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Tadeusz WIESER *

THE LUCIN- AND MESSBACH-TYPE VARISCITES FROM WIŚNIÓWKA (ŚWIĘTOKRZYSKIE MTS.)

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Abstract. Among the formerly described variscite specimens from Wiśniówka (Świętokrzyskie Mts.) small differences in the chemical and optical properties were detected in the two variously shaped and coloured varieties. Unfortunately, after examinations by X-ray powder methods this statement was not confirmed. At present, X-ray diffraction and infrared absorption spectra obtained from the new specimens permitted identification of two well discernable polymorphs of Lucin- and Messbach-type variscites. Both varieties were found together in spherules having internal parts occupied by Messbach- and external — by Lucin-type variscite. This phenomenon judging from the available sources is extremely rare in the nature, though similar physically to frequent co-occurrence of chalcedony and quartz.

INTRODUCTION

In the course of the optical and chemical determinations of variscite specimens from Wiśniówka Quarry (Świętokrzyskie Mts.) performed by Gucwa, Pelczar and Wieser (1960) two kinds of this mineral were discerned. Both occur, as a rule, together in the form of spherules. One of the varieties, microcrystalline-fibrous, of white colour, occupies the inner part of the spherule. Another one, phanerocrystalline-prismatic, of light apple-green colour, builds outer zone or crust of the spherule, taking the shape of radiating rods. White variety is chemically richer in ferric oxide (10,69 per cent) though the goethite films on cleavage surfaces are responsible for the bulk of the Fe_2O_3 content. Another distinguishing mark is a little lower maximum refractive index ($n_\gamma = 1{,}590$). The green variety, on the other hand, revealed the following indices of refraction: $n_\gamma = 1{,}593$, $n_\beta = 1{,}587$, $n_\alpha = 1{,}567$. The Fe_2O_3 content being smaller and equaling 4,03 per cent (by weight) only.

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* Carpathian Division, Geological Institute, Cracow (Kraków, ul. Skrzatów 1).

The more recent studies of minerals of variscite group, especially those carried out by Čech and Slanský (1965) facilitated the distinction of the two kinds of variscites, called now Lucin- and Messbach-types. This undoubtedly large attainment was further revised by infrared absorption spectra studies of the same varieties executed by the same authors three years later. Still later, Salvador and Fayos (1972) not only confirmed the existence of two mentioned polymorphic species of variscites but also elucitated the structural dependences, including those resulted from the appearance of two kinds of water molecules. Moreover, they pointed out the metastable crystalline state of Messbach-type variscite.

Other main object of this paper is also to clarify the genetic relations of strictly coexisting varieties of variscite. This phenomenon is extremely rare in nature, though common of Wiśniówka.

X-RAY DIFFRACTION ANALYSIS

The recently examined material comprised the heretofore and now available samples of variscite from Wiśniówka quarry of Middle Cambrian quartzites. To the formerly observed sequence: chalcedony ± goethite, quartz ± dickite, and variscite ± goethite a new member, namely wavellite should be added, which with illite and the second generation of dickite infills interspaces between variscite spherules. Wavellite appears in the shape of long prismatic, subhedral crystals and exhibits interplanar spacings typical for this mineral (8,42 Å; 5,64 Å; 4,75 Å, a.o.).

Variscite spherules (see Photography 1 and 2) composed of white interiors and green overcrusts were adequately crushed and possibly precisely separated. Analyzed with the Rigaku-Denki-type diffractometer (using CuK$_\alpha$ radiation and Ni-filter) conspicuous X-ray spectra has been revealed, especially but in green (Lucin-type) variety. The small quartz impurities, in addition to NaF used as an internal standard, facilitated measuring of lattice spacings. The full list of observed spacings and intesities of reflections of both Wiśniówka variscite varieties, as well as, of indices and calculated spacings reported by Salvador and Fayos (1972), are presented in Table 1.

The tabulated data, diagrammatically shown in Figure 1, correspond well to relatively pure Lucin- (green = *VL*) and Messbach-type (white = *VM*) polymorphs. As leading marks for Messbach-type may serve spacings with $2\,\Theta = 12{,}8^\circ$ (6,41 Å); 20,15° (4,406 Å); 32,7° (2,740 Å) and for Lucin-type with $2\,\Theta = 18{,}1^\circ$ (4,903 Å), a.o. Confronting the former X-ray D.S.H.-powder data for variscite from Wiśniówka obtained by Kubisz (Gucwa *et al.* 1960, p. 41) with here demonstrated results it may be inferred, that the formerly disponible material was composed in preponderance of Lucin-type variety. This conclusion may also be established taking into account the reported (*op. cit.*, p. 42) DTA-curve of variscite from Wiśniówka. In full agreement with features of this curve thermographic data presented by Čech and Slanský (1965) indicate the Lucin-type as responsible for peculiar thermal effects. The double endothermic peaks approaching to extremal values at 190°C and at 230°C seem to be characteristic only for Lucin-type variscite and differs evidently in respect to single peak for Messbach-type, culminating already at 180°C.

Table 1

X-ray diffraction data for Lucin- and Messbach-type variscites from Wiśniówka (indices and *d* calculated after Salvador and Fayos, 1972)

Lucin-type				Messbach-type			
hkl	*d* calc.	*d* obs.	*I*	*hkl*	*d* calc.	*d* obs.	*I*
111	5.358	5.356	68	012, 111	6,413*	6,410	8
200	4,903	4,908	14	112	5,385	5,382	60
020	4,810	4,806	36	020	4,831	4,829	35
002, 201	4,257*	4,26**	90	113, 210	4,404*	4,406	25
012, 211	3,910*	3,908	37	004, 202	4,288*	4,288	100
112	3,632	3,631	20	014	3,924	3,925	18
220	3,435	3,434	4	212	3,918	3,918	22
202	3,225	3,225	16	122	3,874	3,875	4
022, 221	3,188*	3,190	14	203	3,743	3,744	10
122	3,040	3,042	100	114	3,647	3,648	15
311	2,913	2,913	60	123, 220	3,459*	3,458	20
131	2,871	2,874	46	024, 222	3,210*	3,210	10
?	—	2,673	4	115, 214	3,076*	3,075	5
113	2,635	2,635	27	124	3,052	3,051	28
321	2,579	2,580	14	312	2,933	2,925	13
032, 231	2,566*	2,568	12	132	2,884	2,882	11
132	2,483	2,483	26	313	2,740	2,740	12
203	2,466	2,468**	5	125, 224	2,692*	2,690	20
400	2,454	2,454**	14	116	2,644	2,644	12
213	2,389	2.388	8	322	2,597	2,597	7
123	2,381	2,382	9	206, 400	2,478*	2,475	19
401	2,359	2,359	4	401	2,448	2,450	8
140	2,336	2,335	20	?	—	2,407	10
411, 332	2,291*	2,292	7	035, 140	2,349*	2,347	5
232	2,274	2,276**	8	042, 141	2,325*	2,325	8
331	2,212	2,214	3	117, 315	2,312*	2,311	5
223	2,195	2,196	3	135, 331	2,283*	2,284	6
240	2,160	2,160	4	413	2,209	2,211	3
004	2,140	2,140	15	226, 207	2,203*	2,201	4
313, 042	2,098*	2,098	2	143, 240	2,171*	2,171	2
241	2,094	2,095	3	008	2,147	2,147	28
133	2,083	2,084	20	127, 333	2,136	2,136	5
142	2,050	2,052	8	235	2,121	2,123	2
333	2,019	2,020	9	136	2,090	2,092	4
323, 204	1,963	1,962	16	243, 334	2,029	2,031	6

* One (nearest) of two values.

** Coincidence with quartz.

The introduction of such inconvenient terms as Lucin- or Messbach-type variscites is justificated from historical reasons as was already emphasized by Čech and Slanský (1965). These and other writers have commented upon the remarkable lack of unanimity and discipline in the applied nomenclature of polymorphs with the composition $AlPO_4 \cdot 2H_2O$. Small differences in the physical and chemical properties were interpreted as an evidence for existence of various minerals named separately as: peganite, tangeite, redondite, utahlite, lucinite a.s.o., in addition to the widely adopted names as variscite and clinovariscite or metavariscite. While the last mentioned terms as based on distinct dimorphism (orthorhombic and monoclinic symmetry) must be preserved, the previous ones should be discarded as superfluous.

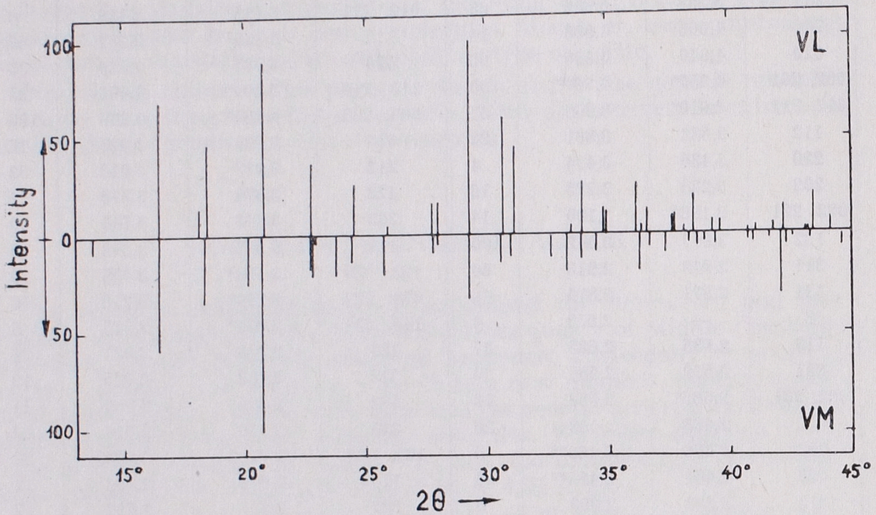

Fig. 1. Diagrammatic illustration of the X-ray spacings and reflection intensities for Messbach (*VM*)- and Lucin (*VL*)-types of variscites from Wiśniówka Quarry

Salvador and Fayos (1972) concluded finally that the duplication of unit cell dimensions along *c* axis, deduced from X-ray patterns of Lucin-type variscite, is the only possible way allowing a complete indexing of Messbach-type variscite. If so, the structural criteria should be taken as a base for nomenclature as was done for mica polymorphs and the inconvenient, long terms could be replaced by simple, short ones.

Further informations regarding internal structure of variscites supply infrared absorption spectra.

INFRARED SPECTROPHOTOMETRIC ANALYSIS

The infrared absorption spectra were recorded with C. Zeiss UR-10 IR-spectrophotometer on the separated samples of Messbach- and Lucin-types of Wiśniówka variscite. Figure 2 shows the curve runs of absorption spectra in the selected ranges limited by 400 and 3800 cm^{-1} frequencies. The smoothed run of curve for Messbach-type variscite (*VM*) is very striking and the divergence could be ascribed to the smaller degree of crystallinity. If a comparison could be given, then the relation between *VM* and *VL* is similar to that demonstrated by chalcedony and quartz, respectively.

Both *VL* and *VM* varieties exhibit strong absorbancy extrema in neighbourhood of 1070, 930, and 650 cm^{-1}. These are due to stretching and bending vibrations of tetrahedral PO_4^{3-}-ions. The interference caused by rotation and translation movements of water molecules hindered the assignment of effects to the corresponding vibration modes. Relative to the v_3 vibrational modes of the PO_4^{3-}-ions are three bands at 1150, 1070, and 1040 cm^{-1}, well discernable in *VL*. In *VM* three bands at 1145, 1070, and 1050 cm^{-1} are less accentuated (especially the splitting producing the last mentioned two peaks) what disagrees with the distinction of only two at 1145 and 1050 cm^{-1} or at 1140 and 1060 cm^{-1} bands by Salvador and Fayos (1972) or Čech and Slanský (1968), respectively. This phenomenon, similarly to the presence of two bands at 905 and 935 cm^{-1} assignable to v_1 modes im *VM* (in *VL* only one band at 935 cm^{-1}) may be interpreted by advancing recrystalization process of *VM* to *VL*. The 935 cm^{-1} peak in *VM* was not observed by Salvador and Fayos (1972).

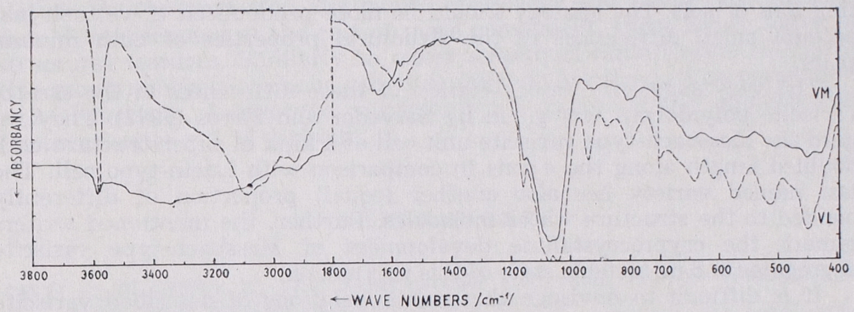

Fig. 2. The infrared absorption spectra of Messbach (*VM*)- and Lucin (*VL*)-type variscites from Wiśniówka quarry

In the region of 3580 and 3100 cm^{-1} frequencies the recorded bands are results of hydrogen bonds of different energy. It must be pointed out that especially those of *VM* appertainance are less marked than in variscites from Zamora (Spain), investigated by Salvador and Fayos (1972) which gave the full interpretation. The mentioned authors explain also two wide bands at about 1630 and 1570 cm^{-1} in the region of water molecule deformations. They infer the existence of two different types of water molecules, W_1 and W_2, explaining in this manner appearance of two endothermic effects near 190 and 230°C. Furthermore, the relative intensity of the bands at 3580 and near 1570 cm^{-1} is lower in *VM* than in *VL* spectrum. This is supposed to be the consequence of the lower content of W_2 water-type in the *VM* lattice ($W_1 : W_2 = 1 : 1$ for *VL* against $3 : 1$ for *VM*). Water molecules of W_1 type, attributed to 1630 cm^{-1} band, should be bonded to the lattice through two hydrogen atoms while molecules of W_2 type possess one link only.

GENETIC RELATIONS

The persistence of occurrence of the Messbach- and Lucin-type variscites in the sequence visible on Photographs 1 and 2 is noteworthy. It may be easily attributed to only possible order of crystallization, beginning with the fast growing, microcrystalline-fibrous Messbach-type variety and ending with slow crystallizing, phanerocrystalline-prismatic Lucin-type variety. Similar succession is observed in chalcedony and quartz deposition order of hydrothermal veins. This principally depends upon the state of saturation (concentration) of solutions with precipitating ions or sols. The analogy should be more pronounced if we took into account small differences in the structural properties of both mineral pairs.

The very suggestive interpretation of these differences in the case of variscite polymorphs was given by Salvador and Fayos (1972). They regard the Messbach-type variscite unit cell as a kind of superstructure with doubled length along the c axis in comparison with Lucin-type cell. The last named variety has also another (equal) proportion of differently bonded to the structure water molecules. Further, the mentioned writers remark the cryptocrystalline development of Messbach-type variscite aggregates and metastable state of this polymorph.

It is difficult to envisage the genetic relations of described variscite polymorphs from only structural standpoint. Their nature and quantitative proportions might vary considerably depending upon both the chemical composition of the solutions and the physical conditions under which the precipitation took place.

None of the true hydrothermal minerals was found in association with variscites in Wiśniówka quarry, as well as, elsewhere. Dickite is rather bounded with epigenetic alterations caused by acid solutions feebly heated geothermally (by deep burial). As remarked above the assemblages: chalcedony ± goethite, quartz ± dickite (I), variscite ± goethite, dickite (II) ± wavellite ± illite found in crevices and voids of quartzites in Wiśniówka Quarry constitute a well discernable sequence. It begins with chalcedony sometimes with goethite, which like quartz from the second assemblage could be deposited from oxidizing and weakly alkaline to neutral solutions. They become even acid, what proves the transformation of kaolinite to dickite or neocrystallization of dickite of first generation. The activity of acid solutions favored dissolution of phosphate minerals, like apatite, noted by Morawiecki (1928) as component of heavy mineral fraction in host rocks (Middle Cambrian quartzites). Furthermore, nearly in all Cambrian sediments the fossils are enriched in calcium phosphate.

Mobilized PO_4-ion was deposited after neutralization of solutions in the form of variscite, which usually together with goethite constituted the third assemblage. In the next assemblage symptoms of renewed acidification of solutions (from ground waters, compare illite illuvial pollution) are revealed by appearance of dickite of second generation. After neutralization, from the more diluted solution wavellite was growing (in place of variscite) as more suited to the changed conditions.

GENERAL REMARKS

The Wiśniówka variscite occurrence confirms the existence of two orthomorphic polymorphs. They may occur together with astonishing regularity of sequence. The Messbach-type variscite, like chalcedony, was deposited from more concentrated solution than his counterpart — Lucin-type variscite; this, like quartz after chalcedony, might be also the product of recrystallization of Messbach-type variscite.

It is proposed to replace now used names of variscite polymorphs. They fulfilled well its task of unification and common understanding of nomenclature. As the next step, the names Messbach- and Lucin-type variscite should be discarded at the cost of more convenient, short terms, based on structural features. Similarly to micas structural classification the variscite group minerals could be called as follows: Messbach-type variscite = 2 O variscite, Lucin-type variscite = 1 O variscite and clinovariscite (metavariscite) = 1 M variscite.

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Tadeusz WIESER

WARYSCYTY TYPU LUCIN I MESSBACH Z WIŚNIÓWKI (G. ŚWIĘTOKRZYSKIE)

Streszczenie

Waryscyty znajdowane w szczelinach i próżniach kwarcytów środkowokambryjskich w kamieniołomie Wiśniówka (Góry Świętokrzyskie) tworzą sferule zbudowane z dwu polimorfonów rombowych. Wewnętrzne partie sferul zajmują mikrokrystaliczny, włóknisty waryscyt typu Messbach a zewnętrzne — słupkowy waryscyt typu Lucin. Wykazały to dyfraktogramy rentgenowskie i spektrogramy absorpcyjne w podczerwieni. Odmiana typu Lucin krystalizowała wolniej z bardziej rozcieńczonych roztworów i jest po części produktem rekrystalizacji odmiany typu Messbach. Roztwory zasobne w aniony PO_4 pochodzą zapewne z rozpuszczenia apatytu, składnika akcesorycznego kwarcytów środkowokambryjskich (Morawiecki 1928) lub skamieniałości kambryjskich i in. wzbogaconych w fosforan wapnia. Ługowanie ułatwiał kwaśny odczyn (por. obecność dickitu) a wy-

padaniu waryscytu sprzyjała neutralizacja roztworów. Z roztworów bardzo rozcieńczonych wodami gruntowymi osadzał się natomiast bardziej uwodniony wavellit.

Autor proponuje zastąpić dotychczasowe niewygodne terminy dla minerałów grupy waryscytu, jak: waryscyt typu Messbach, typu Lucin i klinowaryscyt (metawaryscyt) przez nazwy bardziej zwięzłe, wzorowane na nazewnictwie mik, jak: 2 O waryscyt, 1 O waryscyt i 1 M waryscyt.

OBJAŚNIENIA FIGUR

Fig. 1. Diagram ilustrujący odstępy międzypłaszczyznowe intensywności refleksów u waryscytów typu Messbach (*VM*) i Lucin (*VL*) z kamieniołomu Wiśniówka

Fig. 2. Widma absorpcyjne w podczerwieni waryscytów typu Messbach (*VM*) i Lucin (*VL*) z kamieniołomu Wiśniówka

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Grupa przenikających się wzajemnie sferul złożonych z waryscytu typu Messbach i Lucin, występujących w kamieniołomie Wiśniówka. Delikatne włókna waryscytu typu Messbach łatwo wypadają z wnętrz sferul. Pow. × 12

Fot. 2. Przekrój pojedynczej sferuli waryscytu pokazujący budowę i stosunek skupień kryształów waryscytu włóknistego typu Messbach (partie wewnętrzne) do słupkowego typu Lucin (partie zewnętrzne). Pow. × 27

Тадеуш ВИЗЕР

ВАРИСЦИТЫ ЛЮСИНСКОГО И МЕССБАХСКОГО ТИПОВ ИЗ КАРЬЕРА ВИСЬНЮВКА (СВЕНТОКШИСКИЕ ГОРЫ)

Резюме

Варисциты, наблюдавшиеся в трещинах и пустотах в среднекембрийских кварцитах, обнажающихся в карьере Висьнювка (Свентокшиские горы), образуют сферолитовые формы, состоящие из двух ромбических полиморфных компонентов. Внутреннюю часть образований занимает микрокристаллический, волокнистый варисцит мессбахского типа, а внешние зоны сложены шестоватым варисцитом люсинского типа. Такое строение было определено с помощью рентгеновских дифрактограмм и ИК-спектров поглощения. Разновидность люсинского типа кристаллизовала медленнее из менее концентрированных растворов и частично является продуктом перекристаллизации мессбахской разновидности. Растворы богатые анионами PO_4 возникли очевидно за счет растворения апатита, представленного в виде акцессорного компонента в среднекембрийских кварцитах (Моравецки 1928), или кембрийских окаменелостей и других образований, обогащенных фосфатом кальция. Выщелачиванию способствала кислая среда (присутствие диккита), а выпадение варисцита происходило при нейтрализации растворов. После разбавления растворов грунтовыми водами осаждался вавеллит.

Автор предлагает заменить неудобные термины для минералов группы варисцита (варисцит мессбахского типа, люсиноского типа и клиноварисцит — метаварисцит) более сжатыми названиями, по примере названий слюд: 2 О варисцит, 1 О варисцит и 1 М варисцит.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Диаграмма, изображающая межплоскостные расстояния и интенсивность рефлексов варисцитов мессбахского типа (*VM*) и люсинского типа (*VL*) из карьера Висьнювка

Фиг. 2. ИК-спектры поглощения варисцитов мессбахского типа (*VM*) и люсинского типа (*VL*) из карьера Висьнювка

ОБЪЯСНЕНИЯ К ФОТОСНИМКАМ

Фото 1. Группа взаимно пронизывающихся сферолитовых форм варисцитов мессбахского и люсинского типов, наблюдающихся в карьере Висьнювка. Нежные волокна варисцита мессбахского типа быстро выпадают из сферолитовых форм. Увел. × 12

Фото 2. Разрез отдельной сферолитовой формы варисцита, показывающий строение и соотношение волокнистого мессбахского типа (внутренняя часть) с шестоватым люсинским типом (внешние части) в скоплении кристаллов варисцита. Увел. × 27

Phot. 1. A group of interpenetrating spherules composed of Messbach- and Lucin-type variscite, occurring in Wiśniówka quarry. Delicate fibers of Messbach-type variscite easily fall out the interior of spherules. Enlarged × 12

Phot. 2. Cross-section of a single variscite spherule showing the structure and relation of fibrous Messbach-type (interior part) to prismatic Lucin-type (outer part) crystal aggregates of variscite. Enlarged × 27