

Stanisław MADEJ¹, Krzysztof SADOWSKI²

NEW DATA ON FLUORAPOPHYLLITE FROM STRZELIN

Abstract: Mineralogical investigations of fluorapophyllite from Strzelin were carried out. The mineral forms tabular crystals with the basal pinacoid {001} dominating over tetragonal dipyrmaid {101} and tetragonal prism {110}. Electron microprobe analyses of the material show SiO₂ 51.30, Al₂O₃ 0.50, CaO 24.45, Na₂O 0.23, K₂O 4.56 F 1.52. Unit cell dimensions of the fluorapophyllite are: a=8.971(4) Å, c=15.796 (4) Å and V=1271(1) Å³. DTA measurements record the presence of endothermic reactions at the temperatures of 337°C and 465°C as well as an exothermic one at 824°C. TG analysis shows that the weight loss is 16.7 wt % (up to 1200°C) and generally takes place in two steps (7,4 wt %, 7,7 wt %). The fluorapophyllite crystallisation took place slowly, at low saturation and relatively high temperatures.

Keywords: fluorapophyllite, Strzelin, hydrothermal mineralisation, habit, chemical composition, DTA, TG, XRD

This paper presents results of mineralogical investigations fluorapophyllite crystals found in the main Strzelin quarry. In the quarry occurs fine-grained biotite granite penetrated by veins of biotite-muscovite granite. Ages of these granites, obtained by the Rb-Sr method, were estimated at 347±12 Ma and 330±6 Ma respectively (Oberc-Dziedzic et al. 1996). The granites belong to the Strzelin crystalline massif (Oberc 1966), located in the eastern part of the Fore-Sudetic Block. The postmagmatic mineralisation accompanying the granites was a matter of several studies (Stepisiewicz 1977, Ciesielczuk 2001, Kozłowski, Metz 2003, Ciesielczuk, Janeczek 2004). The authors described several minerals formed in hydrothermal conditions and determined temperatures of their formation using various methods. Apophyllite from the Strzelin granitoids was noted for the first time by Kozłowski and Metz (op.cit.) who investigated samples of pegmatites and veins (the authors did not precise the rock type) from the quarries at Strzelin, Mikoszków and Gębczyce. Using the WDS technique they identified apophyllite and, by means of fluid inclusions analyses, determined the temperatures of its crystallisation.

Fluorapophyllite which is a matter of the present study was found in a 10 cm thick vein cutting the fine-grained biotite granite. The main constituent of the vein

¹ *Institute of Geological Sciences, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland; smad@ing.uni.wroc.pl*

² *Institute of Geology, Adam Mickiewicz University, ul Maków Polnych 16, 61-606 Poznań, Poland, sadowskik@wp.pl*

is quartz with minor amounts of such minerals as chlorite, epidote, prehnite and calcite. The order of crystallisation may be inferred from petrographic observations. The first phase was fine-grained greyish quartz forming xenomorphic aggregates in contact with the granite. Chlorite crystallised next, followed by epidote. Subsequently the second generation of quartz (coarser-grained variety) formed. It is covered by aggregates of crystalline prehnite which is in turn followed by fluorapophyllite. One millimeter big yellow and transparent isometric crystals of calcite ended the crystallisation.

Crystals of fluorapophyllite are transparent to semi-transparent, colourless to white. White colour is related to the presence of secondary alteration of the mineral surface and to the number of inclusions. Fluorapophyllite displaying well-formed all faces is rare as it is mainly present in intergrowths. It forms 5-6mm x 3-4mm x 1 mm tabular crystals. The investigated crystals display three forms: {110}, {101} and {001}. Tetragonal dipyrmaid {101} and tetragonal prism {110} are less developed then the dominant basal pinacoid {001}.

Table 1. Selected chemical analysis of fluorapophyllite (*faph*) and prehnite (*prh*).

Weight percent of oxides						
Sample	<i>faph</i> 2	<i>faph</i> 4	<i>faph</i> 6	Sample	<i>prh</i> 1	<i>prh</i> 8
SiO ₂	51.30	51.39	51.04	SiO ₂	44.02	43.92
Al ₂ O ₃	0.50	0.48	0.43	Al ₂ O ₃	24.39	24.34
CaO	24.45	24.30	24.12	FeO*	0.18	0.18
Na ₂ O	0.23	0.18	0.14	CaO	27.59	27.22
K ₂ O	4.56	4.68	4.72	Na ₂ O	0.01	0.06
F	1.52	1.53	1.48	H ₂ O ^(t)	(4.39)	(4.37)
H ₂ O ^(t)	(18.08)	(18.08)	(18.71)			
Total	100.64	100.64	100.62	Total	100.58	100.09
-O=F	0.64	0.64	0.62			
	(100.00)	(100.00)	(100.00)			
*total Fe= Fe ³⁺						
Numbers of ions on the basis of Si + Al = 8.00.			Numbers of ions on the basis of 24(O,OH)			
Si ⁴⁺	7.909	7.912	7.922	Si ⁴⁺	6.018	6.028
Al ³⁺	0.091	0.088	0.078	Al ³⁺ (T site)	1.982	1.972
Ca ²⁺	4.038	4.009	4.011	Al ³⁺	1.947	1.965
Na ⁺	0.069	0.054	0.041	Fe ³⁺	0.019	0.019
K ⁺	0.897	0.919	0.934	Ca ²⁺	4.041	4.003
∑ cat.	13.005	12.983	12.987	Na ⁺	0.003	0.015
F ⁻	0.741	0.744	0.728	∑ cat.	14.010	14.002
(OH) ⁻	9.297	9.287	9.767	(OH) ⁻	4.000	4.000

Chemical compositions of the fluorapophyllite and prehnite (Tab. 1) were determined using a Cameca electron microprobe (probe current 10 nA, acceleration voltage 15 kV, beam diameter 20µm). Analyses of fluorapophyllite were recalculated assuming the total Si and Al equal 8. H₂O was added to give 100 wt % in the analyses. Based on the chemical composition the following structural formula has been derived for the fluorapophyllite:

(K_{0.90},Na_{0.07})_{0.97} Ca_{4.04} [Si_{7.91}Al_{0.09}O_{19.98}] (F_{0.74},OH_{0.26})_{1.00}·9.04 H₂O. An important feature is the content of F equal 1.5 wt % what gives 0.74 of F ions in formula unit.

X-ray diffraction studies (XRD) were performed by means of Siemens D500 diffractometer using Co-K_α radiation in a range of 10-75° 2θ with a step 0.02° 2θ, at temperature 27°C. The three most intense peaks were observed at d (Å) = 3.945 (100), 2.979 (10), 1.579 (18). Using the WIN-INDEX and WIN-METRIC computer programmes 14 diffraction lines were indexed. Apophyllite group

minerals (except natroapophyllite) show tetragonal symmetry and crystallise in the ditetragonal dipyramidal symmetry class (4/m 2/m 2/m). On basis of the indexed lines, with the tolerance $\pm 0.03^\circ 2\theta$, the following unit cell parameters were obtained: $a=8.971(4) \text{ \AA}$, $c=15.796(4) \text{ \AA}$ and $V=1271(1) \text{ \AA}^3$. The c/a ratio is 1.760.

In order to investigate the fluorapophyllite structure in more detail differential thermal analyses were performed. DTA, DTG and TG curves were recorded using a derivatograph Q-1500D MOM Budapest. The standard heating rate was $10^\circ\text{C}/\text{min}$ up to 1200°C . The DTA curve showed two well-defined peaks (first one being less pronounced) indicating endothermic reactions at temperatures of 337°C and 465°C and an exothermic peak at 824°C . Thermogravimetric measurements, carried out up to 1200°C , recorded the mass loss of 16.7 wt %. Two main stages of the mass loss related to endothermic reactions were observed. The sample lost 7.4 wt % the first and 7.7 wt % during the second stage.

DISCUSSION AND CONCLUSIONS

The apophyllite group is represented by fluor-hydroxyapophyllite (Dunn et al. 1978), natroapophyllite (Matsueda et al. 1981) and NH_4 -fluor, hydroxyapophyllite (Marriner et al. 1990) due to mutual substitutions of K-Na or NH_4 -F, OH. In case of fluorine prevailing over OH group in apophyllite with the composition of $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F},\text{OH})\cdot 8 \text{ H}_2\text{O}$ the phase is called fluorapophyllite (Dunn et al. 1978). Thus the apophyllite from Strzelin ($\text{F}=0.74$, $\text{OH}=0.26$) may be described as fluorapophyllite.

The obtained chemical analyses may evoke some doubts concerning the deficit of cations in the calculated formula. This deficit results in the excess of H_2O (9.04 molecules p.f.u.) comparing to the ideal chemical formula. The concentration of H_2O estimated at 16.7 wt % on the basis of the TG method seems more plausible than the value of 18 wt % assumed at the calculations.

Marriner et al. (1990) compared the unit cell parameters of apophyllites with various fluorine contents and found that the parameters a , c and c/a decrease linearly with increasing substitution of OH by F. With the fluorine amount of 1.5 wt % the approximated parameters should be: $a=8.975(4) \text{ \AA}$, $c=15.83(4) \text{ \AA}$ and $c/a=1.763$ (op. cit.). The parameters obtained for the fluorapophyllite from Strzelin are comparable.

Results of the differential thermal analyses indicate the dominance of F ions over OH groups in the structure of the investigated apophyllite. Two endothermic effects on the DTA curve corresponding with the loss of OH groups (with the first mass loss less intensive) as well as the exothermic effect at 830°C , relating to the formation of wollastonite, are characteristic of fluorapophyllite (Marriner et al. 1990). For instance the exothermic reaction for hydroxyapophyllite takes place at the temperature about 900°C (op. cit.).

Kozłowski and Metz (2003) showed that apophyllite from the Strzelin granites crystallised in the temperature range of $200\text{-}160^\circ\text{C}$. Comparing the order of crystallisation given by Kozłowski and Metz (op. cit) with the one observed in the present study there is a discrepancy in case of epidote, which, according to the

authors (op. cit), formed at temperatures between 230-180°C but after fluorapophyllite.

Fluorapophyllite from Strzelin possesses the habit that was described as tabular (P₂) by Kostov (1975). Doroshenko et al. (1969) calculated the crystallisation temperatures (156-148°C) of apophyllite crystals (0.8 wt % of F and 4.40 wt % of K) from Savinskoye 5 (Transbaikal) which were dominated by the tetragonal dipyrmaid {101}. Such habit was described by Kostov (op. cit.) as dipyrmaid (P₁). According to Kostov (1975) tabular habit of apophyllite (P₂) indicates slow crystallisation at low saturation of the fluid in higher temperature as opposite to the dipyrmaid habit (P₁). Those observations seem to be confirmed by the habit of the crystals from Strzelin and Savinskoye 5.

ACKNOWLEDGEMENTS: Thermal and X ray diffraction analyses were performed at the Department of Mineralogy and Petrology of the Institute of Geological Sciences, Wrocław University. The microprobe analyses were carried out at the Geological Faculty, the Warsaw University. We thank Adam Szuszkiewicz for critical comments on the manuscript.

REFERENCES

- CIESIELCZUK J., 2001: Chemical reactions proceeded in minerals affected by hydrothermal fluid (based on the Strzelin and Borów granites) *Prace Specjalne (Special Papers) PTMin.*, 19: 33-35.
- CIESIELCZUK J., JANECZEK J., 2004: Hydrothermal alteration of the Strzelin granite, SW Poland. *N. Jb. Miner. Abh.*, 179 (3), 239-264.
- DOROSHENKO J.P., IVANOV V.N., PATRUSHEVA N.M., TCHUMACHENKO N.M., 1969: Apophyllite from the polymetallic occurrence Savinskoye No 5 (Transbaikal). *Mineralogiceskij Sbornik*, 4: 424-428.
- DUNN P.J., ROUSE R.C., NORBERG J.A., 1978: Hydroxyapophyllite, a new mineral, and a redefinition of the apophyllite group. I. Description, occurrences, and nomenclature. *Am. Mineral.*, 63: 196-199.
- KOSTOV I., 1975: Apophyllite morphology as an example of habit modification of planar crystals. *N. Jb. Miner. Abh.*, 123 (2): 128-137.
- KOZŁOWSKI A., METZ P., 2003: Post-magmatic mineralisation in the granitoids of the Strzelin massif, SW Poland – a fluid inclusion study. *Prace Specjalne (Special Papers) PTMin.*, 23: 102-104.
- MARRINER G.F., TARNEY J., LANGFORD J. I., 1990: Apophyllite group: effects of chemical substitutions on dehydration behaviour, recrystallization products and cell parameters. *Min. Mag.*, 54: 567-577.
- MATSUEDA. H., MIURA Y., RUCKLIDGE J., 1981: Natroapophyllite, a new orthorhombic sodium analog of apophyllite. I. Description, occurrences, and nomenclature. *Am. Mineral.*, 66: 410-415.
- OBERC J., 1966: Geology of crystalline rocks of the Wzgórza Strzelińskie Hills, Lower Silesia. *Studia Geol. Pol.*, 20: 1-187.
- OBERC-DZIEDZIC T., PIN C., DUTHOU J.L., COUTURIE J.P., 1996: Age and origin of the Strzelin granitoids (Fore Sudetic Block, Poland). 87Rb/86Sr data. *N. Jb. Miner. Abh.*, 171 (2): 187-198.
- STĘPISIEWICZ M., 1977: Fizykochemiczne warunki powstawania minerałów pomagmowych w granitoidach strzelińskich. *Arch. Miner.*, 33 (2): 61-74.