論文　**Original Paper**

Estimated peak metamorphic temperature of the Sanbagawa schists from Nagatoro area, Kanto Mountains, using Raman microspectrometry on carbonaceous materials

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Abstract: The deformation regime of the Sanbagawa metamorphic rocks of the Kanto Mountains have long been controversial, whether it is one plastic continuous body or it is composed of several parts separated by faults or thrusts. One of the key must lie in the area where rocks with different mineral assemblage are found adjacent to each other. Most of the Nagatoro area is categorized as the lowest metamorphic grade zone which is defined by the mineral assemblage without garnet. Several outcrops in this area are known to contain garnet. It has been argued that the appearance of garnet indicates juxtaposition of rocks from different metamorphic grade, suggesting structural discontinuity. To investigate whether the local garnet occurrence was the discontinuity, Raman microspectrometry was applied carbonaceous materials in 27 rock samples in a continuous outcrop in this study. The estimated temperature was 400 to 460℃ with no structural gap or tendency recognizable when mapped. Samples with and without garnet both produced results comparable to each other. No evidence was obtained to show that the local garnet occurrence at the outcrop is due to structural discontinuity. The estimated temperature range was consistent with the beginning condition of the garnet formation. It is likely that the boundary between the garnet bearing rocks and those without garnet was originally continuous, with the condition just on the border to start growing garnet.

Key words: garnet, Sanbagawa metamorphic belt, Kanto Mountains, temperature, Raman spectrometry

Introduction

Reconstruction of the local thermal structure near the earth's surface is important since the temperature condition controls many geological phenomena near the surface of the earth.

Peak metamorphic condition experienced by a metamorphic rock is one of the clues available for geoscientists, since metamorphic rocks record depth (pressure) in addition to the temperature. Many geothermometers using metamorphic rocks have been porposed for that purpose. Most of the traditional geothermometers utilize the chemical composition change of the metamorphic minerals in response to exchange reaction or continuous reaction between more than one minerals. Consequently, the estimation is always limited by the occurrence of the specific mineral assemblage.

Geothermometer using carbonaceous material has become popular as Raman microspectrometry became available to many. The advantage of using the carbonaceous material is that it is applicable to wider range of temperature, not limited by the change of mineral assemblage. Carbonaceous material contained in sedimentary rocks are mostly organic, amorphous matter. During metamorphism, the amorphous matter gradually crystallizes into graphite, the degree of crystallization depending on the temperature and the time duration. Beyssac et al. (2002) has first proposed a calibration using Raman spectra of carbonaceous materials in regional metamorphic rocks and claimed it is valid in the temperature range from 330 to 650℃. Several attempted to extend the temperature range toward the low temperature side after that (Rahl, et al., 2005; Lahfid et al., 2010). Kouketsu et al. (2014) compiled the calibrations to construct a chart for selection of suitable fitting according to temperature range. However, the basic procedure of Beyssac et al. (2002) is still valid in the proposed temperature range.

The deformation regime of the Sanbagawa metamorphic rocks of the Kanto Mountains have long been controversial, whether it is one plastic continuous body or it is composed of several structural sheets. The key to solve the problem is the thermal structure of the area. Though Hashimoto et al.

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(1992) analyzed the carbonaceous material in the area , it was not with the Raman microspectrometry and the result was not calibrated into temperature. In this study, Raman microspectrometry on carbonaceous material was performed in an outcrop of the lower grade Sanbagawa metamorphic rocks. The validity of the results and the correlation with the garnet occurrence is discussed.

Geologic setting

The Sanbagawa Metamorphic Belt lies along arc in the southwestern part of Japan islands. It is one of the most investigated metamorphic belts in the world (e. g., Banno and Sakai, 1989) since it is a well-known relic of the subduction zone. The Belt is originally an accretionary complex, thus the protoliths are mainly trench sediments accompanied by basalt, and lesser amount of limestone and chert. Chronological studies recently revealed that the accretion of the protolith of the Sanbagawa belt occurred in the late Cretaceous (Tsutsumi et al., 2009).

Kanto Mountains lie in the eastern most part of the Belt. The metamorphic zonation in this area have been defined based on the mineral assemblage of pelitic schists by Hashimoto et al. (1992) as zone I, zone II, and zone III in the ascending order. Zone I pelitic schists generally contain quartz, plagioclase, muscovite and chlorite, Zone I is the lowest metamorphic grade zone which is equivalent to the Chlorite Zone defined in the Shikoku Area of the Sanbagawa Metamorphic Belt (Higashino, 1990). The foliation of the schists generally dips slightly north or subhorizontal in the area. The lithology again is known to be subparallel to the foliation.

Most of the Nagatoro area is categorized as the zone I by Hashimoto et al. (1992). Appearance of garnet is the index of zone II, which is the second lowest metamorphic grade zone defined in this area. Several outcrops in this area are known as being the zone II rocks since they contain garnet. Hashimoto et al. (1992) interpreted the appearance of garnet as the structural discontinuity, based on the fact that the crystallinity of carbonaceous materials also varies in the area. That lead to the model with many thin structural sheets (shuffled card structure) (Tagiri et al., 2000). It has been argued, on the other hand, that the model is inconsistent with the known structural history of the western part of the Sanbagawa metamorphism which is largely continuous (Miyashita, 1998).

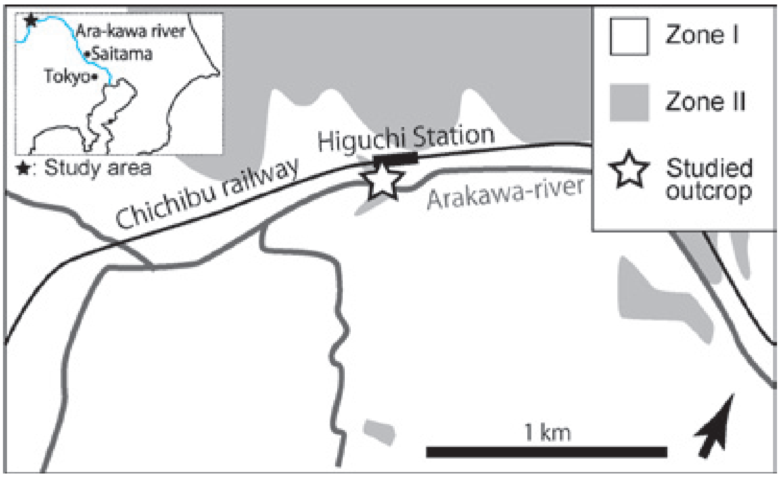

Fig. 1. Sampling locality in this study. Modified after Hashimoto et al. (1992). Zone I is the lowest grade zone of the Kanto Mountains area of the Sanbagawa Metamorphic Belt. Garnet appears in Zone II. The area basically is in Zone I but it has long been known that garnet occurs near the studied outcrop.

The location of the studied outcrop is shown in **fig 1**. The outcrop is marked as garnet bearing, however it is surrounded by Zone I rocks in which garnet is not found. It is one of the argued structural boundary.

Sample description

The studied outcrop consisted mainly of pelitic schists, accompanied by minor amount of green schists. Some of the pelitic parts showed lighter grey color. (They have been described as "psammitic" in some references but they are not distinguished in this study). Mineral assemblage was quartz, plagioclase, muscovite, chlorite. Muscovite and chlorite mainly formed the schistosity. Not all the samples had garnet, calcite, titanite, and zoisite. Garnet grains were small and euhedral, most of them with diameters 50 to 100 micrometers (**fig. 2**). Carbonaceous material was also included in many of the samples, both garnet bearing samples and samples without garnet. Carbonaceous material as inclusion in rigid crystal (mostly albite) was found in 27 samples (**fig. 3**). Analyses hereafter is applied on those samples.

Method

Thin section samples containing carbonaceous materials included in larger crystals were analyzed with Raman microspectrometry. To avoid damage by polishing of the carbonaceous materials (Beyssac et al., 2003), only those carbonaceous materials embedded in other minerals were chosen for analyses. To identify the embedded grains, the grains not observable by the reflexive optical microscope

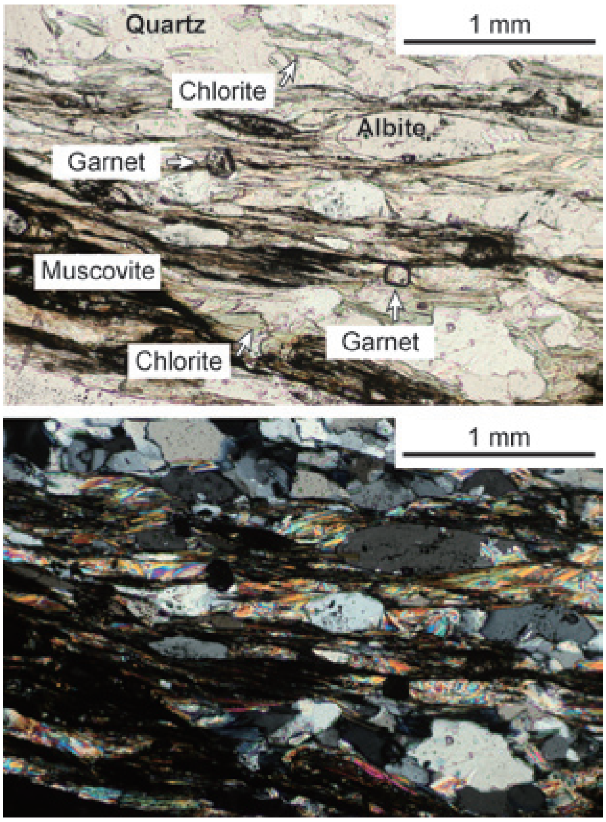

Fig. 2. Photomicrograph of the thin section WT20154 (open nicol, and crossed nicols). Muscovite and chlorite constitute the schistosity. Garnet grains are found in the layers of muscovite and chlorite. Blackish powder-like matter is the carbonaceous materials. Carbonaceous materials are found in the muscovite layers or in the albite.

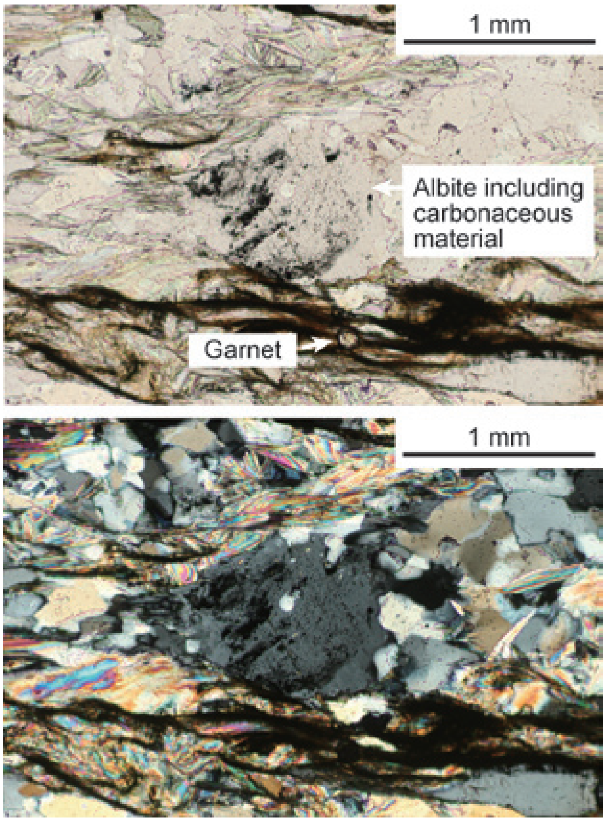

Fig. 3. Photomicrograph of the thin section WT20154 (open nicol, and crossed nicols). Carbonaceous materials are found included in the albite crytal. Carbonaceous materials embedded below the surface of the thin section was analyzed.

was chosen for analyses.

Analyses were performed using JASCO NRS-4100 Laser Raman Spectrometer, at the Kokushikan University. The setup was made basically after Kouketsu et al. (2014). The wavelength of the laser source was 532nm, the laser power was set at 1.6 mW. Grating with 900 and 1800 lines/mm was used to disperse the wave. The objective lens was 100x, making the spatial resolution about 1 μm. Acquisition time was 110 to 130 seconds/run, adding up 3 runs per one measurement. It was confirmed that the laser irradiation did not damage the carbonaceous materials, by radiating several times and verifying the result wave did not change systematically. The wave number was calibrated after the measurement using polystyrene standard.

Calibration into temperature was done after the formula by Beyssac et al. (2002) :

$$T\,[℃] = -445 \cdot R2 + 641$$

$$R2 = (D1/(D1 + D2 + G))$$

The formula requires the area of the peak fitted wave as the parameter. *D1*, *D2*, *G* is the area of the peak wave of the D1-band, D2-band, G-band, respectively. To calculate the area, the measured Raman shift data must be resolved into the three peaks, which was processed by the software Spectra Manager®. G-band (approx. 1580 cm^{-1}) and D1-band (approx. 1350 cm^{-1}) were resolved manually (typing in the center of the peak). D2-band was often difficult to recognize, so in those samples the center of the D2 peak was given as 1614 cm^{-1}. When the basic parameters are given, iterate fitting calculation was performed for 95 times by Spectra Manager® to output the fit curves. The area of each peak wave was then put into the calibration formula.

Results

Fig. 4 shows an example of the measured Raman shift. The wave is resolved into G-band, D1-band, and D2-band peaks as shown in **fig. 4**. The result of the curve fitting calculation and the estimated temperatures are listed in **table 1**. The error range of this calibration is still large and thought to be approximately ±50 ℃, though it is not shown in **table 1** (Beyssac et al., 2002). Variation of the estimated temperature in the outcrop is mapped in **fig. 5**. The

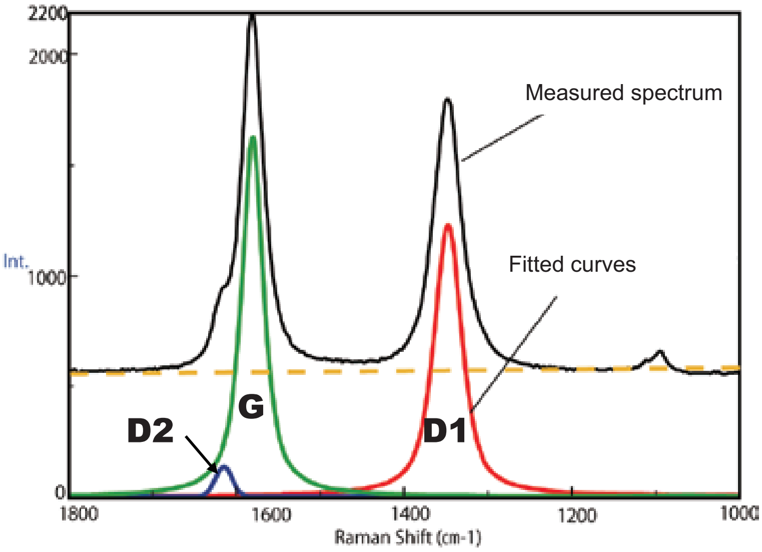

Fig. 4. Example of the measured Raman spectrum (Sample IR2014K). The measured spectrum is drawn upshifted to improve visualization. The measured wave is resolved into G-band, D1-band, and D2-band peaks as shown.

Table 1. The list of the result of the curve fitting calculation. The estimated temperatures are listed in the right most column. The error range of this calibration is thought to be approximately 50 ℃ (Beyssac et al., 2002).

Sample number	Peak of fitted curve			Area			*R2*	*T* (°C)
	D1-band	G-band	D2-band	D1-band	G-band	D2-band		
HT2014a3	1351.37	1583.06	1614.49	274990	339724	9137.45	0.441	445
IR2014J	1349.07	1580.76	1614.68	254656	246515	12105.5	0.496	420
IR2014J	1348.24	1580.47	1618.53	196925	182116	10363.2	0.506	416
IR2014K	1348.07	1580.76	1624.68	137305	149659	6419.97	0.468	433
IR2014K	1349.69	1582.38	1617.31	173813	189200	9085.16	0.467	433
IR2014L	1350.19	1582.38	1618.31	173913	188872	9160.14	0.468	433
IR2014M	1339.59	1566.71	1605.4	403779	474125	23839.9	0.448	442
IR2014M	1348.88	1581.07	1614.49	937384	833804	42999.9	0.517	411
IR2014M	1347.08	1579.76	1614.68	302444	254049	8124.34	0.536	403
IR2014N	1349.97	1581.16	1616.09	146125	126150	7826.34	0.522	409
IR2014x3	1312.33	1569.75	1614.68	356165	271070	31335.9	0.541	400
IR2014x4	1346.07	1578.55	1614.5	301619	299410	18859.1	0.487	424
IR2014x5	1347.02	1580	1614.91	62805.3	62390	3132.91	0.489	423
IR2014O	1348.79	1580.98	1614.95	170058	159508	8667.11	0.503	417
IR2014P	1345.58	1578.26	1614.02	182729	148213	12322.5	0.532	404
IR2014Q	1347.48	1579.17	1614.59	206786	197949	17438.6	0.490	423
IR2014R	1350.18	1581.26	1614.02	272323	298799	15032.8	0.465	434
IR2014S	1347.2	1579.27	1614.13	124462	103970	10671.7	0.521	409
IR2014T	1346.98	1576.17	1613.58	473609	588464	20079	0.438	446
WT20151	1345.63	1577.54	1611.5	280742	205290	43910.6	0.530	405
WT20152	1347.43	1578.33	1614.3	181079	174894	12704.9	0.491	422
WT20153	1349.43	1582.33	1614.3	133972	115587	12080	0.512	413
WT20154	1348.43	1581.33	1614.3	192474	156273	56428.2	0.475	429
WT20155	1350.42	1581.46	1614.3	215037	195523	48485.1	0.468	432
WT20156	1352.25	1584.26	1614.12	197170	124432	35851.1	0.552	395
WT20157	1343.43	1574.34	1614.3	508030	573569	107307	0.427	451
WT20158	1350.64	1580.53	1614.5	132722	162828	30945.2	0.407	460

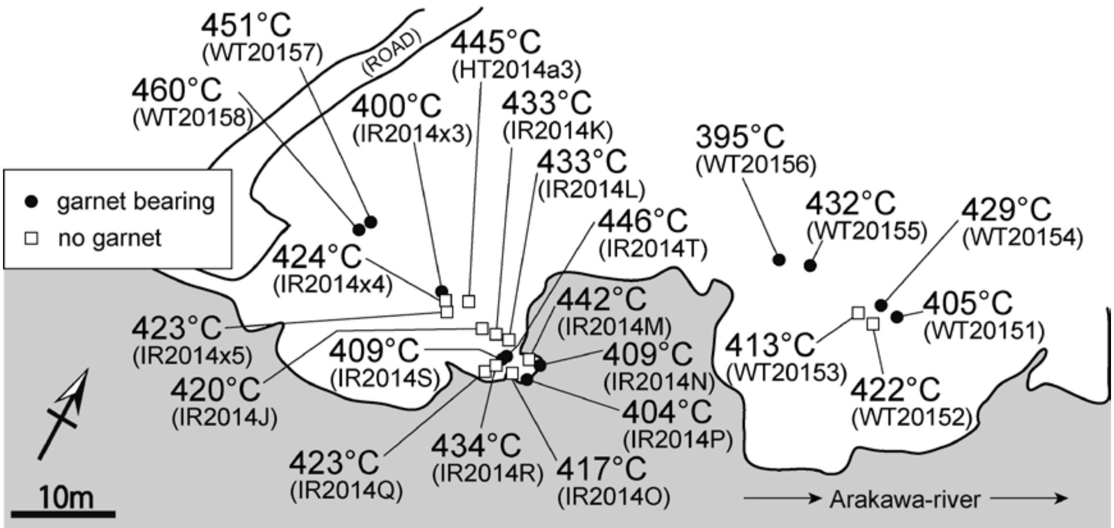

Fig. 5. The estimated temperatures mapped on the outcrop. Occurrence of garnet is also shown. Carbonaceous materials were found both in garnet bearing rocks and rocks without garnet. The temperatures are scattered with no recognizable tendency.

calculated temperatures scattered among 400 to 460 ℃ with no apparent trend concerning the location.

Temperature data of garnet bearing samples were compared to that of samples without garnet (**fig. 6**). The data scattered comparably in both cases, indicating no recognizable temperature difference between the mineral assemblages with or without garnet.

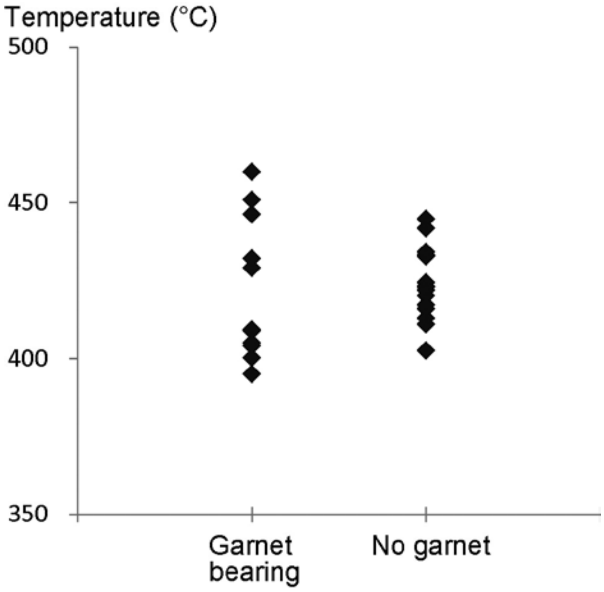

Fig. 6. Comparison of the estimated temperatures between samples with and without garnet. No difference is recognizable between the different mineral assemblage.

Discussion and concluding remarks

Validity of the estimation: The estimation seems valid since the variation range of the estimated temperature in this study is within the application range proposed by Beyssac et al. (2002), 330 to 650℃. The grating density is smaller than the machine used in the preceding work, e. g., Kouketsu et al. (2014), thus the wavelength resolution is smaller. The calibration of used in this study only requires the area of the peaks, not the exact wave number of the peak. Thus, the expected disadvantage of resolution may be small.

The temperature range suggested by this study is consistent with the previous estimation of garnet formation temperature in the Sanbagawa Metamorphic Belt (Enami et al., 1994; Inui and Toriumi, 2002). The peak temperature of the lowest garnet bearing assemblage in the Sanbagawa Metamorphic Belt (Garnet Zone) is estimated in the western part of the Belt as a little higher than 400℃. Calculated starting temperature of garnet formation from chlorite is also between 400 to 500℃, according to Mn content of the bulk rock (Inui and Toriumi, 2004). The deduced temperature condition is consistent that the garnet started to grow in a patchy manner, probably controlled by the slight difference of bulk rock chemistry.

Structural interpretation: At least in this outcrop, no evidence of discontinuity in the metamorphic condition was recognized. This is different from the claim of Hashimoto et al. (1992), which was also based on the estimated crystallinity of the carbonaceous materials. However, Hashimoto et al. (1992) attempted to cover a wide area. Their analyzed points were not dense enough to observe that comparable temperatures are obtained from rocks containing garnet and rocks containing no garnet.

The temperatures did not seem to depend on the existence of garnet. Thus, the occurrence of garnet in this area do not indicate structural discontinuity. It is more likely that the area is a continuous rock body with the metamorphic temperature varying gradually. The outcrop might be an exposed isograd, where garnet has just started to appear (Inui and Tanifuji, 2017). The fact that garnet grains found in this outcrop are all very small and euhedral is consistent with the model that they have just started to grow.

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