

THERMAL STABILITY OF TOCHILINITE
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Introduction. Recognition of Fe-rich tochilinite, a layer-structured sulfide/hydroxide mineral, as a component of the "poorly characterized phases" (PCPs) in C2 chondrites [1] has presented a new opportunity to diagnose the conditions of aqueous alteration on the parent bodies of those meteorites. Because tochilinite is relatively rare on Earth, it has not been studied in detail until recently [2] and its thermodynamic properties have not been determined. We report here the first attempt to measure the heat-capacity function of a terrestrial tochilinite as a step toward estimating chemical-thermodynamic properties that are needed to compute stability relations for tochilinite paragenesis. **Experimental Procedure.** Grains of tochilinite, mechanically separated from skarn gangue rock collected from Stephen Cross Quarry, Wakefield, Quebec, were analyzed by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-2C instrument. The sample was held in a platinum container with loose-fitting lid and heated from 300 K to 1000 K at 10 K/min under continuous purge of dry, high-purity nitrogen gas. After rapid cooling to 300 K and re-equilibration, the sample was reheated. Samples of National Bureau of Standards SRM-720 sapphire, run under the same conditions, were used as heat-capacity standards. **Results.** The original 2.13-mg sample lost 0.31 mg of mass during first heating but sustained no additional mass loss during second heating. Stoichiometric tochilinite, $2 \text{FeO} \cdot 9\text{S} \cdot 1.67 (\text{Mg}(\text{OH})_2)$, contains 11.5 wt. % water so that the 15% weight loss observed for the sample would imply either partial volatilization of sulfur or slight contamination by other hydrous phases. Two observations support the latter interpretation. First, absence of weight loss during second heating implies that sulfur volatilization was not a major process. Second, analysis of a separate sample known to be impure gave 24 % weight loss during first heating (none during second heating) and produced DSC peaks that appear as minor features in the "pure" sample's heat-flow curve.

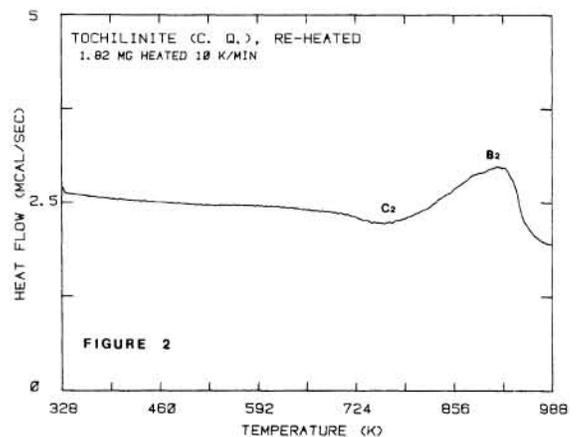
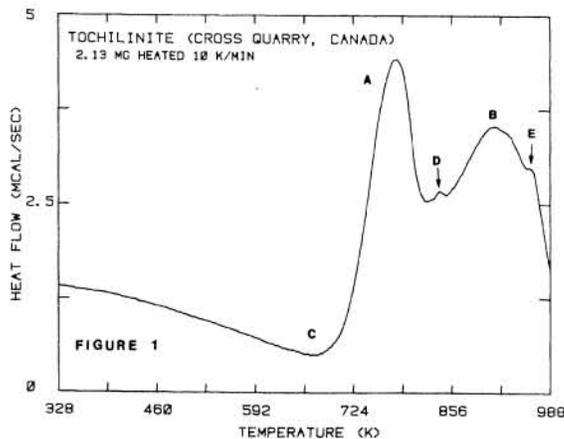
Features A, B/B₂, and C/C₂ in the DSC heat-flow curves for the "pure" sample (Figs. 1-2) are apparently characteristic of tochilinite whereas features D and E (Fig. 1) are most likely attributable to minor hydrous contaminants. Feature A represents dehydroxylation of brucite layers whereas B/B₂ apparently represents either a reversible solid-state transition or a chemical reaction in the dehydroxylated residue (mackinawite + periclase?). The onset of dehydroxylation of Cross Quarry tochilinite occurs at 720 ± 2 K. In contrast, dehydroxylation of "brucite" layers in Mg-serpentine occurs at 850 ± 5 K (reference analyses not presented here). Therefore, tochilinite is significantly less stable with respect to dehydration than is serpentine. Although feature B/B₂ might represent a solid-state transition in a sulfide, peak B₂

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comprises an enthalpy change of 354 ± 18 kJ/mol (i.e., 323 ± 16 cal/g with an assumed gram-formula weight of 262) and indicates a process of much greater energy than the 0.5-2 kJ/mol expected for a solid-state transition in a pyrrhotite-like mineral. Therefore, B/B₂ may indicate a reaction between dehydroxylation products. Feature C represents either an exoenthalpic transition in pristine tochilinite or, possibly, a sample/container reaction. Further experiments in different containers will be required to test the latter hypothesis and eliminate artifacts.

The complex nature of the tochilinite heat-flow curves, especially exoenthalpic feature C, seriously limits the value of heat capacities computed from these measurements. However, it appears that the low-temperature heat capacities of tochilinite may be comparable to those of phyllosilicates with Mg and Al in octahedral layers. The apparent specific heat of Cross Quarry tochilinite at 400 K is 310 ± 22 J/(mol·K) (i.e., 0.28 ± 0.02 cal/(g·K) for 262 g.f.w.), which lies between the values of 285 and 356 J/(mol·K) obtained by mixing calculations based on Kopp's rule and is in the range of values observed for muscovite and talc. **Tochilinite As A Monitor of "Metamorphic" Reheating.** Occurrence of tochilinite would indicate that, subsequent to tochilinite formation, the host rock was never heated above the tochilinite dehydroxylation temperature. Because its decrepitation begins at 720 K, Mg-tochilinite should be a more sensitive monitor of "metamorphic" temperature than are either Mg-serpentine or calcite, which often coexist with tochilinite but which decompose at > 850 K and > 1000 K, respectively. Because substitution of Fe into brucite layers should decrease the dehydroxylation temperature, Fe-rich tochilinites in C2 chondrites might be sensitive to "metamorphic" temperatures < 700 K.



References: [1] Mackinnon I. D. R. and Zolensky M. E. (1984) Nature, **309**, 240-242. [2] Zolensky M. E. and Mackinnon I. D. R. (1986) Amer. Mineral., **71**, 1201-1209.