## MINERALOGY

# Magnesium Szomolnokite $(\mathrm{Fe}, \mathrm{Mg}) \mathrm{SO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ 

by<br>J. KUBISZ

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In the "Staszic" pyrite mine at Rudki near Nowa Slupia a mineral previously unknown here was found in an old, poorly ventilated gallery, where the temperature was nearly $30^{\circ} \mathrm{C}$. Investigations have shown that this mineral is ferro-magnesium sulphate monohydrate ( $\mathrm{Fe}_{0.59}, \mathrm{Mg}_{0.41}$ ) $\mathrm{SO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ ) containing some maganese. The structure and the dimensions of the unit cell of this mineral closely resemble szomolnokite. It seems that the mineral represents one member of the isomorphic series $\mathrm{FeSO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}-\mathrm{MgSO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ not found hitherto in natural conditions. It is suggested to name this mineral magnesium szomolnokite.

Magnesium szomolnokite occurs in the form of compact, finely crystalline aggregates intergrowing an earthy ore containing marcasite and pyrite. Locally it forms parallel intergrowths of acicular crystals. The samples of marcasite intergrown with magnesium szomolnokite are covered on the surface with a crust of ferrous hexahydrite and copiapite.

Physical proprieties: Tabular or acicular habit. Brittle. Facture uneven. Hardness about 2.5. Colourless. Transparent. Vitreous. lustre. In microcrystalline aggregates sugar-white, lustreless. White streak. Optical character positive. Optic axial angle (2V) large. Indices of refraction ( $\mathrm{D}_{\mathrm{Na}}$ ): $\mathrm{N}_{\gamma}=1.629, \mathrm{~N}_{\alpha}=1.558$. Birefringence $=0.071$.

Chemical proprieties: Difficultly soluble in water, undergoes partial hydrolysis. Soluble in HCl . Unstable at room temperature and humidity. X-ray examinations indicate that after several months it is partly altered to tetrahydrate and after one year to a mineral which has not as yet been identified. A small amount of this unknown mineral was detected in magnesium szomolnokite on X-ray pictures taken the next day after the samples had been brought from the mine. Magnesium szomolnokite altered at room conditions can be transformed into monohydrate by heating it to $250-300^{\circ} \mathrm{C}$ during $15-20$ minutes when the heating rate is $15^{\circ} \mathrm{C} / \mathrm{min}$. It seems, therefore, that the unidentified mineral is a higher hydrate of ferro-magnesium sulphate. Probably it is a pentahydrate
(siderotil). The direct determination of water in the alteration product of magnesium szomolnokite is made very difficult by the admixtures of marcasite and pyrite which cannot be eliminated. The X-ray pattern of the product (Table II) is very similar to that of chalcanthite.

Chemical investigations: Crystals selected under binoculars were dissolved in cold $1: 10 \mathrm{HCl}$, iron sulphides were removed by filtration, and the filtrate was analysed (Table I). The water content was estimated by difference.

TABLE I

| Component | FeO | MgO | MnO | $\mathrm{SO}_{3}$ | $\mathrm{H}_{2} \mathrm{O}$ | Total |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| weight \% | 27.49 | 10.42 | 0.18 | 51.53 | 10.48 | 100.00 |

molecular ratio $\mathrm{FeO}: \mathrm{MgO}+1: 0.685$
formula: $\left(\mathrm{Fe}_{0.59}, \mathrm{Mg}_{0.41}\right) \mathrm{SO}_{4} . \mathrm{HO}_{2}$
X-ray examinations: X-ray patterns were made with filtered FeK $1.935978 \AA$ radiation in 114.8 mm . diameter cameras. 80 mm . long $2 \times 1 \mathrm{~mm}$. slit collimators were used. The accuracy of measurements was $\vartheta= \pm 0.02 \mathrm{~mm}$. The intensity of lines was estimated visually. For comparison Table II lists also the calculated data from the X-ray patterns of kieserite $\mathrm{MgSO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ from Klodawa as well as of synthetic pure and zinc-magnesium szomolnokites. The X-ray pattern of synthetic magnesium szomolnokite $\mathrm{FeO}: \mathrm{MgO}=1: 0.33$ is exactly the same at the X-ray pattern of the natural mineral and, therefore, has not been included in the table. The substitution of magnesium or zinc for iron causes small changes in the arrangement of lines and in line to line distances for the range $d=1.72 \AA$ to $d=1.587 \AA\left(\vartheta=34^{\circ}-37.5^{\circ}\right)$. Kieserite is easily distinguished from szomolnokite because, in spiter of the similarity in the arrangements of the first lines, the further ones differ considerably by their $d_{\mathrm{hk} 1}$ values.

Synthesis: Synthetic szomolnokites were obtained in two ways: by dehydration of hydrates (A) and by crystallization from a solution (B).
A. The higher hydrates of iron sulphate are transformed into monohydrate at $95-150^{\circ} \mathrm{C}$. Complete dehydration of the monohydrate takes place in two stages at $320^{\circ} \mathrm{C}$ and $550^{\circ} \mathrm{C}$. These data were obtained from the dehydration curve of the tetrahydrate. It has been found, however, that already above $130^{\circ} \mathrm{C}$ the monohydrate is an unstable phase. X-ray patterns of the tetrahydrate statically heated in air during 30 minutes at a constant temperature of $130^{\circ} \mathrm{C}$ mainly reveal the presence of, $\mathrm{FeSO}_{4}$ and only traces of tetrahydrate. The X-ray paittern of the same substance statically heated during 2 hours at $250^{\circ} \mathrm{C}$ reveals the presence of $\mathrm{FeSO}_{4}$ only. This means that under conditions of static heating at a temperature of more than $130^{\circ} \mathrm{C}$, higher hydrates of iron sulphate are directly transformed

TABLE II

| synthe szomoln |  | magnesium <br> szomolnokite "Staszic" |  | synthetic zinc-magnesium szomolnokite |  | kieserite (Kłodawa) |  |  | alternated szomolnokite |  | synthetic chalcanthite |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| d $\AA$ | I | d $\AA$ | I | d $\AA$ | I | d $\AA$ | I | d $\AA$ | I | $d \AA$ | I | d $\AA$ | I |
| 4.840 | 9 | 4.840 | 9 | 4.824 | 8 | 4.839 | 9 | 1.2456 | 3 | 10.46 | 1 | 10.54 | 1 |
| 3.771 | 4 | 3.793 | 3 | 3.799 | 2 |  |  | 1.2263 | 2 | 5.841 | 6 | 5.752 | 6 |
| 3.441 | 10 | 3.440 | 10 | 3.436 | 10 | 3.409 | 10 | 1.2197 | 2 | 5.641 | 7 | 5.503 | 7 |
| 3.378 | 4 | 3.379 | 3 | 3.372 | 3 | 3.374 | 5 | 1.1990 | 4 | 5.136 | 6 | 5.150 | 4 |
| 3.305 | 8 | 3.309 | 6 | 3.308 | 5 | 3.331 | 9 | 1.1907 | 3 | 4.962 | 10 | 4.739 | 10 |
|  |  |  |  |  |  | 3.111 | 4 | 1.1753 | 3 | 4.366 | 5 | 4.270 | 3 |
| 3.109 | 9 | 3.100 | 8 | 3.086 | 8 | 3.053 | 8 | 1.1725 | 3 | 3.954 | 6 | 3.993 | 9 |
| 2.575 | 7 | 2.577 | 4 | 2.575 | 2 | 2.567 | 8 | 1.1587 | 3 | 3.685 | 9 | 3.719 | 9 |
| 2.528 | 8 | 2.531 | 8 | 2.525 | 9 | 2.527 | 9 | 1.1360 | 3 | 3.444 | 4 | 3.539 | 4 |
| 2.429 | 1 | 2.428 | 3 |  |  | 2.414 | 2 | 1.1191 | 6 d | 3.409 | 3 | 3.454 | 3 |
| 2.400 | 1 | 2.389 | 1 | 2.381 | 1 | 2.383 | 2 | 1.1050 | 1 | 3.260 | 8 | 3.305 | 7 |
| 2.331 | 5 | 2.332 | 3 | 3.333 | 4 | 2.348 | 4 | 1.0983 | 3 |  |  | 3.259 | 3 |
| 2.231 | 7 | 2.215 | 5 | 2.208 | 7 d | 2.189 | 6 | 1.0829 | 1 | 3.176 | 4 | 3.196 | 3 |
| 2.109 | 2 | 2.104 | 3 | 2.110 | 3 | 2.103 | 5d | 1.0791 | 1 | 3.054 | 4 | 3.054 | 6 |
| 2.076 | 6 | 2.065 | 6 | 2.064 | 4 | 2.055 | 9 | 1.0725 | 1 | 3.011 | 1 | 2.902 | 1 |
| 2.043 | 1 |  |  |  |  | 2.028 | 1 | 1.0574 | 2 | 2.964 | 8 | 2.870 | 3 |
| 1.9958 | 7 | 1.9951 | 6 | 1.9882 | 5 | 1.9642 | 5 | 1.0531 | 6 | 2.960 | 5 | 2.826 | 8 |
| 1.9356 | 2 | 1.9330 | 1 | 1.9297 | 1 | 1.9362 | 3 | 1.0613 | 6 | 2.853 | 1 | 2.792 | 1 |
| 1.8941 | 1 | 1.8944 | 3 |  |  | 1.9034 | 5 | 1.0509 | 2 | 2.801 | 7 | 2.743 | 6 |
| 1.8327 | 3 | 1.8276 | 2 | 1.8220 | 4 | 1.8746 | 1 | 1.0457 | 1 | 2.714 | 1 | 2.659 | 6 |
| 1.7457 | 1 |  |  | 1.7480 | 1 | 1.8119 | 6 | 1.0397 | 3 | 2.683 | 7 |  |  |
| 1.7182 | 1 | 1.7179 | 1 | 1.7099 | 2 | 1.7955 | 3 | 1.0372 | 1 |  |  |  |  |
| 1.6863 | 7 | 1.6851 | 5 | 1.6792 | 6 | 1.7276 | 1 | 1.0334 | 2 |  |  |  |  |
| 1.6469 | 4 | 1.6481 | 3 | 1.6475 | 2 | 1.7028 | 4 | 1.0314 | 4 |  |  | - |  |
| 1.6197 | 5 | 1.6240 | 4 | 1.6183 | 5 | 1.6872 | 1 | 1.0291 | 1 |  |  |  |  |
| 1.6000 | 5 | 1.5955 | 4 | 1.5887 | 5 | 1.6613 | 5 | 1.0248 | 3 |  |  |  |  |
| 1.5881 | 3 | 1.5783 | 3 |  |  | 1.6239 | 7 | 1.0218 | 3 |  |  |  |  |
| 1.5668 | 1 |  |  |  |  | 1.6035 | 4 | 1.0204 | 3 |  |  |  |  |
| 1.5528 | 1 |  |  | 1.5388 | 1 | 1.5869 | 6 | 1.0179 | 3 |  |  |  |  |
| 1.5117 | 3 | 1.5113 | 2 | 1.5044 | 4 | 1.5705 | 1 | 1.0132 | 1 |  |  |  |  |
| 1.4660 | 2 |  |  |  |  | 1.5481 | 7 | 1.0103 | 3 |  |  |  |  |
| 1.4545 | 1 | 1.4531 | 1 | 1.4507 | 1 | 1.5364 | 3 | 1.0086 | 1 |  |  |  |  |
| 1.4362 | 1 |  |  | 1.3922 | 1 | 1.5232 | 2 | 1.0010 | 1 |  |  |  |  |
| 1.2893 | 6 | 1.2884 | 3 | 1.2816 | 3 | 1.5041 | 7 | 0.99903 | 2 |  |  |  |  |
| 1.2620 | 5 | 1.2620 | 2 | 1.2616 | 1 | 1.4917 | 2 | 0.99693 | 6 |  |  |  |  |
| 1.2160 | 1 | 1.2140 | 1 | 1.2059 | 2 | 1.4804 | 1 | 0.99514 | 6 |  |  |  |  |
| 1.1959 | 2 | 1.1944 | 1 |  |  | 1.4518 | 6 | 0.99328 | 6 |  |  |  |  |
| 1.1803 | 2 |  |  |  |  | 1.4351 | 4 | 0.99135 | 1 |  |  |  |  |
| 1.1655 | 1 |  |  |  |  | 1.4154 | 5 | 0.98725 | 1 |  |  |  |  |
| 1.1457 | 1 |  |  |  |  | 1.3986 | 2 | 0.98337 | 1 |  |  |  |  |
| 1.1146 | 2 |  |  |  |  | 1.3443 | 1 | 0.98102 | 6 |  |  |  |  |
| 1.1062 | 1 |  |  |  |  | 1.3318 | 3 | 0.97449 | 6 |  |  |  |  |
| 1.0609 | 3 |  |  |  |  | 1.3067 | 2 | 0.97243 | 5 |  |  |  |  |

Table II continued

| synthetic szomolnokite |  | magnesium szomolnokite "Staszic" |  | synthetic zinc-magnesium szomolnotite |  | kieserite (Kłodawa) |  |  | alternated szomolnokite |  | synthetic chalcanthite |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $d \AA$ | I | $d \AA$ | I | d $\AA$ | I | $d \AA$ | I | d $\AA$ | I | d $\AA$ | I | d $\AA$ | I |
| 1.0519 | 2 | 1.0551 | 1 | 1. 534 | 2 | 1.2985 | 3 | 0.97075 | 4 |  |  |  |  |
| 1.0359 | 1 | 1.0389 | 1 |  |  | 1.2777 | 7 |  |  |  |  |  |  |
| 1.0110 | 4 |  |  |  |  | 1.2710 | 1 |  |  |  |  |  |  |
| 0.9973 | 1 |  |  |  |  | 1.2626 | 6d |  |  |  |  |  |  |
| 0.9911 | 2 |  |  |  |  | 1.2524 | 2 |  |  |  |  |  |  |

$d$ - diffused
into $\mathrm{FeSO}_{4}$. Monohydrate can be obtained by dynamic heating in air to temperatures above $130^{\circ} \mathrm{C}$, but most readily to $250-300^{\circ} \mathrm{C}$. The rate of heating should be rather high, $10-20^{\circ} \mathrm{C} / \mathrm{min}$. E.g. pure synthetic szomolnokites were obtained by heating iron sulphate hepta- and tetrahydrate in a furnace at a heating rate $15^{\circ} \mathrm{C} / \mathrm{min}$. Zinc-magnesium szomolnokite was obtained by heating zinc-magnesium melanterite from the "Bolesław" mine near Olkusz to $320^{\circ} \mathrm{C}$ and $380^{\circ} \mathrm{C}$ at the same rate. Although the $\mathrm{FeO}: \mathrm{ZnO}: \mathrm{MgO}$ ratio of this melanterite is $1: 0.954: 0.363$, the X-ray parterns of the obtained szomolnokite manifest no significant changes in the dimensions of the crystal lattice Table II. The colour of szomolnokites obtained by heating is white grey, the grey tint being due to the partial oxidation of iron.
B. Synthetic szomolnokite was also obtained from water solutions of iron sulphate heptahydrate slightly acidified with sulphuric acid. The crystallization temperature measured in the liquid was $60-65^{\circ} \mathrm{C}$. A microcrystalline grey green product was obtained. Its X-ray pattern is shown in Table II. To obtain comparative data, magnesium szomolnokite was also synithesized ( $\mathrm{FeO}: \mathrm{MgO}=1: 0.33$ ). There are no significant differences between the X-ray patterns of synthetic and natural szomolnokite.

Conclusions: The occurrence of szomolnokite with a high content of magnesium substituted for iron ( $\mathrm{FeO}: \mathrm{MgO}=1: 0.68$ ) indicates that representatives of the isomorphic series szomolnokite-kieserite must occur in nature and that the mineral described here belongs to this series. Its formation is associated with the presence of $\mathrm{Mg}^{++}$ions in mine water derived from the dolomite country rocks of the deposit. In spite of the large amount of magnesium substituted for iron, no significant changes of the unit cell dimensions are apparent. Since, as is to be seen from the

X-ray patterns (Table II), there are structural differences between szomolnokite and kieserite, the changes probably take place discontinuously when the amount of magnesium exceeds that of iron. Magnesium szomolnokite with a chemical composition of this kind has not been found so far in nature. In view of the structure identical with pure szomolnokite the mineral under report has been defined as a magnesium variety of szomolnokite.

DEPARTMENT OF MINERALOGY AND PETROGRAPHY, SCHOOL OF MINING AND METALLURGY, CRACOW
(KATEDRA MINERALOGII I PETROGRAFII, AKADEMIA GÓNICZO-HUTNICZA, KRAKÓW)

