

Henryk KUCHAR<sup>xx</sup>, Andrzej WIECZOREK<sup>xxx</sup>

$\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$ , A NEW MINERAL FROM LOWER SILESIA, POLAND

UKD 549.755.2.01.0.6Ca<sub>1-x</sub>Th<sub>1-x</sub>RE<sub>2x</sub>[PO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O/438-14Bogadynia

**A b s t r a c t.** U-5 unknown orthorhombic  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$  with  $a=6.67\pm0.07$ ,  $b=12.06\pm0.12$ ,  $c=6.40\pm0.06\text{\AA}$  is related to the ningyoite group. The mineral in question is formed as a member of the transformation series:  $[\text{Ca,Fe/Th}[\text{PO}_4]_2]$  /monazite group/ -  $[\text{Ca,Fe/Th}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}]$  /rabdophane group/ -  $[\text{Ca,Fe/Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}]$  /ningyoite group/. These transformations are often accompanied by the formation of the mineral  $\text{Fe}_3^{2+}/\text{H}_2\text{O}/[\text{PO}_4]_2$ . The presence of all these members in samples from Bogatynia, Poland, was proved by electron diffraction study.

$[\text{Ca,Fe/Th}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}]$  is hexagonal with cell dimensions  $a=7.08\pm0.07$  and  $c=6.24\pm0.06\text{\AA}$ . The mineral belongs to the brockite -  $\text{Fe}^{2+}\text{Th}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}$  series. A small amount of Fe /2 wt%/ allow one to consider this mineral as brockite.

Amidst the products of the mentioned transformation series, imperfect patterns, probably of an orthorhombic mineral with cell dimensions close to  $a=14.0$ ,  $b=12.0$  and  $c=15.0\text{\AA}$  were identified. It would be related to the  $[\text{Th,Ca,Fe...}/[\text{PO}_4\text{OH}]] \cdot \text{H}_2\text{O}$ ? composition.

## INTRODUCTION

Th-bearing pegmatites and hydrothermal veins located near Bogatynia, Lower Silesia, Poland were investigated. The main Th-minerals are related to monazite, rabdophane, Th-ningyoite and thorogummite groups as well as goethite and  $\text{Fe}_3^{2+}/\text{H}_2\text{O}/[\text{PO}_4]_2$  homologous series /Kucha, 1979/. In samples from these area products of hydrothermal and weathering alteration of Th minerals were found also. The present paper is dealing with one of a small, secondary nests, builded up with altered Th-minerals.

<sup>x</sup>Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy, Cracow /Kraków, Al. Mickiewicza 30/.

<sup>xxx</sup>Institute of Metallurgy, Academy of Mining and Metallurgy, Cracow /Kraków, Al. Mickiewicza 30/



The monazite group with monoclinic symmetry includes: monazite, huttonite /Pabst, 1951/ and cheralite  $\text{CaTh}[\text{PO}_4]_2$  /Bowie and Horne 1953/.  $\text{Fe}^{2+}\text{Th}[\text{PO}_4]_2$  /Kucha, 1979/ is related to the latter.

The rhabdophane group with hexagonal symmetry includes: rhabdophane and brockite  $\text{CaTh}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}$  /Fisher and Meyrowitz 1962/.  $\text{Fe}^{2+}\text{Th}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}$  is related to the latter.

The ningyoite group with orthorhombic symmetry includes virtually only one well characterized mineral of tetravalent uranium - ningyoite  $\text{Ca}_{1-x}\text{U}_x\text{RE}_{3x}\text{Th}_{1-x}\text{Th}_{1-x}/\text{RE}, \text{Fe}^{3+}/2x[\text{PO}_4]_2 \cdot 1-3\text{H}_2\text{O}$  /Muto *et al.*, 1959/.  $\text{Fe}^{2+}\text{Th}_{1-x}\text{Th}_x$  relative,  $\text{Fe}^{2+}\text{Th}_{1-x}\text{Th}_x$  is related to the latter.

One poorly defined pseudohexagonal Th mineral exists in the orthorhombic system. This mineral is referred to /Th,Pb,Ca/ $[\text{PO}_4] \cdot \text{H}_2\text{O}$ ? composition and named grayite /*vide* Fleisher, 1962/.

#### MATERIALS AND METHODS

The chemical composition of materials from Bogatynia pegmatites and hydrothermal veins, as well as microprobe investigations, was described in an earlier paper /Kucha, 1979/.

Electron microscope investigations, were performed with a JEOL JEM-100B microscope at 100 kV. Particles for investigations were taken under microscopic control from areas defined exactly to  $10 \times 10 \mu\text{m}$ . A few dozen particles were studied. They showed chiefly hexagonal, hexagonal partly transformed into orthorhombic, and orthorhombic symmetry referred to the described minerals. Not a single particle has revealed the pattern of an iron hydroxide, but two electron diffraction records showed some interplanar distances of  $\text{Fe}_3^{2+}/\text{H}_2\text{O}/(\text{PO}_4)_2$  scattered amidst the patterns of the minerals in question.

#### CHEMICAL COMPOSITION

The minerals in question failed to be distinguished microscopically one from an other. This was due to close intergrowths and a very small crystal size, far more smaller than the resolving power of a light microscope and even smaller than the dimension of the microprobe electron beam / $1 \mu\text{m}$ /. In reflected light the investigated area seems to be homogenous and only the yielded iron hydroxides form an alien admixture /Phot. 1/. Internal reflections of the area are white-yellow or yellow with red-brown hue. The size of the zone is  $30 \times 250 \mu\text{m}$  /Phot. 1/.

Chemical composition of the area in question is as follows /microprobe number 83/A22/:

wt% - F 1.0, Si 0.8, P 9.8, Ca 4.1, Fe 2.0, RE 1.1, Th 45.4  
atomic proportions Ca 0.30, Fe 0.11, RE 0.02, Th 0.57,  $\text{H}_2\text{O}_{\text{calc.}}$  2.13  
and  $\text{OH}_{\text{calc.}}$  0.0.

Elements sought for but not detected in the area are:  $\text{Cu} \leq 0.1$ ,  $\text{As} \text{Lo} \leq 0.4$ ,  $\text{Pb} \leq 0.35$ ,  $\text{U} \leq 0.45$ .

Chemical formulas of the described minerals are calculated according to the recorded composition and according to isostructural relations to cheralite, brockite and ningyoite, respectively.

#### MONOCLINIC /Ca,Fe/Th $[\text{PO}_4]_2$

The mineral in question seems to be an intermediate member of a solid solution series apparently extending between cheralite  $\text{CaTh}[\text{PO}_4]_2$  and  $\text{Fe}^{2+}\text{Th}[\text{PO}_4]_2$  /Kucha, 1979/. Because of the small Fe content it should be considered as cheralite. The presence of 1.75 wt% Fe in the originally described cheralite /Bowie and Horne, 1953/ confirms this assertion more than enough. The mineral is isostructural with cheralite /Tab. 1/, but it gave only two streaking or streaking-like patterns /Phot. 2/. The character of the recorded electron diffractions implies a relic character of cheralite in the described area. The rest of the primary cheralite is probably entirely transformed into hexagonal and

Table 1

Electron diffraction data for monoclinic /Ca,Fe/Th $[\text{PO}_4]_2$   
partly transformed into hexagonal /Ca,Fe/Th $[\text{PO}_4]_2 \cdot \text{H}_2\text{O}$

| Monoclinic |             | Hexagonal |     | Monoclinic |             | Hexagonal |     |
|------------|-------------|-----------|-----|------------|-------------|-----------|-----|
| d          | hkl         | d         | hkl | d          | hkl         | d         | hkl |
| 4.18       | $\bar{1}11$ | 3.49      | 110 | 2.37       | 220         | 2.06      | 300 |
| 3.51       | 111         | 2.95      | 200 | 2.07       | $\bar{2}22$ | 1.86      | 212 |
| 3.32       | 200         | 2.82      | 102 | 1.82       | 311         | 1.74      | 220 |
| 2.45       | 211         | 2.39      | 112 | 1.74       | 222         | 1.54      | 222 |
| 2.39       | 112         | 2.16      | 211 | 1.38       | $\bar{3}33$ | 1.31      |     |

Monoclinic: zone axis  $uvw$  for monoclinic chiefly  $0\bar{1}1$ , minor  $\bar{1}10$ . d-spacings measured from the streaking pattern /Phot. 2/; then calculated for tilt  $\alpha$  and  $\beta \frac{1}{5}$ , according to Andrews *et al.* /1967/.

Hexagonal: very imperfect pattern. Present only pairs of spots scattered amidst monoclinic pattern.



then into orthorhombic phase. This is strongly supported by the presence of pairs of spots with brockite interplanar distances scattered amidst monoclinic pattern /Phot. 2, tab. 1/. Moreover, the streaking character of the monoclinic spots is evolved probably due to the replacement by hexagonal /Ca,Fe/Th[PO<sub>4</sub>]<sub>2</sub> · H<sub>2</sub>O developing parallel to  $\bar{1}11$  parting plane. This could probably have the same effect on the pattern as stacking faults in artificial, metallurgical materials /Andrews *et al.*, 1967/. Photograph 2 proves the existence of the transformation of cheralite into brockite.

# HEXAGONAL /Ca,Fe/Th[PO<sub>4</sub>]<sub>2</sub> · H<sub>2</sub>O

The described mineral is probably an intermediate member of the solid solution series extending between brockite CaTh[PO<sub>4</sub>]<sub>2</sub> · H<sub>2</sub>O /Fisher and Meyrowitz, 1962/ and Fe<sup>2+</sup>Th[PO<sub>4</sub>]<sub>2</sub> · H<sub>2</sub>O /Kucha, 1979/. The small Fe content, as well as the presence of RE and close structural similarity to brockite /Tab. 2, 3/, allow one to consider it as brockite. Cell dimension /Å/ are:

| /Ca,Fe/Th[PO <sub>4</sub> ] <sub>2</sub> · H <sub>2</sub> O | Fe <sup>2+</sup> Th[PO <sub>4</sub> ] <sub>2</sub> · H <sub>2</sub> O | Brockite                    |
|-------------------------------------------------------------|-----------------------------------------------------------------------|-----------------------------|
|                                                             | /Kucha, 1979/.                                                        | /Fisher and Meyrowitz, 1962 |
| $a = 7.08 \pm 0.07$                                         | $a = 7.04 \pm 0.04$                                                   | $a = 6.89$                  |
| $c = 6.24 \pm 0.06$                                         | $c = 6.36 \pm 0.03$                                                   | $c = 6.40$                  |
| $c : a = 0.88$                                              | $c : a = 0.90$                                                        | $c : a = 0.92$              |

Table 2

Electron diffraction pattern of hexagonal /Ca,Fe/Th[PO<sub>4</sub>]<sub>2</sub> · 2H<sub>2</sub>O  
/a = 7.08, c = 6.24 Å/, raddophane group

| d meas. | hkl | d calc. | d meas. | hkl | d calc. |
|---------|-----|---------|---------|-----|---------|
| 4.37    | 101 | 4.37    | 1.55    | 004 | 1.56    |
| 3.85    | ?   |         | 1.54    | 222 | 1.54    |
| 3.47    | 110 | 3.54    | 1.17    | 115 | 1.18    |
| 3.12    | 002 | 3.12    | 1.15    | 224 | 1.17    |
| 3.05    | 111 | 3.08    | 1.14    | 331 | 1.16    |
| 2.80    | 102 | 2.78    | 1.04    | 006 | 1.04    |
| 2.76    | 201 | 2.75    | 1.03    | 333 | 1.03    |
| 2.36    | 112 | 2.34    | 0.896   | 226 | 0.897   |
| 2.22    | 211 | 2.17    | 0.863   | 117 | 0.864   |
| 2.03    | 300 | 2.04    | 0.858   | 335 | 0.857   |
| 1.95    | 301 | 1.94    | 0.715   | 228 | 0.714   |
| 1.79    | 113 | 1.79    | 0.712   | 337 | 0.711   |
| 1.77    | 220 | 1.77    | 0.601   | 339 | 0.598   |
| 1.70    | 302 | 1.71    | 0.588   | 448 | 0.585   |
| 1.69    | 310 | 1.70    |         |     |         |

Table 3  
Comparison of measured /Phot. 4/ and calculated angles /in degrees/  
in hexagonal /Ca,Fe/Th[PO<sub>4</sub>]<sub>2</sub> · H<sub>2</sub>O /a = 7.08, c = 6.24 Å/

| $h_1 k_1 l_1 \backslash h_2 k_2 l_2$ | 002   |       | 111   |       | 111   |       |
|--------------------------------------|-------|-------|-------|-------|-------|-------|
|                                      | meas. | calc. | meas. | calc. | meas. | calc. |
| 111                                  | 60.5  | 60.4  | 0.0   | 0.0   | 59.0  | 59.1  |
| 111                                  | 118.5 | 119.6 | 58.5  | 59.1  | 0.0   | 0.0   |
| 002                                  | 0.0   | 0.0   | 61.0  | 60.4  | 120.5 | 119.6 |
| 113                                  | 30.5  | 30.4  | 30.5  | 30.0  | 89.0  | 89.1  |
| 220                                  | 90.0  | 90.0  | 30.0  | 30.0  | 30.0  | 29.6  |
| 113                                  | 149.0 | 149.6 | 89.5  | 89.1  | 30.5  | 30.0  |
| 115                                  | 19.5  | 19.4  | 41.0  | 41.0  | 99.7  | 100.1 |
| 224                                  | 41.0  | 41.4  | 19.5  | 19.0  | 79.0  | 78.2  |
| 224                                  | 138.5 | 138.6 | 78.0  | 78.2  | 19.5  | 19.0  |
| 331                                  | 79.0  | 79.3  | 19.0  | 18.9  | 40.5  | 40.3  |
| 331                                  | 100.5 | 100.7 | 41.0  | 40.3  | 19.0  | 18.9  |
| 335                                  | 46.0  | 46.6  | 14.0  | 13.8  | 73.5  | 73.0  |
| 117                                  | 13.5  | 14.1  | 47.0  | 46.3  | 105.5 | 105.4 |
| 228                                  | 23.0  | 23.8  | 37.5  | 36.7  | 95.5  | 95.8  |

/Ca,Fe/Th[PO<sub>4</sub>]<sub>2</sub> · H<sub>2</sub>O is undoubtedly hexagonal, which is shown by the electron diffraction pattern /Phot. 4/ and the exquisite accordance between the measured and calculated for hexagonal symmetry interplanar distances /Tab. 2/ and angles /Tab. 3/. The described brockite is commonly transformed into orthorhombic Ca<sub>1-x</sub>Th<sub>1-x</sub>RE<sub>2x</sub>[PO<sub>4</sub>]<sub>2</sub> · 2H<sub>2</sub>O. A series of electron diffraction records showed the process in different stages of development. The brockite pattern is usually of poor quality, being reduced to pairs of spots scattered amidst the ring pattern of Ca<sub>1-x</sub>Th<sub>1-x</sub>RE<sub>2x</sub>[PO<sub>4</sub>]<sub>2</sub> · 2H<sub>2</sub>O "in statu nascendi" /Phot. 3, Tab. 4/. One rule can be observed here - the worse the quality of the hexagonal pattern, the better the ring pattern of the orthorhombic phase. A feature deserving note is the structural facility of the described transformation. This is because the cell dimensions of brockite calculated in terms of the orthorhombic system a = 6.98, b = 12.10, c = 6.40 are very similar to Ca<sub>1-x</sub>Th<sub>1-x</sub>RE<sub>2x</sub>[PO<sub>4</sub>]<sub>2</sub> · 2H<sub>2</sub>O cell parameters a = 6.67, b = 12.06 and c = 6.46 Å.

Thus electron diffraction study proved the existence of the transformation of brockite into the orthorhombic phase.



Table 4

Electron diffraction data of hexagonal  $\text{Ca}_x\text{Fe}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$   
partly transformed into orthorhombic  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$

| Hexagonal |       | Orthorhombic |     |       | Hexagonal |       | Orthorhombic |     |          |
|-----------|-------|--------------|-----|-------|-----------|-------|--------------|-----|----------|
| $d$       | $hkl$ | $d$          | $I$ | $hkl$ | $d$       | $hkl$ | $d$          | $I$ | $hkl$    |
| 3.92      | ?     |              |     |       | 1.65      | 310   |              |     |          |
| 3.48      | 110   |              |     |       | 1.55      | 004   |              |     |          |
| 3.11      | 002   |              |     |       | 1.33      |       |              |     |          |
| 2.81      | 102   |              |     |       | 1.27      | ?     | 1.27         | 7   | 025, 064 |
| 2.52      | ?     |              |     |       | 1.08      | 422   | 1.09         | 8   | 006, 084 |
| 2.17      | 211   |              |     |       | 1.05      | 006   | 1.04         | 2   | 0.10.3   |
| 2.08      | 003   | 2.10         | 10  | 241   |           |       | 0.832        | 3   | 800      |
| 2.01      | 300   |              |     |       |           |       | 0.806        | 3   | 008      |
| 1.93      | 301   |              |     |       |           |       | 0.736        | 1   | 0.12.6   |
| 1.81      | ?     | 1.81         | 8   | 312   |           |       | 0.695        | 2   | 0.16.4   |
| 1.74      | 220   |              |     |       |           |       |              |     |          |

Hexagonal: usually imperfect patterns. There are only disordered pairs of spots with rabdophane interplanar distances. This effect is caused by replacement of hexagonal lattice by orthorhombic one.  $d$  values with question marks could not be indexed in terms of hexagonal rabdophane group.

Orthorhombic: ring patterns caused by a very fine-grained character of the phase being formed.

UNKNOWN  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$  /U-5/

U-5 seems to be an intermediate member of a solid solution extending between  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Fe}_{1-x}^{2+}\text{Th}_{1-x}/\text{RE}, \text{Fe}^{3+}/_{2x}[\text{PO}_4]_2 \cdot 1-3 \text{H}_2\text{O}$  /Kucha, 1979/. A small Fe admixture in U-5 mineral allows one to consider it as a calcium end member of the considered series. U-5 is certainly orthorhombic, which is shown by a very good accordance between the measured and calculated for orthorhombic symmetry  $d$ -spacings /Tab. 5/ and angles /Tab. 6/. The new-forming U-5 gives ring patterns due to a very fine-grained structure /Phot. 3/, but monocrystallites give excellent spot patterns /Phot. 5/. Cell dimensions of U-5 are as follow /Å/:

| U-5                       | $\text{Fe}_{1-x}^{2+}\text{Th}_{1-x}/\text{RE}, \text{Fe}^{3+}/_{2x}[\text{PO}_4]_2 \cdot 1-3\text{H}_2\text{O}$<br>/Kucha, 1979/: | Ningyoite<br>/Muto <i>et al.</i> , 1959/: |
|---------------------------|------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| $a = 6.67 \pm 0.07$       | $a = 6.77 \pm 0.03$                                                                                                                | $a = 6.78 \pm 0.03$                       |
| $b = 12.06 \pm 0.12$      | $b = 12.06 \pm 0.07$                                                                                                               | $b = 12.10 \pm 0.05$                      |
| $c = 6.46 \pm 0.06$       | $c = 6.41 \pm 0.04$                                                                                                                | $c = 6.38 \pm 0.03$                       |
| $a:b:c=0.553:1$<br>:0.536 | $a:b:c=0.561:1:0.532$                                                                                                              | $a:b:c=0.560:1:0.527$                     |

Table 5  
Electron diffraction pattern of orthorhombic  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$   
 $a = 6.67$ ,  $b = 12.06$ , and  $c = 6.46$  Å/ belonging to the ningyoite group

| $d$ meas. | $hkl$ | $a$ calc. | $d$ meas. | $hkl$    | $d$ calc. |
|-----------|-------|-----------|-----------|----------|-----------|
| 6.48      | 001   | 6.46      | 1.47      | 063      | 1.47      |
| 6.02      | 020   | 6.03      | 1.42      | 044      | 1.42      |
| 4.42      | 021   | 4.41      | 1.37      | 082      | 1.37      |
| 3.23      | 002   | 3.23      | 1.29      | 005      | 1.29      |
| 3.00      | 040   | 3.01      | 1.26      | 025, 064 | 1.26      |
| 2.84      | 022   | 2.85      | 1.24      | 083      | 1.24      |
| 2.74      | 041   | 2.73      | 1.21      | 0.10.0   | 1.21      |
| 2.21      | 042   | 2.20      | 1.20      | 0.10.1   | 1.19      |
| 2.14      | 003   | 2.15      | 1.19      | 045      | 1.19      |
| 2.10      | 241   | 2.11      | 1.14      | 0.10.2   | 1.13      |
| 2.02      | 023   | 2.03      | 1.11      | 084      | 1.10      |
| 2.01      | 060   | 2.01      | 1.08      | 006      | 1.08      |
| 1.92      | 061   | 1.92      | 1.06      | 026      | 1.06      |
| 1.81      | 312   | 1.81      | 1.05      | 0.10.3   | 1.05      |
| 1.75      | 043   | 1.75      | 0.832     | 800      | 0.834     |
| 1.72      | 062   | 1.71      | 0.806     | 008      | 0.808     |
| 1.62      | 004   | 1.62      | 0.736     | 0.12.6   | 0.735     |
| 1.55      | 024   | 1.56      | 0.696     | 0.16.4   | 0.683     |
| 1.51      | 080   | 1.51      | 0.605     | 0.20.0   | 0.603     |
| 1.48      | 081   | 1.47      |           |          |           |

Table 6

Comparison of measured /phot. 5/ and calculated angles /in degrees/  
in orthorhombic  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$  / $a = 6.67$ ,  $b = 12.06$ ,  $c = 6.46$  Å/

| $hkl$  | 001   |       | 020   |       | 021   |       | 022   |       |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|
|        | meas. | calc. | meas. | calc. | meas. | calc. | meas. | calc. |
| 001    | 0.0   | 0.0   | 90.0  | 90.0  | 47.0  | 47.0  | 28.0  | 28.2  |
| 020    | 90.0  | 90.0  | 0.0   | 0.0   | 43.5  | 43.0  | 62.0  | 61.8  |
| 021    | 47.0  | 47.0  | 43.5  | 43.0  | 0.0   | 0.0   | 18.0  | 18.8  |
| 022    | 28.0  | 28.2  | 62.0  | 61.8  | 18.0  | 18.8  | 0.0   | 0.0   |
| 023    | 19.5  | 19.7  | 70.5  | 70.3  | 27.5  | 27.3  | 8.0   | 8.5   |
| 041    | 65.0  | 65.0  | 25.5  | 25.0  | 18.5  | 17.9  | 37.5  | 36.8  |
| 043    | 35.0  | 35.5  | 55.0  | 54.5  | 12.0  | 11.4  | 8.0   | 7.3   |
| 061    | 72.5  | 72.5  | 18.0  | 17.2  | 26.0  | 25.7  | 44.5  | 44.5  |
| 081    | 76.5  | 76.9  | 14.0  | 13.1  | 31.0  | 29.8  | 49.0  | 48.7  |
| 083    | 54.5  | 55.0  | 35.5  | 35.0  | 8.5   | 7.9   | 27.0  | 26.8  |
| 085    | 39.7  | 40.6  | 50.0  | 49.4  | 5.5   | 6.2   | 12.0  | 12.4  |
| 0.10.1 | 79.5  | 79.4  | 10.5  | 10.6  | 32.7  | 32.4  | 51.5  | 51.2  |
| 0.10.2 | 69.5  | 69.5  | 20.7  | 20.5  | 23.0  | 22.5  | 41.4  | 41.4  |



Space group,  $P 222/D_2^1$ , is presumably the same as ningyoite, and so is the unit-cell content  $Z=3$ . The cell dimensions of U-5 are very similar to ningyoite  $Ca_{1-x}Th_{1-x}RE_{2x}[PO_4]_2 \cdot 1-2 H_2O$  and its Fe-Th relative /Kucha, 1979/. However U-5 differs in its chemical formula from the two mentioned minerals, so  $Ca_{1-x}Th_{1-x}RE_{2x}[PO_4]_2 \cdot 2H_2O$  is a new mineral from ningyoite group.

#### GENERAL REMARKS

Electron diffraction study showed the presence of the transformation series: monoclinic cheralite - hexagonal brockite - orthorhombic  $Ca_{1-x}Th_{1-x}RE_{2x}[PO_4]_2 \cdot 2H_2O$ , which is a new mineral. The rise of an unnamed mineral  $Fe_3^{2+}/H_2O[PO_4]_2$  /Kucha, 1979/ was also recorded in the mentioned process, mostly when the monoclinic structure is changed into hexagonal. A few  $Fe_3^{2+}/H_2O/PO_4$   $d$ -spacings were recorded  $/\text{\AA}/$ : 3.55, 2.95, 2.86, 2.67, 2.63, 2.61, 2.39, 2.03 and 1.86. The formation of the iron phosphate is probably due to some  $CO_3$  entering into the brockite structure, when cheralite is transformed into its hexagonal relative.

Among the products of the discussed transformation series, an orthorhombic phase with cell dimensions close to  $a \sim 14$ ,  $b \sim 12$ ,  $c \sim 15 \text{\AA}$  was probably identified. It would be related to  $/Th, Ca, Fe.../ PO_4 \cdot H_2O$  composition. The very imperfect pattern of the mineral in question does not allow a more precise study of its structural properties.

#### REFERENCES

- ANDREW K. W., DYSON D. J., KEOWN S. R., 1967: Interpretation of electron diffraction patterns. Helger and Watts LTD, London, 180 pp.
- BOWIE S. H. U., HORNE J. E. T., 1953: Cheralit, a new mineral of the monazite group. *Miner. Mag.* 30. 93-99.
- FISHER F. G., MEYROWITZ R., 1962: Brockite, a new calcium thorium phosphate from the Wet Mountains. *Amer. Miner.* 47, 1346-1355.
- FLEISHER M., 1962: New minerals names. *Amer. Miner.* 47, 419-420.
- KUCHA H., 1979:  $Fe^{2+}Th/PO_4/2$  monoclinic,  $Fe^{2+}Th/PO_4/2 H_2O$  hexagonal,  $Fe^{2+}Th_{1-x}/RE, Fe^{3+}/_{2x}/PO_4/2 \cdot 1-3H_2O$  orthorhombic and  $Fe_3^{2+}/H_2O/PO_4/2$  monoclinic - four new minerals from Poland. *Miner. Polon.* 10, 1.

#### Streszczenie

W uzupełnieniu badań zespołu minerałów toru, występujących w pegmatytach i żyłach hydrotermalnych w okolicy Bogatyni, opisanych w poprzedniej publikacji /Kucha, 1979/, podano w tej pracy charakterystykę paru następnych minerałów toru, w tym nieznanego minerału z grupy ningyoitu /U-5/.

U-5 jest minerałem rombowym o wzorze chemicznym  $Ca_{1-x}Th_{1-x}RE_{2x}[PO_4]_2 \cdot 2H_2O$ . Parametry komórki elementarnej:  $a = 6,67 \pm 0,07$ ,  $b = 12,06 \pm 0,12$ ,  $c = 6,46 \pm 0,06$ . Mineral ten utworzył się w wyniku szeregu przekształceń:  $/Ca, Fe/Th[PO_4]_2$  /grupa monacytu/ -  $/Ca, Fe/Th[PO_4]_2 \cdot H_2O$  /grupa rabdofanu/ -  $/Ca-Fe/_{1-x}Th_{1-x}RE_{2x}[PO_4]_2 \cdot 2H_2O$  /grupa ningyoitu/. Transformacje te doprowadziły również do utworzenia minerału  $Fe_3^{2+}/H_2O/[PO_4]_2$ . Obecność wspomnianych przemian udowodniona została w oparciu o badania elektronograficzne.

$/Ca, Fe/Th[PO_4]_2 \cdot H_2O$  jest kolejnym minerałem stwierdzonym w toku badań. Jest on heksagonalny i ma następujące parametry komórki elementarnej:  $a = 7,08 \pm 0,07$ ,  $c = 6,24 \pm 0,06$ . Mineral ten należy do szeregu izomorficznego brockit -  $Fe^{2+}Th[PO_4]_2 \cdot H_2O$ . Niewielka zawartość Fe /2% wag./ pozwala uważać go w przybliżeniu za brockit.

Jeszcze jednym produktem opisanego ciągu przemian jest prawdopodobnie rombowy mineral o następujących parametrach komórki elementarnej:  $a \sim 14$ ,  $b \sim 12$ ,  $c \sim 15$ . Ma on przypuszczalnie skład chemiczny zbliżony do  $/Th, Ca, Fe.../ PO_4, OH \cdot H_2O$ .

#### OBJAŚNIENIA DO FOTOGRAFII

- Fot. 1. Mikrofotografia fosfokrzemianów Fe-Th okładujących badany obszar, zaznaczony za pomocą linii kreskowanej. W środkowej części fotografii znajduje się żyłka  $Th_3[PO_4]_4$ . Pole jasnoszare - amorficzne, uwodnione tlenki żelaza, szare - fosfokrzemiany Fe-Th. A 22 - punkt analizy ilościowej w mikroobszarze
- Fot. 2. Elektronogram ilustrujący efekty transformacji jednoskośnego  $/Ca, Fe/Th[PO_4]_2$  z grupy monacytu w heksagonalny  $/Ca, Fe/Th[PO_4]_2 \cdot H_2O$ . Podstawowa dyfrakcja typu "streaking" pochodzi od jednoskośnego monacytu i należy głównie do pasa 011. Streaking jest przypuszczalnie wywołany zastępowaniem fazy jednoskośnej przez heksagonalną po płaszczyźnie równoległej do 111 /płaszczyzna podziału/. Pary punktów z wartościami  $d$  heksagonalnej grupy rabdofanu są rozproszone pośród dyfrakcji jednoskośnej
- Fot. 3. Elektronogram ilustrujący efekt przekształcenia heksagonalnego  $/Ca, Fe/Th[PO_4]_2 \cdot H_2O$  /nieuporządkowane pary punktów/ w rombowy superdrobnoziarnisty  $/Ca, Fe/_{1-x}Th_{1-x}RE_{2x}[PO_4]_2 \cdot 2H_2O$  należący do grupy ningyoitu /dyfrakcja kolista/



- Фот. 4. Dyfrakcja elektronowa heksagonalnego  $\text{Ca,Fe/Th}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}$  z grupy rabdofanu.  $uvw = \bar{1}11$ . Parametry komórki elementarnej wynoszą:  $a \approx 7,08$  i  $b = 6,24$
- Фот. 5. Dyfrakcja elektronowa rombowego minerału  $\text{Ca,Fe}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$  z grupy ningyoiu.  $uvw = 100$ . Parametry komórki elementarnej wynoszą  $\text{\AA}$ :  $a = 6,67$ ,  $b = 12,06$ ,  $c = 6,46$

Хенрик КУХА, Анджей ВЕЧОРЕК

$\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}/\text{PO}_4/2 \cdot 2\text{H}_2\text{O}$  НОВЫЙ МИНЕРАЛ ИЗ НИЖНЕЙ СИЛЕЗИИ /ПОЛЬША/

## Резюме

В качестве дополнения к исследованиям минералов тора, проявляющихся в пегматитах и гидротермальных жилах в окрестностях Богатыни, описанных в предыдущей статье /Куха, 1979/, в настоящей статье приведена характеристика нескольких следующих минералов тора, среди них неизвестного минерала из группы нингиоита /U-5/.

U-5 является ромбоэдрическим минералом с химической формулой

$\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}/\text{PO}_4/2 \cdot 2\text{H}_2\text{O}$ . Параметры элементарной ячейки:  $a = 6,67 \pm 0,07$ ,  $b = 12,06 \pm 0,12$ ,  $c = 6,46 \pm 0,06$ . Этот минерал образовался в результате ряда преобразований:  $\text{Ca, Fe/Th/PO}_4/2$  /группа монацита/ -  $\text{Ca, Fe/Th/PO}_4/2 \cdot \text{H}_2\text{O}$  /группа рабдофана/ -  $\text{Ca-Fe}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}/\text{PO}_4/2 \cdot 2\text{H}_2\text{O}$  /группа нингиоита/. Эти преобразования привели также к образованию минерала  $\text{Fe}_3^{2+}/\text{H}_2\text{O}/\text{PO}_4/2$ . Присутствие вышеуказанных преобразований было доказано на основании электронографических исследований.

$\text{Ca, Fe/Th/PO}_4/2 \cdot \text{H}_2\text{O}$  является очередным минералом, обнаруженным в процессе исследований. Он гексагональный и имеет следующие параметры элементарной ячейки:  $a = 7,08 \pm 0,07$ ,  $c = 6,24 \pm 0,06$ . Этот минерал принадлежит к ряду изоморфического броккита -  $\text{Fe}^{2+}\text{Th/PO}_4/2 \cdot \text{H}_2\text{O}$ . Небольшое содержание /2 % веса/ даёт возможность считать его в приближении за броккит.

Ещё одним продуктом описанного ряда преобразований является по-видимому ромбоэдрический минерал со следующими параметрами элементарной ячейки:  $a \sim 14$ ,  $b \sim 12$ ,  $c \sim 15$ . По всей вероятности его химический состав похож на  $\text{Th, Ca, Fe...//PO}_4$ ,  $\text{OH} \cdot \text{H}_2\text{O}$ ?

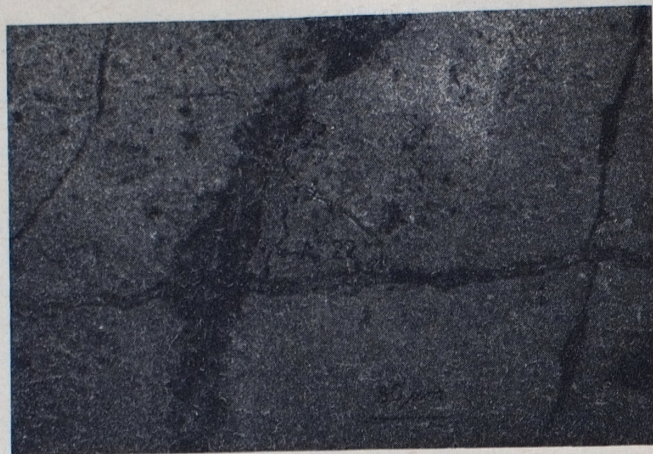
## ОПИСАНИЕ ФОТОГРАФИЙ

- Фот. 1. Микрофотография фосфоросиликатов Fe-Th окклюдированных исследуемый район, обозначенный с помощью штриховой линии. В центральной части фотографии находится жилка  $\text{Th}_3/\text{PO}_4/4$ . Светлосерые - аморфные, гидроокислы железа, серые - фосфоросиликаты Fe-Th. A22 - пункт количественного анализа в микрорайоне
- Фот. 2. Электронограмма иллюстрирующая эффекты преобразования моноклинного  $\text{Ca, Fe/Th/PO}_4/2$  из группы монацита в гексагональный  $\text{Ca, Fe/Th/PO}_4/2 \cdot \text{H}_2\text{O}$ . Основ-

ная дифракция типа "стрекинг" происходит от моноклинного монацита и принадлежит в основном к полосе  $0\bar{1}1$ . "Стрекинг" по-видимому вызван замещением моноклинной фазы гексагональной по плоскости параллельной  $\bar{1}11$  /плоскость раздела/. Пары пунктов с величиной  $d$  гексагональной группы рабдофана рассеяны среди моноклинной дифракции

- Фот. 3. Электронограмма иллюстрирующая эффект преобразования гексагонального  $\text{Ca, Fe/Th/PO}_4/2 \cdot \text{H}_2\text{O}$  /неупорядоченные пары пунктов/ в ромбоэдрический сверхмелкозернистый  $\text{Ca, Fe}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}/\text{PO}_4/2 \cdot 2\text{H}_2\text{O}$ , принадлежащий к группе нингиоита /круговая дифракция/
- Фот. 4. Электронная дифракция гексагонального  $\text{Ca, Fe/Th/PO}_4/2 \cdot \text{H}_2\text{O}$  из группы рабдофана  $uvw = \bar{1}11$ . Параметры элементарной ячейки:  $a = 7,08$  и  $b = 6,24$
- Фот. 5. Электронная дифракция ромбоэдрического минерала  $\text{Ca, Fe}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}/\text{PO}_4/2 \cdot 2\text{H}_2\text{O}$  из группы нингиоита  $uvw = 100$ . Параметры элементарной ячейки  $\text{\AA}$ :  $a = 6,67$ ,  $b = 12,06$ ,  $c = 6,46$





Phot. 1. Microphotograph of Fe-Th phosphosilicates surrounding the investigated grain denoted by means of dotted line. The central part of the picture is cut by a veinlet of  $\text{Th}_3[\text{PO}_4]_4$ . Light grey - amorphous iron oxides, grey - Fe-Th phosphosilicates, A 22 - spot of microprobe analysis. Reflected light, sample 83

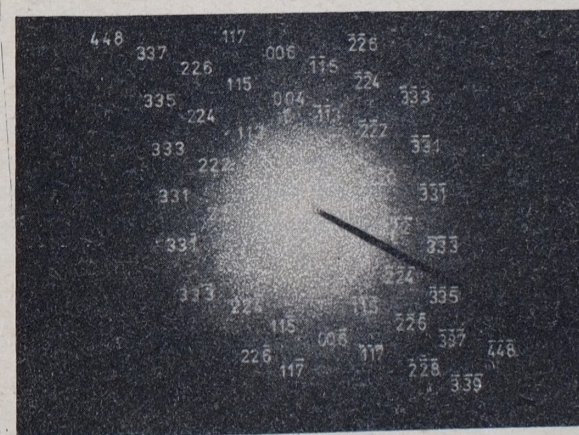


Phot. 2. Electron diffraction pattern illustrating the effects of the transformation of monoclinic  $[\text{Ca,Fe,Th}[\text{PO}_4]_2]$  /monazite group/ into hexagonal /rabdophane group/  $[\text{Ca,Fe,Th}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}]$ . Basal streaking and partly disordered spot pattern is related to monoclinic monazite pattern with spots belonging to  $0\bar{1}1$  zone axis chiefly. Streaking is probably caused by replacement of the monoclinic phase by a hexagonal one, developing parallel to  $\bar{1}11$  /parting plane/. Pairs of spots with interplanar distances related to hexagonal rabdophane group are scattered amidst the monoclinic pattern

H. KUCHA, A. WIECZOREK -  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$ , a new mineral from Lower Silesia, Poland



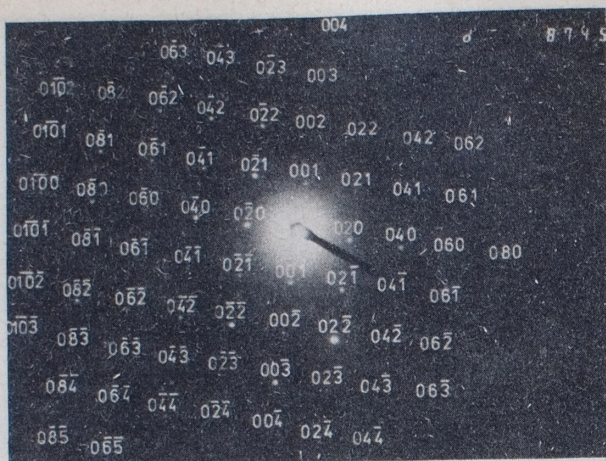
Phot. 3. Electron diffraction pattern illustrating the effects of transformation of hexagonal  $[\text{Ca,Fe,Th}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}]$  /scattered pairs of spots/ into orthorhombic ultrafine-grained  $[\text{Ca,Fe}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}]$  related to ningyoite group /ring pattern/



Phot. 4. Electron diffraction pattern of hexagonal  $[\text{Ca,Fe,Th}[\text{PO}_4]_2 \cdot \text{H}_2\text{O}]$  related to rabdophane group. Zone axis for direction normal to the pattern  $uvw = 110$ . Cell dimensions are:  $a = 7.08$ ,  $b = 6.24$  Å

H. KUCHA, A. WIECZOREK -  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$ , a new mineral from Lower Silesia, Poland





Phot. 5. Electron diffraction pattern of the orthorhombic mineral  $\text{Ca}_{1-x}\text{Th}_{1-x}\text{RE}_{2x}[\text{PO}_4]_2 \cdot 2\text{H}_2\text{O}$  belonging to the ningyoite group. Zone axis for direction normal to the pattern  $uvw = 100$ . Cell dimensions are:  $a = 6.67$ ,  $b = 12.06$ ,  $c = 6.46$