

[EJ] Evening Poster | S (Solid Earth Sciences) | S-MP Mineralogy & Petrology

[S-MP37] Deformed rocks, Metamorphic rocks and Tectonics

convener: Yoshihiro Nakamura (Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology), Yumiko Harigane (Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (AIST))

Mon. May 21, 2018 5:15 PM - 6:30 PM Poster Hall (International Exhibition Hall7, Makuhari Messe)

We invite all researchers who aim to understand the dynamics of the earth's crust and mantle at the plate boundaries, to discuss the latest results from various viewpoints. The scope will include contributions through petrology and structural geology as well as various techniques including rheology and transformation of heat and mass.

[SMP37-P07] A comparative study on graphitization process in limestone and pelites at low pressure contact metamorphism

*Itsuki Muramatsu¹, Yoshihiro Nakamura², Madhusoodhan Satish-Kumar³ (1. Graduate School of Science & Technology, Niigata University, 2. Geological Survey of Japan, AIST, 3. Faculty of Science, Niigata University)

Keywords: Graphitization, Carbonaceous material, Micro-Raman spectroscopy, XRD, HRTEM

Graphitization is a process by which amorphous carbonaceous material changes its crystal structure into a graphitic structure during metamorphism. It is known to be very sensitive to temperature, and therefore widely used as an important Raman spectra of carbonaceous material (RSCM) thermometry to clarify the thermal structure in the temperature range of low- to medium-grade metamorphism (e.g. Beyssac et al., 2002; Aoya et al., 2010; Kouketsu et al., 2014). However, in addition to temperature, the chemical reactions associated with graphitization are also related to pressure, time-scale, deformation, catalysis, fluid activity and so on. Also, it is unclear on how the above factors interact with each other, and indeed there are problems in comparing different natural examples with varying geological conditions. In a previous study based on XRD analysis, it was reported that graphitization progress earlier in carbonate rocks rather than pelitic rocks (Wada et al., 1994). This suggests that there might be a difference between the catalytic effect of silicate minerals and the carbonate minerals. However, micro Raman spectroscopy studies could not detect such a difference. Therefore, in this study, we discussed the catalytic effect of coexisting minerals caused by difference of host rock on Raman spectra of CM. We examined the contact metamorphic rocks to obtain the time-scale for heating in natural samples. We used samples of metamorphosed limestones and pelites surrounding the Tono granite and the Tanohata plutonic complex intruded in to the Kitakami Mountains, Iwate prefecture. Carbonaceous materials extracted by HF-HCl treatments were analyzed by XRD and micro Raman spectroscopy. Furthermore, morphology and microstructure observation by SEM and HRTEM were carried out.

We estimated the effective activation energy of about 280 kJ / mol for Tono samples and about 300 kJ / mol for Tanohata samples, based on Nakamura et al. (2017) model. These values are considerably lower than the activation energy of graphitization reported in previous studies. It can be deduced that actual activation energies for natural graphitization in contact metamorphism could be lower than that was estimated here due to the influence of H₂O activity and/or catalysis. Samples in the temperature range from 350 to 420 °C have bimodal exothermal peaks and reflections in both DTA-TG and XRD, respectively. This suggests that CMs with different crystallinity are mixed in the sample. Therefore, graphitization at low pressure contact metamorphism is an extremely heterogeneous process. In particular, CM in limestone tends to have higher heterogeneity, and each parameter obtained by micro-Raman spectroscopy also has larger error. CM in

limestone has large value of d_{002} spacing, FWHM, and lattice distortion (ϵ_c) in the low temperature side, and the value decreased sharply as temperature increased. When observing such a heterogeneous sample with HRTEM, the CM in the limestone had a unique microstructure in which the amorphous core was covered with a thick graphene sheet. It is thought that this unique microstructure was generated by the reaction between carbonate and CM.

These results suggest that the graphitization of CM in limestone progress rapidly when accelerated by the catalytic effect of coexisting carbonate minerals. Since this process increases error of Raman spectra measurements, it is necessary to take into account the host rock effect in order to accurately estimate metamorphic temperature using RSCM thermometry.

References

Aoya et al., 2010, *Journal of Metamorphic Geology*, 28, 895-914; Beyssac et al., 2002, *Journal of Metamorphic Geology*, 20, 859-871; Kouketsu et al., 2014, *Island Arc*, 23, 33–50; Nakamura et al., 2017, *American Mineralogist*, 102, 135–148; Wada et al., 1994, *Contributions to Mineralogy and Petrology*, 118, 217-228.