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1	Effect of pressure on the thermal cracking and
2	polymerization of pentacosane $(n-C_{25})$, an $n-$
3	alkane
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10 Abstract

11 Hydrocarbons are important carbon components in the subducting slab and that play a crucial role in 12 the Earth's deep carbon cycle. In this study, the thermal reaction of pentacosane (n-C₂₅), a long n-13 alkane, was experimentally investigated under high-pressure and high-temperature conditions at 0.5-14 1.5 GPa and 360–400 °C. The gas chromatography-mass spectrometry (GC/MS) analyses of the 15 reaction products revealed that the radical reaction of $n-C_{25}$ proceeded above 360 °C at 0.5 GPa and 16 above 380 °C at 1.5 GPa, while the rate constant decreased with increasing pressure. Lighter *n*-alkanes 17 and heavier straight/branched alkanes were detected in the reaction products. The formation of lighter 18 *n*-alkanes indicates thermal cracking progression, even at high-pressure conditions. During thermal 19 cracking, lighter 1-alkenes were likely to form, but were instead rapidly added to the initial n-C25 to 20 form heavier alkanes when enhanced by pressure. Thus, lighter 1-alkenes were not detected in the 21 reaction products. As the secondary reaction, the heavier alkanes were polymerized with 22 dehydrogenation to form amorphous carbon when the remaining percentage of the initial material 23 became <10 % and <20 % at 0.5 and 1.5 GPa, respectively, while the lighter *n*-alkanes were detected 24 simultaneously. Both lighter alkanes with high H/C ratios and amorphous carbon with a low H/C ratio 25 eventually formed through the reaction of *n*-alkanes at high-pressure and high-temperature conditions 26 of the deep Earth.

27 Table of Contents graphic

0.5 GPa, 360-400 °C 1.5 GPa, 380-400 °C	Increasing temperature, reaction	time
$\begin{array}{ccc} n\text{-}C_{25} & \xrightarrow{\text{Initiation}} & n\text{-}C_{25} & \xrightarrow{\beta} \\ & & & & \\ & & & \\ & & & \\ & & & &$	3-scission Lighter <i>n</i> -alkanes Lighter 1-alkenes Addition reaction Heavi	Condensation with dehydrogenation (secondary reaction) (secondary reaction) (secondary reaction)
Enhanced by pressure Suppressed by pressure	110471	

28

30 Introduction

31 The stability and chemical reactions of hydrocarbons are crucial in Earth and planetary science 32 because of their widespread occurrence, including the interstellar medium^{1, 2}, carbonaceous 33 meteorites^{3, 4}, and organic sediments at the Earth's surface⁵. Furthermore, hydrocarbons were found 34 in the mantle peridotite xenoliths⁶. Organic sediments including hydrocarbons are likely to be 35 supplied from the Earth's surface to the deep Earth with subducting slabs^{7, 8}. In addition, abiotic 36 hydrocarbons are synthesized in the deep Earth by Fischer–Tropsch reactions⁹, and by the reduction 37 of carbonates^{10, 11}. Stability and chemical reactions of hydrocarbons in the deep Earth are essential for 38 understanding the deep carbon cycles of the Earth, but are currently poorly understood. In the Earth's 39 interior, both temperature and pressure increase with increasing depth. Generally, high temperature 40 would enhance thermal cracking with the production of lighter molecules, whereas high pressure 41 would induce polymerization with the formation of heavier compounds¹²⁻¹⁷. Thus, the chemical 42 reactions of hydrocarbons at high-pressure and high-temperature (HPHT) conditions are expected to 43 be complicated and are the subjects of ongoing debate. 44 Methane, the simplest hydrocarbon, is an important component in C-O-H fluids in the Earth's mantle¹⁸, and its chemical reactions under HPHT conditions have been widely investigated. 45

46 The formation of ethane and heavier hydrocarbons with the dehydrogenation and polymerization of

47	methane progressed above 1,000 K, comparable to the HPHT conditions of Earth's upper mantle and
48	the interiors of icy planets ¹⁹⁻²³ . The reaction advanced significantly with increasing temperature and
49	eventually formed graphitic carbon/diamond above 3000 K. Thermodynamic calculations and
50	theoretical studies have pointed out that alkanes heavier than methane become more stable with
51	increasing pressure and temperature ^{24, 25} , but much less is known on the chemical reactions of heavier
52	alkanes under HPHT conditions. Chemical reactions of propane (C3H8) progressed partially at
53	temperatures of approximately 1000 K and pressures of 3-22 GPa to form both heavier alkanes, such
54	as butane (C_4H_{10}), pentane (C_5H_{12}), and hexane (C_6H_{14}), and lighter hydrocarbons such as methane,
55	suggesting that C-C bond formation and cleavage of C-C and C-H bonds occurred simultaneously ²⁶ .
56	The formation of hydrogenated amorphous carbon from <i>n</i> -hexane at \sim 20 GPa and 1000 K, as well as
57	diamond formation from longer <i>n</i> -alkanes (C ₈ H ₁₈ to C ₁₉ C ₄₀) above 3000 K at 10–20 GPa were
58	reported ^{27, 28} . Theoretical and experimental studies have suggested that when the unbranched alkane
59	chains reach some critical length, the chains assume a folded conformation rather than a linear one ^{29,}
60	³⁰ . Pressure-induced transition from linear to fold molecular conformations was observed in longer n -
61	alkanes (C_7H_{16} , $C_{18}H_{38}$, and $C_{23}H_{48}$), where the reaction pressure decreased as the carbon numbers of
62	n-alkanes increased ³¹⁻³³ . Kinks in fold structures are likely to facilitate cracking of the longer chains,
63	hence, reactions in longer alkanes exposed to high temperatures after compression may be the result

of individual processes on the alkane chain length, and it is necessary to investigate the reaction individually. 32, 33 65

66	Thermal reactions of n -alkanes at lower pressure conditions, such as those of the shallow
67	crust, have been investigated with significant attention in the field of petrochemistry. The complex
68	reaction products were quantitatively and quantitatively evaluated by using gas chromatography-
69	mass spectrometry (GC/MS) analyses. Free-radical reaction pathways are considered to be the
70	dominant reaction pathways of alkanes ³⁴⁻³⁶ . The series of reactions is initiated by the cleavage of C-
71	C bonding, followed by H-transfer to form radicals of the initial alkane. Lighter <i>n</i> -alkanes and 1-
72	alkenes are formed by beta-scissions from the radicals of the initial alkane. Furthermore, heavier
73	straight and branched alkanes are formed by addition reactions between the initial alkane and the 1-
74	alkenes. The effect of pressure on the thermal reactions was also investigated previously ³⁷⁻³⁹ , however,
75	the pressure ranges of most of these studies were limited to below ~100 MPa.
76	In this study, the thermal reaction of a long straight alkane, pentacosane (n -C ₂₅), was
77	investigated experimentally at 0.5 and 1.5 GPa in a closed system. Pentacosane was selected as a

- model hydrocarbon compound due to its occurrence in various environments, including petroleum 78
- crudes⁴⁰, ultramafic hydrothermal field on the Mid-Atlantic Ridge⁴¹, and carbonaceous meteorites^{1,3}. 79
- 80 In addition, *n*-C₂₅ was found in tectonites and mantle xenoliths⁶ thus, its presence in the deep Earth

has been suggested. Investigating the stability and reactions of n-C₂₅ under HPHT conditions are essential for determining its origin, as well as its role in the deep carbon cycle. The complex reaction products were identified and evaluated analytically using GC/MS to reveal the reaction mechanisms and the effect of pressure.

85 Experimental methods

Pentacosane (C₂₅H₅₂, Tokyo Chemical Industry Co. LTD., purity >99.0 %) and aluminum oxide 86 87 (Al₂O₃, FUJIFILM Wako Pure Chemical Corporation) were used as the initial materials for the HPHT 88 experiments. Aluminum oxide was powdered and cleaned with acetone, then heated in an oven at 89 450 °C for 4 h to remove organic contaminants. Pentacosane and aluminum oxide were mixed in an 90 agate mortar with a weight ratio approximately 1:4. A gold sample capsule with a 4 mm outer diameter 91 was cleaned with dichloromethane and heated in an oven at 450 °C for 4 h to remove organic 92 contaminants prior to encapsulating the sample. Approximately 15 mg of the initial material was filled 93 into the gold capsule and welded. The capsule was pressurized using a tungsten carbide piston-94 cylinder type apparatus equipped with a hydraulic press. A cylinder with a 4 mm inner diameter was 95 used without a pressure medium. Sealing plates made of stemless seats and copper/phosphor bronze 96 (0.2 mm thick) were placed at the top and bottom of the sample capsule. The sample was first 97 compressed to the target pressure at room temperature, and then heated using a band-type external

98	heater surrounding the cylinder. The temperature was measured using a K-type thermocouple attached
99	to the top of the cylinder. The detail of the apparatus was described in a previous study ⁴² .
100	The samples after the HPHT experiments were recovered from the capsules in distilled
101	dichloromethane solvent by drilling to prevent the reaction products from escaping. The solution was
102	initially filtered by a membrane filter to extract the soluble products from the insoluble products. For
103	the soluble products, mass spectrometry was performed using a GC/MS (Agilent 6890/5973N)
104	equipped with a 30 m \times 0.25 mm I.D. capillary column, with a 0.25 μm layer of stationary phase
105	(DB-5HT, Agilent Technology Co.). The representative GC column temperature program was as
106	follows; maintained at 45 °C for 3 min, then increased from 45 to 325 °C at a rate of 3 °C/min, and
107	then finally held at 325 °C for 10 min. Helium was used as the carrier gas (1 mL/min). An m/z scan
108	range from 50 to 550 was used. Methyl laurate ($C_{13}H_{26}O_2$) and methyl stearate ($C_{19}H_{38}O_2$) were used
109	as internal standards for the quantitative analyses. Raman spectra of the insoluble products were
110	measured using micro-Raman spectrometry. The applied Raman spectrometer was equipped with a
111	semiconductor laser ($\lambda = 532$ nm) with approximately 5.5 mW output power on the sample surface,
112	an optical microscope with an objective lens, a single polychromator, and a CCD-detector. Scattered
113	light was dispersed using a grating with 1,200 grooves/mm. The Raman bands of naphthalene and
114	neon emission lines were used for Raman shift calibration. The spectral resolution was approximately

115	1 cm ⁻¹ . To check that laser irradiation did not damage the samples, the spectra were measured
116	repeatedly at the same points. Changes in the Raman spectra due to laser damage were not observed.
117	The appearance of the samples was also checked before and after laser irradiation using an optical
118	microscope; there were no considerable changes observed.
119	Results
120	The HPHT experiments with n -C ₂₅ performed at 0.5 and 1.5 GPa and at temperatures ranging from
121	360 to 400 °C are listed in Table 1. Figure 1a and b represents logarithmic plots of the remaining <i>n</i> -
122	C_{25} at 0.5 and 1.5 GPa, respectively. A remarkable decrease in <i>n</i> - C_{25} was observed at 360-400 °C, 0.5
123	GPa and at 380-400 °C, 1.5 GPa, while the reaction was not observed from the samples at 360 °C,
124	1.5 GPa (runs 15 and 16). The remaining ratio of the starting material decreased with both increasing
125	reaction time and temperature. The reaction times and the logarithms of the remaining ratios show a
126	linear relationship, indicating that the reaction is a first-order reaction. Table 2 presents the calculated
127	rate constants for <i>n</i> -C ₂₅ at 0.5 GPa (360–400 °C) and 1.5 GPa (380–400 °C), indicating that the
128	reaction rate decreases with increasing pressure.
129	

Table 1 Experimental Conditions of the Present Study 131

130

Dun no	Pressure	Temperature	Reaction time	Remaining
Kun no.	(GPa)	(°C)	(h)	$n-C_{25}$ (%)
1	0.5	360	48	91.7
2	0.5	360	96	77.2
3	0.5	360	192	47.8
4	0.5	370	48	91.3
5	0.5	370	96	71.0
6	0.5	370	192	26.5
7	0.5	380	24	77.0
8	0.5	380	48	56.7
9	0.5	380	96	27.6
10	0.5	400	8	68.3
11	0.5	400	24	25.7
12	0.5	400	48	8.55
13	0.5	400	48	1.2
14	0.5	400	96	0.4
15	1.5	360	48	100.2
16	1.5	360	96	101.2
17	1.5	380	48	92.7
18	1.5	380	96	82.1
19	1.5	380	192	68.3
20	1.5	400	48	83.8
21	1.5	400	96	27.0
22	1.5	400	96	17.4
23	1.5	400	192	4.6
24	1.5	400	192	1.6

Table 2 Rate Constants Obtained for the *n*-C25 reaction

	0.5 GPa	1.5 GPa
360 °C	1.11×10 ⁻⁶	
370 °C	1.99×10 ⁻⁶	
380 °C	3.75×10 ⁻⁶	5.33×10 ⁻⁷
400 °C	1.68×10 ⁻⁵	5.63×10 ⁻⁶



136 Figure 1 Remaining ratio of n-C₂₅ between 360 and 400 °C at (a) 0.5 and (b) 1.5 GPa.

137	Figure 2 shows a representative total ion chromatogram (TIC) of the reaction products
138	recovered from 0.5 GPa and 400 °C for 24 h (run 11). Many intense peaks were detected with almost
139	equal intervals at shorter retention times than that from n -C ₂₅ . The peaks were identified as lighter n -
140	alkanes (<i>n</i> -C ₉ to <i>n</i> -C ₂₄) by their retention times and the mass spectra. Although <i>n</i> -C ₂₃ and <i>n</i> -C ₂₄ were
141	contained in the initial material, as well as $n-C_{26}$ and $n-C_{27}$, the amounts of these contaminants were
142	significantly lower than those detected in the reaction products (Table S1). In the slightly shorter
143	retention times than that of <i>n</i> -C ₂₅ , the peaks assignable as C ₂₅ alkenes were detected, which had $[M]^{+}$
144	= 350 in their mass spectra (Figure S1a), while peaks from alkenes with carbon numbers < 24 were
145	not detected in the reaction products. Many peaks were detected at longer retention times than that
146	from n -C ₂₅ , suggesting the formation of heavier hydrocarbons. Most of the heavier reaction products
147	had fragmental peaks of $m/z = 57$, indicating that the reaction products were alkanes, some of which
148	were identified as the longer straight alkanes (<i>n</i> -C ₂₆ to <i>n</i> -C ₃₂). An intense fragmented peak of $m/z =$
149	351 was found from most of the other heavier products (Figure S1b-d), which is considered as a
150	fragmented peak of $C_{25}H_{51}$ ⁺⁺ . The results suggest that most of the heavier reaction products were
151	branched alkanes formed by an addition reaction between n -C ₂₅ and alkyl fractions.
152	



154

Figure 2 Representative TIC of GC/MS measurements from the reaction product of the sample at 0.5 GPa
and 400 °C for 24 h (run 11). Numbers 9–27 represent *n*-alkane peaks. Asterisk represents the internal
standard peak. Inset is an enlarged view at 57–70 min. The mass spectra of peaks a–d are represented in
Figure S1.

Figure 3a shows representative molar yields of lighter *n*-alkanes from n-C₉ to n-C₂₄ at 0.5 GPa and 400 °C with different reaction times. The molar yields of the lighter *n*-alkanes increased with

162	increasing carbon numbers up to n -C ₂₂ after reaction times of 8 h (Figure 3a, Table S1). The yields of
163	n-C ₂₃ and n-C ₂₄ were significantly lower than those of the other lighter n -alkanes. It is indicated that
164	C-C bond cracking did not likely occur at the end of the chain, but rather in the interior C-C bonds as
165	reported during the thermal cracking of n -C ₂₅ at lower pressure conditions ³⁹ . After the reactions at 48
166	and 96 h, the molar yields show an opposite trend, namely the molar yields decreased with decreasing
167	the carbon numbers from n -C ₂₂ to around n -C ₁₀ . At 1.5 GPa, a similar trend of the molar yields of
168	lighter <i>n</i> -alkanes was observed (Figure 3b). Namely, molar yields of the lighter <i>n</i> -alkanes increased
169	with increasing carbon numbers up to $n-C_{22}$ after the reaction for 48 h, while the molar yields
170	decreased with decreasing carbon numbers from $n-C_{22}$ to around $n-C_9$ after the reaction for 96 and
171	192h. The sum of the molar yields of the lighter <i>n</i> -alkanes between $n-C_9$ and $n-C_{24}$ shows an
172	increasing trend with the decrease of the remaining n -C ₂₅ , and the total molar yields reached around
173	11 % and 15 % at 0.5 GPa (run 13) and 1.5 GPa (run 21), respectively (Table S1).









177 changing reaction times. The yields are an average of two runs with the same experimental conditions for



(a)

179	Figure 4a shows representative single ion chromatograms of $m/z = 57$ at 0.5 GPa, 400 °C
180	with different reaction times from 8 to 96 h. Many heavier and lighter alkane peaks were observed
181	from the samples after heating for 8 and 24 h, for which the remaining percentages of the starting
182	material were 68.3 % and 25.7 % (runs 10 and 11), respectively. The relative intensity of the peaks
183	from the heavier alkanes decreased and almost disappeared after heating for 48 and 96 h, where the
184	remaining percentages of the initial material were 1.2 % and 0.4 %, respectively (runs 13 and 14),
185	while the light <i>n</i> -alkanes still remained. The total yield of the heavier alkanes was 7.8 wt.% after
186	heating for 24 h (run 11) and decreased significantly to <1 wt.% after heating for 48 and 96 h (runs
187	12-14, respectively) as listed in Table S2. The extracted solutions from runs 12-14 changed to a
188	yellow color, while the solution of the other recovered samples and the starting material were
189	transparent. It is implying the formation of some soluble heavier conjugated organics in runs 12–14,
190	but the organics were not able to be analyzed using the GC/MS analysis applied in this study. For the
191	single ion chromatogram of the reaction products at 1.5 GPa and 400 °C, as shown in Figure 4b, the
192	peaks from the heavier alkanes were still observed, but the total yields decreased from 5.9 to \sim 2 wt%,
193	while the remaining percentage of the initial material decreased from 17.4 % to <5 % with reaction
194	times increased from 96 to 192 h (Table S2). The total yield of the reaction products did not reach
195	100%, suggesting that the lighter <i>n</i> -alkanes less than C_8 and the heavier molecules might be formed

196 by thermal cracking and addition reactions, but those products were not able to be detected by the





Figure 4 Single ion chromatograms (m/z = 57) at (a) 0.5 GPa and 400 °C and at (b) 1.5 GPa and 400 °C

201 for different reaction times. The intensities of the chromatograms were normalized by the peak intensity

202 of methyl laurate, the internal standard. The remaining percentages of $n-C_{25}$ are shown in brackets.

204	Insoluble carbonaceous materials with aluminum oxide were obtained from the samples
205	after heating to 400 °C at 0.5 GPa for >48 h, and to 400 °C at 1.5 GPa, for >96 h (runs 13, 14, and
206	22-24). Figure 5a and b show the representative Raman spectra of the insoluble materials obtained
207	from the sample at 0.5 GPa and 400 °C for 96 h (run 14) and from the sample at 1.5 GPa, and 400 °C
208	for 192 h (run 24), respectively. Peaks were observed at 1254, 1331, 1487, and 1604 cm ⁻¹ (run 14)
209	(the fitting details are shown in Figure S2a and Table S3a), which were assignable as the D4, D1, D3,
210	and G_L bands of carbonaceous material ^{43, 44} . The G_L band consisted of G and D2 bands, but could not
211	be separated. The second-order bands were observed at around 2500–3200 cm ⁻¹ , but were not well-
212	resolved. The peak frequencies and shapes were similar to those of soot ⁴³ and amorphous carbon ⁴⁵ ,
213	rather than amorphous hydrogenated carbon ⁴⁶ . In the case of amorphous hydrogenated carbon, which
214	contains >20 % hydrogen, the peak intensity of the G band is much higher than that of the D band, in
215	contrast to that observed from the insoluble material of the present study. The intensities of $D_{\rm l}/G_{\rm L}$ in
216	runs 14 and 24 samples were 0.73 and 0.70, respectively, suggesting low sp ³ /sp ² ratios ⁴⁵ . The spectra
217	obtained from the insoluble material at 0.5 GPa showed rises in the baseline, which were hardly
218	observed at 1.5 GPa. The rises in the baseline suggest that the insoluble material contained some
219	fluorescent substances such as conjugated organics. Similar Raman spectra of amorphous carbon

- 220 were obtained from the reaction products of *n*-hexane and cyclohexane after the DAC experiments of
- 221 20 GPa and 1000 K²⁸, and from the reactants of the shocked compression of benzene⁴⁷.



Figure 5 Representative Raman spectra for the insoluble products of (a) 0.5 GPa and 400 °C for 96 h (run

224	14) and at (b) 1.5 GPa and 400	°C for 192 h	(run 24)
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225

226 **Discussion**

- 227 The thermal reaction of n-C₂₅ progressed with increasing temperature >360 °C at 0.5 GPa and >380 °C
- 228 at 1.5 GPa. The reaction also progressed with increasing reaction time and followed the first-order

229	fraction. Both lighter <i>n</i> -alkanes and heavier straight/branched alkanes formed via the reaction. These
230	experimental results indicate that the free-radical thermal reaction progressed under high-pressure
231	conditions at 0.5 and 1.5 GPa. The reaction rate of n -C ₂₅ at 1.5 GPa was significantly smaller than
232	that at 0.5 GPa at the same temperature, indicating that initiation of the reaction was suppressed with
233	increasing pressures. The reaction rate of the <i>n</i> -alkanes increased with increasing pressure up to ~ 40
234	MPa, above which it decreased with increasing pressure ^{39, 48, 49} . Similar reaction rate changes with
235	pressure have been reported for n -C ₂₅ at 12–80 MPa ³⁹ . The reaction rate at 350 °C increased from 7.4
236	\times 10 ⁻⁷ s ⁻¹ to 12.3 \times 10 ⁻⁷ s ⁻¹ at 12 MPa and 40 MPa, respectively. Then, the reaction rate decreased with
237	increasing pressure. The reaction rate constant for <i>n</i> -C ₂₅ at 80 MPa was 8.6×10^{-7} s ⁻¹ , which was
238	almost consistent with that at 12 MPa. The reaction rates at 400 °C were 3.75×10^{-6} s ⁻¹ and 1.68×10^{-5}
239	s ⁻¹ at 0.5 GPa and 1.5 GPa, respectively (Table 1), which were considerably smaller than that at 12
240	MPa, $(4.3 \times 10^{-5} \text{ s}^{-1})^{39}$. The results suggest that the decreasing reaction rate of <i>n</i> -C ₂₅ with increasing
241	pressure occurred continuously up to at least 1.5 GPa.
242	The thermal reactions of <i>n</i> -alkanes formed lighter 1-alkenes by beta scission, as well as
243	lighter <i>n</i> -alkanes ³⁴⁻³⁶ , although 1-alkenes with $< C_{24}$ were not detected in the reaction products, even
244	in the low conversion rate both at 0.5 and 1.5 GPa. It is in contrast to that observed in the radical

reactions of *n*-alkanes at lower pressures at around 10 MPa, in which both lighter *n*-alkanes and 1-

246	alkenes were formed from thermal cracking and were obtained in almost the same degree ^{37, 50} . Heavier
247	straight and branched alkanes were detected in this study and were likely to be formed by the addition
248	reaction of 1-alkenes and n -C ₂₅ . It is suggested that lighter 1-alkenes were formed by beta-scission of
249	n-C ₂₅ with <i>n</i> -alkanes at first. Then, the lighter 1-alkenes rapidly reacted with n -C ₂₅ to form various
250	heavier alkanes at 0.5 and 1.5 GPa. Consequently, the radical addition reaction would prefer to
251	progress under higher pressure conditions. Similar pressure dependence for the formation of heavier
252	alkanes was reported in the case of radical reactions of <i>n</i> -hexane and <i>n</i> -hexadecane $(C_{16}H_{34})^{37, 51}$.
253	Polymerization is a common reaction in hydrocarbons under high pressure, especially in the case of
254	unsaturated hydrocarbons, in which the double carbon bonds reacted to form a single bond by addition
255	reaction, reported as the pressure-induced polymerization of ethylene and propene ^{52, 53} . Aromatic
256	compounds were not detected by the GC/MS analysis in this study. However, C_{14+} aromatics were
257	detected from the reaction products of <i>n</i> -C ₂₅ at 12 MPa ³⁹ . Polymerization of aromatic compounds,
258	such as benzene and naphthalene with formation of sp ³ bonding was induced by compression up to
259	<20 GPa, even at room temperature ^{54, 55} . However, no chemical reactions of <i>n</i> -hexane and
260	cyclohexane were detected at least up to 40 GPa at room temperature ²⁸ . It is possible that unsaturated
261	aromatic compounds became less stable at high pressures compared with saturated hydrocarbons and
262	therefore were less likely to form by the thermal reaction of <i>n</i> -alkanes with increasing pressure. While

263 gold capsules were often used in the experiments on hydrocarbon reactions^{39, 49, 56}, it should be noted 264 that catalytic effect of metals on hydrocarbon reactions under HPHT conditions was theoretically 265 predicted²⁵. Further studies are necessary to verify the catalytic effect of gold capsules on hydrocarbon 266 reactions.

267 Amorphous carbon was formed as the product of secondary reactions when the remainder 268 of the initial n-C₂₅ dropped below ~10 and ~20 % at 0.5 and 1.5 GPa, respectively. In the same 269 recovered samples, considerable decreases in the heavier straight and branched alkanes were observed 270 in the GC/MS analyses. These results suggest that condensation with dehydrogenation of heavier 271 alkanes progressed to form amorphous carbon. At 12 MPa, the formation of insoluble carbonaceous 272 products, so-called cokes, by the reaction of n-C₂₅ was reported when the remaining n-C₂₅ dropped below 6 %³⁹. Insoluble amorphous carbon was obtained when the remaining percentage of the starting 273 274material dropped below ~10 and ~20 % at 0.5 and 1.5 GPa, respectively; namely, the secondary 275 reaction initiated even at lower reaction rates with increasing pressure. The secondary reaction with 276 condensation and dehydrogenation would prefer to progress under higher pressure conditions. The 277 lighter *n*-alkanes were still detected with the formation of amorphous carbon, suggesting that both 278 amorphous carbon with a low H/C ratio and lighter *n*-alkanes with higher H/C ratios were formed via 279 the thermal reaction of *n*-alkanes.

280 Conclusions

281 The effect of pressure on the thermal reaction of a long *n*-alkane, pentacosane $(n-C_{25})$ was investigated 282 by using GC/MS analyses of the reaction products recovered from 0.5 and 1.5 GPa and between 360 283 and 400 °C. Radical reactions of n-C₂₅ progressed at HPHT conditions >360 °C, 0.5 GPa and >380 °C, 284 1.5 GPa, while the rate constants of the reaction decreased with increasing pressure. The lighter *n*-285 alkanes of n-C9 to n-C24 and heavier straight/branched alkanes were obtained from the reaction 286 products, while lighter 1-alkenes were not detected even though they were considered to be formed 287 by beta scission. At the high pressures, 1-alkenes were quickly added to the $n-C_{25}$ to form the heavier 288 alkanes, so 1-alkenes were not detected in the reaction products. The addition reaction of unsaturated 289 carbons was shown to proceed preferentially with increasing pressure. The heavier alkanes were 290 polymerized with dehydrogenation as a secondary reaction, eventually forming amorphous carbon at 291 0.5 GPa, 400 °C >48 h and at 1.5 GPa, 400 °C, >96 h when the remaining starting *n*-C₂₅ reduced to 292 <10 % and <20 %, respectively. The HPHT experimental conditions of the present study are 293 comparable to the geotherm of cold subducting slabs up to around 50 km in depth⁵⁷. The experimental 294 results demonstrate that radical beta scission of long *n*-alkanes occurs even under HPHT conditions 295 of the deep Earth. Both lighter alkanes with high H/C ratios and amorphous carbon with a low H/C 296 ratio are likely to form eventually from the reaction of *n*-alkanes.

297 Supporting Information

298	Representative mass patterns of C_{25} alkene and heavier branched alkanes, fitting results of the Raman
299	spectra for the insoluble products, tables of molar yields of shorter <i>n</i> -alkanes, and total yields of the
300	heavier alkanes (PDF).
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