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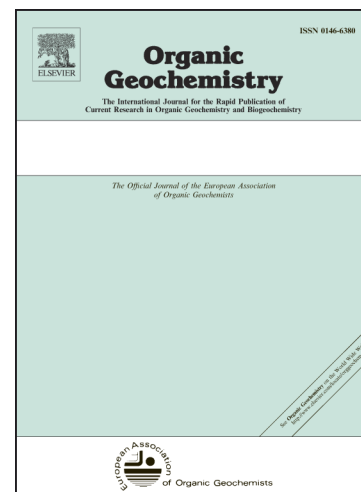
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Early stages of Type I-S kerogen formation revealed by Rock-Eval® 7S analysis of sediment from a modern halo-alkaline lake (Dziani Dzaha, Mayotte)

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Highlights:

- First application of Rock-Eval® 7S to recent lacustrine sediments
- Lake Dziani Dzaha is a modern analog for Type I-S petroleum source rock depositional environment
- Increase of hydrogen index linked to organic-sulfur enrichment
- Pyrolysis thermal stability of sulfurized organic matter increases with depth
- Pyrolysis organic sulfur is released either with CO₂ or HC

Abstract: The Dziani Dzaha (Mayotte Islands, Indian Ocean) is a small, shallow, saline and hyperalkaline maar lake. Its surface waters are characterized by intense primary production, inducing the waters below 2 m depth to remain aphotic and anoxic all year round, at least until 2017, when a ~5 m-long core was taken from the center of the lake. The recovered sediments were described and sampled at high resolution. They consist of laminated microbial mats, mixed with carbonate lenses or nodular beds, and rare silty detrital facies. The inorganic and organic carbon contents of 160 samples were analyzed using the Rock-Eval® method, including the Rock-Eval® 7S device which quantifies both total organic sulfur and total sulfur content, in addition to conventional Rock-Eval parameters. The Dziani Dzaha sediments are characterized by high TOC content (8.5 wt.% on average and up to 27.9 wt.%) and variable inorganic carbon content. HI values average 630 mg HC/g TOC and reach up to 834 mg HC/g TOC. TS content varies from 0.3 to 3.6 wt.%, with TS_{org}/TOC ratios close to 0.01 at the top of the core and fluctuating downcore between 0.02 and 0.05. Interestingly, the pyrolysis thermal stability of sulfurized organic matter increases with depth, and the highest HI values are associated with highest S_{org} content, sulfurization of organic matter being generally accompanied by reductive processes. The hydrogen- and organic-sulfur-rich sediments of Dziani Dzaha can be considered modern analogues of Type I and I-S petroleum source rock deposits, such as the Eocene Green River shales and Kimmeridgian Orbagnoux laminites, with remarkable facies and geochemical similarities. (258 words)

Keywords: Halo-alkaline lake, Laminated sediments, Type I-S kerogen, Organic sulfur, Early diagenesis, Rock-Eval® 7S

1. Introduction

Type I kerogens, characterized by high initial H/C atomic ratios (1.5-1.8) and low initial O/C atomic ratios (<0.1), stand out from the other kerogen types because they are rare and present the highest petroleum potential (Tissot et al., 1974; Durand & Monin, 1980, Vandenbroucke and Largeau, 2007). The reference for Type I kerogen was chosen in the Eocene lacustrine oil shales of the Green River Formation (hereafter called GRS for Green River Shales), which is the source rock of a petroleum system in the Uinta basin (USA) and one of the largest oil shale reserves in the world (Johnson et al., 2011). In accordance with the kerogen's high H/C ratios, the extracts, oils or pyrolysis products of GRS are rich in long-chain *n*-alkanes (C₄₀₊), *iso*- and *anteiso*-alkanes and other microbial biomarkers, suggesting that the initial organic matter (OM) source (probably *Cyanophyceae*) was strongly reworked by microbes during early diagenesis. This lipid-rich biomass was deposited during stable stratified periods of a lake, such as the 49 million-year old Mahogany Zone unit (Dean & Anders, 1991). It is well known that the intramontane lacustrine environment of GRS was not freshwater, as it contains unusual alkaline minerals, in particular specific Na-carbonates, such as dawsonite, nahcolite and trona (Smith, 1983; Tuttle, 1991).

To define Type I kerogens, Tissot et al. (1974) studied not only GRS, but also oil shales from different origins, including Permian torbanite (Scotland), Autunian boghead (France) and recent material from Coorong lagoon (Australia), all of which contain accumulations of the colonial algae *Botryococcus braunii*. Due to the presence of algaenan biopolymers, *Botryococcus*-derived OM can be preserved in environments in which anoxic conditions are not required for fossilization (Vandenbroucke & Largeau, 2007). The organic-rich tasmanite kerogen (Australia), composed almost entirely of the marine prasinophyte algae *Tasmanites*, was also classified as Type I kerogen by Tissot and Welte (1978). Finally, all the samples used to define Type I kerogens comprise various kinds of OM, derived from different biological precursors, deposited under many different preservation conditions and environmental settings.

Kerogens may contain a wide range of sulfur content (Orr, 1978; Durand & Monin, 1980), commonly assessed by the Sorg/C atomic ratio obtained through elemental analysis. It is considered that sulfur-rich kerogens are those where the Sorg/C atomic ratio is > 0.04 (Orr, 1986). Sulfur is a subordinate element in biomolecules, and its enrichment beyond Sorg/C atomic ratio of 0.04 in kerogens is the result of sulfur incorporation into OM during early diagenesis, a phenomenon known as OM sulfurization or natural vulcanization (Sinninghe Damsté & de Leeuw, 1990; Kok et al., 2000a; Adam et al., 2000; Amrani, 2014). In SO₄²⁻-rich environments, reactive Fe is believed to out-compete OM for sulfur incorporation, because of the fast formation of pyrite (FeS₂) or its precursors (Berner, 1985; Sinninghe Damsté et al., 1989; Hartgers et al., 1997). Consequently, it is generally thought that extensive OM sulfurization only occurs when the production of sulfur species exceeds the amount of reactive Fe, i.e. when terrestrial detrital input is low. Deposition in marine environments with low reactive Fe input favors OM sulfurization, and there are many examples of Type II-S kerogens in both ancient and modern environments.

By contrast, Type I-S kerogen occurrence is scarce as lacustrine waters usually have very low SO_4^{2-} contents. Only lakes with sulfate-rich rocks in their watershed and a reactive Fe deficiency appear to be prone to the formation of Type I-S kerogen. This was first recognized for two Catalan oil shales (Sinninghe Damsté et al., 1993) that contain kerogens with H/C atomic ratios > 1.5 and $\text{S}_{\text{org}}/\text{C}$ atomic ratio > 0.05 . The kerogen from one of these organic sulfur-rich deposits (Ribesalbes) is mainly composed of fossilized *Botryococcus braunii* algae. Other examples are the Eocene lacustrine source rocks from the Jiangling-Dangyang area of the Jiangnan Basin in China (Peters et al., 1996; Grice et al., 1998), Miocene Nördlinger Ries post-impact lacustrine sediments from Germany (Zhao et al., 2022a, 2022b), and possibly Eocene oil shales from the Qaidam Basin in China (Huc, 2013).

Although Type I-S kerogens are most often deposited in lakes, they may also be deposited in marine environments, as exemplified by the Upper Jurassic Orbagnoux laminites (Jura, France). This back-reef environment contains laminated organic-rich layers with Type I-S kerogen ($\text{S}_{\text{org}}/\text{C}$ ratio reaching 0.06) deposited under anoxic conditions (Bernier, 1984; Tribovillard et al., 1991, 1992, 1999; van Kaam-Peters & Sinninghe Damsté, 1997; van Kaam-Peters et al., 1998a, 1998b; Mongenot et al., 1997, 1999, 2000; Sarret et al., 2002; Thlajeh et al., 2024).

Few modern settings have been described as analogs of past environments that preserved Type I-S OM. As far as we know, Mud Lake in Florida (Bates et al., 1995; Filley et al., 2001), five lakes in Switzerland (Urban et al., 1999) and the estuarine St. Andrew Bay in Florida (Bürchert and Pratt, 1996) contain sufficient sulfur-rich compounds in both soluble and insoluble OM fractions to be linked to environments prone to produce Type I-S kerogen upon diagenesis. However, none of the proto-kerogens in these recent environments reaches the $\text{S}_{\text{org}}/\text{C}$ atomic ratio of 0.04. This is because the sediment is still in the early stages of diagenesis, and much of the organic sulfur (S_{org}) occurs in the soluble OM fractions and has not yet been incorporated into the kerogen. Estimating the $\text{S}_{\text{org}}/\text{C}$ ratio that these sediments would harbor at a later stage of diagenesis requires quantification of the total organic sulfur (TSorg).

Pyrolysis with the GeoElf Sulfur Analyser, which allows specific detection of sulfur-containing effluents, has been used to determine the $\text{S}_{\text{org}}/\text{C}$ ratio of (proto)kerogens (Jensen et al., 1998). However, because this instrument only analyzes pyrolysis effluents, leaving out the organic-sulfur fractions that react with the mineral matrix during pyrolysis, it does not quantify residual S_{org} . Such data are now available with the newly developed Rock-Eval® 7S (RE7S) apparatus (Vinci Technologies) which analyzes SO_2 effluents in addition to conventional hydrocarbon and CO_2/CO effluents monitored by the Rock-Eval® method (Lamoureux-Var et al., 2019; Carvajal-Ortiz et al., 2021; Espitalié et al., 2023).

We present here the application of RE7S to sediments of Lake Dziani Dzaha, a saline, alkaline sulfidic lake from Mayotte Island (Comoros, Western Indian Ocean). In 2017, a ~5 m-long core was retrieved in the center of this lake and the

collected sediments were described and analyzed at high resolution for their OM content using both RE6 and RE7S devices. The results are compared to the GRS and the Orbagnoux laminites as Type I and Type I-S kerogen references, respectively, demonstrating that Lake Dziani Dzaha is a modern analog for these fossil environments. This work sheds light on the early stages and timing of Type I-S formation.

2. Study site

Mayotte is a group of islands to the southeast of the Comoros (an archipelago in the Mozambique Channel of the Western Indian Ocean, Lat. 12°50 S; Fig. 1A), comprising two main islands (Fig. 1B): Grande-Terre (Mahoré) and Petite-Terre (Pamandzi). Geologically, the islands of Mayotte are the oldest in the Comoros archipelago with an estimated age for the initiation of the volcanism at 26.5 (Masquelet et al., 2022) and the main building phase between 10.6 Ma to 1.25 Ma (Pelleter et al., 2014). During the Quaternary, the latest volcanic phase on land corresponds to phonolitic explosive eruptions (Nehlig et al., 2013; Pelleter et al., 2014; Lacombe et al., 2024), that created maar-craters to the east of Petite-Terre. These maar-craters are open to the ocean except for the one hosting the Dziani Dzaha (from a Mahorese word meaning "volcano lake"), a lake with a surface area of 0.175 km² and a water level located approximately at the current sea level (Figs. 1C and D). On the basis of geomorphological features and dating of volcano-sedimentary material and coral fragments, Dziani Dzaha is considered to be the most recent maar-crater of the area, with an estimated age ranging between 25,000 and 4,000-years BP (Zinke et al., 2003, Lacombe et al., 2024). According to its chemistry (Sarazin et al., 2020), it is probable that the lake was at least initially connected to marine waters through bedrock fractures. The present-day lake watershed is very restricted, limited to the crater rim, which is mostly made of phonolitic pyroclastic rocks.

The lake's bathymetry is predominantly flat, with a depth not exceeding 6 m, with the exception of a narrow 18 m deep circular depression (Fig. 1E). Magmatic degassing in the Dziani Dzaha waters is evidenced by three zones of CO₂-rich bubbling gases (Leboulanger et al., 2017; Milesi et al., 2020; Cadeau et al., 2022). Although the lake water chemistry started to evolve after 2020 in response to an increase in CO₂ bubbling (Cadeau et al. 2022), at the time of the core sampling in 2017 it had been stable at least since 2010 (Sarazin et al., 2020). The lake waters were then slightly hypersaline (with salinity up to 1.5 that of seawater) and strongly alkaline ($[\text{CO}_3^{2-}] \approx 150\text{-}200$ mM, pH = 9.1-9.4; Leboulanger et al., 2017). The water column was stratified, with a permanent oxycline oscillating around 1 m depth and, depending on the season, by one or two aphotic haloclines, associated with a strong sulfide concentration gradient; one non-permanent halocline occurred at 2 m depth during the rainy period and one nearly permanent halocline occurred at the bottom of the pit (Sarazin et al 2020; Sala et al., 2021). Moreover, intense methanogenesis in the lake waters was demonstrated by dissolved methane concentration approaching saturation, below the 2 m deep halocline when present, a bubbling zone of methane-dominated gases (Milesi et al., 2020), high methane fluxes at the air/water interface (Sarazin et al., 2020),

microbial communities and lipid biomarkers (Sala et al., 2021) and carbon isotope mass balance (Cadeau et al., 2020).

The intense primary productivity, to which the lake owes its permanent green color (Fig. 1D), was dominated by planktonic prokaryotes with 90% of the biomass attributed to filamentous cyanobacteria (Leboulanger et al. 2017; Gérard et al., 2018; Bernard et al., 2019; Hugoni et al., 2018; Sala et al., 2021). This strong phytoplanktonic biomass limits light penetration to the first meter of the water column (Leboulanger et al., 2017) which, together with the intense remineralization of this OM induced the aphotic, anoxic nature of the underlying waters and their sulfidic nature below the haloclines when present. Because its relatively high organic carbon sedimentation rate (Cadeau et al., 2020; Sala et al., 2021), Dziana Dzaha is an interesting ecosystem to study the preservation potential of OM in such halo-alkaline euxinic ecosystems.

3. Material and methods

3.1 Coring and sediment sampling

Sediment cores were collected in November 2017 near the center of the lake at a water-depth of ca. 5 m, using a modified "Fanget-Malet 90" gravity piston corer (Nesje type) developed by the EDYTEM laboratory, and PVC tubular liners (9 x 600 cm, diameter x length). The length of sediment retrieved was limited by the presence of an indurated surface, possibly representing either a stromatolite-rich interval or the basement of the crater. The longest core (ca. 480 cm), called core C5, was cut into three sections, and each section was opened and visually described (see section 4.1.). Opening of the three sediment sections released a strong H₂S smell, and an intense hydrocarbon smell was also noted for levels deeper than 100 cm. Sediment layers, 2 cm thick, were taken every 3 cm, making a total of 160 samples. To limit contamination by the PVC liner, each sediment layer was sampled at a distance of one centimeter from the tube walls. Samples were stored in pyrolyzed amber glass vials and kept frozen until returned to the laboratory where they were freeze-dried and homogenized.

3.2 Sample preparation

Given their high salt content, sample aliquots were desalted by rinsing twice with 30 mL demineralized water to preserve the instruments and prevent analytical artifacts during Rock-Eval® analysis (Baudin et al., 2015, 2023a; Wattripont et al., 2019). This rather mild rinsing was shown to limit OM losses (Jovovic, 2020).

3.3 Rock-Eval® analysis

Rock-Eval® analyses were carried out on both RE6 Turbo and RE7S devices (Vinci Technologies). RE6 was applied on 160 desalted samples covering the whole core, using a cycle adapted for recent sediments (Baudin et al., 2015; Copard & Baudin, 2023). The pyrolysis cycle starts at 180°C with a 3 min isotherm followed by an increase of temperature up to 650°C using a ramp of

30°C.min⁻¹. The oxidation cycle ranges from 300 to 850°C with a ramp of 20°C.min⁻¹ and a 5 min final isotherm, as described by Behar et al. (2001) for petroleum source rocks. Several detectors (FID, CO and CO₂ infrared detectors) and thermocouples are used to record the classic Rock-Eval® thermograms and measure the S1, S2, S3, S4, and S5 peaks and their T_{peak} (temperature of oven when effluent yield reaches a maximum). Classical Rock-Eval® parameters were derived from these thermograms: Total Organic Carbon (TOC), Hydrogen Index (HI), Oxygen Index (OI), and Mineral Carbon (MinC), following calculations described by Behar et al. (2001). Systematic duplicates every eight samples and the analysis of a reference sample every nine samples were used to check the replicability and accuracy of the analyses, which are highly reproducible (Pacini et al., 2023).

A selection of 55 of the 160 samples was also analyzed using a RE7S instrument which, in addition to the classical parameters provided by the Rock-Eval® method, analyzes sulfur-containing effluents (SO₂) using an UV detector. Deconvolution of SO₂ thermograms obtained continuously during pyrolysis, as well as during oxidation up to 1200°C, enables organic and inorganic sulfur to be distinguished and quantified (Lamoureux-Var et al., 2019; Carvajal-Ortiz et al., 2021; Espitalié et al., 2023). Total organic sulfur (TS_{org}) and total sulfur (TS) are thus measured by the Rock-Eval® 7S method without the need to separate organic and inorganic forms of S by selective chemical attacks. This allows TS_{org}/TOC to be determined, a parameter equivalent to the S_{org}/C proposed by Orr (1986) and intended to classify sulfur-rich kerogens. As with the HI obtained from the S2 peak, the Rock-Eval® 7S method can be used to calculate an organic sulfur index (SI, in mg S/g TOC) as being equal to S_{2Org}S/TOC x 100. The SI is therefore a parameter allowing quantification of the organic sulfur richness of source rocks (Carvajal-Ortiz et al., 2021; Espitalié et al., 2023).

4. Results

4.1. Macroscopic description of sedimentary facies of core C5

The description of core C5 right after its opening enabled us to identify and describe three main types of facies throughout the core (Fig. 2): (1) microbial mats (m), of different colors, more or less laminated and indurated; (2) almost pure white carbonates (w), forming poorly indurated nodules or nodular beds, with sub-millimeter to multi-centimeter size; (3) detrital facies with a silty granularity. The microbial mats (m) exhibit facies variations described as follows: dark brown laminated microbial mats (ma); lighter, less laminated microbial mats (mb); highly laminated, ochre to purple laminated microbial mats (mc); and black laminated microbial mats (md).

Various allochthonous elements were also identified throughout the core: higher-plant remains (leaves, fibers, wood fragments) in the microbial mat; sub-centimeter smooth phonolite clasts, present indiscriminately in all facies; and

rounded, millimeter-size, very friable black nodules, interpreted as charcoal fragments, isolated or concentrated in microbial mats.

Variations in the distribution of these facies and close-up views of the above described facies are shown in Figure 2. On the basis of these variations, three units were described in core C5, from top to bottom:

- A homogeneous upper unit (0-100 cm) with a gel-like texture, composed of a continuous succession of poorly visible fine laminations and microbial mats (facies md). This unit also contains levels that are probably detrital but could potentially correspond to more indurated and more carbonate-rich microbial mats. The basal level of this unit (99-100 cm) appeared as a peculiar transitional facies, sensitive to photo-oxidation, which changed from dark red to rusty orange in the first few minutes after opening the core.
- An intermediate unit (100-444 cm) of heterogeneous microbial mats (facies ma and mb), ranging from slightly indurated and finely laminated facies to highly indurated and damaged facies, interlayered with carbonate nodules of creamy texture and pure white color and possible detrital levels. This unit can be subdivided into an intermediate unit 1 at top (between 100 and 263.5 cm) where detrital facies are nearly absent, overlying an intermediate unit 2 (between 263.5 and 444 cm), characterized by a higher proportion of detrital and carbonated facies.
- A lower unit (444-477 cm) consisting of finely laminated ochre to purple microbial mats (mc), interrupted by a thick detrital level (459.5-467 cm), interpreted as a single storm-event. The absence of pumice bearing laminae, ash or coral fragments at the base of the core suggests that the early history of the lake is missing from this core.

The possible reasons behind facies changes within and between these three units encompass changes in the elevation of Petite Terre Island induced by regional magmatic activity (Gargani, 2024), the progressive sedimentary filling up of the crater and, of course paleoclimatic changes including sea-level changes. Identifying them is beyond the scope of the present study.

4.2. Organic and inorganic carbon contents

Rock-Eval® analysis results show that the sedimentary record of Dziani Dzaha has always been characterized by high OM and carbonate contents (average TOC = 8.5 wt.% and MinC = 4.8 wt.%). The richest OM levels contain 27.9 wt.% TOC (= 60 wt.% OM, assuming that recent OM typically contains 50 wt.% carbon; Meyers, 2003), and the richest carbonates contain 10.2 wt.% MinC, representing almost pure carbonate.

As facies are not homogeneous along core C5, strong variations appear in organic and inorganic carbon contents (Fig. 3). The main trends observed are consistent with the division into units based on macroscopic descriptions. The upper unit

has fairly homogeneous OM and carbonate contents (TOC \approx 9 wt.% and MinC \approx 3 wt.%) and the upper 50 cm of this unit show particularly low fluctuations. The intermediate unit shows contrasting OM contents with the highest (up to 27.9 wt.% TOC) and the lowest (TOC \approx 0.8 wt.% if pure carbonate levels are excluded), as well as contrasting carbonate contents with MinC fluctuating between 0.8 and 10.2 wt.%. The subdivision of the intermediate unit into two sub-units is not clearly expressed by changes in organic and inorganic contents. The lower unit is made up of poorly contrasted laminae with rather homogeneous OM (TOC \approx 7.5 wt.%) and carbonate contents (MinC \approx 3.5 wt.%).

If facies are examined independently of their place in the core, a number of characteristics emerge, which are well expressed in a TOC vs. TIC plot (Fig. 4). As expected, the white carbonate levels contain the highest MinC and the lowest TOC contents. Silty facies contain on average low TOC and MinC contents, consistent with a strong detrital contribution. Black microbial mats (md) show rather low carbonate content (MinC \approx 2.8 wt.% on average) and relatively high OM content (TOC \approx 10.2 wt.% on average). With a few exceptions, roughly laminated microbial mats (mb) contain on average more carbonate (MinC \approx 7 wt.%) and less OM (TOC \approx 6 wt.%), compared with strongly laminated, ochre to purple microbial mats (mc), which average MinC around 3.8 wt.% and TOC around 8.4 wt.%. Samples from the dark brown laminated microbial mat facies (ma) cover a larger area on the plot (Fig. 4) and exhibit the highest TOC contents.

4.3. Total and organic sulfur contents

TS content ranges from 0.3 to 3.55 wt.%, with an average of 1.05 wt.%, while TSorg content varies from 0.2 to 2.8 wt.%, with an average of 0.7 wt.%. The upper unit shows very homogeneous TS and TSorg values, while the intermediate unit shows wider variations depending on facies (Fig. 3). The TSorg/TOC ratio, similar to the Sorg/C ratio defined by Orr (1986), is close to 0.01 in the upper unit and rises abruptly to \sim 0.05 at the top of the intermediate unit, and then fluctuates downcore between 0.02 and 0.04 (Fig. 5). Interestingly, the organic SO₂ generated during pyrolysis is not always associated with the same effluent. In the upper unit, organic SO₂ is released at the same time as CO₂ (S3 peak), at lower temperatures than the hydrocarbon maximum release (S2 peak), while in the intermediate and lower units, the organic SO₂ peak is released later, and its maximum temperature approaches and sometimes even merges with that of the S2 peak (Fig. 5).

4.4. Type of OM preserved in Dziani Dzaha sediments

Hydrogen Index (HI) values are high in Dziani Dzaha sediments, averaging 630 mg HC/g TOC and maximizing at 834 mg HC/g TOC, which is exceptional for recent sediments. Vertical fluctuations in HI are not obvious along the core C5 (Fig. 3). However, there are two periods with significantly lower HI-values, in the

lower half of the upper unit and at the top of the intermediate unit (mean HI values of ca 500 mg HC/g TOC compared to 680 mg HC/g TOC for the rest of the core). The highest HI-values occur in the intermediate unit.

Excluding one sample with an abnormally high OI-value near 1000 mg CO₂/g TOC, OI values range from 70 to 633, with an average of 178 mg CO₂/g TOC. The upper and lower units have fairly constant OI-values (around 100 mg CO₂/g TOC), while the intermediate unit shows the highest OI-values. It should be noted that the white carbonate facies (w) and the most carbonate-rich microbial mat facies (mb) are those with the highest OI-values (> 250 mg CO₂/g TOC; Fig. 6A). This suggests a carbonate contribution to the CO₂ generated below 400°C during pyrolysis, as some carbonate species decompose at low temperatures (Baudin et al., 2023b). Hydromagnesite (a hydrated carbonate; Mg₅(CO₃)₄(OH)₂·4H₂O), known to occur in the sediments of Lake Dziani Dzaha (Milesi et al. 2018), exhibits a two-stage thermal decomposition, the first being close to 410°C. This temperature is above the 400°C limit which, in the Rock-Eval® method, marks the separation between CO₂ of organic and mineral origin. However, it is likely that the decomposition of hydromagnesite starts at a temperature slightly below 400°C, and that the CO₂ then released is counted as organic, leading to an artificial increase in the OI value.

Excluding the mb and w facies in Figure 6A for this reason, the OM in the sediments of Lake Dziani Dzaha lies in the areas of Type I or hydrogen-rich Type II kerogens defined by the van Krevelen pseudo-diagram (Fig. 6B). It should be kept in mind that this OM is still at the protokerogen stage, and that its diagenetic evolution is not yet complete, which can cause the HI- and OI-values to evolve towards a Type I kerogen (see discussion below).

5. Discussion

5.1. Facies similarities of Dziani Dzaha sediments with Type I and I-S source rocks

If we exclude the thin detrital facies (facies s; Fig. 2), which represents external inputs rather than autochthonous sedimentation, the primary sedimentary facies identified in the core can be divided into three main types: (1) finely parallel laminated facies, more or less dark depending on their richness in OM, with a gel-like texture; (2) wavy to broken laminated facies, with the same variations in color as the finely laminated facies; (3) pure white carbonates with a creamy texture, most often in the form of nodules or lenses and more rarely as a small continuous level at the scale of the core section.

Laminated facies are undoubtedly associated with the production and preservation of cyanobacteria that thrive in surface waters. Parallel laminated facies were deposited in a calm environment, probably during periods of high-water levels, and were not subsequently disturbed. Wavy and broken laminated facies were either deposited during periods of low water level and high lake

agitation, or correspond to post-depositional growth of intralaminar diagenetic carbonate which deformed and broke parallel laminae. This deformation, together with the wide range of nodule sizes (mm to cm in diameter), is a strong argument in favor of the diagenetic origin of the carbonate. It is likely that carbonate nodules originated preferentially in the most OM-rich laminae and that their formation was linked to certain early diagenetic microbial processes, such as fermentation (Reitsema, 1980) or acetoclastic methanogenesis (Kenward et al., 2009).

Remarkably, the tripartite facies association described in Dzani Dzaha sediments (no older than 7,000 years) is reminiscent of certain facies in the 49 million-year-old GRS (Utah, USA) or the 153 million-year-old organic laminites of Orbagnoux (Jura, France), as shown by comparison of the three sedimentary deposits at the same scale (Fig. 7). The same successions of alternating thin laminae, some dark and rich in OM and others more carbonate-rich, can be seen in the present lake as in the fossil analogues. The lamination is sometimes disturbed by undulating characters or by carbonate nodules, whose growth has visibly deformed the sediment.

5.2. Organic and sulfur contents of Dziani Dzaha sediments are comparable to Type I and I-S source rocks

In addition to the similarity of some facies, the sediments of the Dziani Dzaha and the petroleum source rocks of the GRS and the Orbagnoux laminites contain the same Type I OM and similar TOC contents, as illustrated by the van Krevelen pseudo-diagram of HI vs OI Rock-Eval® parameters from the three formations (Fig. 8). The slightly lower HI and slightly higher OI-values observed in the sediments from the Dziani Dzaha compared to those of the two emblematic examples of petroleum source rocks containing Type I kerogen, is explained by OM at the protokerogen stage. It is likely that at a later stage of diagenesis, the OM in Dziani Dzaha sediments would have lost oxygen-rich functionalized compounds (acids, alcohols, ketones, etc.), which would lead to a reduction in OI and an increase in HI values. Finally, the facies of the intermediate and lower units of C5 core contain sulfurized OM with $TSorg/TOC > 0.04$ (Fig. 5), which refers them to the Type I-S like the Orbagnoux facies.

5.3. Incorporation of organic sulfur into Dzani Dzaha sediments and its consequences as shown by RE7S data

According to our pyrolytic data, OM-sulfurization in Dziani Dzaha sediments likely involved different types of organic compounds and mechanisms as a function of depositional conditions. In the top unit, SO_2 is released during pyrolysis at fairly low temperature (290°C) and is perfectly in phase with the CO_2 S3 peak (Fig. 5), suggesting that oxygenated and thermally labile compounds would be preferentially sulfurized. This suggests that carbohydrates were

preferentially sulfurized to lipids (e.g., Kok et al., 2000b). Still, the TSorg/TOC ratio in the upper unit appears much lower than in the underlying sediments (Fig. 5), suggesting strong modifications in the S cycle and OM sulfurization processes between the intermediate and the upper units, in line with preliminary molecular and isotopic studies (Jovovic, 2020, Jovovic et al., 2020). It can also not be ruled out that the SO₂ peak observed at low temperature during pyrolysis of the sediment of the upper unit originates from the Sorg contained in the phytoplanktonic biomass reaching the sediment.

At the top of the intermediate unit, as the OM reaches a TSorg/TOC ratio of 0.05, the SO₂ peak corresponds to HC release (peak S2) rather than CO₂, although a small shoulder remains at the start of the SO₂ peak that could still be linked to sulfurized OM like that in the upper unit. The correspondence of the SO₂ peak with peak S2 suggests the presence of sulfurized lipids in these laminae. The fact that the SO₂ yield maximizes slightly earlier (at 460°C) than the HC peak (480°C) is to be expected, because the activation energy required to thermally break the C-S bond is lower than that of the C-C bond (Baskin and Peters, 1992). Further down the core, samples with TSorg/TOC ratios of ~0.03 show a SO₂ peak emerging between the first CO₂ peak and the HC peak, suggesting an intermediate stage of OM sulfurization. Such a dynamic of sulfur incorporation in recent sediments, with preferential sulfurization of carbohydrate versus alkyl moieties, has been described in sediments from the Cariaco Trough (offshore Venezuela), ranging in age from 900 to 6,000 years (Aycard et al., 2003; Werne et al., 2003).

Sulfurization of carbohydrates can be an important pathway in the preservation of organic matter in euxinic depositional environments and this process has been shown to be involved in the formation of Type II-S kerogens (van Kaam Peters et al., 1998a, 1998b; Kok et al., 2000b; van Dongen et al., 2006). The explanation for changes in the type of OM preferentially sulfurized between the upper and intermediate units remain to be investigated. These changes may be due to variable composition of the OM and reactive inorganic sulfur pools available for sulfurization (i.e., amount of sugars vs. functionalized lipids). In addition, the markedly lower TSorg/TOC ratio in the upper compared to the intermediate unit indicates that sulfur incorporation into OM has been less intense since establishment of the present-day ecosystem, ca 900 years ago. This could be due to changes in environmental and biogeochemical conditions in the lake that led to a sulfide-rich but sulfate-poor environment that could have impacted the speciation of inorganic sulfur compounds available for sulfurization of OM (Jovovic, 2020; Jovovic et al., 2020; Cadeau et al., 2022). This type of environment could, perhaps, be unfavorable for formation of polysulfides (extremely reducing conditions possibly favoring sulfides over polysulfides), which have proved to react efficiently with various organic functions under geochemically relevant conditions (e.g. Schouten et al., 1994; Tribovillard et al., 1994; De Graaf et al., 1995; Poinot et al., 1997). One of the consequences of sulfur incorporation into OM is to make it resistant to microbial degradation (Sinninghe Damsté and de Leeuw, 1990; Adam et al., 2000). In Type II-S source rocks, such as the Kimmeridge Clay Formation (UK), facies with the most sulfur-rich OM are also

those with the best petroleum potential (Bertrand et al., 1994; van Kaam-Peters, 1998a, 1998b). The same relationship seems to occur for Type I-S OM in Dziani Dzaha sediments, as supported by the clear relationship between the % Sorg content of samples and their HI value (Fig. 9). Dark brown laminated facies are clearly those in which sulfurized OM is most abundant, with HI values as high as 800 mg HC/g TOC.

6. Conclusions

Dziani Dzaha is a small saline and hyper-alkaline maar lake characterized by intense primary production and anoxic, seasonally euxinic, bottom waters. Analysis of sedimentary facies from a ca. 480 cm-long core retrieved from the center of the lake shows the dominance of laminated facies rich in OM (up to 28 wt.% TOC) throughout the sedimentological history of the lake. Rock-Eval® 6 and 7S analyses show that this OM is Type I and I-S, with TSorg/TOC ratios as high as 0.05, demonstrating the rapid and efficient formation of such kerogens under favorable conditions. In terms of facies and OM characteristics, the Dziani Dzaha sediments can thus be considered modern analogs of petroleum source rocks, such as the GRS and the Orbagnoux laminites.

These preliminary results obtained from Rock-Eval® 6 and 7S analyses suggest that different mechanisms of OM sulfurization occurred in the lake since its formation (depending notably on primary productivity and the speciation of inorganic sulfur), inducing the selective sulfurization of certain classes of compounds depending on conditions. Variations in the type of mechanisms and sulfurized organic matter in the sedimentary history of Lake Dziani Dzaha are currently the subject of further study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Caption of figures

Fig. 1 – Location and bathymetric maps of the Lake Dziani Dzaha on Mayotte Islands (Indian Ocean). (A) Comoros Archipelago in Western Indian Ocean, (B) Mayotte Islands, (C) Dziani Dzaha in Pamandzi (Petite Terre) Island, (D) Picture of the lake showing its characteristic green color, (E) Bathymetric map of the lake, with location of core C5, and (F) Schematic lake cross-section showing its stratification and water chemistry during the wet season (from Cadeau, 2017).

Fig. 2 – Photograph and simplified sedimentary log of core C5, with close-up views of the main facies on the right.

Fig. 3 –Rock-Eval® parameters along core C5. TOC: Total Organic Carbon; MinC: Mineral Carbon/Total Inorganic Carbon; HI: Hydrogen Index; OI: Oxygen Index; TSorg and TS: Organic Sulfur and Total Sulfur Content, respectively. In the far right column, the green part of the histogram corresponds to mineral sulfur.

Fig. 4 – TOC *vs* TIC plot of 160 samples from core C5, according to their sedimentary facies (see Figure 2 for symbols assignment). The transverse line corresponds to a mixing line between pure calcite (TIC = 12 wt.%; TOC = 0 wt.%) and pure OM (TIC = 0 wt.%; TOC = 50 wt.%).

Fig. 5 – Vertical evolution of the TSorg/TOC atomic ratio along core C5 derived from Rock-Eval® 7S data. The shaded area corresponds to the range of sulfur-rich kerogens (type S) according to Orr (1986). The right panels show examples of the SO₂, CO₂ and HC normalized thermograms recorded by the RE7S. The SO₂ peak maximizes at different temperatures and is associated with either CO₂ or HC depending on the sample and its richness in TSorg.

Fig. 6 – HI *vs* OI plot of the sediment from core C5 according to their sedimentary facies (see Figure 2 for symbols assignment). (A) All facies represented (N=160 samples), (B) Same figure excluding carbonate facies (w and mb), which affect the oxygen index (N=108 samples).

Fig. 7 – Similar occurrence of organic-rich laminated facies (grey and red dots) and carbonate nodules of diagenetic origin (white dots) in Dziani Dzaha

sediments and petroleum source-rocks from the Mahogany Zone of the Green River Formation (borehole PR15-7C, TotalEnergies) and the Orbagnoux laminites (N. Tribovillard, unpublished results).

Fig. 8 – HI vs OI van Krevelen pseudo-diagram of sediments from Dziani Dzaha (this study), Green River Fm (Tuttle, 1991) and Orbagnoux laminites (Tribovillard et al., 1992). The size of the symbols is proportional to wt.%TOC. The shift in the position of the Dziani Dzaha sediment samples towards lower HI and higher OI is explained by the immaturity of these recent sediments, still at the early diagenesis stage compared with >50 Ma old sedimentary rocks.

Fig. 9 – (A) Relationship between %Sorg and the hydrogen index (HI) of sediments from Dziani Dzaha, according to their sedimentary facies (see Figure 2 for symbols assignment), (B) van Krevelen pseudo-diagram of sediments from Dziani Dzaha with symbol size proportional to sulfur index (in mg S/g TOC).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Journal Pre-proofs

Figure1

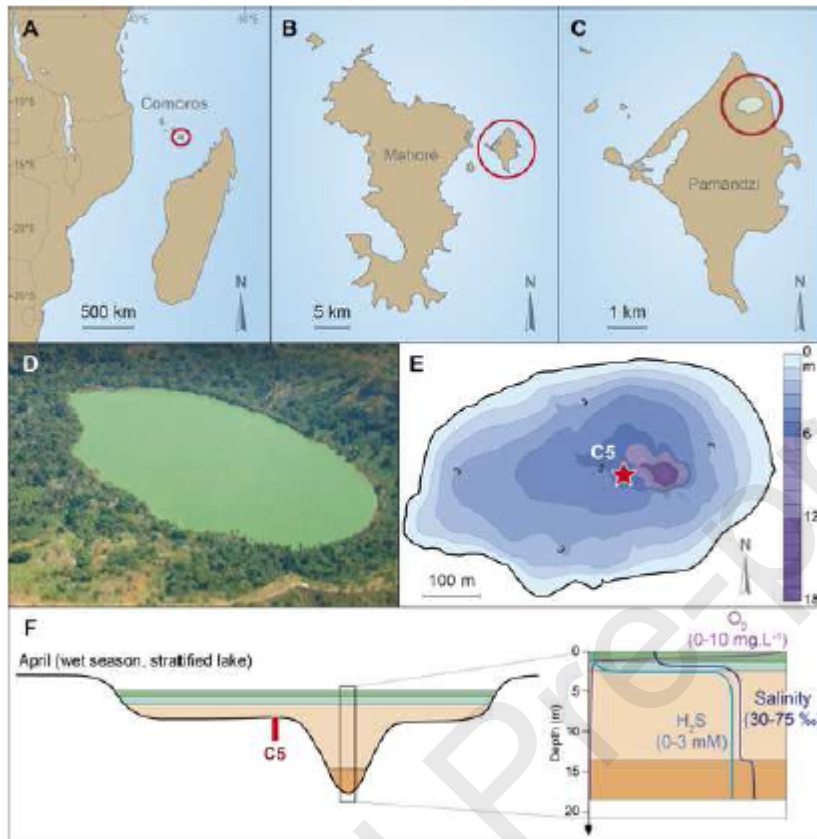
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Figure 2

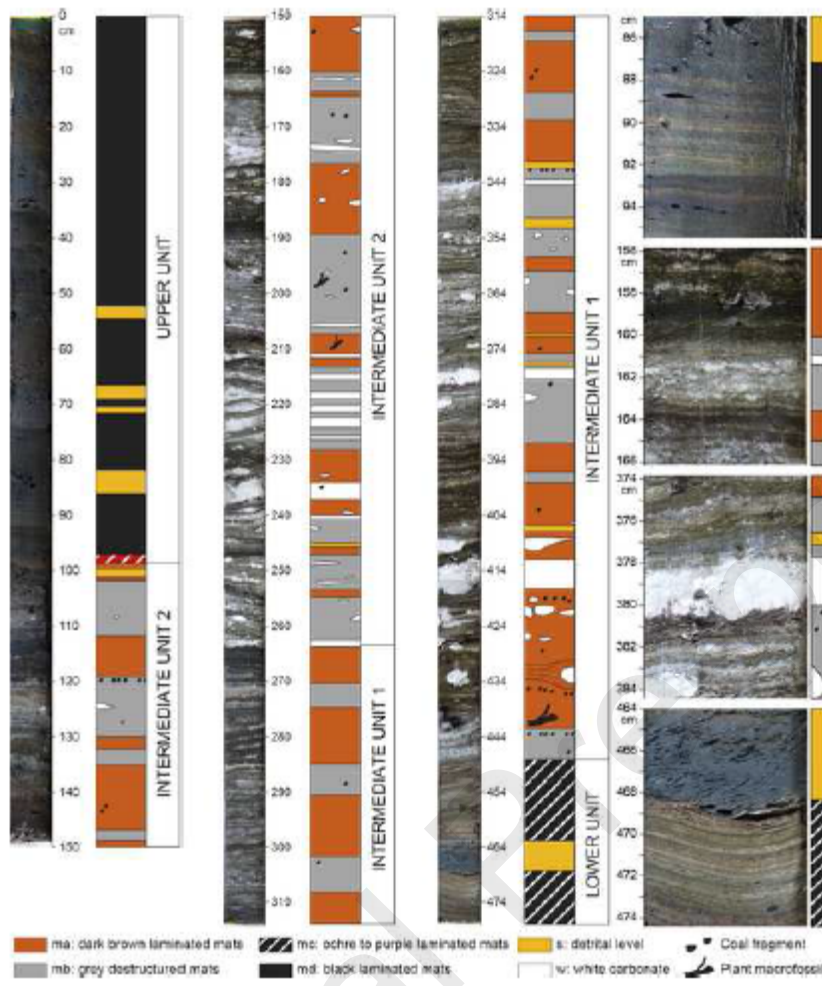
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Figure3

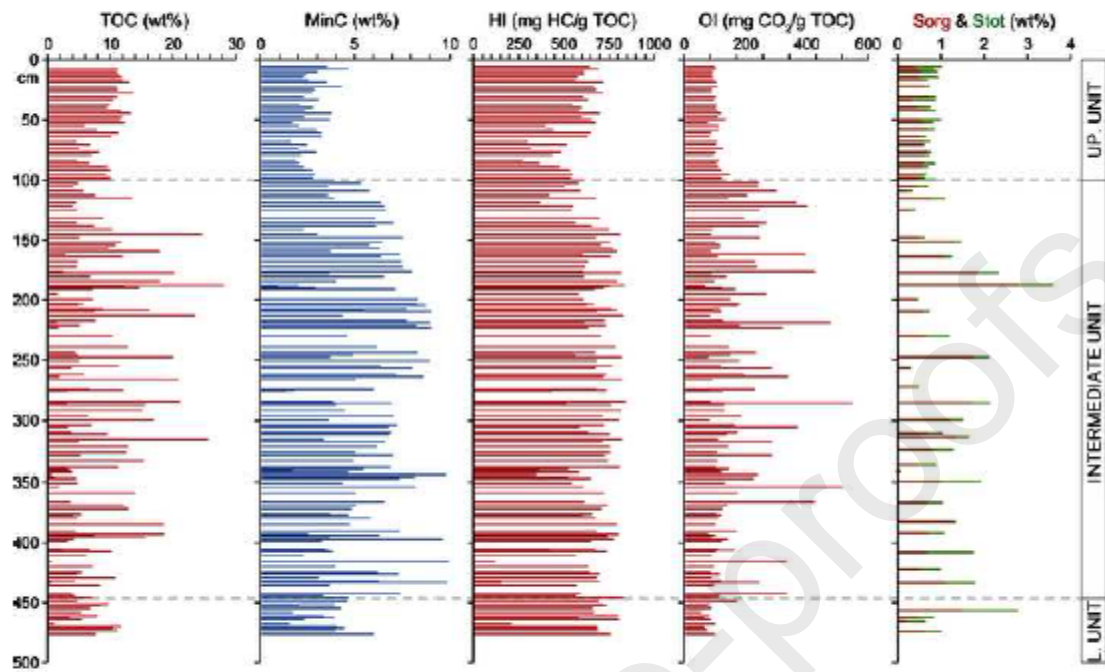
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Figure4

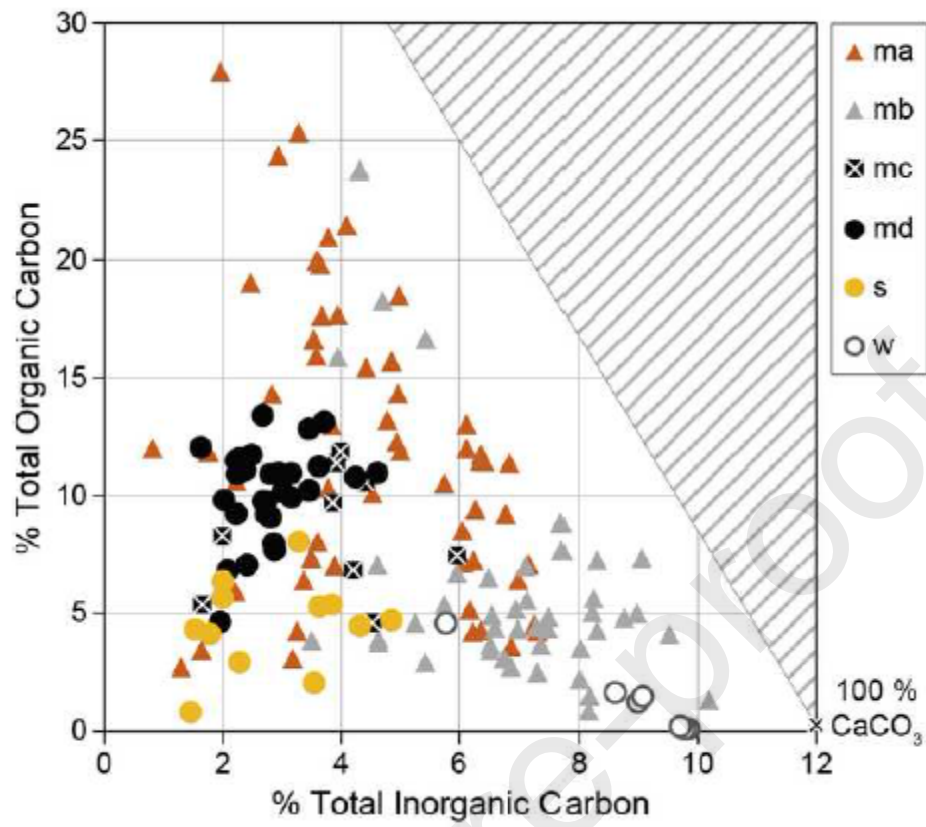
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Figure6

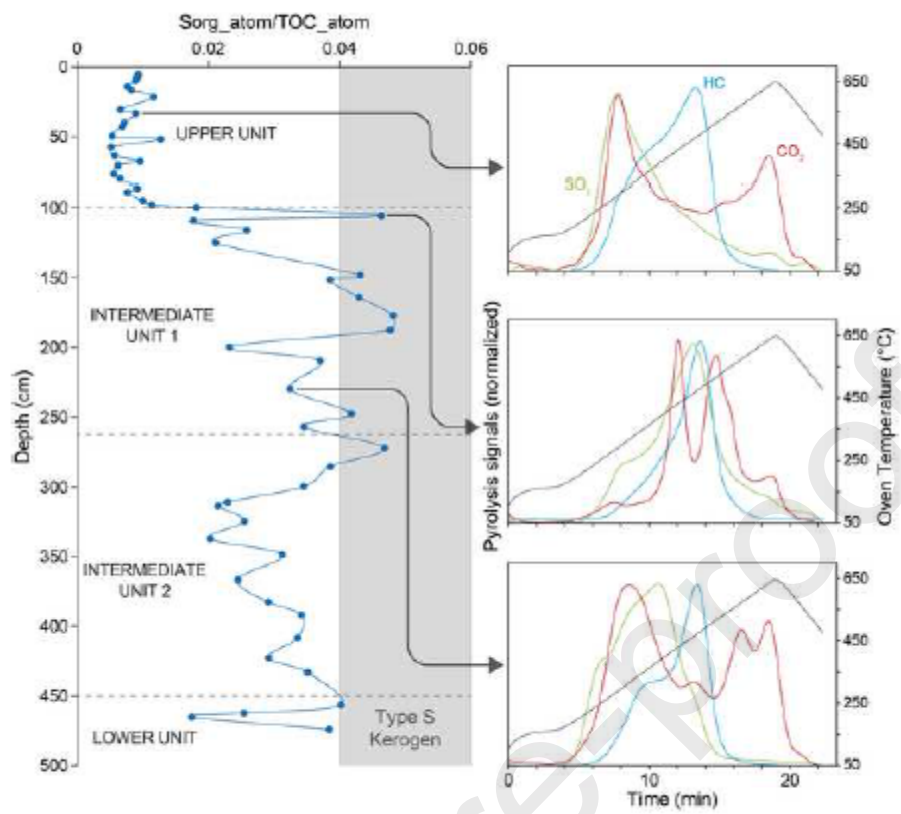
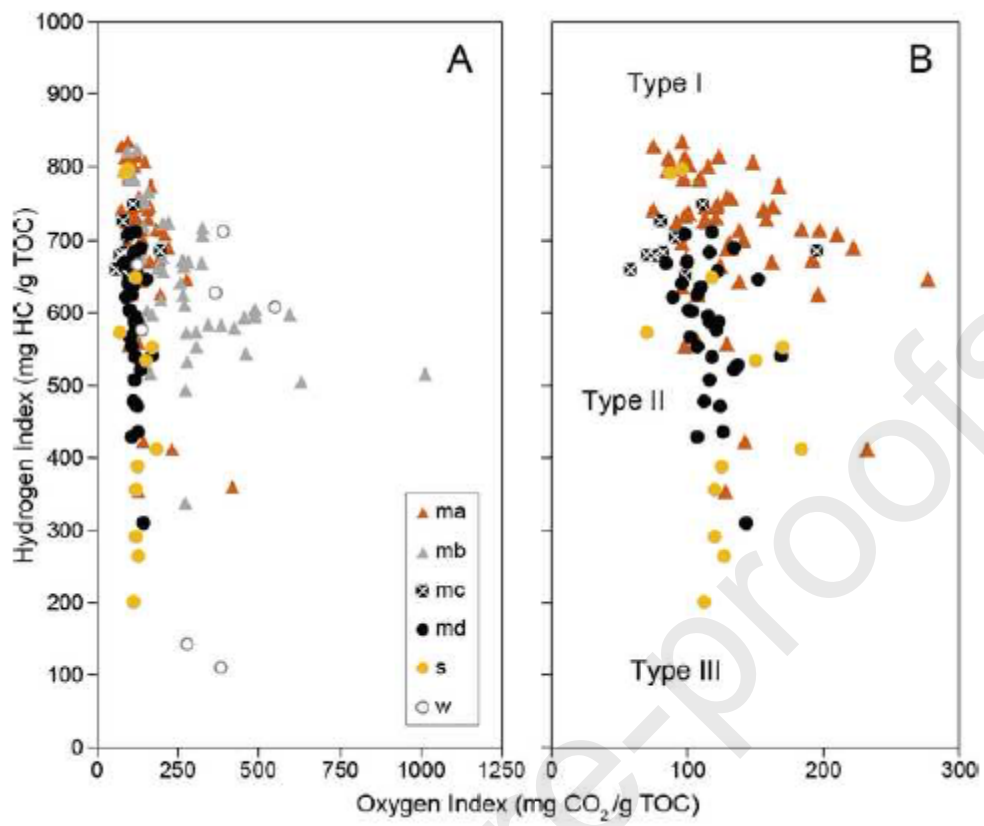
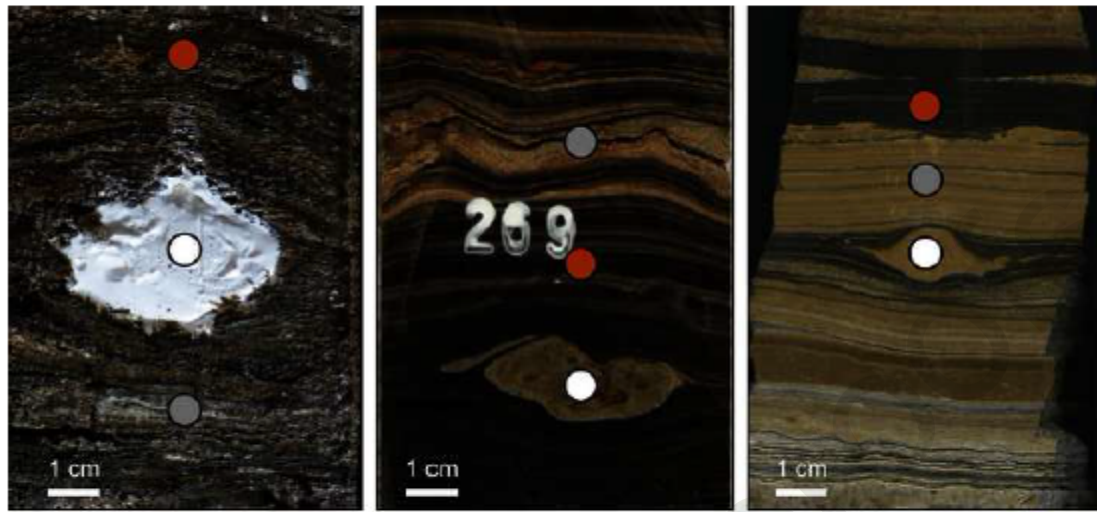
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Figure6

[Click here to access/download;Figure;Figure_6.jpg](#)



Lake Dziani Dzaha
(< 7,000 yrs)

Green River Shales Fm
(49 million yrs)

Orbagnoux Laminites
(153 million yrs)

Journal Pre-proof

Figure 8

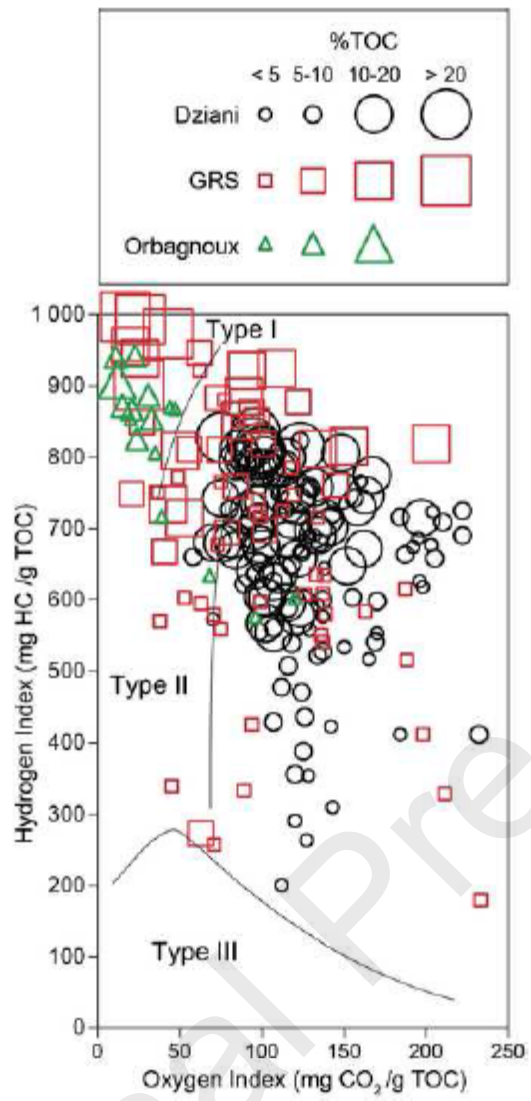
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Figure9

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