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MINERALOGICKÁ URČENÍ NĚKTERÝCH ČESKOSLOVENSKÝCH SERPENTINOVÝCH AZBESTŮ

MINERALOGICAL IDENTIFICATION OF SOME CZECHOSLOVAK SERPENTINE ASBESTOS

(Z referátu na konferenci o azbestových nerostech, Oxford, 21. 7. 1967)
(From a Report on the conference about Asbestos Minerals, Oxford, 21. 7. 1967)

Úkolem této práce i referátu je podat přehled o některých hlavních výskytech serpentinových azbestů na území Československa. Zabývali jsme se azbesty z lokalit Přísečnice, Hrubšice, Nová Ves, Letovice a Dobšiná. Práce obsahuje především mineralogickou identifikaci několika metodami. Rentgenografický výzkum byl prováděn na Guinierově fokusační komoře podle P. M. de WOLFFA. Monokrystaly azbestových minerálů byly snímkovány též na Weissenbergově goniometru. Byly pořízeny rotační diagramy při ose rotace ve směru prodloužení vláken a vypočítány mřížkové parametry v tomto směru. Od všech studovaných vzorků byly provedeny chemické analýzy a z nich vypočítána množství iontů, jež připadají na jednotkovou buňku ideálního vzorce pro serpentiny. Na studovaných vzorcích byl rovněž vyzkoušen účinek kyseliny solné. Optická pozorování byla prováděna na práškových preparátech, u některých vzorků byly určeny indexy lomu na Fjodorovově stolku bivariační metodou. Od všech studovaných serpentinů byly rovněž provedeny křivky DTA. U jednotlivých nalezišť je podána též stručná geologická charakteristika.

Po shrnutí výsledků provedených analýz byly studované vzorky z Přísečnice, Nové Vsi a Hrubšic určeny jako směsi *ortochryzotilu* a *klinochryzotilu,* vzorek z Dobšiné jako téměř čistý *klinochryzotil* a vzorek z Letovic byl určen jako vláknitý *antigorit* se zvýšeným obsahem Fe.

Závěrem děkujeme dr. D. Ulrichové za provedení DTA ve speciálních laboratořích Ústředního ústavu geologického v Praze.

In the territory of Czechoslovakia serpentine asbestoses occur only in deposits of small extent. Deposits have been found in the following areas: western Bohemia, western Moravia, and central Slovakia. The purpose of our work was above all a mineralogical identification of serpentine minerals from the following localities:

Přísečnice — north-western Bohemia
Hrubšice, Nová Ves — western Moravia
Letovice — north-western Moravia
Dobšiná — central Slovakia

In the introduction we submit a brief geological characteristic of these deposits.

Přísečnice — the *serpentine* of this locality is of a coarse rodlike structure, with a greasy lustre, light brownish-yellow to brownish-green. It is based on fine-grained scarn, formed predominantly of *magnetite.* The epigenetic scarn deposit is deposited, together with dolomite, in orthogneiss of from Algonkian to Cambrian age, and also *talc* and *actinolite* occur here.

Hrubšice and Nová Ves — these localities are placed in the largest *serpentinite* body in Moravia. Here *asbestos* forms very fine, from gray-green to gray-brown fibres with a silky lustre.

Letovice — here *asbestos* occurs in greenish *seprentinite* of moldanubic age, which forms an exceptionally strongly stratified rock deposited in gneiss. Here unusual is the occurrence of *calcite.* The *serpentine* of this locality is coarsely rodlike, distinctly partible, gray-green with a greasy lustre.

Dobšiná — here *asbestos* forms the only deposit extracted at present in Czechoslovakia. It occurs in veins of a maximum thickness of 3 cm. Here the mother rocks is a body of serpentinized basic eruptive rock deposited in the lower Trias. If examined macroscopically *asbestos* is very finely fibrous, with silky lustre, and of light-gray-green colour. Here of mineralogical interest are ample occurrences of light green *garnets-andradites* on serpentinite cracks.

In the study of asbestos minerals from these mentioned localities chemical, optic, X-ray, and thermic methods were applied, and of some samples electron optical photographs were made.

Investigations were made on these samples from the collection of the Mineralogical departement of the National Museum of Natural History.

Přísečnice — inv. No. 5.834,
Hrubšice — inv. No. 21.360,
Nová Ves — inv. No. 27.764,
Letovice — inv. No. 31.728,
Dobšiná — inv. No. 52.734.

Chemical composition:

For the determination of the chemical composition of the investigated serpentines chemical analyses were performed. Table 1. contains the results of these analyses of samples from Hrubšice, Dobšiná, and L e t o v i c e . In the individual analyses the numbers of ions belonging to the unit cell in the ideal formula for serpentines — $Mg_3Si_2O_5(OH)_4$ — were calculated on the basis of 9 (O,OH). From the results obtained it can be seen that the chemical composition of serpentines from H r u b - š i c e and D o b š i n á does not differ substantially from the average analyses of chrysotiles. The sample of the L e t o v i c e locality shows a somewhat different chemical composition. It has a slightly increased Al content, which is in conformity with the chemism of platy serpentines as mentioned in the works of F. H. GILLERY (1959) and E. W. RADOSLOVICH (1963). Striking is here the high content of ferrous iron (approximately 5 per cent of FeO, and the lower content of Mg (approximately 34 per cent of MgO than found in average analyses of antigorites. It may be assumed that magnesium is isomorphously replaced by ferrous iron.

The samples were treated also with 1 n HCl at a temperature of 100 °C for one hour. After treatment with hydrochloric acid the X-ray lines disappeared in the X-ray photographs of all samples with the exception of the those from Letovice, in which the treatment with HCl did not change the X-ray photographs. This fact conforms to the results obtained in chemical analyses and confirms the fact that the serpentine from Letovice could be identified as an antigorite and the others as chrysotiles.

O p t i c a l i n v e s t i g a t i o n :

Optical observation of the studied samples was carried out on powder samples.

Under the microscope asbestos from P ř í s e č n i c e appears fibrous, insignificantly pleochroic. In the α direction it is straw-yellow, and in the γ direction greenish-yellow. Its refraction indexes have the following values

$N\gamma$ = 1,571,
$N\alpha$ = 1,562,
birefringence = 0,009.

While the birefringence corresponds to γ-chrysotile, his refraction indexes are extraordinaly high. The mineral was determined safely by X-ray investigation.

Under the microscope the asbestos material from the N o v á V e s locality appears as fine, long-fibrous, at places curved and easily partible. It is colourless and without pleochroism. The sign of elongation was determined as being positive. The indices of refraction were measured as follows:

$N\gamma$ = 1,552,
$N\alpha$ = 1,542,
birefringence = 0,010.

The asbestos mineral from the Hrubšice locality has almost the same optical constants as has the preceding: indices of refraction:

$N\gamma$ = 1,553,
$N\alpha$ = 1,544,
birefringence = 0,009.

sign of elongation positive.

Under the microscope the fibres form up to long-columnar crystals with moderate pleochroism. In the α direction it is from colourless to slightly yellow, and in the γ direction it is greenish-yellow.

Under the microscope the serpentine from Dobšiná appears long and finely filamentous and distinctly pleochroic. In the α direction it is of straw-yellow colour, in the γ direction it is greenish-yellow. The sign of elongation was determined as being positive and the refraction indices have the following values:

$N\gamma$ = 1,656,
$N\alpha$ = 1,534,
birefringence = 0,011,

and sign of elongation positive.

The microscopic picture of serpentine from the Letovice locality shows a yellowish-green colouring and long laths. The refraction indices were measured in this case on an universal stage by means of the double variation method. The following values were determined:

$N\gamma$ = 1,573,
$N\alpha$ = 1,570,
birefringence = 0,003,

sign of elongation positive, and optic sign negative.

Generally it can be said that chrysotile samples show lower values of refraction indices and a higher birefringence, whereas in the case of fibrous antigorite the opposite is true.

X-ray investigation:

Of the samples of the studied asbestos minerals from the five mentioned localities powder X-ray diagrams were made by means of the focusation method in the camera after P. M. de WOLFF with $CuK\alpha$ radiation. Difraction diagrams of three types were obtained. The samples from Přísečnice, Hrubšice, and Nová Ves give almost identical X-ray pictures, whereas those of the samples from Dobšiná and Letovice are different. The X-ray data are given in Tabs 2 and 3.

Comparison of the X-ray data obtained with those given by E. J. W. WHITTAKER and J. ZUSSMAN (1956) revealed the following results: the samples from Přísečnice, Nová Ves, and Hrubšice render X-ray values corresponding to the values of a mixture of orthochrysotile and clinochrysotile, the X-ray values of the sample from Dobšiná conforms to the values of almost pure clinochrysotile. The X-ray diagrams of clinochrysotile and of a mixture of orthochrysotile and clinochrysotile differ practically in the area of d = 2,6 Å to d = 2,4 Å as can be seen also from the record of difraction lines corresponding to the angle area produced in the Müller — Micro difractometer with

Fig. 4.

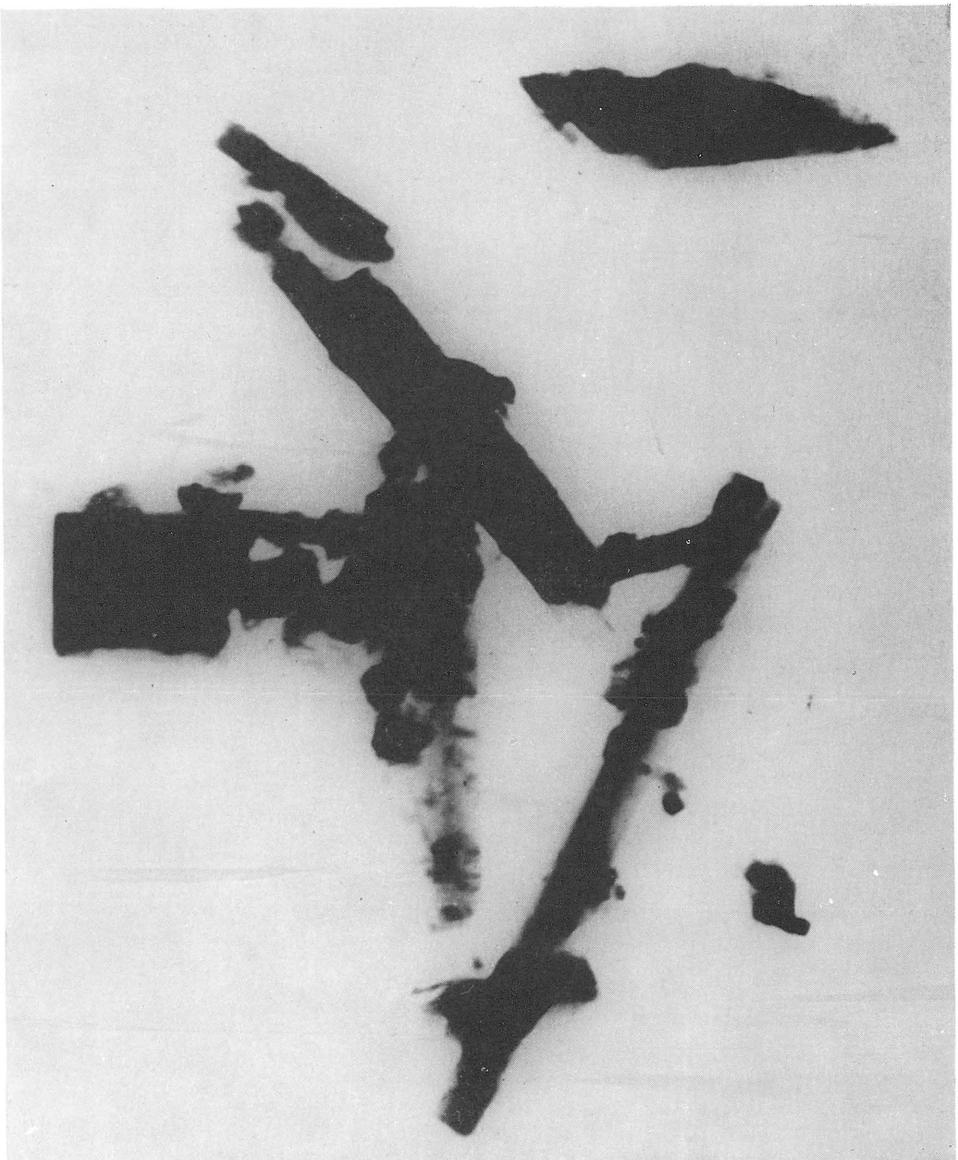
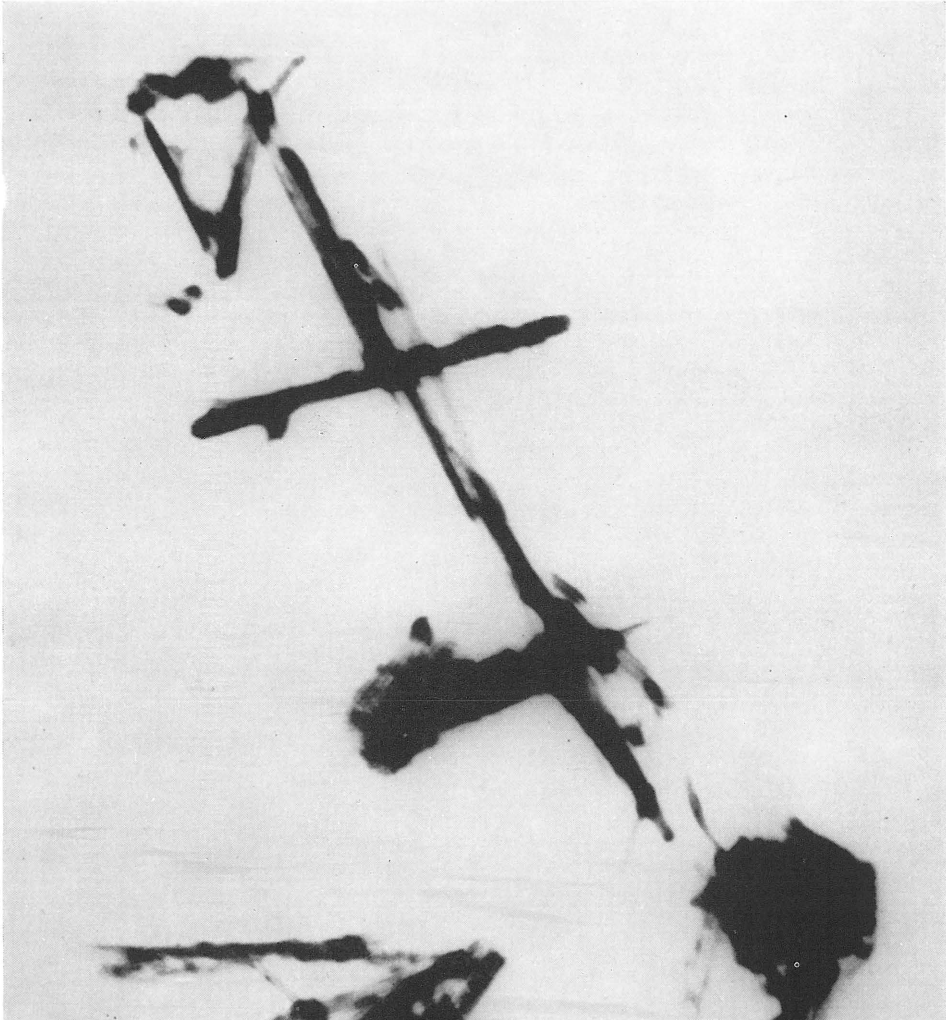


Fig. 5



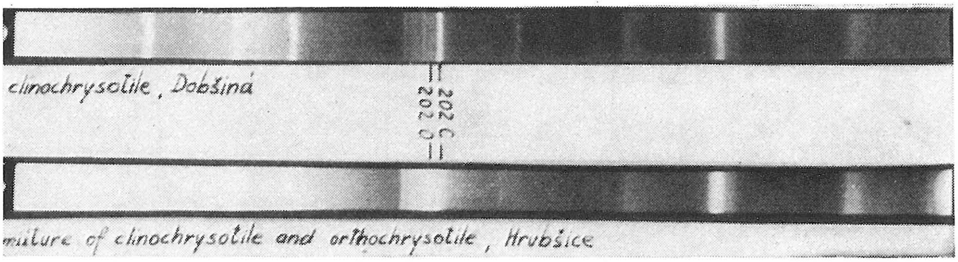


Fig. 1.

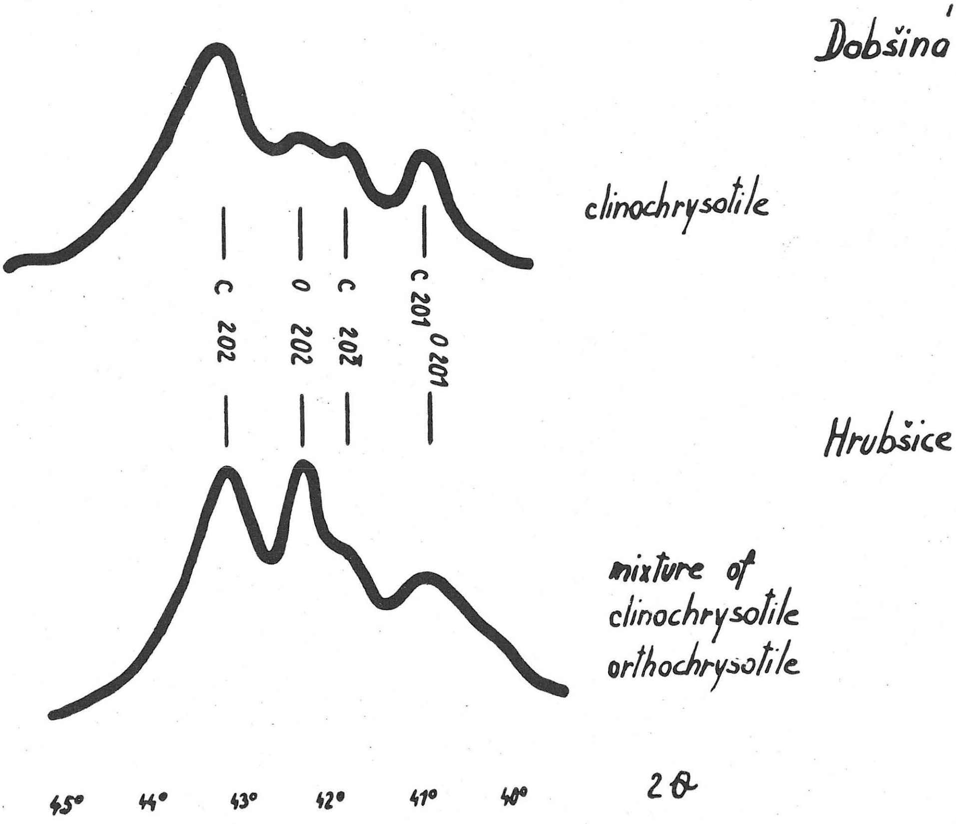


Fig. 2.

the application of Co Kα radiation. (See Fig. 1). The reflection (202) d = = 2,50 Å of orthochrysotile and (202) d = 2,45 Å of clinochrysotile are both present in the difraction diagrams of the samples from P ř í s e č - n i c e, N o v á V e s, and H r u b š i c e and are almost of the same intensity, whereas in the X-ray patern of the sample from D o b š i n á only the (202) d = 2,45 reflection belonging to clinochrysotile is strong. The basal reflection d (002) is 7,3 Å in both cases.

An X-ray pattern differing from the preceding ones was obtained from the sample from the L e t o v i c e locality. The X-ray values obtained from it were compared with VHITTAKER and ZUSSMAN'S (1956) data for antigorite. The basal reflection (001) has a somewhat lower value d = 7,18 Å, and also the reflection from the plains (102) and (102) in the examined sample from L e t o v i c e has a somewhat lower value than mentioned by the above authors.

Apart from powder diagrams rotation diagrams were made along the fibre axis. In all examined serpentines, with the exception of the serpentine from the L e t o v i c e locality, the lattice parameter in the direction of the fibres equalled an average 5,3 Å, from which it can be seen that in these cases the X axis is parallel to the fibre axis. In the case of the serpentine from L e t o v i c e a constant with a value of 9,3 Å was obtained along the fibre axis, and therefore here the Y axis is parallel with the fibre axis.

T h e r m i c s t u d y :

From all investigated serpentines DTA curves were obtained. As can be seen from Fig. 3) they are practically dentical with the exception of the L e t o v i c e sample. In all cases an endothermic reaction corresponding to dehydroxylation takes place at temperatures of from 660 °C to 690 °C. Immediately after this there takes place an exothermic reaction at about 800 °C caused by the recrystallization of olivine. The DTA curve of the L e t o v i c e sample shows a shifting of the endothermic reaction compared with the curves of chrysotile to a temperature of 730 °C. According to W. A. DEER, R. A. HOWIE, and J. ZUSSMAN (1962), and J. KOURIMSKÝ, V. ŠATAVA (1954) in antigorite there occurs a dehydroxylation at higher temperatures as is the case with chrysotiles, which fact was confirmed in our case.

E l e c t r o n o p t i c a l o b s e r v a t i o n :

Of the samples from D o b š i n á and L e t o v i c e pictures of the suspension of their particles were made by means of an electron microscope (see Fig. 4—5) with an enlargement of X 8000. The pictures show the finely filamentous character of chrysotile from D o b š i n á and the lathlike, fibrous antigorite from L e t o v i c e .

C o n c l u s i o n :

After the summarizing of the results obtained in the analyses performed, samples from P ř í s e č n i c e , N o v á V e s , and H r u b š i c e , determined as mixtures of *orthochrysotile* and *clinochrysotile,* the D o b - š i n á sample as an almost pure *clinochrysotile* and the L e t o v i c e sample as a fibrous *antigorite* with an increased Fe content, were examined.

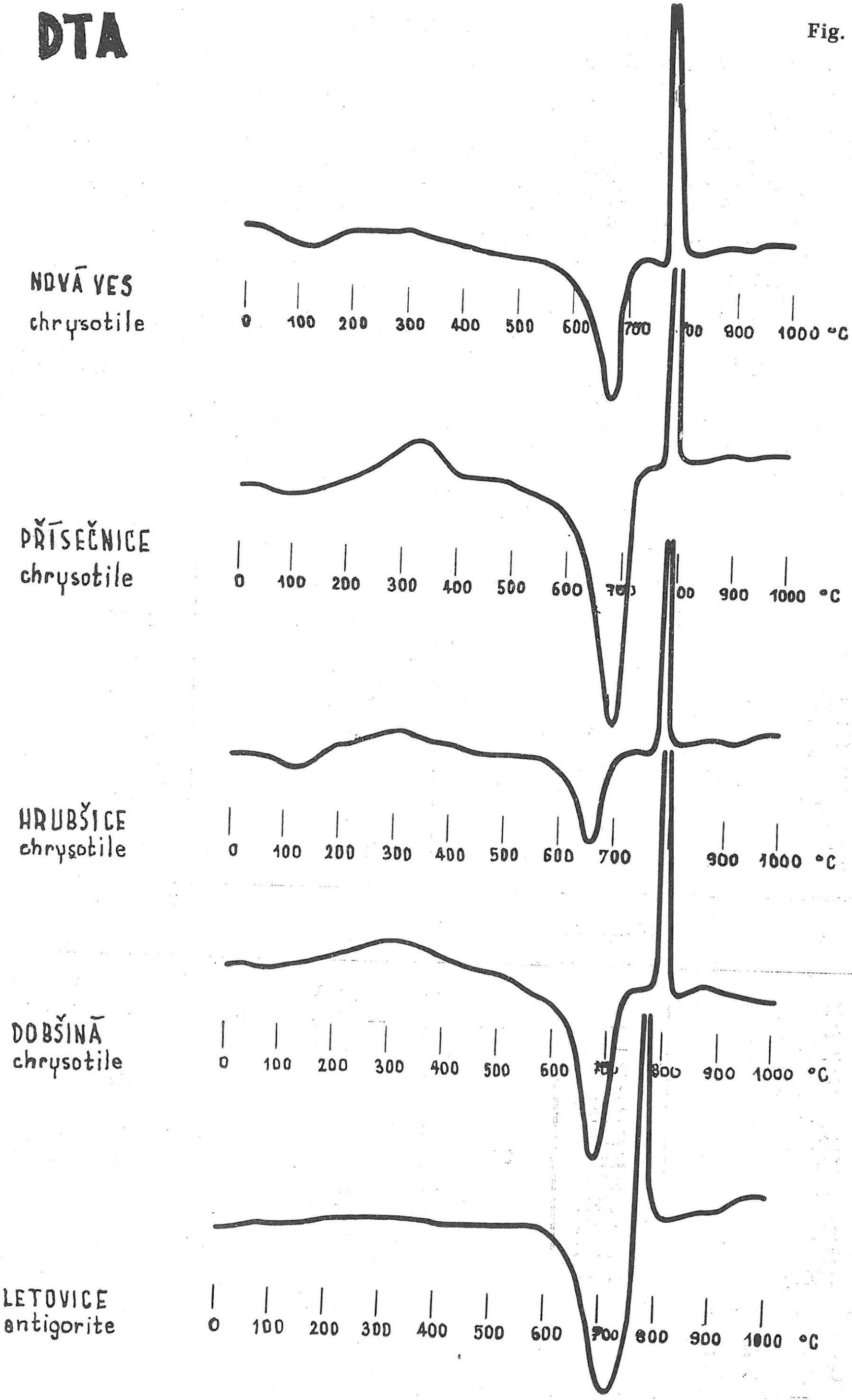

DTA
NOVÁ VES
chrysotile
PŘÍSEČNICE
chrysotile
HRUBŠICE
chrysotile
DOBŠINÁ
chrysotile
LETOVICE
antigorite
0 100 200 300 400 500 600 700 800 900 1000 °C

Fig. 3.

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Table 1. **Serpentine analyses**

	1.	2.	3.
SiO_2	42,21	41,83	42,02
Al_2O_3	0,26	0,87	1,74
Fe_2O_3	2,48	2,12	3,63
FeO	1,49	0,34	4,99
MnO	0,06	0,13	0,13
MgO	37,20	39,94	34,36
CaO	0,72	0,35	0,35
Na_2O	0,05	0,09	0,06
K_2O	0,07	0,20	0,06
P_2O_5	0,16	0,10	0,21
H_2O	15,13	13,25	12,16

Numbers of ions on the bassis of 9 (O,OH)

	1.	1. sum	2.	2. sum	3.	3. sum
Si	1,932	1,93	1,927	1,93	1,990	1,99
Al	—		—		—	
Fe^{3+}	—		—		—	
Al	0,014	2,79	0,046	2,90	0,222	3,00
Fe^{3+}	0,085		0,073		0,129	
Fe^{2+}	0,057		0,001		0,197	
Mn	0,002		0,005		0,005	
Mg	2,536		2,741		2,424	
Ca	0,035		0,017		0,017	
P	0,006		0,001		0,008	
Na	0,004		0,008		0,005	
K	0,004		0,012		0,004	
(OH)	4,617		4,073		3,839	

1. Chrysotile, Hrubšice, West Moravia,
2. Chrysotile, Dobšiná, Slovakia,
3. Fe — antigorite, Letovice, West Moravia.

Table 2. **X-ray powder data for chrysotile**

	hkl	d(Å) calc.	1		2		3		4		5	
			d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
	002	7,32	7,36	vs	7,36	vs	7,31	10	7,34	10	7,31	9
	020	4,60	4,58	m	4,56	m	4,56	9	4,544	8	4,54	8
	022	3,89										
	004	3,66	3,66	vs	3,66	s	3,63	9	3,63	9	3,63	8
	024	2,86										
	130	2,66	2,66	mw	2,66	w	2,65	5			2,64	4
O	201	2,614			2,604	mw	2,61	4				
C	$20\underline{1}$	2,590	2,594	mw			2,576	2	2,572	4	2,579	3
C	202	2,548	2,549	m	2,547	vw	2,527	4	2,513	3	2,520	5
O	202	2,497			2,500	m	2,489	7	2,479	7	2,479	1
C	202	2,454	2,456	s	2,451	ms	2,443	8	2,434	6	2,437	9
	006	2,438										
O	203	2,332					2,322	3				
	040	2,301			2,285	vw	2,284	1				
C	$20\underline{3}$	2,280	2,282	w							2,276	1
C	204	2,214	2,215	w	2,212	vw					2,199	2
O	204	2,148					2,137	3	2,128	2		
C	204	2,094	2,096	m	2,093	mw	2,083	5			2,079	4
O	205	1,966			1,972	vw	1,957	3				
	008	1,829	1,829	w	1,828	w	1,842	2	1,814	1	1,816	2
O	206	1,796					1,796	3	1,786	1		
C	206	1,748	1,748	m	1,746	mw	1,731	5	1,731	3	1,748	5
	310	1,739										
	028	1,698					1,698	1				
O	207	1,643					1,631	2				
	060	1,534	1,536	s	1,531	ms	1,536	8	1,531	8	1,536	s
O	208	1,506					1,498	3	1,494	3		
	001	1,463	1,465	w	1,464	w	1,460	3			1,464	1

1. Data for clinochrysotile by Whitaker E. J. W. and Zussman J. (1956)
2. Data for mixture of clinochrysotile and orthochrysotile by Whitaker E. J. W. and Zussman J. (1956)
3. Data for mixture of clinochrysotile and orthochrysotile studied (Přísečnice — West Bohemia)
4. Data for mixture of clinochrysotile and orthochrysotile studied (Hrubšice — West Moravia)
5. Data for clinochrysotile studied (Dobšiná — Slovakia)

O — typical lines of orthochrysotile
C — typical lines of clinochrysotile

Table 3.

X-ray powder data for antigorite

hkl	1		2	
	d (Å)	I	d (Å)	I
001	7,30	vs	7,16	10
$20\bar{1}$	6,95	—		
$30\bar{1}$	6,52	w		
401	5,80	w	6,06	2
710	5,11	vvw	5,21	3
810	4,67	mw	4,63	5
020	4,64	mw	4,56	8
910	4,27	w	4,14	6
$81\bar{1}$	3,95	mw		
102, $10\bar{2}$	3,63	s	3,56	10
302, 202	3,52	vvw	3,41	2
$14.0.\bar{1}$	2,88	—	2,83	1
15.0.1	2,66	vvw	2,65	3
930	2,60	vw		
17.0.0 $16.0.\bar{1}$	2,57	mw	2,55	3
16.0.1	2,53	vs	2,51	10
931	2,46	m		
003, 18.0.0	2,42	mw	2,42	3
17.0.1, $30\bar{3}$ 10.3.1	2,39	w	2,39	3
403 ?	2,35	mw	2,34	2
15.0.2	2,24	mw	2,28	3
$16.0.\bar{2}$	2,21	mw		
$83\bar{2}$	2,169	ms	2,14	6
16.0.2	2,153	m		
$93\bar{2}$	2,127	w		
$17.0.\bar{2}$	2,113	w		
$11.3.\bar{2}$	2,035	vw		
$15.0.\bar{3}$	1,879	w		
15.0.3	1,832	m	1,826	4
004, $10\bar{4}$ 833	1,813	w	1,794	3
$93\bar{3}$	1,782	m	1,767	3
$10.3.\bar{3}$	1,755	w		
17.0.3	1,738	mw	1,735	4

hkl	1		2	
	d (Å)	I	d (Å)	I
21.3.1	1,688	vw	1,697	3
14.0.$\bar{4}$	1,587	w		
24.3.0	1,563	m		
060	1,541	m	1,555	8
24.3.$\bar{1}$	1,534	m	1,528	10
15.0.4				
16.0.4	1,523	m	1,496	8
22.3.2				
061	1,509	mw		
17.0.$\bar{4}$	1,497	m		
93$\bar{4}$				
934	1,480	w		
18.0.$\bar{4}$	1,468	w		
10.3.4	1,462	—		
20$\bar{5}$	1,452	w		
205	1,448	mw	1,444	2

1. Data for antigorite by Whitaker E. J. W. and Zussman J. (1956)
2. Data for fibrous antigorite studied (Letovice — West Moravia)