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Sodian potassian hydroxonian meta-autunite: first natural occurrence of an intermediate member of a predicted solid solution series

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Abstract

Sodian potassian hydroxonian meta-autunite, $(Na_{0.56}K_{0.29}(H_3O)_{0.16}) \cdot UO_2 \cdot PO_4 \cdot 3.25H_2O$, is a novel member of the meta-autunite group. It occurs in a playa 105 km NNE of Kalgoorlie, Western Australia as void and fracture infillings in near-surface gypsiferous muds. Mineral aggregates are bright greenish yellow with a strong yellow fluorescence under UV light and consist of micaceous crystallites usually 20–50 μm in diameter. The mineral has a R.I. of 1.575–1.580 and is probably uniaxial, optically negative. Reversible dehydration occurs readily on heating or under vacuum; dehydration is complete above 300°C but remains reversible even after partial melting has occurred on heating to 1200°C. Principal X-ray diffraction lines are $d = 4.94(110)$, 3.49(200), 2.47(113) and 220), 1.559(420). By the Guinier powder technique, these lines have intensities 75, 100, 75 and 50 respectively. These correspond to a meta-autunite I structure with tetragonal pseudo-cell dimension $a' = 6.971$Å and $c' = 8.545$Å. Heating did not produce a phase equivalent to the meta-autunite II structure. The sodian potassian hydroxonian meta-autunite is the first reported occurrence of an intermediate member of a predicted solid solution series with potassium, sodium and hydroxonium end members. It differs in origin from other naturally-occurring autunite and meta-autunite minerals in being a direct precipitate from groundwater, rather than an alteration product.

Introduction

Several members of the autunite and meta-autunite groups with monovalent cations in interlayer positions are known as naturally occurring minerals and/or as synthetic compounds. Ross and Evans (1965) suggest that there may exist a solid solution series, the torbernite group, with the general formula: $A(UO_2 \cdot PO_4) \cdot 3H_2O$ where $A = Li^+, Na^+, K^+, Rb^+$ Cs^+ NH_4^+ and/or H_3O^+. This series may also be isomorphous with arsenate minerals with the formula $A(UO_2 \cdot AsO_4) \cdot 3H_2O$.

The known naturally-occurring end members of the monovalent uranyl phosphate series relevant to this paper are meta-ankoleïte, $(K_{0.85}Ba_{0.1})(UO_2 \cdot PO_4)$ $3H_2O$ (Gallagher and Atkin, 1966), sodium meta-autunite (Chernikov *et al.*, 1958) and hydrogen autunite (Camargo, 1971), all of which occur rather sparingly as alteration products. We have examined meta-ankoleïte from the type locality by electron microprobe analysis and have not found barium, so the mineral is probably a true end member of the series. A new phase, sodian potassian hydroxonian meta-autunite, described here, is the first reported natural occurrence of an intermediate member of such a series and differs from them in being a direct precipitate in a playa, rather than an alteration product. This occurrence also is significant in that all other similar enrichments of uranium in drainages in Western Australia are due either to carnotite or to uranium in chalcedonic or opaline silica (Butt *et al.*, 1977). The discovery of this mineral was made by Esso Minerals Ltd. in 1977.

Location

The sodian potassian hydroxonian meta-autunite occurs in Boomerang Lake, 6 km SW of Menangina homestead, about 105 km NNE of Kalgoorlie, Western Australia, at latitude 29°52′10″S and longitude 121°52′25″E (Fig. 1). Boomerang Lake is a playa, situated in a semi-arid region with hot summers and mild winters. At Kalgoorlie, average annual rainfall is 263 mm, and mean daily minimum and maximum temperatures are 18.3°C and 33.6°C in January, and

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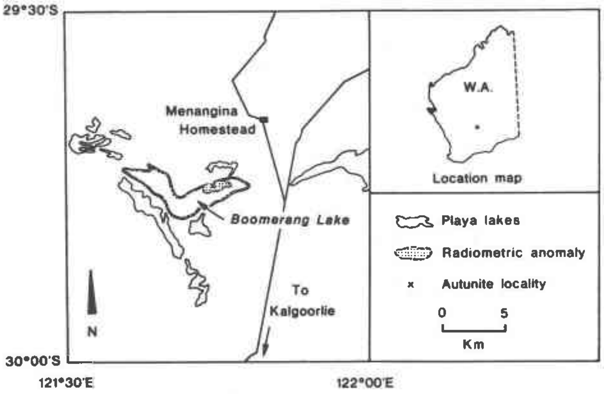

Fig. 1. Map showing site of occurrence of sodian potassian hydroxonian meta-autunite, Menangina, Western Australia.

4.8°C and 16.5°C in July. The playa forms part of a chain of lakes which are the present expression of a now alluvium-choked, ancient trunk valley draining southeastwards across the deeply weathered Archaean Yilgarn Block of southwestern Australia. The lakes are usually dry, and there is surface water flow only after exceptional rains; however, subsurface flow follows the course of the ancient valleys.

The mineral has been found in a small area, approximately 50 × 100 m, close to the northern shore of the lake. It occurs in saline, gypsiferous muds in the saturated zone, mostly at depths of 30–100 cm. It appears as prominent, bright greenish yellow (Munsell 2.5 GY 8/8) disseminations, fracture coatings and veinlet infillings in the red-brown (Munsell 2.5 YR 4.5/7) muds. Colors were determined on wet fracture surfaces. The veinlets, up to 1.5 mm × 20 mm, usually have no depth and the mineral appears to be a late-stage infilling of voids, shrinkage cracks and, occasionally, of cylindrical channels up to 2 mm in diameter, interpreted as root casts and/or insect burrows. Viewed under ultra-violet light, the mineral is finely disseminated throughout the muds. Carefully hand-picked material can still contain small amounts of quartz, gypsum and halite. A uranium oxide phase is also present: electron diffraction data indicate a cubic fluorite type cell, a = 5.46Å corresponding to uraninite. This has probably formed by reduction of the precipitated autunite phase.

Physical properties

Aggregates of the sodian potassian hydroxonian meta-autunite are soft and consist of small crystallites up to 1.5 μm thick and 100 μm diameter (but mostly in the range 20–50 μm), with a micaceous habit and a somewhat resinous luster. Scanning electron micrographs (Fig. 2) illustrate this habit very clearly. The mineral has a strong, bright yellow fluorescence under both long- and short-wave ultra-violet light. Optical characteristics are difficult to determine, due to the small size of the crystallites and, in any case, vary with water content. The mineral appears to be uniaxial (or, if biaxial, 2V is close to zero) and optically negative. The refractive indices are between 1.575–1.580. An attempt to measure the specific gravity by sink-float methods failed because of reaction of the sample with the heavy liquid (Clerici solution). There was insufficient material for classical density measurement, but attempts to use a micropycnometer method result in values between 3.7 and 4.7.

Chemical composition

Handpicked samples were dissolved in concentrated hydrochloric acid, diluted and analyzed by atomic absorption spectrometry for sodium and po-

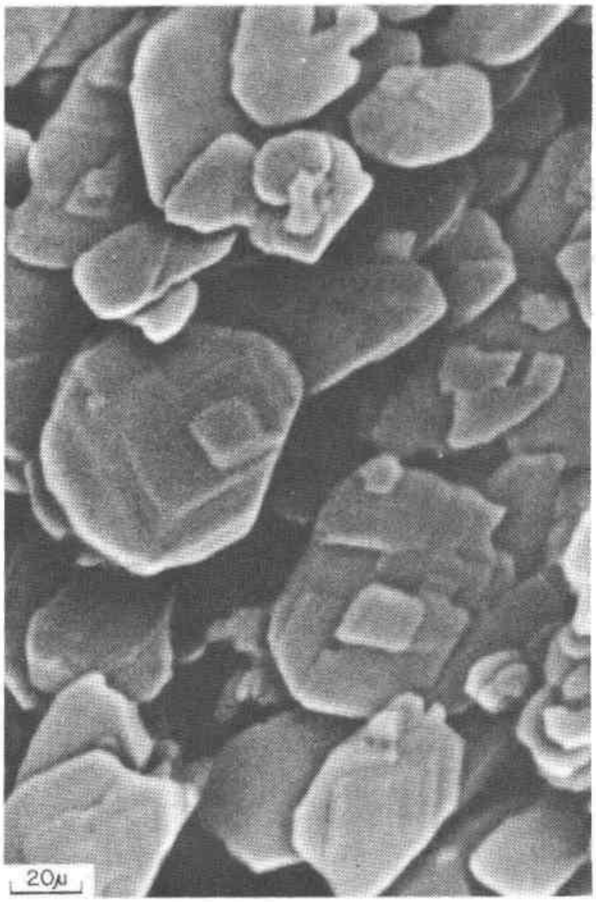

Fig. 2. Scanning electron micrographs of sodian potassian hydroxonian meta-autunite showing platy habit.

tassium, by colorimetry for phosphate (Murphy and Riley, 1962) and by polarography for uranium (Deutscher and Mann, 1977). Samples were also analyzed for water soluble sodium by atomic absorption spectrometry. The mineral was analyzed by the Australian Microanalytical Service for hydrogen using a Pregl combustion train technique and for carbon and nitrogen using a Perkin-Elmer 204 CHN analyzer (MacDonald, 1974). No other alkali or alkaline earth metals, nor any nitrogen, were detected.

The analytical results are shown on Table 1. Analysis A gives the mean analytical data, which have been recalculated in B, assuming a composition of the type $(Na,K,H_3O) \cdot UO_2 \cdot PO_4 \cdot xH_2O$ and omitting, as impurities, NaCl, CO_3 and insolubles. Reversible losses of water on heating vary from 6.6 wt.% at 33°C to 12.3 wt.% at 300°C. The analysis corresponds to a formula $(Na_{0.56}K_{0.29}(H_3O)_{0.16}) \cdot UO_2 \cdot PO_4 \cdot 3.25H_2O$.

Electron microprobe analyses of these samples proved unreliable, even for qualitative use, owing to the mobility of sodium and potassium under the electron beam. Virtually all the sodium is lost after 3 seconds' exposure to the beam, and all the potassium within 60 seconds (Butt and Vigers, in prep.) Consequently, caution must be exercised in assessing electron microprobe analyses of this group of minerals.

Table 1. Chemical composition of sodian potassian hydroxonian meta-autunite

	A	B
U	49.27(3)	52.18
P	6.67(2)	7.06
Na	2.70(2)	2.86
K	2.37(2)	2.51
H	1.47(1)	1.45
C	0.17(1)	-
NaCl	3.16(1)	-
Insoluble	1.60(1)	-
H^+	-	0.10
O: in UO_2	6.62	7.01
in PO_4	13.77	14.58
in CO_3	0.68	-
in H_2O	11.76	11.63
in H_3O^+	-	0.56
Total	100.24	99.95

A = Mean composition in weight percent; numbers in parentheses = number of determinations. NaCl is water-soluble Na calculated as NaCl.

B = Recalculated assuming atomic proportions U:P:$(Na+K+H_3O^+)$ = 1:1:1, omitting NaCl, CO_3 and insolubles as impurities.

Structural considerations

The variable water content mentioned above is a well-known feature of the autunite group of minerals, but its consequences for electron probe analysis and for X-ray diffraction do not appear to have been fully appreciated. Our natural material gave very different diffraction patterns by the Debye–Scherrer and Guinier techniques, because the Guinier camera was evacuated and caused dehydration to a second intermediate phase.

The name autunite is usually reserved for the fully-hydrated tetragonal phase; meta-autunites are more or less dehydrated, with roman numerals designating progressively lower dehydration states. The partially dehydrated tetragonal phase (of which our air-dried material is an example) is called meta-autunite I; and the irreversibly dehydrated orthorhombic phase (not found naturally) is called meta-autunite II (Ross and Evans, 1965). The mineral described here does not fit into this scheme, because there are two distinct but related phases of the meta-autunite I type both showing reversible hydration. In addition this mineral does not form an irreversibly dehydrated phase equivalent to meta-autunite II.

Debye–Scherrer, Guinier and powder diffractometer X-ray data indicate that the air-dried material is well crystallized, with the lattice spacings shown in Table 2. The pattern can be indexed on the basis of a meta-autunite I structure with tetragonal pseudo-cell dimensions $a' = 6.971$Å, $c' = 8.545$Å. By analogy with the known structures, the true cell is probably $a = 19.71$Å, $c = 17.09$Å. The mineral has a marked layer structure and diffractometer patterns have strongly enhanced $(00l)$ reflections. These vary in spacing with varying water content, the most obvious changes being step-wise; two different spacings may occur together, and the pattern of air dried material described above indicates the presence of small amounts of a fully hydrated phase, corresponding to autunite, with a basal spacing of 19.4Å. It is assumed that the observed basal spacing should be doubled, although the (001) reflection is not visible in this phase. Even when wet, the majority of material does not hydrate to this phase, suggesting that only a restricted range of compositions will hydrate fully, and that the sample is somewhat inhomogeneous, perhaps on a micro-scale.

Interestingly, there is a variation of basal spacing with relative humidity in the meta-autunite I phase,

Table 2. Observed and calculated diffraction patterns for air-dried sodian potassian hydroxonian meta-autunite

Index	d_{obs}	d_{calc}	Intensity
001	8.75	8.55	W
011	5.45	5.40	W
110	4.94	4.93	MS
111	4.30	4.27	W
102	3.70	3.64	W
200	3.49	3.49	S
	3.36		V
112	3.23	3.24	V
211	2.94	2.93	VW
003	2.91	2.85	VW
202	2.68	2.70	VW
212	2.54	2.52	VW
113 220	2.47	2.47 2.46	MS
221	2.37	2.37	VW
301	2.24	2.24	VW
203 310	2.20	2.21 2.20	W
004	2.14	2.14	W
222 311	2.124	2.135 2.134	VW
302	2.049	2.041	VW
321	1.887	1.886	VW
214 322	1.766	1.761 1.762	VW
400 313	1.742	1.743 1.743	W
005 401	1.709	1.709 1.708	VW
105 411	1.659	1.660 1.659	VW
330	1.642	1.643	W

Index	d_{obs}	d_{calc}	Intensity
304 412	1.576	1.573 1.572	VW
420	1.559	1.559	M
205 322 314 421	1.534	1.535 1.534 1.534 1.533	VW
422	1.461	1.464	VW
413	1.446	1.453	VW
305 501	1.376	1.377 1.376	VW
116 510 423	1.367	1.368 1.367 1.367	W
315 511 404	1.350	1.351 1.350 1.350	VW
414 502	1.328	1.326 1.325	VW
316 315	1.196	1.196 1.195	VW
117 335 531	1.184	1.185 1.185 1.184	VW
504	1.163	1.167	V
207 514 425	1.152	1.152 1.152 1.152	VW
524	1.109	1.107	V
406 533	1.103	1.103 1.102	VW
227	1.094	1.094	VW

as well as small variations from sample to sample. d_{001} has been observed to vary from 17.1Å to 17.4Å. The *hkl* reflections remain sharp during this swelling, and there are corresponding slight adjustments of the uranyl phosphate layer itself, amounting to a change of 0.2% in the *a*-dimension. This must indicate partial occupancy of the water sites in the meta-autunite structure, and probably also points to the importance of hydrogen bonding on the stability of the uranyl phosphate layer.

A previously unreported phase is obtained by gently heating the meta-autunite I phase (to about 40°C) or by dehydrating it *in vacuo*. The diffraction pattern consists mainly of broad peaks, although the basal reflection of 6.90Å is sharp and the 001 reflection at 13.80Å is now of reasonable intensity; the main lines of the pattern are given in Table 3. A number of these lines can be indexed as *hk*0 reflections from a structure with essentially unchanged uranyl phosphate layers, and since the dehydration is reversible in a few minutes in air, this is probably correct. On examination by electron microscopy, the entire *hk*0 net is easily obtained, although there is a slight discrepancy in spacing (a = 6.98±.02Å by X-rays, 6.89±.02Å by electron diffraction). The difference may be due to a higher vacuum and hence greater dehydration in the electron microscope, or to inhomogeneity in the sample. The electron diffraction patterns showed considerable variations in intensities from crystal to crystal, especially those corresponding to centering reflections with $h + k$ = odd; there was also evidence for the doubling of the *a*-axis in one crystal, and of disorder along the *c*-axis. (*c* could only be measured by X-ray diffraction).

It is not possible to index the diffraction pattern of this dehydrated phase on a tetragonal or monoclinic unit cell without assuming an unreasonably large superlattice; it is therefore probable that the uranyl phosphate layer is slightly distorted, and the true symmetry may be triclinic.

Further heating to 120°C decreases the *c*-dimension slightly to 13.5Å, but behavior at higher temperatures has not been followed as our heating stage will not exceed this temperature. However, heating the mineral in a furnace and allowing it to cool in air shows that dehydration remains reversible to 1200°C, even in apparently melted material. The only evidence of this thermal treatment is a moderate change in relative intensities of diffraction rings. There does not appear to be a phase equivalent to the reported orthorhombic meta-autunite II.

In order to clarify the ranges of stability of the partially dehydrated phases, the natural material and three synthetic uranyl phosphates were studied at several different temperatures. The results are shown in Table 4. The predominant spacing at any temperature is underlined; variation of spacing within a particular phase is seen by looking down a vertical column. Note that the natural material is similar to the synthetic sodium analogue in its behavior, and that the calcium analogue is the only one with appreciable amounts of a fully hydrated phase. There are always at least two phases in the region designated meta-autunite I by Ross and Evans (1965). These differences, which occur very readily, together with the

Table 3. X-ray diffraction pattern (Guinier) of evacuated sodian potassian hydroxonian meta-autunite, showing the *hk*0 reflections

h^2+k^2	d_{obs}	d_{calc}	Intensity	h^2+k^2	d_{obs}	d_{calc}	Intensity
1	6.90	6.98	M		1.894		VW
	5.46		W		1.839		VW
	5.19		VW		1.748		VW
2	4.94	4.94	MS	16	1.742	1.745	W
	4.77		M		1.731		VW
	4.58		MW	18	1.646	1.645	M
	4.30		W		1.628		MW
	3.69		VW	20	1.565	1.561	MS
4	3.49	3.49	S	26	1.372	1.369	W
	3.44		MW	32	1.238	1.234	VW
	3.40		MW	34	1.198	1.197	W
	2.88		VW	36	1.167	1.163	VW
8	2.469	2.468	MS	40	1.108	1.104	W
10	2.214	2.207	S				

Table 4. *d*-spacings of (002) reflections of natural sodian potassian hydroxonian meta-autunite, and synthetic sodium, potassium and calcium autunites and meta-autunites under different temperature conditions, Å. Predominant spacings underlined.

	Natural			Sodium		Potassium					Calcium			
Wet, 20°C	9.9	$\underline{8.89}$		$\underline{8.83}$		$\underline{8.92}$	7.4				$\underline{10.37}$			
Air dry, 20°C	9.9	$\underline{8.80}$		$\underline{8.8}$		$\underline{8.88}$	7.49				$\underline{10.37}$	8.74		
40°C		8.80	$\underline{6.90}$	$\underline{8.74}$		$\underline{8.83}$	7.49				9.8	$\underline{8.49}$		
60°C			$\underline{6.90}$	8.55	$\underline{6.93}$	8.6	7.8	$\underline{6.58}$				$\underline{8.41}$		
90°C			$\underline{6.90}$		$\underline{6.71}$			$\underline{6.57}$					$\underline{7.50}$	6.54
120°C			$\underline{6.74}$		$\underline{6.70}$			$\underline{6.57}$	6.1	5.62			$\underline{7.27}$	6.50
120°C→20°C		$\underline{8.80}$		$\underline{8.72}$	$\underline{7.3}$	$\underline{8.88}$	7.61					$\underline{8.22}$		6.55

difficulty with microprobe analysis already mentioned, stress the need for caution in dealing with these minerals.

Relationship to other autunite and meta-autunite group minerals

The sodian potassian hydroxonian meta-autunite described here appears to be the first known intermediate member of the meta-autunite solid solution series predicted by Ross and Evans (1965). Whether the composition of the mineral from this locality remains constant is uncertain. The interlayer cations of autunite and meta-autunite minerals are exchangeable and this provides the route by which many synthetic varieties are made (Fairchild, 1929). Consequently, the composition will depend upon the activities of K, Na and other species in the groundwater, the pH and the Eh, all of which may vary over the course of a few months. In addition to the diffraction evidence that layer compositions may not be entirely uniform, evidence for a changing composition is provided by the fact that the potassium content for material collected in 1977 was 4.36 wt.% whereas in 1978 it was 2.37 wt.% (wet chemical analyses). Only small amounts of the mineral were available for the earlier analysis and the results cannot be confirmed.

This mineral differs somewhat from other members of the meta-autunite group in its mode of origin and its dehydration behavior. Other autunite and meta-autunite group minerals are usually found as alteration products of pre-existing minerals, whereas this variety has been precipitated directly from saline groundwaters in the playa. On mild dehydration, there are two phases apparently equivalent to meta-autunite I, but there is no equivalent to the irreversibly dehydrated orthorhombic meta-autunite II. Indeed the mineral has the remarkable characteristics of retaining its structure and the property of reversible dehydration to its melting point of 1200°C.

Acknowledgments

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References

Butt, C.R.M., Horwitz, R.C. and Mann, A.W. (1977) Uranium occurrences in calcrete and associated sediments in Western Australia. Australia, CSIRO Division of Mineralogy Report No. FP. 16, 67p.

Camargo, W.G.R.de (1971) Minerais uraniferous de Perus, S.P. Boletim de Instituto de Geociencas e Astronomia, Universidade de Sao Paulo, 2, 85–201.

Chernikov, A.A., Krutetskaya, O.V. and Organov, N.I. (1958) Sodium autunite. American Mineralogist, 43, p.303 (abstract only).

Deutscher, R.L. and Mann, A.W. (1977) Determination of uranium in natural waters by differential-pulse polarography of a trioctyl-phosphine oxide extract. Analyst, 102, 929–933.

Fairchild, J.G. (1929) Base exchange in artificial autunities. American Mineralogist, 14, 265–275.

Gallagher, M.J. and Atkin, D. (1966) Meta-ankoleïte, hydrated potassium uranyl phosphate. Bulletin of the Geological Survey of Great Britain, 25, 49–54.

MacDonald, R.D. (1974) Developments in quantitative elemental microanalysis. Proceedings of the Royal Australian Chemical Institute, 41, 37–40.

Murphy, J. and Riley, J.P. (1962) A modified single solution method for the determination of phosphate in natural waters. Analytica Chemica Acta, 27, 31–36.

Ross, M. and Evans, H.I. (1965) Studies of the torbernite minerals (III): Role of the interlayer oxonium, potassium and ammonium ions, and water molecules. American Mineralogist, 50, 1–12.

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