Dehydroxylation, Rehydroxylation, and Stability of Kaolinite

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Abstract: From hydrothermal experiments three pressure-temperature-time curves have been refined for the system Al_2O_3-SiO_2-H_2O and reversal temperatures established for two of the principal reactions involving kaolinite. The temperatures of three isobaric invariant points enable the Gibbs free energy of formation of diaspore and pyrophyllite to be refined and the stability field of kaolinite to be calculated. The maximal temperature of stable kaolinite decreases from 296 ° C at 2 kb water pressure to 284 ° C at water's liquid/vapor pressure, and decreases rapidly at lower pressures. On an isobaric plot of $[H_4SiO_4]$ vs. $°K^{-1}$, kaolinite has a wedge-shaped stability field which broadens toward lower temperature to include much of the $[H_4SiO_4]$ range of near-surface environments. If $[H_4SiO_4]$ is above kaolinite's stability field and the temperature is <100 ° C halloysite forms rather than pyrophyllite, an uncommon pedogenic mineral. Pyrophyllite forms readily instead of kaolinite above 150 ° C if $[H_4SiO_4]$ is controlled by cristobalite or noncrystalline silica.

Kaolinite and a common precursor, halloysite, are characteristic products of weathering and hydro-thermal alteration. In sediments, relatively little halloysite has survived due to its low dehydration temperature and instability at low water pressure, but kaolinite commonly has survived since the Devonian Period. In buried sediments, the water pressure and $[H_4SiO_4]$ requisite for stable kaolinite generally are maintained. In oxidized sediments and in pyritic reduced sediments, kaolinite commonly has survived, but where alkalies, alkaline earths, or aqueous iron has concentrated in the pore fluid, kaolinite has tended to transform to illite, zeolites, berthierine, or other minerals.

Key Words: Dehydroxylation • Gibbs free energy • Halloysite • Hydralsite • Hydrothermal • Kaolinite • Pyrophyllite

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