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MINERALOGY OF THE ZIPPEITE GROUP

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ABSTRACT

The ill-defined mineral zippeite and a number of zippeite-like minerals, hitherto supposed to be hydrated uranyl sulfates, are found to contain one or another of various monovalent or divalent cations in addition to uranium. They correspond to synthetic phases with the formula $A_x(UO_2)_6(SO_4)_3(OH)_{10} \cdot yH_2O$, where A is K, Na or NH_4 (with $x=4$ and $y=4$) or Co,Ni,Fe^{2+},Mn^{2+},Mg,Zn (with $x=2$ and $y=16$). All are structurally related but three subgroups are indicated by X-ray and chemical evidence: the K and NH_4 members, the Na member, and the divalent cation members. Extensive solid solutions exist between the divalent cation members but not with the K and Na members. The Na member is orthorhombic with *a* 8.80, *b* 68.48, *c* 14.55Å; all of the members are related to an orthorhombic pseudocell with *a* ~8.8, *b* ~17.1, *c* ~7.2Å.

The chemical identity of the type zippeite of J. F. John (1821) from Joachimsthal is not known. A similar mineral described by R. Nováček (1935) from the same locality is identified as the K member and is taken as the neotype. Other identified natural phases include sodium-zippeite (the common member), cobalt-zippeite, nickel-zippeite, magnesium-zippeite and zinc-zippeite. An altered mineral probably representing the iron member also occurs. Efforts to synthesize the Ca and Cu members of the group failed.

SOMMAIRE

La zippéite, minéral mal défini, ainsi qu'un certain nombre de minéraux analogues, étaient considérés jusqu'ici comme des sulfates d'uranyle hydratés; ils s'avèrent contenir, outre l'uranium, l'un ou l'autre de différents cations monovalents ou divalents. Ces minéraux correspondent aux phases synthétiques $A_x(UO_2)_6(SO_4)_3(OH)_{10} \cdot yH_2O$, où A est K, Na ou NH_4 (avec $x=4$ et $y=4$) ou bien Co, Ni, Fe^{2+}, Mn^{2+}, Mg, Zn (avec $x=2$ et $y=16$). Ils sont tous apparentés par leur structure, mais se classent en trois groupes, chimiquement et aux rayons-X, selon qu'ils contiennent: K ou NH_4, Na, ou un cation divalent. De nombreuses solutions solides existent entre pôles à cations divalents, mais non K et Na. Le composé correspondant au pôle Na est orthohombique avec *a* 8.80, *b* 68.48, *c* 14.55Å; tous ces minéraux possèdent une même pseudomaille avec *a* ~8.8, *b* ~17.1, *c* ~7.2Å.

La nature chimique de la zippéite type de Joachimsthal (J. F. John 1821) n'est pas connue. Un minéral analogue, décrit par R. Nováček (1935) et provenant de la même localité, est identifié comme potassique et est considéré comme néotype. D'autres phases naturelles ont été identifiées; ce sont les zippéites de sodium (la plus commune), de cobalt, de nickel, de magnésium et de zinc. Un minéral altéré représente probablement la zippéite de fer. Les efforts faits pour synthétiser les zippéites de Ca et de Cu ont été vains.

(Traduit par la Rédaction)

INTRODUCTION

The first uranium sulfates found in nature were recognized by the German chemist J. F. John in 1821. At that time the only other known uranium minerals were the species subsequently called uraninite, torbernite and autunite. John described and qualitatively analyzed an emerald green *uranvitriol* and a yellow earthy *basisches schwefelsäures uranoxyd* from Joachimsthal, Czechoslovakia. The uranvitriol later was described crystallographically and named johannite by Haidinger (1830). The yellow earthy sulfate was named zippeite* by Haidinger (1845) but without further description.

Minerals attributed to zippeite have since

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*A memorial of František X. M. Zippe (1791-1863), Czech mineralogist, is given by Kettner (1963).

been found at numerous localities but their study has been attended by many difficulties. In part this has been caused by the very fine-grained and admixed nature of the material and by the quite limited samples available for analysis. The main source of trouble, however, has been the long-standing belief that the mineral was a hydrated uranyl sulfate. It is now found that the earlier analyses were incomplete, and that the minerals and synthetic compounds hitherto loosely grouped around the name zippeite contain one or another of various monovalent or divalent cations in addition to the uranyl ion.

The earlier summary accounts of natural and synthetic so-called zippeite by Nováček (1935), Traill (1952) and Frondel (1958) constitute a composite description of a group of related substances. They believed the mineral to be a hydrated uranyl sulfate. This situation gave rise to complications during the 1950's, a period of active study of the mineralogy of uranium, when supposed uranyl sulfates falling within the range of properties attributed to "zippeite" were found at many places. Some of these substances were tentatively referred to by new names, such as the meta-zippeite, meta-zippeite-I, meta-zippeite-II and beta-zippeite mentioned by Gruner *et al.* (1954) and others. A few occurrences became known informally by the name of the mine in which they were found, such as "Happy Jack zippeite" and "Lucky Strike zippeite".

With regard to the identity of the original mineral from Joachimsthal, Nováček (1935) did not succeed in finding type specimens of John's material and based his description and microchemical analyses of zippeite on certain non-type specimens from the same locality. He thought that the rather variable material represented a series of hydrated uranyl sulfates. Frondel (1958) obtained three of these specimens*, found them to be similar to a synthetic compound reported to be a hydrated uranyl sulfate, and described this material as zippeite-proper with the composition $2UO_3 \cdot SO_4 \cdot 5H_2O$.

Following the recognition early in the present study that certain synthetic zippeite-like preparations contained K as an essential constituent, two of Nováček's specimens and the earlier analyzed synthetic compound were re-analyzed and found to be a potassium uranyl sulfate. An extensive program of phase synthesis was then undertaken that led to the recognition of a large group of structurally related compounds. This included members found here to be identical with various natural zippeite-like minerals. The latter have been named zippeite (the K member of the group), sodium-zippeite, cobalt-zippeite, nickel-zippeite, magnesium-zippeite and zinc-zippeite. These names have the approval of the Commission on New Minerals and Mineral Names of the I.M.A.

METHODS OF SYNTHESIS

Zippeite-type phases were precipitated from acid solutions containing uranyl sulfate together with sulfates of K, NH_4, Na, Co, Ni, Fe^{2+}, Mn^{2+}, Mg or Zn. Precipitation was effected at room temperature by the addition of NH_4OH (or NaOH) to solutions containing divalent cations and of KOH, NaOH or NH_4OH to solutions containing the corresponding monovalent sulfates. Experimentation established that the phases are precipitated in acid solutions over a wide range of molar ratios and concentrations. Control of pH is essential. In general, if a dilute alkaline solution is slowly added dropwise with vigorous stirring, bringing the pH up to 4.0–4.2, a precipitate will form on standing for hours or days. Under these conditions only a small proportion of the dissolved cations is precipitated. If the precipitation is effected at somewhat higher pH, becquerelite or other phases in either crystalline or amorphous form may coprecipitate.

The rapid addition of the alkaline precipitant, depending on its normality and the vigor of stirring, may locally give a relatively high pH with accompanying immediate precipitation of becquerelite. This may then redissolve slowly. The rather divergent ratios of UO_3 to SO_3 reported in some analyses of synthetic material may be due to admixture of becquerelite. Uranyl sulfate solutions that are nearly saturated with the monovalent or divalent sulfates, and that have an initial pH below 3, generally yield satisfactory results.

The use of NaOH in precipitating the divalent cation and K members often results in the coprecipitation of the Na member. This precipitates first and may then be followed, on standing, by the divalent cation compound. The Na member is commonly admixed in natural material.

The particle size of the precipitates tends to increase with time when left in the mother solution, but crystals large enough for single-crystal study could not be obtained even after several months. In general the particle size increases with decreasing pH at the level of precipitation and with increasing dilution. Zippeite-type phases containing Ca or Cu could not be synthesized.

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*Kindly supplied by Dr. Karel Tuček of the National Museum in Prague.

GROUP DESCRIPTION

The composition and properties of the members of the zippeite group are summarized in this section. Details of the individual members are given in following sections.

Chemical composition

The 8 chemical analyses of natural and synthetic materials referred to zippeite are summarized by Frondel (1958): they are all believed to have overlooked K or other cations. The 13 new chemical analyses reported here for natural and synthetic material indicate that the general formula for the group is $A_x(UO_2)_6(SO_4)_3(OH)_{10}\cdot yH_2O$, where A includes the monovalent cations K, Na and NH_4 (with $x=4$, $y=4$) and the divalent cations Co, Ni, Fe, Mn, Zn, and Mg (with $x=2$, $y=16$). The monovalent and divalent cations probably occupy all or half of a single structural site.

Syntheses effected from solutions containing varying ratios of K and Na establish that there is a small mutual substitution of K and Na near the end-compositions but that K-rich and Na-rich phases otherwise coprecipitate. The K member slowly recrystallizes to the Na member when immersed in a concentrated solution of NaCl, but the Na member does not convert in a KCl solution. There is a complete solid-solution series between the Co and Ni members in synthetic material and probably also in natural material. Efforts to investigate the solid solubility between the Co, Fe and Mg members by X-ray methods failed because of the very poorly crystallized nature of the precipitates. Extensive mutual substitution between the various divalent cations is indicated in natural material.

X-ray crystallography

X-ray study indicates that all of the members have identical or very closely related structures. Single-crystal study by the Weissenberg and precession methods of an analyzed natural Na member did not afford a satisfactory determination of the unit cell and space group. The unit cell is orthorhombic and very large, with *a* 8.80, *b* 68.43, *c* 14.55Å. There is a marked pseudocell, *C* face-centered, with *a* 2.21, *b* 2.84, *c* 7.275Å. Most of the reflections on both single-crystal and powder photographs can be indexed in terms of larger pseudocells with *a* 8.80, *b* 34.24 or 17.12, and *c* 7.275 or 14.55Å, but the true cell, verified by very strongly exposed photographs, has *b* 68.48Å. The space group is not known. The only systematic extinctions established with certainty are (00*l*) with *l* odd. Single-crystal X-ray study would be very desirable for other members of the zippeite group but suitable crystals are lacking. A partial indexing for the Na member of the group in terms of a pseudocell with *a* 8.82, *b* 17.12 and *c* 7.32Å is given in Table 1.

The X-ray powder data for synthetic and natural members of the zippeite group are given in Table 1. The powder photographs of the members of the group are all similar but three subgroups comprising the K and NH_4 members,

TABLE 1. X-RAY POWDER DATA FOR THE ZIPPEITE GROUP

Zippeite, synthetic*		Zippeite, Joachimsthal**		Sodium-zippeite synthetic†				Cobalt-zippeite Nickel-zippeite synthetic		Nickel-zippeite, Happy Jack mine		Magnesium-Zippeite Lucky Strike mine**		Zinc-zippeite, synthetic		Manganese-zippeite, synthetic	
I	d_{meas}	I	d_{meas}	I	d_{meas}	d_{calc}	hkl	I	d_{meas}	I	d_{meas}	I	d_{meas}	I	d_{meas}	I	d_{meas}
7	8.58	2	8.60	1	8.56	8.56	020	6	9.82	37	9.63	1	9.7	33	9.62	12	8.52
100	6.95	10	7.06	100	7.34	7.32	001	6	8.70	9	9.04	8	7.2	10	8.52	100	7.15
2	6.24	1	6.24	2	4.715	4.705	121	100	7.21	19	8.51	1	4.9	100	7.08	5	6.22
12	5.41	3	5.45	2	4.270	4.280	040	6	5.54	7	7.69	1	4.2	9	5.46	12	5.49
11	4.29	2	4.29	6	4.004	4.009	131	4	4.88	93	7.10	1	3.9	8	5.19	5	4.29
10	4.24	1	3.89	14	3.754	3.777	201	6	4.23	12	6.41	10	3.58	14	4.84	10	4.19
4	3.85	3	3.66	54	3.663	3.660	002	8	3.94	5	6.07	8	3.48	2	4.53	5	3.93
21	3.62	9	3.50	44	3.490	3.480	230	8	3.69	12	5.47	6	3.11	7	4.28	6	3.67
77	3.482	8	3.12	35	3.153	3.150	231	46	3.59	7	5.19	2	2.88	9	4.18	50	3.583
8	3.227	4	2.87	15	2.858	2.853	060	22	3.47	19	4.82	3	2.74	10	3.89	41	3.453
66	3.108	2	2.72	5	2.666	2.675	222	28	3.12	26	4.19	2	2.52	50	3.54	6	3.317
22	2.860	4	2.65	9	2.529	2.526	232	2	3.03	16	3.90	1	2.49	35	3.44	54	3.110
8	2.698	3	2.47	7	2.439	2.440	003	8	2.865	42	3.56			4	3.27	12	2.863
20	2.644	2	2.34	3	2.253	2.250	062	4	2.739	100	3.45			26	3.100	19	2.660
3	2.592	4	2.22	8	2.206	2.205	400	10	2.653	67	3.10			8	2.860	16	2.483
21	2.460	2	2.14	11	2.118	2.119	213	11	2.491	21	2.85			8	2.650	6	2.391
10	2.321	2	2.09	5	2.023	2.030	072,342	8	2.388	15	2.724			15	2.467	2	2.302
7	2.239	3	2.05	8	2.002	2.004	262	4	2.303	30	2.644			3	2.362	9	2.227
13	2.210	3	1.94	7	1.891	1.889	402	5	2.323	31	2.481			4	2.276	5	2.165
13	2.189	1	1.87	11	1.746	1.745	460	4	2.180	10	2.380			6	2.227	4	2.135
7	2.140	2	1.75	6	1.701	1.704	282	1	2.140	7	2.292			6	2.160	10	2.075
8	2.089	2	1.70					6	2.080	21	2.227			6	2.067	5	2.047
12	2.041	1	1.69					2	2.054	12	2.164			4	2.008	6	2.011
22	1.932							12	1.963	19	2.128			15	1.943	18	1.967
9	1.855									10	2.075			3	1.892	4	1.855
6	1.797									7	2.045			3	1.824	8	1.834
8	1.752									15	1.956			2	1.772	4	1.795
15	1.741									7	1.853			7	1.695	6	1.747
12	1.697									12	1.825					6	1.728
12	1.687															10	1.699
																8	1.680

*Diffractometer recording, Cu radiation, Ni filter. Peak heights in arbitrary chart units. **Film recording, 114.6 mm diameter camera. Cu radiation, Ni filter. †Indexing for cell with *a* 8.82, *b* 17.12, *c* 7.32Å.

the Na member, and the divalent cation members can be distinguished. These subgroups correspond to limits in the mutual substitution of the cations involved and to differences in the degree of hydration. Efforts to index the patterns of all members of the group in terms of the stated pseudocells for sodium-zippeite failed although some of the stronger lines can be indexed in common. The three subgroups probably have different although closely related structures. Traill (1952) has described a monoclinic synthetic phase that is very similar in its X-ray powder pattern and refractive indices to the K member, zippeite, but that differs in symmetry and cell geometry from sodium-zippeite.

The natural materials are frequently very fine-grained mixtures that cannot be separated so that extra lines in the powder patterns are a common problem.

Physical and optical properties

In synthetic material, the K and NH_4 members are golden yellow in color, the Na, Mg and Zn members are yellow, the Co and Ni members orange to tan, the Mn member dull orange brown, and the Fe member yellowish brown. All fluoresce bright yellow in both short- and long-wave ultraviolet radiation, somewhat less strongly in the Co, Ni, Mn and Fe members. The hardness could not be determined precisely but is near 2. The specific gravity is more than 3.3 for all members.

Crystals of both the natural and synthetic members are microscopic in size. They comprise rhomboidal to slightly elongate plates with very similar angles in the different members as measured in plane section under the microscope. Rounded rhomboidal crystals together with petal-like, spindle-shaped and lath-like shapes are common. The obtuse internal angle of the rhomboids is near 106°. Vermicular aggregates or stacks of crystals joined by their flat sides are common. Warty crusts and dense to earthy aggregates composed of minute shreds also occur.

Optically, the crystals conform to orthorhombic symmetry. The optical orientation is the same in all members: the acute bisectrix X is perpendicular to the plane of flattening and cleavage, (010), with Z parallel to the elongation or c-axis; $2V(-)$ is moderate to large. All members are pleochroic with X colorless to pale yellow, Y yellow, Z dark yellow to golden yellow. Twinning is common. The most common twin law is on a $(h0l)$ plane with symmetrical extinction Z to Z' of about 28°. Another type of twin, sometimes polysynthetic or repeated as fourlings, has symmetrical extinction Y to Y' of about 74°. There is a perfect cleavage parallel to the flattening, or (010), with a suggestion of a cleavage inclined to this plane.

The indices of refraction fall into two groups: the divalent cation members, with α in the range 1.70 to 1.75, and the Na and K members, with α 1.63 and 1.65 respectively. The optical study of the natural minerals is rendered difficult by the generally fine-grained nature of the material and especially by the frequent admixture of compositional variants, as in efflorescent crusts with a complex history of deposition. Sodium-zippeite and, less frequently, the potassium member, zippeite, occur intimately admixed with other members of the group.

Occurrence

The members of the group are all secondary in origin and typically occur in the oxidized zone of uraninite deposits containing sulfides. They are also found, sometimes abundantly, as efflorescences on the walls of mine workings. Gypsum, uranopilite and johannite are common associates. The sulfate content of these minerals comes from the oxidation of the sulfides, chiefly pyrite and chalcopyrite, but including smaltite-chloanthite and other CoNi minerals in the case of the Co and Ni members of the group. Sodium-zippeite, the more common member of the group, is typical of deposits of the so-called sandstone type. Zippeite is more typical of weathered uraninite vein occurrences in igneous or metamorphic rocks.

ZIPPEITE

The redefinition of zippeite as the K member of the group is based on the re-examination of material studied by Nováček (1935) and on the identity of this material with synthetic potassium uranyl sulfate. An identical mineral also was found on old specimens labelled uranochre from Joachimsthal (acquired in 1821 for the Harvard collection) that probably are contem-

TABLE 2. CHEMICAL ANALYSES OF ZIPPEITE

	1	2	3
K_2O	8.17	7.89	8.06
Na_2O			0.62
UO_3	74.39	75.38	
SO_3	10.41	11.41	
H_2O	7.03	4.92	
Total	100.00	99.60	

1. Calculated for $K_4(UO_2)_6(SO_4)_3(OH)_{10}\cdot 4H_2O$
2. Synthetic material. Jun Ito, analyst. Sample dried at 105°C.
3. Joachimsthal. Jun Ito, analyst. Heavy metals present only in spectrographic traces. Loss at 500°C 10.7%. Optical and X-ray data identical with synthetic material.

TABLE 3. OPTICAL PROPERTIES OF ZIPPEITE

	1. Synthetic (present study)	2. Synthetic (Gruner 1954)	3. Synthetic (Traill 1952)	4. Joachimsthal	5. Colorado (Larsen 1921)	6. Schneeberg	7. Hillside mine, Utah
α	1.654	1.657	1.655	1.655	1.660	1.657	1.657
β	1.716	1.720	1.717	1.716	1.710	1.717	1.720
γ	1.768	1.768	1.765	1.768	1.760	1.767	~1.77

Optically negative with 2*V* large. Pleochroic with *X* colorless, *Y* pale yellow, *Z* yellow.

TABLE 4. OPTICAL PROPERTIES OF SODIUM-ZIPPEITE

	1. Synthetic	2. Delta mine, Utah	3. Atomic King mine, Utah	4. Capitol Reef, Utah	5. W.N. mine, Utah	6. Happy Jack mine, Utah	7. Fruita, Utah (Hess 1924)
α	1.630	1.632	1.637	1.630	1.634	1.629	1.630
β	1.690	1.688	1.688	1.689	1.687	1.685	1.689
γ	1.738	1.738	1.737	1.739	1.735	1.732	1.739

Biaxial negative, 2*V* about 80°. Pleochroic with *X* colorless, *Y* pale yellow, *Z* yellow.

poraneous with the original material of J. F. John (1821).

The X-ray powder data, optical properties and chemical analyses of natural and synthetic zippeite are given in Tables 1, 2 and 3. The NH_4 member of the group has an almost identical X-ray pattern and slightly higher indices of refraction than the K member, zippeite. The reported optical and X-ray data indicate that both phases are represented among the numerous earlier reported syntheses of hydrated uranyl sulfates using KOH or NH_4OH as precipitants. The direct water determinations reported for such material are higher (10–13% H_2O) than that found here.

In addition to the original occurrence at Joachimsthal, where it occurs with gypsum, uranopilite, johannite and other members of the zippeite group, we have identified zippeite from the following localities: Great Bear Lake, Canada, associated with liebigite and uranopilite [this material is different from that called zippeite by Palache & Berman (1933), which probably was uranopilite]; at the Telegraph, Wood and Kirk mines in Gilpin County, Colorado, where it occurs with ill-defined zippeite-type minerals containing Zn and Fe; at the Hillside mine, Yavapai County, Arizona, as one of several zippeite-type minerals; at the Besner mine, Henvey Township, Ontario, as a coating on thucholite; and as a coating on uraninite at Schneeberg, Saxony.

SODIUM-ZIPPEITE

This mineral, the most common member of the group, was recognized as a distinct mineral as early as 1950 by the writers and others on the basis of its optical properties (Table 4) and X-ray powder pattern (Table 1). An adequate description, however, was obtained only after it had been synthesized and analyzed (Table 5). The yellow color of sodium-zippeite contrasts with the golden yellow color of zippeite. The optical properties of sodium-zippeite and zippeite are not materially altered by desiccation over $CaCl_2$ or by exposure to air saturated with water. There are no changes in the optical characters of sodium-zippeite on heating to 61°C; at 101°C, about 0.5% H_2O is lost, the indices of refraction increase (α 1.666 β 1.712, γ 1.770) and the X-ray pattern becomes slightly diffuse.

TABLE 5. CHEMICAL ANALYSES OF SODIUM-ZIPPEITE

	1.	2.	3.	4.	5.	6.
Na_2O	5.53	5.85	4.96	4.91	5.25	5.09
K_2O				0.19	0.47	0.42
UO_3	76.53	73.76	76.79	76.92	75.86	74.1
SO_3	10.71	9.63	10.39	10.22	10.43	12.5
H_2O	7.23	10.25	7.43	7.62	7.99	7.89
Total	100.00	99.49	99.57	99.86	[100.00]	[100.00]

1. Calculated from $Na_4(UO_2)_6(SO_4)_3(OH)_{10}\cdot 4H_2O$
2,3,4. Synthetic materials. Jun Ito, analyst. Analysis 4 on homogeneous material from solution containing Na: K = 4 : 1.
5. Delta mine, Utah, Recalculated to 100 after deduction of 0.1 CaO as gypsum and 4.39 insoluble (SiO_2,Al_2O_3,Fe_2O_3). Jun Ito, analyst.
6. Same. Less pure sample. Recalculated to 100 after deduction of 6.62 insoluble. Jun Ito, analyst.

A notable locality is at the Happy Jack mine in White Canyon, San Juan County, Utah, where it occurs abundantly with other members of the group as efflorescences on the mine walls; also at the Delta mine, in the southwestern part of the San Rafael Swell, Emery County, Utah, in part as cross-fiber veinlets; with andersonite at the Atomic King mine, Cane Springs, Moab County, Utah. Other proven localities, all in Utah, include the Oyler mine, Henry Mountains district, Wayne County; the Lucky Strike No. 2 mine, Emery County; the Parco No. 23 mine, Grand County; the Soda Roll mine, Green River district, San Juan County; and the W. M. mine, Deer Flat, San Juan County. The mineral from Fruita, Utah, analyzed by W. T. Schaller (cited in Hess 1924) is sodium-zippeite. Also found admixed in some specimens of zippeite and of nickel-zippeite from Joachimsthal. Minerals described optically by Nováček (1935) from Joachimsthal and by George (1949) from Gilpin County, Colorado, may be sodium-zippeite in part.

The "zippeite" and zippeite-like minerals listed in many Atomic Energy Commission and U.S. Geological Survey internal reports of the period 1950-1960 as occurring at numerous mines and prospects in the Colorado Plateau region and elsewhere probably are sodium-zippeite in large part. Some of the earlier reported optical and X-ray data, however, cannot be reconciled with any of the present descriptions.

COBALT-ZIPPEITE AND NICKEL-ZIPPEITE

It was found experimentally that a complete solid solution series exists between the synthetic Co and Ni members. The X-ray powder spacings (Table 1) and the indices of refraction (Table 6) of the end-compositions are virtually identical.

TABLE 6. CHEMICAL ANALYSES OF NICKEL-ZIPPEITE AND COBALT-ZIPPEITE.

	1.	2.	3.	4.	5.	6.
MgO			0.54	0.56		
FeO			0.70	0.57		
MnO			0.33	0.27		
NiO	6.01	6.32	2.14	1.87		
CoO			1.33	1.98	6.59	6.03
UO_3	69.09	68.4	66.1	67.2	67.8	69.07
SO_3	9.67	9.57	10.56	10.55	9.48	9.67
H_2O	15.23	15.20	18.1	17.0	15.46	15.23
Total	100.00	99.49	[100.00]	[100.00]	99.33	100.00
	α	1.745	1.73-1.74		1.747	(colorless)
	β	1.777	1.76-1.77		1.779	(pale yellow)
	γ	1.84	1.82-1.83		1.84	(yellow)

1. Calculated for $Ni_2(UO_2)_6(SO_4)_3(OH)_{10}\cdot 16H_2O$
2. Synthetic nickel-zippeite. Jun Ito, analyst.
3. Nickel-zippeite. Happy Jack mine, Utah. Recalculated to 100 after deducting SiO_2 1.23, Al_2O_3 0.5, TiO_2 0.08, $(Ce,Y)_2O_3$ 0.41, 12.0 sodium-zippeite, 1.4 johannite. Jun Ito, analyst.
4. Cobalt-zippeite. Happy Jack mine, Utah. Recalculated to 100 after deducting SiO_2 0.80, 0.98 (TiO_2,Al_2O_3,Ce_2O_3), 8.0 sodium-zippeite, 1.6 johannite. Jun Ito, analyst.
5. Synthetic cobalt-zippeite. Jun Ito, analyst.
6. Calculated for $Co_2(UO_2)_6(SO_4)_3(OH)_{10}\cdot 16H_2O$

Zippeite-type material containing Co, Ni, and other cations in widely varying ratios was abundant at one time at the Happy Jack mine, Emery County, Utah. Here the material occurred as extensive coatings on the mine walls associated with sodium-zippeite, uranopilite, johannite and zeunerite together with chalcanthite, antlerite, siderotil, bieberite, erythrite, epsomite and gypsum. The primary uraninite ores at the mine (Trites *et al.* 1959) were locally rich in gersdorffite and unidentified CoNi minerals, from which the Co and Ni were derived, together with pyrite, chalcopyrite, bornite and sphalerite.

The Co-Ni-zippeite solid solutions are intimately admixed with sodium-zippeite and johannite together with finely divided clayey material. They are also relatively fine-grained, as minute shreds and petal-like crystals, and the somewhat variable optical properties could not be measured with precision. The color of the material varies from tan to brownish yellow and orange yellow. Traversing the mine tunnels with a portable ultraviolet lamp afforded spectacular views.

The fine-grained nature of the material made it impossible to obtain pure samples for analysis. By means of X-ray fluorescence analysis, using standards made of the analyzed synthetic members, the Ni-Co atomic ratio was measured in 19 small hand-picked samples. The ratio was found to range from approximately 4:1 to 1:3. The ratio varied in material from different places in the mine and also in successive layers in a single crust. The analyzed samples probably represented mixtures of grains of different Ni-Co ratio in all instances.

Two complete wet-chemical analyses on composite samples representing the material with Co>Ni and Ni>Co were obtained (Table 6). Further purification of these samples by sedimentation techniques failed to remove admixed sodium-zippeite, as found by optical and X-ray examination. Considerable Mg, Fe and Mn are present in solid solution but Ni or Co are the dominant cations. The occupancy of the divalent cation site in atomic percent in the two analyses is $(Ni_{39}Co_{24}Mg_{18}Fe_{13}Mn_6)$ and $(Co_{34}Ni_{32}Mg_{18}Fe_{11}Mn_5)$. The observed variation in the indices of refraction of individual grains presumably reflects variations in the amount and kind of the substituting cations.

Nickel-zippeite free from admixture was identified in several specimens from Joachimsthal. It had Ni:Co ~10:3 and contained minor Fe and Zn. The content of Ni and Co in this material derives from the smaltite-chloanthite and nickeline in the uraninite veins. Ni and Co also were found as major constituents in zippeite-type minerals, too impure and small in amount for satisfactory study, from Great Bear Lake and Hottah Lake, Canada, and from the Hillside mine, Yavapai County, Arizona. These all had Ni in excess of Co.

MAGNESIUM-ZIPPEITE

This mineral was found as a fine-grained efflorescence in workings of the Lucky Strike No. 2 mine in Emery County, Utah. It occurs very sparingly, associated with sodium-zippeite, gypsum, bieberite, cobaltocalcite and rabbittite. The mineral was originally found by M. E. Thompson, A. W. Weeks and A. M. Sherwood*

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*Priority for the recognition and description of this new mineral belongs to these authors.

but because of understandable uncertainties as to its true identification at that time, it was not mentioned in their account of the mineralogy of the mine published in 1955.

A microchemical analysis by A. M. Sherwood on a hand-picked 12 mg sample gave MgO 6.2, CoO 1.4, UO_3 74.6, SO_3 5.0, H_2O 10.9, total 98.1. The ratios of the analysis are not close to the formula for the zippeite group, but the identification of the mineral as the Mg member thereof is established by the X-ray powder data (Table 1). Co substitutes for Mg to a small extent. Mg also is a significant constituent of the cobalt-zippeite and nickel-zippeite from the Happy Jack mine. A complete series may extend between the Mg-Co-Ni members. The natural material has an orange yellow to orange tan color but the synthetic material is yellow.

Synthetic magnesium-zippeite was too fine-grained for satisfactory optical study; it has $\alpha \sim 1.70$, $\beta \sim 1.74$, $\gamma \sim 1.79$. The natural material examined here has slightly higher indices of refraction, with α 1.72 (pale yellow), β 1.75 (yellow), γ 1.82 (dark yellow), that varied slightly in different specimens probably due to variation in the Mg-Co ratio. Earlier-reported optical and X-ray data apparently represent a mixture with sodium-zippeite. The synthetic preparations all contain small amounts of optically amorphous foreign (?) material and no chemical analysis was made.

ZINC-ZIPPEITE

The X-ray powder data (Table 1) and optical properties of synthetic zinc-zippeite verify the unpublished description of a zinc uranyl sulfate found by Dr. Charles Milton[†] in specimens from the Hillside mine, near Bagdad, Yavapai County, Arizona. It occurs with sodium-zippeite and other zippeite-type minerals as yellow, orange and reddish brown coatings on quartzose ore containing disseminated sulfides and uraninite. Associated minerals include johannite, schroeckingerite, gypsum and bayleyite (Axelrod *et al.* 1951). The analyzed material (Table 7) is yellow and gives an X-ray pattern identical with that of synthetic material.

We also have identified this mineral in more recent specimens from the Hillside mine. It forms shreds and minute curved crystals; the optical properties (Table 7) are somewhat variable. Several other zippeite-type minerals occur at the locality. These include a more or less altered brownish yellow to brown mineral containing both Zn and Fe that is similar to material from Gilpin County, Colorado, described below; also present are one or more fine-grained yellow minerals with relatively low indices of refraction, α 1.61–1.65, and dark orange to brownish orange materials containing Mn, Fe and Ni in variable amounts.

TABLE 7. CHEMICAL ANALYSES OF ZINC-ZIPPEITE

	1.		2.	3.	
Na_2O			0.12		
ZnO	6.52		7.01	3.4	
MgO				0.87	
UO_3	68.71		67.33	69.10	
SO_3	9.62		9.93	9.69	
H_2O	15.15		15.85	14.26	
Rem.				3.7	
	100.00		100.00	101.02	
		α	1.72	1.70-1.715	(colorless)
		β	1.77	1.75-1.763	(pale yellow)
		γ	1.81	>1.7	(yellow)

1. Calculated for $Zn_2(UO_2)_6(SO_4)_3(OH)_{10}\cdot16H_2O$
2. Synthetic material. Jun Ito, analyst.
3. Hillside mine, Arizona. Microchem. anal. on 1.060 mg sample, by F.S. Grimaldi. Rem. is insoluble 2.1, PbO 1.6.

Fe^{2+}, Mn^{2+} AND Cu MEMBERS

Repeated efforts to synthesize the Fe^{2+} member of the group yielded extremely fine-grained precipitates, unsuited for optical study, that at best gave very faint and diffuse X-ray patterns of the zippeite-type. A suite of zippeite-type minerals from uraninite vein occurrences in Gilpin County, Colorado, probably includes the more or less oxidized Fe member of the zippeite group. When uraninite was first recognized in Colorado in 1871 at the Wood mine in Gilpin County, it was noted by Pearce (1895) that some specimens were coated by a "uranium vitriol", formed by oxidation of the pyritic ore, which consisted of johannite (gilpinite) together with a golden brown to apricot mineral. The latter was later described optically and called uraconite by Larsen (1921) and George (1949). Similar material occurred at the Kirk, Telegraph and Calhoon mines. Specimens examined here showed typical rhomboidal, petal-like and spindle-shaped crystals. The material is optically inhomogeneous and variable, probably caused by alteration of a single phase in some instances, but usually representing a mixture of related phases. Many grains are mottled or rimmed by alteration products. Spectrographic examination of hand-picked samples showed either Fe or Zn as the dominant cation; minor cations included Mg, Mn, Ni and Cu. Optically most of the samples are in the range α 1.71–1.74 (pale yellow), β 1.77–1.80 (yellow), γ 1.84–1.86 (golden). Larsen (1921) gave α 1.75, β 1.79, γ 1.85 with $2V$ medium. A sample with

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[†] Data supplied by Dr. Milton. Priority for the recognition of this new mineral belongs to him.

Zn much in excess of Fe had α about 1.71. The X-ray patterns are very poor and variable, but resemble those of the Co-Ni members. Both zippeite and sodium-zippeite occur with this material together with johannite.

The Mn^{2+} member of the group has been synthesized but has not been identified in natural material. The X-ray data are given in Table 1. The indices of refraction are α 1.73, β 1.78, γ 1.83. Mn was found by optical or X-ray spectrography to be a minor or trace constituent in numerous natural samples, especially from the Hillside mine, Arizona, the Happy Jack mine, Utah, and Gilpin County, Colorado.

The name cuprozippeite has been given by Boldyrev (1935) to a mineral containing 5% CuO but it is not known if the substance belongs in the zippeite group. Efforts to synthesize the Cu member of the group failed, johannite or basic copper sulfates being obtained together with sodium-zippeite or zippeite.

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