Pressure dependence of graphitization: implications for rapid recrystallization of carbonaceous material in a subduction zone

Yoshihiro Nakamura¹ · Takashi Yoshino² · Madhusoodhan Satish-Kumar³

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Abstract

We report the results of kinetic experiments of graphitization at various pressures (0.5–8.0 GPa) and durations (1 s to 24 h) at 1200 °C. The natural carbonaceous material in sedimentary rocks from the Shimanto accretionary complex and the Hidaka metamorphic belt, Japan, underwent systematic changes in crystallinity and morphology with increasing pressure. To assess the pressure dependence of graphitization, we adopted three approaches to formulating the graphitization kinetics using a power law rate model, a Johnson–Mehl–Avrami–Kolmogorov model, and a superposition method. Activation volumes of -21.7 ± 3.0 to -45.7 ± 4.5 cm³ mol⁻¹ and -0.7 ± 0.2 to -16.8 ± 1.8 cm³ mol⁻¹ were obtained for pressures from 0.5 to 2.0 GPa and 2.0 to 8.0 GPa, respectively. Such large negative activation volumes might arise from structural modification and compression in the primary carbonaceous material. We applied the experimental data to the Arrhenius-type equation of graphitization, extrapolated to geological P – T – t conditions. Our model predicts that carbonaceous material undergoing metamorphism for ~10 Myr at pressures of 0.5–3.0 GPa will begin to crystallize at around 350–420 °C and transform fully to ordered graphite at around 450–600 °C, depending on the peak pressure. Thus, natural graphitization might proceed much more rapidly than previously estimated, owing to the large negative activation volumes for the reaction rate. This indicates that subducted carbonaceous materials will completely convert to fully ordered graphite by rapid recrystallization and metamorphic devolatilization before reaching sub-arc depths (<100 km).

Keywords Graphitization · Carbonaceous material · HPHT experiment · Activation volume

Introduction

Graphitization of carbonaceous material (CM) is one of the most important and sensitive thermal indicators of very low-grade to amphibolite facies metamorphism (150–650 °C). The process is irreversible and the structural evolution from an amorphous to a turbostratic, and then graphitic crystal structure shows a direct correlation with peak metamorphic temperatures (Buseck and Bessac 2014). Hence, many researchers have investigated natural graphitization in metamorphic rocks using X-ray diffraction (XRD) (Itaya 1981; Okuyama–Kusunose and Itaya 1987; Wada et al. 1994), micro-Raman spectroscopy (Wopenka and Pasteris 1993; Yui et al. 1996; Hilchie and Jamieson 2014), and transmission electron microscopy (TEM) (Buseck and Huang 1985; Zuilen et al. 2012; Nakamura and Akai 2013). Although there are many reasons for investigating natural graphitization, most studies have focused on its application as a user-friendly indicator of thermal conditions during metamorphism, independent of

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✉ Yoshihiro Nakamura
yoshi-nakamura@aist.go.jp

¹ Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, AIST, Tsukuba Central 7, 1-1-1 Higashi, Tsukuba 305-8567, Japan

² Institute for Planetary Materials, Okayama University, Misasa, Tottori 682-0193, Japan

³ Department of Geology, Faculty of Science, Niigata University, 2-8050 Ikarashi, Nishi-ku, Niigata 950-2181, Japan

bulk chemistry and the mineral assemblage. The development of Raman spectra of carbonaceous material (RSCM) thermometry has provided a powerful tool for understanding the geodynamic evolution of metamorphic terrains (Beyssac et al. 2002; Rahl et al. 2005; Aoya et al. 2010; Lahfid et al. 2010; Kouketsu et al. 2014).

Since natural graphitization is thought to be strongly dependent on peak temperature, RSCM thermometry is used to predict peak metamorphic temperatures in combination with various other geothermometers or thermal models (e.g., Beyssac et al. 2002; Aoya et al. 2010). However, laboratory experiments have shown that the synthesis of graphite from amorphous carbon at 1 atm requires a very high effective activation energy of $\sim 1000 \text{ kJ mol}^{-1}$ (Fischbach 1963, 1971). Furthermore, experimental kinetic data suggest that even at 700°C , the synthesis of graphite from amorphous carbon would require $\sim 10^{40} \text{ min}$ ($\sim 1.9 \times 10^{34} \text{ years}$) (Fischbach 1971; Bustin et al. 1995). Thus, besides temperature, other extrinsic factors during metamorphism should be considered.

In the previous literature, it has been argued that natural graphitization is accelerated by extrinsic factors such as hydrostatic pressure and tectonic deformation (Bonijoly et al. 1982; Ross and Bustin 1990; Beyssac et al. 2003; Nover et al. 2005). Recently, a low effective activation energy of $\sim 300 \text{ kJ mol}^{-1}$ was estimated by kinetic experiments for the recrystallization of natural CM to graphite under a pressure of 1 GPa (Nakamura et al. 2017). The experimental data implied that a large negative activation volume is required for the recrystallization of CM to graphite in natural metamorphic rocks. However, there are scarce kinetic data on the pressure dependence of graphitization under high pressures and temperatures. It is necessary to determine the effect of pressure on the kinetics of graphitization to extrapolate the experimental data to geological P – T conditions (0.5–4.0 GPa/400–700 $^\circ\text{C}$). If the process has a large negative activation volume, natural graphitization in a subduction zone might proceed more rapidly than previously thought. Large amounts of volatiles are released during the recrystallization of CM, resulting from the liberation of functional groups and heteroatoms due to recrystallization and reorganization in the CM microstructure (Oberlin et al. 1999). The released carbonic fluids are an important source of isotopically light carbon within the carbon cycle. Hence, it is important to assess the timing and depth of metamorphic devolatilization as well as the recrystallization of CM to fully understand the recycling of subducted carbon.

In the present study, we focused on the pressure dependence of the rate of graphitization at pressures between 0.5 and 8.0 GPa to determine the activation volume of the reaction rate. Our experimental data provide important information on the kinetics of graphitization under high pressures and we propose a new kinetic model for the process of

natural graphitization that incorporates a pressure–temperature–time (P – T – t) relationship.

Methods

Experimental methods

The natural CM used for our high-pressure–high-temperature (HPHT) experiments is identical to that employed by Nakamura et al. (2017), and it was chemically extracted from two different naturally occurring sedimentary rocks, one from the Hidaka metamorphic belt (HMB) in Hokkaido, Japan (Nakamura et al. 2015), and another from the Cretaceous Shimanto accretionary complex (SM) in Kochi, SW Japan (Nakamura et al. 2019). The natural CM is distributed along the grain boundaries of silicate minerals and closely associated with phyllosilicates. Such isolated CM has a narrow range of carbon stable isotopic compositions ($\delta^{13}\text{C}$) between -23.6 and -25.8‰ , which suggests a biogenic origin (Nakamura et al. 2015), and the data demonstrate that the starting material in the HMB is the remnant of organic material trapped in sediments. In the starting material of the SM, primary microstructures of coal such as vitrinite or inertinite have been observed (Ohmori et al. 1997; Nakamura et al. 2019). The CM from the SM represents the aggregation of dispersed organic material in a sediment. The CM from the HMB shows a turbostratic (d_{002} spacing = $3.431 \pm 0.007 \text{ \AA}$) crystal structure in XRD profiles and a high area ratio (1.397 ± 0.158) in micro-Raman spectroscopy (Table 1). The CM from the SM shows an amorphous (d_{002} spacing = $3.505 \pm 0.013 \text{ \AA}$) crystal structure in XRD profiles and a broad D1 band full width at half maximum (FWHM) ($129.4 \pm 8.4 \text{ cm}^{-1}$) in micro-Raman spectroscopy (Table 1).

HPHT experiments were performed at the Institute for Planetary Materials (IPM), Okayama University, Misasa, Japan. The starting materials (HMB and SM) were encapsulated separately in platinum (Pt) tubes with different outer diameters (2 and 3 mm, respectively). Once encapsulated and welded, both samples were placed at the center of a graphite heater with an inserted MgO disk as a pressure medium. This assembly was then mounted in a high-pressure apparatus for pressure treatment under selected conditions of temperature and time. Three different high-pressure apparatus were used: (1) a piston-cylinder (PC) high-pressure apparatus, (2) a DIA-type high-pressure apparatus (AMAGAE), and (3) a Kawai-type multi-anvil high-pressure apparatus. For the PC experiments, the assembly was composed of a talc–Pyrex–graphite furnace with MgO disks as the pressure medium (3/4 inch diameter) for runs at 0.5 and 1.5 GPa. The experimental temperatures were measured by type S (Pt–Pt₉₀–Re₁₀) thermocouples. For experiments

Table 1 Experimental conditions, XRD data, and Raman data of the run products at 1200 °C

Run no.	Type	Pres- sure (GPa)	Time (s)	XRD and micro-Raman analyses						CM in Shimanto accretionary complex									
				d_{002} (Å)	FWHM	$L_c(002)$ (Å)	g^*	Area ratio	$I\sigma$	D1 band FWHM	$I\sigma$	Area ratio	$I\sigma$	D1 band FWHM					
				CM in Hidaka metamorphic belt						CM in Shimanto accretionary complex									
Starting material HMB/SM				3.431	3.06	30	0	1.397	0.16	49.84	2.43	3.505	5.01	18	0	1.643	0.09	129.41	8.37
PC586	PC	0.5	600	3.429	1.93	47	0.028	1.361	0.080	53.38	3.79	3.484	3.72	24	0.136	1.692	0.115	105.43	3.36
A2614	DIA	0.5	3600	3.421	2.09	43	0.133	1.348	0.125	51.01	4.93	3.477	3.50	26	0.184	1.851	0.130	84.71	4.37
PC585	PC	0.5	21,600	3.413	2.06	44	0.229	1.364	0.084	55.39	2.89	3.474	3.09	29	0.207	1.783	0.168	86.64	5.43
PC589	PC	0.5	43,200	3.404	1.59	57	0.349	1.331	0.057	53.28	1.94	3.424	2.69	34	0.537	1.930	0.085	76.95	2.67
PC587	PC	0.5	86,400	3.390	1.48	61	0.536	1.228	0.066	51.48	1.88	3.394	2.66	34	0.738	2.004	0.095	88.01	4.31
PC590	PC	1.5	3600	3.391	1.39	65	0.517	1.369	0.106	48.40	1.94	3.392	1.38	66	0.751	2.075	0.132	52.44	2.23
A2634	DIA	2	600	3.397	1.44	63	0.441	1.315	0.112	49.75	3.13	3.391	1.01	82	0.756	1.824	0.105	58.34	2.81
A2613	DIA	2	3600	3.394	1.23	74	0.479	1.460	0.140	45.15	3.38	3.389	1.76	51	0.767	1.893	0.147	56.11	5.61
A2637	DIA	2	21,600	3.386	1.03	88	0.586	1.080	0.106	44.90	2.27	3.369	0.69	131	0.904	0.813	0.078	37.66	1.61
H505	DIA	2	86,400	3.377	0.77	116	0.708	0.979	0.150	39.66	1.68	3.357	0.52	175	0.977	0.733	0.053	37.06	2.47
1K3186**	MA	4	1	3.401	1.76	51	0.387	1.648	0.133	49.81	3.34	3.418	3.68	25	0.579	1.349	0.134	78.71	8.47
1K3184	MA	4	1	3.395	1.47	62	0.468	1.644	0.106	44.24	2.22	3.401	3.60	25	0.689	1.303	0.079	82.48	3.50
5K3198	MA	4	600	3.385	1.42	64	0.596	1.310	0.091	46.58	3.65	3.379	1.75	52	0.836	1.430	0.138	51.09	3.62
1K2854	MA	4	2400	3.367	0.69	131	0.831	1.019	0.074	39.14	2.11	3.374	1.41	64	0.870	1.768	0.153	79.18	7.81
1K2640	MA	4	3600	3.365	0.82	110	0.852	1.161	0.230	37.38	1.94	3.380	0.75	121	0.830	1.364	0.081	35.49	1.28
1K2855	MA	4	10,800	3.366	0.58	156	0.851	0.897	0.115	41.26	1.55	3.361	0.72	125	0.952	0.865	0.087	43.81	1.29
1K3185	MA	8	1	3.382	1.40	65	0.640	1.584	0.121	48.21	2.74	3.384	3.30	27	0.799	1.094	0.082	92.00	3.77
1K2851	MA	8	600	3.365	1.35	67	0.856	1.504	0.114	51.09	3.62	3.363	1.53	59	0.942	1.196	0.090	60.76	4.93
1K2641	MA	8	3600	3.364	0.73	124	0.868	0.976	0.097	40.59	1.07	3.364	0.41	223	0.933	1.160	0.123	44.11	1.39
1K2853	MA	8	10,800	3.363	0.81	111	0.883	0.802	0.053	44.89	1.84	3.358	0.64	142	0.971	0.676	0.101	51.05	2.53

$L_c(002)$ is calculated by the Scherrer equation ($K = 1.0$). Area ratio (AR) = $\text{area}_{D1} + D4 \text{ bands} / \text{area}_G + D2 + D3 \text{ bands}$. g^* is the calculated degree of crystallinity using initial and final values of d_{002} spacing. High-pressure PC (piston-cylinder), DIA-type, and Kawai-type multi-anvil (MA) apparatus was used for the HPHT experiments. Heating experiment (1K3186**) was conducted by a fast ramping rate of ~ 1000 °C/min

using the DIA-type high-pressure apparatus, cubic pyrophyllite with an edge length of 21 mm was adopted as the pressure medium and tungsten carbide anvils with top edge lengths of 15 mm were used for runs at 0.5 and 2.0 GPa. For experiments using the Kawai-type multi-anvil high-pressure apparatus, the pressure medium was a Cr_2O_3 -doped MgO octahedron with an 18-mm edge length for runs at 4 and 8 GPa. Temperatures were monitored using W_{97}Re_3 – $\text{W}_{75}\text{Re}_{25}$ thermocouples with Al_2O_3 insulating sleeves, for which the junction was placed at the contact between two Pt capsules. Seventeen kinetic experiments were carried out at 1200 °C under pressures between 0.5 and 8.0 GPa, with annealing times of 10 min to 24 h at peak temperature (Table 1). These experiments were performed with a heating rate of ~ 100 °C/min, and quenching was achieved by turning off the furnace power. Three short kinetic experiments (1 s) with a slow (~ 100 °C/min) and a fast ramping rate (~ 1000 °C/min) under pressures of 4 GPa and 8 GPa were also conducted.

Analytical methods

The recovered Pt capsules were mounted in epoxy resin and cut into two halves. One half was used for scanning electron microscopy (SEM) and micro-Raman spectroscopy. In the other half, the sample material was separated from the slab section of the Pt capsule using a hand-held diamond cutter under a binocular microscope. The powder samples were subsequently used for X-ray diffraction analyses and TEM observations. X-ray diffraction (XRD) was performed with a Rigaku ULTIMA IV diffractometer at Niigata University, equipped with $\text{CuK}\alpha$ radiation (40 kV, 40 mA), a graphite monochromator, a slit $2/3^\circ$ – 0.45 mm– $2/3^\circ$ system, and a time constant of $0.5^\circ \text{ min}^{-1}$. The powdered samples of CM were dried on a Si-low background sample holder with an internal standard of silicon (10–20 wt%). The 2θ values of the obtained peaks were calibrated using the peak positions of the internal silicon standard (Iwashita et al. 2004). $L_c(002)$ was calculated using the Scherrer equation, $L_c(002) = K\lambda/\beta\cos\theta$, where K is a constant (1.0), λ the X-ray wavelength ($\text{CuK}\alpha = 1.5419 \text{ \AA}$), β the full width at half maximum (FWHM), and θ the Bragg angle.

Micro-Raman spectroscopy was applied to the CM and graphite in the first-order region using a Jasco NRS 3100 spectrometer at Niigata University, equipped with an 1800 lines/mm grating and a Peltier-cooled CCD-detector (256×1024 pixels, Andor Technology). A $100\times$ microscope objective (Olympus MPlan-BD) and a Nd–YAG laser (wavelength 532 nm) were used. The acquisition time was 10–30 s, and 3–6 spectra were gathered for each data point. Mean values and standard deviations were calculated based on 13–23 analyses for both edge and central parts of samples. Peak analysis of obtained peak profiles was performed by the computer program *PeakFit* 4.12, and

the G (1580 cm^{-1}), D1 (1350 cm^{-1}), D2 (1620 cm^{-1}), D3 ($\sim 1450 \text{ cm}^{-1}$), and D4 ($\sim 1200 \text{ cm}^{-1}$) bands in the first-order region (1000 – 1800 cm^{-1}) were separated (Sadezky et al. 2005). Area ratio (AR; $\text{Area}_{\text{D1} + \text{D4 bands}}/\text{Area}_{\text{G} + \text{D2} + \text{D3 bands}}$) were estimated as a reliable indicator of CM crystallinity.

Transmission electron microscopy (TEM) was carried out using a JEM 2010 electron microscope (JEOL) with a LaB_6 filament at Niigata University as well as a Tecnai Osiris (FEI) with a field emission gun at AIST, operating at 200 kV. Powder samples extracted from the run products were ground and suspended in distilled water. After ultrasonic cleaning in plastic tubes, the solution was deposited on the carbon-coated holey film of the TEM micro-grid. The samples were used mainly to observe the d_{002} lattice fringe along the [010] direction.

Results

Structural evolution of the run products

At 1200 °C, both CM samples showed marked changes in crystallinity and morphology with increasing pressure and duration of annealing (Figs. 1, 2). Details of the structural changes in XRD and Raman parameters are given in Table 1. For the lower pressure regions (0.5–2.0 GPa), a single broad peak that is a composite of the d_{100} and d_{101} peaks can be identified in the 2θ range of 40° – 45° in XRD profiles (Figs. 1a and S1). The peak becomes asymmetric and splits into separate d_{100} and d_{101} peaks with increasing pressure (4–8 GPa; Fig. S1). The Raman bands of the CM in the first-order region (1000 – 1800 cm^{-1}) also display systematic changes from an amorphous to a graphitic structure. The D3 and D4 bands in the Raman profile disappear or become difficult to identify with increasing pressure (Fig. 1b). These peaks are attributed to amorphous sp^2 or sp^3 – sp^2 hybrid sites in organic molecules (Sadezky et al. 2005), and a decrease in the amorphous phase can be observed (Fig. 1b). As the recrystallization of CM proceeded, the intensity ratios of the D1- and G-bands ($I_{\text{D1}}/I_{\text{G}}$) systematically decreased as the pressure increased from 0.5 to 8.0 GPa, and the 2D1 peak in the second order region (2000 – 3500 cm^{-1}) became asymmetric, suggesting the formation of an ABAB structure (Fig. 1b; Cançado et al. 2008).

The time–pressure relationships for both samples clearly show changes in crystallinity with increasing duration of annealing (Fig. 2a–f). In particular, the change in d_{002} spacing is more sensitive than other crystal parameters such as the FWHM of d_{002} spacing and the area ratio ($\text{Area}_{\text{D1} + \text{D4 bands}}/\text{Area}_{\text{G} + \text{D2} + \text{D3 bands}}$). The recovered CM samples display a clear change from amorphous (d_{002} spacing $\sim 3.5 \text{ \AA}$) to turbostratic (d_{002} spacing $\sim 3.43 \text{ \AA}$) and then graphitic (d_{002} spacing $< 3.36 \text{ \AA}$) structures as a result of

Fig. 1 Structural evolution of starting material in samples from the Shimanto accretionary complex (SM) with increasing pressure (0.5 to 8.0 GPa) at 1200 °C for 1 h, as revealed by **a** XRD and **b** micro-Raman spectroscopy. **c** Secondary electron image of flaky graphite

pressure-induced recrystallization (Fig. 2a, d). After HPHT experiments at 8 GPa, the crystallinity and morphological characteristics of the run products of the CM changed completely from a granular to a planar structure with flakes of 1–10 μm in diameter (Fig. 1c). The formation of a graphitic structure, as indicated by morphological characteristics, was supported by the presence of d_{110} and broad d_{112} peaks in the XRD profile (Fig. 1a). The appearance of the d_{112} peak in the XRD profile is a useful indicator of fully ordered graphite (Fig. S1; ABAB. structure; Wada et al. 1994).

Kinetic experiments

The recovered CM samples show a marked change in crystallinity with increasing annealing duration and pressure (Fig. 2 and Table 1). The CM synthesized by a fast (~1000 °C/min) and a slow ramping rate (~100 °C/min) at 1 s shows similar crystallinity (Fig. 2). We considered the effect of heating rate is small even in the rapid kinetic experiments. Hence, it is possible to calculate the pressure dependence of graphitization using time–pressure relationships. We selected the d_{002} spacing of both samples for kinetic analysis because the bulk analysis is sensitive to the change from an amorphous to a graphitic structure (Fig. 2a, d). We first determined the degree of graphitization (g) by applying the following equation (Khawam and Flanagan 2006) to the experimental data:

in sample 1K2851, extracted from the Pt capsule (1200 °C, 8.0 GPa, 1 h). Each silicon peak in the XRD profile is for the internal standard used for calibrating the interlayer spacing of the disordered graphite

$$g = \frac{(d_0 - d_1)}{(d_0 - d_f)} \quad (1)$$

where d_0 is the initial d_{002} spacing of the starting material (Table 1; Murty et al. 1969; Fischbach 1971), d_1 is the observed experimental data, and d_f is the final d_{002} spacing previously reported for fully ordered graphite (d_f 3.354 Å; Fischbach 1971). The d_0 values in the HMB and SM samples were used for d_{002} spacings of 3.431 Å and 3.505 Å, respectively (Table 1). After converting to non-dimensional parameters, we then applied the following power law rate model:

$$g = k_p t^n, \quad (2)$$

where k_p is the rate constant, t is time (s), and n is the reaction order at a given pressure. Taking the natural logarithm of Eq. (2), each kinetic parameter can be estimated by the following differential method:

$$\ln g = \ln k_p + n \ln t. \quad (3)$$

Plotting this equation on a $\ln g$ and $\ln t$ diagram gives a straight line with a slope of reaction order n and an intercept $\ln k_p$ (Fig. 3a, d). The data for HMB and SM fitted by Eq. (3) show good coefficients of determination (R -squared) of 0.90 to 0.98 and 0.75 to 0.95, respectively

Fig. 2 Time–pressure relationships between 1 and 10^6 s at a constant temperature (1200 °C). The parameters **a** d_{002} spacing, **b** FWHM of d_{002} spacing from XRD, and **c** area ratio ($AR = \text{area}_{D1+D4} / \text{area}_{D2+D3+G}$) from micro-Raman spectroscopy are based on

data for the CM in samples of HMB. The same parameters are used in (d), (e), and (f) for the CM in samples of SM. The experimental data for 1 GPa are from Nakamura et al. (2017)

(Table 2). The observed structural changes revealed in the time–pressure relationships show a sigmoidal transformation with increasing pressure and annealing duration (Fig. 2). Hence, the best fit of g was further calculated using the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model. This model, which is especially suitable for analyzing the complex transformation kinetics of heterogeneous nucleation and recrystallization, and is widely utilized in material science and mineralogy (e.g., Francisco et al. 2016), is expressed as follows:

$$g = 1 - \exp(-k_a t^m), \quad (4)$$

where k_a is the rate constant, t is the duration of heating (s), and m is the reaction order, termed the “Avrami index”. Applying the differential method ($\ln$ – $\ln$ plot), Eq. (4) can also be expressed as

$$\ln[-\ln(1 - g)] = \ln k_a + m \ln t. \quad (5)$$

Plotting this equation on a $\ln[-\ln(1 - g)]$ vs. $\ln t$ diagram, the natural logarithm of rate constant $\ln k_a$ and the reaction order (Avrami index) m were simply estimated

from linear regression of the intercept and slope, respectively (Fig. 3b, e). Good coefficients of determination (R -squared) of 0.77 to 0.96 and 0.78 to 0.95 were obtained with the fitting of JMAK model (Table 2). The reaction orders of n and m fitted by both kinetic models changed gradually with increasing pressure and annealing duration. The observed changes of reaction order n , m in the time–temperature relationship are similar to those reported by Huang (1996) and Nakamura et al. (2017). This suggests the change in the rate-limiting step of the reaction took place under HPHT conditions. In principle, the activation volume should not be determined using $\ln k_{p,a}$ values obtained from the different reaction orders because a number of different reaction mechanisms may contribute to the $\ln k_{p,a}$ values.

We, therefore, used the superposition method in our approach to the kinetics of graphitization. The fitting curves of the measured crystal parameter (d_{002} spacing) and the logarithmic treatment time at different pressures can be superposed by proper scale changes on the time axis. The shift in distance is called the time–pressure shift factor α_p , which is given by

Fig. 3 Relationship between $\ln t$ (s) and $\ln g$ for samples of HMB (a) and SM (d) fitted by a power law rate model. Also shown is the relationship between $\ln t$ (s) and $\ln[-\ln(1-g)]$ for samples of HMB (b) and SM (e) fitted by a JMAK model. c and f Composite master curves of unit cell height c for CM in samples of HMB (c) and SM (f) obtained by shifting the 1.0, 2.0, 4.0, and 8.0 GPa curves to combine smoothly with the 0.5 GPa (reference pressure) curve for time-pres-

sure relationships. All the master curves (red lines) were calculated by non-linear best fitting of sigmoidal functions (Hill equation). The master curves (black dotted lines) and experimental data (gray circles) reported by Nakamura et al. (2017) were also overlain to provide a reference for the temperature dependence of the composite master curve

Table 2 Summary of kinetic parameters for the natural carbonaceous materials used in the HPHT experiments

P (GPa)	P (atm)	Power law model					JMAK model					Superposition method			
		$\ln k_p$	1σ	n	1σ	R^2	$\ln k_a$	1σ	m	1σ	R^2	$\ln a_p$	h	1σ	R^2
CM in Hidaka metamorphic belt (HMB)															
0.5	4935	− 3.860	0.249	0.283	0.026	0.975	− 4.201	0.391	0.342	0.041	0.958	0.000	0.657	0.219	0.921
1	9869	− 3.378	0.298	0.265	0.031	0.936	−4.317	0.347	0.405	0.036	0.962	1.386			
2	19,738	− 1.233	0.133	0.079	0.012	0.954	−1.279	0.225	0.133	0.025	0.908	3.219			
4	39,487	− 0.841	0.105	0.075	0.015	0.896	− 0.590	0.199	0.141	0.095	0.767	6.842			
8	78,973	− 0.432	0.038	0.036	0.005	0.957	0.052	0.082	0.088	0.012	0.956	11.650			
CM in Shimanto accretionary complex (SM)															
0.5	4935	− 4.787	0.995	0.368	0.112	0.804	− 5.394	1.350	0.458	0.142	0.777	0.000	0.477	0.205	0.900
1	9869	− 1.532	0.179	0.115	0.019	0.885	− 1.983	0.252	0.220	0.026	0.934	2.398			
2	19,738	− 0.571	0.171	0.046	0.019	0.754	− 0.861	0.619	0.179	0.068	0.908	5.704			
4	39,487	− 0.379	0.044	0.030	0.006	0.889	− 0.536	0.156	0.160	0.022	0.947	8.126			
8	78,973	− 0.218	0.023	0.020	0.003	0.950	0.056	0.139	0.128	0.020	0.954	13.383			

$\ln k_p$ =rate constant of the power law rate model, n =reaction order of the power law rate model, $\ln k_a$ =rate constant of the Avrami model, m =JMAK index (reaction order of the JMAK model), $\ln a_p$ =time-pressure shift factor, and h =Hill coefficient of the sigmoidal master curve (Hill equation)

$$\alpha_p = \frac{t_p}{t_{\text{ref}}}, \quad (6)$$

where t_{ref} is the reference time at a certain reference pressure and t_p is the time required to give the same response at the reference pressure. The crystal properties with regression curves obtained by the superposition method are shown in Fig. 3c, f. The experimental reference pressure here is 0.5 GPa (4934.6 atm). For each reference pressure, a fully superimposed curve generated by the shift factors is fitted by a non-linear regression curve (Hill equation). In principle, the reaction mechanisms in kinetic experiments should have the same reaction order for both pressure dependence and temperature dependence, which means the same Hill coefficient h . Hence, we compared the master curves obtained from pressure and temperature dependence, which were previously reported by Nakamura et al. (2017). The master curves for pressure dependence have slightly lower R -squared values (0.90–0.92) than the previously reported data for temperature dependence ($R^2 = 0.96$ –0.98). This suggests that the temperature dependence is more sensitive to the reaction than pressure dependence. The h values of both samples are the roughly same within an error of one sigma (Fig. 3c, f). These data demonstrate that a similar reaction mechanism of graphitization can be reproduced by a single Hill equation in both kinetic experiments. We conclude, therefore, that the superposition method is more suitable for model fitting in kinetic experiments than other fittings.

Discussion

Pressure dependence of graphitization

Our experimental results suggest that the observed changes in crystallinity and morphology in both CM samples are

strongly related to the duration of annealing and the pressure. Hence, we assessed the activation volume of graphitization using log–linear plots of the power law rate and JMAK models. Pressure dependence in experimental kinetics is given in terms of the activation volume $\Delta V^\ddagger$, which describes the influence of pressure P on the rate constant k (House 2007), and is generally expressed as

$$\left(\frac{\partial \ln k_{p,a}}{\partial P} \right)_T = -\frac{\Delta V^\ddagger}{RT}, \quad (7)$$

where P is pressure (atm), R is the gas constant ($8.314462 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is absolute temperature (K). This equation indicates that if $\Delta V^\ddagger$ is independent of pressure, then a plot of $\ln k_{p,a}$ as a function of P should, within experimental uncertainty, display a linear relationship with a slope of $-\Delta V^\ddagger/RT$. However, our experimental results indicate a power law relationship with regard to pressure, suggesting a change in the rate-limiting step at ~ 2 GPa. Therefore, the rate constants were fitted separately by two linear approximations (Fig. 4a, b and Table 2). Using log–linear plots ($\ln k_{p,a}$ as a function of pressure), we obtained activation volumes of $-21.7 \pm 3.4 \text{ cm}^3 \text{ mol}^{-1}$ and $-33.7 \pm 17.3 \text{ cm}^3 \text{ mol}^{-1}$ for the two samples at pressures between 0.5 and 2.0 GPa. Furthermore, activation volumes of $-0.7 \pm 0.2 \text{ cm}^3 \text{ mol}^{-1}$ and $-2.6 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ were obtained for the two samples at pressures between 2.0 and 8.0 GPa. In addition to the power law rate and JMAK models, the alternative kinetic model (using the superposition method) was applied to determine the pressure effect of graphitization. The natural logarithm of time–pressure shift factor $\ln \alpha_p$ can be inputted into the equation of pressure dependence (7) at constant temperature (1473 K):

$$\ln \alpha_p = -\frac{\Delta V^\ddagger}{RT} P. \quad (8)$$

Fig. 4 Log-linear plots of pressure (GPa) vs. $\ln k_p$ (a), $\ln k_a$ (b), and $\ln \alpha_p$ (c) for both samples. $\ln k_{p,a}$ and $\ln \alpha_p$ as functions of pressure were fitted by power law (dotted lines) and linear regressions (solid lines). The experimental data for 1 GPa are from Nakamura et al. (2017)

Plotting $\ln\alpha_p$ vs. P is another way of calculating $\Delta V^\ddagger$ values. The calculated $\Delta V^\ddagger$ values and fitting data are given in Fig. 4c and Table 2. We obtained activation volumes of $-25.7 \pm 2.9 \text{ cm}^3 \text{ mol}^{-1}$ and $-45.7 \pm 4.5 \text{ cm}^3 \text{ mol}^{-1}$ for the two samples at pressures between 0.5 and 2.0 GPa. Likewise, activation volumes of $-16.8 \pm 1.8 \text{ cm}^3 \text{ mol}^{-1}$ and $-15.7 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ were obtained for the two samples at pressures between 2.0 and 8.0 GPa. The superimposed master curves were fitted by a single sigmoid curve and the log-linear plot between $\ln\alpha_p$ and pressure should be a linear relationship. However, the best fitting of our results seems to be a power law relationship rather than a linear relationship. This implies that the successive reaction of graphitization might be not fully reconstructed by the superimposed master curve of Hill equation.

Previous kinetic experiments in this field are limited to the study of Noda et al. (1968), who proposed activation volumes of -7 and $-9 \text{ cm}^3 \text{ mol}^{-1}$ for graphitization under pressures of 0.1, 0.3, and 0.5 GPa. In comparison, our graphitization experiments performed under a wider range of P - T conditions showed much greater negative activation volumes for the three kinetic models, suggesting a strong effect of pressure-induced graphitization, especially at low pressures. Our results indicate two different rate-limiting steps of the reaction with increasing pressure. At low pressures (≤ 2 GPa), slight structural changes were observed using XRD and micro-Raman spectroscopy (Fig. 2). TEM observations suggest that the small distorted fringe areas are already anisotropic (Fig. 5b). A reorganization of CM nanostructures prior to recrystallization is also supported by the formation of arc-like spots of 002 reflections in the selected area electron diffraction (SAED) pattern (Fig. 5b), and the nanostructures of the recovered samples are obviously different

to the isotropic structure of the starting materials (Fig. 5a). With increasing pressure, the distorted fringes become larger and are realigned along the c -axis. The small stackings of the distorted fringe can be identified as a bright spot in the 002 dark field images (Fig. 5c). At higher pressures (> 2 GPa), the graphitic layers still have stacking defects along the c -axis, even though the distorted graphitic layers convert to a graphite structure as a result of the longer annealing times at higher pressure (Fig. 5d). Under high magnification, fully ordered graphite, which has ABAB... stacking (2H phase), shows an angle of $\sim 72^\circ$ between the (101) and (002) planes, observed along the [010] direction. In contrast, the graphite synthesized in our HPHT experiments shows a range of angles between the (101) and (002) planes, suggesting the presence of a rhombohedral phase ($\sim 78^\circ$; Lin et al. 2012) and other stacking phases (e.g., AA...; Fig. 5d). A rhombohedral phase and stacking defects can be formed by strong shear deformation or induced by ball milling (Lin et al. 2012), and have been observed in natural mylonites (Nakamura et al. 2015). The nanostructural signatures suggest that large negative activation volumes arise from structural modification and compression caused by hydrostatic pressure.

The recrystallization of carbon material is strongly dependent on the nanostructure of the precursor material, and the nanostructures can be divided into two types, called soft (graphitizing) carbon and hard (non-graphitizing) carbon, based on TEM observations (Inagaki et al. 2014). Hard carbon consists of small hollow particles with walls that comprise a few carbon sheets, while soft carbon already has distorted fringes of carbon sheets. Such a difference in nanostructure results in the large differences in final crystal size and annealing temperature when graphite is synthesized from amorphous carbon in the laboratory (e.g., Inagaki

Fig. 5 Representative nanostructural evolution of CM to graphite in sample SM with increasing pressure. **a** TEM image and corresponding SAED pattern of starting material in sample SM. **b** Recovered sample A2614SM ($g=0.184$) at 0.5 GPa and 1 h. The variation in distorted graphitic layers in the area indicated by the rectangle is shown as arc-like spots of 002 reflections in the SAED pattern. **c** 002

dark field image of the distorted fringe in A2613 ($g=0.767$) at 2.0 GPa and 1 h. The bright spots correspond to the distorted fringes of CM along the c -axis marked by the white circle of the SAED pattern. **d** Lattice fringes of graphitic layers corresponding to (002) and (101) planes along the [010] direction in sample 1K2853SM ($g=0.971$) at 8.0 GPa and 3 h

1996). The acceleration of graphitization occurs (even at 0.5 GPa) as a result of the collapse, under hydrostatic pressure, of the small hollow particles with walls (Inagaki et al. 2014). This process is more marked in the hard carbon, resulting in the heterogeneous recrystallization of amorphous carbon to a graphitic carbon. In our experiments, the isotropic structure of the primary CM was destroyed by even low hydrostatic pressures (0.5 to 2.0 GPa) before the start of recrystallization. The changes in the nanostructure of the starting material are quite consistent with previous observations of hard carbon under high-pressure conditions. These structural changes due to an extrinsic factor might enhance the recrystallization of CM and lead to large negative activation volumes in kinetic experiments.

Implications for rapid graphitization in a subduction zone

Our experimental data on graphitization reveal remarkably large negative activation volumes for the natural precursor materials used in our study. Thus, natural graphitization in a subduction zone might proceed much more rapidly than previously thought. We, therefore, made a simplified extrapolation of the graphitization rate dependent on temperature–pressure. The temperature–time dependence of graphitization can be successfully fitted by the Hill equation of Nakamura et al. (2017) since these authors performed their experiments on graphitization kinetics using the same starting materials as we used. In our experiments, we found that the Hill equation can also be applied to the pressure dependence of graphitization, and we obtained similar Hill coefficient values for both our kinetic experiments using a superposition method (Fig. 3c, f). This suggests similar reaction processes were reproduced in our different kinetic experiments, which means that the Hill equation is most suitable for making extrapolations from experiments to geological P – T – t conditions.

Based on the kinetic data of Nakamura et al. (2017), the temperature–time dependence of the sigmoidal master curve from an amorphous structure to a graphitic structure in the kinetic experiments was tested using the unit-cell height c :

$$f(T, t) = \frac{C_{\min} + (C_{\max} - C_{\min})}{1 + \left[\frac{A_1 \exp\left(-\frac{\Delta H}{RT}\right)}{t} \right]^h}, \quad (9)$$

where $C_{\min}$ and $C_{\max}$ are the maximum and minimum values of the unit-cell height c (Å), respectively, A_1 is the pre-exponential factor (s^{-1}), T is the absolute temperature (K), R is the gas constant, h is the Hill coefficient, and ΔH is the activation enthalpy (kJ mol^{-1}). Equation (9) combines the Hill equation and the Arrhenius relationship determined by

time–temperature experiments. In principle, the activation enthalpy under a pressure is strictly expressed by the following equation:

$$\Delta H = \Delta E a + P\Delta V^\ddagger, \quad (10)$$

where ΔH is the activation enthalpy, $\Delta E a$ the activation energy at 1 atm, P the pressure, and $\Delta V^\ddagger$ the activation volume. Because of the power law relationship between $\ln \alpha_p$ and pressure in our experiments (Fig. 4c), it is difficult to extrapolate the activation enthalpy at each pressure using Eq. (10). Therefore, the activation volumes at each pressure were calculated by differentiating the power law relationship between $\ln \alpha_p$ and pressure (Fig. 6). After differentiating, we recalculated the activation volumes from $\text{cm}^3 \text{mol}^{-1}$ to kJ mol^{-1} , and the effective activation energy calibrated for pressure dependence ($P\Delta V^\ddagger$) was calculated from the effective activation energy at 1 GPa (Fig. 6; Nakamura et al. 2017). Combining Eqs. (9) and (10), the pressure–temperature–time dependence inferred from the sigmoidal master curve (Hill equation) is expressed as follows:

$$f(P, T, t) = \frac{C_{\min} + (C_{\max} - C_{\min})}{1 + \left[\frac{A_1 \exp\left(-\frac{\Delta E a + P\Delta V^\ddagger}{RT}\right)}{t} \right]^h} \quad (11)$$

Details of the input parameters for the geological extrapolations are listed in Table 3. The $\Delta E a + P\Delta V^\ddagger$ value was calculated from $\ln \alpha_p$ and pressure (Fig. 6). Thus, it is possible to predict the structural evolution from CM to graphite by the above function of pressure P (atm), peak temperature T (K), and duration of annealing t (s) during metamorphism.

Fig. 6 Calculated activation volumes ($\Delta V^\ddagger$) and effective activation energies corrected by pressure dependence ($\Delta E a + P\Delta V^\ddagger$) between 0.5 and 8.0 GPa using a superposition method. Solid and dotted lines represent the HMB and SM samples, respectively

Table 3 Kinetic parameters used for the geological extrapolations of graphitization

Samples	$C_{\min}$ (Å)	$C_{\max}$ (Å)	h	A_1 (s ⁻¹)	t (s)	$T_{\min}$ (K)	$T_{\max}$ (K)	$P_{\min}$ (atm)	$P_{\max}$ (atm)
HMB	6.859	6.725	0.86	3.4196E-06	3.1536E+14	473	1073	4935	39,487
SM	6.992	6.731	0.69	3.5654E-09	3.1536E+14	473	1073	4935	39,487

The preexponential factor A_1 in Nakamura et al. (2017) was converted from A_1 (min⁻¹) to A_1 (s⁻¹), and t (s) is the input heating duration (~10 Myr) estimated as the average heating duration of regional metamorphism (Viète and Lister 2016)

Applying Eq. (11), we calculated the pressure–temperature dependence of graphitization for 10 Myr (Viète and Lister 2016; Fig. 7). Our kinetic models reveal that both starting materials (HMB and SM) show pressure-induced graphitization at pressures of 0.5–3.0 GPa. The initial crystallinity changes in the starting materials of HMB and SM were observed at around 350 and 420 °C, respectively, and conversion to fully ordered graphite (unit cell height $c \sim 6.72$ Å) occurred at around 450 and 600 °C, respectively (Fig. 7). Thus, the crystallinity of natural CM in sediments shows a rapid change as a function of geological time and peak temperature, due to the effect of pressure. On the other hand, a considerable difference of activation volumes for pressures of 0.5 GPa was identified for both starting materials (Fig. 6). Based on the calculated pressure dependence of the activation volumes at 0.5 GPa, the difference is ~ 40 cm³ mol⁻¹

(Fig. 6). The difference between turbostratic and amorphous structures prior to pressure-induced graphitization might play an important role in natural graphitization under low-pressure conditions. Such nanostructural differences in the precursor material may lead to variability in natural graphitization in various types of metamorphic terrain (Wada et al. 1994; Beyssac et al. 2019). However, the effect of reorganization in the nanostructure becomes small with increasing pressure, and activation volumes of two starting materials demonstrate the similar $\Delta V^\ddagger$ values of $-14 \sim -10$ cm³ mol⁻¹. This suggests that the reaction mechanism of graphitization becomes the same at high pressures (2–8 GPa). The conversion to the fully ordered graphite at around 450 and 600 °C are reasonable temperatures in comparison with the natural occurrences of metamorphic graphite. Our extrapolations demonstrated that natural graphitization

Fig. 7 Pressure–temperature transformation diagrams for HMB (a) and SM (b) samples using the unit-cell height c (Å) for 10 Myr. The kinetic parameters for the Hill Eq. (11) are listed in Table 3. Also shown are the fields of various metamorphic facies and geotherms after Liou et al. (2009): GR granulite, AM amphibolite, EA epidote amphibolite, BS blueschist, GS greenschist, Amp-EC amphibole

eclogite, Ep-EC epidote eclogite, Lw-EC lawsonite eclogite. The pink arrows indicate the rock-based mean P – T conditions for a subduction zone (Penniston–Dorland et al. 2015). P – T conditions of the HMB and SM starting materials are indicated by orange and blue stars, respectively

occurs under realistic geological P – T – t conditions (Fig. 7). The revised kinetic model of graphitization is applicable to a wide range of P – T conditions and will contribute to improvements in geothermometry, geospeedometry, and geobarometry.

Fate of carbonaceous material in a subduction zone

Our data demonstrate that subducted CM in sediments converts to metamorphic graphite by rapid recrystallization under realistic P – T – t conditions for a subduction zone. The recrystallization results in the metamorphic devolatilization of CM until the formation of fully ordered graphite is complete. The precursor material in the CM (the so-called kerogen) contains many functional groups and heteroatoms in aromatic rings. Such organic compounds are liberated as a C–O–H fluid when the amorphous carbon structure is reorganized and are recrystallized into a graphitic structure (Oberlin et al. 1999). Most of the volatile components (e.g., the oxygenated compounds H_2O and CO_2) are released immediately at the start of the carbonization and reorganization of the amorphous carbon, but the production of noncondensable gases (e.g., CH_4 and H_2) continues until graphitization is complete. This metamorphic devolatilization is consistent with the changes of H/C and O/C atomic ratios in the Van Krevelen diagram (Durand and Nicaise 1980; Vandenbroucke and Largeau 2007). In particular, it was reported previously that the H/C atomic ratio of residual CM in metasediments shows a systematic decrease with increasing crystal size $L_c(002)$ during a rise in metamorphic temperatures from 150 to 650 °C (Itaya 1981; Wada et al. 1994; Suzuki et al. 2017). This suggests that the liberation of CH_4 and H_2 continued until the upper amphibolite facies of metamorphism. Hence, it is possible to assess indirectly the timing and depth of the release of volatiles based on the kinetics of graphitization.

The natural starting materials in our HMB and SM specimens are good examples of subducted carbon because the samples come from forearc sediments and the Shimanto accretionary complex. We attempted to extrapolate the subducted CM crystallinity with increasing P – T conditions for different durations of heating. The rock-based mean P – T paths in a subduction zone were applied for our estimations (Penniston-Dorland et al. 2015; Fig. 7). Figure 8 shows the models of recrystallization from amorphous to graphitic carbon using our new kinetic data for the SM and HMB samples. The results suggest that subducted CM can be preserved as amorphous carbon to a depth of ~40 km, but is then converted to graphitic carbon before reaching sub-arc depths (up to 100 km). Our estimations reveal that the release of volatiles continued until a depth of ~90 km as a result of the formation of fully ordered graphite, regardless of variations in the starting material and duration of

Fig. 8 Recrystallization curves for samples of HMB (a) and SM (b) with increasing P – T . The mean P – T conditions for a subduction zone are from Penniston-Dorland et al. (2015). Three different durations of heating (10.0, 1.0, and 0.1 Myr) were modeled for reference. Schematic illustrations of the CM nanostructure are modified from Vandenbroucke and Largeau (2007)

heating (Fig. 8). Such processes result in a large amount of volatiles being released from the subducted CM, which means that a large amount of C–O–H fluid is transported in the subduction zone. Kerrick and Connolly (2001) reported that subducted marine sediments lose all of their CO_2 and most of their initial H_2O before reaching a depth of 90 km, based on thermodynamic calculations. Thus, the carbonic fluids liberated from CM are mixed with other C–O–H fluids, providing a wide variety of carbon stable isotopic ratios in the CO_2 until a depth of ~90 km is reached. On the other hand, it is well known that only ~50% of subducted carbon is returned to the Earth's surface by arc magmatism (Bebout 1995; Wallace 2005). Some of the subducted carbon remains as fully ordered graphite (2H graphite) and is an important source of isotopically light carbon in the deep carbon cycle.

Conclusions

Our experiment results provide new kinetic data on the pressure dependence of graphitization under HPHT conditions. Previously, only the effects of shear deformation and pressure on natural graphitization had been discussed. However,

here we demonstrate, on the basis of the revised Arrhenius-type kinetic model, that natural graphitization proceeds much more rapidly than previously thought. In particular, our new kinetic data show that the rapid recrystallization of CM indicated by Nakamura et al. (2017) can be extrapolated to realistic natural P – T conditions in a subduction zone (Fig. 7; 0.5–4.0 GPa/200–800 °C). This suggests that it might not be necessary to consider the effects of tectonic deformation or fluid activity when attempting to understand natural graphitization in the Earth's crust. In many metamorphic terrains, the recrystallization of metamorphic graphite can be explained by the effects of three important factors: peak temperature, lithostatic pressure, and a realistic duration of heating. Further refinement of the model and a better understanding of the kinetics of graphitization, both in nature and in laboratory experiments, will lead to the development of more reliable indicators of the P – T – t conditions experienced by metasediments in the Earth's crust.

Our experimental data also demonstrate that subducted carbon can be preserved as amorphous carbon in a subduction zone until a depth of ~40 km, after which it is converted to graphitic carbon before reaching subarc depths (up to 100 km). This suggests that the volatile components of the subducted carbon are released at depths of 40–90 km, after which fully ordered graphite becomes a stable phase. The fully ordered graphite then plays an important role as a sink of isotopically light carbon until the phase transition to diamond is reached at depths greater than ~150 km.

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