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Characterization of polycyclic aromatic hydrocarbons and their phenanthroperylene quinone precursors in fossil crinoids using liquid chromatography–atmospheric pressure photoionization mass spectrometry

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ABSTRACT

The distribution and origin of diagenetic products of polycyclic quinone pigments in fossil crinoids was investigated using high-performance liquid chromatography–diode array detection–atmospheric pressure photoionization mass spectrometry (HPLC–DAD–APPI-MS). A number of characteristic higher-molecular-weight polycyclic aromatic hydrocarbons (PAHs) were identified in toluene extracts of diverse crinoid samples, with 1,2,3,4,5,6-hexahydrophenanthro[1,10,9,8-*opqra*]perylene as the main compound. Moreover, phenanthro[1,10,9,8-*opqra*]perylene-7,14-dione (PPQ) and further derivatives were detected for the first time in the fossil record, representing intermediates between hydroxylated phenanthroperylene quinone pigments such as fringelite F and phenanthroperylene PAHs. The widespread presence of PPQ, its derivatives and related PAHs in fossil crinoids which contain phenanthroperylene quinone pigments confirms the diagenetic formation of specific PAHs by reductive degradation of quinone pigments.

1. Introduction

A number of polycyclic aromatic hydrocarbons (PAHs) are thought to be diagenetically derived from natural product precursors (Wakeham et al., 1980). Perylene quinone pigments have been proposed as diagenetic precursors of perylene (Jiang et al., 2000; Grice et al., 2009; Marynowski et al., 2013). Furthermore, several characteristic larger PAHs such as the eight-ring PAH 1,2,3,4,5,6-hexahydrophenanthro[1,10,9,8-*opqra*]perylene (HHPP) have been isolated from fossil crinoids which contain phenanthroperylene quinone pigments (Blumer, 1962; Thomas and Blumer, 1964; Wolkenstein et al., 2006, 2008). HHPP was originally discovered in a millericrinid from the Upper Jurassic of Switzerland (Blumer, 1951, 1962; Thomas and Blumer, 1964; Wolkenstein et al., 2006), but has also been detected in a millericrinid from the Upper Jurassic of Poland (Wolkenstein et al., 2008) and an encrinid from the Middle Triassic of Germany (Wolkenstein et al., 2006). Because of the structural similarity and common occurrence in fossil crinoids, a relationship between phenanthroperylene quinone pigments such as fringelite F and HHPP has been suggested (Blumer, 1962; Thomas and Blumer, 1964; Wolkenstein et al., 2006). However, to date, no intermediate products have been found for either HHPP or perylene that would provide conclusive evidence for the formation of these PAHs from the supposed precursor molecules.

Recently, it has been shown by high-performance liquid chromatography (HPLC)–diode array detection (DAD)–electrospray ionization (ESI)-mass spectrometry (MS) analysis that violet coloured fossil crinoids with preserved phenanthroperylene quinone pigments are much more widespread than previously thought (Wolkenstein, 2015). However, a number of difficulties are associated with the analysis of larger PAHs with molecular weights > 300 Da like HHPP. Due to their extremely low volatility, higher-molecular-weight PAHs cannot be analysed by gas chromatography–mass spectrometry (GC–MS). Nonpolar compounds such as PAHs are also only poorly ionized by conventional ESI (Hanold et al., 2004).

PAHs have been successfully analysed by HPLC–MS with atmospheric pressure chemical ionization (APCI) (Marvin et al., 1999) and more recently using atmospheric pressure photoionization (APPI) (Moriwaki et al., 2004; Itoh et al., 2006). APPI is a relatively new ionization technique for LC–MS and provides high sensitivity for a broad range of analytes, especially nonpolar molecules (Robb et al., 2000; Hanold et al., 2004). The efficiency of analyte ionization in APPI-MS can be enhanced using suitable dopants such as toluene or acetone. Little fragmentation is observed in APPI (Robb et al., 2000), but analyte ions may be isolated and

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fragmented by collision-induced dissociation to obtain structural information.

In order to detect possible diagenetic products of quinone pigments in fossil crinoids, a HPLC–DAD–APPI-MS method for the analysis of higher-molecular-weight PAHs was developed. It was then applied to screen diverse fossil crinoid samples that had already been analysed for the presence of phenanthroperylene quinone pigments (Wolkenstein, 2015).

2. Material and methods

2.1. Fossil samples and reference compounds

Diverse fossil crinoid samples from the Mesozoic and Palaeozoic were selected from collection material (Table 1; for more details see Wolkenstein, 2015). For reference, synthetic phenanthro [1,10,9,8-*opqra*]perylene-7,14-dione (PPQ) and HHPP were used. PPQ prepared according to Falk and Vaisburg (1995) was kindly provided by Prof. Heinz Falk (University of Linz). HHPP was synthesized from PPQ according to Wolkenstein et al. (2002).

2.2. Sample preparation and extraction of fossil crinoids

Samples of fossil crinoids (0.1–3.2 g) were cleaned with acetone. After dissolution of the carbonate with 10 M HCl, the residues were separated by centrifugation, washed thoroughly with distilled water, and dried overnight at room temperature under vacuum (about 10 Torr). Residues were then sequentially extracted by sonication (10 min at 40 °C) and centrifugation in toluene (3 ×) and dimethyl sulfoxide (1×).

2.3. HPLC–DAD–MS analysis

Aliquots of the PAH-containing toluene extracts were filtered using 0.2 µm polytetrafluoroethylene filters (ReZist, Schleicher & Schuell) and were diluted 1:1 (v/v) with acetonitrile prior to injection. HPLC–DAD–MS measurements were carried out on an Agilent 1100 Series HPLC system with a diode array detector coupled to an Agilent 6520 Q-TOF LC–MS time-of-flight mass spectrometer equipped with an APPI source. Separation was performed at 25 °C on a Phenomenex Luna C18(2) column (50 × 4.6 mm i.d., 3 µm). The HPLC program consisted of a linear gradient of acetonitrile:water (70:30, v/v) to 100% acetonitrile in 15 min, followed by isocratic elution at 100% acetonitrile at a flow rate of 1 ml min^{-1}. UV–visible absorbance at multiple wavelengths in the range of 200–800 nm was recorded using a diode array detector. Mass spectra were acquired in the positive-ion mode (nebulizer gas pressure 60 psi, drying gas flow 4 l min^{-1}, drying gas temperature 350 °C, vaporizer temperature 500 °C, capillary voltage 3.0 kV, fragmentor 250 V, skimmer 65 V) over the 100–1100 *m/z* range. Mass calibration and continuous reference correction was obtained using purine and the HP-0621 acetate adduct ($C_{12}H_{18}O_6N_3P_3F_{12}$)

Table 1
HHPP and PPQ occurrence in fossil crinoids compared to fringelite F.

Species	Age	Location	Sample amount (g)	Residue (mg)	Fringelite F[a] concentration (ppm of fossil)	PPQ[b] relative peak area per g of sample	HHPP[c] concentration (ppm of fossil)
Millericrinida							
Millericrinid	Upper Jurassic	Solnhofen, DE	2.1	91.3	n.d.	n.d.	n.d.
Millericrinid	Upper Jurassic	Tendaguru, TZ	3.2	7.7	7.4	0.35	**16.0**
Millericrinus lusitanicus	Upper Jurassic	Vestiaria, PT	2.9	28.1	0.2	n.d.	n.d.
Liliocrinus polydactylus	Upper Jurassic	Angoulins, FR	0.2	0.3	41.6	n.d.	n.d.
Apiocrinites roissyanus	Upper Jurassic	Tonnerre, FR	1.1	0.8	77.1	0.29	**0.1**
Millericrinid	Upper Jurassic	Hannover, DE	2.2	50.2	66.9	1.00	**13.0**
Liliocrinus munsterianus	Upper Jurassic	L'Isle-sur-le-Doubs, FR	1.2	0.9	129.5	<0.01	**<0.1**
Apiocrinites roissyanus	Upper Jurassic	Boncourt, CH	1.8	4.4	85.1	n.d.	n.d.
Angulocrinus echinatus	Upper Jurassic	Malton, GB	1.0	17.1	38.6	0.31	**16.4**
Millericrinid	Upper Jurassic	Villers-sur-Mer, FR	1.1	11.0	<4.3	n.d.	n.d.
Apiocrinites negevensis	Middle Jurassic	Hamakhtesh Hagadol, IL	2.7	3.2	<0.2	n.d.	n.d.
Apiocrinites parkinsoni	Middle Jurassic	Bradford-on-Avon, GB	1.6	6.9	137.5	n.d.	**0.1**
Ailsacrinus abbreviatus	Middle Jurassic	Eastington, GB	1.1	27.2	0.5	n.d.	n.d.
Comatulida							
Solanocrinites sp.	Upper Jurassic	Tendaguru, TZ	0.2	6.5	113.6	n.d.	n.d.
Solanocrinites beltremieuxi	Upper Jurassic	Île de Ré, FR	0.1	1.4	28.2	n.d.	n.d.
Isocrinida							
Pentacrinites dargniesi	Middle Jurassic	Malmesbury, GB	1.4	52.5	13.7	n.d.	n.d.
Hispidocrinus leuthardti	Middle Jurassic	Liestal, CH	2.3	12.8	23.7	n.d.	n.d.
Pentacrinites dargniesi	Middle Jurassic	Develier, CH	3.0	39.0	23.3	n.d.	**4.9**
Encrinida							
Chelocrinus schlotheimi	Middle Triassic	Willebadessen, DE	0.6	9.5	3.7	n.d.	n.d.
Encrinus cf. *brahli*	Middle Triassic	Weißenborn, DE	0.1	0.5	16.4	n.d.	n.d.
Monobathrida							
Strimplecrinus inornatus	Lower Carboniferous	LeGrand, Iowa, US	2.6	8.1	n.d.	n.d.	n.d.
Order indet.							
Crinoidea	Silurian, Ludlovian	Burgen, Gotland, SE	1.2	1.8	n.d.	n.d.	n.d.

For more detailed information on the investigated crinoid samples see Wolkenstein (2015). Countries indicated: DE, Germany; TZ, Tanzania; PT, Portugal; FR, France; CH, Switzerland; GB, United Kingdom; IL, Israel; US, United States of America; SE, Sweden.
n.d. = not detected.
[a] Fringelite F concentrations from Wolkenstein (2015).
[b] Analysis was performed by HPLC–DAD (peak areas at 420 nm). No quantification of PPQ was possible, because of the extremely poor solubility of the compound.
[c] Quantification was performed by HPLC–DAD (peak areas at 310 nm) using HHPP as external standard.

introduced via an internal reference mass kit. Acetone was used as dopant for APPI ionization, delivered at a flow rate of 50 µl min^{-1} via a syringe pump and mixed in a tee-piece with the mobile phase after separation. Further dopants tested were toluene and toluene: anisole (99.5:0.5, v/v). For tandem MS experiments, precursor ions measured at defined retention times during the HPLC run were mass-selected in the quadrupole and fragmented in the collision cell operated at various collision offset voltages. All compounds were fragmented at 40 V except PPQ that was fragmented at 60 V.

Extracts from two additional fossil samples (*Apiocrinites negevensis* and millericrinid from Solnhofen) were analysed only by HPLC–DAD, using an Agilent 1200 Series HPLC system, by applying the same chromatographic conditions as described above.

3. Results and discussion

An HPLC–APPI-MS method was developed for the analysis of higher-molecular-weight PAHs in geological samples. APPI-MS parameters were optimized for extremely-low-volatile compounds, using a high vaporizer temperature of 500 °C. Whereas Itoh et al. (2006) observed the highest ionization efficiency for common PAHs using a dopant mixture of toluene:anisole (99.5:0.5, v/v), the highest ionization efficiency for the higher-molecular-weight PAH HHPP was observed with acetone as the dopant. Using APPI-MS the limit of detection for HHPP was 18 ng ml^{-1}, while using DAD detection (310 nm) the limit of detection was 41 ng ml^{-1}.

Twenty crinoid samples from Mesozoic and Palaeozoic sediments were investigated by HPLC–DAD–APPI-MS and an additional two by HPLC–DAD. In seven crinoid samples the characteristic PAH HHPP was successfully detected and identified by comparison of the spectroscopic data of the fossil compound with those of the standard compound (Figs. 1 and 2, Table 1). The UV–visible spectrum of the fossil compound was identical to that of the HHPP standard, showing an absorption maximum at 310 nm (Fig. 2a and b). In the positive-ion APPI mass spectrum, a corresponding ion at *m/z* 357 is observed (with elimination of six hydrogens) (Fig. 2a and c). Based on the high-resolution time-of-flight mass spectrometry data, a molecular formula of $C_{28}H_{21}$ $[M+H]^+$ was determined (Fig. 2c, Table 2). Characteristic fragmentation was obtained by collision-induced dissociation of the *m/z* 357 ion, revealing elimination of CH_2CH_2 and CH_4 (Fig. 2d). Selected ion traces of *m/z* 371 (peaks 3 and 4) and *m/z* 385 indicated the presence of homologues of HHPP and their isomers that could be attributed to the molecular formulae $C_{29}H_{23}$ $[M+H]^+$ and $C_{30}H_{25}$ $[M+H]^+$ by accurate mass data (Fig. 2a and e, Table 2). In the collision-induced dissociation mass spectra, obvious differences between the isomers were observed (Fig. 2f).

In addition to HHPP and its homologues, further possible diagenetic products were found. Most important was the discovery of small amounts of phenanthro[1,10,9,8-*opqra*]perylene-7,14-dione (PPQ) in the crinoid extracts (Figs. 1 and 3, Table 1). PPQ represents an intermediate between the hydroxylated phenanthroperylene quinone pigment fringelite F and the PAH HHPP and has not been observed in the fossil record until now. By comparison of the retention time, UV–visible spectrum, accurate mass data, isotopic pattern and fragmentation pattern with those of the standard compound, the fossil compound was unequivocally identified as PPQ (Fig. 3). In the UV–visible spectrum it shows an absorption maximum at about 420 nm (Fig. 3a and b). In the positive-ion APPI mass spectrum, a corresponding ion at *m/z* 381 is observed that can be attributed to the molecular formula $C_{28}H_{13}O_2$ $[M+H]^+$ by accurate mass data (Fig. 3a and c, Table 2). Collision-induced dissociation of the *m/z* 381 ion shows characteristic elimination of CHO and CO (Fig. 3d). Moreover, further PPQ derivatives were detected

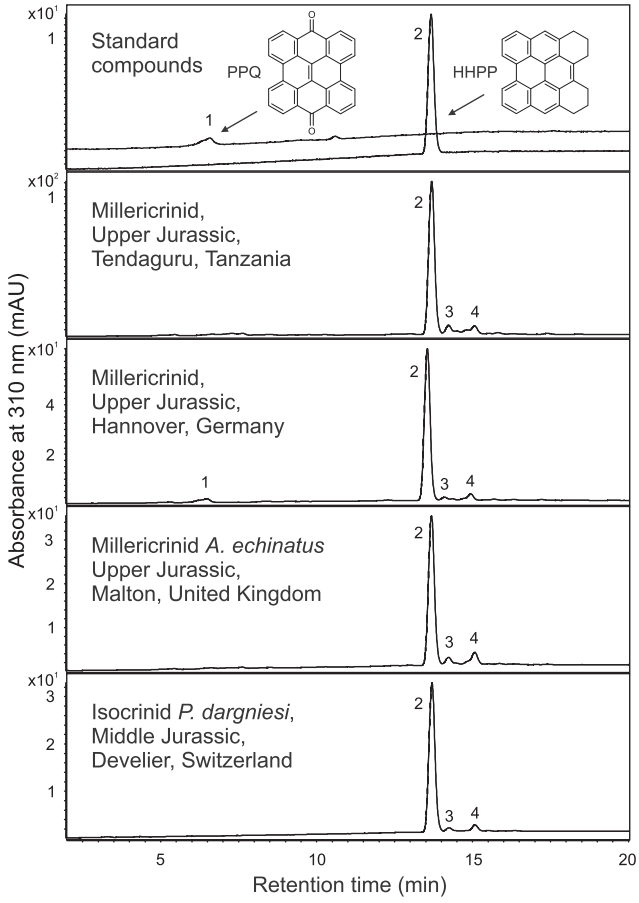

Fig. 1. HPLC–DAD chromatograms of toluene extracts from fossil crinoids in comparison to reference compounds. Compounds 3 and 4 are isomeric homologues of compound 2 (see Fig. 2).

by mass spectrometry (Fig. 4, Table 2). A derivative that could be attributed to the molecular formula $C_{28}H_{13}O_3$ $[M+H]^+$, likely PPQ with one hydroxy group in addition to the two carbonyl groups (Table 2), was found. In addition, a hexahydro derivative of PPQ with the molecular formula $C_{28}H_{19}O_2$ $[M+H]^+$ was detected (retention time 12.34 min, only in the crinoid sample from Hannover) showing elimination of six hydrogens in the mass spectrum and elimination of CO and CH_2CH_2 in the collision-induced dissociation mass spectrum (Fig. 4a and b). Furthermore, two isomers at *m/z* 369 were observed showing elimination of three hydrogens in the mass spectrum. By accurate mass data, they can be attributed to the molecular formula $C_{28}H_{17}O$ $[M+H]^+$, corresponding to trihydro-mono-carbonyl derivatives of PPQ (note differences in the collision-induced dissociation mass spectra) (Fig. 4c and d). Finally, traces of several homologues were identified (Table 2).

In the crinoids studied, no common PAHs like anthracene or perylene were found, and neither were nine-ring PAHs that have previously been detected in small amounts in addition to HHPP in a Jurassic crinoid by Thomas and Blumer (1964). However, it has to be considered that the crinoid sample amounts (0.1–3.2 g) were much smaller than in the study by Thomas and Blumer (1.5 kg) and the method applied in this study was not optimized for PAHs with molecular weights < 300 Da.

Concentrations of HHPP ranged from <0.1 to 16.4 ppm in the fossils, with the highest concentration in the Jurassic crinoid from Malton (UK) (Table 1). These values are similar to those determined in the few previous studies on this PAH (Blumer, 1951; Blumer, 1962; Thomas and Blumer, 1964; Wolkenstein et al.,

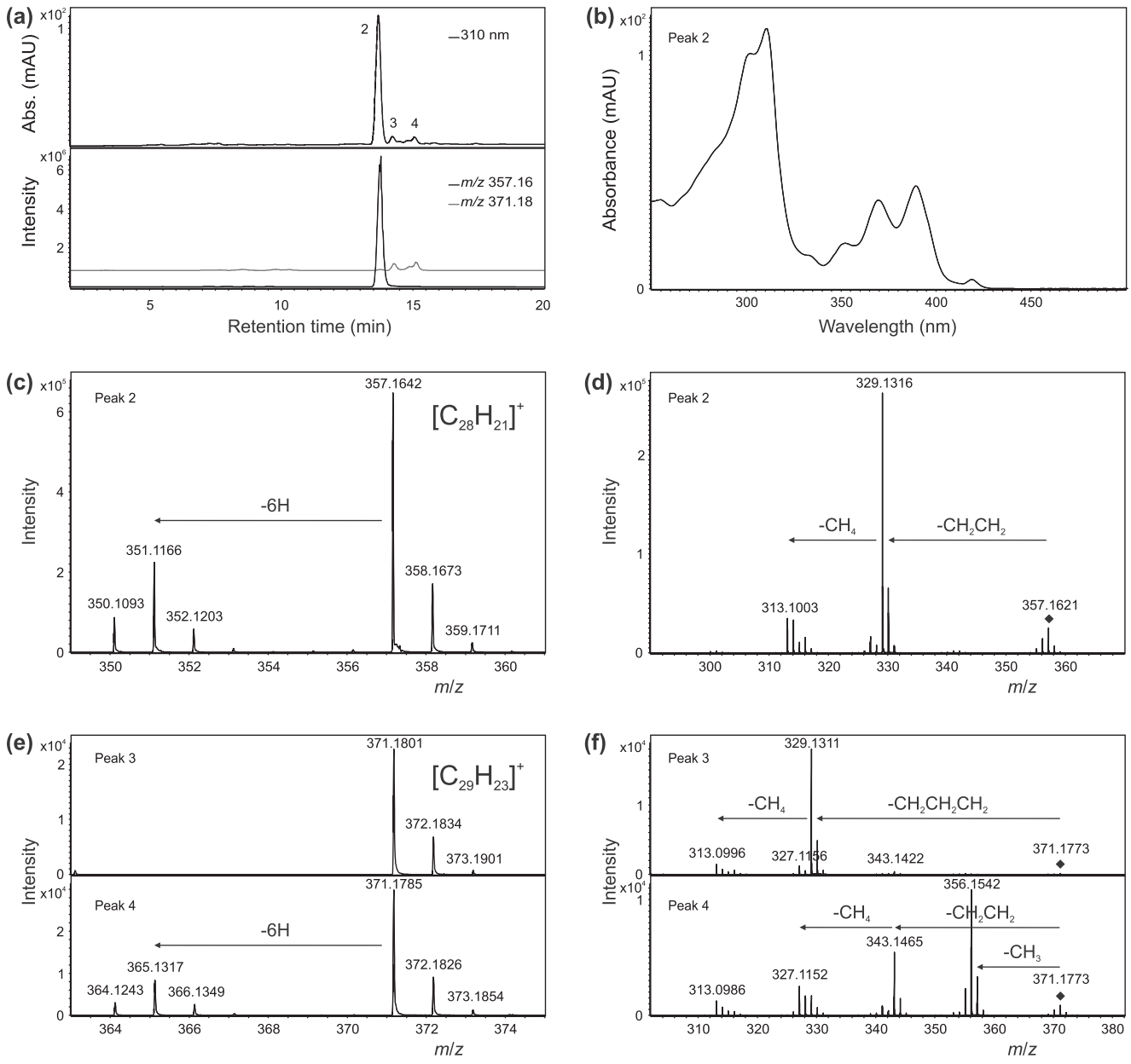

Fig. 2. Analytical data of HHPP (peak 2) and isomeric homologues (peaks 3 and 4) from a fossil crinoid (millericrinid) from Tanzania (Tendaguru): (a) DAD chromatogram (detection at 310 nm) (upper) and ion chromatograms (positive-ion APPI-MS) (lower) of toluene extract; (b) DAD spectrum of peak 2 shown in (a); (c) mass spectrum of peak 2 shown in (a); (d) collision-induced mass spectrum of *m*/*z* 357.16 shown in (c) (peak 2); (e) mass spectra of peaks 3 and 4 shown in (a); (f) collision-induced mass spectra of *m*/*z* 371.18 shown in (e) (peaks 3 and 4).

Table 2
Accurate mass data of PAHs and other diagenetic products of phenanthroperylene quinone pigments from fossil crinoids.

Compound	Retention time (min)	Molecular formula, $[M+H]^+$	*m*/*z* calculated	*m*/*z* observed
HHPP	13.78	$C_{28}H_{21}$	357.1638	357.1642
	14.26	$C_{29}H_{23}$	371.1794	371.1801
	15.12	$C_{29}H_{23}$	371.1794	371.1785
	15.60	$C_{30}H_{25}$	385.1951	385.1943
	8.51	$C_{28}H_{17}O$	369.1274	369.1272
	10.33	$C_{28}H_{17}O$	369.1274	369.1273
	9.47	$C_{29}H_{19}O$	383.1430	383.1435
	11.19	$C_{29}H_{19}O$	383.1430	383.1431
PPQ	6.71	$C_{28}H_{13}O_2$	381.0910	381.0909
	8.54	$C_{29}H_{15}O_2$	395.1067	395.1067
	9.47	$C_{28}H_{13}O_3$	397.0859	397.0854

Mass data are from millericrinid, Upper Jurassic, Tanzania.

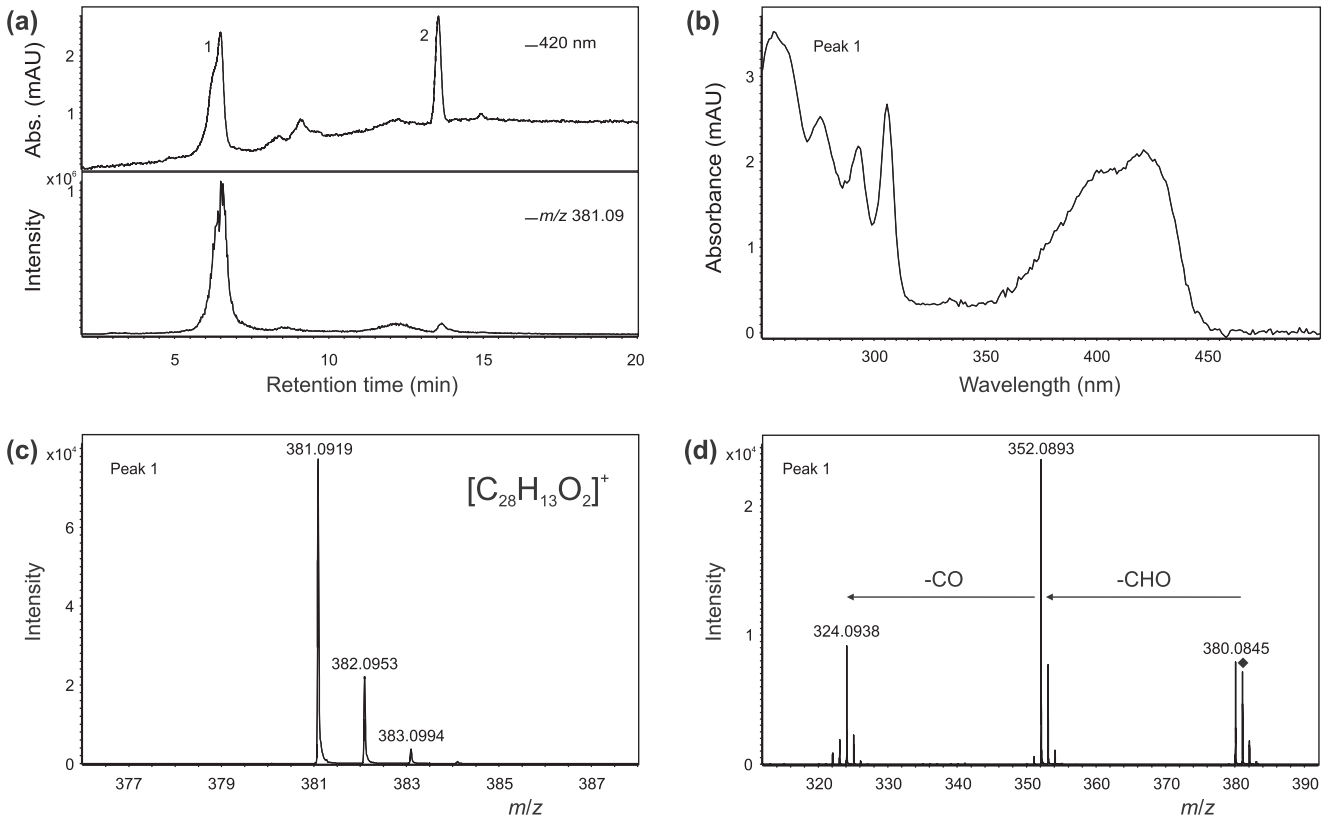

Fig. 3. Analytical data of PPQ from fossil crinoid from Germany (Hannover): (a) DAD chromatogram (detection at 420 nm) (upper) and ion chromatogram (positive-ion APPI-MS) (lower) of toluene extract; (b) DAD spectrum of peak 1 shown in (a); (c) mass spectrum of peak 1 shown in (a); (d) collision-induced mass spectrum of *m*/*z* 381.09 shown in (c) (peak 1).

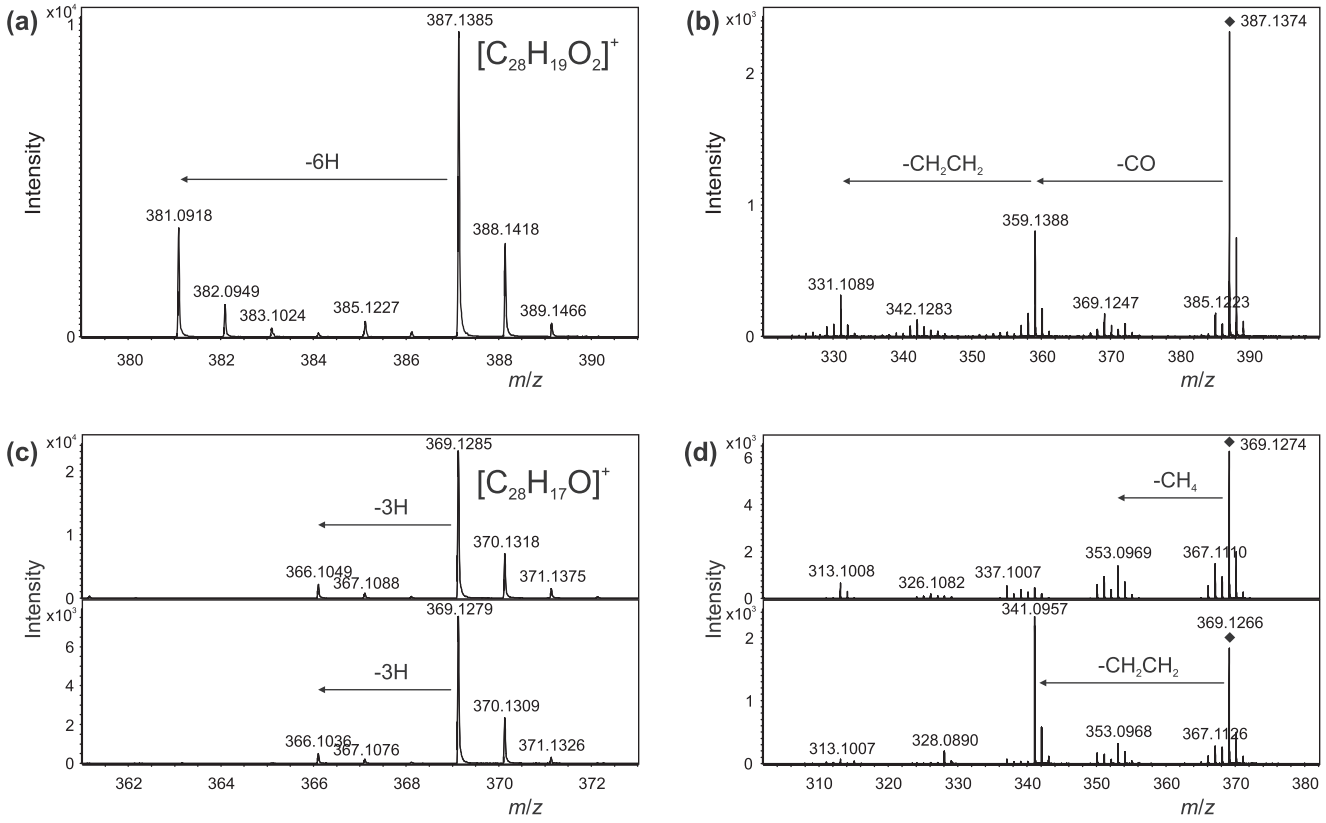

Fig. 4. Analytical data of PPQ derivatives from crinoid from Germany (Hannover): (a) and (c) mass spectra of compounds; (b) and (d) corresponding collision-induced mass spectra of *m*/*z* 387.14 and *m*/*z* 369.13.

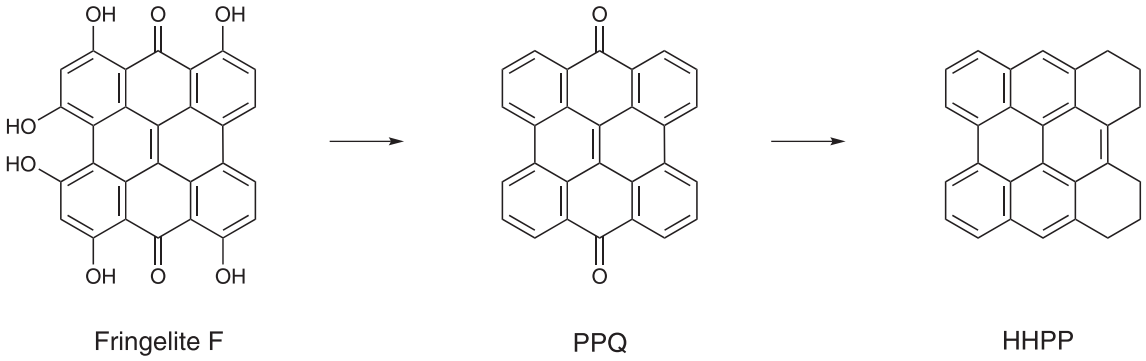

Fig. 5. Proposed diagenetic formation of the PAH HHPP from the phenanthroperylene quinone pigment fringelite F.

2006, 2008). Typically, concentrations of HHPP are small compared to the concentrations of the main quinone pigment fringelite F. Although the primary pigment contents of the individual crinoids are not known, it is remarkable that those samples with the highest absolute amounts of fringelite F yielded only very small amounts of HHPP, whereas most samples with small amounts of fringelite F yielded relatively high amounts of HHPP. One crinoid with one of the highest concentrations of HHPP (millericrinid from Tendaguru) contains even more HHPP than fringelite F. No quantitative information of PPQ could be obtained, due to the extremely poor solubility of the compound in common solvents (see also Falk and Vaisburg, 1995). As estimated from UV absorbance, concentrations of PPQ are thought to be small compared to those of HHPP.

HHPP and the newly identified intermediate PPQ were exclusively found in fossil crinoids that also contain phenanthroperylene quinone pigments. The specific occurrence of the compounds together with the quantitative results mentioned above indicate that HHPP is a diagenetic (possibly early catagenetic) product of fringelite F, suggesting the pathway shown in Fig. 5. The alkyl derivatives of fringelite F hypericin and demethylhypericin are supposed to be precursors of fringelite F (Wolkenstein et al., 2006). Accordingly, homologues of HHPP and PPQ are likely corresponding diagenetic products of hypericin and demethylhypericin.

4. Conclusions

HPLC–APPI-MS analysis of diverse fossil crinoids shows that HHPP occurs more widespread than previously known, with a distribution that is obviously related to co-occurring phenanthroperylene quinone pigments. The discovery of the intermediate PPQ confirms the hypothesis that HHPP is a diagenetic product of the phenanthroperylene quinone pigment fringelite F. The common occurrence of these and various related compounds show that reductive degradation of phenanthroperylene quinones to PAHs is a widespread diagenetic process with a multitude of reaction pathways involved.

Furthermore, the study demonstrates the wide applicability of HPLC–APPI-MS for the characterization of complex organic extracts from geological samples in general. The method has not only allowed for the LC–MS detection of nonpolar compounds, but also led to the discovery of several biomarkers of medium polarity, all of them not accessible to conventional GC–MS because of their low volatility.

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