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PALYNOFACIES AND TOTAL ORGANIC CARBON CONTENT FROM THE BAIA BOREHOLE (MOLDAVIAN PLATFORM)

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Abstract

The studied borehole is located near the city of Fălticeni, in the western part of the Moldavian Platform. The lithology consists of sands/sandstone, claystone and shale. In the present study, for the interpretation of the palynofacies, 16 samples from the Baia borehole, collected at depths between 290 and 1050 m, have been analyzed. For the analysis of the Total Organic Carbon (TOC), 10 samples were prepared and analyzed. For most of the samples, the results for the hydrocarbon potential vary from fair to good. In order to establish the type of kerogen, 4 samples were studied and the H/C and O/C ratios were calculated and plotted in a van Krevelen diagram. The type of kerogen resulted is III. The samples analyzed for the study of the palynofacies mostly belong to field III, according to the Tyson (1995) diagram. This field is characterized by a predominance of phytoclasts, which indicate a fluvial-deltaic source where the palynomorphs are fairly preserved. Amorphous Organic Matter (AOM) is present in low percentage. The color of the sporomorphs in fluorescent light is yellow, which corresponds to a $\lambda \approx 580$ nm wavelength. The same color was noticed for the AOM studied in fluorescent light.

Keywords: Baia locality, Moldavian Platform, palynofacies, kerogen, TOC.

Geological settings

The studied area is located in the Moldavian Platform, which represents the western part of the East European Platform. The Moldavian Platform is composed of a crystalline

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basement and a sedimentary cover. The deposits identified belong to the third stage of sedimentation, ranging between the Upper Badenian and the Maeotian (Ionesi, 1994).

The samples analyzed in the present study are from the Baia borehole, which is located near the city of Fălticeni, in the western part of the Moldavian Platform (fig. 1).

Method

The analyses for Total Organic Carbon (TOC), H, N, S, and O were performed using a EuroEa 3000 EuroVector elemental analyzer. The TOC content is used as an indicator of the potential of hydrocarbon source rocks. Depending on its values, the genetic potential of the source rocks can be established, being estimated between poor and excellent (Peters and Cassa, 1994). The samples analyzed were prepared in the laboratory through two methods:

- the first method consisted of crushing the samples to a particle diameter of 0.1-0.3 mm. Subsequently, they were treated with HCl 2N for 24 hours to remove the carbonates. The remaining material was then washed with distilled water in order to remove any acid and later dried in an oven at 50°C. The resulting samples were afterwards used for TOC analyses.

- a second method aimed at the extraction of the kerogen from the rock and the quantification of C_{org}, H and O. Afterwards, the H/C and O/C ratios were calculated and the results were projected in a van Krevelen diagram in order to identify the type of the kerogen from the analyzed samples.

The extraction of the kerogen from rock was described by Durand and Nicaise (1980; modified by Vandenbroucke 2003; Vandenbroucke and Largeau, 2007). The separation of the kerogen from the mineral fraction is performed using a series of chemical reagents, trying to preserve as much of the original chemical composition of the organic matter as possible. The samples were crushed to a particle size of about 0.1 mm, and then treated with an organic solvent (dichloromethane - DCM) in order to remove the soluble fraction (the bitumen) from the rock. The carbonates and silicates were destroyed through a solution of HCl 6N + HF 40% (1/3-2/3 v/v). The isolation of the kerogen from the minerals undestroyed by the acid attack was carried out through centrifugation in heavy liquid ($ZnCl_2$ with a density of 2). The kerogen extract was then washed with distilled water and treated again with dichloromethane. The kerogen thus obtained was afterwards used in elementary analyses for C, H, O, N and S.

For palynofacies analysis, samples consisting of 50 g of rock were used. These samples were first treated with HCl (37%) in order to remove the carbonates, and then with HF (48%) so as to destroy the silicates. The separation of organic matter was achieved through centrifugation in heavy liquid ($ZnCl_2$ with a density of 2).

The optical study of the organic matter was carried out using a Leica DM1000 microscope with transmitted light (Osram 30W bulb type), and the reflected blue light (fluorescence) with a HBO 50W mercury lamp. The rank of fluorescence of palynomorphs (Robert, 1985) and the Thermal Alteration Index (TAI – Pearson, 1984) were used so as to determine the degree of maturation of the organic matter. As the degree of maturation increases, palynomorphs show a green to bright yellow (equivalent to a vitrinite reflectance VR_0 up to 0.7%), orange ($VR_0 \approx$ 0.7-0.9%) and red fluorescence color ($VR_0 \approx$ 0.9-1.2%) (Smojić et al., 2009). In the over-mature stage, the fluorescence is not visible. Pearson (1984) established the following maturation scale in relation to the Thermal Alteration Index: TAI = 1-2 for the immature stage (up to 0.5% VR_0), TAI = between 2+ to 3+ (0.5-1.3% VR_0) for the mature stage and TAI = 3+ up to 4-5 for the over-mature stage.

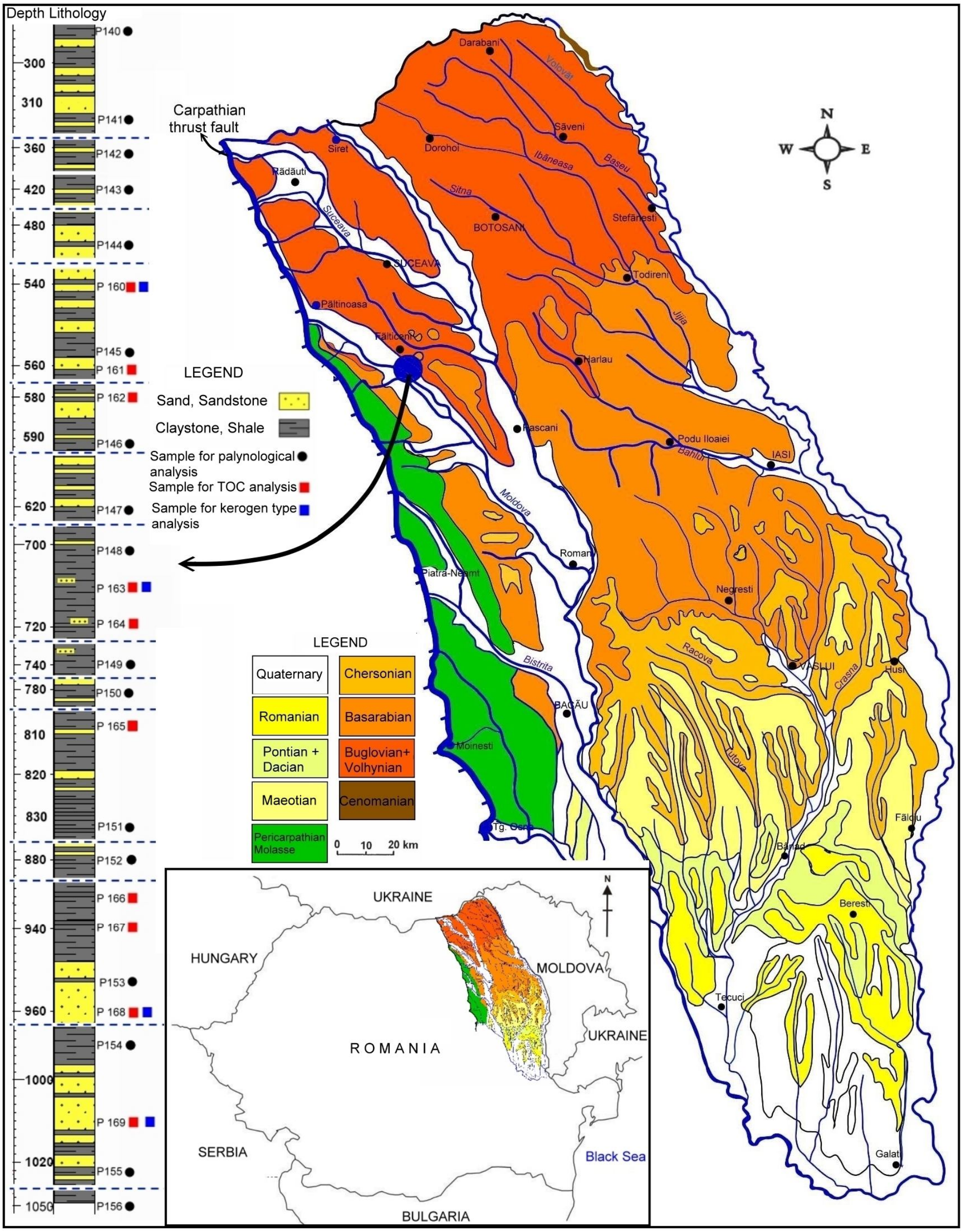

Fig. 1 Location and lithological column of the Baia borehole. The geological map is according to Ionesi (1994).

Results and discussions

In the present study, 10 samples from the Baia borehole have been used for TOC analysis. The results are presented in table 1. The hydrocarbon potential has been established according to Tissot and Welte (1984) and Bordenave (1993). Samples 161 (560 m) and 168 (960 m) have a good hydrocarbon potential, while the other samples analyzed have a fair hydrocarbon potential.

Tab. 1 The results for TOC and H analyses performed on the Baia borehole samples

Sample nr.	Depth	% TOC	% H	Hydrocarbon potential
P 160	540 m	0.75	0.342	Fair
P 161	560 m	1.236	0.595	Good
P 162	580 m	0.778	-	Fair
P 163	710 m	0.998	0.722	Fair
P 164	720 m	0.593	0.265	Fair
P 165	810 m	0.82	0.301	Fair
P 166	930 m	0.873	-	Fair
P 167	940 m	0.756	-	Fair
P 168	960 m	1.156	-	Good
P 169	1010 m	0.708	-	Fair

In order to establish the type of kerogen for samples 160 (540 m), 163 (710 m), 168 (960 m) and 169 (1010 m), we have calculated the H/C and O/C ratios. The results are presented in table 2. The values for the H/C ratio are between 0.8228 and 0.9272, the highest value being calculated for sample 160. The values for the O/C ratio are relatively similar, being comprised between 0.2283 and 0.2758.

Tab. 2 The percentages for N, C, H, S, O and H/C and O/C ratios from the kerogen analyzed

Sample nr.	% N	% C	% H	% S	% O	H/C ratio	O/C ratio
P 160	2.804	54.059	4.177	-	19.880	0.9272	0.2758
P 163	2.743	56.106	4.192	-	17.155	0.8965	0.2293
P 168	2.199	51.131	3.506	-	16.840	0.8228	0.2470
P 169	-	65.263	4.554	1.45	19.871	0.8373	0.2283

The results obtained for kerogen analysis have been plotted in figure 2. The kerogen type resulted from this diagram is III. This type of kerogen has a low H/C ratio (<1.0) and a high O/C ratio (up to ~ 0.3) (Peters and Moldowan, 1993). The kerogen type III is manly formed from vascular plants and it contains great amounts of plants debris represented by vitrinite macerals. It produces natural gas and, occasionally, associated condensate if the thermal maturation is adequate.

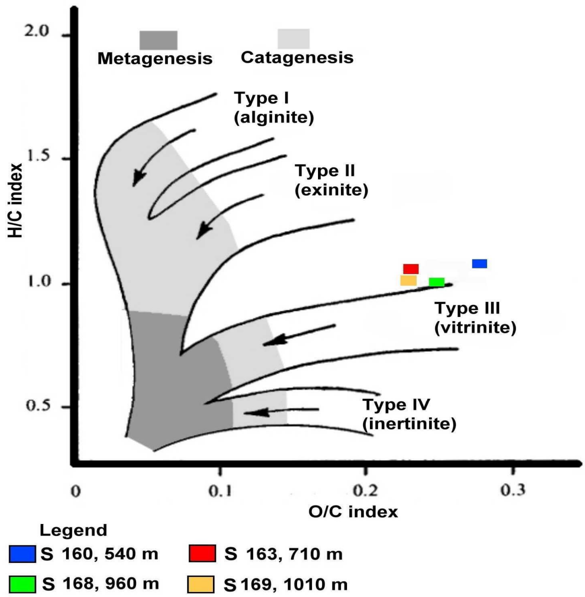

Fig. 2 The H/C and O/C ratios plotted in a van Krevelen diagram.

Palynofacies analysis

In the present study, 16 samples from the Baia borehole, collected at depths between 290 to 1050 m, have been analyzed for palynofacies interpretation (fig. 1). The percentage of phytoclasts, palynomophs and AOM resulted from palinofacies analysis were plotted in a Tyson diagram (fig. 3). Most of the samples (P140, P143, P147, P148, P149, P150, P151, P153, P154, P155 and P156) belong to field III of the palynofacies. This field is characterized by a predominance of phytoclasts, which indicates a fluvial-deltaic source, where the palynomorphs are fairly preserved. The AOM is present in low percentage. According to Tyson (1995), the type of kerogen for this field is mainly III. The same type of kerogen was established based on the van Krevelen diagram (fig. 2). Samples P142 and P146 belong to field VIII of the palynofacies, being characterized by an assemblage dominated by very-well-preserved AOM. Palynomorphs are also present, but in low percentage. At the limit between fields IX and VIII is sample P152, characterized by a high frequency of AOM, with a lower percentage of phytoclasts.

AOM can have both a marine origin, being derived from bacterial degradation of planktonic organisms, and a continental origin, coming from debris degradation of continental plants (Bombardiere and Gorin, 2000). We can distinguish between these two categories of AOM (derived from marine or continental sources) based on fluorescence. Thus, AOM derived from the degradation of phytoplankton displays fluorescence (Plate I, fig. 1a,b and 5a,b), while AOM resulting from the degradation of plant debris is non-fluorescent (Plate I, fig. 2a,b, 3a,b and 6a,b). Another opinion on AOM fluorescence was expressed by Tyson (1995). According to Tyson (1995), AOM presenting fluorescence derives from "well-preserved plankton/bacteria," while non-fluorescent AOM results from “degraded plankton/bacteria”.

The phytoclasts are brown-dark brown in color and mostly angular in shape, which indicates the proximity of the source area (Plate I, fig. 4a, Plate II, figs. 7, 8).

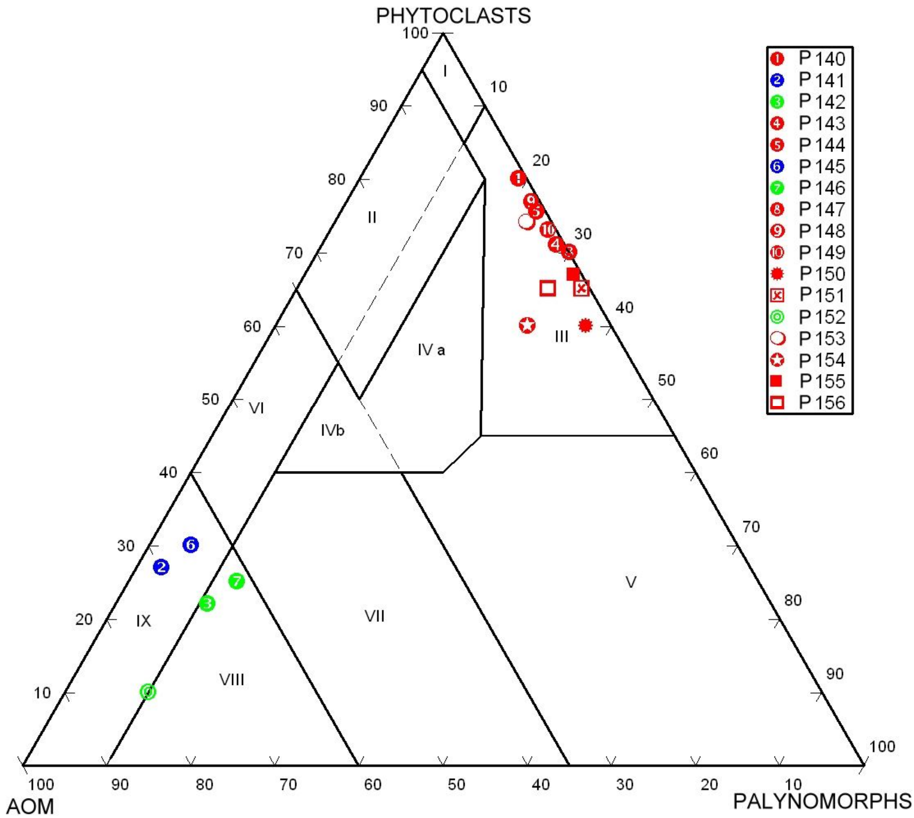

Fig. 3 Samples from the Baia borehole used for palynofacies analysis plotted in the ternary diagram of the kerogen (Tyson, 1995).

Thermal maturation of kerogen

The maturation degree of the organic matter extracted from the bituminous rocks analyzed was derived based on TAI (inferred from pollen specimens) and the color of dinoflagellate fluorescence.

TAI is a numerical scale, based on the changes that occur in palynomorph color (spores and pollen) as the temperature to which they are subjected increases (Pearson, 1984). The visual determination of palynomorph color indicated a TAI between 2 and 2+ (Plate II, figs. 1a, 2a, 4a, 5a, 6a, 7a), suggesting a stage of the organic matter at the limit between the immature and the mature. We have also seen palynomorphs with dark yellow to orange-brown color, corresponding to a TAI of -3 (Plate II, fig. 3a), which indicates a mature phase of liquid petroleum generation.

The fluorescence color of dinoflagellates is yellow to bright yellow, which corresponds to a $\lambda \approx 580$ nm wavelength, and dark yellow to dark brown, corresponding to a $\lambda = 580\text{-}620$ nm wavelength. According to Raynaud and Robert (1976), organic matter that has a color of fluorescence from 580 to 630 nm is in a mature stage in terms of hydrocarbon generation. The bright yellow color of the palynomorphs is equivalent to a vitrinite reflectance (VR_0) up to 0.7% (Smojić et al., 2009). The color of the sporomorphs is yellow, with a $\lambda \approx 580$ nm wavelength (Plate II, figs. 1b, 2b, 3b, 4b, 5b, 6b) and dark yellow (Plate II, fig. 7b).

Based on TAI and the color of the palynomorphs in fluorescent light, we concluded that the Organic Material from the samples analyzed is at the beginning of the mature stage of hydrocarbon generation.

Conclusions

In order to establish the type of kerogen for samples P160 (540 m), P163 (710 m), P168 (960 m) and P169 (1010 m), we calculated the H/C and O/C ratios. The type of kerogen resulted from this study is III, wich may produce natural gas and, occasionally, associated condensate if the thermal maturation is adequate. The percentage of TOC was established based on 10 samples (from the 540-1010 m depth range within the borehole analyzed), mainly a fair/good hydrocarbon potential being determined (TOC < 1%).

Most of the samples belong to field III of the palynofacies, according to Tyson (1995). This field is characterized by a predominance of phytoclasts, which indicates a fluvial-deltaic source, where the palynomorphs are fairly preserved. AOM is present in low percentage. According to Tyson (1995), the type of kerogen for this field is mainly III. The same type of kerogen was established based on the van Krevelen diagram (fig. 2).

Samples P142 and P146 belong to field VIII of the palynofacies, which is characterized by an assemblage dominated by well-preserved AOM. Palynomorphs are present in low percentage. At the limit between fields IX and VIII is sample P152, characterized by a high frequency of AOM, with a lower percentage of phytoclasts.

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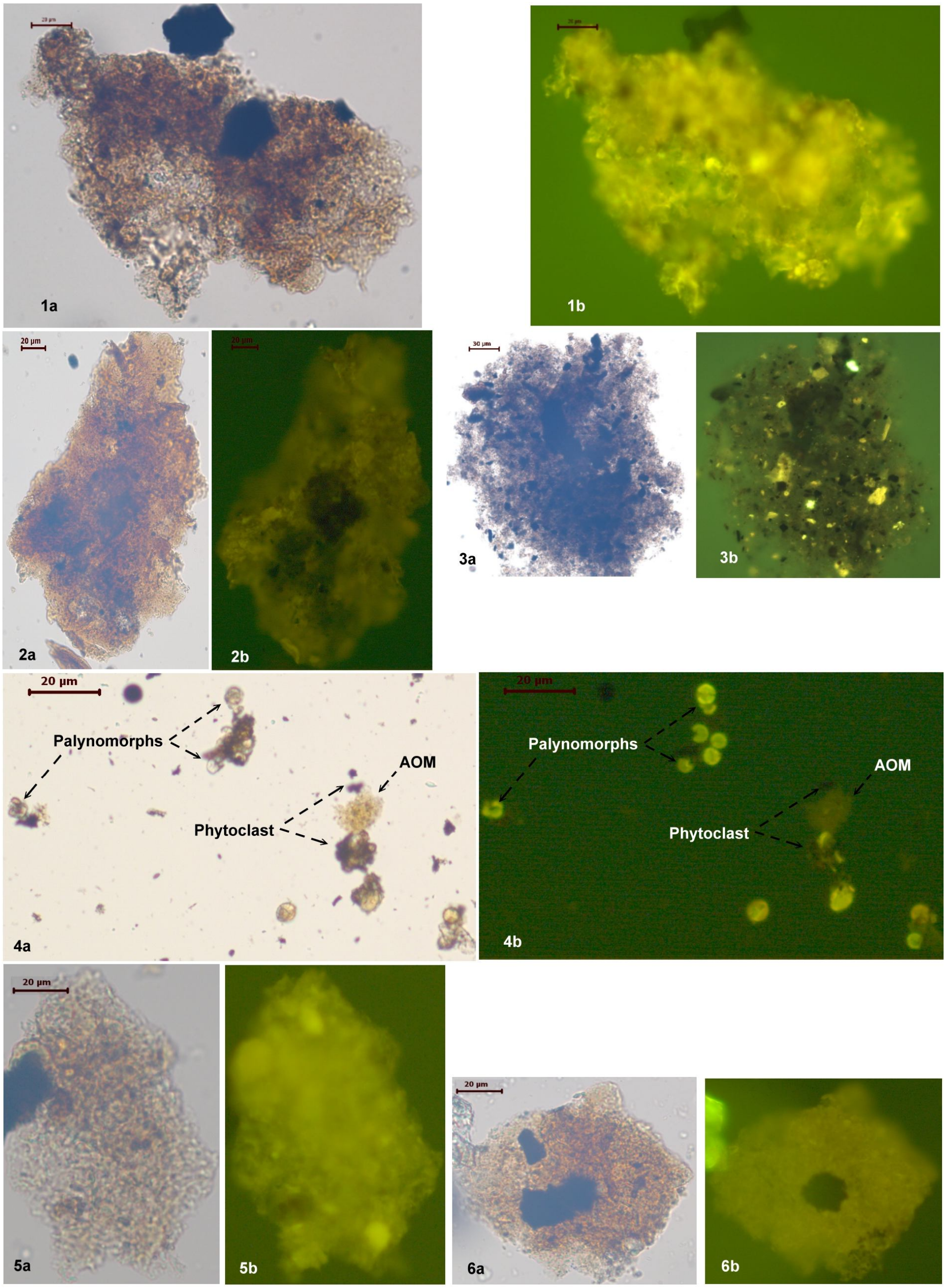
CAPTION OF PLATES

Plate I

1a, 2a, 3a, 5a, 6a. AOM in transmitted light
1b, 2b, 3b, 5b, 6b. AOM in fluorescent light
4a. Phytoclasts, palynomorphs and AOM in transmitted light
4b. Phytoclasts, palynomorphs and AOM in fluorescent light

Plate II

1a. *Pityosporites* sp. in transmitted light
1b. *Pityosporites* sp. in fluorescent light
2a. *Pityosporites* sp. in transmitted light
2b. *Pityosporites* sp. in fluorescent light
3a. *Pityosporites* sp. in transmitted light
3b. *Pityosporites* sp. in fluorescent light
4a. *Intratriopollenites instructus* in transmitted light
4b. *Intratriopollenites instructus* in fluorescent light
5a. *Abiespollenites absolutus* in transmitted light
5b. *Abiespollenites absolutus* in fluorescent light
6a. *Zonalapollenites minimus* in transmitted light
6b. *Zonalapollenites minimus* in fluorescent light
7a. *Leiotriletes* sp. in transmitted light
7b. *Leiotriletes* sp. in fluorescent light
8. Phytoclasts (black coal fragments)
9. Phytoclasts and palynomorphs


1a
1b
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Palynomorphs
AOM
Phytoclast
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6a
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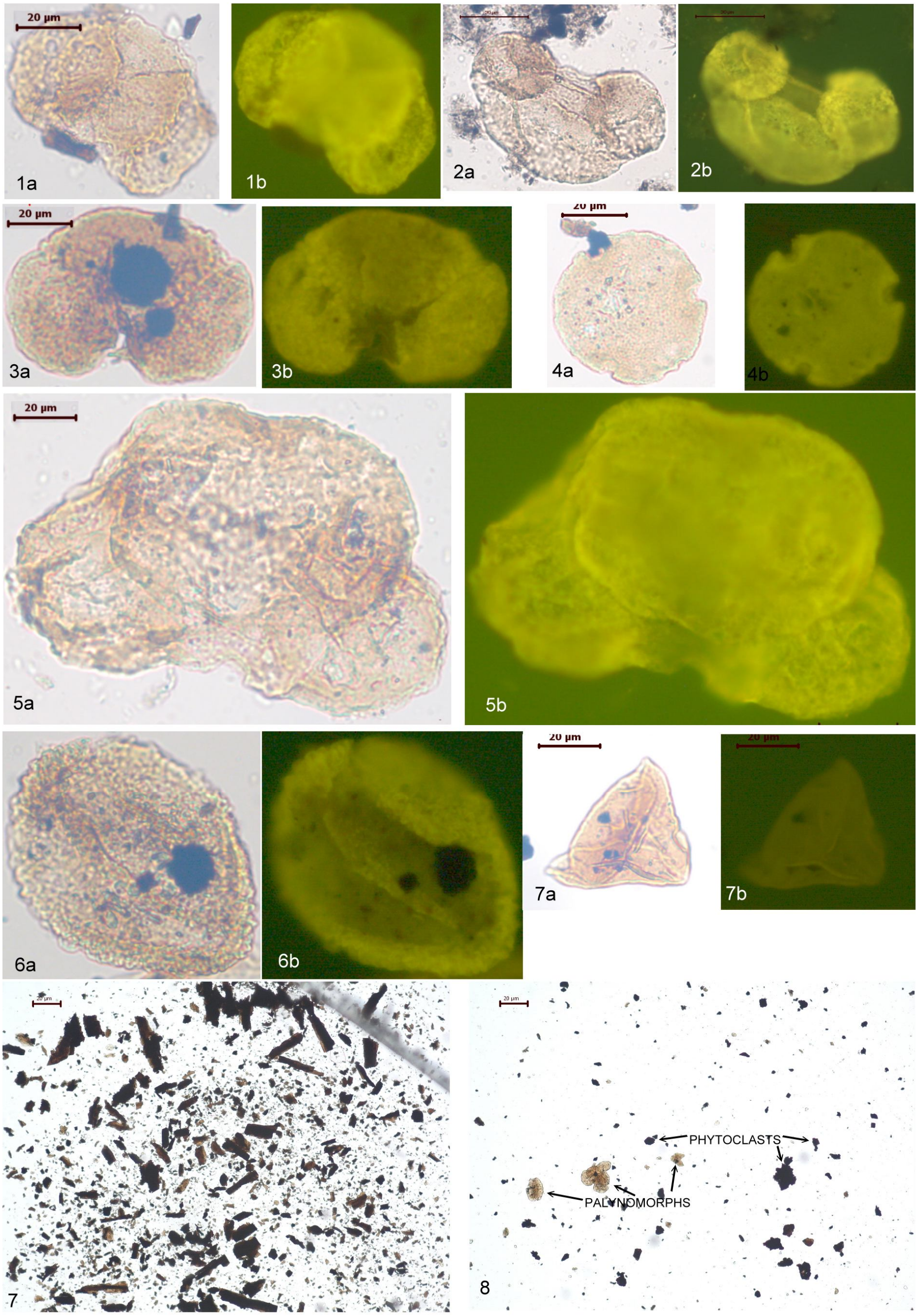
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PHYTOCLASTS
PALYNOMORPHS