71st Annual Meeting of the International Committee for Coal and Organic Petrology

Book of Abstracts

15-21 September 2019, The Hague

BOOK OF ABSTRACTS

SYMPOSIUM ON ORGANIC PETROLOGY WITH SPECIAL FOCUS ON OIL GENERATION FROM COALS AND CARBONACEOUS SHALES

71st ANNUAL MEETING OF THE INETRNATIONAL COMMITTEE FOR COAL AND ORGANIC PETROLOGY

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Cover image:
Photomicrograph of blue-fluorescing oil inclusions in
Najmah Kerogene Fm., U. Jurassic, Kuwait
Oil immersion, UV light-excitation, width 600 μm.

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ORAL PRESENTATIONS

ICCP INPUT IN THE INTERNATIONAL STANDARDS FOR COAL AND ORGANIC MATTER PETROGRAPHIC ANALYSES

Angeles G. Borrego*

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Anybody having a close look to the ISO standards for Coal petrographic analyses and knowing the analytical procedures described in the ICCP handbook would realize that the ISO 7404 standards for vocabulary, sample preparation, maceral and microlithotype analyses and vitrinite reflectance measurements, are entirely based on the ICCP methods and procedures. The first edition of these ISO standards appeared 1988. Much was due to the effort of the pioneering ICCP members and their positions in their respective institutions as representatives for the elaboration of the ISO standards. Worth to mention are: B. Alpern (CERCHAR,FR), R. Nöel (INCHAR,BE), M.Th. Mackowsky (Bergbau Forschung,DE), H. Smith (NCB, UK), V. Hevia (INCAR,ES), G.H. Cady (ISGS,USA) in the early times, although more ICCP members were participating through the national committees. At that time the ICCP was structured in just two Commissions (i) Terminology and Nomenclature and (ii) Methods of Analysis and therefore the establishment of the definitions and analytical methods were the key issues to prepare the Handbook (1963, 1971, 1975). Similarly the equivalent ASTM standards D2797-99 make use of the ICCP methods. In the successive revision of these methods involving the replacement of the photomultiplier by cameras, the incorporation of automated analysis and new preparation methods, ICCP members (i.e. A.C. Cook, W. Pickel, and D. Pearson) have been very much involved, the position of the ICCP being translated by W. Pickel in the latest revision.

Very relevant is also the contribution of the ICCP concepts to the International Classification of in-Seam Coals (ECE/UN 1998) that for the first time use vitrinite reflectance as the main classification criteria replacing volatile matter yield, widely used in the national classification systems, to establish the classes. To this achievement, the successive chairing position of M.Th. Mackowsky, B. Alpern and M.J. Lemos de Sousa of the UN Genève Committee had a key influence. This was the basis also for the ISO 11760 Classification of coals, whose 1st edition appeared in 2005, contributing to a more widespread utilization of optical methods.

More recently, an ASTM standard for Microscopical Determination of the Reflectance of Vitrinite Dispersed in Sedimentary Rocks (ASTM D7708) whose first version in 2011 has been derived from an ICCP working group lead by P. Hackley has been also produced.

The ICCP has tried for years to simplify the complex classification system of metallurgical coke texture (ASTM D5061) and still it has groups working to this aim and to extending the classification to other carbon forms. Currently also work is being carried out to incorporate coke reflectance in the standard characterization of coke. I would like to thank very specially M.J. Lemos de Sousa who guided me to find the key issues of these memories.

PETROLEUM GENERATION POTENTIAL OF PENNSYLVANIAN COALS AND MARINE SHALES IN THE RUHR BASIN, GERMANY.

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The Variscan foreland basin, which extends from the British Isles in the West to southern Poland in the East is subdivided into a series of sub-basins of which the Ruhr Basin is located north of the Rhenish Massif. The sedimentary fill of the Ruhr Basin consists of a clastic terrigenous succession composed of cyclically deposited mudstones, sandstones, some conglomerates and about 80 major coal seams. The thickness of the Namurian sediments reaches up to 2,000 m, that of the Westphalian more than 3,000 m. There is evidence that Carboniferous coals are oil-prone, based on high concentrations of liquid hydrocarbons present in these coals, pyrolysis-GC studies on coals and selected plant material from Carboniferous deposits and microscopic observation of abundant exsudatinite in coals of about 0.8 to 1.0% vitrinite reflectance (high volatile bituminous A coals). While there is a lack of significant oil accumulations related to Carboniferous coals, there is clear evidence that they act as excellent source rocks for natural gas in northwestern Europe.

Thin marine horizons are rare but allow basin-wide correlations. Most important marine layers are the Sarnsbank Horizon at the Yeadonian/Langsettian boundary, the Katharina Horizon at the Langsettian/Duckmantian boundary, the Domina Horizon of Duckmantian age and the Ägir Horizon at the Duckmantian/Bolsovian boundary. In terms of sequence stratigraphy, these marine horizons are interpreted as marine flooding surfaces. The Katharina Horizon is equivalent to the Clay Cross Marine Band in England, the Quaregnon Horizon in Belgium and the Dunbarella Marine Marker Horizon in Poland. The upper part of the Katharina Horizon is again characterized by a brackish and a non-marine association at the very top.

The average TOC content of the Katharina Horizon shales is around 2% with a maximum of 6.7%. TS reaches up to 4.9%. In the TS vs. TOC diagram, all shale samples plot into the field indicating a marine depositional environment. The pristane/nC_{17} vs. phytane/nC_{18} ratio suggests a reducing environment with input of marine algal matter. This is confirmed by a low TAR ratio caused by a dominance of short chained *n*-alkanes typical for marine organic matter over long-chained *n*-alkanes reflecting land-plant input.

Coal seam Katharina is overlain by this marine horizon. TS values are consistently high throughout the coal seam but reach a maximum in the uppermost part, as it is typical for marine flooded peats. Some samples of seam Katharina are rich in exsudatinite and hence, prove the formation of hydrocarbons. Based on geochemical data, Katharina coal has a much higher hydrocarbon generation potential than the adjacent, marine Katharina horizon. However, expulsion efficiency seems to be low, as indicated by high preserved H/C ratios.

Interestingly, coals preserve much of their hydrocarbon generation potential up to the high-medium bituminous coal stage, i.e. up to stages, when type I and II kerogen-bearing source rocks have already realized most of their petroleum generation potential. Data on Ruhr coal seams and adjacent clastic sedimentary rocks indicate that this applies only to coal seams. Reasons for this strong retention and limited expulsion efficiency are discussed.

TOLUENE-SOLUBLE HYDROCARBONS FROM LIGNITES: AN EXAMPLE FROM THE CENTRAL GERMAN LIGNITE BASIN

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The Central German Lignite Basin hosts lignite seams of Upper Paleocene (Thanetian) to Lower Oligocene (Rupelian) age. These seams consist of different lithotypes, that are differentiated especially by their variable color from whitish to yellow to brown and black. Every lignite lithotype shows characteristic properties regarding macroscopical, microscopical and geochemical features. As a result, the behavior of the different lithotypes during upgrading by the use of hydrogenation or extractive procedures varies considerably.

Knowledge of the causal relationships between organic petrology of the different lignite lithotypes and their conversion properties is of fundamental importance. This helps to understand lignites as valuable raw materials for non-energetically usage (e. g. as basis for the chemical industry). But it provides also basic insights to the differing oil generation potential of humic coals for scientific research: By considering lignites as an early diagenetic stage of carbonification and with this as the first step towards a potentially oil generating bituminous coal, detailed knowledge of the thermochemical behavior of aliphatic hydrocarbons from lignites contributes to improve the understanding of the oil formation process.

To characterize the soluble portion of aliphatic hydrocarbons in lignites, results of a liquid-liquid-extraction are presented. The examined coals were extracted under laboratory conditions for three hours in the Soxhlet extractor by using boiling toluene as organic solvent. Internal analyses show that this toluene-soluble part ("bitumen") consists in general of about 84 % of bituminous waxes, about 13 % of resins and another 3 % of an asphalt-like, dark substance.

It is obvious, that high polymer and figurated liptinites (e. g. cutinite, sporinite and some resinites) are hardly soluble by the applied treatment if at all. Contrary to that, low polymer or highly destroyed liptinitic material (e. g. suberinite, alginite, some resinite and liptodetrinite) is significantly depleted in the residual coal compared to the raw material. Another major portion of the extracted bitumen originates from low condensed, non-gelified humic material (e. g. attrinite or textinite). Correlations between the remission degree, the surface fluorescence intensity and the chemical analyses of the untreated raw coal, the residual coal and the extracted bitumen support these observations.

Further investigations on the chemical composition of the extracted bitumen are expected to reveal a broader understanding of the relations between extracted macerals and the individual material properties. This will be done in the future.

RELATIONSHIP BETWEEN BITUMINITE AND SOLID BITUMEN AND THEIR CORRELATION WITH THE KEROGEN GROUP COMPONENTS

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Bituminite is a maceral from the liptinite group with special importance in marine and lacustrine source rocks, especially when occurring in association with secondary organic components like solid bitumen. This maceral is considered to have its origin on the degradation and microbial alteration of various organic precursors (algae, zoo- and phytoplankton, zoobenthos, bacterial biomass, coccolith organisms, bodies of higher-level animals or algal mats), under anoxic conditions, through the action of bacterial and physiochemical agents. The establishment of a link between the macerals and the kerogen group components has been the focus of many attempts, although with little to no success. Within these premises, the goal of this study is to compare the maceral composition (in reflected light - RWL) with the kerogen organic constituents (transmitted light - TWL) from organic-rich samples with predominance of the bituminite maceral.

For this propose was selected a set of organic-rich samples from the Baños de la Hedionda sedimentary section, positioned in the W. part of the Internal Subbetic, representing a sedimentary record of a deep pelagic plateau located in the most distal part of the South Iberian Paleomargin. The studied samples belong to the Black radiolaritic shales Member of the Capas Blancas Formation (Cenomanian-Turonian, *archaeocretacea* biozone), displaying a total organic carbon content ranging from 6.89 to 31.48 wt.%, and insoluble residue of 86 to 90 wt.%.

Based on the objectives, in whole rock polished section, under RWL and blue incident light, the samples are dominated by bituminite (mean random reflectance 0.29%BR_r), mostly under the form of threads and elongated lenses exhibiting a brown fluorescence, and by great quantities of two qualities of solid bitumen (SB-I and SB-II). The SB-I (mean random reflectance 0.31%SBR_r) is characterized by a brown fluorescence, appearing mostly aligned with the bituminite maceral and presenting fractures. The SB-II displays no/weak fluorescence, appears mostly filling voids within the mineral matrix, and presents a mean random reflectance of 0.43%SBR_r (equivalent vitrinite reflectance 0.67%VR_{eq}). The micrinite maceral is mostly present in layered aggregates. Bacterial material with a strong yellow fluorescence, sporinite and zooclasts were also identified.

Under TWL and incident blue light, the kerogen is dominated by the Amorphous Group. This group is characterized by: (i) bacterial AOM that forms uniform cohesive particles with sharp and distinct (sometimes angular) outlines displaying a strong yellow to light orange fluorescence, being directly correlated with the bacterial material identified in RWL; and, (ii) a more heterogeneous AOM with diffuse outlines, exhibiting a brown fluorescence, that is possibly correlated to the bituminite maceral. It is also possible to identify the presence of zooclasts, sporomorphs and solid bitumen. As described under RWL, two types of solid bitumen were also recognized, through their fluorescence properties, being related to SB-I and SB-II.

In both techniques, it is possible to observe that SB-I presents a close relationship with the bituminite/heterogeneous AOM suggesting a syngenetic formation, while the SB-II may be considered a secondary product.

MULTI-PROXY ASPECTS FOR HYDROCARBON POTENTIAL OF BARREN MEASURES SHALES FROM JHARIA COAL BASIN, INDIA

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The pore structures in the shale matrix are the hydrocarbon trapping site which affects the storage capacity of gas in shale beds as well as production performance. Here, in this study, authors have selected twenty borehole shale samples and have made a multi-approach to estimate their hydrocarbon potential. Rock–Eval pyrolysis, Petrographical studies, Raman spectroscopy were used to characterize the kerogen type, organic matter richness, thermal maturity, the microstructural framework and its transformations with the advancing metamorphic degree of organic matter. The storage mechanism, pore size distribution and surface area were estimated using low pressure N2 gas adsorption analysis. XRD analysis was done in order to identify and quantify different mineral phases and ultimately their controls on the pore size distribution.

The TOC content of 3.87 and 15.99 wt.% with a predominance of type III organic matter suggests a very good to excellent hydrocarbon generation potential in all the samples. The samples consist of vitrinite maceral ranging from 5.41–18.57 vol.%, which may correspond to the lignocellulosic organic matter (type-III kerogen) input from terrestrial plants. The mean random vitrinite reflectance values (MVRo: 0.97–1.27%) indicates the gas generation capability of the shale samples. Moreover, the plot between PI and Tmax also shows the potential for gas generation.

In the Raman spectroscopic study, the lowering of Full Width at the Half Maxima (FWHM) of the D4 band with increasing degree of aromatic condensation 1 (DAC1) may reflect the consequence of hydrocarbon expulsion and subsequent improvement in the microstructural ordering. The plot of the MVRO with the distance between the D1 and G band suggest gas generation from these shales. The multipoint BET surface area of the studied shales varies from 2.93 to 12.87 m2/g. The Barren Measures shales exhibit Type H2 and H3 hysteresis patterns specifying to ink bottle-shaped pores and slit-shaped pores respectively. The slit-shaped pores favour the pore network and are characteristically excellent for the flow of gas. Based on the volume of nitrogen adsorbed, the calculated BJH pore volume was observed to vary between 0.003 and 0.010 cc/g. The surface area showed a significant correlation (R2= 0.81) with the total pore volume. The average pore diameter for the shales ranges from 3.0 to 3.7 nm which indicates the samples are dominantly mesoporous in nature. The presence of higher amount of brittle (quartz, felspar) minerals will lead to better development of natural and induced fractures providing migration pathway and accumulation space for gas.

HYDROZOAN-RICH ORGANIC FACIES FOR PALAEOENVIRONMENT CHARACTERIZATION OF A RECENT COASTAL LAGOON SYSTEM: SALGADA LAGOON, BRAZIL

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Lagoa Salgada is a seasonally brackish to hypersaline coastal lagoon located in Rio de Janeiro State, southern Brazil. This lagoon has its formation linked with the evolution of Coastal Plain of the Paraíba do Sul River Delta and has been influenced by the sea level variations with sediments from different sources. As a consequence of the fluctuations in sea levels, the lagoonal systems presented special features as a mixture of continental and marine waters.

This study aims to characterize the evolution of Lagoa Salgada by the correlation of bottom sediments and organic matter with focus on animal-derived debris (hydrozoans) interactions throughout the last 7000 years BP. In this regard, eight sediment cores were drilled from the bottom with different length. The sediment samples were characterized mainly by coarse and fine sand, sandy mud and mud. The deepest sediment core is of 212 cm and in a previous study a chronological model was constructed resulting in a period between 6.300- and 1.300-years cal. BP. The cores were sampled at intervals of 10 cm, totalizing 96 intervals. They were submitted to the analysis of Total Organic Carbon (TOC) aiming to quantify the OM in the sediments. The same sampling intervals were submitted to chemical isolation of OM. All these 77 intervals were studied by Palynofacies analyses. Geochemical data indicates high heterogeneous content with TOC values varying from 0.04 to 9.45 wt.%. Carbonate content ranges from 3 to 90 wt.%. Both results show an increase in the top area, reaching the highest values in the upper mud.

The kerogen assembly is complex for sand and sandy mud sediments with a high allochthonous contribution. For this reason, the results of 34 intervals were submitted to cluster analysis by applying R-Mode and Q-Mode. In these intervals, it is possible to verify opaque phytoclasts, cuticles, sporomorphs, dinocysts, freshwater microplankton, AOM and highest amounts of hydrozoans. The intervals that register the greatest amounts of marine and fresh water palynomorphs show an increase in the concentration of hydrozoans. Meanwhile an opposite effect is observed where the concentration of phytoclasts rises. Based on the results, it is possible to characterize the evolution of the paleoenvironment of Lagoa Salgada over the 6340 years BP and the relation of hydrozoans with the changes in the set.

USING GEOCHEMISTRY TO SUPPORT A FIRE-ORIGIN FOR THE DOMINANT INERTINITE MACERALS OF A No. 4 SEAM UPPER WITBANK COAL, SOUTH AFRICA

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Coal macerals are formed through multiple pathways. Specifically, macerals of the inertinite group may be formed through: (1) aerial oxidation; (2) fungal degradation; (3) freeze-drying; and (4) charring of plant matter. For inertinite-rich Permian South African coals of the Main Karoo Basin, aerial oxidation has been considered to be the main the pathway responsible for the formation of these macerals. Other authors have proposed charring based primarily on palaeoecological and palynological observations.

To investigate the origin pathway for the inertinite macerals, a coal sample from the No. 4 Seam Upper of the Witbank Coalfield was density-fractionated to create an inertinite-rich and a vitrinite-rich sub-sample. The samples, including the parent, were analyzed using electron spin resonance (ESR), nuclear magnetic resonance (NMR), carbon and nitrogen stable isotopes (δ13C and δ15N), X-ray photoelectron spectroscopy (XPS) for the determination of nitrogen functionalities, and classical coal petrography.

In the parent sample, inertinite macerals constitute 48.5 vol.% (mineral matter-free basis), whereas vitrinite macerals constitute 41.6 vol.%. The density-fractionated samples comprise of 63 vol.% inertinite and 81 vol.% vitrinite corresponding to the inertinite-rich and vitrinite-rich samples, respectively. The dominant inertinite macerals for the inertinite-rich sample are fusinite, semifusinite (reactive and inert), and inertodetrinite.

Based on the ESR analysis, the inertinite-rich sample has a higher radical content than the vitrinite-rich, suggesting that the major components were exposed to high temperatures in their geologic history. The NMR analysis revealed the presence of 6-carbon aromatic clusters in the inertinite-rich sample which correspond to guaiacol and syringol, the main products of low-temperature (below 400 °C) lignin pyrolysis.

The inertinite-rich sample has the lower δ15N value, and higher δ13C value relative to vitrinite-rich. Also, the dominant nitrogen functionalities of the inertinite-rich sample are N-pyrrolic and N-oxide complexes, as opposed to N-quaternary and N-pyridinic in the vitrinite-rich.

This is all interpreted to be consistent with a fire-origin for the dominant inertinite macerals of the inertinite-rich sub-sample; fusinite and semifusinite are thus interpreted to represent products of charring of plant matter. Low-reflecting semifusinite (reactive) is interpreted to reflect moderate charring, whereas the higher reflecting counterpart (inert) reflects more severe charring. Inertodetrinite, being a secondary maceral, is interpreted to reflect charred plant matter that was subsequently disintegrated during transport.

A COMPREHENSIVE UNDERSTANDING OF OM-HOSTED PORES IN TRANSITIONAL SHALE: A CASE STUDY FROM PERMIAN LONGTAN SHALE in SOUTH CHINA THROUGH ORGANIC PETROGRAPHY, GAS ADSORPTION and X-RAY DIFFRACTION ANALYSES

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The transitional (coal-associated coastal swamp) Permian shales are important gas-bearing targets in China. However, the nature and formation of OM-hosted pores in this shale facies has not yet been studied in detail from the perspective of organic petrology and geochemistry. In this paper, we selected typical transitional shale samples from Permian Longtan Formation in the northwestern Guizhou Province (NGP) to specially investigate the development of OM-associated pores mainly through organic petrographic analysis and gas adsorption and X-ray diffraction measurements.

Petrographic observations under optical microscope and scanning electron microscope (SEM) reveal that OM in the Longtan shale is composed predominantly of type III kerogens (vitrinite and inertinite), with minor amounts of amorphous solid bitumen. SEM imaging reveals that the secondary OM pores (as a result of devolatilization of gaseous hydrocarbons) were very rare in Longtan shale, only occasionally observed in individual type III kerogen with bubble-like morphology and extremely low surface porosity less than 1.0%.

On the other hand, the high methane adsorption values and their strong linear correlation with total organic carbon contents in the Longtan shales indicate that the type III kerogens contain numerous SEM-invisible micropores (<2nm). By virtue of the combined N2 and CO2 adsorption on the extracted type III kerogens from bulk shale, we demonstrated the existence of SEM-invisible OM micropores (distributed at 0.34-0.36 nm) and quantified their contribution to the surface area and pore volume of OM, as being of 87% and 13%, respectively. XRD further correlated these micropores to the chemical structure of type III kerogens, i.e., the spacing between aromatic rings. As such, it is the interlayer pores between the aromatic rings that are responsible for the sorptive capacity of type III kerogens and also the bulk Longtan shale.

Considering the fact, that the type III kerogens in shales of different sedimentary facies were all revealed to poorly develop the secondary pores in previous studies, we believe that it is the inert solid body (rather than the previously considered weak hydrocarbon potential) of type III kerogens that lead to the undeveloped secondary pores. That is, type III kerogens cannot generate the devolatilization pores without depolymerization of their macromolecular structure during thermal degradation. Overall, the revelation of OM-hosted pores in the transitional shales provides further understanding of shale gas generation and occurrence in China.

REACTIONS AND STABILIZATION OF ORGANIC NITROGEN MOIETIES AND THEIR INFLUENCE ON δ^{15}N PARAMETER IN COALS

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The coal metamorphism, as it evolves the microstructure of the coals, would also have significant influence on the structural transformations and isotopic discriminations of the primary chemical moieties. The present study aims to illustrate the nitrogen functionalities present within the chemical framework of the bituminous coal samples from the Raniganj and the Jharia Basins and anthracite A samples of the fold-thrust belts of the Sikkim Himalayas as well as to document the metamorphic transformations of these nitrogenous moieties with the advent in the degree of coalification.

The stable carbon (-24.08 to -21.67‰ for bituminous coal samples and -23.91 to -21.39‰ for anthracite A samples) and nitrogen isotopes (1.64 to 2.81‰ for the bituminous coal samples; 1.07 to 3.44‰ for the anthracite A samples) do not show any significant variation with the vitrinite reflectance and, therefore, correspond to the terrestrial higher plant sources of the organic matter. Further, the weak shifts of stable nitrogen isotope values in the anthracite A samples may be attributed to the preservation of the organic nitrogen in the thermally stable aromatic and heterocyclic structures.

The TOC/TN ratio, although representing the vascular plant organic matter input into the mire, in the case of bituminous coal samples (33.49 to 43.69), for the anthracite A samples, shows an unusual enrichment of the total nitrogen, which may be the result of the preservation of the organic nitrogen in the stable chemical framework within the microstructure.

The primary alteration of the labile nitrogen-containing groups including the pyrrolic structures would have been initiated by the aqueous fluid entering into the reactive carbonaceous matrix during metamorphism. During these processes, most of the nitrogen atoms would have been quaternarized, and this has been evidenced by strong correlation ($r = 0.96$) between relative area ratio of the graphitic to pyrrolic nitrogen and the mean random vitrinite reflectance. Moreover, the intensity and relative area ratio of the pyridinic to pyrrolic nitrogen are strongly correlated with the mean random vitrinite reflectance ($r = 0.92$ and 0.89, respectively) suggesting entanglement of the nitrogen atoms within the pyridinic forms as well as with increasing metamorphic temperature. These structural rearrangements might have led to an intensification of the cyclazine structures and preservation of the pyridinic forms in the anthracite A samples. Due to increasing surface hydrophobicity and decreasing interlayer spacing, the fluid would have lost its mobile phase and could not invade the carbonaceous core. Thus, the organic nitrogen was preserved within the thermochemically stable functionalities without showing any substantial isotopic variation.

APPLICATION OF ORGANIC MATTER MICROSCOPY IN ENVIRONMENTAL STUDIES

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In areas of former or ongoing coal mining, stream and lake sediments contain organic matter not only of recent biological origin, but also fossil or anthropogenically emitted material such as coal, char coal and fly ash. In such areas, it is useful to distinguish the biogenic from the anthropogenic origin of the organic matter in the stream sediments. Thus, the main aim of this study is to microscopically characterize organic matter in the assessed stream flow section and to distinguish the prevailing source of organic matter.

Ten coal and six dust samples representing the Bílina open-pit lignite mine and 10 stream sediments from the Bílina River were evaluated. The samples were characterized regarding maceral composition and huminite reflectance. The classification of organic matter used for stream sediments differs from coal and dust. There, organic matter was classified as either recent, fossil or carbonized organic matter. This evaluation method helped to distinguish the prevailing organic matter type and thus determine the river sediment potential to sorb toxic metals. Measurements on dust and stream sediments were carried out statistically by evaluating all particles (huminite, inertinite, recent, fossil and carbonized particles) within the measured area (250x190 µm) of 81 random images, covering the whole area of the polished sections. In addition, organic geochemical analysis was applied contemporarily. All samples were subjected to the determination of total organic carbon (TOC) and total inorganic carbon (TIC). Standard sample preparation (ASE extraction, fractionation, sulfur removal) was followed by GC-MS analyses in order to evaluate the selected set of polyaromatic hydrocarbons.

The results from maceral analysis prove that the dominant maceral groups in coal and dust samples are huminite and liptinite. The dust samples are mostly composed by coaly particles from lignite mining whereas the composition of organic matter in stream sediments is very variable. The upper part of the stream flow section is industrially unaffected with the predominance of the recent organic matter, while the number of particles of the fossil and carbonized character started to increase further downstream.

The random reflectance values of huminite in coal range between 0.29 and 0.34% HR_r corresponding to low-rank lignite that is intensely mined in the study area. The random reflectance of particles in dust and stream sediments range between 0.33 and 1.09% R_r.

Indicative PAH ratios make it possible to distinguish dominant pyrogenic and petrogenic derived organic matter. But when evaluating the maceral composition, it is also possible to distinguish biological and coal-derived material and thus more precisely distinguish potential emission sources in heavily contaminated areas.

ORGANOPETROGRAPHIC ATTRIBUTES FOR CARBON NANO-PRODUCTS FORMATION FROM COAL-A CASE STUDY FROM IB VALLY COAL BASIN, ODISHA, INDIA

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Carbon nanotubes (CNTs) and carbon nanoballs (CNBs) have attracted the attention of scientists, technologists, policy makers, and investors nowadays. Authors have taken ten sub-bituminous to bituminous coal samples from Ib valley coal Basin, Odisha, India to synthesize carbon nanotubes and carbon nanoballs by molten caustic leaching (MCL) process. The vitrinite (Vmmf), liptinite (Lmmf) and inertinite (Immf) content of these coals are placed in the range of 40.50-66.55, 2.05-13.92 and 19.56- 57 vol.%, respectively. The volatile matter (VMdaf), ash yield (Ad) and fixed carbon content (FCdaf) varies from 31.18-47.17, 10.27-39.80 and 46.00- 67.26 wt.%, respectively.

The MCL process preferentially oxidized the aliphatic constituents and functional groups containing heteroatoms in coal to form partially ordered carbon layers; followed by the HCl treatment dissolves the non-catalytic mineral matter and facilitates the partially ordered carbon layers into ordered fullerene and graphene structures (Fig. 1). The presence of carbon nano-particles like hexagonal carbon nano-chunks, carbon nanoballs, worm-shaped and necklace shaped carbon nanotubes in the MCL products has been observed through High-Resolution Transmission Electron Microscopy (HRTEM), X-ray Diffraction (XRD) and Fourier Transform Infrared (FT-IR) spectroscopy analyses. The carbon nanoballs are varied in the range from 52–64 nm and the carbon nanotubes with 7-15 nm in diameter.

Oxygen and hydrogen content present in coal has reduced the carbon nano-products (CNPs) yield. FTIR spectra of MCL products exhibit a peak located around 1190 cm-1 as broad with strong intensity signifying the occurrence of carbon nano-materials. Presence of iron content in mineral matter favors the CNPs yield through the MCL process. The CNPs yield increases with increase in A-factor, index of aliphaticity (IAL) in the coal whereas CNPs yield decreases with rise in index of aromaticity (IAR). Micropetrographic study of coal samples indicates that the carbon nano-products (CNPs) formation is favored with an increase in vitrinite and liptinite and decrease of inertinite contents. The presence of more aliphatic bridges and chains in liptinites and vitrinites increases carbon nano-products yield.

An empirical equation viz. petrographic estimate of CNPs (PEC) is proposed. PEC has a good coefficient of determination (R2=0.96) with CNPs yield and it seems to predict the approximate amount of CNPs yield through the MCL process. The MCL process of coal might be a proficient technique for making of nano-carbon at lower cost instead of applying drastic conventional methods.

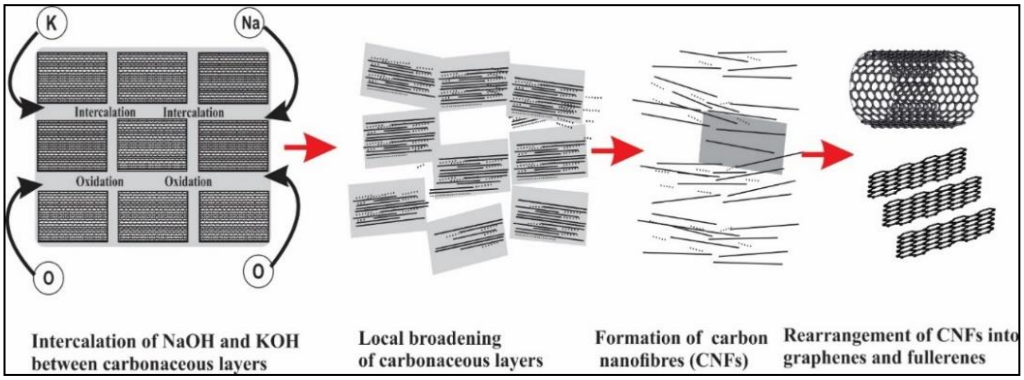

Figure 1: Schematic diagram exhibiting formation of carbon nano-products in MCL process.

LmPy-GCMSMS AS AN ALTERNATIVE METHODOLOGY FOR PROVIDING MOLECULAR DATA OF INDIVIDUAL ORGANIC COMPONENTS IN HETEROGENEOUS MIXTURES: INSTRUMENTAL DEVELOPMENT

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Pyrolysis has been extensively used over the last years as an analytical technique in which large molecules are degraded into smaller volatiles species using only thermal energy. For analytical process improvement, this technique is able to use the chromatographic information to determine the composition or structure of the original sample. GC/MS detection provides molecular analysis of gaseous species and its combination with laser system has relatively derived in a new technique called Laser Micropyrolysis GC/MSMS. LmPy-GCMSMS is a typical hyphenated analytical technique applied using a Pyrolyzer (Laser Source), a Microscope, and a GC/MS system. Among pyrolysis techniques, the LmPy has supplied some success in providing important molecular data on organic fossils such as coals, source rocks, oil shales, etc. Pyrolysis studies of organic mixtures have proven to be an excellent means in which the chemical composition of these heterogeneous materials can be examined.

To any pyrolysis technique, a certain high temperature must be sufficient to break molecule bonds, however a low temperature of degradation is not analytically useful. Consequently, when exposed at very high temperatures the molecule degrades extensively, thus creating very small products. Therefore, the main point in analytical pyrolysis is to select a certain temperature at which a macromolecule can be degraded to produce a wide array of products. In the LaMPy system, the short duration laser beam is collimated by enabling thermal cleavage of isolated components, or a macromolecule, into smaller components with an immense amount of energy. This thermal interaction between laser and material initiates a shock, which in turn produces a range of pyrolysis products that are analyzed by GC/MS. In the LmPy analysis is not possible to control the temperature.

On the other hand, the laser provides a sufficient thermal flux to heat polymeric materials as high as 1000°C/s in a very short time. These extreme heating rates are a characteristic of laser pyrolysis and serve as great purpose in minimizing secondary pyrolysis reactions, thus producing pyrolysis fragments characteristic of original polymers. Consequently, the laser radiation contains high collimated and coherent energy, which can deliver very large amounts of thermal energy on a specific area of small dimension. This means that the directional coherent and monochromatic attributes of high-powered laser irradiation can be focused to pyrolyze very small or small parts of consolidated organic materials, which enables this technique to investigate non-volatile, thermally labile materials at a microscopic level. In other words, the laser beam may affect an area with less than 100 µm using focusing lenses. This allows to individually analyze, in an isolated way, very small components within complex mixtures.

In summary, LmPy-GCMSMS has the potential to improve our understanding of organic composition in heterogeneous materials and isolated organic walled microfossils. In Palynofacies and Organic Facies Laboratory (LAFO-UFRJ - Brazil), the micropyrolysis system refers to a laser and an optical device; a sample chamber and cold trap; and a GC/MSMS to separate and detail the composition of molecular pyrolysis products (i.e. molecular fingerprinting). CSIRO Division of Petroleum Resources (Sydney, Australia) assembled this system exclusively for LAFO/UFRJ with the financial support from PETROBRAS/Brazil and the National Council for Scientific and Technological Development (CNPq-Brazil) supported its development.

WHAT ARE THE EFFECTS OF BROAD ION BEAM MILLING TO SEDIMENTARY ORGANIC MATTER?

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Broad ion beam (BIB) milling is a sample preparation technique widely used in the petroleum industry to enable high resolution scanning electron microscopy (SEM) for imaging of organic nano-porosity in unconventional hydrocarbon reservoirs. However, the recent development and application of BIB milling means that its potential side effects are poorly understood. This includes the possibility that BIB milling creates unintended artifacts, such as the creation of the imaged organic nano-porosity. Our previous work (Valentine et al., 2019, Int. J. Coal Geol. 201:86-10) suggested gentle BIB milling of sedimentary organic matter produced a flattening effect which resulted in increased organic reflectance. Organic reflectance is a well-established proxy for thermal maturation, increasing with thermal advance. However, in our previous work we found no evidence for BIB-induced maturation. Instead, our work suggested increased surface flatness improved specular reflectance and together with decreased diffuse reflectance, resulted in higher reflectance values. To test this hypothesis, we are performing additional experiments to measure reflectance and molecular properties (via Raman and infrared spectroscopies) of organic matter pre- and post-BIB milling.

Four bituminous coal samples with mean vitrinite reflectance (R_o) values from about 1.0 to 1.4% were selected for investigation of BIB milling impacts in the current work. Using a sample map consisting of an image mosaic, R_o measurements determined by ASTM 2798 were collected on 8 individual vitrinite fragments. Four of the same locations were analyzed by Raman spectroscopy and the other 4 locations analyzed by infrared (IR) spectroscopy. Prior to BIB milling, atomic force microscopy (AFM) topography images were collected on 2 of the same vitrinite fragments from which R_o and Raman measurements were collected. Samples were BIB-milled for 5 min, using 4 keV; 15°incline; 360° rotation at 25 rpm; 100% focus (1.5 kV discharge; ~100 µA), then returned to the AFM. Topographic profiles were then collected on the same fields as prior to milling.

Preliminary analysis of AFM topographic data is inconclusive for the flattening effect, where similar, smoother and rougher surfaces were observed post-milling. Instrumental limitations prevent precise measurement of the exact locations pre- and post-milling; however, measurement fields are assumed to be within 10-20 µm of each other and on homogenous vitrinite fragments. We are examining the AFM data to evaluate the impact of measurement location relative to the sample center (milling is best at the sample center) as well as relative hardness of vitrinite (R_o is approximate proxy for hardness, which increases with increasing R_o).

Collection of post-milling IR, Raman and R_o data is ongoing. Based on our prior work and preliminary data, we predict spectroscopic analyses will show no difference in molecular structure and composition after milling, whereas R_o will increase by approximately 20%. The implications of these results to studies which use BIB milling will be evaluated and discussed.

DETERMINATION OF Tmax SUPPRESSION USING ARTIFICIALLY MATURED ORGANIC-RICH, UPPER ORDOVICIAN OUTCROP SAMPLES FROM NORTHEASTERN CANADA

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In this study, artificial thermal maturation via closed hydrous pyrolysis was performed on four organic-rich Upper Ordovician outcrop samples (Red Head Rapids from Northern Ontario and Southampton Island, Amadjuak, and Foster Bay formations from Hudson Bay/Strait and adjacent Foxe Basin) from Northeastern Canada in order to ascertain the true Tmax suppression.

The pyrolyzed and as-received (unextracted and extracted) rock samples were sent for Rock-Eval 6 and the new Hawk/TOC pyrolyses to measure the Tmax and the concentration of other key parameters (i.e. Hydrogen Index, Oxygen Index, Production Index, S1, S2, and S3) in order to determine the amount of Tmax suppression and the possible cause. Outcrop samples and artificial maturation were used to mitigate some of the errors associated with the inherent heterogeneity of geological samples and drilling contamination. Errors associated with both analytical methods were calculated using a large number of Rock-Eval and Hawk/TOC analyses results of standard samples. Additionally, multiple analyses were also performed on selected samples to investigate the possibility of sampling errors.

The results indicate that Tmax suppression does occur, with Hawk/TOC producing a much higher variability (up to 13°C ± 0.24 % margin of errors) than the Rock-Eval 6 (1 to 6°C ± 0.24%) (Fig. 1). The data also show that the high amount extractable organic matter (EOM) retained and adsorbed by the rock matrix during and after oil generation and migration causes significant Tmax suppression. Most notable is the significantly high Tmax suppression in the oil/gas phase of hydrocarbon generation. The overall results indicate that high hydrocarbon potential (i.e., high HI) itself does not cause Tmax suppression but the various extractable hydrocarbon fractions (i.e. heavy oil, soluble solid bitumen) generated during catagenesis. Furthermore, the results also show that both analytical methods are susceptible to EOM saturation resulting in Tmax suppression.

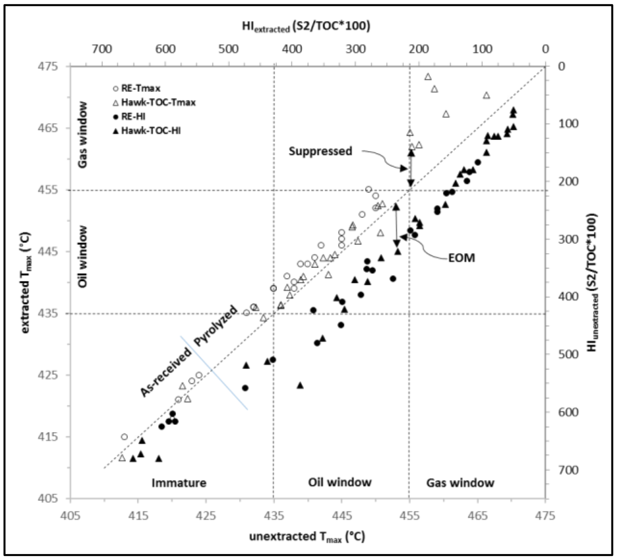

Figure 1. Combined cross plots of Hawk-TOC and Rock-Eval results for T_{max} ($T_{max\ extracted}$ vs $T_{max\ unextracted}$) and Hydrogen Index ($HI_{extracted}$ vs $HI_{unextracted}$ in log scale) before and after organic solvent extraction. The plot suggests that high concentration of convertible hydrocarbon in labile kerogen (S2) does not caused T_{max} suppression but the high amount extractable organic matter (EOM) produced, retained and adsorbed in the rock matrices during hydrocarbon generation and migration. The Hawk/TOC pyrolysis results have a higher variability than the Rock-Eval even with the exclusion of the significant T_{max} suppression in the oil/gas generation window.

POSTER PRESENTATIONS

DEPOSITIONAL PALAEOENVIRONMENT OF SEAMS II & III IN CHOREMI LIGNITE MINE FROM MEGALOPOLIS BASIN (SOUTHERN GREECE)

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The current study aims to determine the organic-petrographic features of Seams II and III in Choremi Lignite Mine, Megalopolis Basin, Southern Greece, in order to assess the coal depositional environment.

One hundred sixty-four samples obtained from organic and inorganic strata at Choremi Mine, were collected by applying channel sampling. Samples were examined by means of proximate and ultimate analyses, gross calorific value determination, coal-petrographical and mineralogical examination and natural radioactivity measurements.

The ash yields range from 4.4 to 74.3% (on dry basis), while the sulphur content is high (up to 8.9%, db). Maceral analysis revealed the predominance of the huminite group (54.7-98.6%), followed by liptinite (<42.4%) and inertinite (<15%), on a mineral matter-free basis. A distinct prevalence is observed either in detrohuminite subgroup (up to 88.6%, mmf) or in telohuminite subgroup (up to 69.7%, mmf), corresponding to changes in the tissue preservation conditions. The huminite reflectance of the examined samples ranges from 0.21 to 0.25%. Quartz, clay minerals, calcite, aragonite, plagioclase and pyrite are the major minerals in the studied samples. The specific activities of ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K display values between 28-558, 3.7-71, 28-402 and 43-828 Bq/kg, respectively.

Frequent lithological alternations at site indicate repeated and sudden changes between limnic and telmatic conditions during peat accumulation, which reflects variations in subsidence rate or/and climatic conditions. Considering the moisture (af) and the gross calorific value (maf), the Choremi coal corresponds to low-rank B and A Lignite. In terms of maturity and along with macroscopic and microscopic features the studied seams include peaty lignite. Macerals from the detrohuminite subgroup (attrinite and densinite) pointing to intense mechanical decomposition of the plant material, mainly derived from herbaceous vegetation. The coal facies data implies that the precursor peat was accumulating in a reed mire, under mesotrophic anoxic conditions, where the water level was high and fluctuating, resulting in high mineral matter influx from the surroundings. The Choremi lignite from Seams II and III is considerably enriched in natural radionuclides in comparison to world coals, but comparable to the lignite from Seam I in Marathousa Mine, pointing out the similarities on the depositional palaeoenvironment of all the seams in Megalopolis Basin.

PRELIMINARY ORGANIC PETROGRAPHICAL STUDY AND THERMAL MATURITY ASSESSMENT OF THE UPPER CRETACEOUS BITUMINOUS LIMESTONE IN VARGIANI SECTION, PARNASSOS-GHIONA UNIT, CENTRAL GREECE

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The Parnassos-Ghiona geotectonic Unit, representing a Mesozoic carbonate platform that occurred between the Pindos Ocean and the Pelagonian Belt, has raised extensive scientific, as well as industrial interest regarding the origin of the hosted, strategic karst-type bauxite deposits. In this platform carbonate sedimentation in a shallow marine palaeoenvironment took place since the Triassic until the Palaeocene, although short-lived episodes of sea regression interrupted the sedimentation processes and led to exposure of the carbonate rocks and to subsequent karstification. Respectively, three main clastic bauxite horizons named b1, b2 and b3 from bottom to top of the sequence were deposited, as an outcome of erosion and transport of the adjacent lateritic material formed in the Pelagonian Belt.

In this sedimentological context bituminous limestone strata have been deposited above the bauxite horizons, and the study of these organic-rich strata, particularly this of Turonian-Senonian age, overlying the b3 bauxite, is the objective of this current research.

In more detail, this study focuses on the systematic organic petrographical characterization, including both maceral analysis and random vitrinite reflectance measurements (Ro%), of the above-mentioned bituminous strata, in order to identify the origin of the organic matter input, as well as the thermal maturation stage. Herein the section V1 near to Vargianni in Parnassos Mt. is presented.

The lithology of the section from bottom to top comprises bauxite b3 layer, being conformably overlain by a 5-10-cm-thick black calcareous shale that turns upwards to dark-grey bituminous limestone.

The total organic carbon (TOC) content of the studied samples ranges up to 1.1 wt.%, whereas maceral analyses show that samples are rich in indigenous vitrinite with an average VRo 1.0%. Additionally, reworked vitrinite fragments with mean VRo 1.3% participate as a secondary, yet significant organic feature. Minor amounts of inertinite fragments and limited fluorescing liptinite macerals, along with non-fluorescing amorphous organic matter are present as well.

The obtained so far results suggest that at least the ending of the lateritic mud deposition occurred in a shallow water-logged palaeoenvironment with significant terrestrial organic matter input, whereas soon it developed to shallow-marine upwards. Furthermore, thermal maturation of the studied strata, as indicated by the Ro% of the indigenous vitrinite population, corresponds to the late catagenesis stage.

GEOCHEMICAL CHARACTERIZATION OF SOURCE ROCKS AND FLUIDS FROM THE TARIJA BASIN, BOLIVIA

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A regional source rock and fluid geochemical evaluation was carried out for the Tarija basin, Bolivia, to determine the spatial and temporal variations in source rock quality, type, and maturity, and to determine the source/sources of the fluids present in producing fields.

At least 4 potential source rock intervals are present in the southern part of the Tarija basin (the Devonian Iquiri, Los Monos and Icla formations, and the Silurian Kirusillas formation), each displaying variable quality, maturity, and hydrocarbon potential. Present-day TOC's range from 0.02-12%, with the majority of samples having <1% TOC. Pyrolysis data indicate mixed Type II-III kerogen in the Iquiri and Los Monos Formations, Type III kerogen in the Icla Formation, and predominantly Type IV kerogen in the Kirusillas Formation. Maceral group composition indicates that the Iquiri and Los Monos Formations are primarily gas-prone (vitrinite-rich) with minor liquid generation potential attributed to terrestrial liptinite originated from spores and leaf skins (sporinite and cutinite, respectively). Kerogen in the Icla Formation is inertinite-rich, and demonstrates little to no hydrocarbon generation potential except for Miraflores-X2, Bermejo-X44 and Palo Marcado-X5 wells, where kerogen becomes rich in oil-prone amorphous organic matter of marine origin. Overall, the maceral assemblages indicate a coastal depositional environment ranging from a fluvial/delta plain setting to a delta top/front system, with distributary channels and interdistributary bays favorable for the local accumulation of sporinite and cutinite macerals (Iquiri and Los Monos Fms). The Icla Fm most likely represents a more distal setting of pro-delta deposits.

GC fingerprints and biomarker ratios for tested fluids are consistent with a deltaic marine environment with significant terrestrial input (e.g. low sterane/hopane, high Pr/Ph). Isotope data for bulk fractions indicates mixing of different maturity liquids from multiple source rocks – lower maturity liquids in the Boomerange Arch sourced from the Lower Devonian/Silurian, and higher maturity liquids in the south sourced from the Middle and Lower Devonian (Los Monos and Icla). The gas in the Margarita and Itau fields is thermogenic in origin (condensate-associated), and is most likely sourced from the Icla Fm. However, the fluids in the AOI show considerable spatial and stratigraphic variability related to maturity variation, charge mixing, biodegradation, and fractionation effects, making correlation challenging.

PETROGRAPHIC STUDY OF A NEW LIGNITE DEPOSIT FROM BILENE (GAZA, MOZAMBIUQUE)

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A Pleistocene coastal lignite was recognized during the geological mapping in the Bilene area and its paleontological content is under investigation within the PaleoMoz Project (www.paleomoz.org). In the Bilene area, three main geological units were identified: Inner Dune system (Units 1A and 1B) formed when sea level was lower than today; Coastal Spits (Units 2A and 2B) that reflect a sea level higher than today's; and, Coastal Bar (Units 3 to 7) indicative of today's sea level but associated to different geomorphological aspects of the coastline and small-scale sea level fluctuations since Late Pleistocene. The lignite outcrops from within these more recent units indicate that its deposition was made in paleolakes/paleolagoons. In this study, the chemical and petrographic compositions of these lignites are reported based on the proximate and ultimate analysis, maceral analysis and huminite reflectance.

The lignite consists of a matrix stratified lignite lithotype. It is a Low Rank C (Lignite C) coal with a huminite reflectance of 0.248% and H/C and O/C atomic ratios within the same range. The proximate and ultimate analysis data show that these lignites have high ash yield (33.9% to 75.0%, d); volatile matter (63.2% to 78.4%, daf), carbon (51.7% to 57.9%, daf), hydrogen (4.7% to 6.3%, daf) and nitrogen (2.2% to 3.2%, daf) contents according to the rank of this coal; and, low total sulphur (0.92% to 2.1%, d). The coal is richer in huminite (86%) than liptinite (10%) and inertinite (4%). Telohuminite subgroup occurs as textinite and ulminite. Textinite cell walls are open or filled with corpohuminite or resinite. Non-lignified tracheids tissues are present. Gelohuminite subgroup appears only as corpohuminite filling suberinite cell cavities and dispersed within attrinite. The detrohuminite subgroup is present essentially as attrinite mixed up with liptinite and inertinite macerals and mineral matter. Liptinite group is represented by cutinite, sporinite, alginite (*Botryococcus* colonies), suberinite, resinite (including fluorinite-type) and, occasionally, chlorophyllinite exhibiting the characteristic blood-red fluorescence. The macerals of the inertinite group are inertodetrinite, fusinite and traces of funginite. The mineral matter includes clay minerals, quartz and framboidal pyrite.

Diessel's and Calder´s petrographic indices and facies and paleoenvironmental diagrams point out to an ecosystem influenced by groundwater level under mesotrophic hydrological conditions. The low inertinite content suggests saturated and humid conditions. The lignite's peat precursor derived mainly from herbaceous plants and *Botryococcus* algae deposited in a topogenous mire (fen) under mesotrophic anoxic conditions.

This work was developed within the PaleoMoz Project (funded by Museu Nacional de Geologia, Programa Aga-Khan/FCT and National Geographic Society Standard Grant CP-109R-17), and co-financed by European Union within FEDER, framed in COMPETE 2020, through the project ICT (UID/GEO/04683/2013) with reference POCI-01-0145-FEDER-007690.

CHARACTERIZATION AND EVALUATION OF BADENIAN SOURCE ROCKS FROM THE CENTRAL – SOUTHERN PART OF THE GETIC DEPRESSION, ROMANIA

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In this study, the rock samples of Badenian age were selected from the center-southern part of the Getic Depression, this area being at the contact between the South Carpathian nappe and the Moesian Platform, Romania. A total of 26 core samples from 10 structures and 17 wells, were analyzed using organic geochemical and petrological methods. The values of total organic carbon (TOC) measurements are from 0.41 wt.% to 1.97 wt.%, the results suggesting a fair to good HC generation potential.

In all samples the presence of terrigenous macerals (vitrinite, sporinite, cutinite, resinite, and inertinite) associated with marine liptinite macerals (alginite as lamalginite and telalginite) is observed. In fluorescent light, the color of liptinite is green-yellow to bright yellow fluorescing (Fig.1). Pyrite is observed as framboidal, and dispersed shapes.

The values of vitrinite reflectance (VRo%) are between 0.42% and 0.55%, and maturity parameters (Tmax) from Rock-Eval pyrolysis are between 409°C - 443°C.

Tmax, values of calculated vitrinite reflectance (VRo%), and thermal alteration index (TAI) show that some of the samples (17) are immature, and another 9 samples are in early maturity part of the oil window. On the pseudo-van Krevelen diagram the analysed rock samples represent mainly Type III kerogen (Fig.2), indicating a gas generative potential.

In some rock samples from the Badenian age vitrinite suppression can be observed, because the Tmax and depth of burial are high, and random reflectance of vitrinite is low. Other factors that influence reduction in reflectance are: high liptinite contents and the frequency of clay minerals in all samples.

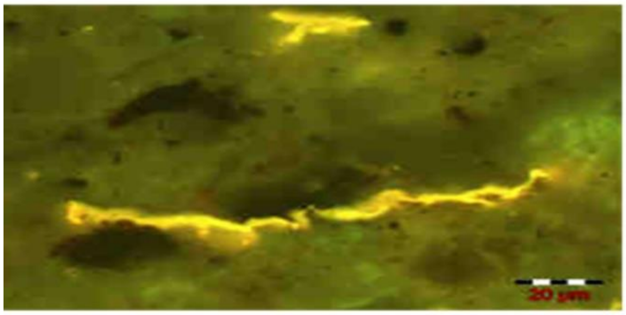

Figure 1. Photomicrograph of Badenian source rock of the Getic Depression, in fluorescent light, oil immersion, X50 objective

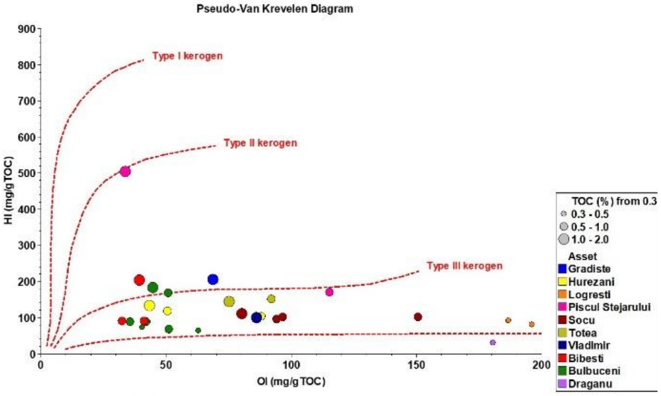

Figure 2. Types of kerogen – pseudo van Krevelen diagram

A STUDY OF SILURIAN GRAPTOLITES FROM DORNES REGION (CENTRAL IBERIAN ZONE, PORTUGAL): THE CONTRIBUTION OF ORGANIC PETROLOGY AND PALYNOFACIES

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Graptolites correspond to marine colonial animals that arose in the Cambrian and persisted until the Carboniferous. Its fossils are important tools in biostratigraphy as well as in organic petrology studies. The aims of this work was to study the organic matter, with focus on graptolites, present in a Silurian sequence from Dornes area (Central Iberian Zone, Portugal) and to determine its thermal maturity, through petrographic studies (both transmitted and reflected white lights). For this purpose, 10 samples of a continuous sequence, that correspond to Foz da Sertã Formation, with thickness approximately 100 m were collected near Dornes village. The Foz da Sertã Fm. includes dark grey mudstones, siltstones and some sandstone layers. The graptolites in this Formation indicate ages between the end of Llandovery to the Wenlock, or even Ludlow (?).

The microscopic analysis shows similar organic content in all samples (graptolites, solid bitumen and amorphous particles).

The observation of the organopalynological slides revealed that the graptolites exhibit a dark color (in transmitted white light) and do not exhibit fluorescence under incident blue light. They showed different shapes, from equant, lath to sharp and appear flattened without specific features on the surface of the particles. In order to improve the graptolite characterization, slides were observed under reflected white light, which revealed distinctive features of the graptolites such as the theca, the theca aperture and the growth lines.

When observed in whole rock blocks and under reflected white light, the graptolites are well preserved, presenting a grey to white color, and are optically anisotropic. The anisotropy increases with the increase of their reflectance. In Foz da Sertã Fm., granular and non-granular graptolites can be distinguished with a dominance of the non-granular. Graptolites can exhibit lath- and blocky-shape, with the characteristic segmented morphology of the graptolite being observed in the lath-shape graptolites together with the theca and thecal apertures. The blocky-shape graptolites present also an important distinctive feature, the fuselar layers of the periderm wall. Graptolites maximum reflectance (lath and blocky) varies from 2.21 to 3.94% and solid bitumen maximum reflectance ranges between 1.09 and 2.22%. Vitrinite equivalent reflectance was calculated using Jacob´s equation (values between 1.97 - 3.72%) pointing out a post-mature stage for the organic matter. No relation has been established with confidence between the reflectance of graptolite and the reflectance of solid bitumen.

The different preparation types and lights used in this study allowed a better characterization of the organic matter present in Foz da Sertã samples, mainly the graptolites. The use of reflected white light, in the palynofacies study, proved to be extremely important in the description of the graptolites features.

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PRELIMINARY ORGANIC PETROGRAPHY OF SHALES FROM ARCHEAN ABITIBI GREENSTONE BELT VOLCANOGENIC MASSIVE SULFIDE (VMS) DEPOSIT, ONTARIO, CANADA

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We present preliminary data, including programmed pyrolysis, correlative light and electron microscopy with energy dispersive spectroscopy (CLEM-EDS) and organic petrography of five black shale samples from the 2.7 Ga Abitibi Greenstone belt in Ontario, Canada. The Abitibi belt is a source of precious metals and serves as an important record of earth's earliest oxygenation events. Much of what we know about when cyanobacteria evolved and how the Earth was first oxygenated is based on the organic and inorganic geochemistry of organic-rich black shale. Though the concentration and isotopic composition of organic matter in black shale is a key variable in these studies, organic petrography generally is not included. Black shale within the Abitibi deposits contain some of the highest total organic carbon (TOC) contents known (up to 17.6 wt.%) in the Archean compared to other locations.

We identified and measured random and maximum reflectance of solid bitumen (SB) sourced from cyanobacteria occurring in Abitibi belt black shale, and evaluated the relationships between SB reflectance, programed pyrolysis data, and mineralogy. Our over-arching goal with this study and subsequent analysis is to apply organic petrography techniques to atypical samples to evaluate potential contributions to precious metals exploration, paleobiology, and to inform Archean petroleum process research.

Preliminary mean SB random reflectance (SBRo, in %) values range from 3.46 to 4.31% SBRo within a 5.5 m (18.2 ft) cored interval, indicative of highly variable, overmature organic matter with high anisotropy. Solid bitumen is abundant, occurring in veins and with intra-matrix, void-filling texture. CLEM-EDS results appear to indicate a positive correlation between SBRo values and clay mineral abundance. For example, SB reflectance was 0.35 to 1.14% higher in mineral-impregnated SB compared to adjacent homogenous SB. However, this preliminary result needs to be substantiated by additional CLEM-EDS and reflectance measurements.

Carbon analyzer results obtained from the five samples indicated a range of 4.87 to 12.01 wt.% TOC. Previous analyses on nearby samples [within 0.15 m (0.5 ft)] using infrared carbon/sulfur analysis ranged from 3.95 to 15.91 wt.% TOC. These results imply that TOC within these samples is highly variable, but still higher than typical deposits of this age. Hydrogen Index values range between 1 and 5 mg HC/g TOC and Production Index values range from 0.23 to 0.50, consistent with the overmature nature of the samples indicated by SB reflectance.

The application of organic petrography in this study highlights potential of this approach to elucidate petroleum processes in Archean black shale. For example, the identification of two separate SB populations (vein and intra-matrix) may indicate two different petroleum charging events, and CLEM-EDS may implicate sub-optical mineral impregnation impacts to SB reflectance measurement and subsequent thermal maturity interpretation. Our future research with Abitibi black shale is intended to lead to better understanding of some of the earliest forms of life on earth, improved interpretations of geochemical data in metal exploration, and expand our understanding of overmature organic matter.

PETROGRAPHIC CHARACTERISTICS AND FACIES INTERPRETATION OF COAL SEAMS 361-510 KWK „MYSŁOWICE-WESOŁA“ (UPPER SILESIA COAL BASIN, POLAND)

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This work is an extensive presentation of the results of petrographic research for the whole profile of coal including seams from 361 to 510, occurring in Upper Silesian Coal Basin. Altogether, the profile includes 11 coal seams. Petrographic analyses such as the quantitative analysis of microlithotypes, macerals and the survey of the studied coal coalification degree have been conducted. For each coal seam, there has been made a detailed macroscopic description including lithology, consisting of emission of coal lithotypes according to criteria proposed by Diessel (1992) and Lipiarski (1975). The currently unstable situation on the fuel market, as well as taking care of the natural environment lead to an increase in the interest in new technologies based on coal use.

The study involves a detailed diagnosis of the coal seams structure and facies research. Coal is a heterogeneous structure, which results from its genesis. The original coal structure has already been shaped at the stage of peat formation. During the process of coalification, it has undergone biochemical and geochemical changes, mainly at increasing pressure and temperature. The most important products possible to be obtained from coal are solar and electrical energy. Since coal consists of components (macerals and minerals) heterogeneous in physical and chemical terms, its usefulness to individual processes is determined mainly by petrographic composition. The macroscopic description itself enables to measure its quality.

A detailed coal seams profiling enables to derive lithotypes and calculate their attendance in the analyzed sections.

The interpretation of deposition environments (facies) of the coal seams 361-510 GZW has been conducted in accordance with the propositions of Donaldson (1969) and Hacquebard (1993). Based on the modified primary method, the interpretation of depositional environment has been conducted, including coal facies on the grounds of three main groups of macerals: vitrinite, inertinite, and liptinite.

The described lithotypes are going to be assigned to a proper area within a paleo-wetland environment in which their plant precursors were probably deposited, which in turn gives information of the genesis of the studied coal from the seams 361-510.

ORGANIC PETROGRAPHICAL AND MINERALOGICAL STUDY OF A META-ANTHRACITE LAYER IN MOLAOI AREA, SOUTH-EASTERN PELOPONNESE, GREECE

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The Phyllite-Quartzite Unit in SE Peloponnese, metamorphosed slightly under greenschist conditions, has been previously reported to host occurrences of Carboniferous-Permian anthracite to meta-anthracite coal. Currently one such outcrop has been discovered approximately 3 km NW of Gkagkania village, Molaoi area, Lakonia Prefecture. The meta-anthracite layer overlays meta-sedimentary strata (sandstone and limestone), whereas it is structurally overlain by the Permo-Triassic volcanosedimentary sequence of the Tyros Beds. This study attempts to define the characteristics of this “meta-coal” occurrence and thus, forms a basis for further research, towards defining the palaeodepositional conditions and geotectonic evolution of the Phyllite-Quartzite Unit.

Channel sampling has been applied to a 5-m-high recent road-cut. Samples were examined by means of proximate and ultimate analyses, as well as organic petrographical and mineralogical studies. The layer proved predominantly corresponding to meta-carbonaceous facies with ash yields 50-71.6 wt.%; only the 1-m-thick, upper part represents meta-coal with ash values up to 37.6 wt.%.

X-Ray diffraction revealed that quartz (up to 68 wt.%) is the predominant mineral for both meta-carbonaceous and anthracite samples, whereas calcite (up to 29 wt.%) and chamosite (up to 16 wt.%) occur subordinately.

Additionally, petrographical examination showed the predominance of vitrinite-group macerals. Random vitrinite reflectance measurements revealed that the meta-coal samples display mean VRo between 4.3 and 4.7%, whereas the meta-carbonaceous samples from 2.5 to 4.8%. The average VRo of 4.5% classifies the studied layer in the borders of ortho- to meta-anthracite.

According to the current study the Gkagkania-Molaoi “coal occurrence” is a low grade, ortho- to meta-anthracite. The analytical results combined with the field lithological relationships point out that there was a period in Carboniferous, where peat-forming conditions were established in the upper part of the sandstone - limestone sequence belonging to the Phyllite-Quartzite Unit. The conditions of organic-matter accumulation were variable providing mostly carbonaceous facies with an accumulating nowadays thickness of ~4 m, whereas telmatic conditions were established towards the upper parts providing ~1m thick anthracite layer. The exact relationship to the Tyros volcanosedimentary sequence, as well as the geodynamic evolution related to the maturation stages are yet to be defined.

THE INFLUENCE OF HIGH-DENSITY POLYETHYLENE ON LIGNITE ORGANIC MATTER DURING PYROLYSIS – INSIGHTS FROM MACERAL AND LIQUID HYDROCARBONS COMPOSITION

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The influence of high-density polyethylene (HDPE) on lignite organic matter (OM) during pyrolysis was studied based on maceral composition of solid pyrolysis products and composition of liquid pyrolysis products, including isotopic carbon signatures ($\delta^{13}C$) of individual hydrocarbons. Pyrolysis of pre-extracted lignite sample (xylite-rich coal, Rr = 0.31±0.03 %), HDPE (plastic bag for food packing), and their mixture (mass ratio 1:1) was performed in the open pyrolysis system under a nitrogen atmosphere for 4 hours, at temperatures 400°C, 450°C and 500°C. This temperature range was chosen according to data from thermogravimetric analysis which indicate that the first significant mass loss (after releasing of moisture) for lignite occurs between 350°C and 500°C, whereas thermal degradation of HDPE starts about 420°C and almost finishes at 500°C. Theoretical and experimental yields of solid, liquid and gaseous products obtained by co-pyrolysis of lignite/HDPE and pyrolysis of lignite at 400°C were almost equal, implying no synergetic effect. On the other hand, co-pyrolysis of lignite/HDPE at 450°C and particularly 500°C resulted in increase of experimental yields of liquid and gaseous products and decrease of experimental yield of solid residue in comparison to the theoretical ones. This result can be attributed to the fact that at 400°C thermal degradation of HDPE almost does not occur.

Petrographic data indicate that at 400°C only the content of liptinite group macerals slightly decreases in solid residue of co-pyrolysate lignite/HDPE in comparison to solid residue of lignite pyrolysis. In solid residue of lignite/HDPE at 450°C the content of liptinite further decreases, which is associated with a decrease in vitrinite content in comparison to solid residue of lignite pyrolysis. At 500°C in addition to liptinite and vitrinite, content of inertinite in solid residue lignite/HDPE is also lower than in solid residue of lignite pyrolysis.

Content of long-chain *n*-alkanes is higher in liquid co-pyrolysis products, lignite/HDPE than in liquid pyrolysates of lignite at 400°C and 450°C, whereas at 500°C, the opposite trend is observed. This suggests that at temperatures below 450°C HDPE is mainly degraded into long-chain hydrocarbons, which is consistent with higher stability of lower molecular units than initial polymer. Vitrinite reflectance increases from 400°C to 500°C. However, at the same temperature no impact of HDPE on Rr is observed. Despite it, liquid co-pyrolysates, lignite/HDPE show higher values of maturity ratios based on methylated naphthalenes, phenanthrenes and chrysenes than liquid pyrolysates of lignite at the same temperature. In accordance with low impact of HDPE at 400°C, depletion in ^{13}C is observed only for long-chain *n*-alkanes in liquid lignite/HDPE product in comparison to those of lignite. At 450°C and 500°C depletion in ^{13}C occurs for full range of *n*-alkanes, as well as for individual aromatic compounds confirming the substantial impact of HDPE on lignite OM during thermal stress.

ORGANIC MATTER PETROGRAPHY AND HYDROCARBON POTENTIAL OF THE PERMIAN DEPOSITS IN THE KOROTAIKHA DEPRESSION, TIMAN-PECHORA BASIN, RUSSIA

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Korotaikha depression is situated in the northeast of the Timan-Pechora Petroleum Basin. Permian deposits form the upper part of the sedimentary section of the depression are available for study in outcrops. The object of our research was the continental sediments of the Lekvorkut Formation of Late Permian age and the Sylov Formation of Middle-Late Permian age from outcrops of the Syryaga and Vorkuta rivers. Organic petrological and organic geochemical analyses were performed on the coal, coaly shale and claystone samples to investigate the source rock characterization and petroleum generation potential. They include total organic carbon (TOC) content, Rock-Eval pyrolysis, bitumen extraction, gas chromatography, maceral composition and vitrinite reflectance measurements.

TOC content varies in the range 37-64% in coals and 0.8-19.7% in coaly shales and claystones. The Sylov Formation samples are characterized by higher S2 and HI values than the Lekvorkut formation samples. The former are in the range of 51-215 mg HC/g rock for S2 and 161-357 mg HC/g TOC for HI, respectively (Fig. 1a) and the latter range between 0.1-5.7 mg HC/g rock for S2 and 7-49 mg HC/g TOC for HI, respectively.

In the studied Permian samples, vitrinite (65-90%) is the most dominant maceral group followed by inertinite (10-35%) and liptinite (5-20%). Vitrodetrinite, telinite, corpogelinite, gelinite and collotelinite are the dominant vitrinite macerals in the analyzed samples. Semifusinite, inertodetrinite and fusinite are the most common inertinite macerals whilst cutinite, sporinite, resinite, liptodetrinite and bituminite are the most common liptinite macerals. These liptinite macerals display distinct fluorescence (Fig. 1b). The studied samples have a similar composition of organic matter, but the Sylov Formation is characterized by an increased content of liptinite macerals (up to 20%) and the structural components of the vitrinite groups and inertinite. The results of petrographic and pyrolysis studies have shown that organic matter in the Sylov Formation is dominated by Type II/III, III kerogen with excellent hydrocarbon generation potential, and the Lekvorkut Formation is represented by Type II/III, III/IV kerogen with low residual generation potential.

The Lekvorkut Formation samples have high thermal maturity with the measured vitrinite reflectance values ranging from 0.75 to 1.0%Ro in the west and 1.75– > 2%Ro in the east of the studied area. The Sylov Formation have vitrinite reflectance values between 0.8–0.85%Ro. This generally corresponds to the peak part of the oil window. It is assumed that the higher S2 and HI values determined in Sylov Formation samples are a function of both elevated liptinite content and lower thermal maturity (rank) compared to those in Lekvorkut Formation.

Permian deposits in the Korotaikha depression are considered as a source of gas hydrocarbons, but elevated liptinite contents (up to 20%), high hydrocarbon yields S2 and HI also suggest their oil generation potential.

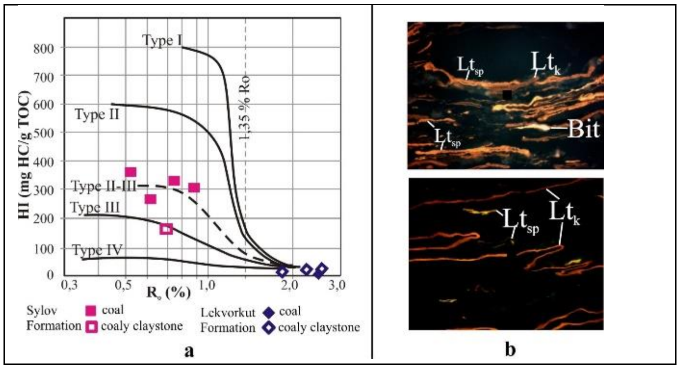

Figure 1. Hydrocarbon potential of organic matter in the Permian deposits. a – distribution of vitrinite reflectance (R$_o$ %) versus hydrogen index (HI); b – photomicrograph of liptinite macerals, UV-light, oil immersion.

ORGANIC PETROLOGY OF BLACK SHALES ASSOCIATED WITH Cu MINERALIZATIONS IN OSSA MORENA ZONE, SOUTH PORTUGAL; THE REGIONAL BACKGROUND

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Black shales (BS) are dark colored mudrocks with variable amounts of organic matter (OM), which accumulate together with silt- to clay-size particles in environments with reducing conditions. The OM present in rocks may have an active role in mineral diagenesis and in mobilization, transport, concentration, reduction, preservation and deposition of metals. The main goal of this work is to characterize the OM present in BS from three different areas that are spatially associated with Cu mineralization in the Ossa Morena Zone (Iberian Variscides), in order to characterize the regional background related with maturation of organic particles during the Variscan orogeny. The BS samples were collected in Alandroal (near the Moviços and Ferrarias occurrences) and Barrancos (near the Minancos ancient mine) districts, which belong to the Sousel-Barrancos metallogenic belt. These three occurrences correspond to Cu mineralized veins, which result from hydrothermal fluids circulation during late Variscan times. The mineralized veins contain quartz, carbonates and sulfides, and cross-cut Paleozoic metasedimentary sequences, namely the Ordovician-Devonian succession. In these occurrences, supergenic enrichments are common.

A total of ten samples of BS were collected in outcrops of Silurian BS from “Xistos com Nódulos” Formation in both districts, all of them near the previous mentioned occurrences, although not or slightly affected by the main mineralized structure. The petrographic analyses to identify and characterize the OM were performed on whole-rock polished blocks prepared under standard procedures. The random reflectance, an indicator of thermal maturation that can be useful to establish the paragenetic sequences of ore deposits, was also measured according to standard procedures.

The petrographic observations allowed the identification of vitrinite-like OM particles in all samples. The organic particles are generally thin and elongated, occurring, essentially, interbedded along mineral matter. The inorganic matter is mainly composed by clays and silicate minerals. The presence of iron oxides and carbonates was also identified occurring in association with OM. The mean random reflectance of vitrinite-like particles from Alandroal varies between 2.93% and 3.86% and between 3.34% and 3.38%, respectively near the Moviços and Ferrarias occurrences, and between 2.05% and 5.05% in Barrancos. The petrographic observations revealed some organic particles exhibiting single flakes graphitic features. In addition, some organic particles observed mainly in Barrancos, appear to be remains of zooclasts, such as graptolites. The occurrence of graptolites in the Silurian “Xistos com Nódulos” Formation is described in the literature. These reflectance values should be representative of the regional background related with the regional metamorphic events. However, previous studies about other Cu mineralization in Sousel-Barrancos metallogenic zone indicated that higher reflectance values are obtained closer to the mineralized veins, as a result of thermal processes associated with the genesis of the mineralization and circulation of hydrothermal fluids.

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PETROGRAPHIC AND GEOCHEMICAL CHARACTERIZATION OF A TRIASSIC-SINEMURIAN SEQUENCE (ALCOBAÇA BOREHOLE, PORTUGAL)

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Alcobaça-1 (ALC-1) borehole, drilled in the onshore of the Lusitanian Basin (Portugal), cut a Triassic - Jurassic sedimentary sequence (3240 m depth). This basin developed over 135 million years ago in the western Iberian margin during one of the fragmentation processes of Pangaea which led to the opening of the North Atlantic Ocean, in the Mesozoic. It is characterized as a distensive basin with continental margin and non-volcanic Atlantic rift type.

The aim of this study is to characterize the dispersed organic matter identified in ALC-1 samples from the Triassic to Sinemurian “Grés de Silves” Group, and Dagorda and Coimbra Formations, using organic geochemistry (total organic carbon - TOC, total sulfur - TS, and insoluble residue - IR) and organic petrology techniques, with special focus on the Coimbra Formation. This Formation (Sinemurian) corresponds to the first carbonated sediments (dolomite and limestone with some OM-rich levels) deposited in the Lusitanian Basin.

The geochemical analysis shows that the TOC content is generally low, varying between 0.12 and 0.78%, with the Silves Group presenting the lowest values (mean value 0.17%). TS ranges from 0.01 and 7.94%, with the Dagorda Formation showing the highest values related to the evaporitic character of this formation. IR shows the carbonate character of the samples from the Dagorda and Coimbra Formations (IR ≤ 50%) and a pelitic character in the Silves Group (IR between 59 and 82%).

In general, the studied samples present organic matter from the three maceral groups (inertinite, vitrinite and liptinite), and also zooclasts (hydrozoan) and secondary products (solid bitumen). In the Coimbra Formation, inertinite and liptinite predominate indicate a type II/III kerogen. Some particles of inertinite appear to result of a natural pyrolysis (charcoal). Regarding the liptinite group, it was possible to observe alginite, bituminite and sporinite, which have a fluorescence color ranging from yellow to orange brown. Vitrinite is scarce, in Coimbra Formation, and generally is small in size, showing reflectance values of, approximately, 0.6%, indicating an early mature stage for the organic matter. Finally, three families of solid bitumen were observed, that have different optical characteristics. According to Jacob's classification, these bitumen correspond to grahamite (≈0.6% Rr), epi-impsonite (≈1% Rr) and meso-impsonite (1.7-3% Rr). The presence of several families of solid bitumen is common in this Basin, having already been reported by several authors. Equivalent vitrinite values, calculated using the Jacob’s formula, seem to indicate that the bitumens present in this Formation are allochthonous.

Further studies on vitrinite and solid bitumen reflectance of the remaining formations will provide a better knowledge of the sedimentary sequence cut by the ALC-1 borehole.

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PETROGRAPHIC ALTERATIONS OF SELF-HEATED CARBONIFEROUS COALS IN WESTERN PART OF PAMIR-ALY (TAJIKISTAN)

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Tajikistan is one of the many countries in the world where self-heating of coals takes place. The process involves Carboniferous coking coals that are currently exploited in open pit mines. This self-heating phenomenon reported to happen in the “burning mountain” and known from ancient times had never been a subject of any major research.

The aim of the preliminary study was to investigate the influence of coal fires on rocks and overlying soils in the region of Takfon, the Fan-Yagnob Valley (Pamir-Aly, Tajikistan) using petrographic and geochemical methods. For that purpose six samples of rocks and three samples of soils from the currently heated places were collected. Total organic carbon (TOC) content was measured using Eltra CS-500 IR-analyser. The samples were grinded to fraction < 1 mm and polished blocks were prepared. Microscopic composition and random reflectance measurements were carried out using Zeiss Axioplan2 reflected-light optical microscope with magnification 500×. The reflectance was measured in 14-100 points depending on the amount of particles suitable for these measurements.

TOC content for three measured samples was in the range from 40 to 54 wt.%, suggesting that soils were highly contaminated by coal. The amount of organic matter present in the samples during petrographic observations differed greatly and was in the range 1-98%. Two samples contained completely altered minerals. In the remaining samples organic matter was the dominating component. It was represented mostly by vitrinite (usually collotelinite, collodetrinite and vitrodetrinite) and inertinite (mostly fusinite, semifusinite, inertodetrinite, and macrinite). Liptinite was rare and represented by sporinite, liptodetrinite, resinite, and cutinite. Three of the samples contained commonly cracked organic particles. Very often the cracks were perpendicular to the external edge of the particle and also to larger cracks that were occurring in the whole particle. Darker in colour oxidation rims were seen together with some cracks. The random reflectance of the altered samples was 0.89-0.92%.

One sample differed from the others as it was unaltered and dominated by clay minerals among which sporinite, cutinite, resinite, and liptodetrinite occurred. The random reflectance of this sample was also the lowest (0.73%).

The presence of cracks and oxidation rims together with the absence of any signs of plasticity indicate low heating rate taking place over limited time. High TOC content suggests the presence of very thin soil strongly contaminated by underlying organic rich rocks.

COMBINATION OF OPTICAL MICROSCOPY AND MICRO-RAMAN SPECTROSCOPY TO STUDY THE CHARACTERISTICS OF MACERALS IN COAL

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The study of coal macerals is being made through the years for nearly one century always with renewed interest and discussion along with new findings and the evolution of the analytical techniques. One of these cases led to the abandon of the term sclerotinite and its division in secretinite and funginite. Although, this division helped to clarify the differences between these two macerals there are now inertinite materials classified as secretinite whose origin is not clear, which eventually could be separated from secretinite based on their reflectance, relief and absence of typical secretinite peculiarities.

The present work focuses on the oil-immersion reflected light microscopy and micro-Raman spectroscopy study of inertinite macerals fusinite, secretinite, and discrete structureless bodies of seven Medium rank C coal samples. The combination of both techniques provides petrographic and dynamic vibrational structure characteristics that allow a more precise distinction of the inertinite macerals studied. Therefore, the petrographic analysis consisted of characterization of shape, color and reflectance measurements, including the measurement of the apparent maximum and minimum reflectance to calculate the Reflectance Indicating Surfaces (RIS), whereas the Raman parameters were calculated from the bands appearing in the spectra.

The petrographic analysis shows that there is a set of discrete structureless bodies with reflectance ranging from semifusinite to 2 R_r% without relief, rims and notches and kerfs. The RIS and the Raman parameters of these materials are different from secretinite and similar to fusinite.

MICROSTRUCTURAL STUDY OF COALS AND NATURAL COKE FROM THE PEÑARROYA-BELMEZ-ESPIEL BASIN (SPAIN)

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Penãrroya-Belmez-Espiel Basin (S Spain) is a narrow tectonic depression parallel to the Precambrian and lower to middle Paleozoic structures of the Central Iberian and the Ossa-Morena tectonostratigraphic zones. It is an intramontane basin filled with late Langsettian and early Duckmantian sedimentary sequence interbedded with coal-bearing units. Two main successive depocentres, which are expanded from NW to SE, were recognized. The early depocentre I (S. Rafael, Santa Rosa, Mellizo, Pardo, Maria and Cervantes Units) was tectonically deformed before the development of depocentre II (Aurora and Cabeza de Vaca Units). This structural pattern is consistent with coal rank and the presence of natural cokes occurring in the depocentre I and is interpreted as the result of continued syn-sedimentary movements on a major strike-slip fault that controlled the SW margin of the basin. The rank of the coals ranges from bituminous coals (depocentre II) to anthracites (depocentre I). The coalification until the anthracites rank was conditioned by fluid circulation from magmatic activity. Natural cokes resulted from the contact metamorphism induced in coals by the emplacement of a doleritic sill. The present study is focused on the microstructural characterization, using Raman spectroscopy, of three samples representative of bituminous and anthracite coals, and a natural coke.

The bituminous coal (Cabeza de Vaca Unit) has a vitrinite random reflectance 0.69% and the following maceral composition: vitrinite 97%, inertinite 1% and liptinite 2%. The anthracite sample (S. Rafael Unit) displays a vitrinite random reflectance of 2.49%, a vitrinite content of 84% and 16% of inertinite. The natural coke exhibits circular and elliptical devolatilization pores, sometimes aligned and folded, is isotropic or, occasionally, presents an incipient anisotropy to fine mosaic texture. The maximum reflectance of the isotropic particles is 6.39%.

The Raman spectral features of the bituminous and anthracite coals show the graphite G band and defect bands D1, D3, D2, linked to the disorder of the material. In the Raman spectrum of the natural coke, D2 band is absent. The G band FWHM shows similar values for the anthracite and coke samples and higher for the bituminous coal, showing that the anthracite and coke have a more ordered structure than the bituminous coals. The anthracite sample displays a lower D1 band intensity than the bituminous coal, with the coke sample presenting the highest value confirming a disordered structure. Thus, considering the G and D1 bands, anthracite presents high structural order but the G band FWHM indicates a more ordered structure for the coke and anthracite.

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PETROGRAPHIC IDENTIFICATION OF CHAR MORPHOTYPES IN COMBUSTION WASTE PRODUCTS OF DIFFERENT ORIGIN

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The aim of the study is to identify morphostructural differences between organic carbon (CHAR) found in two types of combustion waste products: (I) bottom ash sampled from a coal power plant within the CHARPHYTE project (ERA-MIN2015 Joint Call) and (II) poultry litter ashes collected within the DEASPHOR (ERA-MIN2017 Joint Call) project.

The research methods here presented are based exclusively on microscopic analysis. Sample preparation was performed according to ISO 7404-2 (2009) and qualitative analysis according to ISO 7404-3 (2009).

For the classification of char particles the following parameters were used: optical texture (isotropic/ anisotropic), character (burned /unburned).

Analysis of the microstructure and texture of the bottom ash samples highlights (Tab. 1 and Fig. 1): structural similarity and changes which occur during the combustion of coal; identification of the coal type or component of the mixture, which did not burn efficiently; identification and evaluation of structural changes of organic matter in coal during the two phases of combustion: "fast pyrolysis" with the formation of pores that is found in CHAR and "gasification" of CHAR in the presence of oxygen. CHAR which is already converted into a form of carbon in the phase to be subjected to the graphitization process could play a key role as a natural graphite material replacement. Analysis of the residual carbon of biomass origin is easily observed in air pre-combusted aviary samples waste (Fig. 2). The aspect is well defined with how burning is less advanced. Being an aviary litter bed of wheat straw, it is observed that after cellulose incineration char can be detected easily through its porous appearance. As the combustion advancing, degassing pores of the carbon matrix increase by burning.

The morphological identification of residual carbon in the form of partially burnt or unburnt carbon provides important information on its origin (coal and biomass) and details of the combustion parameters of the installation and combustion optimization through thermodynamic parameters. The information brought by petrographic analysis can also facilitate finding ways of reusing/recycling the residual carbon (char), regardless of origin as precursors of synthetic graphite (CHARPHYTE project) or as reducing agent in metallurgical processes (DEASPHOR project).

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Table 1. Petrographic assessment of residual carbon in four bottom ash samples.

Optical aspect	**1**	**2**	**3**	**4**
Weakly degassed char particles	12.8	13.1	13.8	14.2
Degassed char particles	30.0	30.8	31.2	31.3
Combustible components	42.8	43.9	45.0	45.5
Mineral mass/slag	20.0	20.3	19.7	18.6
Minerals in different burning stages	37.2	35.8	35.2	35.9
Non-combustible components	57.2	56.1	55.0	54.5

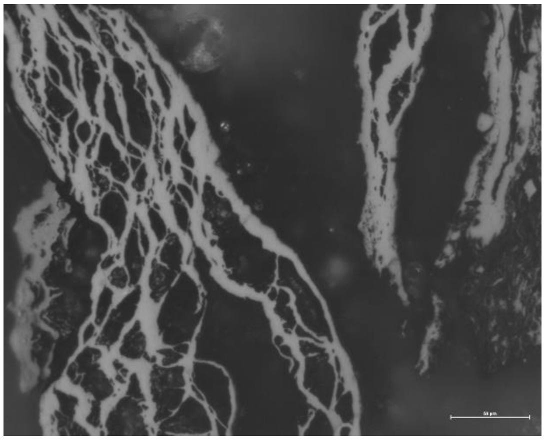

Figure 1. Photomicrographs of degassed char particle in bottom ash, RL, imm., 350x.

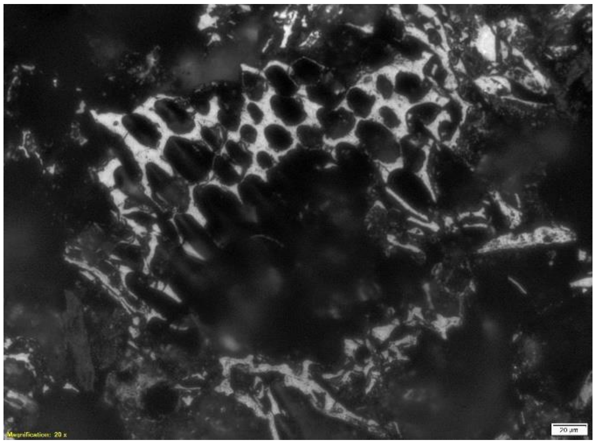

Figure 2. Biomass char particle partially burned in poultry litter ash wastes RL, imm., 500x.

EPIGENETIC PROCESSES AFFECTING THE COALIFICATION IN SANTA SUSANA BASIN, PORTUGAL

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The Santa Susana Basin (SSB) is a Pennsylvanian continental basin, extending over 15 km in a NNW-SSE direction and is up to 1 km wide. The genesis of the SSB was controlled by the NNW-SSE to N-S Santa Susana Shear Zone which separates two tectonostratigraphic zones of the Iberian Massif (the South Portuguese Zone and the Ossa-Morena Zone). Three main outcrops are found in the SSB, from N to S: Jongeis, Remeiras and Vale de Figueira. Previous studies revealed significant petrographic, mineralogical and geochemical dissimilarities between the Jongeis and Vale de Figueira sectors. The main goal of this study is to understand the differences between these two sectors and identify the processes that explain those dissimilarities. The methodologies used for the petrographic and mineralogical study of coal samples included optical microscopy and scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX). The SEM-EDX analyses were used to identify the mineral phases.

The petrographic observations revealed that the organic matter of coal from SSB is mainly composed of vitrinite, by lesser amounts of inertinite and rare liptinite. The organic particles occur isolated or interbedded with mineral matter. However, some hand specimens of coal samples from Jongeis exhibit carbonate veins. Indeed, the coal mass is interwoven with a strong network of epigenetic carbonate veinlets of varying thicknesses and lengths, which are absent in samples from Vale de Figueira sector. The analysis of coal samples from Jongeis sector revealed: slightly higher vitrinite reflectance than the samples from Vale de Figueira, carbonate veins disrupting the coal layers and crushed pieces of vitrinite and inertinite particles agglomerated by carbonates. Besides this, the samples from Jongeis also present high concentration of Ca, Mg and Mn, comparatively with the samples from Vale de Figueira, which seems to be related with the presence of the carbonates. The SEM-EDX analysis demonstrated that the carbonates in samples from the Jongeis sector are dolomite ($CaMg(CO_3)_2$) and ankerite ($Ca(Fe^{2+,}Mg, Mn^{2+})(CO_3)_2$), which is also in accordance with the enrichment in Ca, Mg and Mn in the Jongeis samples. In addition to syn-depositional occurrences, secondary or epigenetic carbonate minerals may also occur in coals as cleat, pore or fracture fillings, precipitated from fluids that permeated through the coal after burial and rank evolution. The reflectance higher than the average and the crushed vitrinite and inertinite particles agglomerated by carbonate s are typical of low thermal and oxidative alteration of coal and also the effect of microtectonic events. These processes are probably of hydrothermal origin and are generated by the thermally driven circulation of fluids. In SSB, the carbonates could result by the hydrothermal activity along the Santa Susana shear zone either associated with the shear zone activity or related with the post-tectonic events taking advantage of previous anisotropies. Therefore, the slightly higher rank of the coals and the occurrence of epigenetic carbonates in samples from Jongeis are attributed to post-depositional processes that included carbonate fluid circulation along the shear zone.

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COAL MINE DRAINAGE IN AN ABANDONED COAL MINE IN DOURO COALFIELD (PORTUGAL)

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The past coal mining activities in Douro Coalfield (NW Portugal) were developed in two principal mining areas, namely São Pedro da Cova and Pejão. The São Pedro da Cova abandoned coal mine operated for almost 200 years and the environmental legacy left by mining operations include negative impacts, among others, on water resources, affecting biodiversity and human health. The São Pedro da Cova mine is located near a population centre and social infrastructures, and it is surrounded by agricultural fields. Besides the leaching occurring in the São Pedro da Cova self-burning coal waste pile that may affect the soils, surface and ground waters. The water circulating inside the underground structures is being drained outside of the mine into a natural water stream.

This study presents the hydrogeochemical characterization of the São Pedro da Cova mine effluents through the analysis of water samples (with and without influence of mine drainage). The concentration of major ions, heavy metals and the priority polycyclic aromatic hydrocarbons (PAH) were determined. The chemical composition of the water drained from inside the mine were compared with the chemical composition of leaches produced through leaching test with the coal waste pile material.

The results indicate that the drainage waters present neutral to almost neutral pH, high electrical conductivity and high concentration of metals, with Al, Fe, As, Mn, and Ni having concentrations higher than values admitted for human consumption. The mine drainage waters present SO_4-Mg facies. The high concentration of metals and the hydrogeochemical facies of these effluents confirm the contamination of streams by mine effluents. Considering organic compounds, some priority PAH were detected in the drainage waters, with high percentage of low molecular weight PAH relatively to high molecular weight PAH, which is common for PAH with petrogenic source. This means that the PAH in the mine effluents result from water circulation through coaly materials inside the underground mining infrastructures. The impact of the use of this water for agricultural irrigation is insufficiently known, and the effect on human health should be investigated.

The water leachable fraction of the São Pedro da Cova mining residues presents higher leachable percentages of Ca, Cd, Co, Mg, Mn, Na, Ni, S, and Zn, indicating that these elements are partly associated with water soluble compounds, and that they are the most easily leached and accessible for percolation and mobilization. These elements were also detected in drainage waters, with some of them with high concentrations, such as the case of Mn and Ni that were found with values higher than those referred in the legislation for human consumption. The results demonstrate that the chemical composition of mine drainage waters discharged into a natural water stream reflects and is affected by the composition of the geological materials through which it percolates, mobilizing heavy metals and PAH to natural systems.

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ASSESSMENT OF THE POTENTIAL FOR EXTRACTION OF REE FROM FLY ASHES AND BOTTOM ASHES DERIVED FROM COMMERCIAL COALS BURNED IN A PORTUGUESE POWER PLANT

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In 2010 an announced China's trade restrictions on rare-earth elements (REE) lead to a price spike in mid-2011. However, the expected widespread shortage of REE did not occur because companies stockpiled REE and alternative materials decreased the use of REE. However, the dependency of the United States of America (USA) and the European Union (EU) became clear. Thus, recycling REE from secondary sources, such as coal ash, was seen as an alternative to primary sources.

In U.S.A., EU and China, studies are focused in coals and respective ashes when there is an indicator of high-REE concentration. However, commercially available coals are ash- and S-poor, which indicates low REE amounts. Nevertheless, the high-amount of coals being burned is a factor to consider.

Therefore, commercial coals burned in Portugal, and respective fly ash (FA) and bottom ash (BA) were studied to characterize their REE plus Yttrium (REY) distribution within time and location in order to determine their potential as raw materials for REY extraction.

Samples of Colombian coal, FA and BA were collected approx. every three months during a year in different locations at Pego power plant (Portugal) and analysed via proximate analysis (moisture, ash and volatile matter), XRF and ICP-MS for major oxides and trace elements, respectively.

Compared to the World Coal Clarke (WCC; REY = 68 ppm) the REY content of the coal samples studied is low (19 ppm in average). Except for Y in one coal sample, the REE elements are depleted in the coal samples analyzed relatively to the WCC, with concentration coefficients <0.5. The REY elements have a significant correlation with the ash yield ($r_{ash} > 0.5$) indicating that are mostly associated with the inorganic matter.

The coal ashes, FA and BA, have higher REY content than the respective coal, 211 ppm in average, and are mainly enriched in heavy REY ($La_N/Lu_N < 1$) in comparison to the Upper Continental Crust. The variation over time of the average REY content ranges between 191 and 227 ppm. Concerning the sampling locations, the lowest REY content was found in the economizer FA whereas the highest in the FA from the 2nd or 3rd row of the electrostatic precipitator (ESP). Regarding the REY content of the ESP FA, two different variation patterns were found: (1) 1st row < 2nd row < 3rd row; and (2) 1st row < 3rd row < 2nd row. Probably due to different temperature conditions, the ratio light REY/heavy REY is also different on the two ESP sides: in one side increases from the 1st to the 3rd row whereas on the other side the reverse occurs.

The outlook coefficient (C_{outl}=((Nd+Eu+Tb+Dy+Er+Y]/ΣREY)/((Ce+Ho+Tm+Yb+Lu)/ΣREY)) versus the critical REY (Y+Nd+Eu+Tb+Dy+Er) percentage in the total REY indicates that all the FA and BA studied are promising raw materials for REY extraction. Further work will be made with the aim to isolate a REY-rich fraction from the coal ashes.

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UV-VISIBLE AND FLUORESCENCE SPECTROSCOPIC STUDY OF SOLVENT-EXTRACTS OF COAL: MACROMOLECULAR INVESTIGATION BASED ON POLYCYCLIC AROMATIC HYDROCARBONS

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Coal has a complex macromolecular network consisting of aromatic-hydroaromatic clusters linked by flexible aliphatic, sulfidic and etheric bridges, and is the most difficult to determine. Compositional makeup as well as the rank of a coal has got tremendous significance in determining the quality of coal for specific applications towards sustainable future. UV-visible absorption and fluorescence (steady-state and synchronous) spectroscopy have the ability to serve as very powerful methods for investigating classes of polycyclic aromatic hydrocarbons (PAH) with fused aromatic ring (FAR) structures present in coal. In the present study, solvent-extracts of coals of different ranks (lignite, sub-bituminous and bituminous) from different coalfields of India were investigated using UV-visible absorption and fluorescence spectroscopy. One solvent extraction involved a mixture of Benzene, Methanol and n-Hexane in the ratio of 3.5:1.5:5 respectively (henceforth BMHx), while the other extraction involved the highly polar chloroform. UV-visible absorption spectra indicate the presence of only carbonyl compounds and n to π* transition in case of the BMHx-extract of lignite, while the chloroform-extract of lignite shows additional presence of alkanes and alkynes with π to π* transition. Solvent (chloroform) extracts of the bituminous samples show the presence of carbonyl compounds with n to π* transition only but sub-bituminous coal-extracts of the same solvent show no such prominent absorption peak like bituminous coal other than the presence of asphaltene and metal porphyrins at 402 and 412 nm, respectively. The lignite samples extracted with chloroform show emission ranging from 420 nm to 700 nm, indicating the presence of 4 and 5 FAR structures while BMHx-extract for the same shows a slightly broader emission (from 320 to 1000 nm) with the presence of wide range (4-10) of FAR structures. The bituminous and sub-bituminous extracts in chloroform have emission ranging from 400 nm to 750 nm, indicating the presence of comparatively smaller (4-6) FAR structures. Distinct peaks in synchronous fluorescence spectra (SFS) of solvent extracts clearly distinguish among the FAR present in the solvent extract portion of different types of coal. The distinct nature of the emissions might be due to the presence of different FAR structure in the extracts, the nature of the solvent used as well as the presence of different soluble FAR in different ranks of coal. The population distribution of smaller and larger fused aromatic ring (FAR) structures present in the solvent-extracts of coal of different rank in this study can lead to understand the innate macromolecular structure with increase in thermal maturity and rank.

PETROGRAPHICAL AND ORGANIC GEOCHEMICAL STUDY OF THE SUBBITUMINOUS COAL FROM THE DUBRAVA FIELD, ALEKSINAC BASIN (SERBIA)

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The Lower Miocene subbituminous coal from the Dubrava field (Aleksinac Basin, Serbia) is studied. Samples were collected from a single borehole, representing different parts of the Main coal seam and coal layers within and under lower oil shale package. Since vitrinite reflectance (%Rr, 0.44 ± 0.03 - 0.46 ± 0.02) and biomarker compositions indicate the same maturity stage of organic matter (OM), corresponding to late diagenesis and early catagenesis, petrographic data, biomarker proxies and stable carbon isotope ratios ($\delta^{13}C$) of individual biomarkers were used to evaluate the origin and depositional environment of OM.

The content of vitrinite group macerals increases from top to bottom of the Main coal seam which is associated with a notable decrease of liptinite and mineral matter (MM). Contents of collotelinite, collodetrinite and corpogelinite increase downward through the Main seam, whereas content of vitrodetrinite shows the opposite trend.

Non-hopanoid triterpenoids and hopanoids are the most abundant hydrocarbons in extractable OM of samples from the Main coal seam. This implies prevalence of angiosperm derived precursor OM, and pronounced microbial activity during diagenesis. Conifer diterpenoids are also present. The ratio of diterpenoids to the sum of diterpenoids and non-hopanoid triterpenoids notably decreases downward through the seam indicating lower conifer input. Typical feature of coal is high content of fernene derivatives, which decreases through the seam. The stable carbon isotopic composition of fernene derivatives implies that they mostly originate from ferns, whereas $\delta^{13}C$ values of the most abundant hopanoids, belonging to 13(18)-neohopene series, suggest in addition to ferns, contribution of chemoautotrophic bacteria.

Content of total *n*-alkanes increases through the seam, which is associated with notable decrease of content of short-chain (C_{15}-C_{20}) and increase of long-chain (C_{26}-C_{33}) homologues. The obtained results suggest lowering of the water table during the formation of the Main coal seam. This change resulted in lesser inundation and deposition of MM associated with smaller input of bacterial and algal OM and higher contribution of angiosperm vegetation. Very similar characteristics are observed for samples in coal layer, located within the lower oil shale package, suggesting the cyclic repetition of environmental conditions. The deepest coal layer, located under the lower oil shale package, contains higher amount of MM, associated with high amount of pyrite. Biomarker composition is relatively similar to that of samples from deeper parts of the Main coal seam and coal layer located within the lower oil shale package, however with slightly higher input of gymnosperm vegetation and hopanoids.

It is noteworthy to mention that compounds with lanosta(eupha)-hexaene skeleton are identified in all samples in relatively high content. Their $\delta^{13}C$ values in range from -28 to -29 ‰ and same concentration trends as observed for non-hopanoid triterpenoids imply angiosperm origin.

BITUMENS (ANTHRAXOLITE) FROM VRCHLABÍ – KRKONOŠE PIEDMONT BASIN, CZECH REPUBLIC

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Investigation of changes in the structure and properties of organic matter in uraniferous rock is an interesting topic, mainly in geological, nuclear and environmental research focused on radioactive materials and wastes. Petrographic, geochemical and mineralogical research (Czech Science Foundation project 19-05360S) was focused on a reference sample of black shale and bitumen from Permian rocks at Vrchlabí in Krkonoše Piedmont Basin (Czech Republic).

The reference sample was formed by laminated black shale with dispersed, mainly liptinite macerals, particularly alginite, bituminite and liptodetrinite, inertinite macerals and rare vitrinite macerals with random reflectance 0.75%. The quartz veins in the black shales were filled up with the brown bitumen of yellow fluorescence colour, with reflectance of up to 0.20%. The pure bitumen which formed part of hard, black lustrous anthraxolite in black shales cross-cut with quartz veins Rudnik Horizon at Vrchlabí contained dispersed mixture of large inclusions and fine micron-scale mineral inclusions, mainly uranium minerals. Rounded or lobate shape of uraniferous bitumen and the isotopic composition of carbon ($\delta^{13}C$= -24.1 to -25.2) indicate their multi-stage formation and coalescence from originally liquid or semi-liquid products of oil migration in an advanced stage of the uraniferous host rock black shales. The content of uranium was up to 3 wt.%. Reflectance of isotropic radioactive bitumen varied between 0.50% and 4.20%, contrary to the reflectance of bitumen without radioactive minerals lower than 0.40%.

Chemically, anthraxolite was composed of extractable solid bitumen and a non-soluble residue of kerogen type. Generally, the extractable fraction was low (0.03-3.45 wt.%) and reversely proportional to the uranium content in the samples. Also, the high uranium concentrations accompanied by decrease in hydrogen and oxygen contents, increase in carbon content, and decrease of H/C and O/C atomic ratios. This is a result of total increase in aromaticity and degree of condensation indicated by the content of only alkanes with unimodal distribution of n-C_{16-28} and with traces of acyclic isoprenoid compounds pristane and phytane, as was found by GC/MS extract analysis. Py-GC/MS method was also used and the pyrolysis required a high temperature of 800°C to break the highly condensed matter. Low molecular weight aromatic compounds, namely toluene and alkylbenzenes, together with alkanes and alkenes were identified.

CHARACTERISTICS OF DISPERSED ORGANIC MATTER OF THE MENILITE BEDS (CARPATHIAN Mts., SE POLAND)

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The Menilite Beds were first described by Glocker in Moravia in 1843. Since then, they have become the subject of intensive research, most times focused on various geochemical aspects. Their high organic matter content and wide distribution within the Carpathian area are the reasons why they play a key role in analyzing petroleum systems of this region. However, geochemical interpretations are not complete unless they are supplemented with optical characteristics of dispersed organic matter. Unfortunately, petrography of organic matter in the case of the Menilite Beds is often either completely marginalized or limited only to vitrinite reflectance measurements. Therefore, publications where the results of microscopic investigations of organic matter are presented are rather rare. This work is focused on microscopic characterization of organic matter, while the results of geochemical analyzes (Rock-Eval pyrolysis) are used here only to make it more complete. The aim is to present the maceral composition of the Menilite Beds within the eastern part of Carpathian Mts (SE Poland).

Samples representing Menilite Beds were collected from 29 outcrops from Skole, Silesian and Dukla Units. The total number of investigated samples was 131. The collected rocks represented a variety of the lithological types - mainly various shale types (clay, marly or carbonate) and in smaller quantities mudstones, siltstones, sandstones and sporadically cherts and micrite limestones. Organic matter most often occurs in the form of elongated laminae or fine, dispersed fragments with a slight elongation in the studied rocks. The content of organic matter (determined on the basis of Rock-Eval pyrolysis results - TOC parameter) ranges from 0.17% to 13.29% (average 3.53%). In its composition, macerals from vitrinite, liptinite and inertinite groups are observed. Macerals of the liptinite group (alginite, bituminite and liptodetrinite) are dominating, while macerals of the vitrinite group (collotelinite and vitrodetrinite) were less often observed. Macerals of the inertinite group (fusinite, semifusinite, inertodetrinite) are usually limited to single occurrences within the entire investigated sample area. Apart from macerals mentioned, fish remains and solid bitumen can also be observed. On the basis of alginite and bituminite content, several types of maceral associations can be distinguished.

Investigated organic matter is most times immature as evidenced by vitrinite reflectance <0.5% and Tmax <435°C. Only small areas of Fore-Dukla Zone and Świątkowa Tectonic Window show higher degree of thermal alternation (oil window). Most of the samples represent type II, II/III and III of kerogen. Organic matter of the Menilite Beds, in terms of its composition and maturity, shows no major regional changes and is rather uniformed within the whole investigated area.