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TUNISITE, A NEW CARBONATE FROM TUNISIA

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Abstract

Tunisite, $NaHCa_2Al_4[(CO_3)_4(OH)_{10}]$ is a new carbonate found at the Pb–Zn deposit, Sakiet Sidi Youssef, Tunisia. It occurs in fine-grained white aggregates or in small tabular crystals associated with pyrite, marcasite, sphalerite and calcite in hydrothermal veins.

The new mineral is tetragonal; $D^7_{4h}-P4/nmm$; $a=11.22\pm0.01$, $c=6.582\pm0.001$ Å, $c/a=0.5866$; $V=828.6$ Å³, cell contents: $2\{NaHCa_2Al_4[(CO_3)_4(OH)_{10}.\}$. The strongest lines in the X-ray powder photograph are: 5.615 (10), 2.592 (9), 3.551 (8), 3.288 (7), 2.526 (7) Å.

Tunisite is colorless. $H=4.5$; ρ 2.51 ± 0.02 (meas.), 2.48 (calc.). Basal and prismatic cleavage very good. Optically uniaxial $(+)$, $\omega=1.573\pm0.001$, $\epsilon=1.599\pm0.001$.

The chemical analysis: Na_2O 4.77, K_2O 0.35, CaO 18.08, Al_2O_3 32.56, CO_2 28.66, H_2O^+ 15.04, H_2O^- 0.51, Σ 99.97 wt.%. DTA shows a strong endothermic peak at 440° (escape of $8CO_2+7H_2O$) and an exothermic peak at 850° (formation of new crystalline phases and escape of $2H_2O$). IR spectrum shows absorption bands at 680 s, 850 s, 1155 s, 1530 vs, 1725 w, 1860 vw, 1920 w, 2330 vw, 2650 w, 3500 s cm⁻¹.

Introduction

A mineral, later established as a new species, was found by one of the co-authors (Z.J.) on the dumps of the Pb-Zn ore deposit of Sakiet Sidi Yousseff, Tunisia, in 1965. This new Na, Ca, Al carbonate was called tunisite after the country of its first occurrence (Tunisia).

The ore deposit of Sakiet Sidi Yousseff is situated in the vicinity of the Algerian frontier at a road connecting the town of Le Kef with that of Souk Ahras. The now abandoned mine lies at about 2 km to the southeast of the village on the slope of Djebel-er-Ressas (elevation 828 m).

Similar to the majority of Tunisian Pb-Zn ore deposits, the deposit of Sakiet Sidi Yousseff is developed on the tectonic boundary between the so-called extrusive Triassic and other geological units represented in this case by the Upper Cretaceous (Cenomanian-Maestrichtian) sediments (Sainfeld, 1952).

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The mineralization is developed in a series of small veins parallel to the anomalous Triassic boundary occuring in a zone of approximately 10 m width and 160 m length (Sainfeld, 1952), as well as in the transversal dislocations. The latter type of veins reaches a thickness of up to 1.5–2 m and a length of about 300 m.

The gangue material is almost exclusively calcite. Quartz occurs only very sporadically. On the basis of the study of material found on the dumps it appears that some parts of the veins were enriched in barite. The following ore minerals were identified by Sainfeld (1952): galena, sphalerite (colloform, "Schalenblende"-type), marcasite, and pyrite.

So far only two specimens of tunisite have been found. It fills the cavities in the white calcite part of the veins, or it is developed as fine covers on the calcite crystals. It apparently belongs to the latest hydrothermal stage.

Qualitative Spectrochemical Analysis

The analysis was performed (analyst Z.Houdkova) by means of a Zeiss (Jena) Q 24 UV-spectrometer (intermittent arc, slit width 0.0045 mm, electrode distance 5 mm, time of exposure 90 sec.). The elements determined were visually divided into five concentration ranges (the elements underlined are near to the boundary of the higher concentration range, those in brackets are close to the upper limit of the lower concentration range). The specimen used for the spectrochemical analysis gave the following results: 10^1: Al,Ca,Na; 10^0: K,Mg; 10^{-1}: Mn,(Pb),(Si); 10^{-2}: Ag,Cr,Zn,V,Sr; $10^{-3}\%$: Cu,Fe,Zr(?).

Chemical Analysis

Tunisite is easily soluble in concentrated inorganic acids, except nitric acid. If dilute inorganic acids are used, the decomposition is accompanied by a strong hydrolysis of the Al-salt thus produced; especially so during prolonged boiling. The hydrate formed is then practically insoluble in acids.

A sample weighing about 0.5 g was used for the analysis. It was dissolved in concentrated hydrochloric acid at room temperature and then carefully at higher temperatures. When the decomposition was completed, the solution was oxidized by a few ml of nitric acid, then diluted to the volume of 100 ml and boiled shortly in order to expel the nitrogen oxides. After cooling, the solution was transferred to a 250-ml volumetric flask and brought up to the 250-ml volume. Amounts suitable for separate determinations were then taken from this solution. Calcium was determined by volumetric titration in a strongly basic medium using the solution of Complexon III and fluorexon as a metafluorescent indicator. Aluminum was analyzed indirectly by determining the amount of ethylendiamintetracetic acid released after the reaction of complexonates with fluoride ions. The determination was made with the aid of a Zn-salt solution in a weakly acid medium (pH 5) during a biamperometric indication using ferrocyanide/ferricyanide oxy-redox system added in a very small amount. Alkalies were determined from the reserve solution by means of flame photometry in the medium of hydrochloric and phosphoric acids.

For the analysis of water and CO_2 separate weights of 0.2g were used. Water was determined gravimetrically according to Penfield using lead sesquioxide as a flux. Carbon dioxide was determined by means of volumetric-absorption gas analysis method.

TABLE 1. CHEMICAL ANALYSIS OF TUNISITE

	1	2	3	4	5
Na_2O	4.77	4.80	0.1548⎫	1	4.98
K_2O	0.35	0.35	0.0074⎭		
CaO	18.08	18.18	0.3242	2.00	18.03
Al_2O_3	32.56	32.74	0.6422	3.96	32.77
CO_2	28.66	28.81	0.6548	4.04	28.30
H_2O^+	15.04	15.12	1.6790	10.35	15.92
H_2O^-	0.51				
Σ	99.97%	100.00%			100.00%

P. Povondra, Analyst.

1—Weight %.
2—Weight % recalculated.
3—Atom proportions.
4—Mole ratios.
5—Theoretical composition for $NaHCa_2Al_4[(CO_3)_4(OH)_{10}]$.

The results of the chemical analysis (Table 1) yield the empirical formula:

$$(Na_{0.95}K_{0.05})_{1.00}Ca_{2.00}Al_{3.96}H_{0.78}[(CO_3)_{4.04}(OH)_{9.58}],$$

formula weight $= 616.96$.

The ideal chemical formula of tunisite can therefore be expressed as

$$NaHCa_2Al_4[(CO_3)_4(OH)_{10}].$$

X-Ray Study

Despite the small size of tunisite crystals, oscillation and Weissenberg photographs (Cu/Ni) about the [001] axis were obtained and the c parameter $= 6.58 \pm 0.01$ Å was derived from them. The zero layer-line was indexed with the use of the linear relation of d_{hk0} and a. Tunisite is tetragonal with the following unit cell dimensions:

$$a = 11.22 \pm 0.01 \text{ Å}$$
$$c = 6.582 \pm 0.001 \text{ Å}$$

$c/a = 0.586$; $V = 828.6$ Å³; $Z = 2$; the calculated specific gravity is 2.48. The specific gravity of tunisite determined by the pycnometer method is 2.51 ± 0.02. The unit cell contains $2\{NaHCa_2Al_4[(CO_3)_4(OH)_{10}]\}$.

Laue class $D_{4h} - 4/mmm$. The results of the indexing of the Weissenberg photographs show only systematic absence of $hk0$ reflexions with $h + k \neq 2n$. Space group of the mineral is $D_{4h}^7 - P4/nmm$. The indexed X-ray powder pattern of tunisite is given in Table 2. The intensities of

TABLE 2. X-RAY POWDER DATA FOR TUNISITE
(Cu/Ni; λ = 1.5418 Å; Camera Diameter 114.59 mm)

I	d(meas)Å	d(calc)Å	hkl	I	d(meas)	d(calc)	hkl
3	7.92	7.934	110	3	1.831	1.829	512
4–5	6.59	6.582	001	6	1.800	1.799	601
10	5.615	5.610	200	3	1.760	1.760	522
6	5.070	5.066	111	4	1.729	1.728	403
3	4.267	4.270	201	6	1.698	1.699	442
5	3.993	3.992	211	6	1.650	1.652	423
8	3.551	3.549	310			1.645	004
1	3.403	3.399	221	3	1.628	1.628	104
7	3.288	3.292	002			1.626	602
6	3.128	3.124	311	2	1.587	1.587	550; 710
3	3.035	3.040	112	1–2	1.576	1.579	204
3–4	2.811	2.814	321	1	1.558	1.557	701
		2.805	400			1.556	640
7	2.754	2.752	212	1	1.549	1.547	542
9	2.592	2.581	401	1	1.514	1.514	641
7	2.526	2.533	222			1.511	523
1	2.454	2.454	331	3	1.492	1.493	314
2	2.412	2.413	312			1.491	632
5	2.347	2.345	421	1–2	1.475	1.473	730
1	2.269	2.261	322	3	1.440	1.441	702
1	2.200	2.200	510			1.438	731
		2.194	003			1.437	650
3	2.153	2.153	103	2	1.425	1.423	603
6	2.125	2.124	501; 431	2	1.407	1.408	414
1	2.096	2.097	412			1.407	642
1	2.040	2.043	203	3–4	1.396	1.397	334
5	2.010	2.010	213			1.396	722
5	1.988	1.986	521	1–2	1.377	1.376	424
		1.983	440	2–3	1.345	1.345	732
1	1.900	1.903	303	1–2	1.334	1.332	821
		1.899	441	1–2	1.322	1.322	660
5	1.866	1.870	600				
		1.866	313				

001 diffraction lines on the X-ray powder pattern are enhanced due to preferential orientation resulting from the very good basal cleavage.

PHYSICAL PROPERTIES

In the specimens studied tunisite most frequently forms fine-grained aggregates of pure white color which are composed of microscopic sub-hedral crystals. Occasionally, the aggregates consist of euhedral or skeleton crystals of the same size. In the latter case they are developed as thin
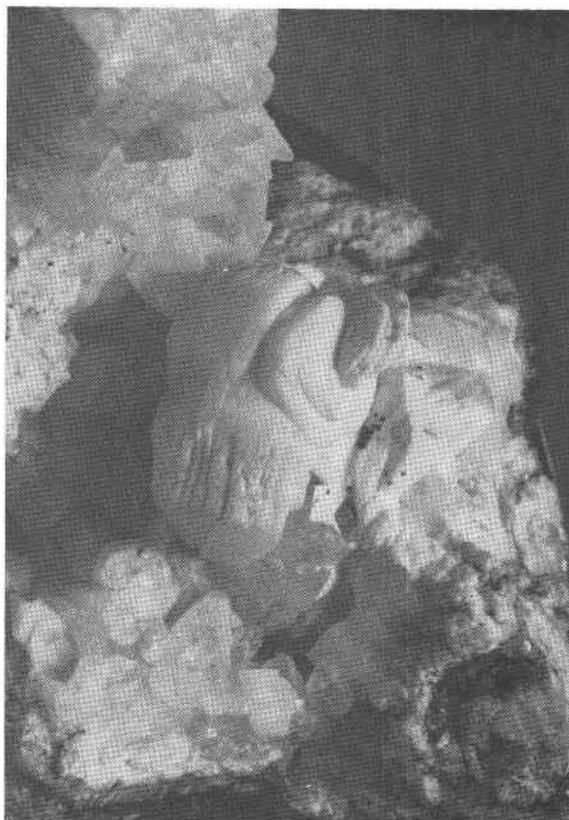
FIG. 1. Tabular tunisite crystals in a cavity of calcite. 4✕.

covers on calcite crystals. Tunisite occurs very rarely in macroscopic tabular crystals which form parallel groups (Fig. 1). The form of the microscopic crystals can be seen on Figure 2. The tetragonal crystals of tunisite are tabular with strongly developed basal pinacoid. This face predominates even on skeleton crystals. The size of tunisite crystals may be expressed mostly in hundredths of mm; quite exceptionally microscopic crystals of 0.2 mm in size were observed. The dimensions of macroscopic crystals range between 2 to 8 mm. Beside the (001) and the (110) there is also observed the (100) and (10l). Two crystal types were observed, the schematic drawings of which are given in Figure 3. Unfortunately, owing to the size of the crystals and their parallel grouping, it was not possible to perform any goniometric measurements.

The hardness of the crystals measured on the (001) face is 4.5 (in terms of Mohs scale); the hardness of the aggregates is 3.5. Tunisite has a per-
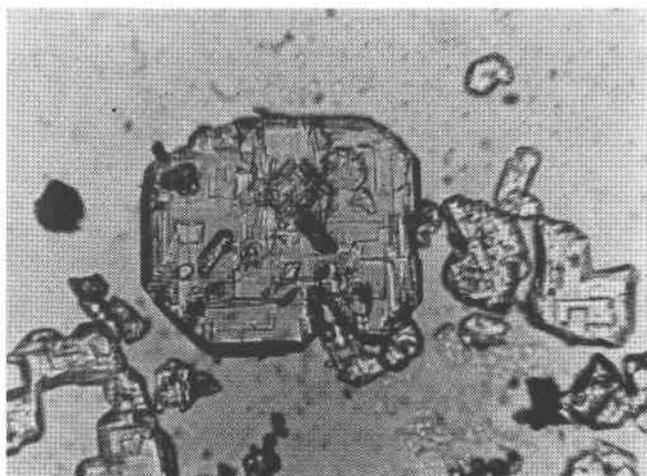
FIG. 2. Microscopic tetragonal and skeleton crystals of tunisite. 120✕.

fect basal and prismatic cleavage. The mineral is optically uniaxial (+). The indices of refraction (for sodium light) are: $\omega = 1.573 \pm 0.001$ $\epsilon = 1.599 \pm 0.001$, $\epsilon - \omega = 0.026$.

THERMAL STUDY

The DTA curve of tunisite (Fig. 4) is characterized by the presence of an endothermic peak at 440°C and an exothermic one at 850°C. The form of the curve on heating the sample in an inert atmosphere (argon) is not changed, except that the peak temperatures are slightly shifted towards lower values (420 and 830°C respectively).

A

B
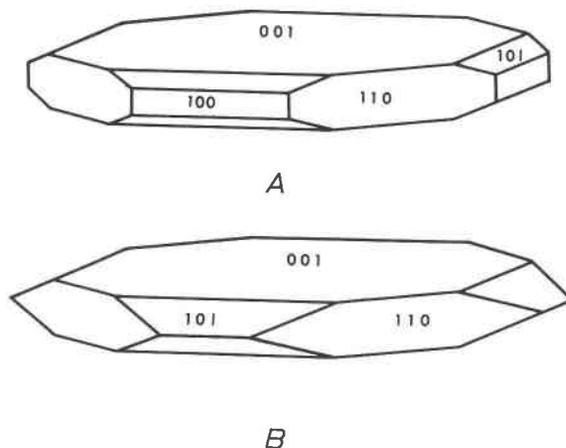
FIG. 3. Schematic drawings of two tunisite crystal types.
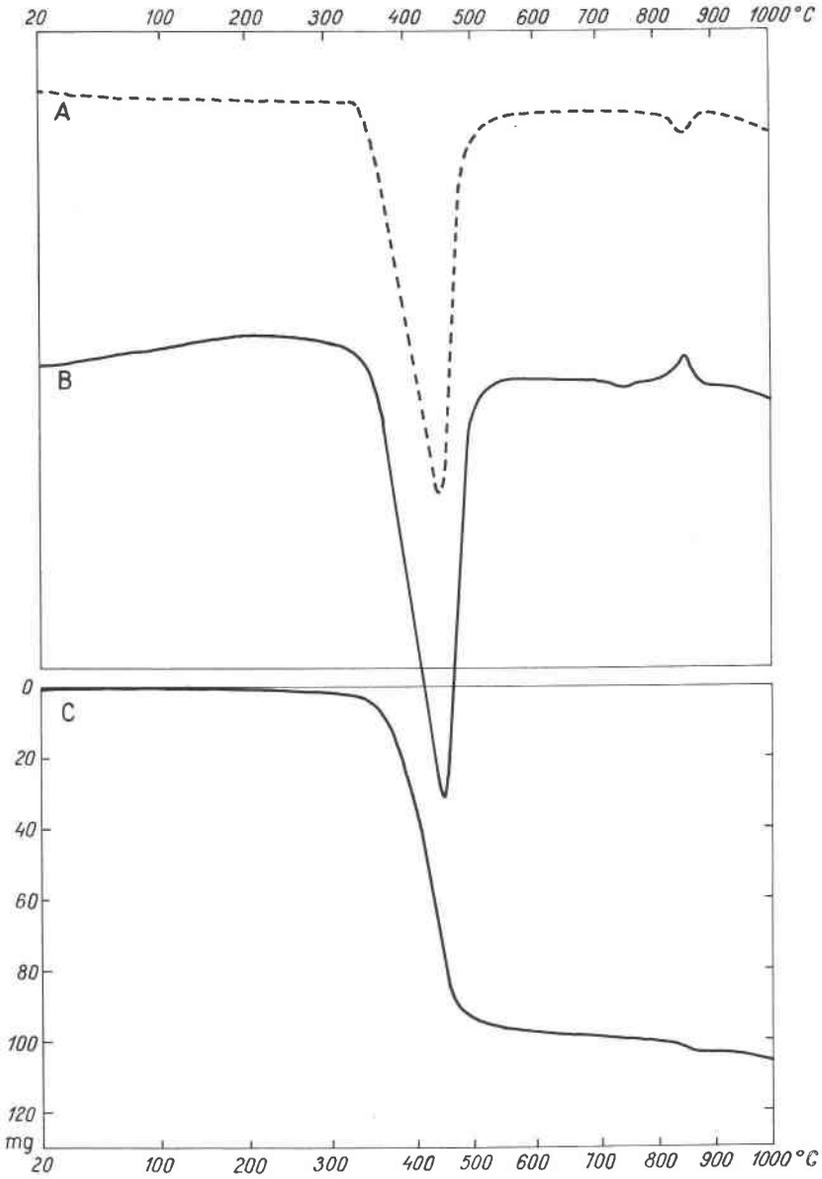
FIG. 4. The DTA (B) and thermogravimetric (C) curves of tunisite.
Curve A is the first derivative of C.
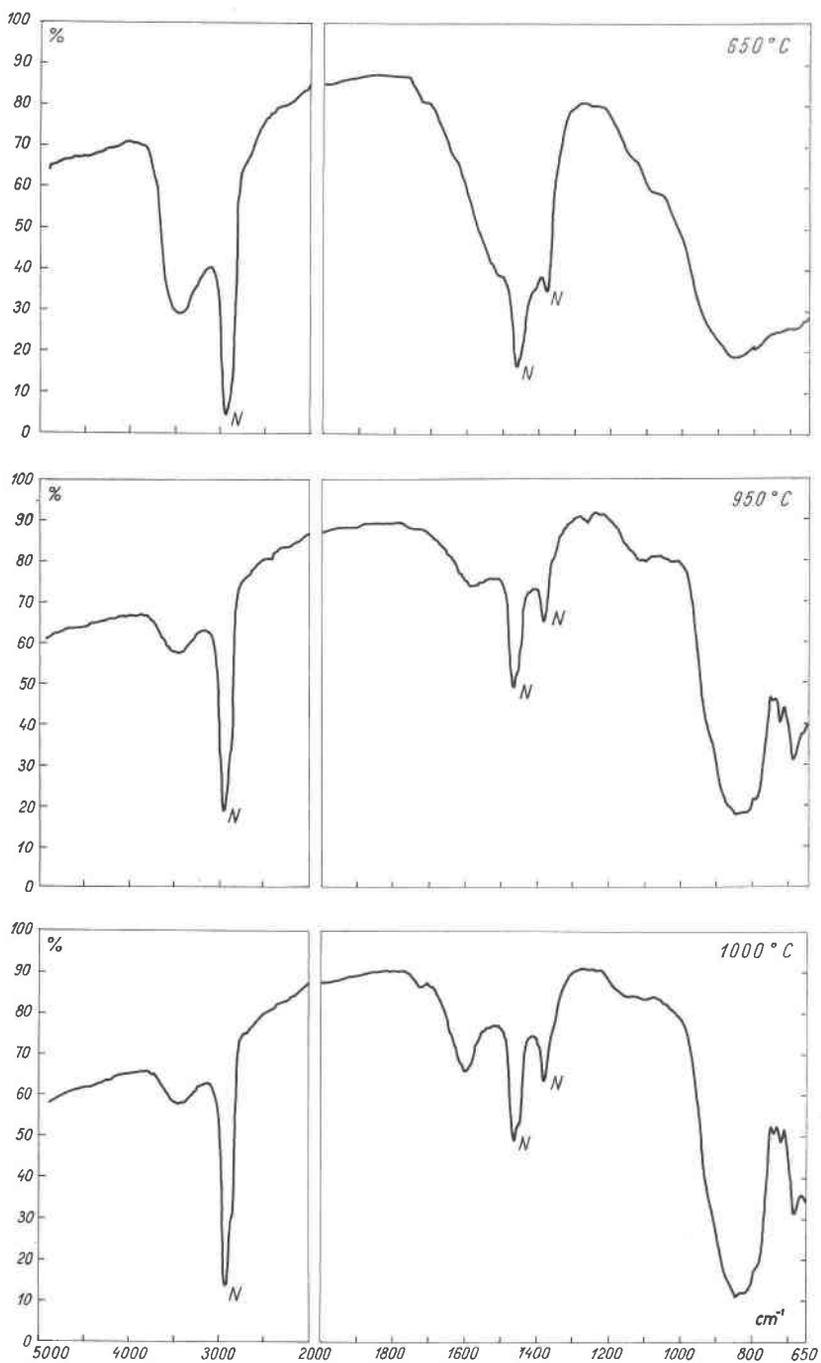
FIG. 5. Infrared absorption curves of tunisite heated to 650,950, and 1000°C respectively. N—Nujol peaks.

According to the thermogravimetric curve (Fig 4) the endothermic re-action corresponds to the loss of weight of 38.2 percent. The entire loss of weight up to 1000°C calculated from the thermogravimetric curve equals 40.8 percent. The exothermic reaction at 850°C is accompanied by a loss of weight of 2.6 percent. Taking into account the amount of CO_2 and H_2O determined by the chemical analysis it may be concluded that the endothermic reaction is caused by the simultaneous escape of CO_2 and H_2O. By calculation it can be established that the reaction at 420°C is due to the decomposition of the mineral accompanied by the simulta-neous escape of 8 $CO_2 + 7$ H_2O. Theoretically, the loss of weight of 38.4 percent corresponds to this escape which is in good agreement with the loss of weight recorded by the thermogravimetric curve. At 850°C, $2H_2O$ are expelled (the theoretical loss of weight is 2.9%) and at the same time the crystallization of several phases takes place. Comparing the results of the thermogravimetric analysis with the CO_2 and H_2O contents deter-mined by the chemical analysis it is apparent that at the temperature of 1000°C two water molecules are still present in the specimen. In fact, their presence can be detected from the infrared absorption curves of tunisite heated to 1000°C (Fig. 5). On the same figure the curves of infra-red absorption spectra of tunisite specimens heated to 650 and 950°C re-spectively are given for the purposes of comparison. The O–H absorption band at 3500 cm^{-1} is for obvious reasons also distinctly recorded on them.

The products resulting from heating the tunisite specimens to the mentioned tempera-tures were subjected to X-ray powder diffraction study with the following results:

1. After the escape of 8 $CO_2 + 7$ H_2O, the specimens are composed for the most part of an amorphous phase. Besides, but in a smaller amount, a crystalline phase is present giving a simple X-ray powder pattern that can be indexed on the basis of a cubic unit cell with $a = 2.818$ Å. The chemical composition of this phase which we denote as phase α could not be established.

2. The amorphous product occurring at 440°C crystallizes at the temperature of 850°C (exothermic reaction). As can be concluded from Table 4, in addition to phase α, the presence of $12CaO \cdot 7Al_2O_3$ and $CaO \cdot Al_2O_3$ was detected. There are still some other phases present in this material. However, they could not be identified.

TABLE 3. X-RAY POWDER DATA FOR TUNISITE HEATED TO 650° C
(Cu/Ni; $\lambda = 1.5418$ Å; camera diameter 114.59 mm)

I	d(meas)Å	d(calc)Å	hkl
10	2.823	2.818	100
9	1.993	1.993	110
3	1.625	1.627	111
2	1.409	1.409	200
3	1.261	1.260	210
2	1.151	1.151	211

TABLE 4. X-RAY POWDER DATA FOR TUNISITE HEATED TO 950° C

Tunisite heated to 950°C[a]		Phase α		12 CaO·7 AP$_2$O (ASTM Card 9-413)		CaO·Al$_2$O$_3$ (ASTM Card 1-0888)	
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*
2 vb	5.54 Å					3	5.6
5	4.90			95	4.89		
1	4.66					13	4.69
3	4.396					2	4.41
2 b	4.014					5	4.05
1	3.746			15	3.79	7	3.71
6	3.480					1	3.50
Diffuse band	3.273– / 3.186			25	3.204	4	3.20
1	3.058						
10	2.966			45	2.998	100	2.97
8	2.830	10	2.823			7	2.85
1	2.735					1	2.75
7	2.664			100	2.680		
3	2.585			17	2.556		
9	2.512					42	2.52
5	2.436			50	2.447	27	2.41
6	2.392						
2 b	2.329					7	2.33
7	2.181			40	2.189	10	2.20
2	2.132					5	2.13
1	2.092					3	2.08
2	2.049			9	2.054		
9	2.002	9	1.993				
2 vb	1.949			30	1.945		
6	1.918					20	1.92
3 b	1.833					5	1.84
2	1.797						
1	1.760					3	1.75
3	1.728			11	1.730		
2 b	1.692			7	1.695	3	1.69
5	1.658			30	1.662	5	1.65
4	1.630	3	1.625	9	1.630		
5	1.601			30	1.601		
2	1.579					5	1.58
1	1.552						
9 vb	1.490			5	1.498	20	1.53
3	1.478			7	1.475		
8 b	1.455						
1	1.432						
2	1.409	2	1.409				
2	1.392			17	1.393		
3	1.371						
1	1.356			3	1.356		
2	1.340			7	1.340		
3	1.308			7	1.307		
1	1.298			5	1.292		
2	1.279			5	1.277		
5	1.263	3	1.261	5	1.263		

[a] (Cu/Ni; Camera diam. 114.59 mm)

TABLE 5. X-RAY POWDER DATA FOR TUNISITE HEATED TO 1000°C

Tunisite heated to 1000°C[a]		$12CaO \cdot 7Al_2O_3$ (G. Hentschel, 1964)		$CaO \cdot Al_2O_3$ (ASTM Card 1-0888)		$3CaO \cdot 5Al_2O_3$ (ASTM Card 1-0572)	
I	d	I	d	I	d	I	d
2	5.52 Å			3	5.6		
6	4.91	s	4.91				
1	4.68			13	4.69		
2	4.44			2	4.41	40	4.46
1	4.220	vw	4.23				
2	4.050			5	4.05		
1	3.810	vw	3.82				
1	3.605						
5	3.521					100	3.50
1	3.203			4	3.20		
1	3.079					40	3.09
10	2.979	m	3.00	100	2.97	27	2.96
3	2.871			7	2.85	33	2.87
1	2.762					40	2.73
7	2.695	vs	2.69				
4	2.603					100	2.60
9	2.525			42	2.52		
4	2.448	ms	2.45			47	2.44
5	2.411			27	2.41		
3	2.344	w	2.36	7	2.33		
7	2.196	m	2.19	10	2.20		
1	2.145						
1	2.097						
1	2.058	w	2.06			40	2.05
3	2.023			7	2.02		
2	1.948	m	1.95				
8	1.925			20	1.92		
2	1.834			5	1.84		
1	1.799					30	1.80
1	1.767					33	1.76
2	1.731	m	1.73				
1	1.694	w	1.70	3	1.69		
4	1.662	m	1.66				
1	1.637	w	1.64	5	1.65	40	1.62
3	1.605	m	1.60				
2	1.579			5	1.58		
1	1.544						
7	1.532			20	1.53	67	1.53

[a] (Cu/Ni; Camera diam. 114.59 mm)

TABLE 6. THERMAL REACTIONS OF TUNISITE

Reaction	Temperature	% Loss of Weight	Interpretation of the reactions
Endothermic	440°C	38.2	Escape of $7H_2O + 8CO_2$, occurrence of the cubic α phase and an X-ray amorphous phase
Exothermic	850°C	2.6	Escape of $2H_2O$, crystallization of $CaO \cdot Al_2O_3$, $12\ CaO \cdot 7Al_2O_3$ and of other unidentified phases

3. The diffraction lines of the phase α were not found on the X-ray powder pattern of the specimen heated up to 1000°C (Table 5). Of the other phases, $CaO \cdot Al_2O_3$, $3\ CaO \cdot 5\ Al_2O_3$, and $12\ CaO \cdot 7\ Al_2O_3$ were identified.

Taking into account the chemical composition of tunisite, it is noteworthy that in the heated specimens no phase containing sodium in essential quantity has been identified. The results of the thermal study of tunisite are summarized in Table 6.

INFRARED ABSORPTION ANALYSIS

The infrared absorption curve of tunisite (Fig. 6) was obtained with a UNICAM 200 infrared absorption recording spectrometer using Nujol method. The infrared spectrum of tunisite is characterized by the presence of absorption bands with peaks at 680 s, 850 s, 985 s, 1155 s, 1530 vs, 1725 w, 1860 vw, 1920 w, 2330 vw, 2650 w, and 3500 s cm⁻¹.

Because of the similarity in the chemical composition of dawsonite and
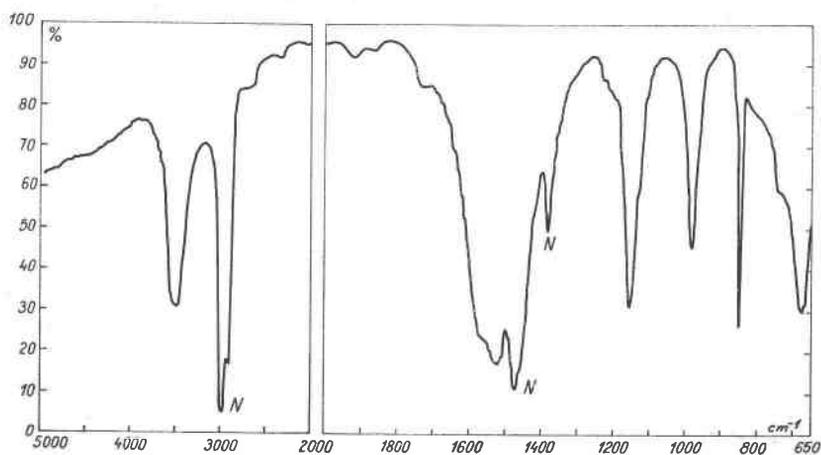
FIG. 6. Infrared absorption curve of tunisite. N—Nujol peaks.

tunisite it was possible to use the results of the paper by Frueh and Golightly (1967) for the interpretation of the infrared absorption spectra of tunisite. To the CO_3^{2-} vibrations correspond the absorption bands at 850 s, 1155 s, and 1530 vs cm^{-1}. Compared with the results obtained by Stubićan and Roy (1961), it is possible that the absorption at 985 s cm^{-1} is caused by O–H–Al vibrations. The latter authors expressed the opinion that these vibrations were essentially due to OH^- vibrations the occurence of which could take place in the presence of another element, in this case Al. The absorption at 680 s cm^{-1} may be due to Al–O vibrations (Frueh, Golightly, 1967). The remaining weak absorption peaks could not be explained. It is noteworthy that within this region some absorption bands were established by Frueh and Golightly (*op. cit.*) for dawsonite as well.

The specimens of tunisite are kept in the mineralogical collection of the National Museum in Prague (specimen No. 53823). The new mineral was approved by the Commission of New Minerals and Mineral Names of I.M.A. in November 1967.

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