controls in such systems, be it absolute permeability of the reservoir matrix and fracture systems or the relative permeability to gas of the pore fluids. For many unconventional gas systems it is not yet clear which of these controls will dominate. Thus University-sited

research centres, such as CeREES, with a broad range of expertise in stratigraphy, sedimentology, regional tectonics, structural regimes, geomechanics and geofluids provide an important knowledge house for companies seeking new exploration ventures. An introduction to CeREES-led research in the shale and coal basins of NE England will be given which emphasizes how a combination of good natural outcrops and large amounts of legacy data can be used to build analogues for more poorly explored systems elsewhere.

SUPERGIANT PETRIFIED OIL FIELD IN TWO-BILLION-YEAR TURBIDITIC GREYWACKE-SHALE SUCCESSION IN THE EASTERN FENNOSCANDIAN SHIELD

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Key words:

Palaeoproterozoic, turbiditic shale, petrified oil, carbon isotopes

32

The c. 2.0 Ga Zaonezhskaya Formation (ZF) from the Onega Basin in Russian Fennoscandia records an unprecedented accumulation of C_{org} -rich (up to 75 wt% organic carbon) rocks with an estimated original petroleum potential comparable to a modern supergiant oilfield. The ZF represents rocks accumulated worldwide during the Shunga Event that occurred in the stage of progressive oxidation of terrestrial environments and in the aftermath of the positive $\delta^{13}C$ excursion in sedimentary carbonates (Lomagundi-Jatuli isotopic event), the greatest perturbation of the carbon cycle in Earth history (Melezhik et al., 2005).

Approximately 650 m of core recently obtained by the Fennoscandian Arctic Russia–Drilling Early Earth Project of the International Continental Scientific Drilling program offers a unique opportunity for detailed sedimentological and geochemical investigation of the turbiditic greywacke-shale-dolostone succession and associated supergiant petrified oil field. The objective of the research is an organic carbon isotope study of the source rocks and generated petroleum.

Currently obtained results show that the ZF exhibits a stratigraphic trend in $\delta^{13}C_{org}$ from -22‰ to -40‰. A shift from -25 to -22‰ in its lower, c. 5 m-thick interval is associated with thermal alteration of kerogen and an apparent methane release caused by emplacement of a gabbro body. The overall, two-step, stratigraphic shift by 15‰ within the upper 200 m of the succession provides evidence for a temporary but massive reversal of the long-term global carbon cycle. This reversal event is known as

the 2.0 Ga Shunga Event (Melezhik et al., 2005), and it was the time when oxidation of organic carbon from the crust dominated the global carbon cycle (Kump et al., 2011).

The uniquely preserved petrified oil field includes evidence of oil traps, oil migration pathways, and subaqueous and surface oil seeps. Despite the 15‰ stratigraphic shift in $\delta^{13}C_{org}$, no isotopic fractionation has been identified between pyrobitumen veins and host-rock carbonaceous matter. However, a massive subaqueous oil seep forming c. 20 m-thick interval shows a $\delta^{13}C_{org}$ of -25‰, hence contrasting with the -30‰ in overlying and underlying shales, and suggesting a genetic link to source rocks in the lower part of the succession.

The surface expression of a petroleum migration pathway appears as clasts of original bitumen redeposited in lacustrine turbidites of the Kondopoga Formation, which is separated from the ZF by a 600 m-thick pile of mafic lava. The $\delta^{13}C_{org}$ of clastic pyrobitumen ranges between -35.4 and -36.0‰. Assuming either a limited or no isotopic fractionation between original kerogen and generated petroleum (the evidence discussed above), these isotopic data would link surface oil seeps to source rocks located within the upper part of the ZF.

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RELATIONSHIPS AMONG POROSITY, PERMEABILITY AND SEISMIC VELOCITY IN MUDSTONES AND SHALES



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Key words:

shale gas, isotopes, biomarkers, adsorption capacity, Illinois Basin

33

Mudstones and shales are the most abundant lithologies and fill around 70% of the world's most sedimentary basins. The permeability of mudstones and shales and its relationships with porosity and velocity are thus fundamental to the quantification of a range of geological processes and geo-engineering applications such as (a) fluid flow modeling and the development of high pore fluid pressures; (b) top seal evaluation of hydrocarbon traps, radioactive waste disposal and storage of CO₂; (c) optimal production of shale gas; (d) subsurface geological processes, such as erosion and flow slides and (e) evaluation of foundation settlement and landfill liner design. Knowledge of interrelationships between porosity, permeability and velocity are also important for well log interpretation, subsurface imaging and remote prediction of permeability from seismic data. Permeability and other rock physical properties of mudstones and shales vary greatly as a function of primary textural and mineralogical composition. For a given porosity, mudstone permeability varies over a range of 2–5 orders of magnitude (Mondol et al., 2008; Mondol, 2009; Mondol et al., 2010; Yang and Aplin, 2010). The most common clay minerals—the primary constituents of mudstones and shales— are smectite, illite, chlorite and kaolinite. When the silt and sand content exceeds 40–50% there may be a grain-supported structure, and this marks the transition into clay-rich siltstones and sandstones. A relatively large fraction of grains may be larger than clay size, but as long as the larger particles are floating in a finer matrix the properties are dominated by the clay-sized particles. This study focuses on relationships among porosity, permeability and seismic velocity of natural and reconstituted mudstones and shales. A total of thirty well characterized, brine-saturated (34000 ppm NaCl) synthetic mudstones of varying textural and mineralogical compositions were compacted mechanically both in a triaxial cells (K₀-loading) and a high stress uniaxial oedometer under controlled pore pressure and proper drained conditions. The samples were mixtures of known amounts of smectite, illite, kaolinite and also silt-sized quartz grains. All experiments

were performed at room temperature, which was between 19°C and 21°C. The stainless steel oedometer cell has a highly polished inner surface. There will be some effects of side friction on the results, but they are considered to be small. The experiments were performed as uniaxial strain tests (UST). Uniaxial strain condition was obtained by controlling the triaxial cell oil pressure directly applied onto the specimen enclosed in a rubber membrane so that no radial strain occurs. The consolidation tests followed by constant-rate-of-strain (CRS) protocol (Sandbaekken et al. 1986) were conducted at the Norwegian Geotechnical Institute (NGI). The rate of strain was adjusted so that excess pore pressure at the undrained bottom should preferably not exceed about 7% of the effective stress at top of the specimen. Porosity reduction, density variations, vertical and horizontal velocities (both V_p and V_s) and vertical and horizontal permeabilities were measured at different stress levels during progressive compaction from 0 to 50 MPa.

Results show that kaolinite dominated mudstones compact more and retain higher density, permeability and velocity than smectite dominated mudstones at same stress level. The differences of porosity, permeability and velocity are relatively small at low stresses but increase drastically with increasing effective stress. Permeability of pure kaolinite ranges from 0.1 to 0.001 mD while in pure smectite it varies from 0.004 to 0.00006 mD at stresses 1 to 50 MPa. Permeability decreases logarithmically with increasing stress, density and velocity and decreasing porosity. Permeability differs over a range of 2-5 orders of magnitude at the same porosity for different clays. The fact that kaolinitic clays may have permeabilities that are several orders of magnitude higher than smectitic clays should be considered when evaluating shales as source/reservoir/seal for hydrocarbon exploration. Applications of the Kozeny-Carman equation, relating porosity to permeability in clays, would therefore produce highly erroneous results. Furthermore, laboratory investigations demonstrate that the smectite content is critical to build up overpressure in mudstones and shales

and reduce the permeability in cap rocks. For relationships between velocity and permeability in pure kaolinite and pure smectite, maximum differences up to a 4 orders of magnitude were observed. Velocities can therefore not be used to estimate permeability of mudstones and shales. The dependence of Vp on permeability for a wide range of synthetic mudstones is indeterminable due to a large scatter. When the samples are grouped into identical porosities the scatter is reduced and Vp increases with decreasing clay content. The effect is attributed to both porosity reduction and clay mineralogy. The magnitude of intrinsic velocity anisotropy is particularly high in compacted, low-porosity kaolinite dominated mudstones compared to their high-porosity equivalents caused by rearrangement of clay particles due to higher stress. The maximum S-wave anisotropy value of 0.6 is attained in synthetic mudstone contained 50:50 kaolinite-silt mixture.

Mudstones and shales should not be treated as single lithology in connection with basin analyses, seismic interpretation and well log analysis, but in reality they span a wide range of properties determined by the diversity of mineral composition and grain-size distribution. Permeability of mudstones and shales varies greatly as a function of primary textural and mineralogical composition and it is nearly impossible to accurately predict the effective permeability of a sequence of shales forming flow barriers. For a given porosity, mudstone permeability varies over a range of 2–5 orders of magnitude. Mudstone permeabilities are also direction dependent, with higher values usually parallel to bedding. This phenomenon reflects two factors: particle alignment and material heterogeneity. Material heterogeneity relates primarily to sediment deposition (e.g. provenance and depositional environments) and is most obviously linked to conditions leading to the formation of sand-silt-clay lamination. Particle alignment is linked to the subsequent mechanical compaction govern by effective stress and chemical diagenesis of clay minerals (e.g. alteration of smectite and kaolinite to illite) controlled by thermodynamics and kinetics and is therefore a function of temperature and time. Laboratory investigation also shows that the shale rock properties depend not only on the strength of the sediment particles (mostly clay minerals), but also on their surface properties and chemical bonds which are controlled by the composition of the pore fluids.

Data from this experimental study can simulate mechanical compaction at relatively shallow depth (2–2.5 km, 70–100°C) prior to significant chemical compaction. However, in cold basins with low geothermal gradients, it could be useful at greater depth. The relationships between permeability and other rock physical properties presented in this study could be used to predict permeability by sorting mudstone units as a function of clay mineralogy. However, the extrapolation of these results to natural systems must be done with caution since this study is based on mechanical compaction of silt-clay mixtures only and does not consider the sand content, organic matters or any diagenetic effects. In addition to the existing database, the experimental data may improve the calibration of fluid flow modeling, seismic and well-log interpretation, mechanical compaction behavior and evolution of shale rock properties. The experimental results may also be of importance for structural design, slope stability analysis and waste disposal efforts.

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FROM BLACK TO GREEN SHALE – ANOXIC SEAS AND GREENHOUSE LANDS IN DISTURBED JURASSIC WORLD

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Key words:

anoxia, greenhouse effect, black shale, green shale, carbon isotopes, Toarcian

34

A black shale is a black/dark grey mudstone rich in organic carbon (>5% by weight) generally formed in anoxic marine bottom waters, usually connected with Oceanic Anoxic Events (OAE). They were formed when a high rate of organic burial globally over a brief interval of time has led to the deposition of organic-rich sediments. Many parts of Europe contain prime targets for shale gas exploration, one of these is the Posidonia Shale (Early Toarcian, ~183 Ma ago) of northern Germany and approximately coeval black shales from Paris Basin (France) and Cleveland Basin (England). In the same time, in the Polish basin, poorly consolidated green/grey mudstones, claystones and siltstones ("verdine" facies) with subordinate sandstone intercalations (Ciechocinek Formation) were deposited in a large embayment/lagoon. The Ciechocinek Formation has the maximum geographic extent of Early Jurassic sedimentary strata in the Polish Basin, consistent with the Early Toarcian sea-level rise also recorded from other European basins. Both black and green shales deposition in early Toarcian is associated with abrupt and large-magnitude changes in the global carbon cycle (Carbon Isotope Excursions – CIE), which appear to be recurrent phenomena during greenhouse periods of Earth history. The Early Toarcian CIE is one of the largest (~–6‰) $\delta^{13}\text{C}$ in Phanerozoic. This CIE has been ascribed to the release, in discrete stepwise pulses, of isotopically light carbon into the ocean–atmosphere system, triggered by injection of magmatic/volcanic CO_2 into the atmosphere and the consecu-

tive destabilisation of methane hydrate in a series of rapid bursts. Carbon-isotope data from terrestrial organic matter (phytoclast separates) show that the shift to light carbon isotope values in the woody organic matter, and therefore also in atmospheric carbon dioxide occurred in major steps, similarly as in the oceans. The steps identified in green shales in Poland were correlated with those identified from marine organic matter (black shales), where they have previously been attributed to 100 kyr eccentricity forcing of climate. Polish basin is a setting where hinterland climate and sea-level change are well recorded. Additionally a link between the carbon-isotope steps and shoreline movements can be demonstrated. Individual peaks of the negative excursion are mostly associated with facies indicative of sea-level rise (flooding surfaces), but at the same time accelerated weathering and erosion in the hinterland of Polish basin, and consequently increased sediment supply caused progradation and some mismatches between isotope shifts and inferred sea-level changes. Enhanced abundance of megaspores derived from hydrophilic plant groups, and marked increase in kaolinite, are coincident with the overall development of the negative isotope excursion. The combined data suggest that each 100-kyr cycle in carbon-isotope values was characterized by increasingly severe palaeoclimatic change, culminating in extremely hot and humid conditions co-incident with the peak of the final most negative carbon-isotope excursion and black shale deposition in West Europe.

LOWER SILURIAN „HOT” SHALES IN POLAND – STRATIGRAPHY AND DEPOSITIONAL ENVIRONMENT

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Key words:

Llandovery, black shales, graptolites, East European Craton, Poland

35

Dark clays and muds are the dominant rock type of the thick Silurian series of the Polish part of the East European Craton. Detailed stratigraphic, facies, palaeontological and geochemical analyses of the Ordovician and Silurian rocks show that some rock horizons are characterized by increased concentration of organic matter and contain increased amounts of radioactive substances and heavy metals. On wireline logs, these rocks are conspicuous by remarkable increased gamma ray records (PG), as compared to the surrounding rocks. The very characteristic rock series that form the potential hydrocarbon source rocks within the Llandovery (Rhuddanian) succession is the Jantar Bituminous Claystone member which is the lowermost part of the Pasłek Formation (Modliński et al., 2006). These organic-rich (“hot”, Lüning et al., 2000) condensed, clay-dominated black shale deposits, with high total organic carbon (TOC) values indicate an anoxic event related to initial postglacial transgression and highstand episodes in mid-to outer shelf of SW Baltica as a response to the melting of the late Ordovician ice cap on the Gondwana paleocontinent and glacioeustatic rise of sea-level (Podhalańska, 2009).

A rich graptolite fauna occurs in the bituminous black shales of the Jantar member. This graptolite assemblage can be referred to the *Akidograptus ascensus*, *Parakidograptus acuminatus* and *Coronograptus cyphus* Zones. In most cases these black shales were deposited directly above the lowstand upper Ordovician marls and sandstones but an eustatic sea-level rise and a transgression could commence even during the latest Ordovician *persculptus* graptolite Zone. Within the black shales of Jantar Member, graptolite rhabdosomes are

preserved usually as flattened periderm, suggesting anoxic bottom conditions, with an excess of H₂S in the sediment. Rarely preserved three-dimensionally rhabdosomes (filled with pyrite) suggest temporarily and short-lived more oxygenated conditions at the bottom-water interface during deposition of the “hot” shales.

Detailed biostratigraphic studies, mainly graptolites, indicate that the deposition of the organic rich black shales was a synchronous event of Llandovery (Rhuddanian) age during the Early Silurian over wide areas of North Africa, Saudi Arabia, the Interior basins of the US, Russia and Czech Republic. Are the Polish Rhuddanian black shales of Jantar Bituminous Claystone member the same “hot” shales ?

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GAS AND OIL SHALE FORMATIONS IN CENTRAL EUROPE – AN OVERVIEW

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Key words:

shale gas, shale oil, exploration risk assessment, Central Europe

36

During the last years attempts were made in Europe to apply shale gas and shale oil exploration concept, previously developed in United States and Canada. For this reason many of well understood European sedimentary basins were reevaluated with new approach. Significant part of new exploration activity concentrated in Central Europe. To constrain exploration potential the historical geological data appeared to be useful, allowing for basic characteristics of shale gas and shale oil prospects. This refers to shale thickness and recent burial depth, type of kerogen, TOC contents, GR API and thermal maturity, timing of hydrocarbon generation, style of tectonic deformation, and stress regime. However the key data for exploration and production from shale reservoir are in Central Europe at present unavailable. This is truth for shale porosity and permeability, mechanical properties, gas or oil saturation and pressure, hydrocarbon composition, IP and EUR, or even shale mineralogy. Irrespective of this limitations shale gas and shale oil potential of sedimentary basins located in Central Europe was analyzed. In a case of basins located in Poland the assessment utilized mainly personal research, while for the basins in neighbor countries it was based on literature studies. The Lower Paleozoic basins with shale gas/oil potential are developed primarily on the western slope of the East European Craton. In its NW part the most important formation is the Upper Cambrian Alum shale in Sweden and Baltic offshore. Gas retention appears to be problematic in this case, due to specific burial and HC generation history. Further SE the Upper Ordovician–Lower Silurian shale in Baltic Basin in Poland, Kaliningrad region of Russia and Lithuania, as well as in Podlasie Depression in Poland is currently a subject to intensive exploration. In this case the main risk factor is relatively low thickness of organic rich interval, as well as high clay contents. Similar characteristics is valid for the Lower Silurian shale in the Lublin region in Poland, SW Ukraine and Moldova further SE.

Silurian shale is considered for shale gas/oil exploration also on Moesian Platform in southern Romanian and northern Bulgaria, as well as in Prague Basin in Czech Republic and in SE Anatolia in Turkey. The Upper Paleozoic basins with shale gas potential are mainly forelands of Variscan orogen, with Namurian shale in Germany being probably the most prospective. In SW Poland in the Visean–Namurian flysch complex north of the Sudety Mts a hybrid system of interbedding shale and tight gas might have developed. However the exploration potential is limited in this case by tectonic deformation and locally also by overmaturation. The Permian–Mesozoic basins are less perspective in this part of Europe, however Toarcian Posidonia shale in the Lower Saxony Basin could be an exception. In the Vienna Basin the Upper Jurassic Mikulov shale and marl have characteristics favorable for development of shale gas, except of high burial depth. In the Outer Carpathians the Lower Oligocene Menilite shale proved to be an unconventional reservoir for oil and liquids, however high degree of tectonic deformation in the fold-and-thrust belt is an obstacle for exploration.

In Central Europe the basins most prospective for shale gas/oil exploration are of the Lower Paleozoic age. This is in contrast with North America where the only such old shale formation with unconventional resources is the Ordovician Utica shale, and the major shale reservoirs are commonly of the Upper Devonian to Lower Carboniferous age. In Central Europe the Upper Paleozoic basins with shale gas/oil potential often suffers tectonic deformation, causing technological challenges. Hydrocarbons in the Paleozoic basins of Central Europe were commonly generated during Variscan time, rising uncertainty as for gas retention. The other specific of Central Europe basins is that thermal maturity often is not high enough for dry gas, and considerable parts of the analyzed basins might have liquids and oil potential.

ENVIRONMENTAL CONCERNS RELATED TO GAS AND OIL PRODUCTION FROM SHALE RESERVOIRS – IMPACT RELATED TO TECHNOLOGICAL APPROACH VERSUS IMPORTANCE OF LOCAL GEOLOGICAL SETTING



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Key words:

unconventional reservoir, hydraulic fracturing, environmental impact, human health

37

Shale gas and shale oil exploration and production recently provokes a vital discussion on its possible impact on natural environment and human health. This impact is related on one side to specifics of technology used for production from unconventional reservoirs, creating challenges common across all explored and producing basins. On the other hand local geological setting might be a reason for number of specific considerations.

Technological approach applied to unconventional reservoirs results with dense grid of production wells on field, and therefore with their high number. For each well long lateral sections are drilled for which often several hydraulic fracturing stages are completed, requiring some 10,000 to 70,000 m³ of water per well. This consumption is generally minor comparing to other industrial or agriculture water usage, however accessibility of water is location specific. The sources of water are typically aquifers, surface waters, shallow low salinity brines, municipal or industrial waste waters. Apart of water a fracturing fluid contains sand (or proppant), and some 0.5–1% of chemical additives (friction reducers, gelling agents, breakers, biocides, scaling agents, corrosion inhibitors, HCl acid, etc). At average some 20% of injected fluid comes back to the surface, and is partly reused for next fracturing. Concentrations of the additives in the frack fluid are relatively low, and once mixing with formation brines further decreases. For this reason the adjectives in flow back water are not a major concern. Environment risk related to the additives is connected rather with possible accidents and spills of concentrated components prior to their underground injection. In a case of flow back fluid the main environmental concern is dissolved solids washed out of reservoir formation and incorporated

from formation brines, primarily salts, sulfates and metals (e.g. Ba, Sr, Fe). Because of this components flow back fluid requires treatment prior to reuse. Composition and concentration of dissolved solids in flow back fluid depends on shale and brine composition in a given locality, and could vary significantly between basins. In some cases organic rich shale are characterized by elevated concentrations of radiogenic components, which could cause elevated radiogenic record of brines and rock debris. This is however negligible from the human health point view.

Possible migration of frack fluid or natural gas from reservoir formation to shallow aquifers due to fracturing attracts considerable public attention. The ability for gas and fluids to migrate up-section is in most of geological setting highly unlikely, and limited only to cases when fractured formation is at very low burial depth (e.g. 500 m) and no seal overburden is present. Therefore in practice such cases are extremely rare. There are however documented cases of gas migration from the reservoir up section due to improper cementing. In a specific cases fracturing could also induce earth tremors, however only in seismic regions.

With the current level of technology landscape footprint of shale gas/oil production was significantly reduced with compare to early stages of technology development. Due to lateral drilling techniques well pads could currently be at a distance of 3–7 km from each other. Individual pad could cover 2–4 ha, however is used only for several months and afterwards the land is reclaimed. Drilling and fracturing activity results with air emissions. These are related mainly to engines exhaust, evaporation of pits for flow back water, flared gas, and methane release. Methane venting and leakage is a concern as a green house gas emission. However its impact on ozone layer is low

NANO- AND MICROPORE STRUCTURE AND ACCESSIBILITY IN SOURCE ROCKS AND TIGHT RESERVOIRS AS DETERMINED BY NEUTRON AND X-RAY SCATTERING



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Key words:

hydrocarbon generation, tight shale, accessible porosity, small angle scattering

38

Small angle and ultra-small angle scattering of neutrons and X-rays (SANS, USANS, SAXS and USAXS) are non-invasive tools for ex-situ analysis of the pore micro-architecture and pore content in sedimentary rocks. Originally these tools have been used to determine the pore size distribution in shales, sandstones, carbonates and coals in various geological contexts (1). These types of rocks turned out to have very broad, fractal-like pore size distributions, extended in the range from several Å to about 20 µm across.

As the scattering contrast for neutrons depends strongly on the natural content of the pore space, SANS/USANS turned out to be ideal tools for following the progress of hydrocarbon generation and primary migration in source rocks. With increasing depth formation waters contained in the pore space of source rocks are gradually replaced by generated bitumen, which, in turn, at yet lower depths is cracked into lighter fractions (2).

With the development of pressure cells capable of reproducing the subsurface temperature and pressure conditions, the pore-size-dependent sorption capacity as well as sorption kinetics for CO₂ and CH₄ in the micro- and nanopores of coals and shales have been measured (3, 4). Perhaps the most significant recent development has been the determination of both accessible and inaccessible nano- and microporosity in tight shales as well as direct comparison of scattering results with the traditional gas sorption data.

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MUD MOBILIZATION AND FOLDING HISTORY IN THE SOUTH CASPIAN BASIN



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Key words:

shale tectonics, overpressure, syn-sedimentary deformations, detachment folding, Caspian Sea

39

This study examines the three-dimensional geometry and reconstructs the folding history of one of the anticline culminations that deform the thick sedimentary depocentre of the western margin of the South Caspian Basin (offshore Azerbaijan). We have examined how syn-sedimentary folding was accompanied here by subsurface mud migration and vertical ascent, which shaped complex diapirs, and how seafloor instability processes occurred linked to some of the deformation pulses. We have conducted this analysis using a post-stack 3D seismic cube migrated in depth tied with information from two exploration wells.

The South Caspian Basin is an important oil and gas productive region and contains one of the thickest sedimentary accumulations of the world, with > 10 km of Pliocene to Recent sediments. The highest rates of deposition occurred during the late Miocene to middle Pliocene, accompanying the rapid subsidence of the basin floor constituted by an oceanic crust. During this epoch, a thick sequence (~6 km) of shallow marine to continental sediments was deposited in the western margin, which represents the main hydrocarbon reservoir, known as the Productive Series (PS, 5.9 to 3.1 Ma). An important unconformity separates PS from the younger fluvial-to-deltaic package formed by the Akchagyl to Gelasian series.

The PS sequence is folded shaping a sigmoidal, NW-SE anticline culmination with a shallow accumulation of overpressured muds. The seismic signal of the mobilized mud is a chaotic facies with many artifacts due to lateral diffractions and a likely error during acquisition and processing procedures. The 3D geometry of the mobilized muds in the anticline culmination depicts an upper teardrop diapir with abundant lateral extrusions.

The complete shape of the folded surfaces has been fit by nonparametric regression methods. We implement the standard length and area-balanced algorithms to estimate the shortening magnitudes and rates. The syn-growth sediments evidence two different pulses of folding accompanied by seafloor instability processes. A minor event is registered during the middle Pliocene toward the end of the deposition of the PS, whereas a maximum shortening episode is recognized just after the Akchagyl Unit at ~1.7 Ma. We believe that this anticline structure constitutes a good example to study how fluid- and clay-rich sediments behave under shallow compression and how their subsurface migration may generate seafloor instability processes.

CLAY MINERAL AND ORGANIC DIAGENESIS OF MALMIAN MARLSTONES, VIENNA BASIN



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Key words:

diagenesis, illite/smectite, illitization, marlstones, Vienna Basin

40

Autochthonous Malmian marlstones of the Mikulov Formation are the main source rock for oil and gas in the Vienna Basin. The Vienna Basin is a Neogene pull-apart basin which is situated between the Eastern Alps to the West, the Carpathians to the North-East and the Pannonian Basin to the East.

In this study the clay mineralogy and the organic parameters of 46 core samples from nine different wells were characterized. The wells penetrate the Mikulov Formation over a depth range of 1400 m to 8550 m and this gives a unique opportunity to study the diagenetic changes of one formation from shallow to deep burial.

The clay mineralogy was quantified with X-ray diffraction applying the mineral intensity factor (MIF) – method of Moore and Reynolds (1997). The clay fraction of the marlstone contains a prominent illite/smectite (I/S) mixed-layer mineral (20 to 70 wt%), illite (20 to 70 wt%), chlorite (0.5 to 12 wt%) and kaolinite (2 to 17 wt%). The amounts of I/S and kaolinite decrease with depth, whereas illite and chlorite increase. A gradual transformation of smectite to illite through mixed-layer I/S intermediates is recognized. With increasing depth the illite content in I/S intermediates in-

creases from 25% to 90%, in the same interval the ordering of the mixed layer I/S changes from R0 (25% illite in I/S) to R1 (60-80% illite in I/S) to R3 (90% illite in I/S). R3 ordering prevails at depths greater than 4000 m.

Illite crystallinity was determined using standards from Warr and Rice (1994). Illite crystallinity increases with temperature and depth, but the deepest sample at 8551 m has not yet reached the anchizone. Vitrinite reflectance values range from 0.4% Ro in the shallowest samples to 3.3% Ro in the deepest samples and indicate a mature stage in the diagenesis of kerogen for the deeper samples. The R1 ordering of the mixed-layer minerals corresponds with vitrinite reflectance values of 0.4% to 0.6% and a depth of approximately 3000 m.

The total organic carbon (TOC) values range between 0.37 and 3.09 wt% with an average of 1.3 wt%. Rock-Eval pyrolysis data (HI, OI) imply type II to III kerogen for the organic matter, hence the marlstones are oil and gas, as well as gas prone.

There is a good correlation of the illitization trend of the mixed-layer mineral I/S and the organic maturity parameters.

AN OVERVIEW OF EXPERIMENTAL MUDSTONE SEDIMENTOLOGY – RESULTS OF EXPERIMENTS AND APPLICATIONS TO THE ROCK RECORD



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Key words:

sedimentology, flocculation, flume studies, depositional environment, depositional processes

41

The processes affecting the transport and deposition of mud in natural environments are still poorly understood, yet, understanding these processes is important because much of the earth's surface is covered with muddy substances. Two thirds of the sedimentary rock record consist of mudstones and shales, mud accumulation impacts water reservoirs, harbors, and shipping lanes, and mudstones and shales are an increasingly important energy resource. From the perspective of a sedimentologist, the need for experimental work in mudstone sedimentology comes from the realization that many mudstones contain small-scale sedimentary structures that can potentially provide information about depositional conditions and history. However, as soon as one attempts to harness these features for interpretation of environments of deposition, one realizes that there simply is not much information available that allows us to link features observed in the rock record to measurable sets of physical variables in modern environments. Although one might hope to glean the required information from studies of modern mud accumulating environments, the heterogeneity of modern sediments makes it quite difficult to connect observed sedimentary features and measured process variables. Thus, study under control-

led conditions in flumes and other experimental apparatuses is essential for true improvement of our understanding of mud deposition.

Flumes can be used to obtain quantitative information about depositional and erosional parameters, but it is of critical importance that the flume be designed in a way that flocculated materials move under shear stress conditions that would be reasonable in natural environments. Recent flume studies have shown that muds can form deposits at flow velocities and shear stresses that would suffice to transport and deposit medium grained sand. Muddy suspensions are prone to flocculation and the resulting floccules travel in bedload and form ripples that accrete into beds. The latter finding suggests that for example many laminated shales were deposited from currents rather than by settling from slow moving or still water. There are many other sedimentary features in shales that can be reproduced in flume studies. As continued progress is being made, these will in coming years provide a quantitative basis for shale sedimentology, as well as offer the potential to better understand the parameters that determine the performance of shale gas reservoirs.

RADIOLOGICAL SAFETY OF METAMORPHOSED BLACK SHALES OF THE NIEMCZA ZONE (NZ) AND THE NIEMCZA – KAMIENIEC ZĄBKOWICKI METAMORPHIC UNIT (N-KZMU)

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Key words:

Poland, Sudetes, uranium, black shales, quartz-graphitic schists

42

Objectives

Radiological safety assessment of metamorphosed black shales (quartz-graphitic schists) of two structural units of the Foresudetic Block (SW Poland), where radiometric anomalies have been described by Solecki (1999, 2000)

Procedures

K, U and Th content of metamorphosed black shales was measured by means of portable RS230 gamma spectrometer. Measured activity of ^{40}K was recalculated into total K (%) content. Measured activities of ^{214}Bi and ^{208}Tl were recalculated into equivalent uranium (eU) and thorium (eTh) concentrations (ppm). Obtained results were analysed in terms of F1 and F2 indices according to Polish Law.

Results

Summary of 110 results of measurements is presented in Tab.1.

Conclusion

Studied rocks are of slightly increased uranium content but do not pose significant radiological risk.

K, U, Th content can be used as a tool of discrimination between metamorphosed black shales of the NZ and the N-KZMU.

Strong correlations between K, U, Th in the case of Żelowice indicates the role of primary clastic accessory minerals as radionuclide carriers.

U enrichment in Brodziszów is of secondary character.

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Tab.1. K, U, Th results from the Niemcza Zone (1-3) and the Niemcza – Kamieniec Ząbkowicki Metamorphic Unit (4-5)

	K (%)		eU (ppm)		eTh (ppm)		Pearson coefficient	
	mean	max	mean	max	mean	max	K/U	U/Th
1. Brodziszów	1.2	1.9	11.2	25.6	6.1	9.7	-0.26	-0.5
2. Zwrócona	1.5	1.7	2.0	2.3	8.2	9.1	0.25	0.0
3. Sulisławice	2.0	2.6	3.4	8.1	9.8	12.9	-0.46	-0.3
4. Żelowice	2.1	4.9	4.7	14.1	10.6	18.8	0.89	0.81
5. Żelowice without anomalous	1.8	3.6	3.5	6.8	9.7	17.5	0.94	0.95

THIN-SKINNED EXTENSION AND SHALE TECTONICS IN A TILTED BASIN MARGIN: THE CASE OF THE NORTHERN ALBORAN SEA (MEDITERRANEAN)



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Key words:

mud volcanoes, overpressure, syn-sedimentary deformations, shale tectonics, Mediterranean

43

We have studied the tectonic evolution of the northern margin of the West Alboran Basin (offshore Spain), a south-dipping margin containing important sedimentary accumulations of Miocene to Recent fine-grained, marine sediments and active mud volcanoes in the seafloor.

The analysis of this sedimentary basin has been conducted through seismic interpretation of a dense grid of 2D seismic lines. This interpretation has been tied with well data, which provide lithological and bio-stratigraphic information. Our analysis of the logging data in some of the commercial wells in this margin confirms the occurrence of overpressured sediments in the lowermost levels of the basin, formed by Early Miocene, shale-rich sediments. This sequence constitutes the source rock for the widespread shale diapirs that characterized the deeper West Alboran depocentre.

We have conducted a detailed reconstruction of the geometry of the shale-cored diapirs and the relationships with the overburden, analyzing the geometries and timing of the syn-sedimentary deformations. It is inferred the

occurrence of a punctuated history of deformations in basin margins through the Middle to Late Miocene, conducted by syn-sedimentary normal faults that root in the basement-to-cover surface, which represents a low-angle detachment surface. We reconstruct that thin-skinned extension in basin margin promoted down-slope migration of the overpressured shales forming diapir structures that evolve shaping progressively shale rollers, shale anticlines, walls and allochthonous shale sheets driven by thrusts in the thicker and deeper portions of the basin.

We interpret that pulses of syn-sedimentary extension in basin margins, mainly during the Middle Miocene, drove the down-slope migration of the overpressured shales. This processes occurred probably during a continuous tilting of the basin floor, which was accompanied by massive sedimentation and burial of fine-grained sediments.

The Alboran Basin therefore is a useful area for analysis of the structural pattern associated with shale tectonic processes and a key basin for comparing the geometries and evolution of shale with structures formed in salt basins.

IDENTIFICATION, INTEGRATION AND UPSCALING OF MUDROCK TYPES IN POLAND – A PATHWAY TO UNLOCKING SHALE RESOURCES



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Key words:

mudrock characterization, lithofacies, microfacies, upscaling, texture

44

A multidisciplinary approach to shale characterization, when applied to a variety of North American hydrocarbon-rich shale plays, has led to improved understanding and characterization of the complex bulk physical, chemical and mechanical properties of these deposits and their heterogeneity. This effort is leading to successful exploitation of these enigmatic resources. Microfacies analysis of mudrocks provides a platform for upscaling from the “nano” to regional scale, and results in comprehensive mudrock characterizations.

Rock-based investigations build on the conventional core material that is available for the basins within Poland in conjunction with newly acquired conventional cores and rotary sidewall cores (RSWC) taken in exploration wells. These rock samples undergo an integrated petrologic analysis to capture their textural and compositional variability. Microfacies analysis of mudrock types within select stratigraphic intervals in each basin leads to the recognition of mudrock lithofacies. The heterogeneity within mudrocks and their associated microfacies are identified and described using a combination of varied techniques including scanning electron microscopy (SEM), thin section petrography, computed tomography (CT) scans, biostratigraphic data and macro core descriptions. By using standard petrographic techniques coupled with newly enhanced and emerging technologies, most issues associ-

ated with mudrock characterizations can be ameliorated. Mudrock lithofacies definitions that are based on integrated petrologic analyses capture the mudrock compositional and textural variability and facies associations. Lithofacies reflect how much variability is present in a mudrock interval and increase our understanding of the geologic history of a deposit. Mudrock lithofacies can connote “significant” differences in lithologies including what boundary thresholds matter to, or are reflected in, the petrophysical properties, the mechanical stratigraphy, and the permeability pathways.

Lithofacies identification allows for documentation of basin-specific variations in mudrock composition and microfabrics, recognition of the distribution of organic-rich members of these intervals, calibration of petrophysical models, definition of the mechanical stratigraphy for completion design, and provides the litho-stratigraphic building blocks for regionally specific, predictive sequence stratigraphic models.

Successful exploration and exploitation of mudrocks as hosts for oil and gas resources can be advanced when the recognition of mudrock lithofacies provides a methodical means of combining geologic, chronostratigraphic, geochemical and petrophysical data from a spectrum of scales and disciplines.

RELATIONSHIP BETWEEN MINERALIZATION AND FABRIC IN THE NONESUCH SHALE: IMPLICATIONS FOR FLUID MIGRATION PATHWAYS IN FINE-GRAINED ROCKS

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Key words:

Nonesuch, copper, fabric, shale, permeability

45

The Proterozoic Nonesuch Fm., Michigan, U.S.A., hosts generally stratiform Cu likely deposited by fluids migrating from the underlying Copper Harbor Conglomerate. Fabric details reveal information about the movement of the fluids through low permeability mudstones. A drill core transect at White Pine shows the Copper Harbor-Nonesuch contact rising toward the center of the ore deposit, moving up the limb of a syncline. Going up the syncline limb, mineralization intensifies, suggesting that more of the mineralizing fluids were forced upward into the Nonesuch. Mineralization, primarily Cu with minor Ag, is most pronounced in the lowest 5 m of the Nonesuch, with some enrichment in other metals, including As, Sb, Cd, and Pb about 15 m above the base. The Nonesuch shales and siltstones, likely lacustrine, host varve-like laminations that include some carbonate-rich laminations. The carbonate-rich laminations host organic matter, but show little mineralization, suggest-

ing they were relatively impermeable. Disrupted laminations, above which there is additional mineralization, suggest upward moving mineralizing solutions were able to break through in discrete places. Also suggesting focused break through of migrating fluids is localized disruption of bedding-parallel alignment of phyllosilicate grains within the mineralized zone. In places, carbonate veinlets crosscut laminae indicating another possible fluid pathway. Some of these veinlets host mineralization, further suggesting mineralizing fluids utilized, and possibly created, discrete discontinuities in fabric. Mineralization is also particularly concentrated in thin laminations immediately beneath clay-rich laminations. This may indicate that fluids migrating upward through silty layers were commonly impeded at clay-rich laminations. These fabric observations suggest that laminated fine grained rocks may permit cross cutting fluid flow at discrete points, but more broadly block flow.

CONTROLS ON DISTRIBUTIONS OF METHYLPHENANTHRENES IN SEDIMENTARY ROCK EXTRACTS: CRITICAL EVALUATION OF EXISTING GEOCHEMICAL DATA FROM MOLECULAR MODELLING

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Key words:

methylphenanthrenes, molecular modelling, MPI

46

The thermodynamic stability of methylphenanthrene isomers and the kinetics of reactions involved in their natural destruction/formation have been studied via molecular modelling. The results were combined with published methylphenanthrene abundances in extracts of rocks containing Type III kerogen of a wide maturity range, to evaluate the utility of methylphenanthrene maturity parameters. These parameters track the isomer evolution toward equilibrium, leading to enrichment in the stable 2- and 3-methyl isomers relative to the less stable 9-, 1- and 4-methyl isomers. The pathways from kinetically to thermodynamically controlled distributions remain unclear but probably involve isomerisation, transmethylation and demethylation reactions. To understand the importance of each pathway, ab initio quantum chemical calculations (DFT) have been performed, leading to the identification of possible transition states and to the determination of activation energies for reactions in aqueous solutions. Acid catalysis significantly lowers modelled reaction barriers to an extent consistent with the changes observed in nature.

The equilibration can start at very low maturation with acid catalysed 1,2-methyl shifts (isomerisations) regarding low energy barriers. Alternative isomerisation pathways through tertiary carbon centres are ineffective. A reverse transmethylation, e.g. modelled methylations of phenanthrene with either a terpenoid alcohol with a gem-dimethyl or polymethyl aryl carotenoid moiety can preferentially lead to 9-methylphenanthrene due to a relatively lower

energy barrier. The appearance of 9-methylphenanthrene at very early maturation stages suggests effective heterogeneous catalysis by the mineral matrix. The reaction is however reversible, which means that 9-methylphenanthrene tends to demethylate with much higher rates than the other isomers but only when suitable methyl acceptors are available. In turn, free radical demethylation which is likely at advanced levels of maturity would not significantly influence relative proportions of the isomers due to very similar barriers for all the isomers. However the reverse reaction would produce all isomers thus equalising all isomer concentrations.

The discussed reactions are only a few of many reactions in which phenanthrene and methylphenanthrenes are potentially involved in nature to mention only biotic (biodegradation) and abiotic methylphenanthrene demethylation, and that there is no a single reaction that determines the fate of these molecules. Therefore, the commonly applied maturity index MPI-1 does not entirely reflect thermal maturity but is instead a molecular expression of complex processes and is dependent partly on catalytic effects of the mineral matrix. Analysis of the published data on methylphenanthrene abundance in rocks containing Type III kerogens indicates that there is no inversion of the MPI-1 trend above $R_r = 1.35\%$ as has been suggested previously. The maturity parameter MPR, defined as the 2-/1-MP ratio seems more closely dependant on thermal maturity than MPI-1.

TIMING AND THE MAXIMUM PALEOTEMPERATURES OF DIAGENESIS OF THE LOWER PALEOZOIC SHALES ON THE PERI-TORNQUIST MARGIN OF THE EAST EUROPEAN CRATON EVALUATED FROM CLAY MINERAL DATA

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Key words:

burial history, illite-smectite, Peri-Tornquist margin, shale diagenesis, shale gas

47

Both the age and the level of the maximum paleotemperatures experienced by a basin in its geological history can be evaluated directly by studying diagenetic mixed-layer illite-smectite, commonly present in sedimentary rocks. The age is available via K-Ar dating of illite-smectite separated from bentonites. The maximum paleotemperatures can be calculated from percent smectite (%S) in illite-smectite, measured from the X-ray diffraction patterns of oriented preparations of fine clay fractions of shales. Such combined approach has been used to study two sectors of the Peri-Tornquist margin: Baltic Basin and the Dniester slope. The materials available from the Baltic Basin included Silurian and Ordovician bentonite samples from the outcrops in Norway, Denmark, Sweden, Estonia and from the cores in Pomerania, Poland, as well as shale samples from several cores in Pomerania and NE Poland. The sample material from the Dniester slope are Silurian bentonite plus Silurian and Lower Devonian shale outcrop samples from the Dniester gorge, and Silurian and Lower Devonian core shale samples from areas located N and S of the Dniester gorge.

In the Baltic Basin XRD data indicate very advanced diagenesis (ca. 200°C) close to the Caledonian fronts, decreasing to ca. 100°C farther on the craton (N Sweden, Estonia, Latvia). Published apatite fission track (AFT) data are consistent with this interpretation. The ages of the maximum paleo-

temperatures range from Lower Devonian-Lower Carboniferous in the central zone between Denmark and Estonia to Upper Devonian to Carboniferous/Permian boundary to N and S of this zone. Such distribution of K-Ar ages is interpreted as indicating a heating event (metamorphic fluid migration?) in the central zone and deep burial under Devonian-Carboniferous cover closer to the Caledonian fronts. On the Dniester slope XRD data detect very advanced diagenesis (ca. 200°C) of entire Dniester gorge area, decreasing to the north and increasing to the anchimetamorphic temperatures in the Rava Ruska zone at the very border of the craton, in accordance with the published CAI zonation. Like in Pomerania, the K-Ar dates for bentonites range from the Upper Devonian to Carboniferous/Permian boundary. They document former extension of a thick cover of Upper Devonian and Carboniferous sediments of the Lublin-Lviv basin far to SE, not accounted for by current paleogeographic reconstructions. Long-lasting erosion of this cover is reflected by the Cretaceous AFT dates obtained from the Silurian bentonites.

Similar Upper Paleozoic burial histories, reconstructed for both areas, argue in favor of a more widespread Variscan cover of the Peri-Tornquist margin than assumed by current paleogeographic reconstructions.

MINERAL DIAGENESIS IN CLAY- AND SILT-RICH MUDSTONES: THE MANCOS SHALE, BOOK CLIFFS, UTAH

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Key words:

mudstone, shale, diagenesis, quartz, Utah

48

An understanding of the nature and scales of diagenetic variability within organic-rich mudstones is critical to the accurate assessment of shale-gas reservoir properties, as well as for elucidating chemical evolution pathways within mudstones. Here we integrate field observations with thin section descriptions, and petrographic and mineralogical data for the Blackhawk Member time-equivalent Mancos Shale in Book Cliffs, Utah. Our objective is to determine the impacts of early and burial diagenesis on this mudstone succession.

The detrital assemblage in the Mancos Shale is quartz-silt, feldspar, clay minerals, dolomite and organic matter (TOC of 1 to 2.5%). Biogenic silica is negligible. Field mapping reveals laterally continuous (km-scale) brittle ferroan dolomite cements ($d^{13}\text{C} = +1$ to -2 per mil, $d^{18}\text{O} = -2$ to -5 per mil), up to 30 cm thick, marking coarsening-upward units 1-3 m thick, and stacked coarsening-upward units 5-15 m thick, which correlate to bedsets and parasequences in up-dip settings. These are early diagenetic in timing and are interpreted to result from enhanced bacterially-mediated diagenesis at sediment hiatus during marine flooding events. In more distal settings these cements become isolated, septarian concretions which contain generations of

dolomite, calcite and kaolinite cements, thereby containing a record of chemical mobility during burial. The dominance of dolomite cements highlights the importance of macroscopic-scale diagenetic carbonate mobility in these mudstones. Pyrite is an important early diagenetic mineral phase throughout the mudstones.

In addition to carbonate-cements, diagenetic alteration and precipitation of quartz and alumina-silicate minerals are also important in these mudstones. Kaolinite takes the form of shelter porosity infilling and as vein fills within septarian concretions. These are interpreted to be early diagenetic in origin and indicate that both silicon and aluminium are mobile during early diagenesis. Burial diagenetic kaolinitisation of feldspar grains is also apparent. Quartz cement takes the form of quartz overgrowths, grain replacement and micro-quartz crystals, and is interpreted to be the result of feldspar replacement or silica expelled from the smectite to illite transformation. These mineral phases highlight that microscopic-scale diagenetic mobility of silica is important even within mudstones lacking biogenic silica and is likely to be an important processes in a wide range of mudstones.

OPAL AS A CARRIER OF URANIUM IN MENILITE SHALES

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Key words:

Carpathians, uranium, opal, autoradiography

49

Objectives

Identification of mineral phases responsible for increased uranium content of menilite shales in Bezmiechowa area, where maximum uranium enrichment supposed to be epigenetic was found by Kita-Badak et al. (1965).

Procedures

Gamma spectrometric profiling by means of portable RS230 gamma spectrometer has been performed in the Bezmiechowa profile. Polished thin section of the sample of the highest uranium content was studied by means of autoradiographic micromapping using CR-39 solid-state nuclear track detector (SSNTD).

Results

Alpha tracks observed in CR-39 SSNTD concentrate at red-brown crystalline silica-phases such as chalcedony up to crypto- and/or microcrystalline quartz, probably resulting from recrystallization of primary menilite opal derived from diatomic remains.

Conclusions

The anomalously high content of stable silica-phases replacing primary menilite indicate that the sample analysed could have suffered an intensive diagenesis.

The influence of fluids generated by the Silesian Unit over thrust zone can explain both uranium migration and opal recrystallisation.

Obtained results fit well to the description of uraniferous opal from Virgin Valley, Nevada which occurs as replacement of diatomite (Zielinski, 1982) and uraniferous opal from the Nopal I uranium deposits, Mexico.

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TECTONIC DECOUPLING ALONG THE SILURIAN SHALE COMPLEX IN THE LUBLIN BASIN, SE POLAND



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Key words:

Palaeozoic, shale, tectonic deformation, seismic data, Lublin Basin

50

The Lublin Basin (SE Poland) is a multistage polygenetic basin developed mainly during the Neoproterozoic to Paleozoic times. The Lower Paleozoic shale complex of this is a part of sedimentary cover of the western slope of the East European Craton, which is currently a primary target for shale gas exploration in Europe. The Neoproterozoic to Paleozoic sedimentary cover of the Lublin Basin is characterized by complex structural development. Lithological variability within section of the basin results with rheological contrasts between individual complexes. Of particular importance for development of tectonic deformations is a presence of 1000-2000 m thick complex of relatively ductile Silurian sediments, composed mainly of mudstone, marl and claystone. Below more brittle Ordovician limestone and marl, as well as the Ediacaran-Cambrian sandstone and mudstone are present. The Silurian complex is covered also by more competent sediments, including the Lower Devonian sandstone and mudstone, as well as the Middle to Upper Devonian and Carboniferous carbonates and clastics. Tectonic deformations of the Precambrian to Carboniferous deposits in the southern part of the Lublin Basin

were analyzed using seismic reflection data that provided insight particularly into the Caledonian and Variscan deformation systems. Special attention was paid to the role of the Silurian shale complex. Results of seismic data interpretation demonstrate differences of tectonic deformations above and below the Silurian section, expressed by different types of structures. The lower complex (Cambrian-Ordovician one) represents regional flexure towards SW. The seismic data allows to document development of syn-sedimentary extensional faults of the Late Silurian (to Early Devonian?) age. These deformations are interpreted here as expression of flexural extension in the Caledonian foredeep basin. The upper complex (Devonian-Carboniferous one) is characterized by folds related to NE compressional shortening of limited scale, developed during late Carboniferous time. Moreover set of low angle reversed faults passing up section into flexures are observed in this complex. Neither folding nor reversed faults are observed in the lower complex. This is interpreted here as a result of local tectonic decoupling along more ductile Silurian shale complex.

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GEOMECHANICAL ASSESSMENT OF THE ELASTIC PROPERTIES OF RESERVOIR ROCKS UNDER HIGH PRESSURES AND TEMPERATURES



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Key words:

geomechanics, high pressure and temperature, Young modulus, Poisson ratio

1

Exploitation of hydrocarbon deposits at great depths requires appropriate stimulating techniques adapted to local geological conditions, which are particularly complex in the case of shale gas, where fracture treatments require the consideration of anisotropy of the rock mass caused by a layered structure of shale.

The designing of the hydraulic fracture treatments requires the knowledge of elastic properties of the rock mass: Young's modulus (E) and Poisson's ratio (ν) because these parameters are commonly used in the available national simulation programs. Thus the selection of the values of E and ν plays a key role in predicting the fracture geometry as well as the success of the whole treatment. The basis for determining the two values are either direct geomechanical laboratory tests in thermo-pressure chambers, where conditions adapted to pressure and temperature at a given depth are created in triaxial stress state, or indirect correlation geophysical tests.

As the results of geomechanical strength and strain tests in conditions modelling depths down to 3.5 km done in the Department of Geomechanics of the University of Warsaw indicate, the elastic parameters obtained in this way are not comparable with the data known from the surface conditions. The changes of the static Young's modulus (E_{st}) and static Poisson's ratio (ν_{st}) along with depth are non-linear, depend on pressure and temperature as well as are different for different types of rocks. It was observed that at the circular pressure $P = 90$ MPa and temperature $T = 120^\circ\text{C}$ in weakly compact Ciężkowice sandstones the strain modulus (E_{st}) increased almost 4 times – from 5 GPa in atmosphere pressure conditions to over 20 GPa in conditions corresponding to the depth of 3.5 km. In similar conditions, in compact Krosno sandstones, the modulus in-

creased from 30 MPa to 45 MPa – less but also significantly. At the same time the direct laboratory measurements indicate, that in the Ciężkowice sandstones following the rise of E_{st} along with the depth, the Poisson's ratio decreases from the value of 0.40 at the surface down to 0.15 at the modelled depth of 3.5 km, whereas it fluctuates with minor variations in Krosno sandstones around 0.25. Therefore the studies indicate the need for verification of surface data in relation to the deposit conditions.

Facilitation of such verification as well as reference to indirect geophysical methods can be simultaneously conducted measurements of the ultrasonic wave velocity during geomechanical tests in conditions of high pressure and temperature. Initial studies on samples of Ciężkowice and Krosno sandstones done in the Department of Geomechanics of the University of Warsaw indicate, that the longitudinal wave velocity (V_p) in the direction parallel to the direction of the load increases in Ciężkowice sandstones almost 3 times and in Krosno sandstones about 50%. In the case of stratified centers, such as shales, another difficulty of assessment of elastic properties is created by the anisotropy of these rocks. The parameters obtained by means of mechanical as well as geophysical (ultrasound) tests may be radically different depending on the measurement's direction. Therefore the prediction of fracturing conditions based on the selection of elasticity parameters (E and ν) must take into account not only lithological variability of the rock mass in vertical profile but also the conditions of pressure and temperature within the rock mass as well as representativeness of measurement directions to the predicted fracturing direction.

TWO-STAGES GAS GENERATION IN THE CARBONIFEROUS SHALES OF THE SOUTHERN PART OF THE FORE-SUDETIC MONOCLINE (SW POLAND)



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Key words:

gas, generation, Fore-Sudetic Monocline

2

The Carboniferous shales in the Fore-Sudetic Monocline (FSM) are regarded as a second target for shale gas exploration in Poland (Poprawa, 2010). In the study area the Carboniferous sedimentary succession exceeds 1000-2000 m in thickness and is composed of clastic deep-marine sedimentary rocks (Mazur et al., 2006). In this work the organic maturity modelling of the Carboniferous sediments was carried out in several boreholes by means of PetroMod software in order to reconstruct the gas generation processes in the Carboniferous gas-source rocks containing III type kerogen and mixed type II/III kerogen. The quantity of the organic matter is variable with averages of 0.5–2% TOC. In the study area maturity is in the range from 0.7 to 2.0% Rr (Pletsch et al., 2010). The results of the modelling indicates that Carboniferous sediments attained their thermal maturity between the Late Carboniferous and Cretaceous. The best-fit calibration has been achieved by means of applying increased heat flow values (~90-100 mW/m²) in the Carboniferous-Early Permian period probably related to the volcanic processes and hydrothermal activity in the study area. The Late Permian-Mesozoic and Cainozoic period were characterized by moderate heat flow (~50-60 mW/m²). Probably, several stages thermogenic gas generation and expulsion could be distinguished. Lower Carboniferous source rocks generated gas in two phases: in the Late Carboniferous and later from Early Triassic until Late Cretaceous. Whereas, Upper Carboniferous source rocks generat-

ed gas only in the Mesozoic, due to insufficient burial in the Variscan stage of the development. As suggested in some German part of the basin (Pletsch et al., 2010), Westphalian gases replace and displace older gases coming from Lower Carboniferous source rocks. It caused a mixing of gases in conventional gas fields (Pletsch et al., 2010). Generally, the hydrocarbon potential of Carboniferous shales in the study area is high, which is also supported by the existence of many conventional gas fields in that area.

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THE SECONDARY OXIDATION OF COPPER BEARING SHALE WIN THE KOZUCHOW AREA

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Key words:

Zechstein, Kupferschiefer, post-diagenetic process, iron oxides, red spots

3

Zechstein copper bearing series occur in most parts of the Polish territory, covering an area more than 170 000 km², and the most important for economic reason and exploratory considerations is Kupferschiefer (T1) - copper bearing shale. This paper presents petrographic and mineralogical characteristics as well as the regularities between occurrence of red spots in Kupferschiefer and post-diagenetic processes. Material for the study came from a borehole Podbrzezie K-6 located in the region of Kozuchow (south-western part of the Fore-Sudetic Monocline). Profile of Podbrzezie K-6 borehole is characterized by the widespread presence of shales with lots of red spots, where Kupferschiefer is underlain by White Sandstone (Bs) and overlain by Zechstein Limestone (Ca1).

Detailed microscopic examination and observation of shales, in reflected and transmitted light, reveals their fine-crystalline texture and laminated structure. Kupferschiefer consists of dark-coloured and light laminae. The dark laminae are built of clay with carbonate admixtures, whereas light laminae consist mainly of carbonate material. Flat and wavy types of lamination are dominant. In places, significant admixtures of fine-grained quartz, feldspar, and muscovite are observed, which makes up to 5% of the rock. Detrital grains are usually dispersed or arranged in laminae. Locally,

relics of grey, spot-free Kupferschiefer can be observed between the red-spotted laminae.

In red-coloured shales iron oxides are commonly observed in the form of: (1) irregular fine grains, (2) mineral aggregates, (3) hematite pseudomorphs after framboidal pyrite and (4) hematite pigment dispersed throughout the sediments or concentrated in the form of lenses, impregnations of carbonates and earthy masses. Variable concentrations of these components are responsible for the presence of red spots dispersed throughout the rocks. Morphology of red spots and the boundaries of fan-shaped brown streaks are irregular and discordant in relation to the Kupferschiefer lamination.

The oxidized nature of the studied shales are considered to be the result of post-sedimentary diagenesis. Many evidences can be mentioned: considerable amounts of hematite pseudomorphs after early diagenetic pyrite, the presence of coarse-grained hematite of hydrothermal origin, cutting the borders of individual laminae of shale by red spots and brown streaks, hematite intergrowths in carbonate minerals and their replacements by very fine-grained hematite (dusty hematite). Secondary processes contributed to precipitation of iron oxides giving the rock red-coloured parts.

THE UNCONVENTIONAL GASES RESOURCES OF ROMANIA. CASE STUDY: SILURIAN FROM MEOSIAN PLATFORM

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Key words:

Moesian Platform, Palaeozoic formation, shale gas, maturity rock

4

The Palaeozoic formations in Romania attracted lately and in the present a lot of companies interested in unconventional shale gas exploration. These formations are present in several geo-structural units. Among these are: Moesian Platform, Moldavian Platform, Scythian Platform (Barlad Depression).

The Moesian Platform is a major structural unit surrounded to the north and west by the South Carpathians, north-east by the North Dobrogea Orogene and to the south by the Balkans, geological unit which stretches on the both sides of the Danube lower course. Moesian Platform is the one of the most important petroliferous basin of Romania. This major sedimentary basin has all geological conditions for hydrocarbons generation, migration and accumulation. Sedimentary cover consists of the Palaeozoic, Mesozoic, Paleocene-Eocene, Miocene, Pliocene and Quaternary formation and was resulted during four major sedimentary cycles: Upper Cambrian-Carboniferous, Permian-Triassic, Jurassic-Cretaceous and Neozoic.

The first Palaeozoic cycle of sedimentary cover start with the Ordovician and the upper Cambrian (siliciclastic sandstones). Silurian facies is represented, especially in the lower part by the graptolitic shales („shelly fauna” levels = black argillites and neritic sedimentation). In the Upper Silurian these shales are mixed with other sediments (green siltstones, sandstones, marly or sandy argillites, black argillites, quartzitic conglomerates, etc). Only in the East Moesia, the „shelly fauna” level contains graptolites. The Pridoli has been identified in the mixt facies of the graptolite shale facies. The thickness of the Silurian sediments is between 50 and 1200 meters. The Devonian is represented by the basal argillitic facies (Lochkovian-Emsian) and consists of various argillites, argillaceous shales, marly or sandy argillites, dark siltstones with quartzitic sandstones and

conglomerates. The Carboniferous (the lower part) consist of carbonate sediments – limestones and dolomites (the Devonian continuous sedimentation) – named Călărași and Dobromiru Formation while in the upper stage this is represented by the terrigenous deposits of paralic type (Vlașin Formation – dark mudstones, siltstones, sandstones, coal layers). The Permo-Triassic lower interval is represented by the Rosiori Formation (the redish detritic lower formation): shales, ferruginous silts or redish silts, sands, quartzitic sandstones, limy sandstones and microconglomerates interbedded with marls, limestones and dolomites.

In the recent years, the Silurian deposits were reviewed and revised, the biostratigraphical reevaluation being based to the micro and macropalaeontological studies. In the same time, were made the XRD analysis of the samples from the Silurian in the East Moesia which showed the existence of clay minerals who content the rest of the organic material. Also, were made some studies, respectively, technical analyses concerning the basin modeling of the Moesian Platform. These studies have been based to the 1-D modeling numerical tools such as the Genex software at the regional scale. In order to this, using the data from more than 10 wells, were created the diagrams which contain different information concerning the source rocks from the all lithological column of this wells: fluid pressure, porosity vs. depth, temperature, geothermal gradient, vitrinite reflectance, kerogen transformation ratio, Rock-Eval temperature Tmax, Rock-Eval hydrogen index, Rock-Eval S1/TOC, Rock-Eval production index, sedimentation and subsidence rates geohistory, tectonic subsidence geohistory, temperature windows geohistory and maturity windows geohistory.

The geological information helps to calibrate and integration these information on the thermal maturation of hydrocarbon source rocks. In parallel were made the geochemical

MINERALOGY OF SILURIAN SHALES FROM THE LUBLIN BASIN (EASTERN POLAND)

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Key words:

shales, mineralogy, geochemistry, Silurian, Lublin Basin

5

Several hundreds wells targeted for hydrocarbons have been drilled in the Cambrian formations in the East European Craton. They passed through Ordovician and Silurian shales; these, however, are poorly known because of insufficient coring and difficult log interpretation of old wells. Petrophysical anomalies in logs have been interpreted as "strange shales". In the last years, Ordovician and Silurian shales from the western slope of the East European Craton are interpreted as perspective rocks for the presence of shale-gas formations. Therefore, modern mineralogical study of shales is the most important step to recognize their composition, texture and petrophysical properties. The aim of this work was to investigate the mineralogical composition of these shales using X-rays diffraction (XRD) and scanning electron microscopy (SEM) combined with energy-dispersive spectrometer (EDS) analysis.

Samples were taken from boreholes located in the Palaeozoic Lublin Basin (eastern Poland). XRD analysis was performed on powdered specimens using the X'Pert Pro PANalytical diffractometer (CoK radiation). Mineral phases present in a the samples were identified using X'Pert HiScore software combined with the ICDD PDF-2 database. SEM imaging and electron microprobe analysis were performed using a JEOL JSM-6380 LA device. The Rietveld analysis was performed using the FullProf computer software written by Juan Rodriguez-Carvajal.

EDS analysis confirmed the presence of both di- and trioctahedral clay minerals and revealed the chemical composition of carbonates in the investigated samples. Samples from the Lublin Basin were taken only from Silurian rocks. Besides quartz, and illite, samples of Llandovery age contain high amounts of carbonate (calcite and dolomite, sometimes ankerite) and pyrite. In turn, Wenlockian samples contain relatively more clay minerals (mainly trioctahedral illite and chlorites). SEM data revealed that the textures of clay minerals are very strong, especially for illite. The same behaviour of illite was observed in XRD specimens. The experimental pattern showed the best agreement with the calculated pattern when the preferred orientation along the (001) face of clay minerals was incorporated into the refined parameters.

The next step is the correlation of mineralogical data with geochemical, sedimentary and geophysical results. Mineralogical results will be used for the calibration of geophysical data (e.g. clay content and petrophysical properties), interpretation of sedimentary conditions, compaction, burial history and volume of organic matter. Mineralogical results can be very useful for stratigraphic correlation and interpretation of tectonic settings. All these results are very important for modelling the evolution of Silurian sedimentary basins.

PHENYL DERIVATIVES OF PACS IN THE SILURIAN SUCCESSION OF THE BARDZKIE MTS, POLAND

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Key words:

Silurian, phenyl derivatives, maturity

6

Lower Palaeozoic shale succession outcropped in the Żdanów village of the Bardzkie Mountains (Middle Sudetes). Investigations of this section during the 70's allows to divide the informal lithostratigraphic units named as: jodłownik beds, lower and upper graptolitic shales and żdanów shales. The shale sequence in Żdanów included sedimentary rocks from Ordovician to Devonian (e.g. Chorowska & Oberc, 1980, Porębska, 1982), but nowadays only the Silurian black siliceous shales and creamy shales interbedded by lydites are well outcropped. The only more detailed inorganic geochemical investigations were performed by Porębska & Sawłowicz (1997) which concerned mainly Silurian-Devonian boundary. Phenyl (Ph) derivatives of polycyclic aromatic compounds (PACs) were for the first time undoubtedly identified in the Permian Kupferschiefer of the Fore-Sudetic Monocline, Poland and in the Devonian carbonates and shales of the Holy Cross Mountains, Poland (Marynowski et al., 2001, 2002; Rospondek et al., 2009), and it is believed that their origin is connected with hydrothermal organic matter oxidation. Here we are presenting the gas chromatography - mass spectrometry (GC-MS) results, showing the high concentrations of these compounds in the Żdanów section. Analyzed samples characterized by occurrence of all previously described Ph-PAHs, including: phenylnaphthalenes, phenylphenanthrenes, terphenyls, phenyldibenzofurans, phenyldibenzothiophenes and quaterphenyls between which phenylnaphthalenes and phenylphenanthrenes are the most abundant compounds. In all samples the more thermally stable isomers clearly dominating, while that with ortho- and a- configuration are present only as traces or do not occur. It suggests the high maturity of the investigated section, what is additionally confirmed by other molecular and petrographic thermal maturity parameters (Grafka & Marynowski, 2011). Taking into account the general increase of organic matter (OM) maturity towards the younger rocks through the section and high concentration of Ph-PAHs originated from OM oxidation by migrating flu-

ids, we suggests that major factor controlling OM maturation was intensive hydrothermal activity.

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NATURAL FRACTURES IN LOWER JURASSIC BLACK AND GREY SHALE, CLEVELAND BASIN, UK



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Key words:

shale, basin, natural fractures

7

The Toarcian Whitby Mudstone Formation (WMF), Cleveland Basin, UK, comprises 70 m grey and black shales. The mean total organic carbon (TOC) is 3%, locally increasing to nearly 20%. The WMF underwent subsidence during the Mesozoic, reaching the oil window during the Late Cretaceous. It was then cooled and uplifted during Tertiary inversion. Clean coastal exposures make the WMF an excellent natural laboratory to investigate controls on natural fracturing in mature, shale-dominated successions. We have identified 3 distinct structural styles within the WMF. (1) Regularly spaced, sub-vertical extension fractures with large height-spacing ratios and thin calcite infills. These fractures occur away from tectonic faults, but opened parallel to the regional extension direction. We interpret these structures as tensile hydraulic fractures that developed under conditions of low differential stress and vertical maximum principal stress. (2) Regularly spaced arrays of moderately dipping shear fractures and sub-vertical extension fractures that display mutual cross-cutting relationships. These fractures occur in the footwalls of tectonic normal faults and have accommodated

E-directed extension. Sub-vertical fractures contain calcite infills; shear fractures contain brecciated shale, but calcite

is rare. We interpret these structures as shear and tensile hydraulic fractures that developed under conditions of vertical maximum principal stress and fluctuating differential stress and fluid overpressure. (3) Regularly spaced arrays of sub-horizontal and sub-vertical fractures, which contain drusy calcite and bituminous material and are associated tectonic faults that display dip- and strike-parallel slickenlines. Sub-vertical fractures consistently abut sub-horizontal fractures, implying that the maximum principal stress flipped from horizontal to vertical. The most parsimonious explanation is that the fractures developed under conditions of high fluid overpressure and low differential stress at the onset of basin inversion. Poroelastic effects caused the horizontal stress to decrease in proportion to the fluid pressure, allowing reorientation of the stress field. These observations suggest that spatial and temporal variations in fluid overpressure under conditions of low differential stress are the primary controls on the style and orientation of natural fractures in shale-rich basins. Compositional variations (e.g. TOC) appear to have a second-order influence.

INTEGRATED STRATIGRAPHY AND CORRELATION OF THE UPPER SILURIAN PERIPLATFORM SHALE SUCCESSION IN THE MIELNIK IG1 AND GOŁDAP IG1 BOREHOLES (EASTERN POLAND)

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Key words:

spectral gamma ray, magnetic susceptibility, carbon isotope, graptolite stratigraphy, Silurian

8

Expected high shale gas potential of the Polish Silurian basin makes it a subject of interest of petroleum industry. The abundance of graptolites and conodonts in Silurian succession allows for a construction of biostratigraphic framework, however, incompleteness of the drillcore sections and insufficiency of the material may cause a gap in a biostratigraphic scheme. Spectral gamma-ray measurement (SGR), magnetic susceptibility (MS) and carbon isotope analyses are the methods that can be used for improvement of stratigraphical resolution in the basin. Prior to their potential implementation in new drillcore sections, the method has been tested in well dated and easy to correlate, full-cored reference sections.

The Silurian sedimentary rocks covering the south-western margin of the East European Craton in NE Poland represent a periplatform setting of low-latitude carbonate platform.

A long distance (~150 km) SGR-based correlation is presented between the Mielnik IG1 and Gołdap IG 1 mid-Ludfordian

borehole sections of NE Poland. The correlation is controlled biostratigraphically and independently by the mid-Ludfordian Carbon Isotope Excursion as well as magnetic susceptibility data.

In the studied sections, characteristic negative peaks of potassium and thorium, together with high uranium content are coincident with occurrence of high diversified, specialized graptolite assemblages. As these horizons are believed to mark flooding surfaces, they allow for possible correlation of parasequences between the sections. The whole procedure is possible mainly due to synchronous facies changes controlled by sea-level fluctuations and wide facies unification in the offshore setting.

Spectral-gamma ray, magnetic susceptibility and carbon isotope analyses, calibrated with the reference sections, can be used as powerful stratigraphic tools. It is important especially in case of either a lack of graptolite fauna or incompleteness of a drillcore material.

LIPID BIOMARKERS AND D15N AS GEOCHEMICAL TRACERS OF ORGANIC MATTER IN EARLY SILURIAN SILICEOUS SHALES OF POLAND

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Key words:

biomarkers, thermal maturity, nitrogen isotopes, organic matter

9

Silurian siliceous shales and black cherts of Poland are rich in organic matter (OM) with C_{org} values ranging from 0.4% to 8.1% (Bauersachs et al., 2009). Recently, it has been found that Early Silurian shales of Poland may be exploitable as unconventional gas reserves. We examined the OM of Early Silurian siliceous deposits to investigate their origin and thermal maturity (Bauersachs et al., 2009). Samples from the Holy Cross Mts (HCM) and Bardzkie Mts (BM) were analyzed to compare the preservation of lipid biomarkers in variously thermally affected rocks. Despite similarity in microfossil preservation, samples from both regions showed different thermal maturity. The BM cherts exhibited a higher degree of maturity than the HCM cherts, which is expressed in variation in OM coloration in thin sections. Cyanobacteria, radiolaria, algae (acritarchs) and graptolites comprise the main part of the preserved microfossils in the studied cherts and shales (Kremer and Kaźmierczak 2005; Kremer 2006). The $d^{13}C_{org}$ of the bulk OM ranged from -28‰ to -31‰ for the BM cherts and ca.-31‰ for the HCM cherts. Nitrogen isotope values for the BM varied from +0.1‰ to -1.1‰ and were slightly heavier than those for the HCM cherts, ranging from -0.4‰ to -2.2‰. This seems to be in agreement with values observed for biological dinitrogen fixation. The $22S/(22S+22R)$ $17\alpha,21\beta(H)$ -hopane ratio and the $20S/(20S+20R)$ $13\beta,17\alpha(H)$ -diasterane ratio of the HCM cherts were both at equilibrium values, indicating a thermal maturity that equals at least the onset of the oil generation window (MacKenzie et al 1980; Seifert and Moldowan 1980). Maturity indices based on the isomerisation ratio of the C29 regular sterane, i.e., $20S/(20S+20R)$, have

not reached equilibrium and range from 0.48–0.52, indicating a maturity close to the peak stage of oil generation. $Ts/(Ts+Tm)$ ratios varied from 0.6–0.8 and corresponded to the peak level of oil generation, in agreement with the sterane maturity parameter. The OM of the BM has reached a higher degree of maturity than the OM of the HCM, but assessment of the maturity, due to the lack of suitable biomarker maturity parameters, was more difficult. Aliphatic fractions of the extracted OM were dominated by n-alkanes in the range of 15 to 36 carbon atoms exhibiting unimodal distribution with a maximum between C_{17} and C_{19} . The most immature cherts contained hopanoids dominated by 22S-isomers attesting to the relative high maturity of the organic matter. The dominance of hopanoids over steranes and the presence of 7-methyl and 8-methyl alkanes in the HCM are in agreement with the presumed cyanobacterial origin of the organic matter. In contrast, the more mature sediments of the BM did not contain recognizable cyanobacterial biomarkers, which were most likely lost during thermal alteration.

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THE KUPFERSCHIEFER IN THE WARKA IG-1 BOREHOLE, MAZOVIA

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Key words:

The Kupferschiefer, early-diagenetic, sphalerite and galena mineralization, pyrite-marcasite mineralization, dolomitic slate-clay

10

The Warka IG-1 borehole is located 50 km south of Warsaw, near Warka village. The borehole was drilled in 1972 by the Polish Geological Institute during a geological study of central Poland. Preliminary research on the Zechstein cupriferous series was carried out in the 90's. In the borehole the Kupferschiefer was reached at 2428 m depth, and the thickness of the shale was 30 cm, which is the average thickness of the Kupferschiefer in Poland.

The studied Kupferschiefer rocks are black or dark gray, shaly and split readily along close-spaced bedding planes. Microscopic analysis showed the laminar structure of the shale, expressed in the presence of thick (up to 200 micrometers) light carbonate laminae, separated by discrete dark matrix (of variable thickness up to several micrometers), composed of clay minerals and organic matter. The carbonate laminae are strongly disturbed to form wavy and cranky mode of lamination. Sharp-edged quartz and feldspar grains (mainly potassic feldspars) are scattered within the light laminae and dark matrix; muscovite, apatite, rutile, zircon and monazite, the clay minerals; illite and chlorite are minor constituents.

Sulfide minerals occur as finely disseminated grains (up to 2 mm in size) and in the form of thin (up to 3 mm) streaks of sulphides. The sulfide mineralization is dominated by marcasite and pyrite occurring mainly as aggregates of framboids and as single idiomorphic grains. Pyrite with marcasite encrusts fragments of microfauna, mainly crushed clam shells, ostracod and foraminifera (Agathammina). Marcasite is a major component of the sulfide streaks, arranged parallel to the slate shale lamination. In addition, sphalerite, and galena crystals occur as large, irregular particles (commonly to 300 micrometers in diameter). Mutual intergrowths of these minerals and replacements of carbonate material and quartz and feldspar grains, by galena and sphalerite can be observed. In addition, sphalerite

and galena cement brecciated and fractured grains of marcasite and pyrite.

EDS and EPMA analyses showed that the light carbonate laminae are composed predominantly of dolomite with a high content of iron and manganese. Carbonates occasionally contain high values of lead and zinc (wt% Zn up to 1.5% and wt% Pb up to 0.8%). Due to the high content of dolomite, rocks can be classified as dolomitic-clay shale. There are no significant impurities in the iron and lead sulphides. It is notable that sphalerite has a high average content of cadmium 1.2 wt% (ranging up to 8 wt%) and averages about 0.8 wt% iron (up to 2 wt%). Small (up to 1 micrometers) cadmium sulfide inclusions occur within sphalerite crystals (mainly in the marginal zones of sphalerite grains).

The irregular lamination of the shale, the large thickness of carbonate laminae, the strongly disturbed structure of the laminae, and the presence of numerous skeletal grains indicate sedimentation on a shallow shelf. Abundant admixture of fine-grained terrigenous material (quartz, feldspar, and accessory minerals typical of mafic rocks) derived from adjacent East European Craton. Sphalerite and galena replacing carbonates, quartz and feldspar, as well as crack fillings cracks in iron sulphides, should be interpreted as secondary mineralization postdating iron sulphides and superimposed on early-diagenetic pyrite-marcasite composites. The enrichment of dolomite with iron, manganese, lead and zinc can be attributed to the influence of infiltrating metal-bearing fluids during subsequent stages of progressive diagenesis. The strong predominance of iron sulphides over galena and sphalerite and the lack of copper sulphides indicate a significant distance from the feeder areas for the Lower Zechstein copper mineralization.

PERSPECTIVE OF SHALE GAS EXPLORATION IN THE LOWER PALEOZOIC DEPOSITS OF VOLYNO-PODILLYA, UKRAINE

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Key words:

Paleozoic, shale gas, petrophysics, geochemistry

11

Early Paleozoic deposits of the sedimentary basin of the south-western margin of the East-European Platform are being considered presently as one of the most prospective targets for shale gas exploration. In Ukraine these are the marine deep-water sediments of Silurian and Ordovician, which extend in south-eastern direction from the Polish border to Romania. Though from the point of view of general geology these deposits are rather well studied, only few publications consider the problems of localization and criteria of possible shale gas occurrence in them. Therefore, we performed the complex laboratory investigations of the available core material, sampled from the wells which have been drilled for exploration of conventional hydrocarbons, with the purpose of study of their material composition, petrophysical, mineralogical-petrographic and geochemical peculiarities, organic matter content, extent of catagenetic transformation, thermal maturity. In summary the following results have been obtained. The rocks under study are the dark-grey, almost black argillites, horizontally laminated with short micro-fractures, with graptolites, enriched with organic matter. Intercalations of siltstones are present. Mineralogical composition of rocks is rather uni-

form. The light fraction makes 80-100% and is represented by the sericite-clayey paragenesis and quartz (0.5-1.2%). The heavy fraction consists mainly of pyrite (90-100%). SiO₂ content changes from 45 to 60%. The following petrophysical parameters are characteristic for the argillites: open porosity – 0.5-2.5%, the total one – 1-5%. The rocks are practically impermeable, permeability factor is less than 0.001 μm²·10⁻³. The natural radioactivity of rocks changes within 9–18 mCr/hr, apparent electric resistance is 20–150 Ohmm, interval time of longitudinal waves spreading is 126–365 mcs/m. A significant anisotropy of petrophysical parameters is observed. Total organic carbon content is 0.5 to 2.5%. Catagenesis stage is MK3-AK2. Taking into account the above-mentioned data it can be concluded that the main features (depth of occurrence, mineralogical-petrographic and petrophysical properties, organic matter content etc.) of the prospective for shale gas exploration deposits are characteristic for the investigated rocks. However, for the reliable estimate of shale gas prospects at the territory under study it is necessary first of all to drill pilot wells and to perform purposeful investigations of core material.

TEMPESTITES FROM MIDDLE JURASSIC ORE-BEARING CLAYS FROM THE SILESIAN-CRACOW UPLAND



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Key words:

dark grey mudstones, laminated shales, storm deposits, Ore-Bearing Częstochowa Clay Formation, S Poland

12

The Ore-Bearing Częstochowa Clay Formation, known also as the ore-bearing clays, is the Middle Jurassic (upper Bajocian – upper Bathonian) mudstone complex, exposing in several clay pits in the Silesian-Cracow Upland. It was deposited in a marginal part of the shallow epicontinental sea, called Polish Basin, which was the easternmost arm of the Central European Basin System. Ore-bearing clays consist of dark grey, organic-rich, calcareous mudstones and shales with horizons of siderite and calcareous concretions and clayey siderite bands. They are developed as the two varieties: more common bioturbated mudstones and rare laminated shales. Sedimentological analysis, including detailed field examination and thin section analysis of both deposit types, revealed that storms were an important agent influencing their deposition.

Thin silt-rich laminae, up to 25 mm thick, mark deposition in the most distal settings by weak storms. They show structures pointing to deposition from waning suspension flows, including normally graded laminae with sharp bottom and gradational upper contacts, thin graded rhythmites and inversely graded laminae showing transition from the silt-poor

to silt-rich mud, which mark current reworking of bottom sediment. These structures are discernible in thin sections and were commonly observed in laminated shales; in bioturbated mudstones they were obliterated by organic reworking. Strong storms in distal settings led to formation of lenticular silt-sand laminae (up to 12 mm thick) with low-angle and cross lamination, resulting from the traction movement of the coarsest material. These structures are discernible in the outcrop and were observed in both laminated shales and bioturbated mudstones. The lack of wave generated structures and distinct erosional scours suggest that all mentioned above tempestites were deposited below the storm wave base. The strongest storms in more proximal settings led to formation of the thickest tempestite layers, which are up to 6 cm thick. They include horizontally laminated accumulations of fine sand, silt and shell debris (up to several metres extensive) as well as isolated, narrow bottom scours, filled with parallel-laminated sand. Thanks to their thickness they were not obliterated by benthic animals and are well visible even in intensely bioturbated mudstones.

TURBIDITIC SHALES VERSUS HEMIPELAGIC SHALES IN THE MAGURA BEDS OF GLAUCONITIC FACIES (UPPER EOCENE–LOWER OLIGOCENE, POLISH OUTER CARPATHIANS)

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Key words:

shales, turbidites, hemipelagites, flysch Palaeogene, Carpathians

13

The Magura Beds of Glauconitic Facies (MBGF) are a lithostratigraphic unit composed of interbedded sandstones, subordinately conglomerates and different fine-grained deposits commonly called “shales”. This unit occurs in the upper part of the flysch succession in the Siary zone of the Magura Nappe, in the Polish Outer Carpathians. Shales are subordinate to dominant constituents of the MBGF.

Detailed macroscopic examinations of outcropped sections in twelve traverses across the MBGF together with complex laboratory analyses have shown that the unit includes shales of two lithofacies of a basically different origin, i.e. the turbiditic and hemipelagic shales. The turbiditic shales (TS) are greenish-grey and dark-grey to black calcareous mudshales that predominate in the MBGF, whereas the hemipelagic shales (HS) are dark-green, noncalcareous clay shales to mudshales, typically occurring in 1–20 mm thick layers at the top of shale beds, and rarely separate the TS beds.

The TS occur in a few centimetres to several metres thick beds showing sharp or transitional bases and tops and a general fining upward. Transitional top occurs in beds capped with the HS. Some very thick beds display fluctuating sand-size,

detrital quartz content in vertical section. The TS are massive except for basal parts of beds that show wispy to continuous silt or sand laminae, and tops that tend to be bioturbated. The massive shales in thick beds are either free of foraminifera or contain only rare reworked specimens. In contrast, more abundant foraminifera usually occur close to the top of beds capped by the HS. TOC content of 0.11–5.06% and kerogen type III have been recorded in the TS.

The HS typically occur in layers showing sharp upper boundary. They are subtly mottled, show distinct trace fossils and are always much richer in foraminifera than the TS. The foraminiferal assemblages consist almost exclusively of agglutinated taxa characteristic of bathyal depths, below the foraminiferal lysocline. The shales usually show a small admixture (below 1 vol%) of detrital sand-size quartz. Their TOC range from 0.13 to 0.7%. The very thick beds of the TS were deposited by large ponded and deflected turbidity currents. They indicate sedimentation of the MBGF in a confined basin. The HS consist of particles settled from water column and of fossilized biota of autochthonous deep-water benthos, mainly foraminifera.

THE HANGENBERG BLACK SHALE AND OTHER EUXINIC EVENTS THROUGH THE FAMENNIAN SUCCESSION OF THE HOLY CROSS MOUNTAINS, POLAND

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Key words:

Famennian, Hangenberg event, redox conditions, volcanic activity

15

Famennian (Late Devonian) was a time of the world ocean perturbations as exemplified by the occurrence of several global events including the well-known Hangenberg extinction event and the less significant Dasberg and Annulata events (House, 2002). All these events are well-recorded in the form of black, organic-rich shales occurring within the Upper Devonian sequence of the Holy Cross Mountains, Poland (Marynowski & Filipiak, 2007; Marynowski et al., 2010; Racka et al., 2010). Inorganic and organic redox indicators for the all black shale horizons indicate that bottom water redox conditions changed periodically from being mainly anoxic/euxinic to oxic or being partially depleted in oxygen. The Hangenberg black shale (HBS), as an example, is characterized by U/Th values above 1.25, Ni/Co above 7 and V/(V+Ni) above 0.8 in the lower part of the HBS section which all point to anoxic/euxinic conditions, as do high total organic carbon contents (TOC) above 10% and a degree of pyritisation (DOP) values around 0.75%. However, the presence of benthic fauna above the lower part of the HBS indicates opportunistic colonisation of the sea-floor during short-term oxic episodes. Evidence for similar, but much more frequent, oxic episodes has also been recognised in the middle part of the HBS, where the U/Th values are below 1.25, Ni/Co below 4, V/(V+Ni) below 0.8, TOC from 3% to 5.5% and DOP from 0.4% to 0.75%, and the benthic fauna commonly occur. Anoxic conditions returned during the deposition of the upper part of the HBS, though, they were not as well developed as during deposition of the lower part of the HBS. On the other hand, small-sized pyrite framboids and isorenieratane biomarkers in the all analysed black shale samples suggest, that euxinic conditions persisted in the photic zone of the water column. Interestingly, a 20 cm thick layer of volcanogenic deposits (tuffites) is present in the middle part of the HBS, the geochemical characteristics of which are typical for ocean-floor basalts. What is also symptomatic,

samples from the HBS show $\delta^{13}\text{C}_{\text{org}}$ values within the range of -27.6 to -28.8‰ and are depleted in $\delta^{13}\text{C}$ by ca. 3‰ as compared to deposits that both underly and overly the HBS. Taking the all other data into account, a decrease of $\delta^{13}\text{C}_{\text{org}}$ values could be caused by episodes of intense volcanic activity, a concomitant release of CO_2 and an increase of atmospheric $p\text{CO}_2$. The occurrence of volcanogenic material below and within the HBS, together with the absence of calcium carbonate over its upper part, the presence of a bundant tetrads just above the black shale, important decline of $\delta^{13}\text{C}_{\text{org}}$ values and a drastic decrease in faunal frequency in the upper part of the HBS, all these imply that volcanism may have caused oceanic acidification (and/or hypercapnia) that in turn potentially may have influenced the Hangenberg mass extinction event.

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INFLUENCE OF THE INTERLAYER CATIONS HYDRATION ON SMECTITE ELASTIC PROPERTIES BY FIRST PRINCIPLE CALCULATIONS

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Key words:

smectite, clay-rich sediments, elastic constants, water content

16

This contribution looks for analyze and compute the elastic properties, and in consequence infer the sonic velocities, of one of the more abundant clay mineral in shale-rich sediments: smectite. This mineral phase is known to have varying mechanical properties depending on the water content. One of the main goals of our analysis is to calculate the resultant elastic tensor for varying contents of Na, K and water in smectite to compare with the bulk elastic properties measured in laboratory.

We have studied the influence of the hydration of the interlayer cations on the elasticity of Na- and K-smectite models by means of first-principle calculations, within the framework of the Density Functional Theory with the SIESTA3.0 code. Norm-conserving pseudo-potentials and generalized gradient approximation have been used.

Different monocrystal models with increasing H₂O content (up to three molecules per interlayer cation) in the interlayer space were built and the cell parameters and internal geometry were optimized. The elastic stiffness constants (EC) were calculated with the help of the finite-strain method. The stress tensor for the different strains of the unit cell was calculated

by optimizing the internal geometry of the crystal, allowing the determination of the elastic constants tensor via the Hooke equation for anisotropic solids. The crystals were in the setting $x||a, y||b, z||c^*$. Acoustic wave velocities along the different directions of the crystal can be calculated by solving the Christoffel equation, for which a Fortran 90 program was developed.

Results show that hydration of the interlayer cation leads to a decreasing of C_{33} ; a small increase of C_{11} and C_{22} was observed for low hydration. Bulk and shear moduli of the polycrystalline aggregate were estimated from the EC tensor. It is inferred that the Coulomb forces between the cations and the interlayer space weaken with increasing hydration conditions and in consequence, the stiffness along the [001] direction is reduced.

These results can be extrapolated to common geological conditions. The occurrence of oriented smectite with moderate water-content in clay-rich sediments would weaken the sedimentary sequence promoting fractures or flow under relatively low differential stresses.

METHODOLOGY AND FIRST RESULTS OF AN ASSESSMENT OF SHALE GAS RESOURCES IN GERMANY



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Key words:

shale gas, Gas-In-Place, Germany, Lower Carboniferous marine shales, Lower Jurassic Posidonia shale, Lower Cretaceous Wealden formation

17

A general assessment of unconventional hydrocarbon resources in Germany is on its way and we present the methodology and first results of a study on the shale gas potential in Germany.

In this study, three formations are screened with regard to their gas potential. These are the Lower Carboniferous marine shales, the Lower Jurassic Posidonia shale and the Lower Cretaceous Wealden formation. Public domain data and maps are compiled to perform the assessment.

In a first step, the areal extent of the shale formations was determined by using the following screening criteria: TOC > 2%, depth range between 1000 and 5000 m, a minimum thickness of 20 m and a thermal maturity between 1.2 and 3.5% Ro. A volumetric gas-in-place approach was applied to estimate the shale gas potential for each formation. Gas is trapped in shales as free gas within the pore space and also adsorbed by the clay matrix and the organic matter. Thus two separate calculations are needed to estimate the total

quantity of gas in place. The amount of free gas for a given areal extent is determined by the thickness of the strata, the gas-filled porosity and a gas expansion factor. The gas expansion factor is necessary to correct the volume at atmospheric pressure and temperature. In addition the adsorbed gas phase is given by the properties rock volume, rock density and gas content. The Langmuir isotherm is an established method to estimate the adsorption capacity of shales. Several rock characteristics such as porosity or Langmuir parameters are poorly known. Therefore, a Monte-Carlo-Simulation was performed to quantify the uncertainties of the different properties.

The results of the assessment show, that the distribution of potential shale gas units resembles in general the known major hydrocarbon source regions in Germany. Therefore, the highest potential for shale gas prospects is expected in the North German Basin.

NEW PERSPECTIVES OF MICROFOSSIL AND HEAVY MINERALS EXTRACTION FROM THE FINE-GRAINED SEDIMENTS WITH THE USE OF THE LIQUID NITROGEN METHOD [LN₂]



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Key words:

fine-grained rock disintegration, microfossil extraction, heavy minerals extraction, liquid nitrogen method

18

Disintegration of the rock samples is a common procedure prior different kind of analyses carried out for various purposes in geological research e.g. extracting of microfossil, separation of heavy minerals and many other. Different kind of methods are used to decompose the rock to fraction of interest – e.g. for microfossil examination, however, most of commonly used methods are very time consuming limiting their usefulness. Moreover, fine grain sediments are generally very resistant to disintegration by commonly used methods preventing much kind of analyses.

Here we present an extremely cheap, fast, easy, and clean method of rock disintegration, especially for extracting microfossil, from variously lithified rocks with the use of liquid nitrogen [LN₂] (compare Remin et al., 2012). This method markedly limits the time of rock disintegration from days, sometimes weeks, to only minutes. It is safe for at least some kind of microfossil, does not require special chemical labs and gives new perspectives in research of fine grain sediments.

Here [poster] we present the step by step procedure of how to use LN₂ method to disintegrate fine grain sediments such as lower Cambrian, lower Silurian shale and lower Carbonif-

erous mudstone. The LN₂ method allows to decompose that kind of rock to a very fine fraction in time not exceeding one or two hours. Based on previous studies (Remin et al., 2012) we conclude that LN₂ method can be applied for extraction from the fine grain sediments at least some kind of microfossil like acritarchs, ostracodes and possibly conodonts, allowing to reach new biostratigraphic data, as well as extraction of heavy minerals for petrographic and sedimentologic studies (Remin et al., *in prep*).

This simplification in microfossil extraction from the fine grain sediment allows to properly balance the time required for thinking about them during drinking a glass of wine, instead of preparing them.

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LOW-GRADE METAMORPHIC SLATES, A POTENTIAL HOST-ROCK FOR HIGH-LEVEL AND/OR LONG-LIVED RADIOACTIVE WASTE DISPOSAL



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Key words:

geological disposal, slates, radioactive waste

19

Three main types of host rock are currently considered for the geological disposal of high-level and/or long-lived radioactive waste: homogeneous crystalline rocks (e.g. granite, gneiss), salt, bedded or in domes, and argillaceous rocks, from plastic clays to indurated claystones.

We propose to expand the category of argillaceous rocks with low-grade metamorphic slates. To date, this rock type has been considered unqualified as a potential host rock for radioactive waste disposal. Moreover, applying the criteria that are designed for a disposal system relying on the intrinsic properties of the plastic clays and indurated claystones as geological barrier (e.g. self-sealing capacity; hydraulic conductivity), to slates inevitably leads to their exclusion as potential host rock. Pelites – i.e. fine-grained, siliciclastic rocks – represent a wide range of rock types, contrary to other types of potential host rock, such as granite, gneiss, salt or plastic clays. The different types of pelite can be positioned on a near-continuum in between indurated claystones and crystalline schists. Therefore, we define two end-member categories, the shale category and the slate category. The main distinctive criterion is whether or not the concept of a layered geological forma-

tion – i.e. the formation concept – is still applicable. In the case of the slate category, the secondary tectonic fabric – i.e. slaty cleavage – becomes the dominant anisotropy, so that the formation concept fails and needs to be replaced with a domainal concept, very comparable to the approach of crystalline host rocks.

Based on a preliminary survey of the Palaeozoic pelites in the Brabant-Ardenne-Eifel realm in Belgium we demonstrate that pelitic rock bodies that are strongly affected by a tectonometamorphic influence in low-grade greenschist metamorphic conditions, may have a potential as host rock for the disposal of high-level and/or long-lived radioactive waste.

Slate belts are potentially interesting target areas for the geological disposal of radioactive waste, primarily when considering its geological stability and isolation. Slates as a potential host rock need, however, a proper approach with a new set of evaluation criteria, taking into account the particular qualities as a geological barrier (e.g. hydraulic conductivity, sealing capacity). Furthermore, slates need a proper design of the disposal system, rethinking the engineering barrier accordingly.

PERYLENE AS AN INDICATOR OF FOSSIL WOOD DEGRADATION BY WOOD-DEGRADING FUNGI

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Key words:

fossil wood, perylene, Middle Jurassic, biomarkers

20

Perylene is a five-ring aromatic compound identified in recent marine and terrestrial sediments, peats and brown coals, crude oils and sedimentary rocks. The recent investigations of perylene occurrence in Holocene sediments rich in fungi spores and their isotopic relationships implicated that main source of this compound is associated with wood-degrading fungi (Grice et al., 2009). Here we presenting the occurrence of perylene in Middle Jurassic fossil wood from the ore-bearing marine clays of Poland. These wood remains characterized by very low thermal maturity (c.a. 0.3% R_p), excellent preservation of biomarkers and biomolecules as well as generally good preservation of anatomical structure due to early diagenetic mineralization (Marynowski et al., 2007a & 2007b). Moreover, for this study only non weathered wood pieces were selected based on macroscopic observations and a lack of oxidation-indicating goethite mineral (Marynowski et al., 2011). Our investigations of 31 taxonomically defined wood fragments show the negative correlation between perylene concentration and the concentration of typically identified terrestrial biomarkers including: cadalene, dehydroabietane, simonellite and retene. What also interesting the linear correlation ($R^2 = 0.7$) between the ratio of perylene to terrestrial biomarkers listed above and (phenanthrene + fluoranthene + pyrene) to these terrestrial biomarkers is observed. It suggests that the high concentration of perylene in fossil wood indicates its extensive degradation by fungi during decay (mortification),

transportation and early diagenesis. We defined the *fossil wood degradation index*: $WDI = \text{perylene}/(\text{perylene} + \text{cadalene} + \text{retene} + \text{simonellite} + \text{dehydroabietane})$, and obtained wide range of values, from 0.1 for less degraded wood to up to 0.9 for highly degraded examples.

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COMPARISON OF THERMAL MATURITIES FROM LOWER JURASSIC AND LOWER CRETACEOUS SEDIMENTS FROM THE SOUTHERN MARGIN OF THE LOWER SAXONY BASIN, NORTHWEST GERMANY, USING ORGANIC GEOCHEMICAL AND PETROGRAPHICAL METHODS



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Key words:

organic geochemistry, organic petrography, natural gas, shale gas, Lower Saxony Basin

21

The Posidonia Shale (Lower Jurassic) and the organic-rich shales from the German Wealden (Lower Cretaceous) came into consideration as a potential play for unconventional hydrocarbons because of their high amounts of organic material. To determine the thermal maturity of these formations RockEval Pyrolysis and organic petrographical analyses were carried out on 29 outcrop samples. The RockEval Pyrolysis is a bulk rock analysis whereas the petrographical observations refer to single macerals in the sediments. Maturities derived by these two methods could differ significantly and the effects on the estimation of palaeoburial depth and heat flows are shown in this study.

The samples are outcrop samples from the Osnabrück area to the Rehburger saddle at the southern margin of the Lower Saxony Basin, northwest Germany.

The Wealden samples have oil window to wet gas window maturities. The Jurassic sediments experienced higher temperatures and hence they have reached the dry gas window. The different stages of maturation indicate variable heat flow and subsidence histories for this part of the Lower Saxony Basin.

The thermal maturities were also used to estimate the maximum burial depth and the heat flow during that time. Porosity data was used to verify the results and the heat flow estimation.

GLACIO-EUSTATIC AND PALAEOCEANOGRAPHIC IMPLICATIONS OF THE HIRNANTIAN AND RHUDDANIAN SEDIMENTARY RECORD IN THE HOLY CROSS MOUNTAINS (POLAND)

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Key words:

Ordovician, Silurian, chert, mudstone, graptolites

22

The uppermost Ordovician in the Holy Cross Mountains (HCM, SE Poland) is made up of mudstones and sandstones of the Zalesie Formation (~ 4–7 m in thickness), interpreted as regressive deposits related to the early Hirnantian glacio-eustatic event (Trela, 2007). Their deposition was punctuated by reworking and redeposition processes manifested by the textural and compositional immaturity of the sedimentary record. These deposits yielded the Middle Ordovician peri-Gondwanian acritarch species (*Frankea*) occurring within the Hirnantian microphytoplankton community (Trela and Szczepaniak, 2009). It appears to be associated with redeposition of this exotic taxon from the Avalonian terrane that collided with Baltica in the Late Ordovician. This scenario seems to be feasible since during the considered time span the HCM were positioned at the SW margin of Baltica. The overlying black radiolarian cherts and shales of the Bardo Formation yielded graptolites indicative for the Rhuddanian biozones:

- *ascensus - acuminatus* zone identified due to occurrence of *Parakidograptus acuminatus* (Nicholson), preceded by *Akidograptus ascensus* Davies in Bardo Stawy, and accompanied by *Neodiplograptus* and *Normalograptus*.
- *vesiculosus* zone with index taxon of *Cystograptus vesiculosus* (Nicholson) and *Huttagraptus*, *Dimorphograptus*, *Atavograptus*, *Pristiograptus*.
- *cyphus* zone including first occurrence of *Coronograptus cyphus* accompanied by *Huttagraptus*, *Neodiplograptus*.

A favorable combination of factors driving force behind the accumulation of the Rhuddanian organic-rich unit in the HCM

include: 1) a rapid post-glacial sea-level rise initiated in the latest Hirnantian, 2) location in the zone of the SE trade winds, and 3) the presence of palaeohigh in the central part of the HCM. The starvation of coarse-grained siliciclastics during the early Silurian post-glacial flooding provided basis for increased organic carbon burial and related anoxic bottom water. The SE trade winds induced upwelling along the palaeohigh facilitating increase of primary productivity and massive appearance of radiolarians supported by chert unit of the Bardo Formation. These conditions favoured blooms of macroaggregates preserved as laminae or lens-like nodules of whitish chalcedony within the black radiolarian cherts (Kremer, 2005).

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ORGANIC-RICH SHALES OF THE PROTO-SILESIAAN BASIN IN POLISH-CZECH CARPATHIANS



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Key words:

flysch, Carpathians, Protosilesian Basin, organic-rich shales, Jurassic, Cretaceous

23

The Protosilesian Basin was well developed within the Alpine Tethys during the Late Jurassic times and existed as undivided entity until the significant Late Cretaceous reorganization. The deposits originated within this basin were incorporated into different structural units: Silesian, Subsilesian and Skole.

The present authors analysed the possibilities of founding Upper Jurassic-Lower Cretaceous organic-rich shales in the western part of Flysch Carpathians in Poland and Czech Republic. The Upper Jurassic organic-rich Mikulov marls represent world-class source rocks. These 1400 m thick organic-rich rocks with TOC value 0.2–10% sourced oils in the Vienna Basin and Carpathian subthrust in Czech Republic and Austria. The similar source rocks perhaps exist in the deeper subthrust areas in Poland. The shale and marls of Vendryné Formation do not contain significant amount of organic carbon. The organic-rich rocks from Vendryně near koło Trzyniec (Czech Republic) display TOC 0.91–1.04%, from Gomna near Cieszyn 1.43–1.77%, from Nowa Marglownia in Golezów 0.99–1.36%. The increased TOC was encountered within the organic-rich shales of Veřovice Forma-

tion and uppermost part of Hradište Formation. These rocks represent global anoxic event OAE 1b. Veřovice Formation contains potential source rocks for the Outer Carpathians systems with reservoirs various in age. The shales within the Hradište Formation in Moravia (Czech Republic) contain the following TOC amounts: profile Skalice near Frýdek and Ostravice near Frýdlantu 0.6–1.5%, profile Pindula Pass between Frenštátem and Rožnovem under Radhošt Mountaun display 2–2.5%. The organic-rich shales from Rzyki near Andrychow (Poland) display TOC 0.38–3.0%, from Zasań near Myślenice (Poland) 1.56–3.72%, from Veřovice in Moravia (Czech Republic) 0.31–3.66%. Sedimentological development of the Veřovice Formation (Czech Moravia) is presented, according to Early Cretaceous (Valanginian – Albian) geotectonic-eustatic changes in the Protosilesian Basin. Those processes were a consequence of a gradual rebuilding the architecture of the Alpine-Carpathian realm. The geological events well correspond with the global sequence stratigraphy

PETROLEUM POTENTIAL OF KIMMERIDGIAN AND TITHONIAN STRATA OF THE POLISH LOWLANDS AS DETERMINED BY HYDROUS PYROLYSIS



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Key words:

Kimmeridgian, Tithonian, Polish Lowlands, hydrocarbon potential, hydrous pyrolysis

24

Introduction

Kimmeridgian strata are considered as one of the world class source rocks responsible for hydrocarbon generation of large petroleum accumulations in the Norwegian and North Seas (Espitalie et al., 1991). However, exploration of these strata in Poland did not record commercial accumulation of petroleum.

Our present study deals with the preliminary results of qualitative estimation of oil and gas generated from Kimmeridgian and Tithonian strata of the Polish Lowlands based on the results of hydrous pyrolysis (HP) experiments.

Procedures

A total of 148 core samples were analysed: 84 from the Kimmeridgian and 64 from the Tithonian strata. Screening pyrolysis analyses were made on a Rock-Eval II instrument equipped with a TOC module. The kerogen elemental analysis was conducted on Carlo Erba EA1108 analyser. The HP experiments were performed on four samples containing immature organic matter (OM) with TOC values from 4.2 to 9.6 wt%, T_{max} values from 405 to 422°C, hydrogen index (HI) values from 322 to 671 mg HC/g TOC and S/C atomic ratio values from 0.005 to 0.068. The experiments were for 72 hrs and were carried out in 1-liter reactors at 330 and 355°C.

Results and discussion

Rock-Eval pyrolysis gives total organic carbon (TOC) contents from 0.14 to 9.6 wt% in the Kimmeridgian samples and from 0.19 to 12.5 wt% in the Tithonian samples. Gas-prone Type-III kerogen dominates in the Kimmeridgian strata (the median value of HI = 133 mg HC/g TOC), oil-prone Type-II kerogen prevails in the Tithonian strata (median of the HI = 358 mg HC/g TOC). The maturity of organic matter in both rock units ranged from immature through the oil generation.

The quantity of oil and gaseous petroleum generated during HP maturation up to T_{max} values of 446 to 452°C was respectively from 138.6 to 335.7 and from 33.6 to 53.6 mg/g TOC. The Tithonian strata with Type-IIS kerogen yielded the highest amounts of gas and oil.

Conclusions

1-D modelling of the petroleum generation (Więclaw, Kosakowski, 2011) reveal that in selected deeply buried structures of Poland, the Upper Jurassic source rocks reached comparable maturities (0.7–1.0% R_o) to those reached in the HP experiments. Therefore, the amount of generated petroleum during HP with noted corrections (Lewan et al., 2002) may be a first step to calculating oil and gas reserves especially in areas where rapid sealing of Cretaceous strata has occurred.

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COMPARISON OF GEOLOGICAL SETTING OF TWO, SHALE GAS – BEARING, VARISCAN FORELAND BASINS – FORT WORTH BASIN, TEXAS, USA AND SILESIAN BASIN, S POLAND



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Key words:

unconventional hydrocarbons, shale gas, foreland basin, Barnett Shale, Moravice Formation

25

Unconventional hydrocarbon deposits have been known for over one century.

However, their importance had stayed out of focus of interest for many decades due to economic reasons and the lack of appropriate technology developments. The last two decades have been especially important for the comprehension of the unconventional hydrocarbon deposits. The most spectacular and well recognized example of such hydrocarbon deposits are the Mississippian Barnett shales, explored in 2000. The organic-rich Barnett Shale is the primary source rock and the main unconventional reservoir in the Fort Worth Basin, Texas, formed within the Ouachita foreland basin of the Mississippian age. In terms of age, tectono-sedimentary history and geological setting of this basin are very similar to the Upper Silesian foreland basin of the Variscan Orogeny. The Early Carboniferous Moravice formation located in the Silesian Basin

(Moravian-Silesian Fold and Thrust Belt) is the possible source rock in southern Poland and it is the Polish equivalent of the Mississippian Barnett formation. The study concerning similarities and differences between the Moravice Formation and Barnett Formation has been done in order to demonstrate unconventional reservoir potential of the Early Carboniferous deposits of Southern Poland. The comparison of the two formations concerns: depositional environment, tectonic setting, thickness, depth, organic and geochemical properties and thermal maturity. Both formations display similar depositional setting and they are organic matter-rich. The Moravice formation is however penetrated by only a limited number of generally shallow wells in comparison to the Barnett Shale, so this study should bring some prerequisites to other more advanced researches focused on hydrocarbon potential of the Silesian play.