Kozerenko, S.V.[1], Fadeev, V.V.[1], Organova, N.I.[2], Rusakov, V.S.[3], Chistyakova, N.I.[3], Kolpakova N.N.[1], Senin, V.G.[1] Synthesis, formation conditions and crystallochemistry of tochilinites – iron, magnesium and sodium hydroxide-sulfides

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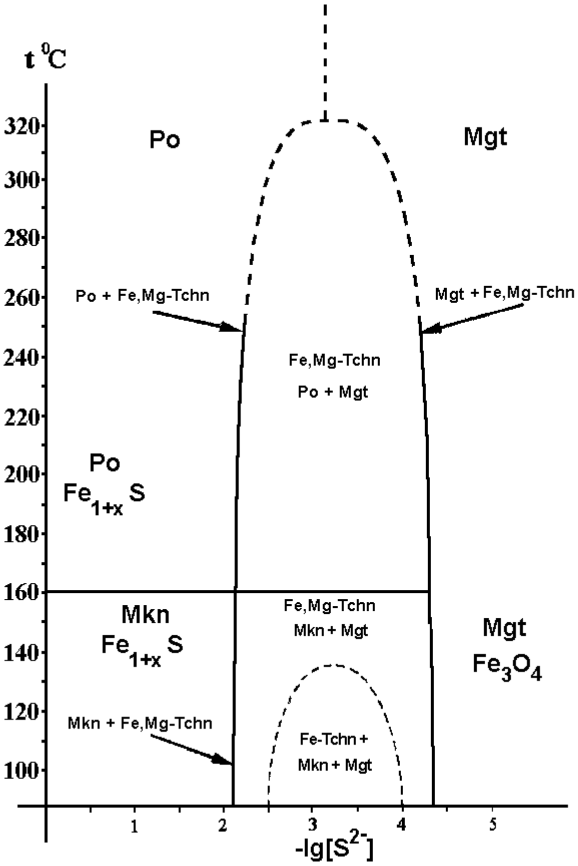
key words [synthesis, hydroxide-sulfides, tochilinites, extraterrestrial substance]

Tochilinites are the minerals of the mixed-layered hydroxide-sulfide group. Within their structures the tetrahedral FeS mackinawite-like bands are regularly alternated with the octahedral brucite-like Mg,Fe(OH)$_2$ bands. The tochilinite formula is $2FeS\cdot nMe(OH)_2$, where Me=Fe, Mg, and the n value varies from 1.5 to 1.75 [1, 2]. Interest in this group of minerals is associated with their wide abundance in meteorites (mostly carbonaceous chondrites of CM and C1 type), cosmic dust, and also in the earth conditions (magnesium skarns, serpentenites, hydrothermal ore deposits) [1-4].



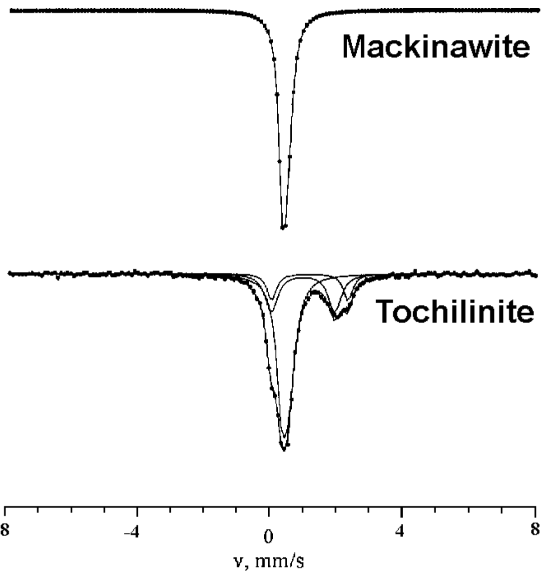


Fig. The scheme of the phase ratio of tochilinites

We were the first to realize the tochilinite synthesis in laboratory conditions [5]. The experiments were conducted in the 80-360°C T-range in titanium vessels or autoclaves (higher than 200°C) in hydrogen sulphide bearing solutions. The sulfide sulfur concentration was measured by a sulfide – silver electrode (with the detection limit of 10^{-6} M). The fresh prepared iron chloride (II) was used as the iron source. Tochilinite forms in neutral or alkaline medium with relatively low content of sulfide sulfur. The magnetite+mackinawite association or the magnetite + hexagonal pyrrhotite association at temperature higher than 160°C form instead of tochilinite in acidic medium. The best tochilinite specimens were obtained in alkaline solutions (pH 11.0±0.5). The iron variety of tochilinite with the formula $2FeS\cdot 1.51(Fe^{2+},Fe^{3+})(OH)_2$ and the magnesium-iron one with the composition $2FeS\cdot 1.54(Fe_{0.7}Mg_{0.3})(OH)_2$ were synthesized. Tochilinite forms, as a rule, in the mixture with mackinawite and/or magnetite at pH of 10.5-11.5 and $C_S^{2-}=10^{-1}$-10^{-6} M. The hexagonal pyrrhotite forms at temperature higher than 160°C instead of mackinawite. The tochilinite stability field depending on temperature and sulfide sulfur concentration is presented in the diagram. The major parameter defining tochilinite formation is sulfide sulfur concentration. The latter decreasing lower than 10^{-4} M results, at first, in mackinawite or pyrrhotite formation and then tochilinite formation at its further decrease. The stability features of the iron and the ferromagnesian tochilinites differ substantially from each other. The former are the metastable phases forming as intermediate compounds during interaction of iron hydroxide (II) with hydrogen sulfide. The upper temperature limit for their formation is 130±10°C. Addition of magnesium stabilizes the tochilinite structure. The ferromagnesian specimens were obtained up to 320°C.

The structural studies of the synthetic tochilinites were performed by electron diffraction and Mössbauer spectroscopy. The broad diffraction picks are typical of Fe-tochilinties, which indicates low ordering of the phase. The sharp diffraction picks characterize Fe-Mg-tochilinites. However, the generalized image of picks is the same, and it can be interpreted as combination of square (reflection of mackinawite-like bands, a_S=3.60 Å) and hexagon (brucite-like structure, a_{OH}=3.145 Å) nets.

Their mutual orientation corresponds to the most common variety of natural tochilinite [1]. The tochilinite Mössbauer spectra are a superposition of the three partial quadruple duplets. The super-thin parameters of one of them are similar to makcinawite with Fe^{2+} ions in low-spin condition. The presence of that duplet is due to the sulfide layer in tochilinite. The other two duplets are due to the presence of iron ions in the brucite layer. Their super-thin parameters correspond to Fe^{2+} at high-spin condition. The Mg atoms occur in the brucite layer, predominantly in one of the revealed non-equivalent positions in Fe-Mg tochilinites. It is confirmed that the same quantity of the mackinawite and brucite layers is combined in synthetic tochilinite.

At highly alkaline conditions (pH 11.5-12.5) an additional phase with the diffraction patterns close to tochilinite appears in synthesized sediments. However, the d value of the most intensive line corresponds to 11.16 Å in contrast to tochilinite with 10.4-10.8 Å. Microprobe analysis detected Na (~ 6 wt.%) in the phase composition. This phase was called sodium tochilinite. Its electron diffraction investigation showed that the sulfide layer was similar to that in Fe-Mg-tochilinite, and the hydroxide layer was different. The presence of sodium results in tetrahedral construction of hydroxide constituent of the phase. The compound is unstable and decomposes at temperature of higher than 100°C with mackinawite formation.

Therefore, the conducted research allows the conclusion that tochilinites are the minerals with a hybrid structure. Due to their composition features tochilinite formation is extremely sensitive to variations in sulfide sulfur concentration and, thus, can be an excellent indicator of mineral formation conditions. The iron tochilinite is metastable and its formation is, first of all, defined by kinetic factors. From this point of view the repeatedly noticed observation becomes clear: mackinawite is typical of the earth mineral parageneses, and tochilnite is typical of meteorites. Short-term mineral formation processes within the parental bodies of carbonaceous chondrites associated with impact metamorphism [4] favors retention of metastable forms. The Na-tochilinite is unstable, and nothing is known about its occurrence in nature. However, the unknown sulfide of composition $NaFeS_2(OH)$ is described in [6]. Based on the results of microprobe studies this phase is similar to the synthesized one.

The work was supported by RFBR no. 00-05-65372

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