Pressure dependence of structural evolution of CM: Implication for fast graphitization in subduction zone

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We report here new kinetic experiments in the pressure range of 0.5 to 8 GPa at 1200˚C for 10 min to 24 hours. Natural CMs extracted from sedimentary rocks in the Shimanto accretionary complex (SM) and Hidaka metamorphic belt (HMB) changed their morphology and crystallinity with increasing pressure. The time-pressure relations of each crystal parameter by X-ray diffraction and micro-Raman spectroscopy demonstrated sigmoidal transformations from an amorphous to a graphitic structure, suggesting the pressure-induced recrystallization at constant temperature (1473 K). Utilizing the relationship between log rate constant (ln*k*) and pressure (atm), we obtained the activation volumes of −22˜− 44 cm^3/mol during graphitization using a power rate model and a Johnson-Mehl-Avrami-Kolmogorov model. Combining the activation volumes and data on Nakamura et al. (2017), the structural evolution of CM based on experimental kinetic model can be expressed by three different factors of pressure *P*(MPa), metamorphic temperature *T* (K) and duration *t* (min):
$f(P, T, t) = C_{min} + (C_{max} - C_{min}) / \{1+[((-22P + 286686)/RT)/t]^h\}$,
where C_{min} and C_{max} are the maximum and minimum values of each parameter, respectively, *A* is the intercept of the Arrhenius plot, *R* the gas constant, and *h* is the reaction rate of the sigmoid function (named as the “Hill coefficient”). It is thus possible to calculate the progress of graphitization at any *P-T-t* conditions during metamorphism. Utilizing the kinetic model, we tried to compare the experimental model based crystallinity of CM with natural metamorphic *P-T-t* conditions. In the case of Hidaka metamorphic belt, the natural CMs along the field *P-T* path of HMB proceeded structural evolution of CM from around 350 ˚C and form a graphite at around 450 ˚C. On the other hand, calculated structural evolution of CM started to recrystallize at around 400 ˚C, and form graphite at over 500 ˚C in a duration of ca.10 million years. Although there still exist some factors for fully understanding the natural structural evolution of CM to graphite, the experimental kinetic model can be applicable as a thermal indicator in a wide range of *P-T* conditions between 0.5 and 2 GPa at 400˜800 ˚C. The most important implication of our finding is that natural CM in crust has proceed fast recrystallization from an amorphous to a graphitic structure by temperature and pressure compared with the laboratory at 1 atm. Our data provide a new kinetic model for not only geothermometry but also geospeedometry and geobarometry in subduction zone.

Keywords: Carbonaceous material, Graphitization, Chemical kinetics, HPHT experiments