

TOCHILINITE PRODUCED IN LABORATORY

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Tochilinite was firstly identified in the serpentinites from Voronezh region, Russia, in 1971 [1] and described in more details in [2-3]. Later this mineral was recognized to be a major matrix phase of the most primitive carbonaceous chondrites (CI, CM) where tochilinite as a mixed-layer structure occurs among serpentine group minerals, olivine, pyroxene, pyrrhotite etc (see, for example, [4]). Terrestrial tochilinite has been suggested to result from low-temperature hydrothermal alteration of serpentinite [3]. The origin of the chondritic tochilinite is still not known, partly because of failure to synthesize this mineral. As far as we know, since 1971, there was no publication about successful synthesis of tochilinite. Here we present results of the first laboratory synthesis of tochilinite as a product of interaction of Fe(II) hydroxides with H₂S at 80°C, and total concentration of reduced sulfur ions in solution lower than 10⁻⁴M at pH 7.8 and lower than 1M at pH 11.5.

Experimental techniques. Input materials were prepared just before runs from solutions of ferrous chloride (with concentrations varied from 0.35 M to 1.1 M), added by NaOH and contemporarily bubbled by H₂S gas. Formed instantly ferrous hydroxide continued to react with H₂S during one hour upon mixing. During this procedure, NaOH added only to remain the required pH value. The solid/liquid ratio of the initial suspensions were determined by ferrous chloride concentration in initial solutions. Reaction vessel 40 ml in volume was either of pyrex glass (at pH ≤ 11), or of titanium (at pH > 11). A vessel was filled in half by the freshly prepared suspension with the fixed values of pH, closed hermetically, and heated up to 80°C. Duration of the runs described here varied from 30 to 150 days. After runs, a vessel was cooled and opened. The liquid product was measured in pH and reduced sulfur ions (S²⁻, HS⁻ etc.) total content the latter referred here as pS. Sulfur content was measured by Ag-Ag₂S electrode pair. A part of the dried solid material after run was studied by method of X-Ray diffraction (XRD)

Results and Discussion. The results of 13 runs are presented in the Fig.1 that demonstrates position of XRD-identified solid final products relative to the values of pH and pS in final liquid. Tochilinites with characteristics reflections $d_{001}=10.9\text{\AA}$ and $d_{002}=5.45\text{\AA}$ were identified in association with magnetite and mackinawite. The magnetite - associated tochilinite produced at pH= 8.2 and pS= 4.8 was studied by selected area electron diffraction (SAED) that confirmed the identification and derived its formula $2\text{Fe}_{1-x}\text{S}1.5\text{Fe}(\text{OH})_2$ (see below for details). Mackinawite - associated tochilinite was produced at pH= 8.0 and pS= 4.0, and pH= 11.2 and pS= 1.0. This pair allows to trace a way of the successful synthesis of tochilinite. Tochilinite reflection $d_{002}=5.45\text{\AA}$ and mackinawite reflection $d_{004}=5.04\text{\AA}$ are very similar. If the tochilinite produced would be more amorphous the overlapping of these reflections would be formed a pattern of a broad maximum at $d= 4.9-5.4\text{\AA}$ that could not be ascribed unambiguously tochilinite. So, the major problem was to produce well-crystallized tochilinite. In a preliminary series of our runs, we found that crystalline products were formed when the run duration was > 60 days (the crystallization rate increased with increasing the pH value in the initial liquid). Also, we found that the total reduced sulfur-ions content in the final liquid was roughly correlated with the solid/liquid ration the initial suspension. These two findings allowed us to control on both degree of crystallinity and pS values.

Structural study. For the magnetite associated tochilinite, diffractograms and Debay-Scherrer patterns contain two tochilinite reflections: $d_{001}=10.9\text{\AA}$ and $d_{002}=5.45\text{\AA}$. All others belong to magnetite phase. More information has been received with electron microscopy and microdiffraction accompanied by Kevex. All micro-particles with Fe and S were not perfect single crystals. But it was possible to have some additional structural information from SAED pattern for the particles with slightly disoriented crystals. The tochilinite studied showed two different layers - Fe_{1-x}S with square two dimensional unit cell ($a_s=3.60\text{\AA}$) and hexagonal brucite-like $\text{Fe}(\text{OH})_2$ with $a_{\text{OH}}=3.145\text{\AA}$. The regular interchanging of two kinds of layers builds the tochilinite structure. The crystallochemical formula can be written as $2\text{Fe}_{1-x}\text{S}1.5\text{Fe}(\text{OH})_2$. The value of the latter coefficient

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can be evaluated only approximately and may be more exact determined with the better microcrystal. It is clear that such formula is near to "limasolite" - tochilinite-like mineral from Limasole (Phase 1 in [2] and is in accordance with assumption by one of the authors [3] about this coefficient value for the pure iron brucite-like tochilinite. The a_s and a_{OH} axes orientation is similar to usual tochilinite one but is accompanied by the mutual systematic turning in the both components. Mutual different layer displacement can be recognised after receiving full X-Ray pattern of tochilinite.

So, the sample produced in laboratory is a new variety of tochilinite with formula $2Fe_{1-x}S_{1.5}Fe(OH)_2$. It consist of two different chemical and metric interchanging layers. Their mutual orientation is similar to those of usual Mg- tochilinite, but with high symmetry of each layer kind (square and hexagonal for sulfide and hydroxide components, respectively and their different mutual turnings (three in sulfide, two in hydroxide).

Fig.1. Experimental data on tochilinite synthesis at 80°C

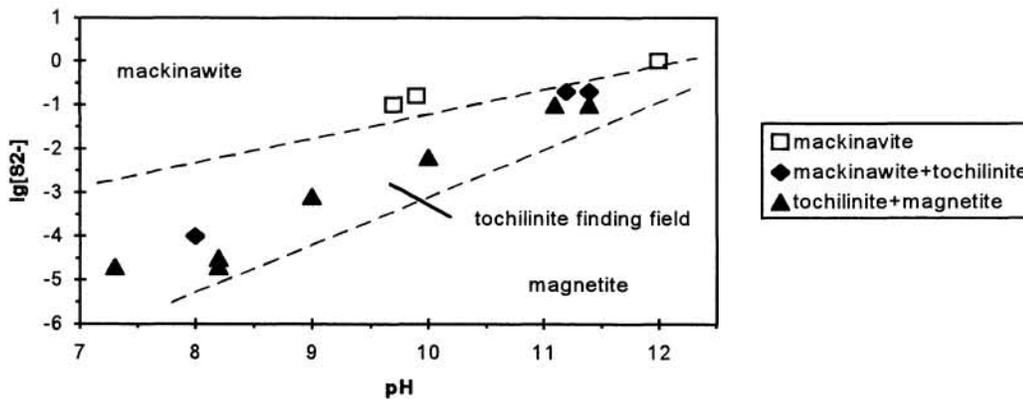
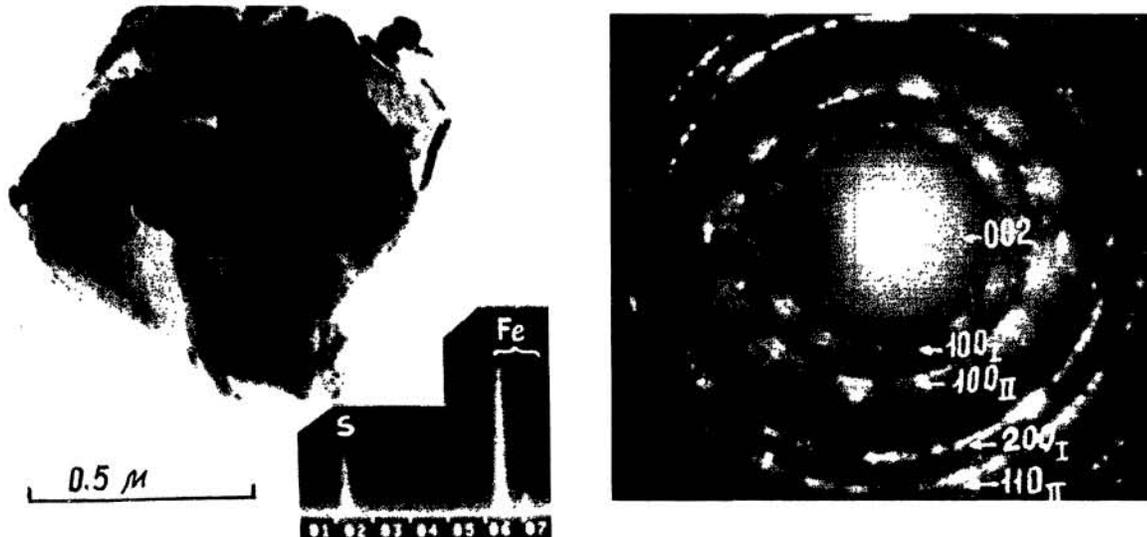


Fig.2. Typical transmission electron microscopy image of tochilinite particle with its EDS analyses. Fig.3. SAED pattern of tochilinite. I - reflection of sulfide, II - of hydroxide components.



References: [1] Organova N.I. et al. (1971), Zap. Vses. Miner. Ob, 100, 4, 477-487 (in Russian). [2] Organova N.I. et al. (1974), Amer. Miner., 59, 190-200. [3] Organova N.I. (1989), Crystallochemistry of incommensurated and modulated mixed-layer minerals., M.: Nauka, 144 p.p. (in Russian). [4] Zolensky M. et al. (1993), GCA 57, 3123-3148.