

Czesław AUGUST\*

## COPIAPITE FROM BORÓW NEAR STRZEGOM (LOWER SILESIA)

UKD 549.766.424+546.46'621 ] .01.08:551.311.23: 552.321.1/.4: [549.324.31+549.623.7 (438-35  
wałbrzyskie, Borów k. Strzegomia)

**A b s t r a c t.** Incrustations of secondary minerals of the hydrated sulphates series have been noted on the surface of weathering granitoid rocks in the Strzegom-Sobótka massif. X-ray, thermal, microscopic and IR spectroscopic studies, as well as chemical analysis have shown that the dominant component in the sulphate associations is copiapite, accompanied by metaaluminite and gypsum. It has been found that these minerals form within the zones of hydrothermally altered granitoid rocks, as the products of reactions occurring during the weathering of pyrite and chlorite.

### INTRODUCTION

Copiapites represent hydrated sulphates that form in the process of secondary alteration of sulphide minerals, mainly pyrite. The structure of copiapites was discussed extensively by Fanfani et al. (1973) on the basis of their own studies and the data of other authors (Bandy 1938, Berry 1947, Palache et al. 1946, Süsse 1970), while their chemical formula was presented by Zodrow (1980). Earlier, in 1964, Kubisz made a comprehensive crystallochemical study of copiapites from Poland. It is now generally held that copiapite, characterized by a tetra-octahedral chain structure, has the following chemical formula:  $XR_4^{3+}(SO_4)_6(OH)_2 \cdot nH_2O$ , where  $n \approx 20$ , and extensive substitution of mono- and bivalent cations (e.g.  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ) and also of trivalent aluminium is possible at the X site.

In Poland, copiapites were reported from the Staszic mine at Rudki (Wieser 1949), the Bolesław zinc and lead ore mine (Żabiński 1960), Dobrzyń on the Vistula (Mazur 1962), a pyrite-bearing schist quarry at Wieściszowice (Kubisz 1964), and from the brown coal mine in Turoszów (Stępisiewicz 1983).

Most copiapites described so far occur in sedimentary formations mineralized with sulphides, where the conditions are suitable for the migration of solutions and the precipitation of sulphates. Much less common are sulphate occurrences in crystalline rocks. Such occurrences are represented by copiapite found by the present author at Borów near Strzegom, Sobótka Zachodnia and Zarów near Świdnica. Detailed investigations were carried out on samples collected from a quarry at Borów.

\* Institute of Geological Sciences, Wrocław University, 50-205 Wrocław, ul. Cybulskiego 30.

During field investigations carried out in the granitoid massif of Strzegom-Sobótka in the years 1981–1983, the author found lemon-coloured mineral concentrations on the weathered surface of hydrothermally altered granite that generally forms narrow, nearly vertical zones. These zones comprise granite crosscut by quartz veinlets of varying thickness, showing hydrothermal-pneumatolitic mineralization (Kowalski 1967, Majerowicz 1975). Besides rock-forming minerals typical of granite (quartz, K-feldspar, plagioclases), the rock in question has an increased content of pyrite and chlorite. Planimetric analysis has shown that pyrite makes up 0.9 and chlorite 1.0 vol. % of the rock. Both the mineralogical composition and the structural and textural features of this granite variety favour the formation of secondary sulphate minerals (August, in press). Depending on the progress of hypergene processes in the zones in question, granite is either bleached due to the illitization and kaolinitization of feldspars and mica (August, in press), or has a green colour when Fe sulphides alone are subject to weathering.

Copiapite in the form of lemon-coloured microcrystalline efflorescences coats with a thin, up to a few mm, layer the weathered surface of granite, or to be more precise, the illite-kaolinite weathering crust of granite. The copiapite efflorescences are accompanied by other secondary sulphate minerals, of which larkspurs and rosette-like aggregates of gypsum needles are readily detectable under the microscope. Single acicular crystals of another mineral, most likely metaaluminite, have also been identified. Since the percentage of these accompanying minerals is very low, they will not be the object of further studies.

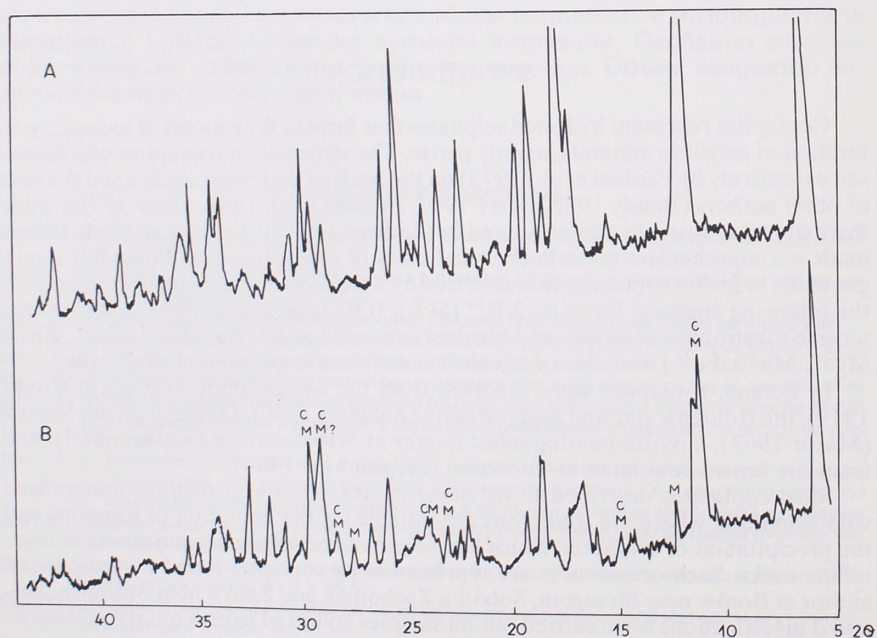


Fig. 1. X-ray diffraction patterns of copiapite from Alcaparossa (A) and Borów (B)  
C – copiapite, M – metaaluminite

Investigations were carried out on lemon-coloured concentrations picked out under the microscope. Though the selection was made with utmost care, the samples contained slight admixtures of other mineral substances.

Microscopic observation in transmitted light was carried out on a sample cold embedded in epoxy resin. The sample was also subjected to scanning electron microscope studies.

Thermal analysis was made with a 1500°C-type Derivatograph under standard conditions at a heating rate of 5 and 10°C/min., taking weighed portions of 660 and 190 mg.

X-ray diffraction patterns were recorded with a DRON-2 X-ray diffractometer, using Fe-filtered CoK<sub>α</sub> radiation.

Infrared spectra were obtained with a Perkin-Elmer 180 spectrometer.

Chemical determinations were carried out on a dissolved sample. Owing to the free water solubility of copiapite, the solution to be analysed was free from insoluble admixtures which were detected during phase analysis. Water content was determined with TG method, taking the mean value of two thermal analyses.

To establish the stoichiometric formula of copiapite, the model of linear equations devised by Zodrow (1980) was employed and solved using an Odra 1305 computer.

RESULTS AND DISCUSSION

Microscopic observation in transmitted light permitted the determination of basic optical features only. Viewed under the microscope, copiapite appears to be a flaky mineral of yellowish colour. It shows very weak pleochroism (from pale-yellow to yellow) and low interference colours. In the marginal zones of flaky concentrations, the crystals become brown due to the sulphate passing into iron hydroxide. The yellowish copiapite concentrations are accompanied by gypsum appearing as idiomorphic lamellae. In the scanning electron microscope, tabular crystals of copiapite are visible, forming botryoidal concentrations (Photos. 1, 2).

X-ray diffraction patterns are presented in Fig. 1. Worth noting are the strongest reflection (about 18.3 Å) displaced towards low angles, and the two partly overlapping 9.22 and 9.04 Å peaks. It is also interesting to note that the intensity of certain characteristic reflections is reversed relative to the corresponding peaks on the powder pattern of copiapite from Alcaparossa (e.g. 18.3 and 9.22; 6.13 and 5.90; 4.13 and 4.02 Å). Moreover, some basal lines (9.22, 6.19, 5.58, 4.69, 4.48, 4.33, 3.88 Å) are split or their peaks are not sharp, which suggests the presence of two substances of similar structures, displaying reflections in similar angle ranges. The X-ray data obtained accord well with those presented by Kubisz (1964). According to this author, the 18 Å reflections displaced towards low angles are typical of pseudocopiapites containing aluminium at the X site. The present results are also in good agreement with the data obtained for aluminocopiapite from Alaska (Jolly, Foster 1967). On the other hand, they differ in some respects from copiapite from Alcaparossa, which is regarded to be a magnesium copiapite (Süsse 1970). The X-ray diffraction pattern of copiapite from Borów also shows reflections corresponding to the main peaks of metaaluminite (e.g. 8.31, 6.88, 5.72, 4.39 Å) described by Frondel (1968).

The results of thermal analysis of the sample from Borów (Fig. 2) are typical of copiapites (Kubisz 1964, Fanfani et al. 1973). Three peaks appearing on DTA, DTG and TG curves correspond to three kinds of endothermic reactions. Their mechanism

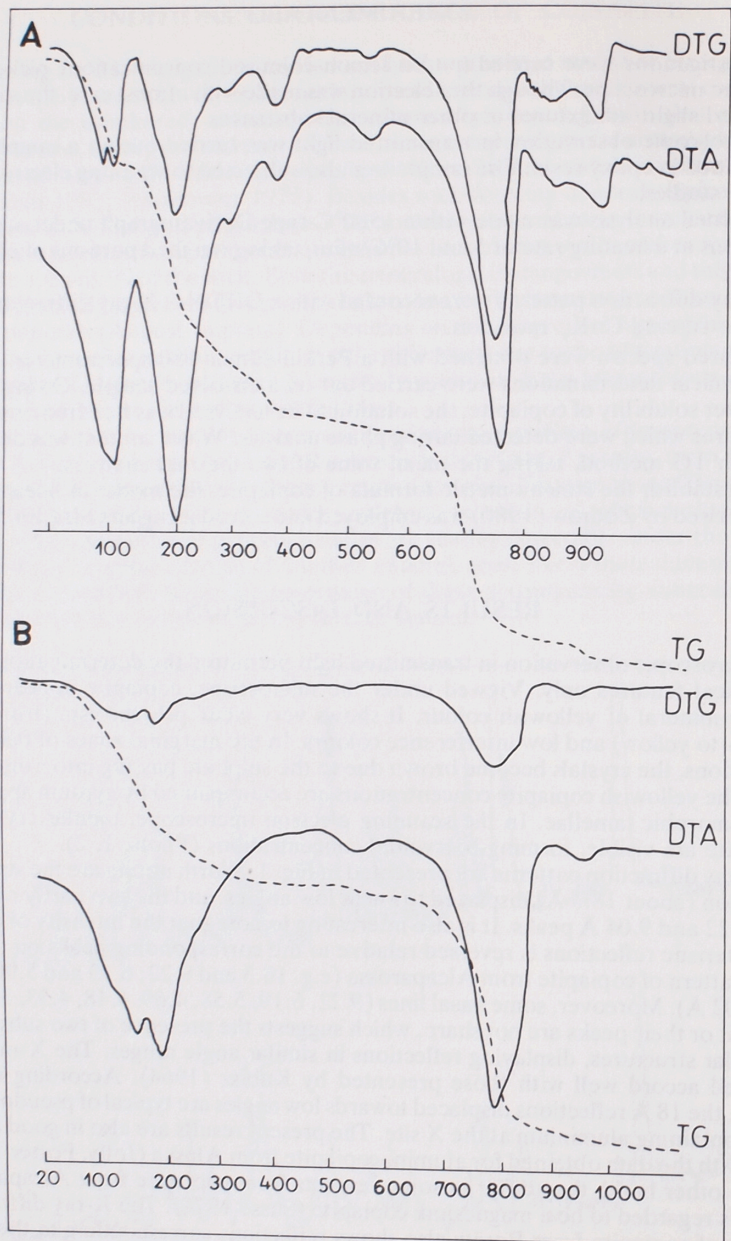


Fig. 2. DTA, DTG and TG curves obtained for copiapite from Alcaparossa (A) and Borów (B). Heating rate 10°C/min., weighed portion 660 mg.

was discussed extensively by Kubisz (*l.c.*). The dehydration of the Borów copiapite involves three stages, producing endothermic peaks at 150, 190 and 240°C on DTA curves, with the corresponding weight loss on TG curves of 9.1, 11.8 and 5.0 wt.% respectively. The three-stage dehydration of copiapite was accounted for by Kubisz by the presence of water of different bonding energy. His suggestions were confirmed by the structural studies of Fanfani et al. (*l.c.*). The dehydroxylation of copiapite occurs at 340 and 540°C, the weight loss being 1.8 and 1.2 wt.% respectively. It is generally held that it should take place at about 340°C (dissociation of compounds of the  $\text{Fe}_2(\text{OH})$  and  $\text{Fe}(\text{OH})$  type). However, Kubisz assumes that this process may be completed at 540°C. Though this is conceivable, it must be pointed out that in the sample studied, a certain undetermined amount of OH groups are removed during the dehydroxylation of kaolinite. The presence of a very small amount of the latter mineral was detected by X-rays. The dissociation of sulphate compounds in copiapite produces a strong endothermic peak with a double maximum at 740 and 810°C, and a weaker but pronounced peak at 960°C. The weight loss corresponding to dissociation is 30 and 3.3 wt.% respectively. Thermal analysis made at a heating rate of 5°C/min. shows that the latter peak is double as well. The shape of the presented endothermic peaks is presumably a result of the successive processes of dissociation of iron, magnesium and aluminium sulphates that form as intermediate phases during the heating of copiapite. One the latter effects (940 or 960°C) has been attributed to the dissociation of metaaluminite, which was detected in a small amount by X-rays.

The infrared absorption spectrum of the Borów copiapite contains bands typical of sulphates (Fig. 3). It shows absorption bands characteristic of the tetrahedral, yet slightly deformed, configuration of  $\text{SO}_4$  ions, which is evidenced by  $\nu_1$  ( $\sim 1000 \text{ cm}^{-1}$ ) and  $\nu_2$  ( $\sim 450 \text{ cm}^{-1}$ ) vibrations (Kubisz, Żabiński 1979). A weak absorption appearing close to  $2450 \text{ cm}^{-1}$  testifies to the presence of  $\text{H}_3\text{O}^+$  ions (Kubisz, Żabiński 1979). Moreover, there are strong absorption bands caused by vibrations of crystallization water ( $\sim 1620 \text{ cm}^{-1}$ ) and OH groups ( $\sim 3530 \text{ cm}^{-1}$ ). Compared with the infrared spectrum of copiapite from Borate, California (Fig. 3) (Van der Marel, Beutelspacher 1976), the respective bands are somewhat displaced, which is presumably due to the differences in chemical composition of the two copiapites.

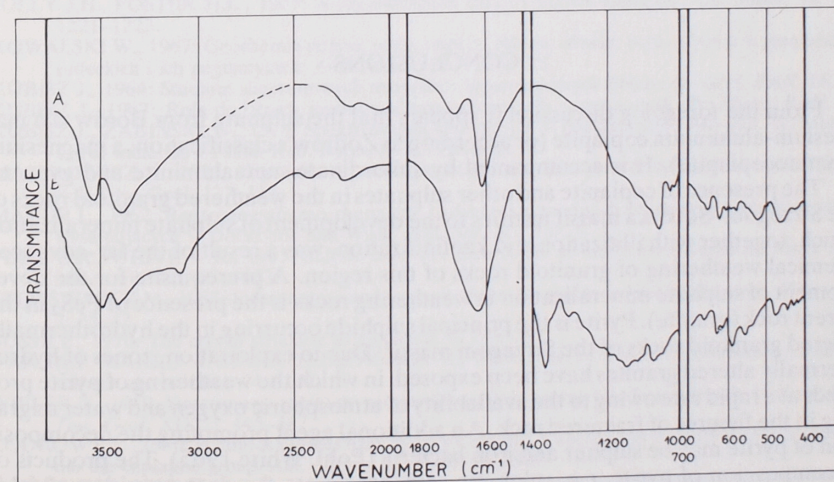


Fig. 3. Infrared absorption spectra of copiapite from Borate, California (A) and Borów (B)

The chemical analysis of copiapite from Borów is presented in Table 1. The constituents entering into the composition of metaaluminite were not isolated since it was assumed that the content of this mineral in the sample prepared for chemical analysis was insignificant. As was mentioned earlier in this paper, the atomic percentage of chemical elements was calculated by solving a set of linear equations. Deriving from the general crystallochemical formula  $(XR_4(SO_4)_6(OH)_2 \cdot nH_2O)$ , this model assumes that cations at the X site should satisfy the conditions  $0 < X < 1$ , while  $0 \leq R^{3+} \leq 1$  (Zodrow 1980), it was also assumed in this paper that aluminium present in copiapite partly occupies the R site (as a complement to  $Fe^{3+}$ ) and partly (after deducting the amount at the R site) the X site.

On the basis of chemical data and the above assumptions, the following stoichiometric formula was established for the Borów copiapite:  $\square_{0.112}Na_{0.010}Ca_{0.006}Mg_{0.159}Mn_{0.009}Fe_{0.311}^{2+}Al_{0.393}(Fe_{0.873}^{3+}Al_{0.127})(SO_4)_6(OH)_2 \cdot 20H_2O$ . Since the sum of cations at the X position is less than the theoretical values equal to 1 (it is 0.888), the problem of full occupancy at this site remains an open question. Because of the lack of detailed studies, some assumptions may only be made regarding the occupancy at the X site. In the author's opinion, there are three possibilities of filling this position in the Borów copiapite:

1. The vacant X sites are occupied by hydronium ions  $H_3O^+$  (they have been found at this position in some sulphates, Kubisz 1967).
2. Trivalent aluminium at the X position compensates for the opposite charges in the structure of copiapite, although the X position itself is not fully occupied (Fanfani et al. 1973).
3. Both (1) and (2) occur in the copiapite studied, generally maintaining the electrochemical equilibrium in the crystal lattice.

For the lack of sufficient data, the author does not feel equal to solving the problem of occupancy at the X site in the structure of copiapite from Borów.

The above remarks and doubts concerning the chemical composition of the Borów copiapite do not interfere with determining its position in the mineral series of the copiapite group. Taking into consideration Zodrow's (*l.c.*) crystallochemical criteria of classification, the copiapite studied is a magnesium-aluminium member of this series.

## CONCLUSIONS

From the foregoing discussion it appears that the sulphate from Borów is a magnesium-aluminium copiapite (or according to Zodrow's classification, a magnesium aluminocopiapite). It is accompanied by subordinate metaaluminite and gypsum.

The presence of copiapite and other sulphates in the weathered granitoid rocks of the Strzegom-Sobótka massif testifies to the development of sulphate mineralization which, together with illitization and kaolinitization, was a result of the far-advanced chemical weathering of granitoid rocks of this region. A prerequisite for the development of sulphate mineralization in weathering rocks is the presence of  $FeS_2$  in the parent rock (granite). Pyrite is the principal sulphide occurring in the hydrothermally altered granitoid rocks of the Strzegom massif. Due to exploitation, zones of hydrothermally altered granites have been exposed, in which the weathering of pyrite proceeds at a rapid rate owing to the availability of atmospheric oxygen and water migrating in the fissures of fractured rock. An additional agent promoting the decomposition of pyrite may be sulphur and iron bacteria (Pohl, White 1965). The products of decomposition of pyrite, e.g. sulphuric acid, accelerate the decomposition of feldspars and chlorite which are the main source of aluminium, magnesium, calcium and

Table 1  
Chemical analysis of copiapite from Borów

Chemical component	Weight %	Molecular number
Na <sub>2</sub> O	0.06	Na 0.010
MgO	0.51	Mg 0.159
CaO	0.03	Ca 0.006
MnO	0.05	Mn 0.009
FeO	1.78	Fe <sup>2+</sup> 0.311
Al <sub>2</sub> O <sub>3</sub>	1.85	Al 0.520
Fe <sub>2</sub> O <sub>3</sub>	22.13	Fe <sup>3+</sup> 0.873
SO <sub>4</sub>	49.10	6.06
H <sub>2</sub> O	25.00	20.04
	100.51	

other elements entering into the composition of copiapite and the coexisting sulphates found in the weathered granitoid rocks of the Strzegom-Sobótka massif.

*Acknowledgments.* The author is grateful to Prof. A. Majerowicz for critical reading the manuscript, and to Dr J. Janeczek for carrying out X-ray analyses and discussions on the results. Thanks are also due to Dr J. Kassner for performing scanning electron microscopic photographs, to H. Siagło M. Sc for chemical analyses and to Z. Płoski M.Sc for electronic computations.

Translated by Hanna Kisielewska

## REFERENCES

- AUGUST C.: Mineralizacja siarczanowa w zwietrzelinach granitoidów masywu Strzegom-Sobótka (komunikat) (w druku) *Pr. Geol.-Miner.*
- FANFANI L., NUNZI A., ZANAZZI P.F., ZANZARI A.R., 1973: The copiapite problem: The crystal structure of a ferrian copiapite. *Am. Miner.* 58, 3-4, 314-322.
- FRONDEL C., 1968: Meta-aluminite a new mineral from Temple Mountain Utah. 53, 5-6, 717-721.
- JOLLY J.H., FOSTER H.L., 1967: X-ray diffraction data of aluminocopiapite. *Am. Miner.* 52, 7-8, 1221-1223.
- KOWALSKI W., 1967: Geochemia potasu, sodu, wapnia, rubidu, ołowiu, baru i strontu w granitoidach sudeckich i ich pegmatytach. *Arch. Miner.* 27, 1, 56-225.
- KUBISZ J., 1964: Studium siarczanowych minerałów hipergenicznych Polski. *Pr. Geol. PAN.* 26.
- KUBISZ J., 1967: Rola dodatnich jonów wodorowo-tlenowych w minerałach. *Pr. Miner. PAN.* 11.
- KUBISZ J., ŻABIŃSKI W., 1979: Spektroskopia absorpcyjna w podczerwieni. 404-427. W: Metody badań minerałów i skał. Red. Bolewski A., Żabiński W.
- MAJEROWICZ A., 1975: Zagadnienia petrologiczne plutonu Strzegom-Sobótka. *Przew. XLVII Zj. Pol. Tow. Geol.* 127-137.
- MAZUR L., 1962: Rentgenograficzno-chemiczne badania siarczanowych produktów wietrzenia pirytu występujących w Dobrzyniu nad Wisłą. *Stud. Soc. Sci. Tor.* 4, 2.
- POHL E.R., WHITE W.R., 1965: Sulfate minerals: their origin in the Central Kentucky Karst. *Am. Miner.* 50, 9, 1461-1463.
- STĘPIEWCZAK M., 1983: Sideronatrite and copiapite from Turoszów, Lower Silesia. *Arch. Miner.* 38, 2, 35-42.
- SÜSSE P., 1970: The crystal structure of copiapite. 6, 286-287.
- VAN DER MAREL M.W., BEUTELSPÄCHER M., 1976: Atlas of Infrared Spectroscopy..., sulfur, sulfates and sulfides. 249-251.
- WIESER T., 1949: Siarczanowe produkty wietrzenia na złożu żelaza Gór Świętokrzyskich. *Rocz. Pol. Tow. Geol.* XIX, 3, 445-447.
- ZODROW E.L., 1980: Hydrates sulfates from Sydney Coalfield, Cape Breton Island Nova Scotia, Canada: the copiapite group. *Am. Miner.*, 65, 9-10, 961-967.
- ŻABIŃSKI W., 1960: Charakterystyka mineralogiczna strefy utleniania śląsko-krakowskich złóż kruszców cynku i ołowiu. *Pr. Geol.* 1.

## КОПИАПИТ З БОРОВА КОЛО СТРЕГОМИА, ДОЛНЫ ШЛАСК

## Streszczenie

W obrębie granitoidowego masywu Strzegom–Sobótka, w strefach hydrotermalnie przeobrażonych, zaobserwowano na zwietrzałych powierzchniach granitów cytrynowożółte wykwity. Największy zasięg tych wystąpień stwierdzono w kamieniołomie w Borowie koło Strzegomia. Badania fazowe wykazały, że mikrokryształiczne skupienia wtórnych minerałów składają się głównie z копиапиту, któremu towarzyszą metaalumin i gips. W elektronowym mikroskopie scanningowym копиапит з Борова ujawnia się jako minerał o pokroju tabliczkowym tworzący groniaste agregaty (fot. 1, 2).

Wyniki badań rentgenowskich i termicznych копиапиту з Борова są zbliżone do danych dla aluminocопиапиту з Аляски i magnezowego копиапиту з Alcaparossa. Analiza chemiczna dokładnie wyseparowanych skupień копиапиту wykazała, że należy on do magnezowo-glinowego członu grupy uwodnionych siarczanów. Jego stechiometryczna formuła obliczona metodą zaproponowaną przez Zodrowa przedstawia się następująco:  $(\square_{0.112} \text{Na}_{0.010} \text{Ca}_{0.006} \text{Mg}_{0.159} \text{Mn}_{0.009} \text{Fe}_{0.311}^{2+} \text{Al}_{0.393}) (\text{Fe}_{0.873}^{3+} \text{Al}_{0.127}) (\text{OH})_2 \cdot 20\text{H}_2\text{O}$ . Problem niepełnej obsady pozycji X w strukturze копиапиту autor próbuje rozwiązać przyjmując następujące możliwości:

1. w pozycji X, poza stwierdzonymi kationami, występują również jony hydrogenowe  $\text{H}_3\text{O}^+$ .

2. kationy  $\text{Al}^{3+}$  występujące w pozycji X kompensują brakujące ładunki kationów jedno- i dwuwartościowych (wg koncepcji Fanfani'ego i in. 1973).

3. W badanym копиапите zachodzą oba w/w przypadki.

Obecność копиапиту i innych minerałów siarczanowych w zwietrzelinach granitoidów masywu Strzegom–Sobótka świadczy o zaawansowanym procesie wietrzenia pirytu i chlorytu oraz o zaistnieniu w ostatnich latach sprzyjających warunków klimatycznych (ciepłe i suche okresy letnie 1980–1983) dla krystalizacji siarczanów.

## OBJASNIENIA FIGUR

Fig. 1. Dyfraktoqramy rentgenowskie копиапиту з Alcaparossa (A) i з Борова (B)

C – копиапит, M – metaalumin

Fig. 2. Derywatogramy копиапиту з Alcaparossa (A) i з Борова (B). Szybkość grzania  $10^\circ\text{C}/\text{min}$ , waga próbki 660 mg

Fig. 3. Spektrogramy absorpcyjne w podczerwieni копиапиту з Борате, California (A) i з Борова (B)

## OBJASNIENIA FOTOGRAFII

Fot. 1. Groniaste skupienia копиапиту з Борова. Pow.  $600\times$

Fot. 2. Kryształy копиапиту o pokroju blaszkowym. Pow.  $2000\times$

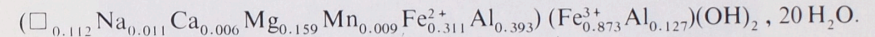
Zdjęcia wykonano na SEM Tesla 300.

## КОПИАПИТ ИЗ БОРОВА ВОЗЛЕ СТШЕГОМЯ, НИЖНЯЯ СИЛЕЗИЯ

## Резюме

В гидротермально измененных зонах гранитного массива Стшегом–Собутка на выветрелых поверхностях гранитов были замечены лимонножелтые выцветы. Наибольшее распространение этих выцветов замечено в камнеломнях в Борове возле Стшегома. Фазовые исследования показали, что микrokристаллические скопления вторичных минералов состоят главным образом, из копиапита, с сопутствующими в подчиненном количестве metaалюминитом и гипсом. В электронном сканировом микроскопе копиапит из Борова наблюдается в виде минерала табличатой формы, образующего гроздевидные агрегаты (фот. 1–2).

Результаты рентгеновских и термических исследований копиапита из Борова подобны результатам полученным для алюмокопиапита из Аляски и магниевый копиапита из Алькапарроса. Химический анализ тщательно отсепарированных скоплений копиапита показал, что он принадлежит к магниево-алюминиевой группе гидратированных сульфатов. Его стехиометрическая формула, рассчитанная по методу предложенному Зодровым, следующая:



Проблему неполного заполнения позиции X в структуре копиапита автор пытается решить, принимая:

1. В позиции X, кроме отмеченных катионов, имеются также гидроновые ионы  $\text{H}_3\text{O}^+$ .

2. Катионы  $\text{Al}^{3+}$ , занимающие место в позиции X, компенсируют недостающие заряды одно- и двухвалентных катионов (по концепции Фанфани и других (1973)).

3. В исследуемом копиапите имеют место оба вышеперечисленные случаи. Присутствие копиапита и других сульфатных минералов в коре выветривания гранитоидов массива Стшегом–Собутка свидетельствует о развитом процессе выветривания пирита и хлорита а также о появлении в последних годах климатических условий, способствующих кристаллизации сульфатов (теплые и сухие летние периоды 1980–1983).

## ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Рентгеновские дифрактограммы копиапита из Алькапарроса (A) и из Борова (B)

C – копиапит, M – metaалюминит

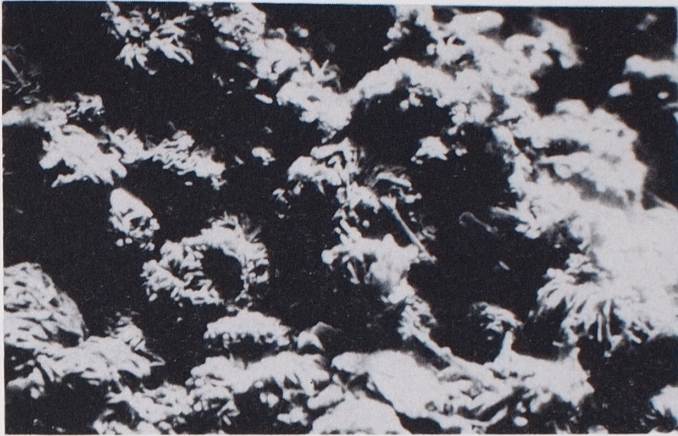
Фиг. 2. Дериwатogramмы копиапита из Алькапарроса (A) и Борова (B). Скорость нагревания  $10^\circ\text{C}/\text{мин.}$ , вес пробы 660 мг.

Фиг. 3. ИК-спектры поглощения копиапита из Борате, Калифорния (A) и из Борова (B)

## ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото. 1. Скопления копиапита гроздевидной формы из Борова. Увеличение  $600\times$

Фото. 2. Кристаллы копиапита пластинчатой формы. Увел.  $2000\times$ . Фотографии выполнены на СЭМ Tesla 300



Phot. 1. Botryoidal copiapite clusters. Magn.  $\times 600$



Phot. 2. Flaky copiapite crystals. Magn.  $\times 2000$

Photographs were taken in SEM Tesla 300.