Thermal Stability of Halloysite by High-Pressure Differential Thermal Analysis

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Abstract: Platy (Te Puke, New Zealand), cylindrical (Spruce Pine, North Carolina), and spherical (North Gardiner mine, Huron, Lawrence County, Indiana) halloysite samples were analyzed by high-pressure differential thermal analysis (HP-DTA) to determine the effect of morphological and chemical differences on their respective thermal stability. In halloysite, these morphological differences imply structural features. The metastable phase relations of each are analogous to those of kaolinite. At 1 bar, the platy, cylindrical, and spherical samples showed peak temperatures (maximum deflection in the dehydroxylation endotherm) of 560 ° , 578 ° , and 575 ° C, respectively, whereas at about 600 bars the peak temperatures were 622 ° , 655 ° , and 647 ° C. At low pressures the observed reaction is related to dehydroxylation: halloysite (H) metahalloysite (MH) + vapor (V), whereas higher pressures produce melting reactions, either H + V = metaliquid (ML) for conditions of $P(H_2O) = P(total)$, or H + MH = ML for $P(H_2O) < P(total)$. The PT conditions of the invariant point, H + MH + ML + V, for each system are: Te Puke, 612 ° ± 4 ° C, 25 ± 7 bars; Spruce Pine, 657 ± 2 ° C, 30 ± 7 bars; North Gardiner, 652 ° ± 2 ° C, 34 ± 7 bars. The lower thermal stability of the Te Puke sample may be related to its higher iron content, although additional data are necessary to confirm that it is not related also to the platy structure. Furthermore, morphological differences between the cylindrical and spherical varieties appear to have had little effect on the energy required to dehydroxylate these halloysite structures. Exceptionally high values obtained for the dehydroxylation enthalpies using the van't Hoff equation, compared with values derived using other methods, may be explained by a 10 – 15-bar excess in the intracrystalline H_2O fugacity during dehydroxylation. Intracrystalline fugacity is defined here as the H_2O fugacity within crystallites and is not related to the partial pressure of H_2O around individual particles.

Key Words: Dehydroxylation • Halloysite • High-pressure differential thermal analysis • Morphology • Phase relations • Thermal stability

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