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The influence of heating rate on the kinetics of mineral reactions: An experimental study and computer models

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ABSTRACT

Startling results were obtained in kinetic experiments that varied the initial heating history of the mineral reaction: 1 dolomite + 2 quartz → 1 diopside + $2CO_2$. The experiments were carried out at 5 ± 0.05 kbar, $X_{CO_2} = 0.9$, and 680 ± 3 °C, which is 65 °C higher than that of equilibrium. The heating history was varied from the conventional procedure [about 1 h reported by Lüttge and Metz (1991)] by various techniques. The experimental temperature in externally heated cold-seal pressure vessels is attained within 10 min by preheating with a furnace running at 1000 °C, and quickly switching to a furnace set at the temperature of the experiment when T reaches 670 °C. Percent conversion, measured by CO_2 production as a function of time for the period 5 to 288 hours, is linear and fit by the equation, $\alpha = kt$, with $k = 5.64 \times 10^{-2}$ [%conversion/h]. Compared with results produced by the conventional heating procedure, our conversion rate is slower and results show an order of magnitude less scatter. The variation in the magnitudes of the rates measured after the fixed experimental conditions were reached for different heating procedures as well as the large differences in the degree of the scatter of the experimental rate data for different heating procedures are contrary to earlier claims made by most experimentalists and required a rethinking of our kinetic interpretation of the data.

A kinetic model developed to simulate the initial period of a mineral reaction experiment provided a reasonable explanation of many of the unusual facets of the experimental results. The model follows the variation of concentration, ΔG of the reaction, surface area, nucleation rates, and volume of the product as a function of time for the different heating histories used in the experimental study. The key problem ignored in earlier work is the significant effect of a complex nucleation history during the heating conditions on the entire subsequent kinetics, even though the latter are carried out for much longer times and under constant P and T conditions. Results show that faster heating rates cause faster nucleation rates, and the duration of the nucleation period is shorter. Two different scenarios were compared: (1) a reaction product growing independently of the reactant surface (as may occur in hornfelses with fine grain size); and (2) a reaction product growing on the surface of a reactant. The latter case leads to a significantly reduced reaction rate for faster heating rates (as was observed experimentally), because the surface of the reactant is covered by an armoring rim of product crystals early in the experiment.

Application of the results of this study to natural systems suggests how the kinetics of mineral reactions behave quite differently if there are different nucleation conditions, even if the P-T-X conditions of the rock are the same.