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VESUVIANITE FROM THE GARBY IZERSKIE MT., LOWER SILESIA, POLAND

Abstract. The brownish vesuvianite from the calc-silicate rocks occurring on the Garby Izerskie Mt. was studied by means of chemical, optical, X-ray, thermal, as well as infrared and Mössbauer spectroscopic methods. The relatively high titanium and fluorine content and the shape of IR-absorption spectrum in the OH-stretching region are typical of the high-temperature, disordered structural form of this mineral.

Key-words: vesuvianite, Garby Izerskie Mt., Lower Silesia, Mössbauer spectroscopy.

INTRODUCTION

Vesuvianite was till quite lately one of the least understood rock-forming minerals. Only over the last 10 years a series of papers has made a considerable progress in our knowledge of chemistry, structure and physical properties of this mineral (e.g. Groat et al. 1992, 1993; Ohkawa et al. 1992, 1994). The discovery of the existence of two structural forms of vesuvianite, related to its origin: the high-temperature, disordered vesuvianite, typical of metamorphic calc-silicate rocks, and the low-temperature, ordered one, occurring in rodingite-type rocks (Allen, Burnham 1992; Ohkawa et al. 1994; Żabiński et al. 1994), is one of the most interesting results of these investigations.

The occurrences of vesuvianite in Lower Silesia, Poland, are known from at least 20 localities (Lis, Sylwestrzak 1986) but only in few cases were they the subject of modern investigations (e.g. Platonov et al. 1995). Therefore, it seems reasonable to supplement with detailed studies at least some of them, particularly the newly found ones like the vesuvianite from the Garby Izerskie Mt.

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GEOLOGICAL SETTING AND MINERALOGY

Calc-silicate rocks containing vesuvianite are exposed in the 'Stanisław' quarry, the Garby Izerskie Mt., which mines a quartz vein, developed in a dislocation zone. The dislocation zone of the Rozdroże Izerskie is associated with the Izera metamorphic rocks (probable Precambrian), which form the northern cover of the Variscan granitoid massif of the Karkonosze and together with it build the Karkonosze-Izera block (Fig. 1).

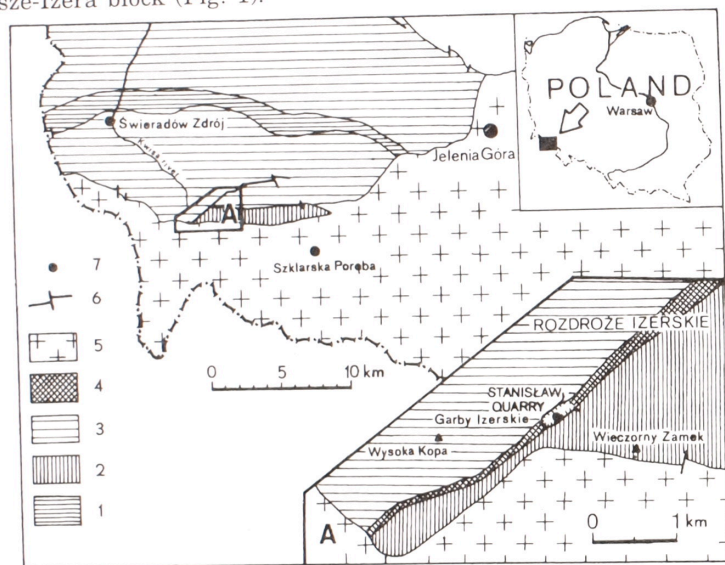


Fig. 1. Sketch geological map of a fragment of the Karkonosze-Izera block, after A. Kozłowski (1978)

1 — mica schists, 2 — hornfelses, 3 — Izera gneiss, Rumburk granite and leucogranite, 4 — quartz vein, 5 — Karkonosze granite, 6 — faults, 7 — skarn location; A — fault zone of Rozdroże Izerskie

The dislocation zone in question stretches over some kilometers from the Jastrzębia Mt. to NE, to the Piaskowa Mt., Rozdroże Izerskie, Garby Izerskie Mt., reaching the Karkonosze granite to SW (Fig. 1A). Its width ranges from 100 m to 300 m and pitch is 70° to SE (J. Szałamacha, M. Szałamacha 1966). It is strongly permeated with quartz and represents probably a deep fault, developed along a shear zone, accessible to penetration by mineral-forming solutions.

The cover of the quartz vein from NW blastomylonitic gneisses, Izera gneisses and granitogneisses, while from SE the vein contacts with cordierite hornfelses and hornfels schists with andalusite. Within the hornfelses there are streaks of calc-silicate rocks, often strongly permeated with quartz. Both the hornfelses and skarns were formed as a result of contact and metasomatic influences of the Variscan intrusion of the Karkonosze granite.

The hornfelses and skarns are intersected by granitic and pegmatoidal apophyses, containing hornblende, muscovite, tourmaline (schorl) and fluorite. Thin granitic apophyses are strongly enriched with andalusite along their contacts with the hornfelses. Their chloritized parts are strongly mineralized with pyrite and chalcopyrite.

The mineral composition of calc-silicate rocks is differentiated. Among skarns Kozłowski (1978) distinguished some varieties. Quartz-wollastonite rocks are the most often. Fibrous wollastonite forms sometimes bands with the thickness up to 10 cm, containing occasionally aggregates of greenish diopside and more rare ones of brownish garnet and vesuvianite. Slightly less often are rocks composed of diopside, quartz and wollastonite, of garnet, quartz, vesuvianite with wollastonite, epidote and diopside, and of garnet, diopside and quartz. The distinguished varieties most often grade continuously one into another. In places almost monomineral segregations have been formed, containing garnets (red) and vesuvianite (honey-brown). In most skarns, variable amounts of calcite and multicoloured fluorite may be found. Plagioclases (oligoclase-andesine), chlorites, Ti minerals represented by more often sphene and rare rutile are subordinate, while apophyllite, siderite and zeolites represent mineralogical rarities. Pure carbonate rocks — marbles — complete the rock inventory in the Garby Izerskie Mt.

In the skarns, a disseminated ore mineralization has also been found, represented mainly by pyrrhotite impregnations, accompanied by chalcopyrite. Pyrite, marcasite, sphalerite, tennantite, ilmenite, magnetite, hematite, covellite, and bornite after chalcopyrite are rare ore minerals. The chalcopyrite contains traces of native gold, whose local concentrations reach 4 g/t.

MATERIAL

The vesuvianite sample from Garby Izerskie was taken from quartz-garnet-vesuvianite skarn with a minor diopside content. The vesuvianite occurs there with garnets in the form of a pocket in the marginal zone between a light, quartz-diopside rock (hornfels?) and accumulations of coarse-crystalline quartz. The vesuvianite and garnet are most often intergrown, but sometimes their monomineral aggregates were observed. The vesuvianite of the brown-olive colour usually forms intergrowths of idiomorphic individuals, while well-developed crystals with sizes reaching 5 mm are rare. The crystals of vesuvianite with the same hand specimen features were also found in quartz-wollastonite-diopside skarn, where the mineral in question occurs as wide (2–3 cm) but flat (up to 1 mm) individuals, which form most probably polycrystalline intergrowths. No quartz was observed close to such a vesuvianite.

In the thin section the vesuvianite shows a very weak birefringence without anomalous interference colours, which are sometimes observed in vesuvianites. The indices of refraction are: $n_e \approx 1.709$ and $n_w \approx 1.710$.

CHEMICAL ANALYSIS

The vesuvianite was analysed using 'wet' chemical methods. The mineral was fused with Na₂CO₃ analytically pure and, for determination of alkalis, also dissolved in HF with a small admixture of H₂SO₄ (both analytically pure). SiO₂ was analysed by weight and supplemented by the amount of the silica remaining in the solution and determined colorimetrically with molybdenum-silica heteropolyacid. Also the amounts of H₂O(−) and H₂O(+) were determined by the weight method as the losses on ignition respectively at 110°C and 1000°C. The contents of FeO_(total),

TABLE 1

Chemical analysis of vesuvianite from Garby Izerskie Mts.

Component	wt. %	Number of cations on the basis of 78 (O, OH, F)	
SiO ₂	36.60	Si	18.028
Al ₂ O ₃	14.77	Al	8.575
B ₂ O ₃	0.04	B	0.034
TiO ₂	1.47	Ti	0.545
Fe ₂ O ₃	4.75	Fe ³⁺	1.761
FeO	2.73	Fe ²⁺	1.125
MnO	0.19	Mn	0.079
MgO	1.36	Mg	0.999
ZnO	0.024	Zn	0.009
Li ₂ O	0.006	Li	0.012
CaO	34.53	Ca	18.223
Na ₂ O	0.11	Na	0.105
K ₂ O	0.08	K	0.050
F	1.33	F	2.072
H ₂ O(+)	2.28	OH	7.491
Total	100.27		
− F = O	0.56		

Al₂O₃, CaO and MgO were determined by the complexometric methods in the presence, respectively, of salicylic acid, PAN, calces, and eriochrome black T as indicators. The true contents of FeO and Fe₂O₃ were estimated from the ratio Fe²⁺/Fe_(total), determined from Mössbauer spectrometry (see below). TiO₂, B₂O₃ and F were determined colorimetrically using, respectively, the peroxide, carmine, and Zr-eriochromo-cyanine methods. The alkalis (Na₂O, K₂O and Li₂O) and ZnO and MnO contents were determined by means of flame photometry and atomic absorption spectroscopy, using a PHILIPS 9100 B spectrometer and setting conditions recommended by the producer.

The results of the chemical analysis of vesuvianite from Garby Izerskie are presented in Table 1.

X-RAY INVESTIGATIONS

X-ray powder diffraction patterns were obtained by means of a DRÖN-3 (former USSR) diffractometer, using Ni-filtered CuK_α radiation. Interplanar spacings are presented in Table 2. They support the identification of this mineral and the purity of the examined sample. Its cell parameters are: *a* = 15.57(5) Å, *c* = 11.84(4) Å.

THERMAL INVESTIGATIONS

DTA and TG curves (Fig. 2) were recorded by means a Hungarian MOM Derivatograph controlled with microprocessor, the heating rate being 10°C/min.

TABLE 2

X-ray powder data for vesuvianite from the Garby Izerskie Mt.

Vesuvianite Garby Izerskie		Vesuvianite JCPDS 38—473		<i>hkl</i>	Vesuvianite Garby Izerskie		Vesuvianite JCPDS 38—473		<i>hkl</i>
<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	I		<i>d_{hkl}</i>	I	<i>d_{hkl}</i>	I	
11.063	6	10.989	2	110			2.604	40	531, 423
		9.434	1	011	2.599	47	2.591	55	600, 522
6.038	1	5.988	2	210	2.532	4	2.532	5	314
5.917	5	5.917	6	002	2.502	1	2.494	2	611, 442
5.491	1	5.495	2	220	2.460	48	2.457	40	620
5.205	1	5.208	1	112			2.439	10	324, 433
4.929	1			310	2.441	9	2.427	4	503, 532
		4.739	2	301	2.410	1	2.404	2	621, 513
4.713	4	4.717	5	202	2.378	6	2.375	6	541, 602
		4.525	1	311	2.350	6	2.353	6	404, 612
4.506	1	4.505	1	212			2.342	3	105
		4.049	4	321	2.328	6	2.326	10	414, 523
4.033	6	4.016	9	222	2.300	5	2.299	5	334
3.897	2	3.876	3	400	2.277	3	2.268	4	622, 631
		3.774	1	312	2.235	2	2.242	2	215
3.674	1	3.663	1	330	2.205	8	2.208	4	550, 710
3.483	11	3.472	9	420, 322	2.185	3	2.193	5	701
		3.425	1	213			2.179	3	711
3.356	6	3.333	1	421	2.164	4	2.155	5	640, 632
3.252	5	3.247	7	402			2.151	4	305, 613
3.191	1	3.175	2	412	2.146	2	2.141	3	434
3.157	3	3.135	1	303			2.132	12	641, 514
		3.115	1	332	2.126	13	2.119	10	315
		3.067	7	510	2.105	1			721
3.055	4	3.040	12	501, 431	2.086	4	2.083	5	325, 623
3.006	8	2.994	10	422			2.066	4	543, 524
2.952	19	2.950	35	004, 511	2.065	3	2.058	4	712, 552
2.908	4	2.907	4	323	2.045	6	2.041	6	730
2.850	5	2.849	3	114	2.027	3	2.024	4	642
2.819	1			521	2.013	7	2.008	4	444, 722
		2.762	12	432, 204			2.004	3	415, 633
2.752	100	2.767	100	440	1.998	5	1.996	9	534
		2.717	2	413, 214	1.979	1	1.976	1	006
		2.703	1	512	1.967	4	1.961	4	651
2.671	3	2.660	4	530			1.953	2	604, 524

The DTA curve shows an endothermic reaction (dehydroxylation) beginning at ca. 900°C, with a peak maximum at 1035°C. This peak is followed by a small exothermic peak at 1070°C. On the TG curve the weight loss of ca. 1.5% in the temperature range 900—1100°C was recorded.

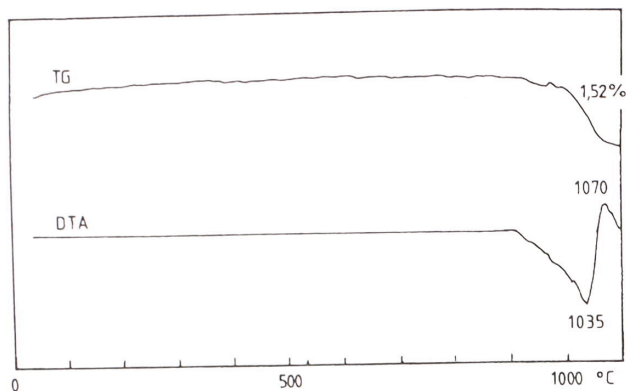


Fig. 2. DTA and TG curves of vesuvianite from the Garby Izerskie Mt.

INFRARED SPECTROSCOPY

FTIR spectrum (Fig. 3) was recorded using a BIORAD FTIR spectrometer. Sample was prepared as a KBr disc in a proportion of 1 mg sample to 300 mg KBr.

From the point of view of structure ordering the most characteristic is the OH-stretching vibration region of the spectrum (Żabiński, Paluszkiewicz 1994).

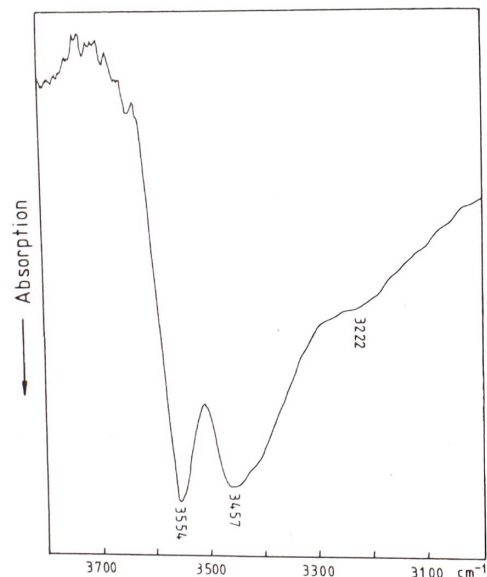


Fig. 3. IR spectrum of vesuvianite from the Garby Izerskie Mt. (the OH-stretching region)

The weak absorption band (inflection) ca. 3200 cm^{-1} , a sharp one ca. 3550 cm^{-1} and only weak absorption features in the region $3600\text{--}3700\text{ cm}^{-1}$ are typical of rather high (disordered) vesuvianites. An intensive band ca. 3460 cm^{-1} cannot be attributed only to water molecules (interstitial water, fluid inclusions etc.), since only weak band due to H_2O -bending vibrations ca. 1650 cm^{-1} appears. Groat et al. (1995) in their detailed, excellent paper on the OH-stretching region of vesuvianite, state that 'there is no evidence for H_2O groups in crystalline vesuvianite, although spectral features characteristic of H_2O were observed in radiation damaged samples'. Since this is not the case of our sample, the problem of 3400 cm^{-1} band requires further studies.

MÖSSBAUER SPECTROSCOPY

The Mössbauer spectroscopic investigations were carried out at the Institute of Nuclear Physics in Cracow-Bronowice. The $^{57}\text{Co(Rd)}$ with a radioactivity of about 25 mCi was used as a source. An absorbent was made in the form of a disc with the area of 2 cm^2 , the iron concentration was about 10 mg/cm^2 . The spectra were recorded at the room temperature. The numerical analysis of the spectra was done with a computer programme that fitted Lorenz curves to the experimental points using the smallest squares method. Isometric shift were given against $\alpha\text{-Fe}$.

The spectrum (Fig. 4) was divided on the three main doublets A-C and a very weak but distinct one D. On the basis of similarity of IS and QS parameters in our spectrum and those described by Polshin et al. (1995) the interpretation of the doublets is as follows: A (IS = 0.33 mm/s , QS = 0.56 mm/s , S = 44%) — Fe^{3+} in square pyramid $\text{Y}_1(\text{B})$ site (LK 5), B (IS = 0.39 mm/s , QS = 1.40 mm/s , S = 17%) — Fe^{3+} in $\text{AlFe}(\text{Y}_3)$ octahedra, C (IS = 1.16 mm/s , QS = 2.55 mm/s ,

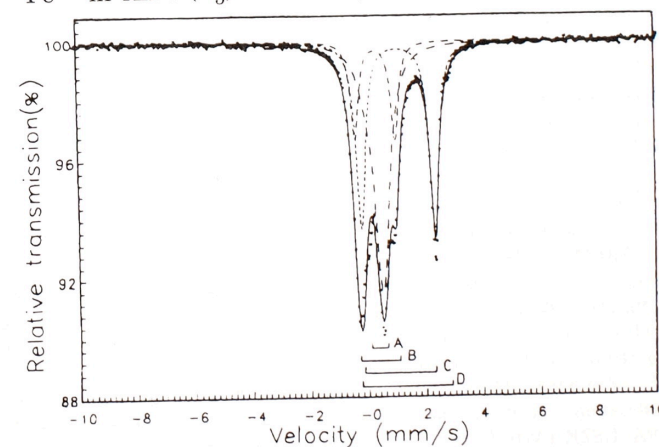


Fig. 4. Mössbauer spectrum of vesuvianite from the Garby Izerskie Mt.

S = 38%) — Fe^{2+} in AlFe (Y_3) octahedra. Weak doublet D (IS = 1.36 mm/s, QS = 3.16 mm/s, S = 1%), not described by Polshin et al. (1995), might correspond to the occurrence of trace amounts of Fe^{2+} in 8-coordinate Ca sites (Manning, Tricker 1975).

The above presented interpretation of the Mössbauer spectrum permitted to define rather precisely the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the vesuvianite studied.

CONCLUSIONS

Geological setting of the vesuvianite studied, which occurs in metamorphic calc-silicate rocks, determines it as a high-temperature, disordered variety (Allen, Burnham 1992). This is in accordance with its chemical composition, and particularly with relatively high Ti and F contents. Infrared spectrum in the OH-stretching region is also typical of high-vesuvianite.

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WEZUVIAN Z GARBÓW IZERSKICH (DOLNY ŚLĄSK)

Streszczenie

Przedmiotem badań był brunatny wezuwian występujący w skarnie kwarcowo-granatowo-wezuwianowym odsoniętym na terenie dawnej kopalni kwarcu „Stanisław” na Garbach Izerskich. Odznacza się słabą dwójłomnością, $i_e \approx 1,709$ i $n_o \approx 1,710$. Stosunkowo wysoka zawartość tytanu i fluoru, jak również charakter widma absorpcyjnego w podczerwieni w zakresie drgań rozciągających grup OH, są typowe dla wysokotemperaturowej, nieuporządkowanej odmiany strukturalnej wezuwianu, co pozostaje w zgodzie z geologicznymi warunkami jego występowania. Interpretacja widma Mössbauera pozwoliła określić pozycje sieciowe zajmowane przez jony Fe^{3+} i Fe^{2+} oraz stosunek ilościowy tych jonów.