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NEW DATA ON GASTUNITE, AN ALKALI URANYL SILICATE

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ABSTRACT

Gastunite is an alkali uranyl silicate with the composition $(K, Na)_2(UO_2)_3(Si_2O_5)_4 \cdot 8H_2O$. Chemical analysis, recalculated after deducting impurities, gives SiO_2—31.2, UO_3—53.8, K_2O—4.6, Na_2O—0.9, H_2O—9.5, total 100.0 per cent. The proposed formula is supported by infra-red absorption data. *X*-ray study shows the mineral to be orthorhombic, space group *Pnna* (W. Outerbridge), a_o—14.24, b_o—35.84, c_o—14.20, calculated specific gravity 3.97 (3.96±0.03 measured). Indexed powder pattern shows the strongest lines to be 7.12 (10), 3.56 (9), 9.10 (8), 4.83 (7), 3.31 (7). Optically biaxial positive with $\alpha=1.604$, $\beta=1.610$, $\gamma=1.621$: 2V moderate, anomalous blue interference color. Habit: radiating acicular to fibrous aggregates. Hardness 2. Perfect (010) cleavage. Gastunite occurs as a secondary mineral in radial aggregates coating chalcedony at the Red Knob mine, Muggins Mountains, Yuma County, Arizona; and in vesicular cavities in welded tuff at the Mammoth prospect, Presidio County, Texas. Also present in dense fine-grained pseudomorphs after uraninite from the Easton area, Pennsylvania. Hydrothermal synthesis data for the potassium, potassium plus sodium, sodium, ammonium, and hydronium analogues of gastunite are presented.

INTRODUCTION

Systematic investigation of secondary uranium minerals in the Harvard collection as part of a research project concerning the uranyl silicate minerals has revealed a second potassium uranyl silicate. The mineral is similar to uranophane in general aspect and occurrence, but on close examination is quite distinct in all respects. The mineral was first noted by Professor Clifford Frondel on specimens from the Red Knob mine, Muggins Mountains, Yuma Co., Arizona; and soon thereafter on specimens from the Mammoth prospect, Presidio Co., Texas, and the Easton area, Pennsylvania.

A search of the literature on the uranyl silicate minerals reveals that this new mineral bears a striking resemblence to gastunite, a provisional description of which was published by Haberlandt and Schiener (1951). More complete data is here presented, and a comparison made with the original data for gastunite.

HABIT, PHYISCAL PROPERTIES, AND OPTICS

Gastunite occurs as radial aggregates of acicular to fibrous crystals coating cavities, and in the Easton material as a dense microcrystalline aggregate pseudomorphous after uraninite. The color varies from yellow to greenish yellow in the radial aggregates, and is a dull straw yellow in the dense material. The specific gravity, determined from three fragments of the radial aggregates is 3.96±0.03 (3.97 calculated). Hardness 2.

There is a perfect (010) cleavage. Luster vitreous to pearly. The mineral does not fluoresce under either long- or short-wave ultraviolet excitation.

Optical data are listed in Table 1. Specimens of the Easton, Pennsylvania material and of the synthetically prepared material are seen on optical examination to be extremely fine-grained, and yield only an average index of refraction.

X-RAY DATA

The small grain size of material available to the writer precluded morphological and single crystal *x*-ray study, but it was found that the powder diffraction pattern could be indexed on a tetragonal cell. Resolution of the unit cell problem was made possible by data supplied from electron diffraction studies by W. Outerbridge of the U. S. Geological Survey (M. H. Staatz, personal communication). Outerbridge found the mineral to be orthorhombic, with marked pseudotetragonal symmetry.

TABLE 1. OPTICAL DATA

Analysis sample—Red Knob mine, Muggins Mountains, Yuma Co., Arizona		
α—1.604	Colorless	Biaxial positive
β—1.610	Very pale yellow	2V—moderate
γ—1.621	Pale yellow	Anomalous blue interference color
		Parallel extinction
		Elongation = Z
Mammoth prospect, Presidio Co., Texas		
α—1.596	Colorless	Biaxial positive
β—1.605	Very pale yellow	2V—large
γ—1.620	Pale yellow	Anomalous blue interference color
		Parallel extinction
		Elongation both parallel to and perpendicular to Z
Thomas Range, Utah (M. H. Staatz, personal communication)		
α—1.596		
β— —		
γ—1.606		
Easton, Pennsylvania		
Average n—1.61		
Synthetic products (too fine-grained for complete optical data):		
Potassium gastunite—average n—1.62. Anomalous blue.		
Potassium plus sodium gastunite—average n—1.611.		
Sodium gastunite—average n—1.61.		
Ammonium gastunite—average n—1.604.		
Hydronium gastunite—average n—1.601.		

TABLE 2. X-RAY CRYSTALLOGRAPHIC DATA

Gastunite—Orthorhombic (pseudotetragonal), space group Pnna, a:b:c=0.39732:1:0.39621. Calculated S. G. 3.97 (measured 3.96±0.03). Z=11.

	Honea	*Outerbridge*
a	14.24±0.01A	14.26±0.05A
b	35.84±0.02A	35.88±0.10A
c	14.20±0.01A	14.20±0.02A

Table 2 compares the data of Outerbridge with that of the writer, whose information was obtained from an indexed powder pattern. Spacings on the powder pattern are given in Table 3.

ANALYTICAL DATA

X-ray fluorescence analyses were made of material from the Texas and Arizona localities (Table 4), and a quantitative chemical analysis made by Jun Ito of the Harvard Mineralogical Laboratory on the material from Arizona. Great difficulty was encountered in separating sufficiently pure material for analysis, and it became necessary to compromise on a sample containing known impurities of wulfenite, vanadinite, and cuprite. The separation was accomplished by coarse grinding of material flaked off the specimen and subsequent removal of larger grains of impurities. The portion remaining was then separated in methylene iodide (S. G. 3.29) and the light fraction rejected. The heavy fraction was then ground slightly finer (−60 mesh), rerun through the heavy liquid, and then carefully hand-picked under the binocular microscope. It immediately became obvious that a complete separation was impossible because certain of the impurities were intimately intergrown with and included in the gastunite. For this reason enough of each visible impurity was taken for preparation of a powder spindle for identification and subsequent subtraction from the analysis.

Results of the chemical analysis are given in Table 5. Molecular amounts of the principal components after recalculation of the analysis indicate a composition of $(K, Na)_2O \cdot 3UO_3 \cdot 8SiO_2 \cdot 8H_2O$. The analysis, infra-red absorption data, and physical properties suggest a phyllosilicate formula, $(K, Na)_2(UO_2)_3(Si_2O_5)_4 \cdot 8H_2O$.

INFRA-RED ABSORPTION SPECTRA

Infra-red absorption data was obtained using a Perkin-Elmer instrument with sodium chloride prism. Samples were prepared for analysis by pressing a wafer containing 5 mg of very finely ground mineral in 0.7 grams of potassium bromide mounting medium. Since not enough ma-

Table 3. Indexed Powder Pattern of Gastunite. Orthorhombic (Pseudo-tetragonal), Space Group Pnna (W. Outerbridge), a_0—14.24, b_0—35.84, c_0—14.20. Cu Radiation, Ni Filtered, Wavelength 1.5418 Å

d_{meas}	I	hkl	d_{calc}	d_{meas}	I	hkl	d_{calc}	d_{meas}	I	hkl	d_{calc}
9.10	8	031	9.14			$2\underline{11}1$	2.90	2.18	2	$1\underline{16}1$	2.19
7.12	10	200	7.12			$1\underline{11}2$	2.90			$4\underline{13}0$	2.18
		002	7.10	2.81	2	462	2.81			661	2.18
6.59	1	220	6.62			$3\underline{10}1$	2.80			642	2.18
		022	6.60			392	2.80			$4\underline{12}2$	2.18
5.57	7	042	5.57	2.51	3	$0\underline{10}4$	2.52	2.10	4	$0\underline{17}0$	2.11
		240	5.57			404	2.51			662	2.11
4.83	3	071	4.82			$3\underline{11}2$	2.51			$3\underline{15}1$	2.11
4.58	5	260	4.58	2.41	4	562	2.42			680	2.10
		062	4.57			$2\underline{13}2$	2.42			$0\underline{17}1$	2.09
4.45	2	311	4.45			$0\underline{14}2$	2.41			086	2.09
3.84	5	322	3.85			$2\underline{14}0$	2.41	1.991	3	$4\underline{14}2$	1.995
		262	3.84			$4\underline{11}0$	2.40			$0\underline{18}0$	1.991
		091	3.83	2.38	5	$0\underline{15}0$	2.39			731	1.986
3.56	9	400	3.56			$0\underline{13}3$	2.38	1.973	4	$0\underline{10}6$	1.975
		004	3.55			$2\underline{14}1$	2.38			604	1.973
3.31	7	440	3.32			$4\underline{10}2$	2.38			406	1.971
		431	3.31			$3\underline{12}2$	2.38	1.927	3	732	1.930
3.18	7	450	3.19			600	2.37			$0\underline{17}3$	1.923
		402	3.18			006	2.37	1.903	5	$6\underline{11}1$	1.901
		204	3.18	2.29	5	631	2.30			$2\underline{18}1$	1.900
		381	3.18			046	2.29			$1\underline{10}2$	1.900
		$0\underline{11}1$	3.18			$4\underline{12}0$	2.29	1.872	2	$0\underline{19}1$	1.870
		412	3.17			640	2.29			$4\underline{16}1$	1.869
		222	3.17			591	2.29	1.830	2	$4\underline{16}2$	1.832
3.13	1	422	3.13			582	2.28			$0\underline{15}5$	1.828
		372	3.13	2.24	3	602	2.25			772	1.827
		292	3.12			206	2.25	1.778	4	800	1.780
		$2\underline{10}1$	3.12			$0\underline{16}0$	2.24			$3\underline{18}2$	1.778
		$1\underline{10}2$	3.12			$2\underline{15}1$	2.24			008	1.775
2.99	4	442	3.00			$1\underline{15}2$	2.24	1.743	3	$6\underline{13}2$	1.744
		461	2.99			651	2.23			048	1.741
		$0\underline{12}0$	2.99	2.20	4	632	2.21			$3\underline{19}1$	1.740
		391	2.98			066	2.20	1.725	4	$6\underline{14}1$	1.728
2.91	7	470	2.92			660	2.20			802	1.727
		$2\underline{10}2$	2.92			$5\underline{10}1$	2.20			208	1.722
		452	2.91			592	2.20			$0\underline{11}7$	1.722

d_{meas}	I	d_{meas}	I	d_{meas}	I	d_{meas}	I
1.689	4	1.322	3	1.088	½	0.903	½b
1.658	3	1.298	2b	1.063	1b	0.861	½b
1.592	3b†	1.260	1b	1.052	1	0.858	½b
1.562	4b	1.244	2	1.029	1	0.812	½b
1.518	1b	1.226	1	1.018	2	0.805	1
1.481	½	1.188	2b	0.989	1b	0.797	½b
1.458	1	1.174	2	0.979	1	0.794	½
1.431	2b	1.154	1	0.968	1	0.791	½b
1.404	3	1.125	½	0.952	1b	0.779	½
1.384	1	1.113	2	0.935	1	0.777	½
1.357	1b	1.101	1	0.912	½		

† b = broad.

Table 4. *X*-ray Fluorescence Analysis of Gastunite from Arizona and Texas

Red Knob mine, Muggins Mountains, Yuma Co., Arizona
Major—U
Minor—Pb, Mo, V, Cu, Fe
Mammoth prospect, Presidio Co., Texas
Major—U
Minor—Ba, Fe

terial was available from the chemical analysis sample, data from the Presidio County, Texas material is compared with that of synthetic products in Figure 1.

All three absorption spectra show maxima near 3.0 and 6.2 microns that correspond to the stretching and bending vibrations respectively of the hydroxyl (or HOH) bond (Randall, *et al.*, 1949). The absorption curve for ammonium gastunite (Figure 1C) also has lower wavelength

Table 5. Chemical Analysis of Gastunite from the Red Knob Mine, Muggins Mountains, Yuma Co., Arizona. Analyst Jun Ito

	A	B	C	D	E	F
SiO_2	23.1	3,846	31.2	5,195	8.21	30.47
UO_3	39.8	1,391	53.8	1,881	2.97	54.42
K_2O	3.4	361	4.6	488	1.00	5.97
Na_2O	0.7	113	0.9	145		
H_2O	7.0	3,885	9.5	5,273	8.33	9.14
CaO	1.1	196	—			—
PbO	11.4	511	—			—
MoO_3	7.2	500	—			—
V_2O_5	0.6	33	—			—
Cu_2O	1.2	84	—			—
MnO	0.2	28	—			—
Fe_2O_3	0.3	19	—			—
Rem.	2.9		—			—
Total	98.9		100.0			100.00

A. Analysis of sample containing known impurities of wulfenite, vanadinite, cuprite and "limonite." Rem., determined by semi-quantitative spectrographic analysis on 3 mg. of material, contains NiO—0.03, CoO—0.x, ZnO—0.X (Zn>Co), MgO—0.0X, Cr_2O_3—present, ZrO_2—present, TiO_2—present, In and Tl—present.
B. Molecular amounts calculated from analysis.
C. Principal components of gastunite recalculated to 100% after deducting impurities.
D. Molecular amounts for recalculated analysis.
E. Molecular proportions.
F. Theoretical composition of $K_2(UO_2)_3(Si_2O_5)_4 \cdot 8H_2O$.

peaks at 3.2 and 7.15 microns, the stretching and bending vibrations characteristic of the ammonium ion (Bellamy, 1954). Strong absorption in the region from 9 to 12 microns includes the wavelengths of 9.4 to 10.4 microns shown by Launer (1952, p. 782) to be typical of silicate bonding of the phyllosilicate type.

Comparison with Launer's data might also lead one to suspect a single chain structure (maxima in region from 9.2 to 11.6 microns) except that the chemical analysis shows there to be insufficient cations to balance the resulting anion charge. Shifts from the wavelengths cited by Launer (1952, p. 781) may result from differences in bond energies in uranyl silicate minerals as compared to the clay and mica minerals from which his data are taken. Also, Bellamy (1954, p. 309) tentatively assigns an absorption maximum near 11 microns to the uranyl ion, adding further to a resemblence of the above spectra to that of the phyllosilicates.

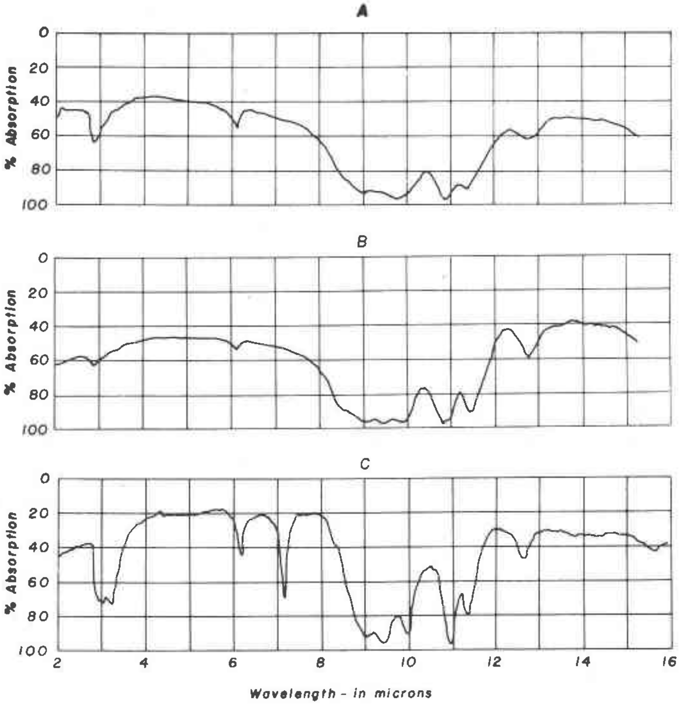

FIG. 1. Infrared-absorption spectra of natural and synthetic gastunite. A. Gastunite—Mammoth prospect, Presidio County, Texas. B. Synthetic potassium gastunite. C. Synthetic ammonium gastunite.

SYNTHESIS

Gastunite was first synthesized by the writer in July, 1956, and has since been noted as a synthetic product by A. M. Pommer (personal communication). The mineral has been prepared in low temperature runs (90° C.) by coprecipitation of soluble salts containing the essential ions. Precipitation is accomplished by raising the pH using NH_4OH or other similar base. The mineral persists in hydrothermal bomb runs to 250° C., becoming slightly more coarsely crystalline in runs allowed to heat for two weeks. Unfortunately the writer has not succeeded in obtaining crystals large enough for complete optical data.

As shown in Table 6 the potassium, potassium plus sodium, sodium, ammonium, and hydronium analogues of gastunite have been prepared in the laboratory. It will be noted in the table that gastunite appears in runs containing divalent cations, but the divalent cations are not believed essential to the structure. All of the analogues listed above yield *x*-ray powder patterns with essentially identical spacings and only slightly different intensities than those of the natural mineral as listed in Table 3.

Boltwoodite, the first of the alkali uranyl silicates to be described (Fondel and Ito, 1956), appears in some of the above syntheses. It is significant that boltwoodite is consistently the stable phase at higher pH when it does appear. Contrary results have been noted by A. M. Pommer (personal communication), but his method of synthesis is quite different and composition of the system would be expected to influence stability relations.

OCCURRENCE

The occurrence of the Easton, Pennsylvania material as pseudomorphs after uraninite indicates a definite secondary origin for gastunite, and by analogy with this occurrence and that of the other uranyl silicate minerals (Fondel, 1956) a similar origin is proposed for the better crystallized material from the other two localities studied by the writer. The Texas and Arizona material show no trace of original uraninite, and it is believed that the component ions were transported for short distances and deposited in cavities. The associated minerals; chalcedony, wulfenite, vanadinite, cuprite, and "limonite" in the Arizona specimen; and uranophane with smaller amounts of sklodowskite in the Texas specimen also indicate a secondary origin.

Specimens from the Red Knob mine, Muggins Mountains, Yuma County, Arizona, typically have gastunite as radial aggregates of acicular crystals coating, and intergrown with, the minerals listed above. The

TABLE 6. SYNTHESIS OF GASTUNITE

Reagents	pH	Temp.	Product	Bomb Run	pH	Product
Potassium silicofluoride Uranyl acetate Potassium hydroxide	8	90°	Boltwoodite	48 hrs. @ 235°	7	Potassium gastunite Boltwoodite
Potassium silicofluoride Uranyl acetate Potassium hydroxide	8	90	Boltwoodite	46 hrs. @ 243	6	Potassium gastunite
Sodium metasilicate Uranyl acetate Potassium acetate Potassium hydroxide	8	90	Amorphous	48 hrs. @ 249	7	Potassium-sodium gastunite
Ammonium silicofluoride Uranyl acetate Sodium acetate Sodium hydroxide	7½	90	Sodium gastunite	48 hrs. @ 235	6	Sodium gastunite
Potassium silicofluoride Uranyl acetate Sodium hydroxide	7½	90	Boltwoodite	48 hrs. @ 240	7	Sodium-potassium gastunite
Sodium orthosilicate Uranyl acetate Calcium acetate	11	85	Amorphous	48 hrs. @ 235	7	Sodium gastunite
Ammonium silicofluoride Uranyl acetate Ammonium hydroxide	7	90	Ammonium gastunite	48 hrs. @ 152	6	Soddyite
Sodium metasilicate Uranyl acetate Calcium acetate Ammonium hydroxide	8	95	Ammonium gastunite	41 hrs. @ 230	8½	Soddyite
Ammonium silicofluoride Uranyl acetate Lead acetate Ammonium hydroxide	8	95	Ammonium gastunite	48 hrs. @ 235	5	Kasolite
Ammonium silicofluoride Uranyl acetate Magnesium acetate Ammonium hydroxide	7	95	Ammonium gastunite	45 hrs. @ 252	5½	Hydronium gastunite
Ammonium silicofluoride Uranyl acetate Strontium acetate Ammonium hydroxide	7	90	Ammonium gastunite	48 hrs. @ 246	5	Hydronium gastunite Strontium fluoride

Mammoth prospect, Presidio County, Texas, material occurs as a lining of acicular to fibrous gastunite in vesicular cavities in a welded rhyolite tuff. The mineral occurs in a more highly bleached portion of the rhyolite, and is slightly deeper in color than the more abundant uranophane of the area. Chalcedonic and opaline quartz are also present in the cavities. Staatz (oral communication), who first noted the mineral several years ago from the Easton locality, has noted several localities unknown to the writer. These include several mines and prospects in the Thomas Range, Utah, and localities in California and Mexico.

COMPARISON WITH ORIGINAL DATA FOR GASTUNITE

It appears likely that the mineral herein described is identical with gastunite as provisionally described by Haberlandt and Schiener (1951). The lack of *x*-ray and analytical data in the original description makes a precise comparison impossible, but the available information is summarized in Table 7. The habit, occurrence, and optical data indicate the probable identity.

TABLE 7. COMPARISON OF PRESENT DATA WITH PUBLISHED DATA FOR GASTUNITE

	Gastunite	Present mineral
Color	Greenish yellow	Yellow to citron yellow
Crystal habit	Radial aggregate of needle-like crystals	Radial aggregates of acicular to fibrous crystals
Optics	nX—1.596 Colorless to pale yellow Anomalous blue nY nZ—1.597 Darker citron yellow Elongation =Z	nX—1.596–1.604 Colorless nY—1.605–1.610 Pale yellow nZ—1.606–1.622 Pale yellow to greenish yellow Biaxial (+), anomalous blue, Z either 11 or ⊥ to elongation
Composition	Spectrographic analysis—main components U, Ca, Si, Pb	Chemical analysis—main components U, Si, K, Na. Ca present, but is non-essential
X-ray powder pattern	Not identifiable with any other	Distinct from all known uranyl silicates

Gastunite occurs at the hot springs at Bad Gastein, Salzburg, and is named from the locality.

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