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An experimental kinetic study on the structural evolution of natural carbonaceous material to graphite

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Abstract

We report here new experimental kinetic data on the structural evolution of carbonaceous material (CM) to graphite during heating at various temperatures (1000 to 1450 °C) for various durations (10 min to 115 h) under a pressure of 1 GPa. Natural CMs extracted from sedimentary rocks in the Shimanto accretionary complex and the Hidaka metamorphic belt of Japan transformed in morphology and crystallinity with increasing temperature and annealing duration to become fully ordered graphite (d_{002} spacing ~3.36 Å). Transmission electron microscopy showed that both samples have undergone microstructural evolution from amorphous carbon to platy graphitic carbon. These changes match the evolution of the samples' X-ray diffraction (XRD) patterns and micro-Raman spectra. The time–temperature relations of crystal parameters obtained by XRD and micro-Raman spectroscopy demonstrated a sigmoidal transformation curve from an amorphous to a graphitic structure, suggesting complexity of these successive and/or parallel chemical reactions are responsible for graphitization. To assess these complex chemical processes, we adopted three different approaches for formulating the graphitization kinetics using a power rate model, a Johnson-Mehl-Avrami (JMA) model and a superposition method. Irrespective of the models employed, the effective activation energies were estimated to lie between 259 and 339 kJ/mol, which are much lower than those reported previously for graphitization. Summarizing the previous studies and our results between 0.1 and 1000 MPa, we found that the effective activation energies systematically decrease as a function of pressure. Based on the experimental results in this study, the sigmoid functions obtained from the time–temperature relations can be extrapolated to low-temperature conditions at 1 GPa. Our kinetic model using unit-cell height *c* predicts that CM undergoing metamorphism for about 1 m.y. will begin to crystallize at ~410 °C, and will transform to fully ordered graphite at over ~520 °C. Thus, natural graphitization undergoes a much faster transformation than reported in previous studies at 1 atm and could be explored in laboratory experiments using natural precursor materials under pressure conditions and time spans that reflect natural conditions in the Earth's crust.

Keywords: Graphitization, carbonaceous material, kinetic model, HPHT experiment