Geological extrapolation based on Arrhenius relation of graphitization experiments
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Previous studies have argued that natural graphitization process cannot be directly explained by Arrhenius relation between peak metamorphic temperatures and duration of heating. One of the most important issues is extremely high activation energy (≈ 1000 kJmol⁻¹) required to form fully ordered graphite, as reported in experimental data (e.g. Fischbach, 1971). In this study, we carried out graphitization experiments and estimated enthalpies based on more realistic temperature and pressure conditions (1000–1450 °C, and 1GPa) than the previous studies. The results obtained from XRD and micro-Raman spectroscopy were analyzed using a superposition method in which the crystal parameters were superposed in to reference temperature (1000 °C) with non-linear regression curves (Sigmoidal functions). Using this method, the effective enthalpies of 274 +/- 16 kJmol⁻¹ and 334 +/- 9 kJmol⁻¹ for two different natural CM (SM; Shimanto accretionary complex, HMB; Hidaka metamorphic belt), were obtained. The data were further evaluated to extrapolate the geological temperature-time conditions of graphitization process, which is controlled by the Arrhenius relation. The sigmoidal master curves can be extrapolated to represent low temperature condition (300–800 °C), and was tested using the parameters of the unit cell height c;

\[ f(t) = C_{\text{min}} + (C_{\text{max}} - C_{\text{min}}) / \{ 1 + (A \exp(m/T))/t \}^n \]

where both \( C_{\text{min}} \) and \( C_{\text{max}} \) are maximum and minimum ranges of each parameter. \( t \) is the annealing duration, \( t_{\text{half}} (A \exp(m/T)) \) is the inflection point obtained from this function, and \( n \) is the reaction rate. Thus, it is possible to predict the structural evolution of CM to graphite by the above function of peak temperature \( T \) and annealing duration \( t \). Our kinetic model predicts that if the CM underwent metamorphism for about one million years, it begins to crystallize at \( \approx 420 \) °C and transform to fully ordered graphite at over \( \approx 510 \) °C (path 2; Fig. 1). Thus, natural graphitization process could be explained by the laboratory experiments using natural precursor materials under realistic pressure conditions in the Earth’s crust.