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Assessing Possibilities and Limitations for Biomarker Analyses on Outcrop Samples: A Case Study on Carbonates of the Shibantan Member (Ediacaran Period, Dengying Formation, South China)

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Abstract: The Shibantan Member (Dengying Formation, South China) represents one of only two carbonate settings with Ediacara-type organisms and offers a rare opportunity to study the biogeochemistry of these ecosystems. To evaluate possibilities and limitations for future biomarker studies on fossil-bearing outcrop samples of the Shibantan Member, we analysed the spatial distribution of hydrocarbons in extractable organic matter (i.e. bitumen) on a millimetre scale. Our study demonstrates that the sample and most likely also other rocks from the same setting are contaminated with petroleum-derived compounds that bear the potential for erroneous interpretations in palaeo-reconstructions. The contamination was revealed by distribution patterns and amounts of extractable *n*-alkanes and acyclic isoprenoids. The contamination is linked to the external weathering surfaces but also to cracks within the rock, and the extent most likely depends on concentration gradients between these contamination sources. Here we show that contamination can successfully be distinguished from syngenetic signals obtained from non-extractable organic matter (i.e. kerogen) using catalytic hydropyrolysis (HyPy). However, we observed that decalcification is necessary to achieve sufficient yields of kerogen-bound hydrocarbons and to avoid artificial alteration of the biomarker signals due to matrix effects.

Key words: Ediacaran, biomarkers, contamination, syngeneity, slice-experiments, catalytic hydropyrolysis (HyPy)

1 Introduction

Contamination and thus introduction of non-syngenetic information into a rock is a serious problem for biomarker studies based on extractable hydrocarbons. In addition to the natural migration of petroleum-derived fluids into the geological formation of interest, there are numerous further possibilities for organic contamination of rock samples during exposure in the outcrop, sampling (e.g. drilling), storage, preparation, or analyses. Sources of contaminants range from immature organic compounds (e.g. organic material derived from ubiquitous higher land-plants or epi-/endolithic microorganisms) to mature organic material (e.g. petroleum-derived fluids). Regardless of the source, such naturally or artificially introduced compounds potentially obscure syngenetic hydrocarbons within a sample and are thus problematic with respect to palaeoenvironmental interpretations (e.g. Eigenbrode, 2004; Sherman et al., 2007; Brocks et al., 2008; Brocks, 2011). The contamination problem is generally addressed by strictly adhering to well established laboratory protocols for cutting, cleaning, crushing and extraction (Sherman et al., 2007). Cutting off the outer layer of a rock sample and subsequent separate analyses of the internal and external parts (i.e. interior vs. exterior experiments; cf. Brocks et al., 2008) is commonly used to identify and to eliminate possible surficial contaminants (Sherman et al., 2007; Brocks et al., 2008). However, contamination is not necessarily restricted to the external weathering surfaces of rock samples but can also be linked to internal surfaces (e.g. cracks). Both contamination paths can be evaluated by measuring concentration gradients of hydrocarbons on a millimetre-scale (i.e. slice-extraction experiments; Brocks et al., 2008; Brocks, 2011). Micro-ablation-technique was

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suggested as potential tool to remove contaminated surfaces and to conduct interior vs. exterior experiments on a sub-millimetre scale, enabling to analyse small sample fragments remaining after exposure of internal crack-surfaces (Jarrett et al., 2013). Other useful strategies include an evaluation of the bitumen maturity with regard to the thermal history of the host rock, as well as comparisons of stable carbon isotope ratios and molecular characteristics of extractable (i.e. bitumen) versus macromolecular organic matter (i.e. kerogen) (cf. e.g. Brocks et al., 2003a, b; Eigenbrode, 2004; Sherman et al., 2007; Rasmussen et al., 2008). The immobile kerogen fraction is commonly considered to be less prone to contamination and molecular structures that are covalently bound to the kerogen matrix are likely syngenetic (cf. Brocks et al., 2003b). Sequential chemical degradation (e.g. Michaelis and Albrecht, 1979; Boucher et al., 1991; Richnow et al., 1992) as well as analytical pyrolysis (e.g. Py-GC/MS; e.g. Larter and Horsfield, 1993) allow isolation and characterisation of subunits of the kerogen (Whelan and Thompson-Rize, 1993), but in both cases the pyrolysate yields are relatively low (Love et al., 1995). In contrast, catalytic hydropyrolysis (HyPy) was shown to release high yields of covalently-bound hydrocarbons from the kerogen and to maintain their biologically-inherited stereochemistries largely intact by using high pressure and temperature in an H_2 atmosphere (Love et al., 1995). Consequently, HyPy was successfully applied for numerous palaeo-reconstruction studies (e.g. Brocks et al., 2003b; Love et al., 2008, 2009; Blumenberg and Wiese, 2012; Duda et al., 2014).

Precambrian rocks are particularly prone to contamination because of their commonly (i) long geological history, (ii) high thermal maturities and thus, (iii) low abundances of syngenetic biomarkers. This is probably also true for the Shibantan Member (Dengying Formation, ca. 551–541 Ma; Condon et al., 2005; Walker et al., 2013) in South China, one of only two known pure carbonate settings in the world with Ediacara-type fossils (e.g. Sun, 1986; Xiao et al., 2005; Shen et al., 2009; Chen et al., 2014). These fossils of architecturally complex soft-bodied organisms include the first stem-group metazoans (e.g. *Dickinsonia* and *Kimberella*) and are thus an important milestone in the evolution of animals (e.g. Narbonne, 2005; Xiao and Laflamme, 2009; Narbonne et al., 2012; and references therein). Preliminary biomarker analyses on the bitumen fractions extracted from the Shibantan Member indicated that the organic matter is highly mature and contamination might be an essential problem (Kelly, 2009; Duda et al., 2014). In a previous study we were though able to analyse evidently syngenetic biomarkers released from the kerogen by HyPy and to demonstrate the syngeneity of aromatic hydrocarbons in the bitumen (Duda et al., 2014). Abundant thiophenes in the Shibantan carbonate have been attributed to a highly sulphidic palaeoenvironment during earliest diagenesis (Duda et al., 2014). The preservation of syngenetic biomarkers is important since biomarkers are only known from one further setting with Ediacara-type organisms (i.e. the White Sea setting in Russia; Kelly, 2009). Further biomarker-studies on the Shibantan Member could therefore be promising, but the general contamination pathways and sources of the allochthonous bitumen compounds are still unclear. This study aims at critically assessing the possibilities and limitations of biomarker studies on thermally mature outcrop samples from the Shibantan Member, with implications for the analysis of similar rocks in other ancient settings. Pathways for hydrocarbon contamination were elucidated via slice-extraction experiments (*sensu* Brocks et al., 2008; Brocks, 2011) and the potential of the direct use of extraction residues for HyPy was critically assessed.

2 Material and Methods

Analyses were conducted on one fresh and representative outcrop sample from the Shibantan Member collected in 2011 in the still exploited Zhoujia'ao Quarry in the Yangtze Gorges close to Yichang (Figs. 1, 2). In the quarry the Shibantan limestone is mined and directly calcined for lime production. The analysed sample was characterised by an Ediacara-type organism exposed on the outer surface (Fig. 2). The bitumen and decalcified extraction residue of the innermost part of the sample (i.e. slice 6; Fig. 3) have previously been analysed and respective data are already published (Duda et al., 2014).

For biomarker analyses, all glassware and silica gel were heated to 500°C for 3 h. The sample block was roughly formatted and all but one external surfaces were removed using a pre-cleaned (with acetone) rock saw. For analyses of the bitumen, adjoining slices of 6.5 mm (slice 1; i.e. the external weathered surface) and 3 mm (slices 2 to 5) thickness were cut from the sample block perpendicular to the bedding planes (cf. Brocks et al., 2008; Brocks, 2011) using a pre-cleaned high precision saw (Buehler; Isomet 1000) (Fig. 3). Slice 6 stems from the innermost part of the big sample block and was thus not immediately adjacent to slice 5 (Fig. 3). After cutting, all slices were carefully crushed and powdered using a pebble mill (Retsch MM 301). The sample powder (slice 1: 25.0 g; slices 2 to 5: 11.5 g) was extracted with 40 ml (slice 1) and 20 ml (slices 2 to 5) each of methanol, dichloromethane/*n*-hexane (1/1; v/v) and then *n*-hexane using ultrasonication (15 min). The sample powder of

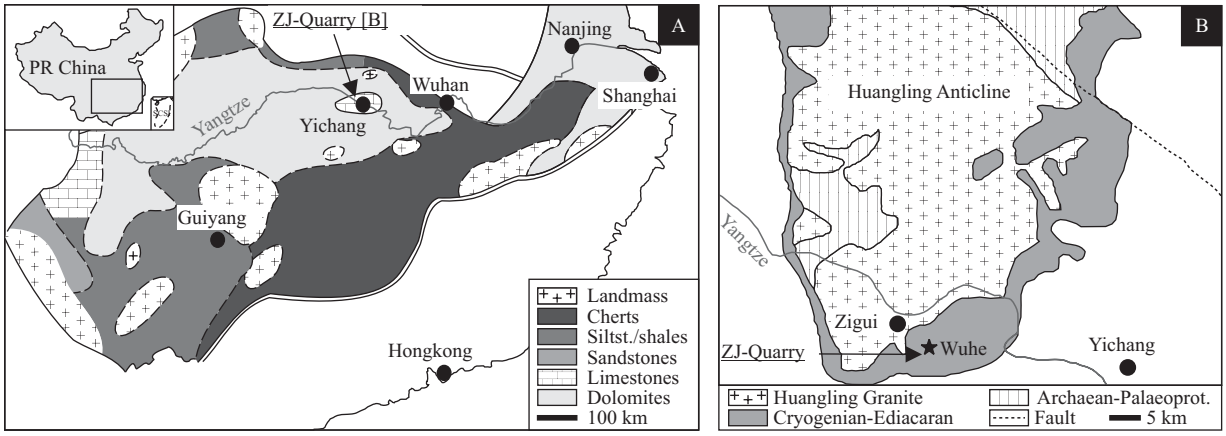

Fig. 1. General overview (A) and exact location (B) of the Zhoujia'ao (ZS-) Quarry in South China.
A: modified after Zhu et al. (2007); B: modified after Chen et al. (2013).

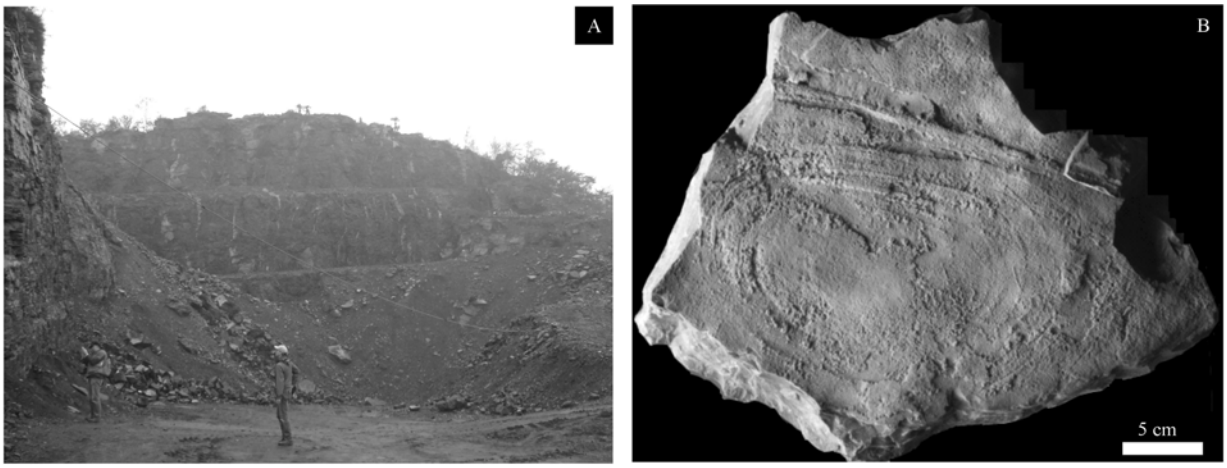

Fig. 2. Sampling location with the outcropping Shibantan carbonates in the Zhoujia'ao Quarry (A) and top view of the analysed sample block with Ediacara-type fossil (B).

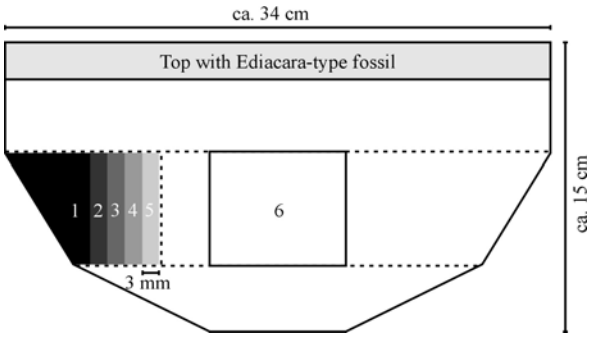

Fig. 3. Sketch of the analysed sample block from the Shibantan Member (side view of Fig. 2b). HyPy analysis was only conducted on slice 6.

slice 6 (99 g) was extracted with 100 ml each of dichloromethane, dichloromethane/*n*-hexane (1/1; v/v) and *n*-hexane using ultrasonication (15 min.) (Duda et al., 2014). Extracts were combined, desulphurised with activated copper and gently dried in a pre-cleaned rotary evaporator followed by N_2. The samples were not completely dried in order to avoid evaporative loss of short-chain *n*-alkanes (cf. Ahmed and George, 2004).

For HyPy, an aliquot of the extraction residue of slice 6 (core of the sample block; Fig. 3) was again Soxhlet extracted using dichloromethane/methanol (9/1, v/v; 24 h), and subjected to HyPy without further treatment. The overall load of the HyPy reactor was about 3.05 g (2.30 g bulk sample + 0.30 MoS_2 catalyst + 0.45 g sand). A second aliquot of the extraction residue was analysed with HyPy after decalcification with HCl (~3 mol/l), and subsequent extraction of the residue with dichloromethane, dichloromethane/*n*-hexane and *n*-hexane (Duda et al., 2014). Because the sample consisted of virtually pure limestone it was not additionally treated with hydrofluoric acid. The overall load of the HyPy reactor was about 1.05 g (0.49 g decalcified sample + 0.06 g MoS_2 catalyst + 0.50 g sand). Samples were pyrolysed using a Strata HyPy system (Strata Ltd., Nottingham, UK) according to Snape et al. (1989) and Love et al. (1995). The temperature program included heating from ambient temperature to 250°C at 50°C min^{-1} and from 250°C to 500°C at 8°C min^{-1}. A hydrogen pressure of 150 bar was applied at a flow of 5 L min^{-1}. The hydrocarbons released

were trapped downstream in a dry ice cooled silica gel trap (see Meredith et al., 2004). The hydropyrolysates were eluted from the silica gel with *n*-hexane, and elemental sulphur was removed with activated copper.

Bitumen extracts and HyPy products were subsequently fractionated into a saturated (F1), an aromatic (F2) and a polar fraction (cf. Blumenberg et al., 2012). F1 and F2 were analysed by combined gas chromatography–mass spectrometry (GC-MS) using a Varian CP-3800 GC coupled to a Varian 1200L triple quadrupole MS. The GC was equipped with a deactivated retention gap (internal diameter (i.d.) 0.53 mm) connected to a fused silica capillary column (Phenomenex Zebron ZB-5MS, 30 m, 0.32 mm i.d., 0.25 μm film thickness). He was used as carrier gas. The GC oven was programmed from 80°C (held for 3 min) to 310°C (4°C min^{-1}; held for 25 min.). Fractions were injected on column using a PTV injector. The injector was initially held at 80°C for 0.2 min and then heated by 150°C min^{-1} to 320°C (held for 15 min). The ion source in the MS was operated at 200°C in electron ionisation mode at 70 eV ionisation energy, and analyses were conducted in full scan and selected ion monitoring (SIM) modes. Hydrocarbons were identified by comparing mass spectra and retention times with published data and/or reference compounds. For SIM analyses of the polycyclic aromatic hydrocarbons (PAHs) selected mass fragments were used (*m*/*z* 178 for phenanthrene; *m*/*z* 192 for methylphenanthrenes; *m*/*z* 184 for dibenzothiophenes; *m*/*z* 198 for methyldibenzothiophenes; *m*/*z* 252 for perylene).

3 Results

3.1 Extractable hydrocarbons (bitumen)

Considerable differences in the distributions and abundances of extractable hydrocarbons were observed between the analysed samples. The *n*-alkanes in slice 1 ranged in carbon chain length from C_{16} to C_{36} and showed a bimodal distribution with maxima at *n*-C_{18} and, less pronounced, at *n*-C_{29} (Fig. 4). The high abundance of short-chain *n*-alkanes (i.e. < *n*-C_{23}) was not found in slices 2 to 5, where homologues ranged from *n*-C_{18} to *n*-C_{35} and displayed a smooth distribution with a maximum around *n*-C_{29} (Fig. 4). The slice 6 was fairly similar to slices 2 to 5, with *n*-alkanes ranging from *n*-C_{16} to *n*-C_{39} (maxima at *n*-C_{27} and, less pronounced, at *n*-C_{36}) and low amounts of short-chain *n*-alkanes (i.e. < *n*-C_{23}) (Duda et al., 2014) (Figs. 4, 5). Considerable differences in the abundances of hydrocarbons were observed between the samples, with aliphatic compounds in slices 1 and 5 being higher concentrated than in the other slices (corrected for sample weight; Fig. 4).

Acyclic isoprenoids (i.e. pristane and phytane) were only detected in slice 1, where pristane/*n*-C_{17} and phytane/*n*-C_{18} ratios were 0.57 and 0.95, respectively.

3.2 Non-extractable hydrocarbons (HyPy-treated extraction residue)

HyPy on the bulk extraction residue resulted in *n*-alkanes with carbon chain lengths from *n*-C_{18} to *n*-C_{39} and a bimodal distribution with maxima at *n*-C_{22} and, less pronounced, at *n*-C_{30} (Fig. 5). *n*-Alkanes cleaved from the decalcified extraction residue had carbon chain lengths from *n*-C_{16} to *n*-C_{40} and a bimodal distribution (maxima at *n*-C_{18} and, more pronounced, at *n*-C_{22}) as reported previously (Duda et al., 2014) (Fig. 5). Amounts of the released *n*-alkanes were about twenty times higher after decalcification (corrected for sample weight and TOC content; Fig. 5).

The HyPy products of the bulk extraction residue were found to be rich in PAHs such as (methyl-) phenanthrenes and, less pronounced, sulphur bearing PAHs such as various (dibenzo-) thiophenes. The same was observed for the decalcified extraction residue (Duda et al., 2014) (Fig. 6). If compared to the decalcified extraction residue, however, the ratio between PAHs and thiophenes was higher in the bulk extraction residue (Fig. 6).

4 Discussions

4.1 Contamination sources and impact on the organic inventory

The different distribution patterns and higher amounts of extractable *n*-alkanes, as well as the presence of acyclic isoprenoids clearly reveal contamination of the external weathered surface (slice 1), as it has been described for another outcrop sample from the Shibantan Member (Kelly, 2009). Similarly, *n*-alkanes in the innermost part of the block (i.e. slice 6) have been attributed to contamination with fossil (i.e. already matured) compounds because of a different chain-length distribution and dissimilar δ^{13}C-signatures compared to the kerogen-bound compounds (Duda et al., 2014). While no voids or cracks were macroscopically visible in the innermost part of the sample (i.e. slice 6; Fig. 3), a few very thin cracks were detected by thin section analysis (Fig. 7). However, other cracks were only visible because slight wet rims persisted after defrosting, indicating that they have not been cemented. Contamination via such tiny cracks plausibly explains the similar absolute concentrations of aliphatic hydrocarbons in slices 1 (i.e. the external weathered surface) and 5 (representing an internal crack), as well as in slices 2 to 4 which were positioned between these two contaminated rock volumes. The innermost part

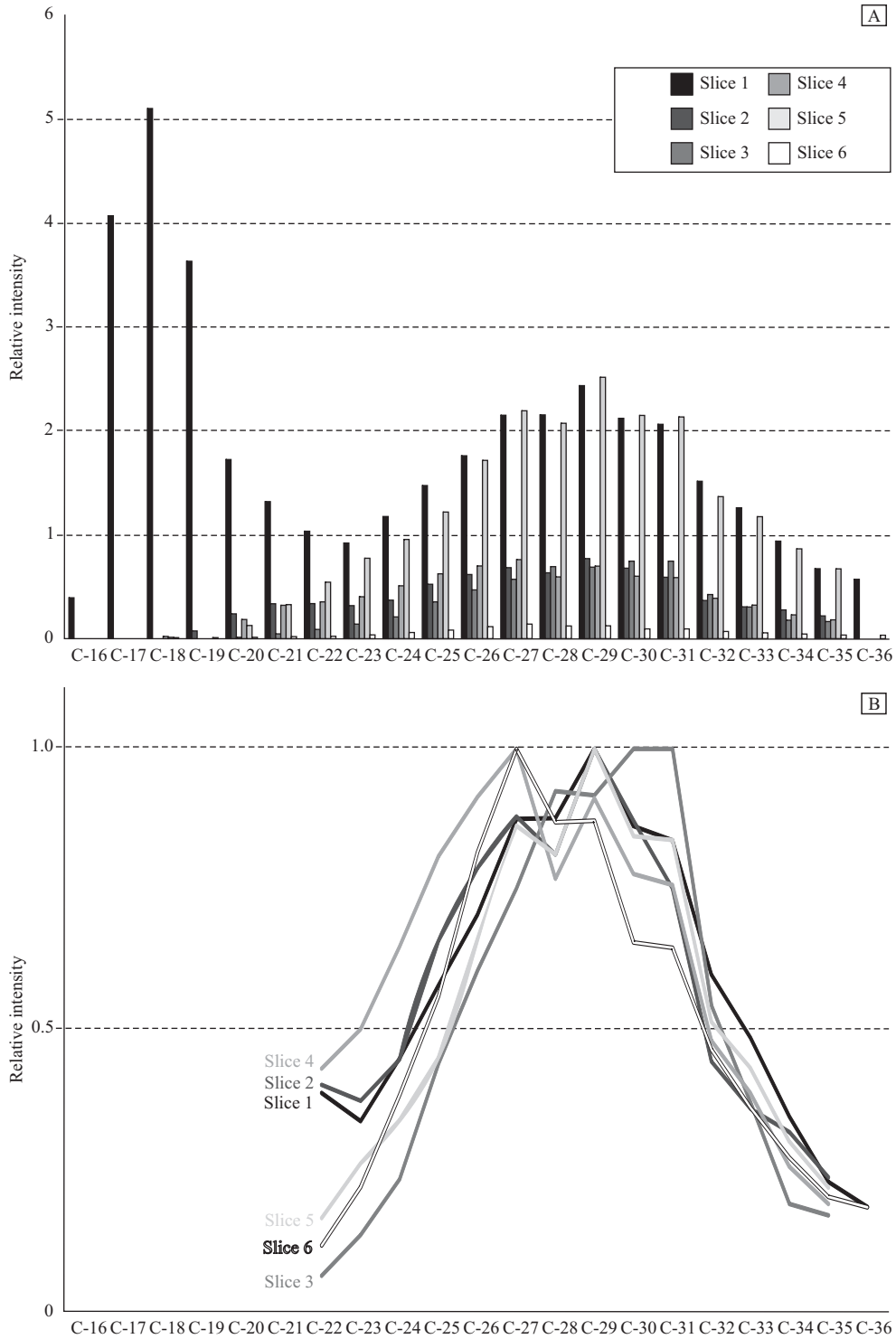

Fig. 4. *n*-Alkane yields (corrected for sample weight) and distribution patterns in bitumen of the analysed slices 1-6.

Comparison of *n*-alkane distribution patterns in a bar chart (A) and a line chart (most significant peak of each slice normalised to 1; only the C_{22}-C_{36} range shown) (B). Data of bitumen from slice 6 from Duda et al. (2014).

of the block (slice 6, Fig. 3), however, shows the same *n*-alkane distribution as slices 2 to 4 but even lower concentrations of these compounds (Fig. 4). This underlines that the grade of contamination of outcrop samples from the Shibantan Member is not only controlled by the weathering surface but also by cracks. Therefore, slice experiments (Brocks et al., 2008; Brocks, 2011) as well as careful thin section analysis are important to understand the sources and distribution patterns of biomarkers and to assess the likeliness of contamination.

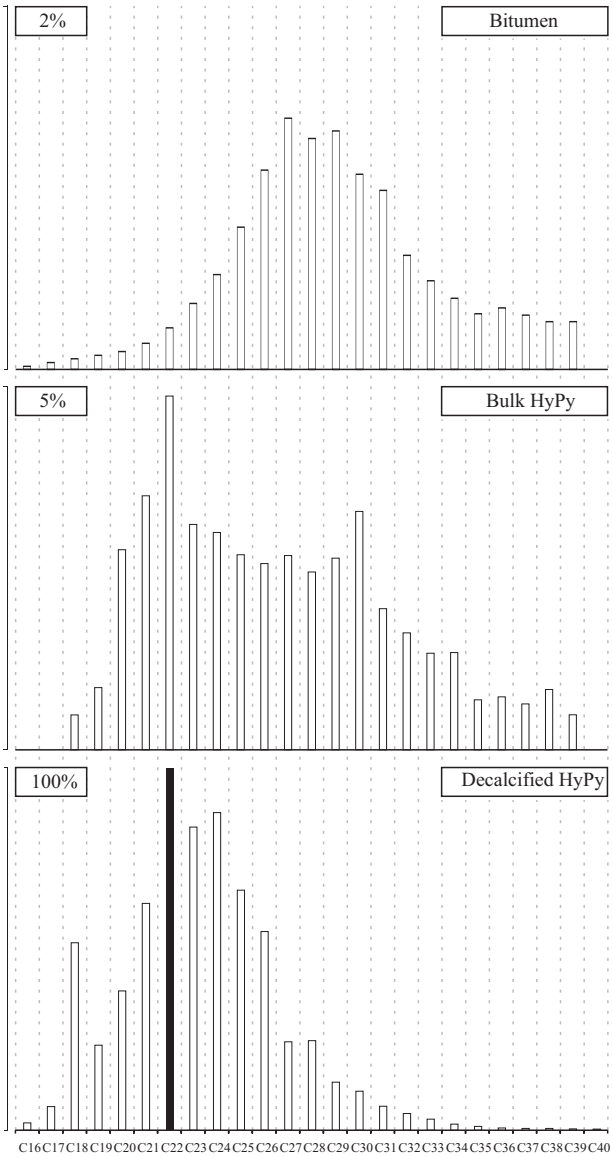

Fig. 5. Comparison of yields of *n*-alkanes in bitumen and extraction residue (bulk and decalcified) of slice 6 (corrected for sample weight and TOC content) relative to main compound (i.e. the C_{22} *n*-alkane in kerogen; indicated by black bar). Data of decalcified extraction residue and bitumen from Duda et al. (2014).

The occurrences of short-chain *n*-alkanes and acyclic isoprenoids (pristane and phytane) on the external weathered surface (i.e. slice 1; Fig. 3) are in good agreement with an external, petroleum-derived contamination, but these compounds are absent in the slice 5 in the vicinity of the inner crack (Fig. 4). An analytical bias due to excessive evaporation of short-chain *n*-alkanes during sample preparation (drying with N_2) (Ahmed and George, 2004) can be excluded since all slices were treated in parallel under the same conditions and should therefore be influenced equally by the work-up procedure. A possible explanation is therefore that the external weathered surface was affected by a second contamination source. Taken together, however, the distribution patterns of *n*-alkanes and acyclic isoprenoids clearly show that aliphatic hydrocarbons in the Shibantan bitumen are indeed not syngenetic.

4.2 Applicability of bulk extraction residues for HyPy

HyPy has already been successfully used on the decalcified extraction residue from the Shibantan carbonate (Duda et al., 2014). Decalcification prior to HyPy, however, is time consuming and involves further risks for contamination. Therefore the use of excessively pre-extracted bulk rock powder, i.e. without decalcification, was tested. The resulting *n*-alkane concentrations and distributions, however, greatly differed from those released from the decalcified sample, whose hydrocarbon yields were about 20 times higher after correction for the sample weight and TOC content, and short chain *n*-alkanes were much more prominent than long-chain *n*-alkanes (Fig. 5). As the long-chain *n*-alkanes in the Shibantan bitumen were suspected to represent a contamination (see 4.1), we argue that the respective *n*-alkanes found in the pyrolysate may represent non-entirely extracted bitumen contaminants that had been sequestered in the carbonate lattice, and thus escaped extraction (Fig. 5). Consequently, decalcification of carbonates is required for a complete extraction of the bitumen and the removal of contaminations contained therein.

A further potential problem that has to be addressed when omitting decalcification are matrix effects. The overall load in the HyPy reactor was three-fold higher for the bulk extraction residue as compared to the decalcified extraction residue (~3g and ~1g, respectively). After correction for the respective sample weight and TOC content much lower yields of syngenetic short-chained *n*-alkanes are evident for the bulk extraction residue (Fig. 5). A possible explanation is that the different sample loads had an impact on the bond cleaving- and product removal processes within the HyPy reactor. Evidence for such matrix effects can also be deduced from the relative distributions of PAHs and thiophenes in the HyPy products of the decalcified and bulk sample. The observed conspicuous drop in thiophene concentrations relative to PAHs in the HyPy products of the bulk extraction residue (Fig. 6) may be explained by an ineffective removal from the hot zone and thus a longer dwell time of released compounds in the reactor because of the high sample load. Though thiophenes are usually regarded as relatively stable (e.g. Koopmans et al., 1995, and references therein), the sample containing the carbonate matrix obviously experienced a partial thermal decomposition during the

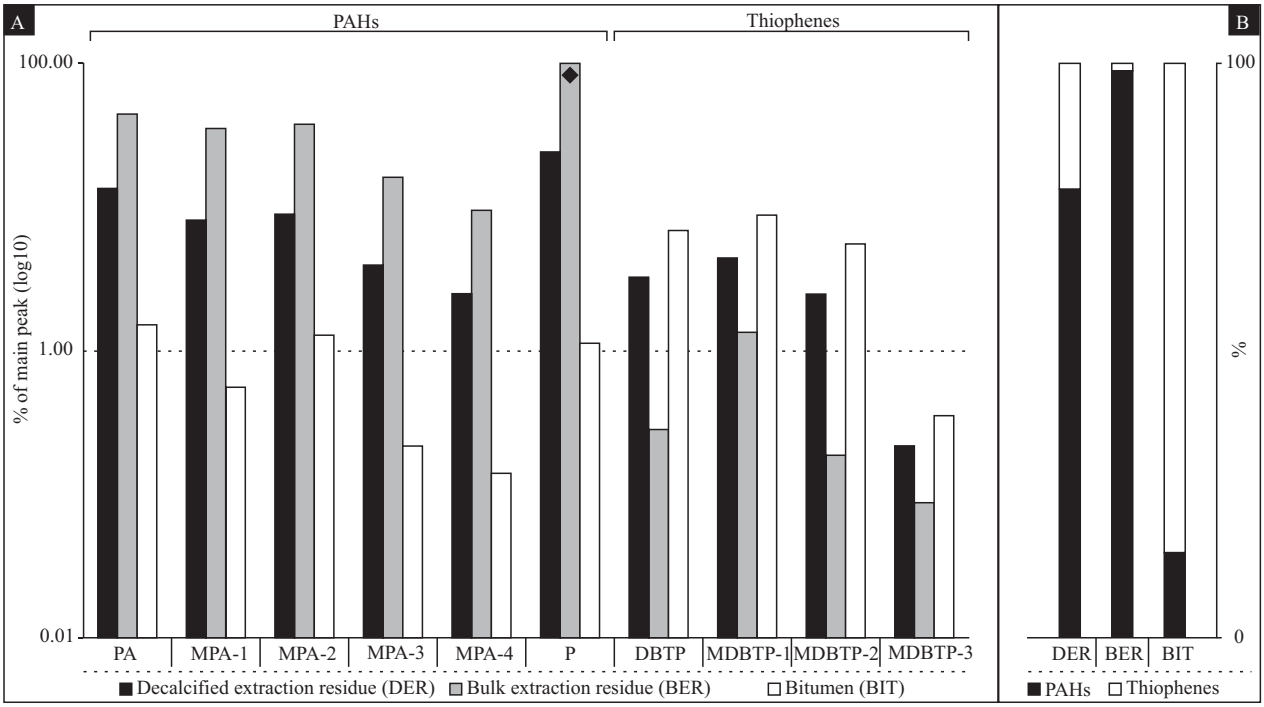

Fig. 6. Relative yields of aromatic compounds from slice 6 (corrected for sample weight and TOC content).
A: Various PAHs and thiophenes in bitumen and extraction residue (bulk and decalcified) relative to P in bulk extraction residue (indicated by black diamond). B: Relative ratios of PAHs (PA, MPA) and thiophenes (DBTP, MDBTP). PA: Phenanthrene; MPA: Methylphenanthrenes; P: Perylene; DBTP: Dibenzothiophene; MDBTP: Methyldibenzothiophenes. Data of decalcified extraction residue and bitumen from Duda et al. (2014).

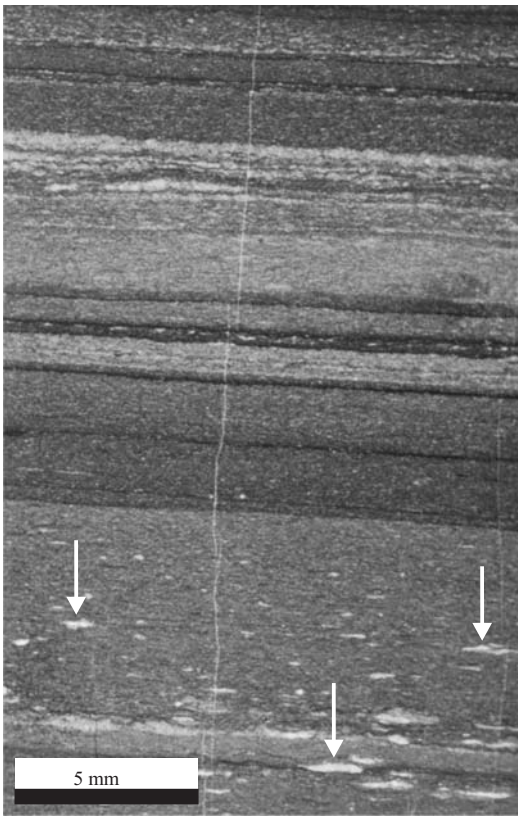

Fig. 7. Thin section of the innermost part of the sample (i.e. slice 6; Fig. 3). Note that no voids are visible (compounds marked by arrows are grains) and that observable cracks are negligible.

HyPy-process, i.e. cleaving of C-S bonds of thiophenes and production of PAHs from dibenzothiophenes. The vulnerability of (dibenzo-) thiophenes to decomposition during HyPy has been previously reported, and consequently ratios of methyl homologues of dibenzothiophene should not be used for kerogen-bound biomarkers (Lockhart et al., 2007). Given that a moderate sample load is the precondition for a rapid removal of the released moieties from the hot zone of the reactor, the decalcification of carbonates prior to HyPy is necessary to concentrate the organic matter and to avoid artificial alteration of the signal, particularly for biomarker-lean carbonate rocks with a high maturity.

5 Conclusions

Bitumens in outcrop samples of the Shibantan Member are affected by contamination with mature organic material, most likely introduced through anthropogenic activity. In addition to severe contamination of the external weathered surface, it has been demonstrated that contamination is also linked to cracks. The degree of contamination in different parts of the sample depends most likely on concentration gradients between these contamination pathways. The distribution patterns and concentrations of short-chain *n*-alkanes and acyclic isoprenoids demonstrate that the external contaminations

are largely petroleum-derived, thus precluding reliable palaeo-reconstructions based on biomarker analyses of the Shibantan bitumen. Our study supports the utility of slice experiments for assessing the existence and extent of contamination and underlines the usefulness of thin section studies conducted in parallel with biomarker analyses.

Biomarkers released from the extraction residue through HyPy are most likely syngenetic. However, decalcification of the samples as well as extraction prior and after decalcification are necessary to obtain these compounds in high yields from the kerogen. Decalcification also avoids artificial alteration of the released compounds due to high sample load in the HyPy reactor, which may otherwise severely influence the distributions of released biomarkers, such as the relative amounts of thiophenes versus PAHs.

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