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THE OCCURRENCE OF α-$MnSiO_3$ IN THE MANGANESE-BEARING ROCKS OR THE TATRA MOUNTAINS

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A b s t r a c t. Manganese-bearing rocks occurring in the upper par of the Liassic crinoidal limestones in the Chochołowska Valley in the Tatra Mts. underwent silification. This process gives rise to manganese silicate. The chemical and X-ray analyses have shown that it is α-$MnSiO_3$ unown in nature. Liebau *et al.* (1958) obtained this modification by synthesis and demonstrated that it has the structure of triclinic, pseudohexagonal pseudowollastonite $Ca_3[Si_3O_9]$ with the ring structure of the silico-oxygen anion.

Manganese limestones occur in the upper part of the Liassic crinoidal limestones belonging to the Jurassic subalpine series of the Tatra Mts. They are located mainly over the Hucisko Glade in the Chochołowska Valley and beneath the Banie Peak over the Lejowa Valley. In these places there are old adits and dip-headings in which manganese ore was mined in the last century. Geological works were carried out in this area in the years 1953 and 1954 (Krajewski, Myszka 1958).

Samples for analysis were collected in the adits over the Hucisko Glade; some were taken from the collections of professor Krajewski.

The manganese rocks in question appear in the form of carbonate formations. The rock matrix of complex structure and red colour is made up essentially of calcite, manganocalcite and rhodochrosite. Among these formations there are streaks and concentrations of manganese oxides. The occurrences of oxidized compact black ore are rare. The crinoidal limestones together with the manganese-bearing beds were intensely silicified. This is evidence by hornfels laminae cutting the limestones and by a hornfels layer underlying them over a substantial length. In the bottom parts of the limestones silification due to remobilization of the silica from the hornfels rocks may be observed (Oszacka 1974).

Over the bottom of the deposit in one of the adits an ore has been noticed that differed from the other samples in greater hardness and darker

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red colour. A chemical analysis has shown the MnO content averaging 71% in the red part of the sample. In the material reduced to the grain size 0.2 mm, raspberry-red grains and violet-red compact fragments have been found besides the few black (manganese oxides) and white (calcite, silica) grains. After separating the black and white grains, this material was subjected to X-ray analysis, which has shown the presence of reflections characteristic of rhodochrosite and some weaker ones, indicating the presence of another crystalline phase. X-ray microanalysis in the selected microvolume, visible on the topographic electron image (Phot. 1), implied the presence of manganese silicate (Fig. 1). On the electron image

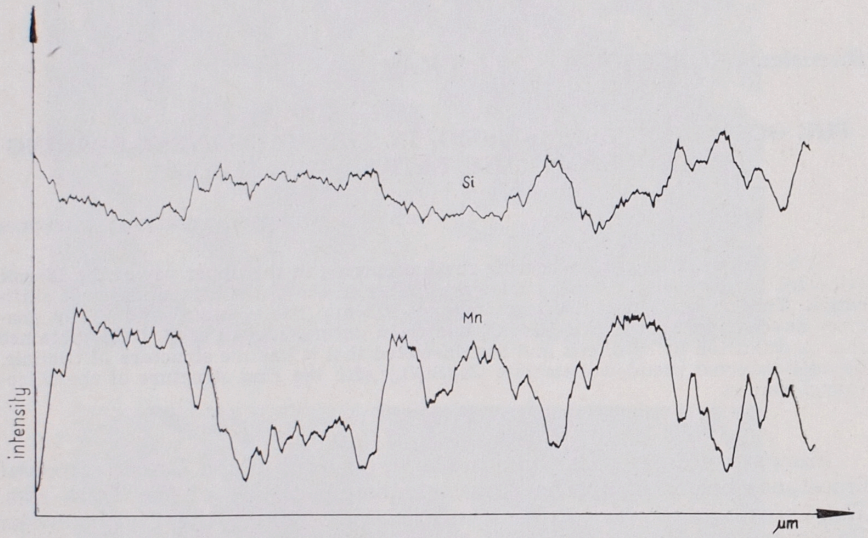

Fig. 1. Mn and Si distribution along the A—A′ line on the polished surface of sample (marked on Phot. 1)

of the manganese and silicon distribution in the given microvolume, areas with a substantial Si content (Phot. 2) and fairly high Mn content (Phot. 3) can be seen. In such regions, local analyses were performed, which have shown that the content of SiO_2 is 41.5%, that of MnO — 50.0% and of CaO — 0.7% (total: 92.2%). Also trace amounts of Fe and the lack of other components have been ascertained. The analyses were carried out on the electron microprobe MS-46 Cameca, using the following parameters: accelerating voltage 20 kV, beam current 150 μA, sample current 15 μA. The sample surface was coated with gold, and manganese and SiO_2 were used as standards *.

Parallel to these analyses, attempts were made at separating the violet-red substance from the broken up material by eliminating red rhodochrosite. To attain this, rhodochrosite grains were picked out manually, and

* The analysis was performed in the Institute of Metallurgy of the Academy of Mining and Metallurgy in Cracow.

then the broken sample was treated with ln HCl for 1 hour at room temperature. The two samples thus obtained were subjected to X-ray analysis (Tab. 1, columns 1*a* and 1*b*). It has been found that the recorded reflections correspond to the d_{hkl} values given by Liebau *et al.* (1958) for the synthetic α-$MnSiO_3$ (Tab. 1, column 3). To check whether the identification of α-$MnSiO_3$ was correct, the synthesis of this silicate was carried out by the present author, following the instructions given in the latter quoted publication. This permitted an X-ray analysis of the natural and synthetic silicate to be made under the same experimental conditions. Pure natural silica and manganous carbonate p.a. in the 1 : 1 molar ratio were used for synthesis. The reaction was run in argon atmosphere in Mettler thermoanalyser. The pressure in the reaction space was equal to the external pressure. Thermocouples Pt-PtRh 10% and platinum crucibles of the volume 0.99 mm^3 were employed, and Al_2O_3 was used as neutral substance. The sample was heated from 20 to 650°C at a rate of 10°/min. The product was kept isothermally for 2 hours at the temperature attained. As appears from the DTA and TG curves, the decomposition of $MnCO_3$ began at 270°C, with the maximum falling at 370°C (Orewczyk, Oszacka 1974). The resultant product of synthesis was subjected to X-ray analysis which has shown that the recorded reflections correspond to the d_{hkl} values of α-$MnSiO_3$ reported by Liebau *et al.* (1958) (Tab. 1, column 3). X-ray examinations of the sample insoluble in ln HCl (Tab. 1, column 1*b*) were carried out by film technique in VEM apparatus with a 114.6 cm camera, applying CoK_α radiation (λ = 1.788896 Å) with Fe filter, a voltage of 35 kV and a current of 10 μA. The other samples were analysed on TUR M 61 diffractometer with filtered CoK_α radiation (λ = 1.7889 Å), at a counter speed of 1°/min for the synthetic product (Tab. 1, column 2) and 0.5°/min for the natural sample (column 1*a*) and a tape feed rate of 600 mm/h. The position of the reflections was calibrated with quartz. The silicate under study is so fine-crystalline that X-ray examinations on a monocrystal are not possible.

A photograph made by means of scanning microscope at 1000-fold magnification (Phot. 4) reveals the presence of narrow, intergrown, tabular crystals.

In hypergenic processes, in which crinoidal limestones were formed and then mineralized, a temperature of 650°C that was applied for the synthesis is unattainable. However, tectonic movements, e.g. displacement of a manganese limestone layer reported by Krajewski and Myszka (1958) as well as numerous faults causing in places the brecciation and crumbling of rocks, could have resulted in a local increase in temperature of the limestones, though certainly not to 650°C. It is known from thermal analyses that the heating rate affects considerably the temperature of some thermal effects, its reduction causing, as a rule, a decrease in this temperature. A decrease in the temperature of $MnCO_3$ decomposition with a reduction in the heating rate has been noted by Orewczyk (1973). Under the geological conditions, the process rate must have been incomparably lower; this could have resulted in a substantial decrease in both the temperature of rhodochrosite decomposition and the reaction temperature of the products of its decomposition with the colloidal silica solution. There seems to be a similarity between the rise of this silicate and the formation of

X-ray data

Investigated silicate from Tatra Mts				Synthetical α $MnSiO_3$ (made by author)		Synthetical α $MnSiO_3$ (Liebau *et al.* 1958)	
a		*b*					
I	d_{hkl}(Å)	*I*	d_{hkl}(Å)	*I*	d_{hkl}(Å)	*I*	d_{hkl}(Å)
1				2		3	
a		*b*					
4	4,931		—	3	4,920	*m*	4,923
	—		—		—		
5	3,090	4	3,097	6	3,095	*m*	3,091
						w	2,888
8	2,773	9	2,756	2	2,775	*vs*	2,773
10	2,490	10	2,491	10	2,490	*vs*	2,490
3	2,364	—	—	3	2,360	*vw*	2,366
2	2,033	4	2,027	2	2,044	*m*	2,046
	—	3	1,802		—	*w*	1,802
	—				—	*vw*	1,700
4	1,578	5	1,578	7	1,571	*s*	1,579
4	1,543	5	1,543	6	1,547	*s*	1,546
		3	1,443		—	*w*	1,444

chamoisite, which in the laboratory conditions forms as a product of high--temperature reactions whereas in nature it owes its origin to low-temperature processes (Ramdohr 1960). The above considerations account for the formation of the silicate in question in the discussed Tatra rocks.

Basing on thermal and X-ray analyses, Liebau *et al.* (1958) distinguished three polymorphic modifications of $MnSiO_3$. The gamma modification has a 5-repeat-unit chain silico-oxygen anion $[Si_5O_{15}]$; it is represented in nature by rhodonite with the formula $Mn_{0.8}\ Ca_{0.2}(SiO_3)$ (Tab. 1, column 4). The parameters of the unit cell are given in table 2. The beta modification has a 3-repeat-unit chain silico-oxygen anion $[Si_3O_9]$, being isotypic with beta-wollastonite and bustamite (Ca, Mn) $[SiO_3]$ occurring in nature (Tab. 1, column 5 and Tab. 2). The α-$MnSiO_3$ modification has been known so far as a synthetic product (Liebau *et al.* (1958)), obtained in microcrystal-

Table 1

for $MnSiO_3$

γ $MnSiO_3$ (Liebau *et al.* 1958)		Natural rhodonite (Liebau *et al.* 1958)		β $MnSiO_3$ (Liebau *et al* 1958)		Natural bustamite (Liebau *et al.* 1958)	
I	d_{hkl} (Å)	*I*	d_{hkl} (Å)	*I*	d_{hkl}(Å)	*I*	d_{hkl} (Å)
4				5			
a		*b*		*a*		*b*	
w	4,067		—		—	*vvw*	7,190
vw	3,830		—		—	*vvw*	4,780
vw	3,560	*vw*	3,566			*vvw*	4,490
vw	3,349	*vw*	3,349	*w*	3,692	*vw*	3,700
w	3,133	*w*	3,124			*vvw*	3,560
vs	2,960	*s*	2,981	*w*	3,389	*vw*	3,410
s	2,758	*s*	2,773		—	*vvw*	3,290
vw	2,677		—	*w*	3,153	*m*	3,190
vw	2,605		—		—	*vvw*	3,096
vvw	2,513	*vvw*	2,519	*w*	2,988	*m*	2,989
vw	2,449		—	*vs*	2,893	*vs*	2,880
w	2,268	*w*	2,220		—	*w*	2,711
w	2,188	*w*	2,169	*vvw*	2,567	*vw*	2,621
vww	2,129	*w*	2,112		—	*vvw*	2,556
vvw	2,083		—	*vvw*	2,462	*vw*	2,462
vvw	1,896		—	*vw*	2,394	*vvw*	2,408
vvw	1,823			*vw*	2,273	*vw*	2,260
vw	1,730	*vvw*	1,724	*w*	2,193	*vw*	2,227
vw	1,694	*vvw*	1,693	*vw*	2,121	*w*	2,117
vvw	1,670					*vw*	2,082
vvw	1,600					*vw*	2,016
vvw	1,548			*vvw*	1,922	*vvw*	1,956
vw	1,484	*vw*	1,476	*w*	1,787		
w	1,428	*w*	1,432	*vw*	1,733		

line form. Its debeyogram shows a striking similarity to that of pseudo-wollastonite, which is characterized by ring structure of the silico-oxygen anion $[Si_3O_9]^{6-}$ (Tab. 1, columns 3 and 6). The structural data are given in Table 2.

It appears then from the investigations performed that manganese silicate that has been recorded in the Tatra manganese-bearing rocks may be regarded as the natural modification α-$MnSiO_3$.

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Table 2

Structural data of some Mn and Ca silicates (after Strunz 1970)

Mineral	Formula	Unit cell	
		type	parameters
Rhodonite	$CaMn_4[Si_5O_{15}]$	Triclinic $C_i^1 = P\bar{1}$	a_0 7,79, b_0 12,47, c_0 6,75 $a_0 : b_0 : c_0 = 0{,}625 : 1 : 0{,}541$ α 85°10′ β 94°04′ γ 111°29′ $Z = 2$
Bustamite	$(Mn, Ca)_3[Si_3O_9]$	Triclinic $A\bar{1}$	a_0 7,74, b_0 7,16, c_0 13,82 $a_0 : b_0 : c_0 = 1{,}081 : 1 : 1{,}930$ α 90°31′ β 94°35′ γ 103°52′ $Z = 2$
Pseudowollastonite (Cyclowollastonite)	$Ca_3[Si_3O_9]$	Triclinic (pseudohexagonal)	a_0 6,90, b_0 11,78, c_0 19,65 $a_0 : b_0 : c_0 = 0{,}586 : 1 : 1{,}668$ $\alpha = \beta = 90°$ $\gamma = 90°48'$ $Z = 8$

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O WYSTĘPOWANIU α-$MnSiO_3$ W TATRZAŃSKICH UTWORACH MANGANOWYCH

Streszczenie

Utwory manganowe występujące w górnej partii liasowych wapieni krynoidowych pomiędzy Doliną Chochołowską i Lejową w Tatrach podlegały sylifikacji. Jednym z przejawów tego procesu jest powstanie krzemianu manganu. Przy pomocy badań chemicznych i rentgenowskich ustalono, że jest to α-$MnSiO_3$. Odmianę tę, nieznaną dotychczas w przyrodzie, otrzymali na drodze syntezy Liebau i współpracownicy. Ustalili oni, że ma ona strukturę trójskośnego (pseudoheksagonalnego) pseudowollastonitu $Ca_3[Si_3O_9]$ o pierścieniowym anionie krzemotlenowym.

OBJAŚNIENIE FIGURY

Fig. 1. Krzywa koncentracji Mn i Si wzdłuż linii sondowania A—A′ na polerowanej powierzchni próbki

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Elektronowy obraz topograficzny 200×200 nm. Pow. × 215

Fot. 2. Obraz rozmieszczenia Mn—Kα. Pow. × 215

Fot. 3. Obraz rozmieszczenia Si—Kα. Pow. × 215
Analiza rentgenospektralna w mikroobszarze. CAMECA MS-46 pow. × 215

Fot. 4. Skupienie osobników badanego krzemianu manganu. Mikroskop scanningowy S 410 (Cambridge). Pow. × 1000

Бронислава КОРЧИНЬСКА-ОШАЦКА

О РАСПРОСТРАНЕНИИ α-$MnSiO_3$ В МАРГАНЦЕНОСНЫХ ПОРОДАХ ТАТР

Резюме

Марганценосные породы, залегающие в верхнем интервале лейасовых криноидных известняков между долинами Хохоловской и Лейовой в Татрах, подверглись силицификации. Одним из проявлений этого процесса является образование силиката марганца. Химическим и рентгеновским анализом был определен его состав α-$MnSiO_3$. Эта разновидность была получена путем синтеза Либау и его сотрудниками и до сих пор в природе не встречалась. Указанными авторами было установлено, что она обладает структурой триклинного (псевдогексагонального) псевдоволластонита $Ca_3[Si_3O_9]$ с кольцевым кремнезёмным анионом.

ОБЪЯСНЕНИЯ К ФИГУРЕ

Фиг. 1. График концентрации Mn и Si по линии зондирования A — A′ на полированной поверхности образца

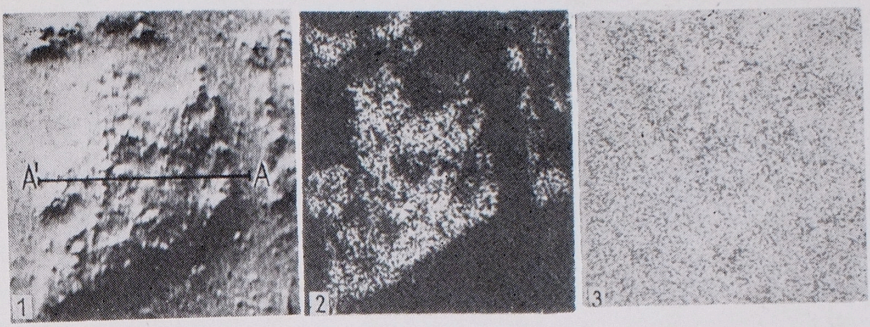
ОБЪЯСНЕНИЯ К ФОТОСНИМКАМ

Фото 1. Электронный топографический образ 200 × 200 μм. Увел. ×215

Фото 2. Образ распределения Mn-Kα. Увел. ×215

Фото 3. Образ распределения Si-Kα. Увел. ×215
Рентгеноспектральный анализ на микроучастке CAMECA MS-46. Увел. ×215

Фото 4. Скопление индивидов силиката марганца. Сканинг-микроскоп S 410 (Кембридж). Увел. ×1000



1. Image of secondary electrons (topography) 200×200 μm. Enlarged × 215. 2. Mn—Kα distribution. Enlarged × 215. 3. Si—Kα distribution. Electron-probe microanalyse. CAMECA MS-46 × 215. 4. Aggregate of plates of investigated Mn silicate. Scanning electron micrograph. Enlarged × 1000

Bronisława KORCZYŃSKA-OSZACKA — The occurrence of $MnSiO_3$ in the manganese-bearing rocks of the Tatra Mountains