DILLNITE AND ITS RELATION TO ZUNYITE

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Abstract

New data on dillnite from Banská Belá, Czechoslovakia, are given. Dillnite is cubic, and occurs in minute tetrahedrons, with $n = 1.563$ and $G = 2.87$. The formula is $Al_{15}Si_6O_{25}(OH, F)_{18}Cl$. A new analysis has been made, with special attention to the determination of OH, F and Cl.

Dillnite and zunyite form a series in which OH and F can substitute for each other within broad limits, but the content of Cl is nearly constant. Zunyite has a low F content and higher refractive index, and the name dillnite is used for material with high F content and lower index.

Introduction

Dillnite from Banská Belá (formerly Dilln) near the old mining region of Banská Štiavnica in Czechoslovakia, was described in 1849 by A. Hutzelmann. A historical survey of dillnite has been given (Konta, 1955). According to six published analyses, dillnite contains 22.33–24.97 SiO_2, 53.00–56.40 Al_2O_3, and the loss on ignition is 18.4–21.75%.

Until recently, dillnite was not considered to be a specific mineral, but rather a mixture of kaolinite and diaspore. During a systematic study of the clay minerals of Czechoslovakia, dillnite was reexamined in our laboratory by x-ray, D.T.A., gravimetric thermal analyses and determination of the refractive index. It was found that it is not a mixture, but a specific mineral (Konta, 1955). As the material studied was named dillnite in 1849, one of the authors (J.K.) did not think it necessary to now change the name.

Dr. W. T. Schaller, of the U. S. Geological Survey, noticed that the x-ray pattern of dillnite as reported (Konta, 1955) was practically identical with those of zunyite, and suggested to us that further investigation was needed. It was then that the F and Cl content of dillnite was discovered.

Optical Data

The dillinite from Banská Belá occurs in minute tetrahedrons, mostly below 2 microns in size. It is isotropic, and the refractive index of 1.563 is essentially lower than those of known zunyites (Table 1). This value (originally given as 1.559) was confirmed by Drs. J. Kouřimský and V. Šípek, from the National Museum in Prague.

It was thought possible that the lower index of dillnite might be caused by a thin film of some amorphous material such as opal or allophane. However, after successive boiling for 30 minutes in HCl,

HNO₃ and finally HF, with washing with hot water after each acid treatment, the refractive index remained unchanged.

DETERMINATION OF VOLATILE CONSTITUENTS

Since the determination of F, Cl and OH in this insoluble silicate presents a difficult analytical problem, we describe briefly the methods used. The data were obtained on finely pulverized dillnite, sieved through a 200-mesh screen (aperture 0.074 mm.), and dried at 110° until the weight was constant.

TABLE 1. REFRACTIVE INDICES OF DILLNITE AND ZUNYITE (Na LIGHT)

This paper	J. Kouřimský	V. Šípek
	Dillnite	
1.563	1.563 ± 0.003	1.563 ± 0.001 (single crystal)
		1.564 (aggregates)
	Zunyite	
Zuñi Mine, Colorado	Lake Balkhash	
(Quoted by Nell, 1930	1.590–1.594 Astashenko and Moleva, 1939	
1.595 Gossner and Mussgnug		
1.6022 M. Albis	Postmasburg, S. Africa	
	1.600 ± 0.001 Vermaas, 1952	
1.589 ± 0.003 E. S. Larsen	Palembang, Sumatra	
	1.595 Druif, 1948	

Total loss on ignition

Three 1 gm. samples were heated repeatedly to 1000° C. until the weight was constant, and the loss in weight was determined to be 20.75, 20.72 and 20.70% respectively. A 2 gm. and a 1 gm. sample were heated at 1100° C. until the weight was constant, and showed losses of 20.97 and 21.04% respectively.* The value of 21.04% was considered to be the most reliable.

The dehydration data and the D.T.A. curves are given in the paper of Konta (1955). The newly obtained curves are the same.

Volatile components remaining in the ignited sample

The samples which had the loss of 20.97 and 21.04% were used to determine the residual amounts of F and Cl. For the first, this proved to be Cl 0.23–0.20%; F 0.15%. For the second sample, Cl 0.12%; F 0.07–0.05%. Fluorine remains in smaller quantity than chlorine, although its

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* After the emptying of the powder, some still adhered to the walls and bottom of the crucible in the 2 gm. sample. The 1 gm. sample came out in a smooth-surfaced single piece.

original content is nearly six times as great. The chlorine can be released only with great difficulty, from which it seems apparent that it is more firmly bound in the structure of dillnite than is fluorine.

Determination of hydroxyl

During ignition all three volatile components escape simultaneously. Hence the determination of OH was done by a modified method of Penfield (1894). Three different $\frac{1}{2}$ gm. samples of powdered dillinite were each mixed with 0.5 gm. of PbO (dried at 600° C.) and placed in small glass bulbs made of high temperature glass. The mixture was covered with 0.5 gm. of PbO. These determinations gave the values 6.35, 6.65 and 6.41%, with an average of 6.47% of H_2O. The water gave negative tests for F and Cl.

TABLE 2. CONTENT OF FLUORINE IN DILLNITE FROM
BANSKÁ BELÁ, CZECHOSLOVAKIA

	a	*b*	*c*	*d*	*e*	*f*	Average value
Fluorine determined by pyrohydrolysis in platinum apparatus	12.34	12.31	12.37	12.38	12.39	12.46	12.38% F
	g	*h*	*i*				
Fluorine determined in glass apparatus:	12.52	12.48	12.61				12.54% F
Final average value							12.46% F

Determination of fluorine

Results of the determination of F in dillnite by two different methods are given in Table 2. First, F was determined on 6 different 0.1 gm. samples (*a–f*) by pyrohydrolysis in a platinum apparatus according to Fresenius *et al.* (1949) and Warf *et al.* (1954). The catalyst was U_3O_8. Final volumetric determination of HF was done by 0.05 M thorium nitrate after previous neutralizing and by addition of buffer (pH = 3.8) in the presence of alizarine sodium monosulfonate as indicator.

Other determinations were made in a glass distilling apparatus after the method of Willard and Winter (1933), modified by Richter (1942) and by the volumetric method of Hoskin and Ferris (1936). Three 0.2 gm. samples of dillnite (*g–i*) were analyzed. Final determination was

made by titration with 0.05 M. thorium nitrate as stated above. The experiences of Romo and Roy (1957) and of Turková (1957) were taken into consideration in this determination.

We consider the determination of fluorine in the glass-apparatus to be more reliable, because the analyzed specimens were fused in a mixture with 1 to 2 grams of sodium and potassium carbonate and thus completely decomposed. The liberation of fluorine during the dissolving of the carbonate fusion was complete.

A final determination of the hydrofluoric acid after pyrohydrolytic treatment was also made by titration with sodium hydroxide solution. Phenolphtalein was used as indicator. The results differed considerably (14.76%, 16.32% and 15.46%), and are too high, as follows from the comparison of the sum of the determined amounts of fluorine, chlorine, and hydroxyl water with the total loss of ignition. Therefore we consider the determination of fluorine by sodium hydroxide solution to be less accurate, even after the correction for chlorine.

Determination of chlorine

This was determined by two methods after water extraction of finely pulverized dillnite fused with sodium and potassium carbonate. In the first three samples the chlorine was determined by potentiometric titration of the extraction of the carbonate fusion, neutralized with nitric acid, after removing the silicic acid and the sesquioxides. The titration was done with $AgNO_3$, as described in detail by E. Müller (1942). The values obtained were 2.26, 2.17, 2.30; average 2.25% Cl. In the remaining three samples the Cl was determined gravimetrically as AgCl, after removing the silica and sesquioxides (according to Hillebrand *et al.* 1953), with values of 2.19, 2.16, 2.16; average 2.17% Cl, giving a final average of 2.21% Cl.

Determination of SiO_2, Al_2O_3 and other oxides

Owing to the high fluorine content it was necessary to use a different method than usual for the silicate analysis. All of the existing analyses of dillnite (collected in the paper by J. Konta, 1955) are in error because of the presence of fluorine. If it is not first removed, it has an adverse influence during the whole analysis. Part of the Si volatilizes as SiF_4, after the dissolution of the carbonate fusion during the coagulation of the silicic acid from the chloride solution, and also during the dehydration of the silica by ignition. Thus the real content of SiO_2 may be reduced several per cent. The presence of fluorine also affects the determination of CaO, for part of the F forms CaF_2, which is weighed with the SiO_2

TABLE 3. NEW CHEMICAL ANALYSIS OF DILLNITE FROM
BANSKÁ BELÁ, CZECHOSLOVAKIA

	No. 1	No. 2	No. 3	Average	Mol Quotients	Atomic ratios	
SiO_2	26.55	26.61	26.30	26.48	0.4409	Si	0.4409
TiO_2	0.76	0.79	0.80	0.78	0.0098	Ti	0.0098
Al_2O_3	56.21	56.00	56.30	56.17	0.5510	Al	1.1020
Fe_2O_3	0.05	0.07	0.05	0.06	0.0004	Fe	0.0007
CaO	0.82	0.79	0.88	0.83	0.0142	Ca	0.0142
MgO	0.19	0.19	0.18	0.19	0.0047	Mg	0.0047
MnO	0.01	0.01	0.01	0.01	0.0001	Mn	0.0001
H_2O^+	6.47	6.47	6.47	6.47	0.3591	OH	0.7182
F	12.50	12.50	12.50	12.50	0.6579	F	0.6157
				(−0.8)	(−0.0422)		
Cl	2.20	2.20	2.20	2.20	0.0620	Cl	0.0620
Less O for F, Cl	5.66	5.66	5.66	5.66		O	1.8637
	100.10	99.97	100.03	100.03	Al:Si:O = 15:6:25		
					OH:F:Cl~10:8:1		

and partially with the Al_2O_3, whose apparent content is thus increased, with the CaO being correspondingly decreased.

The influence of boron was eliminated by the evaporating of the borax fusion with methyl alcohol saturated with dry HCl. After complete removal of boron, the SiO_2 was determined as usual. The other oxides were determined as follows: Al_2O_3 was determined gravimetrically by orthohydroxyquinoline, by drying at 140° C.; TiO_2, Fe_2O_3 and MnO were determined colorimetrically; CaO and MgO were determined compleximetrically, CaO with calcion as indicator (Körbl and Vydra, 1957), and MgO with eriochrome black (Přibil, 1953).

Table 3 gives the results of the quantitative chemical analysis of dillnite from Banská Belá from three 0.5 gm. samples. After the subtraction of 0.8% F, which is probably present as fluorite (Konta, 1955), the approximate formula of dillnite is

$$Al_{15}Si_6O_{25}(OH, F)_{18}Cl$$
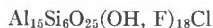
Comparison of these results with earlier analyses shows that errors were mainly in the determination of SiO_2 and CaO, as well as in hydroxyl water, F and Cl.

Density of dillnite

The density determined pycnometrically at 20° C. is 2.87. In the original work there is a misprint: namely 2.67_5.
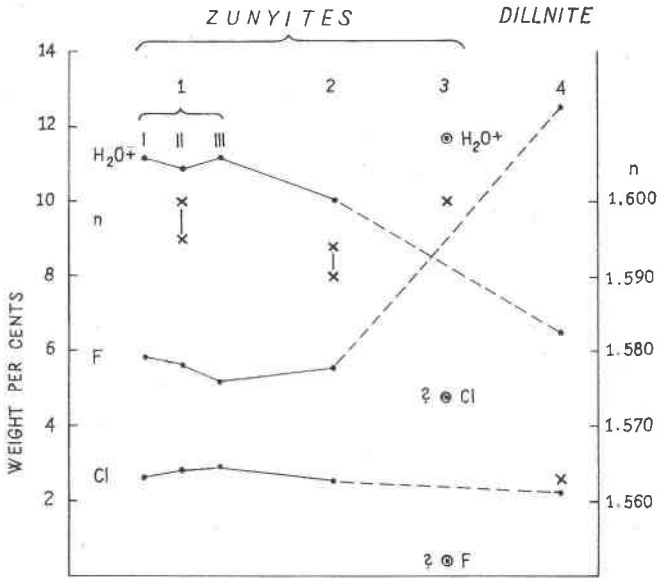
FIG. 1. The chief differences in chemical composition and refractive indices (indicated by x) of zunyites and dillnite.

(1) Zunyite from Zunyi mine, Colorado. (Nel, 1930, writes "Zuni" mine). Gossner and Mussgnug (1929): I H_2O^+ 11.12%, F 5.81, Cl 2.62; II H_2O^+ 10.89, F. 5.61, Cl 2.91; III H_2O^+ 11.12, F 5.19, Cl 2.90, $n = 1.595$ (detd. by the authors), $n = 1.6022$ (detd. by M. Albis, 1921) and quoted by Nel, (1930).

(2) Zunyite from Karabas, near Lake Balkhash in Kazakhstan. Astashenko and Moleva (1939) H_2O^+ 10.03, F 5.52, Cl 2.56, $n = 1.590$–1.594.

(3) Zunyite from Postmasburg, South Africa. Vermaas (1952) H_2O^+ 11.65, F 0.40, Cl 4.80, $n = 1.600 \pm 0.001$.

(4) Dillnite from Banská Belá, Czechoslovakia. H_2O^+ 6.47, F 12.46, Cl 2.2, $n = 1.563$.

THE RELATION OF DILLNITE TO ZUNYITE

From the determined data, it is evident that dillinite and zunyite form an isomorphous series in which within fairly broad limits the fluorine and hydroxyl can replace each other. The content of chlorine is relatively constant in all of the samples studied (Fig. 1).

The formula of zunyite given by Pauling (1933) as $Al_{13}Si_5O_{20}(OH, F)_{18}Cl$ seems to correspond better with the results on dillnite than the formulas $Al_8Si_3O_{12}(OH,F,Cl)_{12}$ (Palache, 1932) and $Al_{13}Si_5O_{20}(OH,F, Cl)_{19}$ (Vermaas, 1952).

Material with lower fluorine and higher refractive index is named zunyite, and that with higher content of fluorine and lower index is named dillnite.

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