

Opening up a window into ecosystems with Ediacara-type organisms: preservation of molecular fossils in the Khatyspyt Lagerstätte (Arctic Siberia)

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Abstract The Khatyspyt Formation in Arctic Siberia is one of only two carbonate settings with Ediacara-type fossils. As a potential hydrocarbon source rock, it contains abundant molecular fossils that may help to expand our understanding of these ecosystems. Unfortunately, however, the molecular fossil record in geological materials is commonly biased by secondary processes such as thermal maturation, migration of bitumen compounds or surface contamination. In this study, we evaluate the preservation of molecular fossils in a sample from the Khatyspyt Formation and elucidate their paleobiological meaning. Our results reveal that the organic matter is remarkably immature (oil window maturity) and shows little effect of biodegradation. Petrographic observations, exterior/interior experiments, and the similarity between free bitumen, mineral-occluded bitumen, and kerogen pyrolysate point to the syngeneity of the molecular fossils. Abundant hopanes, cyclohexylalkanes, and methyl-branched alkanes indicate a bacterial source of the organic matter, likely including cyanobacteria and anaerobic bacteria. At the same time, a carbonaceous compression fossil

on top of the sample and abundant steranes indicate the presence of eukaryotes. The steranes show typical distributions for the Ediacaran (i.e., dominance of stigmastane). Given the exceptional preservation of the body fossils, trace fossils, and molecular fossils, the Khatyspyt Formation can be considered a fossil lagerstätte *sensu* Seilacher (1970: Begriff und Bedeutung der Fossil-Lagerstätten. *Neues Jahrbuch für Geologie und Paläontologie, Monatshefte*: 34–39). The combined analysis of sedimentary facies, paleontology (body, trace, and molecular fossils), and biogeochemistry will provide a more complete understanding of ecosystems with Ediacara-type fossils.

Keywords Ediacaran · Fossil lagerstätte · Ediacara-type organisms · Carbonaceous compression fossils · Molecular fossils · Catalytic hydrolysis (HyPy)

Kurzfassung Die Khatyspyt-Formation im arktischen Sibirien ist eines von lediglich zwei karbonatischen Ablagerungsräumen mit Ediacara-Fossilien. Gleichzeitig ist sie auch ein potentielles Kohlenwasserstoff-Muttergestein. Nicht zuletzt aufgrund der daher reichlich enthaltenen molekularen Fossilien birgt sie das Potential, unser Verständnis dieser Ökosysteme zu verbessern. Das Inventar an in geologischen Materialien erhaltenen molekularen Fossilien ist jedoch häufig durch diverse sekundäre Prozesse, wie z. B. thermische Maturierung, die sekundäre Migration von Kohlenwasserstoffen oder Oberflächen-Kontamination, verfälscht. In dieser Studie evaluieren wir die Erhaltung molekularer Fossilien in einer Probe der Khatyspyt-Formation und diskutieren ihre paläobiologische Bedeutung. Unsere Ergebnisse zeigen, dass das organische Material eine bemerkenswert niedrige Reife aufweist (Ölfenster) und kaum durch Biodegradation beeinflusst wurde. Petrographische Beobachtungen,

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Exterieur/Interieur-Experimente, und die Gleichheit zwischen freiem Bitumen, mineral-gebundenem Bitumen und Kerogen-Pyrolysat unterstreichen die Syngenität der enthaltenen molekularen Fossilien. Hopane, Cyclohexane, und and methylverzweigte Alkane deuten auf die Anwesenheit von Bakterien, wahrscheinlich inklusive Cyanobakterien und anaeroben Bakterien. Gleichzeitig belegen ein organisch erhaltenes Makrofossil auf der Probenoberseite und häufige Sterane, welche ein für das Ediacarium typisches Verteilungsmuster aufweisen (Dominanz von Stigmastan), die Existenz von Eukaryoten. Aufgrund der außergewöhnlichen Erhaltung von Körper-, Spuren- und molekularen Fossilien kann die Khatyspyt-Formation als Fossilagerstätte *sensu* Seilacher (1970: Begriff und Bedeutung der Fossil-Lagerstätten. *Neues Jahrbuch für Geologie und Paläontologie, Monatshefte*: 34–39) interpretiert werden. Die zukünftig gemeinschaftliche Analyse von sedimentärer Fazies, Paläontologie (Körper-, Spuren- und molekulare Fossilien) und Biogeochemie wird ein kompletteres Bild von Ökosystemen mit Ediacara-Fossilien ermöglichen.

Schlüsselwörter Ediacarium · Fossilagerstätte · Ediacara-Organismen · kohlig erhaltene Fossilien · molekulare Fossilien · katalytische Hydroxylyse (HyPy)

Introduction

The Phanerozoic began with a bang—the celebrated “Cambrian explosion” of ecological and morphological complexity (e.g., Erwin and Valentine 2013; Zhang et al. 2014, and references therein). Some million years earlier, the Earth was experiencing several major climatic perturbations, possibly to the extent of global glaciations (i.e., “Snowball Earth”; Kirschvink 1992; Hoffman et al. 1998). The Ediacaran (635–541 Ma) is sandwiched between these events and represents one of the most fundamental transitions in the biosphere (Knoll et al. 2004, 2006; Narbonne et al. 2012). The worldwide occurrence of macroscopic complex organisms, including the first undoubted fossil metazoans, is a particularly striking feature. Although these organisms are important with regard to the diversification of complex life on Earth, their biological affinities, paleobiology, and ecology are still enigmatic (e.g., Seilacher 1989, 1992; Seilacher et al. 2003; Narbonne 2005; Grazhdankin et al. 2008; Xiao and Laflamme 2009).

Efforts to gain a better understanding of Ediacaran ecosystems with macroscopic complex organisms continue to be hampered by taphonomic issues. Ediacara-type fossils (see, e.g., Billings 1872; Gürich 1930a, b, 1933 for early descriptions) are usually preserved as imprints in siliciclastic and volcanoclastic rocks (e.g., Narbonne 2005;

Callow and Brasier 2009). Consequently, biological details and biogeochemical signatures are commonly poorly preserved (Grazhdankin et al. 2008; Duda et al. 2014a). In the last few years, research has shown that carbonate settings are ideal for obtaining a more complete understanding, as the fossils retain high anatomical resolution (e.g., Xiao et al. 2005; Grazhdankin et al. 2008; Shen et al. 2009; Chen et al. 2014). Moreover, sedimentary features and biogeochemical proxies are also well preserved (Duda et al. 2014a, 2015). However, only two known carbonate settings with macroscopic complex organisms exist worldwide: the Shibantan Member of the Dengying Formation in South China and the Khatyspyt Formation in Arctic Siberia (Russia).

Ediacara-type macrofossils in the Khatyspyt Formation include arboreomorph frond structures, aspidellamorph and mawsonitomorph holdfast structures, rangeomorphs, palaeopascichnids, and microbial colonies (Sokolov and Fedonkin 1984; Vodanjuk 1989; Fedonkin 1990; Grazhdankin et al. 2008; Nagovitsin et al. 2015). The fossils are preserved by carbonate cementation (Grazhdankin et al. 2008), very similar to the Shibantan Member. Another feature is the ubiquitous presence of meniscate backfilled burrows (Rogov et al. 2012, 2013a, b). Similar structures have been observed in the Dengying Formation of South China, although interpreted as compressed annulated tubular structures (Shen et al. 2007; Dong et al. 2008). In contrast to the Shibantan Member, the Khatyspyt Formation also contains carbonaceous compression fossils (Grazhdankin et al. 2008). The Khatyspyt Formation can therefore be considered a fossil lagerstätte *sensu* Seilacher (1970), providing a unique, albeit not necessarily representative, window into ecosystems with Ediacara-type organisms.

Molecular fossils are produced by all types of organisms, and could offer additional insight into the structure and functioning of ecosystems with Ediacara-type organisms (cf. e.g., Treibs 1934, 1936; Eglinton and Calvin 1967; Brocks and Summons 2003). Unfortunately, however, the molecular fossil record of geological materials is commonly biased by secondary processes such as maturation, migration, and contamination (e.g., Brocks et al. 2003, 2008; Brocks 2011; Duda et al. 2014b; Mißbach et al. 2016). It has been demonstrated, for instance, that molecular fossil analyses on the Shibantan Member are problematic due to the high thermal maturity of the host rock and surface contamination in the outcrops (Duda et al. 2014a, b). Molecular fossil studies on less mature rocks from a similar setting, therefore, could provide a rare view of the geobiology of ecosystems with Ediacara-type fossils.

Neoproterozoic–Phanerozoic sedimentary rocks of Arctic Siberia are generally characterized by low thermal maturities (Kashirtsev 1988, 2003; Kontorovich et al. 2013). This is mainly due to the geological history of the region: strata from the eastern slope of the Olenek uplift,

for instance, have never been buried deeper than 1 km, as evidenced by vitrinite reflectance data and molecular fossils (Kashirtsev 1988, 2003; Kontorovich et al. 2013). The Khatyspyt Formation is considered a potential petroleum source rock, with total organic carbon (TOC) content of up to 4.19 % (Kontorovich et al. 2009; Kashirtsev et al. 2010; Parfenova et al. 2010, 2011), and thus may contain abundant molecular fossils (also “organic biomarkers” or “lipid biomarkers”). On the other hand, the preservation of molecular fossils may have been affected by regional processes such as penetration by diatremes.

In this study, we evaluate the preservation of molecular fossils in an outcrop sample from the Khatyspyt Formation that has been kept in storage cabinets at the Trofimuk Institute of Petroleum Geology and Geophysics in Novosibirsk (i.e., room temperature, no protection against potential secondary contamination) since sampling in 2009. First, we critically assess the thermal maturity, biodegradation, and syngeneity of molecular fossils in the hydrocarbon fractions of the extractable portion (i.e., bitumen) and non-extractable portion (i.e., kerogen) of the organic matter. We then elucidate the paleobiological meaning of the obtained data and discuss implications for future studies. Our results highlight the potential of the Khatyspyt Lagerstätte to provide a more complete understanding of ecosystems with Ediacara-type organisms through comprehensive geobiological studies.

Geological setting

The ca. 190-m-thick Khatyspyt Formation crops out in the Olenek uplift of the northeastern Siberian Platform in Arctic Siberia (Russia) (Fig. 1). It consists of alternating thin layers of limestone and shale, finely laminated thin- to

medium-bedded limestone, planar- to wavy-laminated thick-bedded limestone, and intraclastic dolomitized limestone (Knoll et al. 1995; Nagovitsin et al. 2015). It was deposited in distal, low-energy carbonate ramp environments below storm wave base (Knoll et al. 1995).

The Khatyspyt Formation lies between the Maastakh Formation and the Turkut Formation (Fig. 1). The Khatyspyt Formation, together with the overlying Turkut and Syhargalakh formations, is penetrated by diatremes (Rogov et al. 2015). A U–Pb zircon age of 543.9 ± 0.3 Ma for a tuff breccia from one of these diatremes provides an upper constraint on the deposition of the Khatyspyt and Turkut formations (Bowring et al. 1993; Knoll et al. 1995; Nagovitsin et al. 2015).

The Turkut Formation contains skeletal fossils of the anabaritid *Cambrotubulus decurvatus*, first appearing 1.4 m above the boundary with the Khatyspyt Formation. The Khatyspyt Formation itself contains the meniscate trace fossil *Nenoxites*, which is remarkably similar to *Helanoichnus helanensis*, *Shaanxilithes ningqiangensis*, *Palaeopascichnus minimus*, *Palaeopascichnus meniscatus*, and *Palaeopascichnus jiumenensis* from China (Shen et al. 2007; Dong et al. 2008). As the latter fossils are a potential biostratigraphic marker for the middle Dengying Formation in South China (Shen et al. 2007), the Khatyspyt Formation could thus be broadly coeval with the Shibantan Member.

Sample and methods

Sample characterization

One sample was investigated for microfacies and molecular fossils (Figs. 1, 2). Petrographic analysis was conducted using a Zeiss Stereo Discovery.V8 stereomicroscope

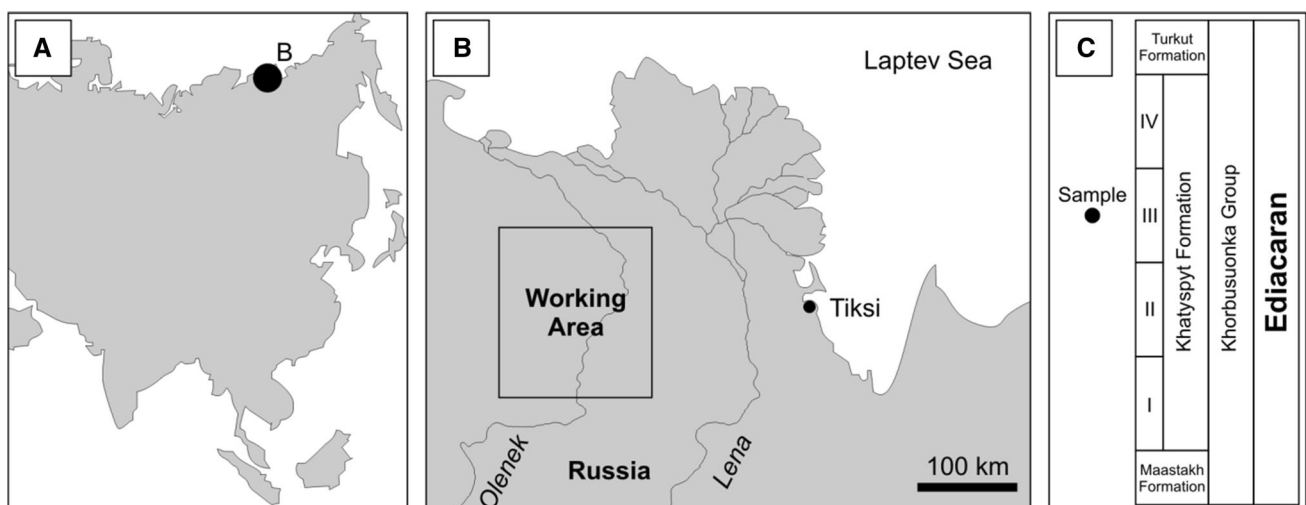


Fig. 1 Sample location (a, b) and stratigraphic overview of the Khatyspyt formation (c) (after Nagovitsin et al. 2015, modified)

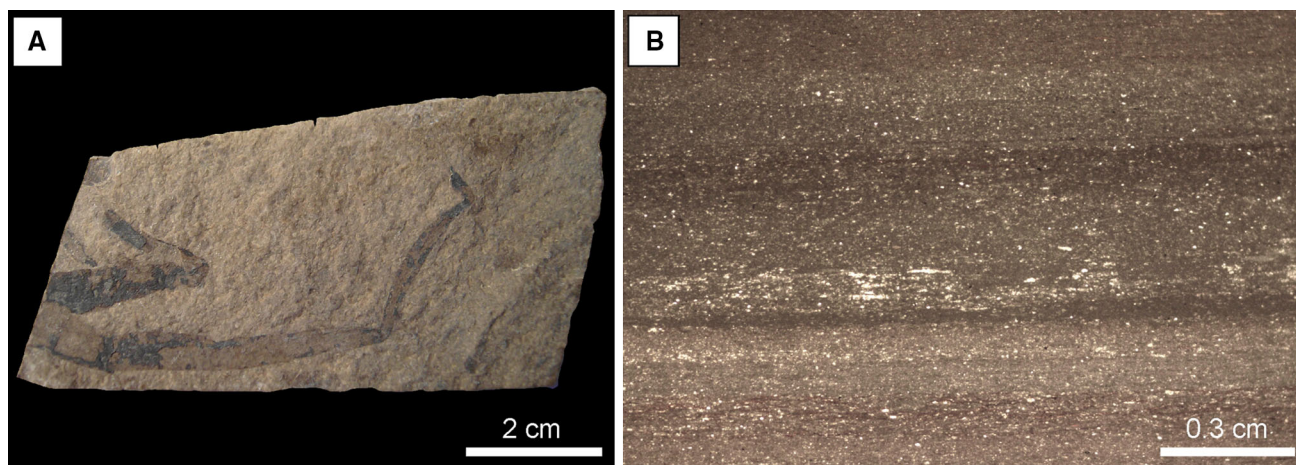


Fig. 2 Paleontological and petrographic characteristics of the analyzed sample. **a** Carbonaceous compression fossil on a parting surface. **b** Thin section showing layers of dense micritic carbonate. Please note the lack of cracks, fissures, pores, and voids

(transmitted and reflected light) linked to an AxioCam MRc5 5-megapixel camera. Bulk C/N/S analysis was performed using a HEKAtech Euro EA CNS analyzer. The total organic carbon (TOC) was determined by combustion infrared detection using a Leco RC612 analyzer.

For the analysis of molecular fossils, all materials were heated to 500 °C for 3 h and/or extensively rinsed with acetone. A laboratory blank prepared and analyzed in parallel was run to monitor laboratory contaminations.

For the analysis of the free bitumen (bitumen 1; see Hallmann et al. 2011), the sample was first separated into exterior and interior parts using a carefully pre-cleaned precision saw (Buehler IsoMet 1000). Both samples were then crushed and powdered using a pebble mill (Retsch MM 301). Ground sample material (ca. 30 g) was extracted with dichloromethane (DCM), DCM/*n*-hexane (1/1; v/v), and *n*-hexane using ultrasonication (20 min). For the analysis of mineral-occluded bitumen (bitumen 2; see Hallmann et al. 2011), the extraction residue of the interior part of the sample was decalcified with hydrochloric acid (HCl; 10 %) and then extracted as described for bitumen 1.

For the analysis of the kerogen, the decalcified extraction residue of the interior part of the sample was Soxhlet-extracted using DCM/MeOH (9/1; v/v; 24 h). The kerogen was then isolated using HCl and hydrofluoric acid (HF) (Durand 1980), and again Soxhlet-extracted with DCM/MeOH (9/1; v/v; 24 h). The isolated kerogen was pyrolyzed using a catalytic hydropyrolysis (HyPy) system from Strata Technology Ltd. (Nottingham, UK), following Snape et al. (1989) and Love et al. (1995). Briefly, samples were heated in the presence of a sulfided molybdenum catalyst (the ambient temperature was raised to 250 °C at 50 °C/min, and then from 250 to 500 °C at 8 °C/min) under hydrogen pressure of 150 bar at a flow rate of 5 L/

min. The hydrocarbons released from the isolated kerogen were trapped downstream on silica powder cooled with dry ice (see Meredith et al. 2004). The HyPy-pyrolysate was eluted from the silica trap with *n*-hexane.

All resulting isolates (bitumen 1, bitumen 2, and HyPy-pyrolysate) were desulfurized with activated copper and gently concentrated using a pre-cleaned rotary evaporator and N₂ to avoid a major loss of low-boiling compounds (Ahmed and George 2004). The isolates were then dried onto a small amount of silica gel and fractionated by column chromatography (1.5 cm in diameter, 8 cm in height; 7 g of dry silica gel). The saturated fraction (F1) was eluted with 27 mL *n*-hexane, the aromatic fraction (F2) with 32 mL *n*-hexane/DCM (1/1; v/v), and a polar residue (F3) with 40 mL DCM/MeOH (1/1; v/v).

Gas chromatography mass spectrometry (GC–MS) analyses were carried out with a Thermo Scientific Trace 1300 Series GC coupled to a Thermo Scientific Quantum XLS Ultra MS. The GC instrument was equipped with a capillary column (Phenomenex Zebron ZB–1MS/Phenomenex Zebron ZB-5, 30 m, 0.1 μm film thickness, inner diameter 0.25 mm). Fractions were injected into a splitless injector and transferred to the GC column at 270 °C. The carrier gas was He, at a flow rate of 1.5 mL/min. The GC oven temperature was ramped from 80 °C (1 min) to 310 °C at 5 °C min^{−1}, and held for 20 min. Electron ionization mass spectra were recorded in full scan mode at an electron energy of 70 eV with a mass range of *m/z* 50–600 and scan time of 0.42 s.

Pristane/phytane (Pr/Ph), Pr/*n*-C₁₇, and Ph/*n*-C₁₈ were calculated based on peak integrals in non-filtered total ion current chromatograms (TICs). The carbon preference indexes (CPI) as well as hopane- [22S/(22S + 22R); Ts/(Ts + Tm)] and sterane-based indexes [20S/(20S + 20R); ββ/(ββ + αα); diasterane/sterane ratios] were calculated

by integrating peaks in filtered chromatograms (m/z 85, 191, and 217, respectively) following established formulae (Bray and Evans 1961; Seifert and Moldowan 1978, 1980, 1986; Mello et al. 1987; Killips and Killips 2005; Peters et al. 2005).

Results

Sample characterization

The sample originates from an interval in which Ediacara-type fossils and carbonaceous compression fossils co-occur (8.86–12.29 m in section 0605; see Nagovitsin et al. 2015). The top of the sample contains a carbonaceous compression fossil (Fig. 2a). Thin-section microscopy reveals that the sample consists of layers of dense micritic carbonate (i.e., no pores or voids) without any evidence of biolamination (Fig. 2b). No cracks or fissures are observed.

The TOC content of the analyzed sample was 0.7 wt%. The sulfur and nitrogen content were relatively low (each were 0.02 wt%).

Molecular fossils

Alkanes and acyclic isoprenoids

The chromatograms exhibit no hump of an unresolved complex mixture of organic compounds (UCM) (Fig. 3).

In bitumen 1 and 2, the *n*-alkanes range from C_{11} to C_{36} , with a maximum at C_{17} (Fig. 3). In the HyPy-pyrolysate, the *n*-alkanes range from C_{11} to C_{35} , with a maximum at C_{15} (Fig. 3). A slight odd-over-even carbon number predominance (OEP) is observed for all analyzed fractions. The CPI_{24–34} index (Bray and Evans 1961) is 1.10 for bitumen 1, 1.06 for bitumen 2, and 1.06 for the HyPy-pyrolysate (Table 1; Fig. 3). Unlike the bitumen fractions, the HyPy-pyrolysate contains alkenes, ranging from C_{11} to C_{32} (Fig. 3).

Terminally methyl-branched alkanes (*iso*- and *anteiso*-isomers) are present in the range of C_{13} (i.e., methyl- C_{12}) to C_{27} (i.e., methyl- C_{26}) in bitumen fractions 1 and 2 and from C_{12} (i.e., methyl- C_{11}) to C_{27} (i.e., methyl- C_{26}) in the HyPy-pyrolysate (Fig. 3). In all cases, the terminally branched alkanes are most abundant in the range C_{15} (i.e., methyl- C_{14}) to C_{20} (i.e., methyl- C_{19}). Only small amounts of mid-chain methyl-branched alkanes are found in bitumen fractions 1 and 2 (Fig. 3).

Cyclohexylalkanes are prominent compounds in all fractions (Fig. 3), where they range from C_{11} to C_{26} , with C_{max} at C_{16} and C_{17} . In bitumen fractions 1 and 2, cyclohexylalkanes have an OEP in the range C_{21+} , while no OEP is present in the HyPy-pyrolysate.

Among the acyclic isoprenoids, 2,6,10-trimethyldecane (farnesane), 2,6,10-trimethyltridecane (TMTD), and 2,6,10-trimethylpentadecane (norpristane) occur in sizeable amounts in all fractions (Fig. 3). Furthermore, 2,6,10,14-tetramethylpentadecane (pristane, Pr) and 2,6,10,14-tetramethylhexadecane (phytane, Ph) are prominent in bitumen fractions 1 and 2 (Pr/*n*- C_{17} = 0.48 and 0.52, respectively; Ph/*n*- C_{18} = 0.60 and 0.61, respectively), while only very small amounts are present in the HyPy-pyrolysate (Pr/*n*- C_{17} = 0.08; Ph/*n*- C_{18} = 0.15) (Table 1; Fig. 3). The Pr/Ph ratio is higher in bitumen fractions 1 and 2 (Pr/Ph = 1.14 and 1.13, respectively) than in the HyPy-pyrolysate (Pr/Ph = 0.65) (Table 1).

Tricyclic triterpanes (cheilanthanes)

Cheilanthanes are observed only in trace amounts (bitumen fractions 1 and 2) or close to the detection limit (HyPy-pyrolysate).

Steranes

Both bitumen fractions and the HyPy-pyrolysate include cholestane (C_{27}), ergostane (C_{28}), and stigmastane (C_{29}) isomers ($\alpha\alpha$ S + R and $\alpha\beta$ S + R, respectively) (Fig. 4). Notably, the C_{27} and C_{28} steranes are present only in small amounts, whereas the C_{29} steranes represent the most prominent pseudohomologues (e.g., bitumen 1: $C_{27}:C_{28}:C_{29}$ = 20:17:64 %; HyPy-pyrolysate: $C_{27}:C_{28}:C_{29}$ = 18:13:69 %). C_{27} and C_{29} diasteranes (S + R) occur in traces in both bitumen fractions but could not be identified in the HyPy-pyrolysate. 4-Methyl stigmastane was found in all fractions (Fig. 4). Additionally, traces of 5 α (H)-pregnane and diginane ($\alpha\alpha\beta$) were identified in the bitumen fractions based on published spectra (Philp 1985; Requejo et al. 1997).

Hopanes

Hopanes in bitumen 1 and 2 include C_{27} (Ts and Tm), C_{29} (Ts, $\alpha\beta$ and $\beta\alpha$), C_{30} ($\alpha\beta$ and $\beta\alpha$), and the C_{31} – C_{35} isomers ($\alpha\beta$ and $\beta\alpha$, S + R, respectively) (Fig. 4). The HyPy-pyrolysate contains the same compounds except the C_{27} and C_{29} Ts isomers (Fig. 4). It further shows considerable amounts of hopenes. The most prominent of these compounds were tentatively identified according to published mass spectra (Summons and Jahnke 1992; Meredith et al. 2008) as the C_{27} 22,29,30-trisnorhop-17(21)-ene, the C_{30} hop-17(21)-ene (co-eluting with C_{30} hopane), the C_{30} 17 α (H)-hop-20(21)-ene, the C_{30} 17 β (H)-hop-20(21)-ene, and the C_{31} 17 α (H)-homohop-20(21)-ene (Fig. 3).

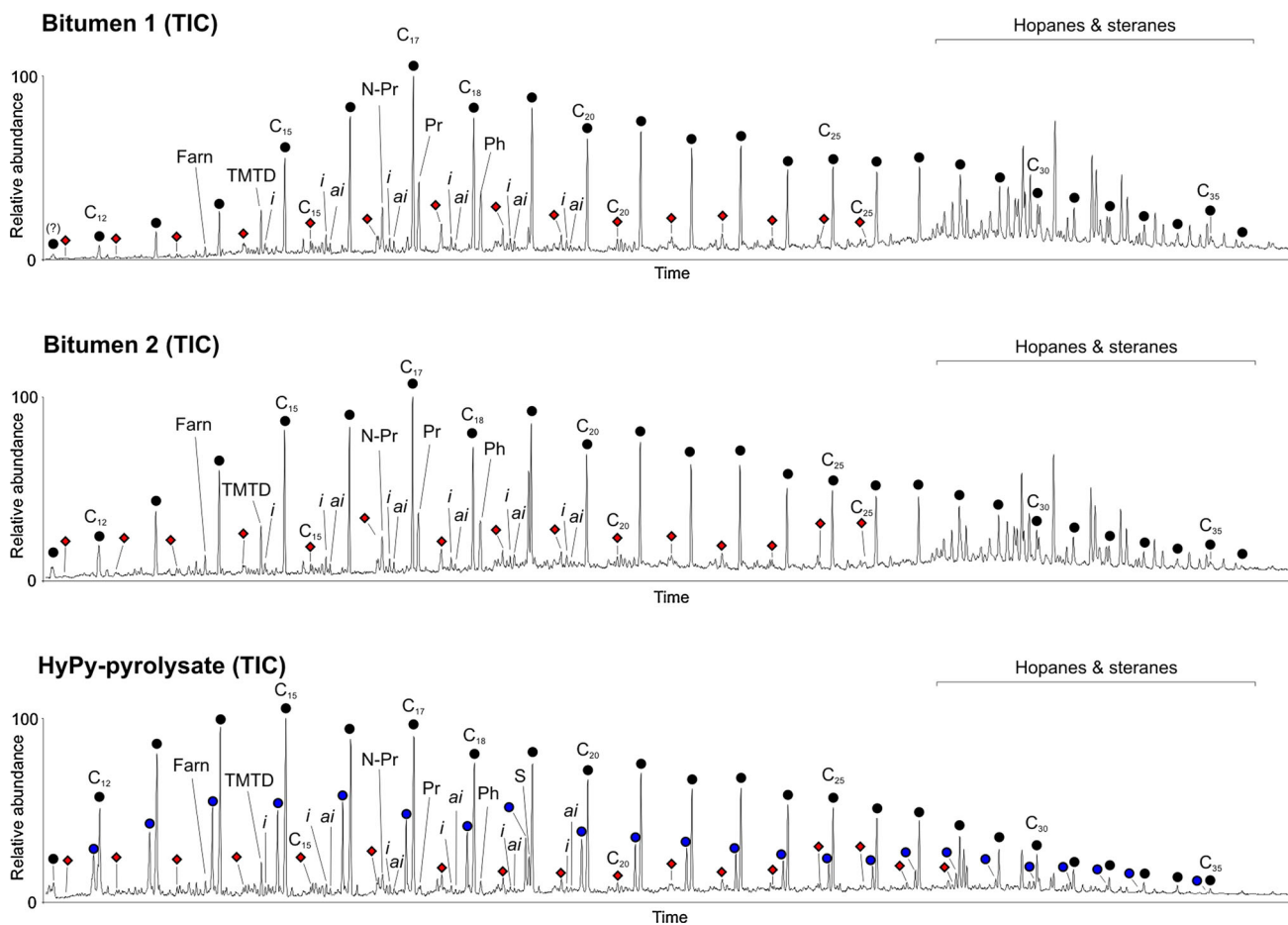


Fig. 3 Chromatograms (total ion current; TIC) of the hydrocarbon fractions from bitumen 1, bitumen 2, and the HyPy-pyrolysate. *Black circles* n-alkanes, *blue circles* n-alkenes, *red diamonds*

cyclohexylalkanes, *Farn* farnesane, *TMTD* 2,6,10 trimethyltridecane, *N-Pr* norpristane, *Pr* pristane, *Ph* phytane, *i* iso-alkanes, *ai* anteiso-alkanes

Discussion

Maturity, biodegradation, and syngeneity of molecular fossils

The CPI values around unity calculated for bitumen fractions 1 and 2 (1.10 and 1.06, respectively; Table 1) indicate that the organic matter is generally thermally mature (Bray and Evans 1961). This is further supported by C₃₁ hopane [22S/(22S + 22R); bitumen 1 = 0.55; bitumen 2 = 0.57; Table 1] and C₂₉ sterane indexes [20S/(20S + 20R); bitumen 1 = 0.48; bitumen 2 = 0.47; ββ/(ββ + αα); bitumen 1 = 0.26; bitumen 2 = 0.28; Table 1], which all suggest early oil window maturity (Seifert and Moldowan 1980, 1986; Killups and Killups 2005; Peters et al. 2005). Low C₂₇ (bitumen 1 = 0.15; bitumen 2 = 0.18; Table 1) and C₂₉ diasterane/sterane ratios (bitumen 1 = 0.08; bitumen 2 = 0.08; Table 1) are also in line with a carbonate-dominated source rock and early oil window maturity (Peters et al. 2005). This estimate agrees with other reports [e.g., 20S/(20S + 20R) sterane stereoisomer indexes of ca.

0.5, Ts/Tm values averaging at 0.58; Kontorovich et al. 2009; see also Parfenova et al. 2010, 2011] and the age of the host rock, although analysis of a larger sample set would be necessary for a more precise maturity evaluation.

The lack of a UCM indicates that the impact of biodegradation is notably low (Fig. 3) (Peters et al. 2005). Biodegradation is controlled by a variety of factors, including temperature, the availability of water, and rock characteristics (e.g., lithology, grain size, porosity, and permeability) (Peters et al. 2005). The generally dense micritic matrix and the virtual absence of pores and fissures in the analyzed sample probably limited the availability of electron acceptors for hydrocarbon-degrading microbes. Furthermore, surface biodegradation during outcrop exposure in recent times was probably hampered by the cold Arctic climate, which prevented the penetration of liquid water into the rock and limited the delivery of nutrients to potential organotrophic microbes.

In addition to biodegradation, the migration of younger hydrocarbons into the rock formation of interest can lead to overprinting of the syngenetic molecular fossil inventory.

Table 1 Selected indexes calculated for the hydrocarbon fractions of bitumen 1, bitumen 2, and the HyPy-pyrolysate

Index	Bitumen 1	Bitumen 2	HyPy
CPI	1.10	1.06	1.06
Pr/Ph	1.14	1.13	0.65
Pr/ <i>n</i> -C ₁₇	0.48	0.52	0.08
Pr/ <i>n</i> -C ₁₈	1.65	1.64	6.55
22S/(22S + 22R) hopane (C ₃₁)	0.55	0.57	0.53
22S/(22S + 22R) hopane (C ₃₂)	0.60	0.62	0.52
Ts/(Ts + Tm)	0.39	0.37	–
20S/(20S + 20R) sterane (C ₂₉)	0.48	0.47	0.44
ββ/(ββ + αα) sterane (C ₂₉)	0.26	0.28	0.25
Diasteranes/steranes (C ₂₇)	0.15	0.18	–
Diasteranes/steranes (C ₂₉)	0.08	0.08	–
Sterane/hopane	0.37	0.32	0.16

Pristane/phytane (Pr/Ph), Pr/*n*-C₁₇, and Ph/*n*-C₁₈ were calculated based on peak integrals in non-filtered TICs. The carbon preference indexes (CPI) as well as hopane- [22S/(22S + 22R); Ts/(Ts + Tm)] and sterane-based indexes [20S/(20S + 20R); ββ/(ββ + αα); diasterane/sterane ratios] were calculated by integrating peaks in filtered chromatograms (*m/z* 85, 191, and 217, respectively) following established formulae (Bray and Evans 1961; Seifert and Moldowan 1978, 1980, 1986; Mello et al. 1987; Killips and Killips 2005; Peters et al. 2005)

However, the dense micritic matrix and the absence of pores and fissures in the analyzed rock argue against a major emplacement of younger fluids. The presence of alkenes and hopenes in the HyPy-product generally indicates that these compounds have been covalently bound to the kerogen, although the exact formation pathway of the identified hopenes is still ambiguous (original constituents of the kerogen vs. artificial formation from other hopenes during hydrolysis; see Meredith et al. 2008). Further, the organic geochemical indexes for the HyPy-pyrolysate [e.g., CPI = 1.06; C₃₁ hopane 22S/(22S + 22R) = 0.53; C₂₉ sterane 20S/(20S + 20R) = 0.44; Table 1] are slightly lower than those of the bitumen fractions and thus indicate lower maturities of the kerogen-bound moieties. Likewise, the presence of Ts and Tm in both bitumen fractions [Ts/(Ts + Tm); bitumen 1 = 0.39; bitumen 2 = 0.37; Table 1], along with the absence of Ts in the HyPy-pyrolysate, is consistent with a lower maturity of the HyPy product (cf. Bishop et al. 1998; Peters et al. 2005). Such an offset between the bitumen and the corresponding kerogen is typically observed in HyPy studies of source rocks (Love et al. 1995, 2008; Bishop et al. 1998), and supports a syngenetic origin of the bitumen from the Khatyspyt Formation.

A further potential problem that needs to be excluded is contamination during exposure in the outcrop, transport, storage, and saw cutting (Brocks et al. 2003, 2008; Brocks

2011; Schintie and Brocks 2014; Duda et al. 2014b; French et al. 2015). In addition to the use of comprehensive laboratory blanks, contamination was assessed by comparing bitumen 1 vs. bitumen 2 (see Hallmann et al. 2011) and conducting exterior/interior (E/I) experiments (see Brocks et al. 2008, 2015; Brocks 2011). In the analyzed sample, the bitumen fractions 1 and 2 are virtually identical (Fig. 3), indicating no difference between the free and mineral-occluded compounds. The observed E/I ratios of *n*-alkanes, hopanes, and steranes range between 0.9 and 1.0 (Table 2), which lends additional support to an in situ origin of the molecular fossils. The observed OEP of cyclohexylalkanes C₂₁₊ in the bitumen fractions 1 and 2 could indicate a slight contamination by polyethylene byproducts (Grosjean and Logan 2007; Brocks et al. 2008), especially as there is no such OEP in these compounds in the HyPy-pyrolysate. Apart from that, however, contamination appears to be very minor in all fractions studied.

Paleobiology

Although *n*-alkanes are ubiquitous in the biosphere and are therefore not specific (e.g., Brocks and Summons 2003), the observed predominance of short-chain *n*-alkanes with maxima at *n*-C₁₇ (bitumen fractions 1 and 2) and *n*-C₁₅ (HyPy-pyrolysate) is generally in line with a bacterial or algal source (e.g., Blumer et al. 1971; Hoffmann et al. 1987; Peters et al. 2005). Pristane and phytane, along with the other short-chain isoprenoids observed, are most commonly considered to derive from the phytol side chain of chlorophyll *a* (e.g., Tissot and Welte 1984; Philp 1985; Peters et al. 2005, and references therein). This indicates an abundance of photoautotrophs, namely cyanobacteria and algae, in the Khatyspyt environment.

Abundant hopanes indicate the importance of bacterial organic matter sources (e.g., Rohmer et al. 1984; Peters et al. 2005). The presence of mid-chain branched alkanes may point to direct contributions from cyanobacteria (e.g., Gelpi et al. 1970; Shiea et al. 1990; Peters et al. 2005). Terminally methyl-branched alkanes (*iso*- and *anteiso*-isomers) in fossil samples are often considered as being derived from *iso*- and *anteiso*-fatty acids. These compounds are widespread in anaerobic bacteria, including sulfate-reducing bacteria (see Kaneda 1991, and references therein). However, the lack of distinctive isomer preferences of methyl-branched alkanes could also reflect formation during catagenesis (Kissin 1987). Cyclohexylalkanes may derive from cyclohexyl fatty acids, which occur in various bacteria (De Rosa et al. 1971; Suzuki et al. 1981). It is not clear whether these compounds could also represent diagenetic products of straight-chain fatty acids or polyaldehydes (e.g., Rubinstein and Strausz 1979; Gelin et al. 1994). Taken together, however, the presence of both

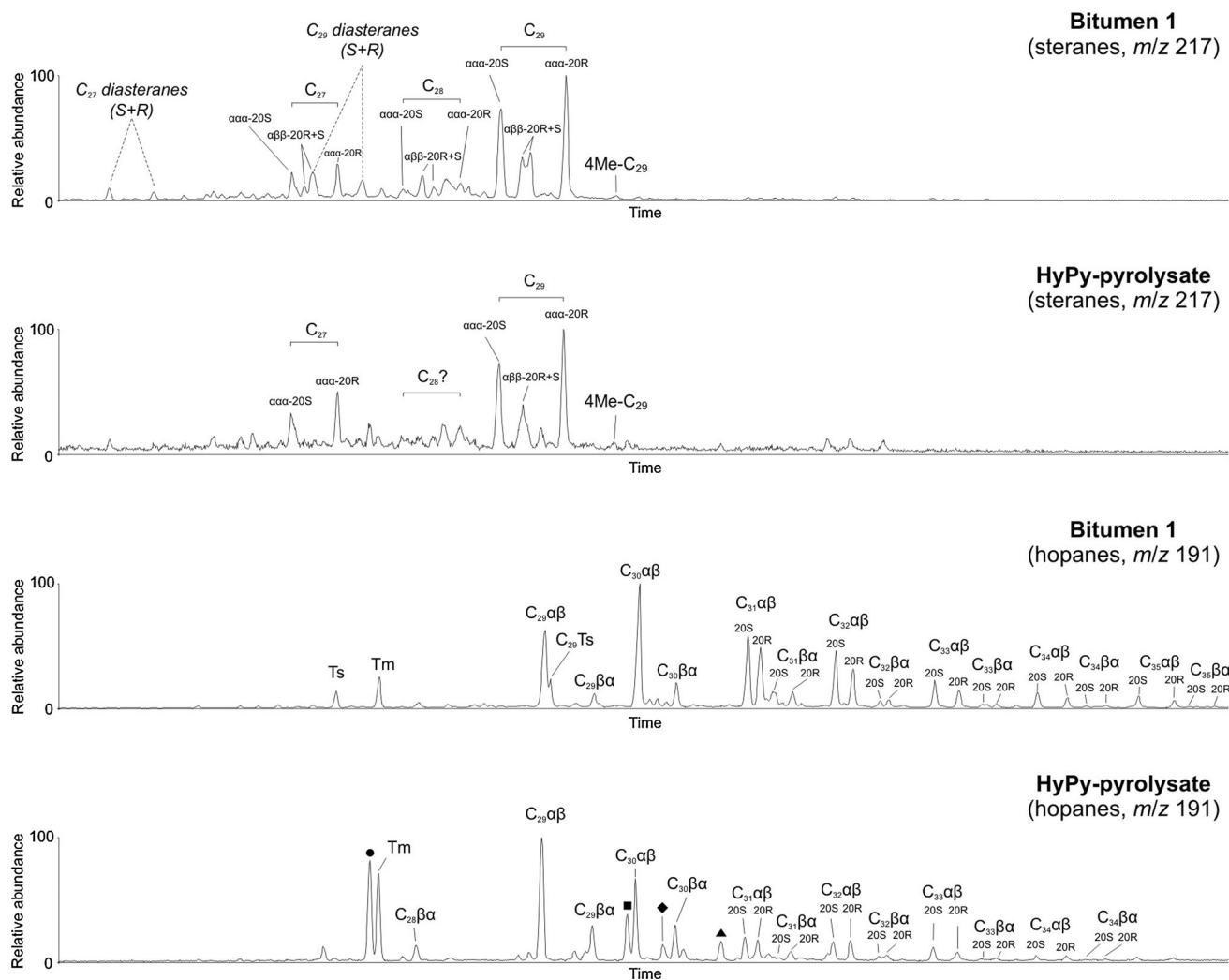


Fig. 4 Filtered chromatograms of the hydrocarbon fractions from bitumen 1 and the HyPy-pyrollysate (m/z 217 for steranes; m/z 191 for hopanes). *Circle* 22,29,30-trisnorhop-17(21)-ene, *square* 17- α (H)-hop-20(21)-ene, *rhombus* 17- β (H)-hop-20(21)-ene, *triangle* 17 α (H)-

homohop-20(21)-ene, *Ts* and *Tm* trisnorhopanes (C_{27}), 4Me- C_{29} 4-methyl stigmastane (tentatively identified). Please note that the hop-17(21)-ene co-elutes with the C_{30} hopane

autotrophic and heterotrophic bacteria in the studied paleo-environment is likely.

The carbonaceous compression fossil on top of the sample (cf. Grazhdankin et al. 2008) and the abundance of steranes (e.g., Volkman 2003; Peters et al. 2005) indicate the presence of eukaryotes. The observed preference for stigmastane (C_{29}) over cholestane (C_{27}) and ergostane (C_{28}) is typical for the Ediacaran (Knoll et al. 2007; Brocks et al. 2015). Examples include other Siberian platform oils (e.g., Kontorovich et al. 1981; Fowler and Douglas 1987; Summons and Powell 1992; Aref'yev et al. 1993; Kashirtsev et al. 2010; Kelly et al. 2011) and Ediacaran rocks from the South Oman Salt Basin (e.g., Grantham 1986; Grantham et al. 1990; Grosjean et al. 2009). This phenomenon is commonly explained by abundant chlorophyte varieties in Ediacaran ecosystems (Grantham and

Wakefield 1988; Summons and Powell 1992; Knoll et al. 2007). Likewise, cheilanthanes may originate from eukaryotic algal lipids, though their exact biological source is still unknown (Brocks and Summons 2003; Brocks and Pearson 2005). Together with the steranes, these compounds indicate that eukaryotic primary producers were abundant in the Khatyspyt ecosystem, which is in good accordance with the most likely chlorophyll-derived molecular fossils pristane and phytane (see above).

Sterane/hopane ratios (Ster/Hop) are commonly used to evaluate the relative importance of bacteria vs. eukaryotes in past environments (e.g., Peters et al. 2005). Ster/Hop ratios in the analyzed sample are well below 1 (bitumen 1 = 0.37; bitumen 2 = 0.32; HyPy-pyrollysate = 0.16; Table 1), suggesting greater contributions from bacteria. However, low Ster/Hop ratios of Precambrian organic

Table 2 Exterior/interior (E/I) ratios for selected molecular fossils of the hydrocarbon fractions

Molecular fossils	E/I
<i>n</i> -C ₁₁ to <i>n</i> -C ₃₄ (mean)	1.0
Norhopane (C ₂₉)	0.9
C ₃₀ hopanes	1.0
C ₃₁ hopanes	1.0
C ₃₂ hopanes	0.9
C ₂₇ steranes	1.0
C ₂₉ steranes	1.0

All ratios were calculated by integrating peaks in filtered chromatograms (*m/z* 85, 191, and 217, respectively)

Norhopane (C₂₉) and C₃₀ hopane include the $\alpha\beta$ isomers. C₃₁ and C₃₂ hopanes include $\alpha\beta$ (S + R) isomers. C₂₇ and C₂₉ steranes include $\alpha\alpha\alpha$ (S + R) and $\alpha\beta\beta$ (S + R) isomers

matter could also be due to benthic microbial mats that impact the transfer of organic compounds from the water column to the sediment (i.e., the “mat-seal effect”; Pawlowska et al. 2012; Blumenberg et al. 2015). Furthermore, the low Ster/Hop ratios could be due at least in part to the greater thermal stability of hopanes compared to steranes (“thermal taphonomy”) (Requejo 1994; Norgate et al. 1999; Mißbach et al. 2016). Molecular fossil analyses of different biofacies and/or taphofacies of the Khatyspyt Formation could help to determine the influence of these taphonomic processes in greater detail (see “[Implications for future studies](#)”).

Implications for future studies

Given the exceptional preservation of body fossils (Grazhdankin et al. 2008), trace fossils (Rogov et al. 2012, 2013a, b), and molecular fossils (this study), the Khatyspyt Formation can certainly be considered a fossil lagerstätte sensu Seilacher (1970). Although fossil lagerstätten provide a unique window into past ecosystems, they are not necessarily representative, as they were formed under rather unusual conditions (Seilacher 1970). The extent to which the Khatyspyt Lagerstätte is similar to other settings with Ediacara-type fossils has yet to be demonstrated. This could be achieved by a critical comparison of different settings with respect to the geological framework, sedimentary facies, paleontological features, and biogeochemical characteristics.

The Shibantan Member in South China is particularly suitable for such a comparison. Both the Khatyspyt Formation and the Shibantan Member consist of bituminous limestones and comprise somewhat similar Ediacara-type

fossils (cf. Sun 1986; Xiao et al. 2005; Grazhdankin et al. 2008; Shen et al. 2009; Chen et al. 2014; Duda et al. 2014a, 2015). Unlike the Shibantan Member, however, the Khatyspyt Formation also contains carbonaceous compression fossils (Grazhdankin et al. 2008) and vertical bioturbation (Rogov et al. 2012, 2013a, b). Detailed comparisons of the Khatyspyt Formation and the Shibantan Member will enable scientists to distinguish ecological and taphonomic influences on the respective fossil records.

It has been proposed that the Khatyspyt Formation and the Shibantan Member were at least temporarily stratified, with an anoxic lower and an oxygenated upper water layer (Dzik 2003; Duda et al. 2014a; Kaufman et al. 2014). However, no molecular fossils indicative of stratification (e.g., gammacerane; Sinninghe Damsté et al. 1995), anoxic conditions (e.g., 28,30-bisnorhopane and 25,28,30-trisnorhopane; Peters et al. 2005), or even photic zone anoxia (e.g., isorenieratane or okenane; Koopmans et al. 1996; Brocks and Schaeffer 2008, respectively) were observed in the sample from the Khatyspyt Formation. This may support earlier suggestions of heterogeneous and fluctuating redox conditions in the Khatyspyt and Shibantan environments (Duda et al. 2014a; Kaufman et al. 2014). It remains to be determined, however, whether the analyzed sample is representative of the entire Khatyspyt Lagerstätte. In future studies, more detailed investigations of molecular fossils will improve our understanding of how ecological conditions in these Ediacaran environments fluctuated in time and space.

Conclusions

Organic matter in the Khatyspyt Formation is remarkably immature (oil window maturity) and almost unaffected by biodegradation. Petrographic observations, exterior/interior (E/I) experiments, and the similarity between free bitumen, mineral-occluded bitumen, and HyPy-pyrolysate point to syngeneity of the observed molecular fossils. Abundant hopanes, cyclohexylalkanes, and methyl-branched alkanes indicate a bacterial source of the organic matter, likely including cyanobacteria and anaerobic bacteria. At the same time, the carbonaceous compression fossil on top of the sample and the ample steranes indicate a high abundance of eukaryotes. The steranes show typical distributions for the Ediacaran (i.e., dominance of stigmastane). No molecular fossils indicative of stratification, anoxic conditions, or photic zone anoxia were observed. Given the exceptional preservation of body fossils, trace fossils, and molecular fossils, the Khatyspyt Formation can be considered a fossil lagerstätte sensu Seilacher (1970). The combined analysis of sedimentary facies, paleontology

(body, trace, and molecular fossils), and biogeochemistry in future studies will enable a more complete understanding of the Khatyspyt Lagerstätte and will improve our understanding of how ecological conditions fluctuated in time and space.

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