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NEW DATA ON TARNOWSKITE (TARNOWITZITE) FROM TARNOWSKIE GÓRY

UKD 549.742.27.08:548.3:549.742.24(438.232 Tarnowskie Góry)

Abstract. A sample of tarnowskite (tarnowitzite) from Tarnowskie Góry (Upper Silesia) containing on the average more than 3.0 wt. % Pb ($> 3.9\%$ PbCO_3) was investigated by electron microprobe, X-ray, thermal and IR spectroscopic methods. It was found that not more than 1.5—2.0 mol.-% of CaCO_3 is replaced isomorphously by PbCO_3 , the remaining part of PbCO_3 being present in the form of finely dispersed cerussite.

INTRODUCTION

The name *tarnowitzite* was given by Breithaupt (1841) to a Pb-rich variety of aragonite first found in the area of Tarnowskie Góry in Upper Silesia (German name: Tarnowitz). In view of the fact that Tarnowskie Góry is an ancient Polish mining town, Bolewski (1975) suggested that the name tarnowskite be used for this mineral.

Tarnowskite from Tarnowskie Góry was described, e.g. in the papers of Traube (1888, 1889, 1894), who also mentioned earlier publications of other authors. More recently tarnowskite from Tarnowskie Góry has been studied by Heinze (1962) while Strzelska-Smakowska and Szuwarzyński (1978) described tarnowskite from Trzebionka near Cracow. This mineral was also reported from other countries: from Tsumeb (SW Africa), Castelminier (Ariege), and Postenje (Serbia) (Heinze 1962, Goni *et al.* 1965). Heinze thought it possible that in tarnowskite from Tarnowskie Góry lead substitutes for calcium in the crystal lattice of aragonite. He maintained, however, that lead occurs there mainly as dispersed cerussite.

Electron probe micrographs obtained by Goni *et al.* (1965) show clearly that cerussite and aragonite are separate phases in tarnowskite from Tsumeb. Goni did not detect lead in the crystal lattice of aragonite, so

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he assumed that its content must be lower than the detection limit of the method used.

Having a specimen (holotype) of tarnowskite from Tarnowskie Góry, coming from the collections of the Mineralogical Museum of the Wrocław University, the present author thought it advisable to investigate it using modern instrumental methods, presuming that they would throw some light on the controversial nature of this mineral.

EXPERIMENTAL

The mineral studied is a compact, radial crystal aggregate, light-green in colour. In places there are pronounced lighter, nearly white, bands of varying thickness, running perpendicular to the elongation of crystals.

This specimen was subjected to chemical, X-ray, thermal, and infrared spectroscopic investigations.

Chemical investigations

Chemical analysis was made using atomic absorption, X-ray fluorescence, and electron microprobe methods.

Atomic absorption was used to determine the total lead content in the sample, separately for the greenish and white parts. The data obtained on a Pye Unicam apparatus are as follows:

- greenish parts of the sample — 2.93% Pb, i.e. 3.8% PbCO₃
- white parts of the sample — 4.60% Pb, i.e. 5.9% PbCO₃.

The maximum lead content noted in tarnowskites from Tarnowskie Góry was ca. 7 wt. % Pb (or 9% PbCO₃, Traube 1888).

X-ray fluorescence was applied to check which trace elements are present in tarnowskite. Investigations were made on a Rigaku-Denki X-ray spectrometer. The spectrum (Fig. 1) displays pronounced peaks

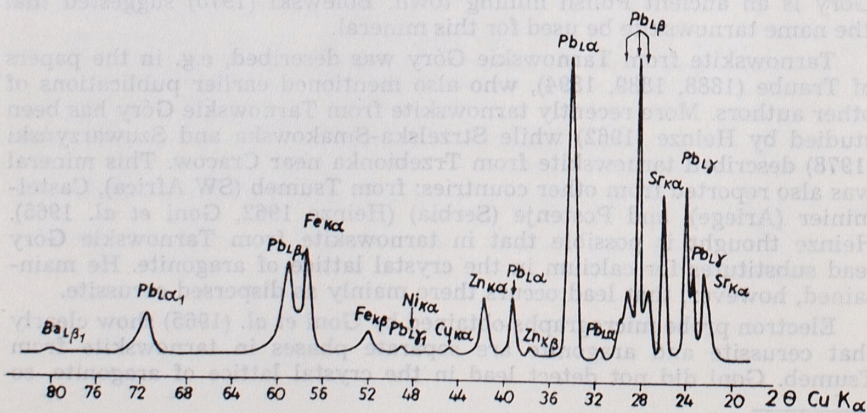
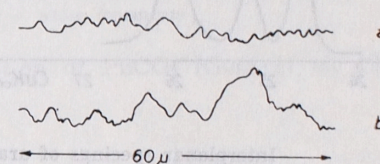


Fig. 1. X-ray fluorescence spectrum of tarnowskite from Tarnowskie Góry

owing to the presence of the following elements: Pb, Sr, Fe, Zn and traces of Ba, Cu, Ni. Worth noting is the substantial amount of strontium, which fact was already reported by Traube (1894), who found that some tarnowskite varieties from the former Fryderyk mine in Tarnowskie Góry had an SrO content up to 0.35%. The zinc content is relatively high as well, and Traube (1894) also noted this in one of his samples.

Surface distribution of lead was analyzed on a Jeol electron microprobe in the Institute of Physics and Chemistry of Metals, Silesian University. It has been found that lead is unevenly distributed in different parts of the sample, which is particularly conspicuous on images of back-scattered and secondary electrons, and less so on the image of surface lead distribution (Phot. 1). Apparently, slight changes in lead content affect markedly the electron images of the sample. This thesis was substantiated by linear analysis of lead distribution along a profile oriented transversely to the bands visible on electron images of tarnowskite (Photos 2a, 2b). These bands form zones from 2 to 20 micrometres in width. Figure 2

Fig. 2. Microprobe scan along the line for
a — Ca, b — Pb



presents Pb and Ca distribution along another profile. In places, antagonistic variations in the content of these elements were recorded. This, however, is no evidence of isomorphous substitution of Pb for Ca because lead can form a finely dispersed cerussite phase of grain size smaller than the electron beam diameter (Heinze 1962, Goni *et al.* 1965). Nevertheless, it will be noted that surface lead distribution shows clearly that this element is disseminated in all parts of the sample, seen as white and dark bands.

X-ray investigations

X-ray patterns were obtained with a Rigaku-Denki Geigerflex diffractometer, using powder technique and Ni-filtered Cu-K_α radiation. Instrument settings were: $U = 30$ kV, $i = 20$ mA, scanning speed $2^\circ/\text{min.}$, chart speed 20 mm/min.

X-ray diffraction pattern of the greenish parts of the sample did not show the presence of cerussite while the diffractogram of the whiter parts (Fig. 3) displayed not only aragonite reflections but reflections arising from cerussite as well ($d_{hkl} = 3.59$ and 3.49 Å).

To investigate the possible effect of lead on the lattice constants of aragonite, precise measurements of interplanar spacings were made for lead-free aragonite and for tarnowskite. To eliminate the error of non-axial alignment of the sample surface with the goniometer axis, quartz was used as internal standard. X-ray diffraction patterns were recorded

in the 2θ angle range from 67° to 83° , and the instrument settings used were: $U = 30$ kV, $i = 20$ mA, chart speed 5 mm/min., scanning speed $1/4^\circ$ /min. The results are listed in Table 1. Differences between the interplanar spacings of tarnowskite and aragonite are slight but marked. Assuming a linear change of the interplanar spacings with Pb content

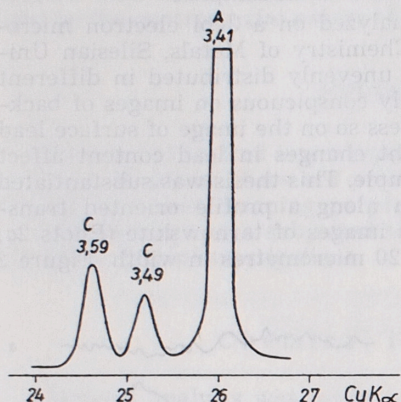


Fig. 3. A fragment of X-ray diffractogram taken for the white part of tarnowskite

A — aragonite, C — cerussite

Table 1

Interplanar spacings of aragonite, tarnowskite and cerussite

hkl	d_{hkl} (Å)		
	aragonite	tarnowskite (Tarnowskie Góry)	cerussite
153	1.189	1.190	—
243, 062	1.205	1.206	1.282
134	1.224	1.225	—
400	1.240	1.241	1.296
332	1.261	1.262	1.330

(Vegard's law) and insignificant influence of other cations present in tarnowskite, it has been estimated that not more than 1.5—2.0 mol % of CaCO_3 is replaced by PbCO_3 in the crystal lattice of aragonite.

Thermal investigations

Thermal analysis was made by differential scanning calorimetry method on a Du Pont thermoanalyzer in the Textile Institute in Bielsko-Biała. The DSC curve for an averaged sample of tarnowskite (Fig. 4a) shows the same endothermic peaks as for standard aragonite, as well as an additional peak at $t_{\text{max}} = 948^\circ\text{C}$ due to melting of PbO (Goni *et al.* 1965). The thermal curve obtained for the white parts of the sample exhibits aragonite peaks, as well as additional endothermic peaks at $t_{\text{max}} = 316$ and

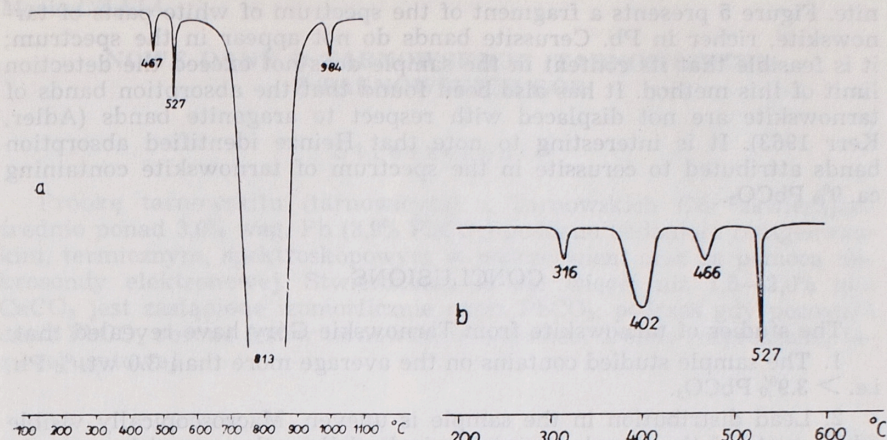


Fig. 4. DSC curves of tarnowskite
a — averaged sample, b — white fragments

402°C corresponding to step dissociation of PbCO_3 (Goni *et al.* 1965; Varne, Bayliss 1962).

Infrared spectroscopic investigations

Infrared spectra were obtained with a Zeiss Jena SPECORD 71 spectrometer using KBr discs. The spectra of tarnowskite (averaged sample and separated white parts) are similar to the spectrum of standard arago-

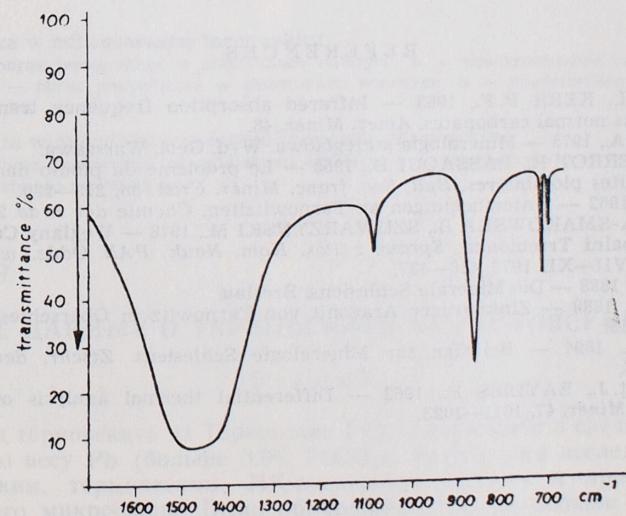


Fig. 5. IR absorption spectrum of the white parts of tarnowskite

nite. Figure 5 presents a fragment of the spectrum of white parts of tarnowskite, richer in Pb. Cerussite bands do not appear in the spectrum; it is feasible that its content in the sample does not exceed the detection limit of this method. It has also been found that the absorption bands of tarnowskite are not displaced with respect to aragonite bands (Adler, Kerr 1963). It is interesting to note that Heinze identified absorption bands attributed to cerussite in the spectrum of tarnowskite containing ca. 9% $PbCO_3$.

CONCLUSIONS

The studies of tarnowskite from Tarnowskie Góry have revealed that:

1. The sample studied contains on the average more than 3.0 wt. % Pb, i.e. $> 3.9\% PbCO_3$.
2. Lead distribution in the sample is uneven. Macroscopically visible white parts of the sample are richer in lead than the greenish parts. In the sample studied, the lead content in the white and green parts is 4.60% and 2.93% Pb, respectively. Due to electron microprobe analysis, well-defined, distinct zones 2—10 micrometres wide, differing in lead content, were detected.
3. There are limits to the substitution of lead for calcium in the lattice of aragonite. As appears from X-ray investigations, in the tarnowskite studied not more than 1.5—2.0 wt. % of $CaCO_3$ is replaced by $PbCO_3$ in the crystal lattice of aragonite. The remaining lead occurs as fine-crystalline cerussite.
4. Differentiation in the lead content in zones perpendicular to the direction of crystal growth testifies to rhythmical changes of the physico-chemical conditions of crystallization of tarnowskite.

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Maria CZAJA

NOWE DANE O TARNOWSKICIE (TARNOWICYCIE) Z TARNOWSKICH GÓR

Streszczenie

Próbkę tarnowskitu (tarnowicytu) z Tarnowskich Gór zawierającą średnio ponad 3,0% wag. Pb ($3,9\% PbCO_3$) poddano badaniom rentgenowskim, termicznym, spektroskopowym w podczerwieni oraz za pomocą mikroskopy elektronowej. Stwierdzono, że nie więcej niż 1,5—2,0% mol $CaCO_3$ jest zastąpione izomorficznie przez $PbCO_3$, podczas gdy pozostała część $PbCO_3$ obecna jest w tarnowskicie w postaci drobno rozproszonyj fazy cerusytowej.

OBJAŚNIENIA FIGUR

- Fig. 1. Spektrogram fluorescencji rentgenowskiej tarnowskitu z Tarnowskich Gór
- Fig. 2. Rozmieszczenie ołowiu i wapnia wzdłuż wybranego profilu
a — Ca, b — Pb
- Fig. 3. Fragment dyfraktogramu rentgenowskiego białej części tarnowskitu
A — aragonit, C — cerusyt
- Fig. 4. Krzywe DSC tarnowskitu
a — próbka uśredniona, b — białe fragmenty
- Fig. 5. Widmo absorpcyjne w podczerwieni białej części tarnowskitu

OBJAŚNIENIA FOTOGRAFII

- Fot. 1. Analiza w mikroobszarze tarnowskitu
a — obraz powierzchni w elektronach odbitych, b — powierzchniowe rozmieszczenie Pb, c — obraz powierzchni w elektronach wtórnych, d — powierzchniowe rozmieszczenie Pb
- Fot. 2. Analiza w mikroobszarze innego fragmentu tarnowskitu
a — obraz powierzchni w elektronach odbitych, b — rozmieszczenie Pb wzdłuż profilu zaznaczonego na Photo 2a

Марья ЧАЯ

НОВЫЕ ДАННЫЕ О ТАРНОВСКИТЕ ИЗ ТАРНОВСКИХ ГУР

Резюме

Образец tarnowskitu из Tarnowskich Gur, содержащий в среднем более чем 3,0% по весу Pb (больше $3,9\% PbCO_3$), подвергался исследованиям: рентгеновским, термическим, ИК-спектроскопическим и при помощи электронного микроскопа. Было обнаружено, что не больше 1,5—2,0% грамм-молекулярных $CaCO_3$ изоморфно заменены $PbCO_3$, в то же время

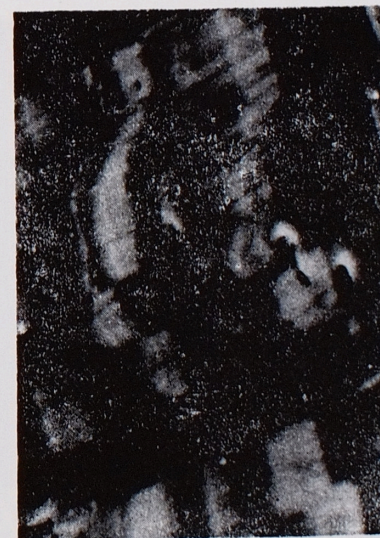
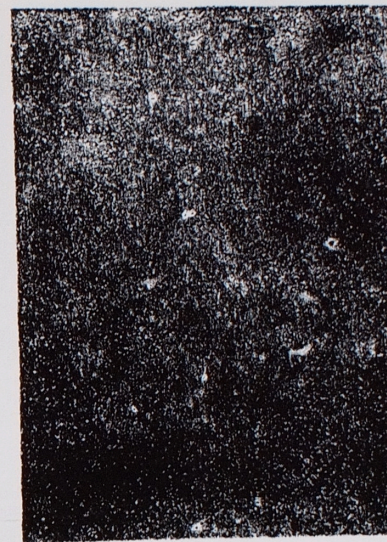
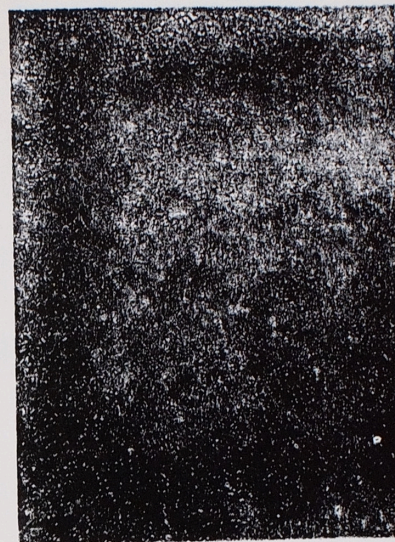
остальная часть $PbCO_3$ присутствует в тарновските в форме разрозненной церусситовой фазы.

ОБЪЯСНЕНИЯ К ФИГУРАМ

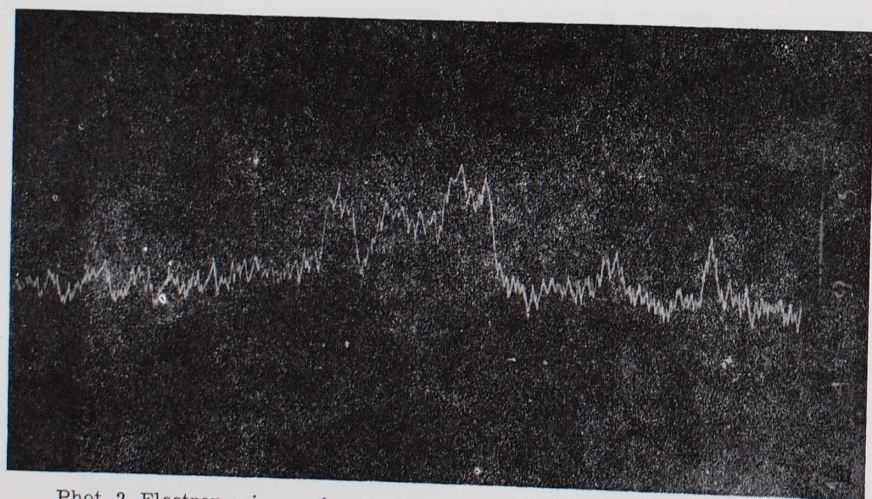
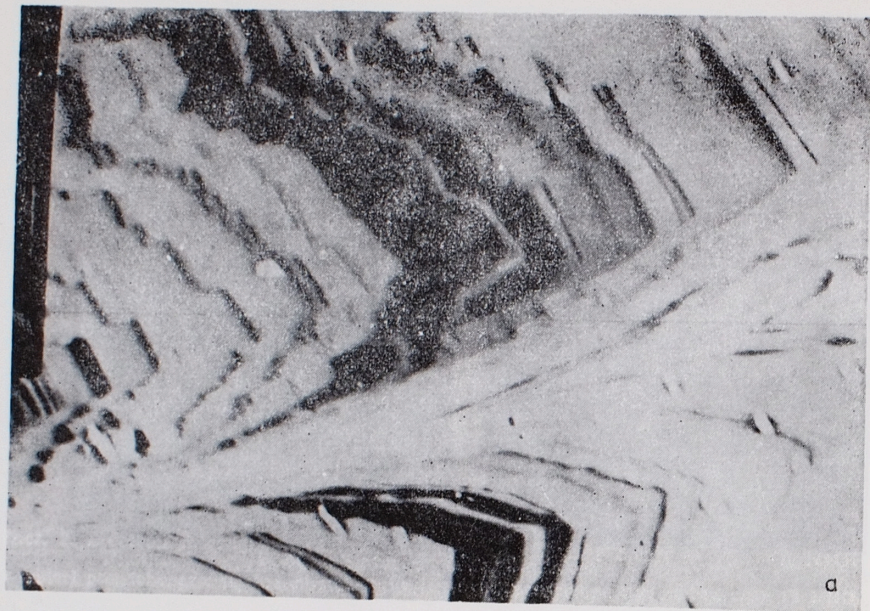
- Фиг. 1. Спектрограмма рентгеновской флуоресценции тарновскита из Тарновских Гур
Фиг. 2. Расположение свинца и кальция вдоль избранного профиля
а — Ca, б — Pb
Фиг. 3. Часть рентгеновской дифрактограммы белой части тарновскита
А — арагонит, С — церуссит
Фиг. 4. Кривые DSC тарновскита
а — усреднённый образец, б — белые части
Фиг. 5. ИК-спектр поглощения белой части тарновскита

ОБЪЯСНЕНИЯ К СНИМКАМ

- Фото 1. Анализ в микрозоне тарновскита
а — изображение поверхности методом отражённых электронов, б — поверхностное расположение Pb, с — изображение поверхности методом вторичных электронов, d — поверхностное расположение Pb
Фото 2. Анализ в микрозоне другой части тарновскита
вдоль профиля обозначенного на снимке 2а
а — изображение поверхности методом отражённых электронов, б — расположение Pb



Phot. 1. Electron-microprobe analysis of tarnowskite
a — backscattered electron image, b — Pb image, c — electron image, d — corresponding Pb image



Phot. 2. Electron microprobe analysis of another fragment of tarnowskite
a — backscattered electron image, *b* — scan for Pb along the line marked on the Phot. 2*a*

Maria CZAJA — New data on tarnowskite (tarnowitzite) from Tarnowskie Góry