

CARBONACEOUS MATERIALS IN THE FLUID INCLUSIONS OF THE ACCRETIONARY COMPLEX SOUTHWEST JAPAN - RAMAN MICRO-SPECTROSCOPIC STUDY

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Introduction

Dehydration and degassing from the accretionary complex is one of the major sources of crustal fluids. To investigate the geochemistry of the crustal fluids, we carried out gas analysis of the fluid inclusions in the vein minerals of the Shimanto accretionary complex Southwest Japan and found that carbonaceous materials (CM) were often accompanied with methane-rich fluid inclusions. In this article, we will present mode of occurrences of the CM in conjunction with its Raman micro-spectroscopic characteristics and will discuss its origin.

Geological settings

Shimanto accretionary complex of the studied area is Cretaceous accretionary complex nowadays uplifted and eroded out on the land surface. It consists dominantly of trench-fill facies (sandstone and mudstone) and subordinately of melange facies (basalt, chert, limestone, sediment) and slope and forearc facies (sandstone and mudstone). The formations of this complex often host quartz vein and calcite vein. Imprint of the regional thermal structure, maximum P-T condition as 250°C and 260 MPa (Th of methane-rich inclusion is about -120°C), and vein systems after the accretion of the geologic units were estimated from the illite crystallinity, vitrinite reflectance and fluid inclusion micro-thermometry (Sakaguchi, 1999).

Samples

Vein samples were collected from the outcrops along the seashore about 10 km across the various geologic units; melange and trench facies. Veins are one to several millimeters wide and thought to be syn- or post-kinematic stage of the tectonic deformation from their mode of occurrences. Fifteen doubly polished thin sections were prepared from the samples including quartz or calcite vein for the Raman micro-spectroscopy. Fluid inclusions are mainly thought to be secondary inclusions from their linear or plainer distribution in the host minerals. They generally range 1 to 5 µm in size and show two distinct types; 1) liquid dominant two phase inclusions and 2) single phase dark inclusions due to high relief (few inclusions contain soot-like dusts).

Analytical method

Fluid inclusions in the vein quartz and calcite in the doubly polished thin sections were analyzed under the laser Raman micro-spectrometer (Horiba Jobin-Yvon T64000 at the Fukuoka University) with 514.5 nm excitation line of Ar laser, single path mode and twice accumulations of 30 sec measurement. Spectral window is from 1000 cm⁻¹ to 3000 cm⁻¹. Error of peak position is within 1 cm⁻¹. Due to the thermal vulnerability of the CM, low laser power (10 mW) was selected for the CM analysis and 50 mW for the gas analysis. Diameter of the laser probe is about 1 µm. As strong background fluorescence has hidden the high wave number peaks of the inclusions in calcite host minerals, the results of the calcite veins are not further considered. For the comparison, detrital

CMs in the rock matrix of the same samples and two graphitic carbon samples of other localities (Sri Lanka and Kamioka Mine) are also analyzed under the same analytical condition.

Results

The Raman spectral peaks of gaseous species CH₄, N₂, CO₂ and carbonaceous materials were identified. Sixty-four fluid inclusions are classified into nine types (A-I shown in table 1) based on the Raman spectroscopy. Under the microscope, careful observation identifies sooty dust in some CM detected fluid inclusions but not for all. The ν_{1,CH4} band of methane in type C, D, E, G, H inclusion is around 2913-2917 cm⁻¹, while that of type A and B shifts lower wave number 2908-2912 cm⁻¹.

Characteristics of the Raman peak of CM are as follows; "G peak" from

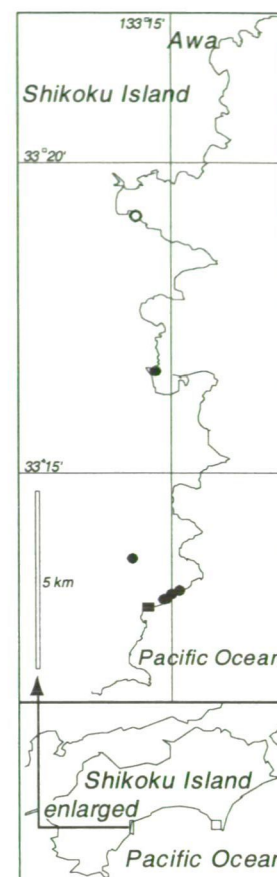


Fig. 1 Sample localities and fluid inclusion type; open circle: CI, closed circle: A(BF)I, open square: CGHI, closed square: AC(DE)GI, (): minor quantity.

Table 1 Characteristics of various fluid inclusion types. +: detected, -: not detected.

Type	Phase	CH ₄ (cm ⁻¹)	N ₂	CO ₂	CM
A	one	2908-2912	-	-	+
B	one	2908-2912	-	-	-
C	one	2913-2917	-	-	-
D	one	2917	+	-	-
E	one	2917	+	-	+
F	one	-	-	-	+
G	two	2917	-	-	-
H	two	2914-2916	-	+	-
I	two	-	-	-	-

1600 to 1611 cm^{-1} higher than typical graphite 1582 cm^{-1} peak. These peak positions are similar to those of kerogen in Wopenka and Pasteris (1993). On the other hand, peak width of CM in the fluid inclusions, measured as full width at half maximum (FWHM), distributes left side of the Wopenka and Pasteris (1993)'s kerogen. "D peak" around 1350 cm^{-1} is identified for all CM Raman spectra. "S peak" (secondary peak of G peak) is weak or not identified. These characteristics suggest low crystallinity CM such as kerogen, anthracite, glassy carbon or CM precipitated from CH_4 rather than graphite. Figure 2 shows G peak characteristics on Raman shift (cm^{-1}) and peak width (FWHM in cm^{-1}). This figure reveals that peak width of CM in the fluid inclusions is narrower than those of detrital CM in the rock matrix which overlie on the Wopenka and Pasteris (1993)'s kerogen. Even in the same sample, FWHM of CM in the fluid inclusion is narrower than that of detrital CM in the adjacent rock matrix.

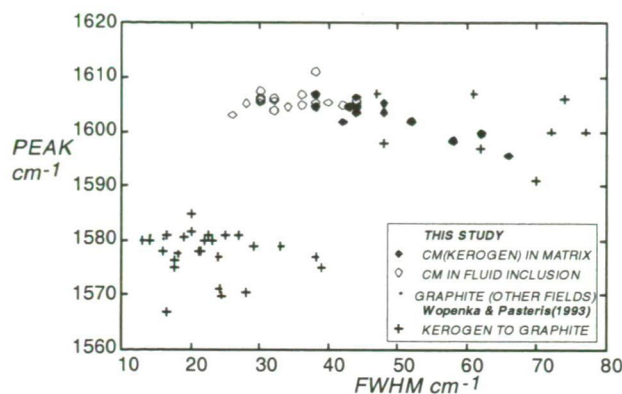


Fig. 2 Comparison of Raman G peak of CM in this study and in Wopenka & Pasteris (1993)

Discussions

It is noticed that many of CM detected fluid inclusions are associated with methane (type A), Raman spectral character of CM in the fluid inclusions is different from that in surrounding rock matrix and ν_{1,CH_4} band of associated methane is slightly lower than that in CM free inclusions. To explain these characteristics and its origin, we examined following three models. The first is that methane was trapped in the fluid inclusion, and CM was directly precipitated from methane. The second is that thermal cracking produced the methane from CM which was transported from the detrital CM and trapped in the fluid inclusions. The last is that CM and methane were both trapped in the fluid inclusions at the same time. For the direct precipitation of graphite from methane, high temperature is required to proceed this reaction (e.g. PASTERIS and CHOU, 1998). TAKENO and TAGUCHI (2002) discussed the possibility of this model from the point of view of thermal heat source as local movement of the fault which produced the rock melting called "pseudotachylite". But, we think that instantaneous frictional heat of pseudotachylite is not enough for this wide distribution of type A inclusions and that regional maximum temperature of 250°C is also not enough for it. Then we discarded the first model. In the case of the second model, thermal cracking process of CM should produce not only methane but also CO_2 and hydrocarbon other than methane. However, we did not detect such gaseous species in the fluid inclusions. Furthermore, it cannot account the type B fluid inclusions. This seems to flaw the second model. In the last model, immiscible methane-rich fluid has carried away ultra fine CM from the crashed rock matrix during the vein opening and was trapped in the fluid inclusions together with CM in the vein minerals. This model seems convincing but still requires an explanation for the narrow G peak width of CM and lower ν_{1,CH_4} band shift of methane. The ν_{1,CH_4} peak position of methane is known to be sensitive to pressure (SEITZ et al., 1993), so this might indicate that dense (high pressured) methane-rich fluid readily transported CM.

Conclusions

We discovered that CM is included in many methane-rich single-phase inclusions and its peak width is narrower than that of detrital CM in the surrounding rock matrix. The ν_{1,CH_4} band of methane with CM in the fluid inclusions is lower-shifted to 2908-2912 cm^{-1} compared with that of vapor methane (2917 cm^{-1}). For the origin of this CM in the fluid inclusions, direct precipitation of CM from the methane and in-situ thermal cracking origin of methane from the CM are ruled out, and trapping of methane-rich fluid together with ultra fine CM in the fluid inclusions is proposed as possible model.

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