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HALOTRICHITE, SZOMOLNOKITE, AND ROZENITE FROM DOLLIVER STATE PARK, IOWA

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ABSTRACT

Abundant sulphate efflorescences on Pennsylvanian sandstones of Dolliver State Park have previously been considered to consist of melanterite. X-ray diffraction, infrared absorption, and differential thermal, thermogravimetric, and chemical analyses have now shown that they consist of halotrichite, szomolnokite, and rozenite. Melanterite may occur in place of the lower hydrate, rozenite, during times of high humidity.

INTRODUCTION

One of the most interesting localities for sulphate minerals in Iowa is near Fort Dodge, in Webster County, where they have been known since the publications of White (1870), Keyes (1893), and Wilder (1902). The chief location for sulphates, other than gypsum, is along Prairie Creek in Dolliver State Park, where sulphate efflorescences occur on outcrops of Pennsylvanian sandstones and conglomerates. One outcrop, especially noted for the occurrence of ferrous sulphate minerals, was designated as the « Copperas Beds » by early Iowa geologists because of the occurrence of ferrous sulphate, copperas. Ever since chemical analyses performed by the Iowa Geological Survey in the late 1800's disclosed that the minerals consisted of hydrated ferrous sulphate, they have been considered to be melanterite, $FeSO_4.7H_2O$.

The fact that recent studies of melanterite (Jambor & Traill 1963; Ehlers & Stiles 1965) have shown that it rapidly dehydrates into rozenite, $FeSO_4.4H_2O$, under conditions of low and moderate humidity suggested that the earlier identification of the Copperas Bed minerals as only melanterite was incorrect. The present study has confirmed this, for melanterite was not present in the samples collected for study. Three less common minerals were identified: halotrichite, $FeAl_2(SO_4)_4.22H_2O$, szomolnokite, $FeSO_4.H_2O$, and rozenite, $FeSO_4.4H_2O$. This is the first reported occurrence of any of these minerals in Iowa, and, as far as the authors are aware, the first report of szomolnokite in the midcontinental United States.

DESCRIPTION AND OPTICS OF THE COPPERAS BED MINERALS

Samples, referred to in this report as the copperas mixture, were collected from the Copperas Beds in October, 1970. The minerals occurred on outcrop as a fibrous, white, three-quarter inch long layer of thin elongate crystals intermixed with a mass of very fine-grained crystals. Microscopic examination showed that the fine-grained crystals were equant in habit and apparently were a second mineral different from the elongate crystals. Very minor amounts of a third mineral with a higher birefringence than the other two were also observed.

All three minerals were readily soluble in cold water, but the elongate crystals dissolved more rapidly than the other two. Isolation of the fine-grained material by hand-picking and by differential dissolution in water was unsuccessful because the minerals were closely intergrown and did not differ enough in their dissolution rates. Indices of refraction of the elongate crystals in sodium *D* light *are* $\alpha = 1.470$, $\beta = 1.486$, $\gamma = 1.489$. These are similar to data given in Palache, Berman & Frondel (1951) for halotrichite ($\alpha = 1.480$, $\beta = 1.486$, $\gamma = 1.490$). The equant crystals were too small to allow accurate refractive index determination.

EXPERIMENTAL METHODS

X-ray diffraction analyses were performed on a Norelco diffractometer equipped with a pulse height analyzer, and using CuK_α radiation and scan rate of 1° 2θ per min. from 5° to 65°. The diffractometer-determined peak locations were verified with a 57 mm powder camera using Cr radiation. Differential thermal analyses were performed on a Stone instrument, model 202, using a heating rate of 10°C/min. and an air atmosphere. Thermogravimetric analysis used a Dupont thermogravimetric analyzer, model 950, and N_2 atmosphere. A heating rate of 1°/min. with horizontal scale expansion was employed from ambient to 200°C to determine if stepwise dehydration of the minerals could be detected, and 10°/min. from 200°C to 950°C. Results obtained in air and N_2 atmospheres were nearly identical except that reactions occurred at a slightly lower temperature in air.

Infrared analyses were performed on a Perkin-Elmer IR spectrophotometer, model 21, using a standard KBr disk mounting technique. IR spectra were obtained on unheated samples and on samples after heating to different temperatures in an oven for about one hour and then quenching in air. Chemical analyses for magnesium, iron and aluminum were performed on a Perkin-Elmer atomic absorption spectrophotometer, model 303.

In any study of hydrated minerals, there is a possibility of hydration changes between outcrop and final analytical results. In the present study, hydration changes of halotrichite and szomolnokite should be unimportant. Once formed, both minerals are very stable and samples have been stored in museums for decades without noticeable changes. This stability was demonstrated in our study when we attempted to rehydrate the minerals by suspending them over steaming water for 6 hours. No significant shifts in the diffraction traces of these two minerals were found upon analysis immediately after treatment. Changes in hydration are also possible during grinding, and for this reason grinding was kept to a minimum and performed immediately before analysis.

TABLE 1. COMPARISON OF X-RAY DIFFRACTION DATA FOR COPPERAS BED MINERALS, HALOTRICHITE, ROZENITE, AND SZOMOLNOKITE

Copperas Minerals		Halotrichite				Rozenite		Szomolnokite			
		Bauer & Sand 1957		Caillere & Prost 1968		Kubisz 1960*a*		(this paper)		Kubisz 1960*b*	
d Å	I/I°	d Å	I/I°	d Å	I/I°	d Å	I/I°	d Å	I/I°	d Å	I/I°
15.66	18			13.51	30						
10.52	12	10.4	15	10.49	30						
9.56	12	9.5	13	9.48	30						
9.11	8										
7.94	15	7.82	10	7.90	30						
6.94	8			7.07	10	6.85	50				
6.70	8										
6.41	10										
6.05	35	6.02	30	6.06	40						
5.79	8			5.81	10						
5.47	22			5.48	20	5.46	90				
5.27	12	5.24	15	5.26	20	5.17	5				
4.84	25			4.91	70			4.87	50	4.84	90
								4.82	35		
4.79	100	4.77	100	4.80	80	4.73	10				
		4.62	30								
4.48	25			4.55	40	4.47	100				
4.38	10										
4.35	12	4.29	55	4.31	100						
4.11	10	4.09	45	4.12	80						
3.95	30	3.95	35	3.98	40	3.97	70				
				3.87	20						
3.77	35	3.75	40	3.76	30			3.77	10	3.77	40
				3.64	20						
3.50	95	3.48	100	3.49	100						
3.44	40							3.45	100	3.44	100
3.39	10					3.40	60	3.39	25	3.38	40
3.35	10			3.33	10						
3.29	20	3.30	20	3.28	10	3.27	10	3.30	30	3.31	80
						3.22	50				
3.11	15	3.16	15	3.16	20			3.12	50	3.11	90
		3.05	15	3.04	20						
2.96	15	2.96	20	2.95	20	2.98	40				
						2.95	50				
2.89	15	2.86	30	2.85	20	2.91	5				
2.83	15										
2.78	20	2.76	20	2.76	10	2.77	10				
						2.72	10				
2.68	12	2.67	25	2.67	20	2.67	5				
2.66	10										
2.61	12	2.61	20					2.59	20	2.58	70
2.52	14	2.55	20	2.55	20	2.57	40	2.53	30	2.53	80
2.46	12	2.45	10			2.47	5				
2.43	10			2.44	10	2.43	30	2.43	20	2.43	10
								2.40	8	2.40	10
		+ additional lines						+ additional lines			

Acetone or alcohol were not used because sulphate minerals often form organic complexes with alcohol and some of the sulphates are soluble in acetone (M. Mrose, USGS, personal comm. 1971). These hydration changes of these two minerals were unimportant is also shown by the fact that x-ray diffraction analyses run over a period of several weeks under different humidity and temperature conditions disclosed no differences for haltotrichite and szomolnokite peaks between analyses. This conclusions does not apply to rozenite, however, which changes rapidly and reversibly to melanterite under humid conditions (Jambor & Traill 1963). This mineral has probably changed in the lab although similar changes undoubtedly took place several times on outcrop. Probably melanterite could be found in Dolliver Park during times of high humidity, but prevention of its dehydration to rozenite during analyses would be difficult.

Discussion of Results

A comparison of x-ray diffraction peaks (Table 1, Fig. 1) of the copperas mixture with those of halotrichite (or pickeringite, the magnesium end member of a solid solution series between iron and magnesium) szomolnokite, and rozenite shows that nearly all the peaks correspond. Relative intensities are not always similar, however; this is especially obvious when comparing Kubisz data (1960b) for szomolnokite to similarly-located peaks of this artificial mineral corresponded very closely to those recorded szomolnokite under the instrumental conditions used in the present study, the artificial mineral was synthesized according to the method summarized by Standard-Messo Duisburg Gesellschaft (1967). The positions of x-ray peaks of this artificial mineral correspond very closely to those recorded by Kubisz (1960b), but the peak intensities differ (Table 1). The intensities here determined correspond closely to those suspected of belonging to szomolnokite in the copperas mixture.

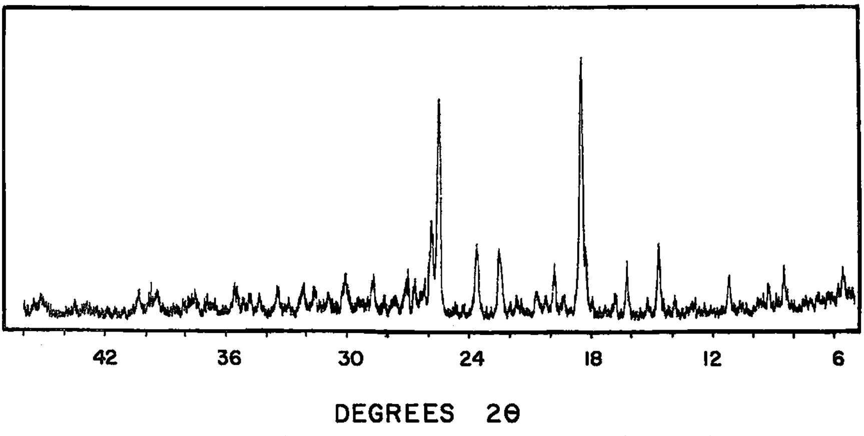

Fig. 1. X-ray diffraction pattern of Copperas Bed minerals.

A few peaks, e.g. that a 15.66 Å, were not satisfactorily accounted for. Whether these unidentified peaks correspond to another unidentified mineral in the mixture or to one of the three identified minerals and result from compositional or minor structural differences between these minerals and previously-studied examples is not known. Atomic absorption analysis of the Copperas Bed minerals (Table 2) shows the mixture contains little magnesium, thereby eliminating the possibility of pickeringite in the samples. The small amount of magnesium present undoubtedly replaces iron in one or more of the minerals present. In addition, the copperas mixture contains more iron, less aluminum, and less water than ideal halotrichite. All these features are consistent with the presence of a low-hydrate iron sulphate, such as szomolnokite, which dilutes the aluminum, increases the iron, and decreases the water content of the mixture. Assuming an ideal composition for halotrichite in the mixture, the chemical analysis indicates that halotrichite and szomolnokite each constitute about 40-50 per cent of the sample, and that rozenite is present in minor amounts. This conclusion is supported by relative intensities of *x*-ray peaks associated with each of these minerals, and by visual observation. Evidently, the elongate crystals are halotrichite, the fine-grained equant crystals are szomolnokite, and the highly birefringent crystals are rozenite.

Some of the excess iron and lesser aluminum in the mixture could also result from minor replacement of aluminum by ferric iron in the halotrichite structure. Although a relatively rare ferric analogue of halotrichite, bilinite, $Fe^{2+}Fe_2^{3+}(SO_4)_4.22H_2O$, is known, the absence of major amounts of bilinite is shown by comparing the infrared spectrum (Fig. 2) of the Copperas Bed minerals with a published spsectrum of bilinite (Sitzia 1966) ;

TABLE 2. CHEMICAL ANALYSIS OF COPPERAS BED MINERALS

	Copperas Minerals	Artificial Halotrichite * $FeAl_2(SO_4)$. $22H_2O$	Artificial Pickeringite * $MgAl_2(SO_4)$. $22H_2O$	Rozenite (Kubisz 1960a) $FeSO_4 . 4H_2O$	Artificial Szomolnokite * $FeSO_4 . H_2O$
$FeO + Fe_2O_3$	22.8%	8.07	0.00	31.13	42.28
MgO	0.05	0.00	4.69	0.97	0.00
Al_2O_3	4.91	11.45	11.87		0.00
SO_3	32.0[1]	35.97	37.29	36.29	47.12
H_2O	33.9[2]	44.51	46.15	32.98	10.60

* Palache, Berman & Frondel (1951).

1. Corresponds to weight loss from 475°C to 900°C.
2. Corresponds to weight loss from ambient to 475°C.

sulphate absorption bands at about 1110cm^{-1} in bilinite are not present in the Copperas Bed mineral spectrum.

The infrared absorption spectrum of the Copperas Bed minerals corresponds approximately to that of halotrichite and rozenite (Omori & Kerr 1963). The spectrum obtained on an unheated sample (Fig. 2) shows a single broad ν_3 sulphate band at 1110cm^{-1}; the ν_1 sulphate at 1019 cm^{-1} (which is forbidden in the near IR range but which often occurs because the unsymmetrical bonding between sulphate molecules and other atoms in a mineral structure), and a small sulphate ν_4 band at 663 cm^{-1}. The single broad ν_3 band is characteristic of many sulphate minerals, including halotrichite and rozenite. The small ν_1 band found in the copperas spectrum has not been observed for halotrichite or rozenite.

Typical water bands occur at 3300 cm^{-1} and 1640 cm^{-1} but the presence of shoulders at 3030 and 2540 cm^{-1} on the high frequency band indicates that water is bound in the mixture with different bond strengths. Other water bands occur at 1505 cm^{-1}, 950 cm^{-1}, and 824 cm^{-1}. These bands have been observed in several sulphate compounds (Duval & Lecompte 1959; Gamo 1961; Campbell *et al.* 1970). Assignment of these three bands

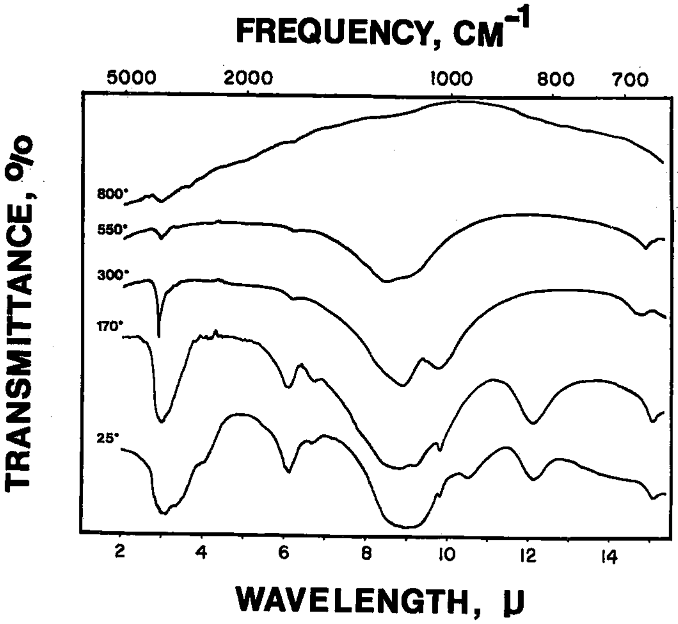

Fig. 2. Infrared absorption spectra of heated and unheated Copperas Bed minerals.

to water is based upon analogy with similar assignments by Gamo (1961) in his study of copper sulphate monohydrate. Of the water absorption bands found in the IR spectra of the Copperas Bed minerals, the bands at 1505 cm^{-1} and 824 cm^{-1} have not been reported for halotrichite or rozenite (Omori & Kerr 1963) ; the 950 cm^{-1} band was observed for halotrichite, but it was not nearly as intense as the corresponding band in the Copperas Bed mineral spectrum.

Omori & Kerr (1963) have shown that halotrichite and rozenite cannot be easily distinguished by their infrared spectra, but the copperas mixture also has several distinctive bands which are not characteristic of either of these minerals. The bands are the ν_1 sulphate band at 1019 cm^{-1}, and the two water bands at 1505 cm^{-1} and 824 cm^{-1}. Artificial szomolnokite (Table 3, Fig. 3) exhibits all of the above bands, in addition to some bands which are not found in the spectrum of the Copperas Bed minerals. The significance of the extra bands is not understood since, to the authors'

TABLE 3. OBSERVED INFRARED ABSORPTION FREQUENCIES OF ARTIFICIAL SZOMOLNOKITE

Absorption Freq. cm^{-1}	Assignment	Absorption Freq. cm^{-1}	Assignment
3250	Water	1012	$SO_4\nu_1$
1620	Water	883	Water (?)
1495	Water	845	Water (?)
1395	Water (?)	820	Water
1275	Water (?)	663	$SO_4\nu_4$
1140	$SO_4\nu_3$	660	$SO_4\nu_4$
1080	$SO_4\nu_3$		

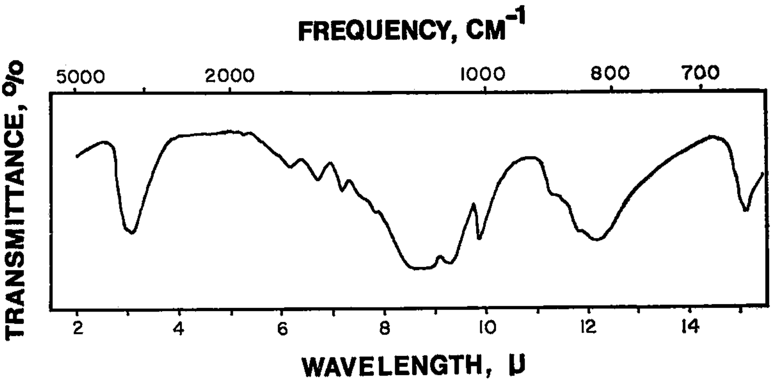

FIG. 3. Infrared spectrum of artificial szomolnokite.

knowledge, they have not been observed in other sulphate minerals. They may result from the synthesis method employed, but they do not represent acetone which was used to wash the material since they do not correspond to any reported for acetone (Thermo. Res. Center, 1970, card No. 283). The similarity of IR spectra of the artificial szomolnokite with bands of the copperas minerals is additional evidence for the presence of this mineral in the mixture.

The DTA curve for the copperas mixture (Table 4, Fig. 4) does not correspond closely to published data on halotrichite (Cocco 1952; Caillere & Frost 1968; Bretsznajder & Rojkowski 1969), but is very similar to that of rozenite from the Thames River gravel of England (Midgley 1962). Several copperas peaks occur at much lower temperatures than analogous peaks for halotrichite. Although wide variation in peak position has been previously obtained in three different studies of halotrichite (Table 4) these variations are too large to result from instrumental effects, and must result from compositional variations between different samples. Thus, the differences between curves of the Copperas Bed minerals and those of halotrichite cannot be considered as evidence against the occurrence of this mineral in the mixture.

TGA and infrared analyses performed after heating the copperas mixture to temperatures just above each DTA peak indicate the reactions

TABLE 4. DIFFERENTIAL THERMAL ANALYSIS OF COPPERAS BED MINERALS

ENDOTHERM	Copperas Minerals	Halotrichite 1	Halotrichite 2	Halotrichite 3	Pickeringite[3]	Rozenite[4]
TEMPS. °C						74 W
	125 S	120 M	100 S	120 S	100 S	114 S
		150 S	200 M	135 S		
	270 W	320 M	300 M	280 W	330 M	
				320 M	400 M	
	620 M	550 W	770 W	770 M	770 W	555 M
	740 M	805 M	900 M	790 M	900 M	700 M
				810 M		
EXOTHERM	450 M			520 VW		275 W (pyrite)
TEMPS. °C						400 M

S = stong, M = medium, W = weak, VW = very weak.

1. Cocco (1952).
2. Caillere & Prost (1968); temperatures estimated from their diagram.
3. Bretsznajder & Rojkowski (1969).
4. Midgley (1962).

corresponding to each peak. TG analysis (Fig. 5) shows a major weight loss at about 100° C corresponding to the lowest temperature DTA endotherm. The IR spectrum of a sample heated to 170° C shows the disappearance of water bands at 3030 cm^{-1}, 2540 cm^{-1}, and 950 cm^{-1}, proving that the low temperature endotherm corresponds to dehydration. This reaction is probably limited to halotrichite because szomolnokite would yield steps in the TG curve, and rozenite is present in quantities too small to affect either the DTA or TGA curves.

Some water remains in the mixture above 170° C as shown by the persistence of water bands in the IR spectrum of the heated sample. The water bands remaining seem to correspond to coordinated water which is

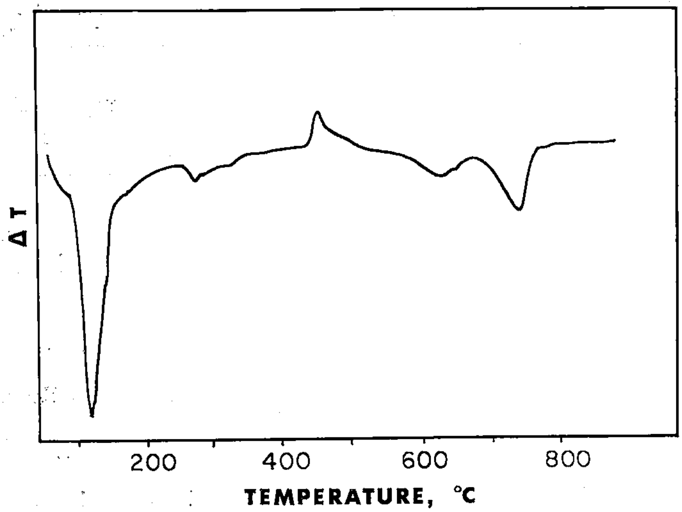

Fig. 4. Differential thermal analysis curve for Copperas minerals. Air atmosphere.

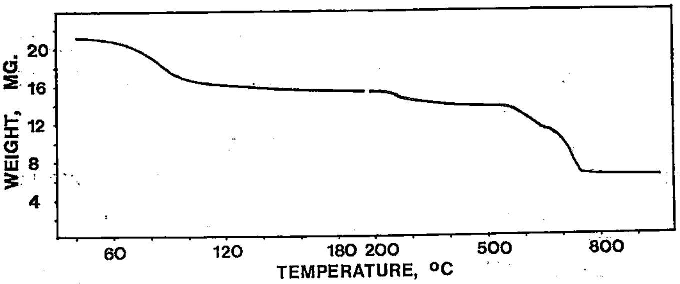

Fig. 5. Thermogravimetric analysis curve for Copperas Bed minerals. Nitrogen atmosphere.

strongly held in the mineral structure. This water is probably entirely associated with the monohydrate, szomolnokite. The magnitude of water bands in the heated sample is somewhat surprising since only minor amounts of water could be present, but this is consistent with corresponding bands of artificial szomolnokite (Table 3, Fig. 3).

A second endotherm at about 270° C corresponds to a minor weight loss involving coordinated water as shown by the disappearance of water bands from the sample heated to 300° C. Szomolnokite evidently loses its single water molecule at 270° C.

Heating to 300° C also affects the sulphate molecules in the mixture. The single broad ν_3 sulphate band at 1110 cm^{-1} which characterized the unheated sample has split into two bands at 1127 cm^{-1}. In addition, the ν_4 sulphate band has broadened and probably represents two overlapping ν_4 bands. According to Adler & Kerr (1963), the single broad sulphate band at about 1100 cm^{-1} represents highly symmetric bonding of the sulphate molecules within a mineral lattice; under these conditions the ν_3 vibration becomes triply degenerate so that a single absorption band occurs rather than three bands at slightly different frequencies which are characteristics of sulphate molecules bound in an unsymmetric manner. In this highly symmetric environment, the sulphate molecule is said to be located in a lattice site possessing T_d symmetry. Heating of the mixture to 300° C seems to have rearranged the sulphate molecules so that they now occupy lattice sites of lower, probably C_{3v}, symmetry; that is, one of the bonds between a cation and an oxygen of the sulphate molecules is not equivalent to the other three bonds.

In addition to rearrangement of the sulphate molecules, heating below 300° C also releases some sulphur as indicated by a very strong sulphur smell. The exact amount of sulphur lost at low temperatures is unknown, but the assumption that all weight loss of the mixture below 475° C

TABLE 5. X-RAY DIFFRACTION DATA FOR COPPERAS BED MINERALS AFTER HEATING TO 550°C

d Å	*I/I°*	*d* Å	*I/I°*
6.30	35	3.02	30
4.48	20	2.80	20
3.66	100	2.77	60
3.08	20	2.70	10
		2.57	30

(Table 2) corresponds to simple dehydration is therefore not precisely correct.

The 450°C DTA exotherm is very similar to one noted by Midgley (1962) for siderotil. This peak does not correspond to any weight change in the copperas mixture, and therefore must result from a phase change. *X*-ray diffraction and IR analyses support this. A new crystalline phase with characteristic *x*-ray peaks was observed for a heated sample (Table 5). and the sulphate IR band in the sample heated to 550° C is different than in the 300° C sample (Fig. 2). Evidently the higher temperature treatment has expelled some sulphur and perhaps has reorganized the sulphate molecules into another higher symmetry lattice site.

The 620° C endotherm corresponds to major loss of sulphur, probably as SO_2 gas by analogy to melanterite dehydration (Gallagher *et al.* 1970). The 740° C endotherm corresponds to additional sulphur loss, probably as SO_3 gas (Gallagher *et al.* 1970). This two-stage removal of sulphur is indicated by the two high temperature endotherms and by the two-stage weight loss shown on the TGA curve. Complete loss of sulphate above 740° C is indicated by the complete disappearance of sulphate absorption bands from a sample heated to 800° C.

Origin of the Copperas Bed Minerals

The Copperas Beds are located in a geologic setting ideal for a variety of saline sulphate minerals. These rocks are porous and permeable, are iron-stained and contain locally abundant iron concretions, and interfinger with pyritic coals and black shales within a short lateral distance. In this type of setting, there is an abundant source of substances required for the formation of many saline minerals, and the porous and permeable sandstones and conglomerates of the beds allow easy groundwater transport of dissolved materials. Surface evaporation of the groundwater then concentrates the dissolved substance, leading to precipitation of the sulphates. These strata seem extraordinarily rich in relatively unusual sulphates in addition to the minerals described here. In April 1971, after the present analyses were finished, another visit to Dolliver Park was made to collect additional minerals. A preliminary *x*-ray diffraction study disclosed that the sulphates obtained on the last trip were entirely different than those found in 1970. The minerals precipitated at this locality are apparently dependent on seasonal conditions. Usually the efflorescences dissolves after heavy rains and new ones precipitate during drier weather. Undoubtedly the minerals species that precipitate will vary, depending on weather conditions during precipitation. Study of these additional sulphate minerals is now in progress.

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