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Organic signatures in Pleistocene cherts from Lake Magadi (Kenya) – implications for early Earth hydrothermal deposits

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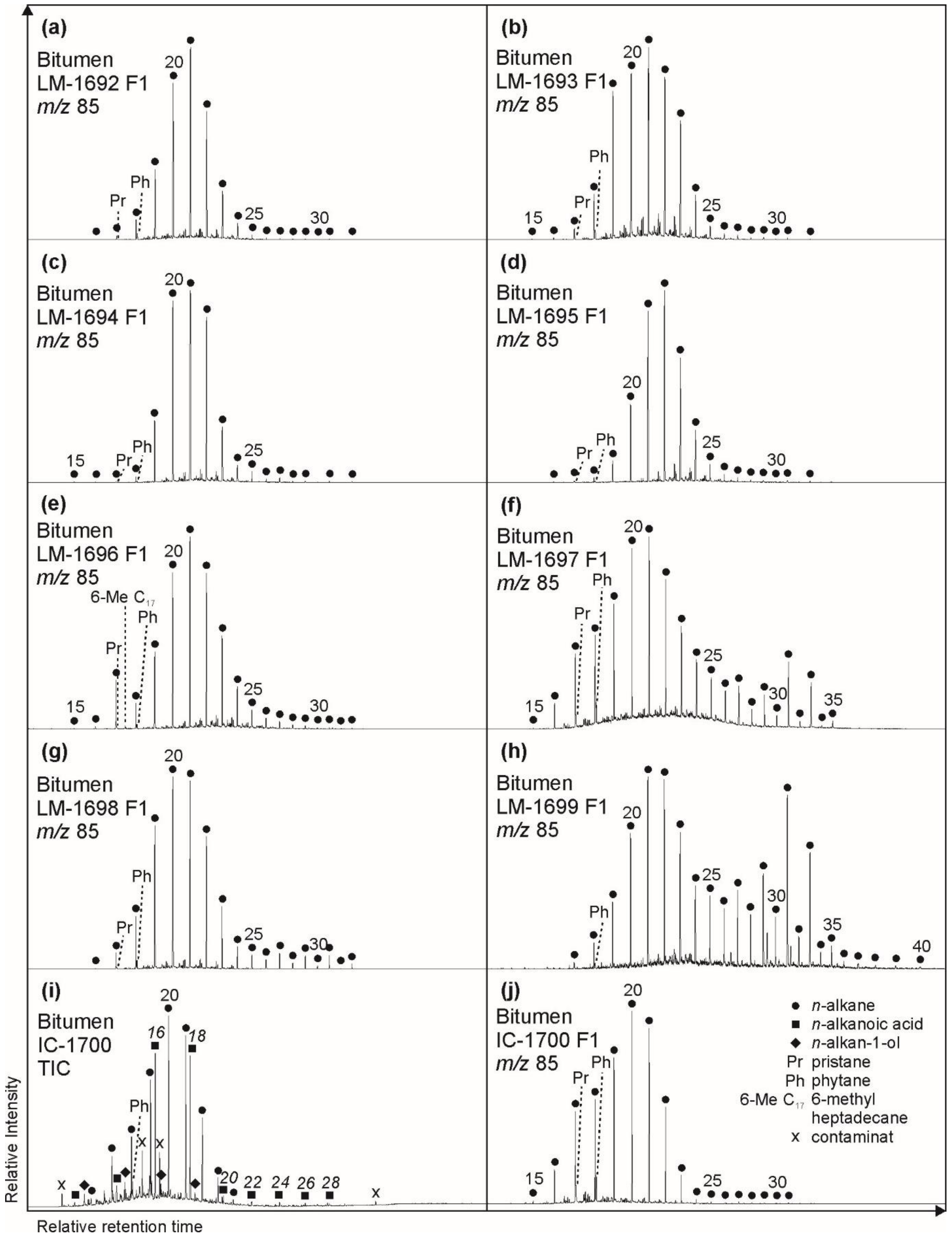
Interior–*versus*-exterior experiments (LM-1692 and LM-1695)

Crushed and powdered surface cut-offs (exterior) and the inner blocks (interior) of LM-1692 and LM-1695 were extracted and derivatized using a similar protocol as described in Section 2.2. In brief, 10 g sample powder (2 × interior and 2 × exterior per sample) was ultrasonically extracted with 20 mL DCM / MeOH (2/1, *v*/*v*), DCM / MeOH (3/1, *v*/*v*) and DCM (10 min, respectively). All TOEs were desulfurized with reduced Cu and hydrolyzed using TMCS / MeOH (1/9, *v*/*v*; heated at 80 °C for 1 h 30 min). Subsequently, the extracts were derivatized with BSTFA / pyridine (3/2, *v*/*v*; heated at 40 °C for 1h). All samples were analyzed via GC-MS using the parameters described in Section 2.4.



(a)
Bitumen
LM-1692 F1
m/z 85
(b)
Bitumen
LM-1693 F1
m/z 85
(c)
Bitumen
LM-1694 F1
m/z 85
(d)
Bitumen
LM-1695 F1
m/z 85
(e)
Bitumen
LM-1696 F1
m/z 85
6-Me C17
(f)
Bitumen
LM-1697 F1
m/z 85
(g)
Bitumen
LM-1698 F1
m/z 85
(h)
Bitumen
LM-1699 F1
m/z 85
(i)
Bitumen
IC-1700
TIC
(j)
Bitumen
IC-1700 F1
m/z 85
n-alkane
n-alkanoic acid
n-alkan-1-ol
Pr pristane
Ph phytane
6-Me C17 6-methyl heptadecane
x contaminat
Relative Intensity
Relative retention time

Figure S1. Partial GC-MS ion chromatograms (*m/z* 85; 10–60 min) of the hydrocarbon fractions (F1) from bitumens of the Magadi cherts (LM-1692–1699; a–h). A total GC-MS ion chromatogram (TIC; 10–60 min) and a partial GC-MS ion chromatogram (m/z 85; 10–60 min) of the Great Geysir reference sinter (IC-1700) is shown in (i) and (j), respectively. A narrow bell-shaped *n*-alkane distribution in the mid-chain range (around *n*-C_{21}) is visible in all samples analyzed. Additionally, odd-numbered long-chain *n*-alkanes are abundant in bitumens from most of the Green Bed cherts (LM-1697–1699; f–h). Notably, 6-methyl heptadecane appears in LM-1696 (e).

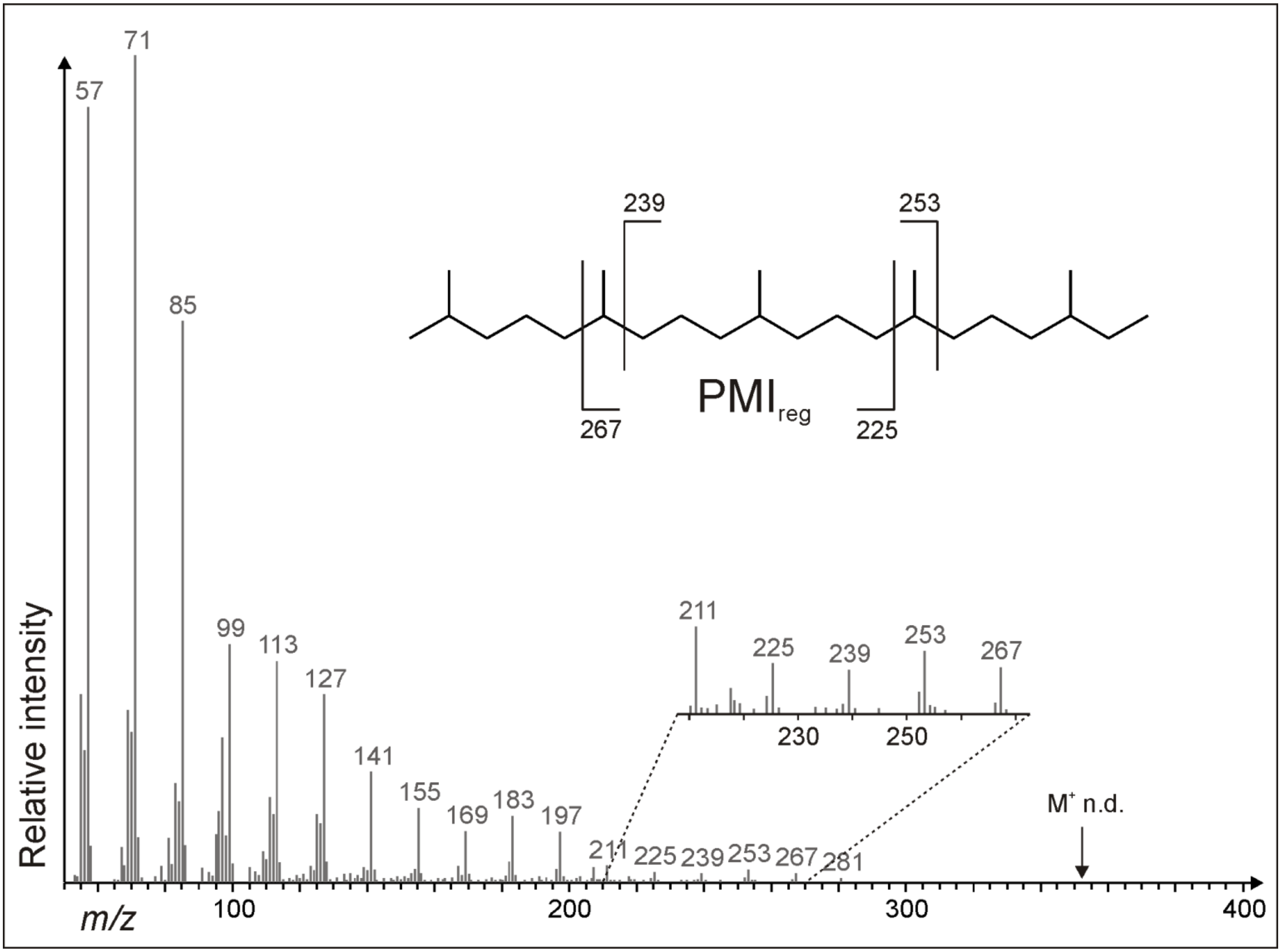


Figure S2. Mass spectrum of the regular C_{25} isoprenoid 2,6,10,14,18-pentamethylicosane (PMI_{reg}) from kerogen of LM-1693 (similar in kerogen pyrolysates from LM-1692 and LM-1695). Typical for this C_{25} isoprenoid isomer is the higher abundance of the fragments at 225 and 253 u, as compared to 239 and 267 u (Risatti et al., 1984; Greenwood and Summons, 2003).The molecular ion (M^+) at 352 u was not detected (n.d.).

Table S1. Mean $\delta^{13}C_{V\text{-}PDB}$ values in ‰ of fatty acids from bitumens

	LM-1692		LM-1693		LM-1694		LM-1695		LM-1696		LM-1697		LM-1698		LM-1699		IC-1700	
	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±
$C_{12:0}$	−25.7	0.1	−25.0	0.1													−26.5	0.1
$C_{13:0}$			−26.1	0.5													−21.2	0.2
$C_{14:0}$	−26.1	<0.1	−27.5	0.1	−27.4	<0.1	−32.2	0.1			−28.5	0.8					−26.4	0.2
i-$C_{15:0}$			−25.3	<0.1	−27.3	0.1											−18.2	<0.1
ai-$C_{15:0}$	−30.9	<0.1	−28.8	0.1	−29.5	0.1											−21.2	0.7
$C_{15:0}$	−27.8	0.1	−28.0	0.2	−26.1	0.1	−31.4	0.2			−21.5	0.4	−29.2	<0.1	−23.9	0.1	−24.8	0.2
$C_{16:1}$													−26.9	0.5				
$C_{16:1}$													−23.7	0.5				
$C_{16:0}$	−28.3	<0.1	−25.3	<0.1	−26.4	<0.1	−23.9	0.1	−27.0	0.5	−27.5	0.1	−23.9	<0.1	−25.3	0.1	−26.1	<0.1
ai-$C_{17:0}$	−34.0	<0.1	−30.0	0.3	−25.7	0.1												
$C_{17:0}$	−29.4	0.2	−27.3	0.2	−24.8	0.7	−27.3	<0.1	−18.8	0.1	−22.8	0.1	−24.1	0.9	−30.5	0.5	−24.2	0.2
$C_{18:2}$			−27.8	1.0	−18.3	0.7			−35.2	0.2			−27.5	0.2				
$C_{18:1}$	−29.1	0.1	−26.5	0.1	−25.8	<0.1			−26.9	<0.1	−28.1	0.5	−23.2	0.2	−30.2	0.1		
$C_{18:1}$	−21.7	0.2	−22.5	0.1									−21.2	0.2				
$C_{18:0}$	−28.3	0.2	−26.3	0.1	−29.1	0.1	−29.6	0.1	−26.2	0.4	−28.7	0.1	−25.1	0.2	−28.4	0.7	−27.2	0.1
$C_{19:0}$											−22.1	0.1	−32.0	0.1			−27.9	<0.1
$C_{20:0}$	−28.8	0.6	−28.2	<0.1	−27.2	<0.1			−20.2	0.1	−20.8	0.1	−27.3	0.7	−27.5	0.2	−21.1	0.1
$C_{21:0}$											−21.3	<0.1	−30.9	0.3				
$C_{22:0}$									−30.5	0.3	−24.3	0.1	−28.0	0.7	−26.7	<0.1	−33.7	0.3
$C_{23:0}$											−25.7	<0.1	−30.8	0.1			−30.6	<0.1
$C_{24:0}$	−24.5	0.1	−28.0	0.1	−22.2	0.1	−28.9	0.1	−28.5	0.3	−26.3	0.1	−27.5	0.1	−28.8	<0.1	−29.5	0.1
i-$C_{25:0}$			−24.8	0.2														
ai-$C_{25:0}$			−27.1	0.2														
$C_{25:0}$			−22.5	0.2							−26.8	0.1	−24.7	0.7			−33.8	0.1
$C_{26:0}$	−25.8	0.2	−30.6	<0.1	−30.4	0.4			−16.3	0.2	−24.6	0.2	−30.0	0.3	−30.5	0.3	−35.4	0.1
$C_{27:0}$											−22.5	0.2					−31.9	0.2
$C_{28:0}$											−25.4	<0.1					−32.0	<0.1

Table S2. Mean $\delta^{13}C_{V\text{-}PDB}$ values in ‰ of alcohols, ketones, mono- and diethers from bitumens

	LM-1692		LM-1693		LM-1694		LM-1695		LM-1696		LM-1697		LM-1698		LM-1699		IC-1700	
	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±
Alkan-1-ols																		
C_{12}																	−29.9	0.4
C_{13}																	−25.2	0.1
C_{14}	−28.5	0.2	−39.5	0.1	−37.3	0.1	−19.6	0.5	−27.1	0.7			−19.4	0.2			−30.2	0.1
C_{15}																	−27.3	<0.1
C_{16}	−34.8	0.2	−25.1	<0.1	−35.5	0.4	−36.0	0.3	−35.9	0.2	−33.1	0.2	−33.6	0.4	−30.9	0.3	−24.4	0.1
C_{18}	−37.2	0.3	−31.9	0.2	−35.0	0.3	−35.9	0.4	−34.8	0.1	−33.2	<0.1	−35.1	0.4	−32.8	0.4	−29.4	0.3
C_{20}	−30.9	0.1	−29.9	0.6	−32.7	0.1	−30.3	0.2	−29.8	0.1	−24.8	0.2	−29.5	0.1	−30.9	0.1		
C_{21}							−33.3	0.2										
C_{22}	−29.6	0.4	−32.4	0.3	−28.7	0.1	−30.3	0.2	−25.2	0.4	−34.6	0.2	−26.7	0.3	−31.5	0.3	−25.9	0.2
C_{23}													−31.1	0.1	−20.2	0.4		
C_{24}	−20.2	0.3	−36.5	0.1	−28.3	0.3	−32.3	0.6	−30.1	0.7	−22.6	0.8	−25.0	0.2	−30.0	0.3	−24.0	0.1
C_{25}													−17.5	0.2	−25.3	0.2		
C_{26}	−32.1	0.5	−33.8	0.7	−17.4	0.2	−28.5	0.9	−26.5	0.3	−29.2	0.1	−21.7	0.3	−21.8	0.2	−27.7	0.5
C_{27}													−26.4	0.3				
C_{28}	−21.3	1.0	−26.7	0.5	−20.6	0.4	−26.6	1.0	−18.7	0.3	−22.8	0.1	−25.4	<0.1	−23.5	0.1	−23.0	0.2
C_{30}					−14.6	0.3					−20.3	0.7			−19.6	0.1	−29.5	0.5
C_{32}	−26.4	0.7																
Glycerol mono- and diethers																		
i-$C_{16:0}$	−21.8	0.1	−20.3	<0.1	−12.2	<0.1												
$C_{16:0}$	−20.4	0.1	−20.2	0.7	−11.4	0.4												
10Me-$C_{16:0}$	−21.5	0.1	−23.0	0.1	−19.7	<0.1												
i-$C_{17:0}$	−25.2	0.2	−21.3	0.5														
ai-$C_{17:0}$	−17.4	0.1	−25.0	0.7														
$C_{17:0}$	−19.0	0.1	−26.9	0.1	−10.7	0.2												
Me-$C_{17:0}$	−22.1	0.1	−17.9	0.4	−10.9	0.1												
Me-$C_{17:0}$	−22.5	0.3	−9.8	<0.1	−9.4	<0.1	−18.6	0.1										
$C_{18:1}$	−20.9	0.2	−15.7	0.1														
$C_{18:1}$	−19.1	0.8	−22.9	0.7	−7.0	0.2												
$C_{18:0}$	−12.5	0.2	−19.0	0.8	−5.7	0.4												
A	−21.7	0.4	−18.5	0.5	−12.2	0.4	−22.2	0.1	−14.8	0.5					−16.6	0.4		
ExA	−18.3	0.6	−19.9	0.2	−15.3	0.4	−19.4	0.5	−19.6	0.5								
Other compounds																		
Tetrahym.							−33.3	0.3	−27.7	0.1	−25.4	0.2	−24.1	0.5	−29.3	0.2		

Table S3. Mean $\delta^{13}C_{V\text{-}PDB}$ values in ‰ of alkanes and isoprenoids from bitumens

	LM-1692		LM-1693		LM-1694		LM-1695		LM-1696		LM-1697		LM-1698		LM-1699		IC-1700	
	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±
n-C_{16}																	−37.1	0.1
n-C_{17}			−30.5	0.6					−30.1	0.6	−38.0	1.2					−32.9	<0.1
6Me-C_{17}									−30.3	0.2								
n-C_{18}	−32.5	<0.1	−32.1	<0.1	−31.8	0.5	−35.6	0.5	−33.8	<0.1	−34.4	0.1	−34.3	0.1			−33.4	<0.1
n-C_{19}	−32.0	0.2	−31.6	0.1	−32.0	0.1	−33.3	0.3	−32.9	0.5	−33.3	0.4	−32.9	<0.1	−14.7	0.5	−35.2	0.1
i-C_{20}	−31.1	0.1	−30.0	<0.1	−34.1	0.3							−29.8	0.2				
ai-C_{20}	−32.1	0.8	−33.2	0.1	−29.0	0.8							−27.5	0.1				
n-C_{20}	−31.4	<0.1	−30.7	0.2	−30.9	0.3	−32.3	0.4	−33.2	<0.1	−32.6	0.4	−32.7	0.2	−38.9	0.3	−33.6	<0.1
i-C_{21}	−32.3	<0.1	−31.2	<0.1	−32.7	<0.1	−30.9	0.1	−34.4	0.7	−35.3	0.5	−33.2	0.3				
ai-C_{21}	−29.8	<0.1	−31.5	<0.1	−30.5	0.3	−31.9	0.4	−28.6	0.1	−36.5	0.3	−32.2	0.1				
n-C_{21}	−31.6	<0.1	−31.0	0.2	−31.2	0.4	−31.9	0.1	−32.9	<0.1	−31.6	<0.1	−33.6	<0.1	−35.0	0.7	−34.0	<0.1
i-C_{22}	−29.9	0.8	−33.2	0.1	−29.6	0.1	−34.0	0.3	−34.1	0.1	−34.9	0.1	−33.6	0.1				
ai-C_{22}	−29.1	0.2	−37.4	0.8	−28.9	0.1	−34.4	0.2	−33.3	<0.1	−32.6	0.1	−33.3	0.3				
n-C_{22}	−32.1	0.2	−31.7	<0.1	−32.0	0.3	−32.3	0.1	−32.8	<0.1	−31.6	0.2	−34.4	0.2	−36.7	0.3	−37.5	<0.1
i-C_{23}	−33.8	0.1	−30.3	0.1	−29.1	0.1	−32.1	<0.1	−31.4	<0.1	−36.5	0.1	−31.3	0.2				
ai-C_{23}	−33.7	0.2	−27.3	0.1	−28.8	0.1	−33.1	0.1	−32.1	0.1	−39.1	0.4	−30.2	0.4				
n-C_{23}	−32.1	<0.1	−32.2	0.2	−32.2	<0.1	−32.4	0.1	−32.6	0.3	−34.5	<0.1	−33.4	0.1	−25.4	0.1	−39.6	0.1
i-C_{24}	−31.8	<0.1	−33.9	0.1	−32.5	<0.1	−29.8	0.4	−35.2	<0.1			−36.3	0.3				
ai-C_{24}	−26.2	0.5	−32.6	0.2	−31.5	0.1	−29.0	0.1	−34.3	0.3			−29.5	0.7				
n-C_{24}	−32.7	0.2	−33.7	<0.1	−31.6	<0.1	−31.8	0.2	−32.5	0.5	−30.6	0.2	−32.2	0.1	−27.6	0.2	−39.2	<0.1
i-C_{25}	−30.8	<0.1	−31.2	0.4	−25.3	<0.1	−34.6	0.1	−28.4	0.4								
ai-C_{25}	−26.8	0.4	−35.9	0.4	−22.6	0.2	−30.4	0.7	−28.0	0.2								
n-C_{25}							−32.0	<0.1	−30.2	0.1	−34.7	0.1	−34.9	0.2	−25.6	0.1		
n-C_{26}							−29.8	0.1	−29.9	0.2	−34.0	0.2	−25.8	<0.1	−34.8	0.3		
n-C_{27}											−36.3	0.2	−23.7	0.1	−30.8	0.1		
n-C_{28}											−33.8	0.2	−24.2	0.3	−27.9	0.1		
n-C_{29}											−28.8	0.4	−23.9	0.5	−21.5	0.2		
n-C_{30}															−26.9	0.1		
n-C_{31}											−20.9	0.6	−24.4	0.1	−21.1	0.4		
n-C_{32}															−24.5	0.2		
n-C_{33}															−25.8	<0.1		
Isoprenoids																		
Pr			−31.7	0.1					−30.2	0.1	−32.2	0.2	−35.8	0.1			−34.5	0.2
Ph	−33.3	<0.1	−30.9	0.4	−30.0	0.6	−36.1	1.2	−34.7	0.1	−33.8	0.1	−35.3	<0.1			−38.6	0.1

Table S4. Mean $\delta^{13}C_{V\text{-}PDB}$ values in ‰ of alkanes and isoprenoids from kerogens

	LM-1692		LM-1693		LM-1694		LM-1695		LM-1697		LM-1698	
	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±	Mean	±
n-C_{15}							−30.5	0.6				
n-C_{16}							−30.4	0.1			−30.9	0.1
n-C_{17}							−30.3	<0.1	−26.0	0.3	−31.3	<0.1
n-C_{18}	−36.3	0.7	−35.0	0.9			−31.5	0.2	−25.4	0.4	−34.9	<0.1
n-C_{19}	−32.0	0.3	−29.2	0.7			−27.2	0.1	−24.0	<0.1	−34.6	0.1
n-C_{20}	−27.8	0.6	−33.7	0.8	−34.6	0.6	−26.9	0.1	−22.1	<0.1	−35.8	0.2
n-C_{21}	−28.1	0.4	−31.5	0.3	−29.6	0.5	−27.6	0.7	−22.0	0.2	−34.3	0.8
n-C_{22}	−31.1	<0.1	−30.9	0.2	−26.6	0.1	−28.8	0.1	−23.0	0.9	−32.9	0.1
n-C_{23}	−31.8	0.1	−29.3	0.4	−21.0	0.1	−27.3	<0.1	−22.4	0.1	−34.5	0.8
n-C_{24}	−26.5	0.6	−30.5	0.3	−24.7	0.4	−26.9	0.2	−22.9	0.5	−35.3	0.2
n-C_{25}	−28.7	0.5	−30.9	1.0	−22.7	0.2	−27.3	<0.1	−24.4	0.3	−34.9	<0.1
n-C_{26}	−26.6	0.5	−27.4	0.1	−23.3	0.2	−25.4	<0.1	−24.1	0.1	−29.7	0.1
n-C_{27}	−29.8	0.3	−30.6	0.1	−18.9	0.1	−24.8	<0.1	−22.9	0.4	−28.0	0.1
n-C_{28}	−30.4	0.4	−28.8	0.7	−24.3	0.4	−23.6	0.3	−22.6	0.3	−28.0	0.1
n-C_{29}	−25.9	<0.1	−29.1	0.8	−16.8	1.0	−25.8	0.2	−22.8	0.2	−26.3	0.3
n-C_{30}	−29.6	0.6	−32.3	0.4	−22.0	0.8	−24.3	0.3	−22.1	<0.1	−26.0	0.1
n-C_{31}	−24.7	0.2	−31.0	0.4	−23.0	0.4	−23.5	<0.1	−22.4	0.1	−27.1	0.6
n-C_{32}	−26.7	0.4	−31.3	1.0	−21.9	0.6	−22.6	0.4	−21.5	<0.1	−24.1	0.6
n-C_{33}	−24.8	0.7			−26.0	0.3	−23.6	0.2	−21.4	0.4	−26.2	0.2
n-C_{34}	−27.6	0.1			−24.6	1.0	−23.2	0.1	−21.2	0.1	−25.4	<0.1
n-C_{35}	−28.9	0.3			−26.0	0.4	−24.4	0.7	−20.4	0.5	−28.2	0.5
n-C_{36}					−26.1	0.2	−27.4	0.7	−21.0	0.1	−23.7	0.4
n-C_{37}							−27.7	0.9	−20.8	0.4	−26.9	0.2
n-C_{38}							−25.6	<0.1	−19.3	0.6	−25.3	<0.1
n-C_{39}									−21.8	0.1		
n-C_{40}									−21.6	0.5		
Isoprenoids												
Far							−33.0	0.2				
Nor							−35.3	0.1				
Pr							−32.3	0.3				
Ph	−25.1	0.3	−26.8	0.2			−28.5	<0.1				
PMI_{reg}	−22.0	0.3	−24.0	0.4	−14.5	<0.1	−24.6	0.1				

Table S5. Coefficients of determination (R^2) for Raman fittings

	LM-1692	LM-1693	LM-1694	LM-1695	LM-1696	LM-1697	LM-1698
Flake 1	0.995	0.996	0.995	0.975	0.985	0.984	0.989
Flake 2	0.996	0.997	0.995	0.989	0.992	0.987	0.975
Flake 3	0.994	0.998	0.992	0.982	0.989	0.987	0.984
Flake 4	0.988	0.992	0.994	0.986	0.994	0.987	0.991
Flake 5	0.996	0.997	0.989	0.992	0.997	0.984	0.986
Flake 6	0.996	0.997	0.994	0.974	0.989	0.986	0.985
Flake 7	0.996	0.997	0.995	0.954	0.992	0.979	0.986
Flake 8	0.995	0.998	0.979	0.992	0.982	0.970	0.981
Flake 9	0.997	0.998	0.988	0.987	0.992	0.985	0.986
Flake 10	0.998	0.995	0.991	0.991	0.989	0.987	0.992
Mean	0.995	0.996	0.991	0.982	0.990	0.984	0.986

Table S6. Mean concentrations of selected *n*-alkanes, archaeol (A) and extended archaeol (ExA) in the interior and exterior of LM-1692 and LM-1695 (mg/g TOC).

	n-C_{18}	*n*-C_{19}	*n*-C_{20}	*n*-C_{21}	*n*-C_{22}	*n*-C_{23}	*n*-C_{24}	*n*-C_{25}	A	ExA
1692 exterior	0.02	0.11	0.13	0.18	0.13	0.16	0.03	0.02	0.21	0.12
1692 interior	0.02	0.09	0.12	0.22	0.20	0.16	0.04	0.03	0.17	0.12
1695 exterior	0.08	0.35	0.42	1.20	0.96	0.74	0.42	0.25	0.24	0.09
1695 interior	0.07	0.32	0.49	1.83	1.33	0.76	0.32	0.13	0.42	0.16