

COMPARISON OF MOURITE FROM KARNES COUNTY, TEXAS WITH MOURITE FROM THE U.S.S.R.¹

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ABSTRACT

Mourite, ideally $4[(U^{6+}O_2) \cdot 2Mo^{5+}O_2(OH)_2 \cdot 3Mo^{6+}O_2(OH)_2]$ or $4[(U^{4+}O_2) \cdot 5Mo^{6+}O_2(OH)_2]$, depending upon whether the reducing power of the sample is ascribed to molybdenum or to uranium, occurs at the Boso-Hackney prospect in Karnes County, Texas, the first reported locality outside the Soviet Union. Mourite forms spherulitic masses of purple bladed fibers elongated parallel to b and flattened on $\{100\}$; the cleavage on $\{100\}$ is pronounced. The indices of refraction exceed 1.79, with many fibers being opaque; other fibers are pleochroic in shades of dark blue-violet and greenish blue-black. Unit cell measurements derived from a refinement of the powder diffraction data are $a=24.443(9)$ Å, $b=7.182(1)$, $c=9.901(2)$, $\beta=102^\circ 13'(2)$. The principal reflections in the powder diffraction pattern are $d(400)=5.98$ Å, ($I=100$); $d(003)=3.226$ ($I=35$), $d(\bar{2}22)=2.888$ ($I=31$), $d(800)=2.986$ ($I=22$), $d(\bar{4}03)=3.132$ ($I=21$), and $d(001)=9.66$ ($I=13$).

A new chemical analysis for Russian mourite shows 99.3% hydrous uranium molybdenum oxides, whereas the original analysis shows 93.19% hydrous uranium molybdenum oxides and 7.35% oxides of other cations. Unit cell measurements derived from a refinement of the powder diffraction data are $a=24.426(6)$ Å, $b=7.185(1)$, $c=9.895(1)$, $\beta=102^\circ 10'(1)$. The new interplanar spacings for the Russian mourite include a different set of strong reflections from those previously reported.

INTRODUCTION

A molybdenum uranium mineral was separated from the uranium ore samples collected by Weeks in 1955 and 1956 at the Boso-Hackney prospect in Karnes County, Texas. The prospect is located at the foot of the north end of Tordillo Hill (named on the Fashing quadrangle, Texas, $7\frac{1}{2}$ minute topographic map of the U. S. Geological Survey). The location is 12 miles southwest of Falls City, Texas, and 100 yards southeast of Farm Route 791 at Tordillo Hill. This prospect was one of many small near-surface deposits which stimulated further drilling down the dip and led to the finding of much larger deposits. Reference to this uranium molybdate mineral was made by Weeks in a joint paper by Frondel and Weeks (1958).

This mineral was first designated "Unknown 8653" because its X-ray powder diffraction pattern differed from that of other molybdenum uranium minerals. Its identity with mourite (Kopchenova *et al.*, 1962) was first suspected from chemical data which indicated Mo:U=5:1.04, whereas Mo:U=5.5:1 was reported for type mourite. A sample of

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mourite from the U.S.S.R. was obtained through the courtesy of Professor G. P. Barsanov of the Fersman Mineralogical Museum, Moscow, U.S.S.R. The chemical analysis and X-ray diffraction data obtained in the present study from this specimen established the identity of the Texas mineral with mourite. Karnes County, Texas, is the second reported occurrence for mourite.

GEOLOGIC OCCURRENCE

The general geologic setting of the Karnes County uranium deposits is described by Eargle and Weeks (1968), and Weeks and Eargle (1963). At the Boso-Hackney prospect the host rock is a sandy and tuffaceous member (known as the Stone Switch Sandstone Member) of the Whitsett Formation, Jackson Group of late Eocene age. The sandstone is highly lithic and feldspathic with many grains of slightly to highly altered volcanic fragments, zoned feldspars, and moonstone-sanidines. Some ore sand is very friable, some firmly cemented with interstitial clinoptilolite; and locally, as at the mourite occurrence, it is very tightly cemented with opal and chalcedony. Interbedded with the sand is tuffaceous clay containing plant impressions. Abundant glass shards are preserved at nearby uranium localities, although not directly at the mourite prospect.

Small amounts of molybdenum are present in many of the Texas Coastal Plain deposits forming yellow molybdates, such as iriginite, near the surface, or dark blue water-soluble ilsemannite in leachings from the walls of the deep open ore pits. A unique feature at the mourite locality is a tight silica cement found at the surface of the ground. The cement preserves a reducing environment in which mourite, pyrite, and marcasite can survive. The opal coating of the sand grains and the interstitial filling of opal and chalcedony enclose microscopic needles of mourite. The interlocking of the opal cement with the mourite grains made the purification of the analysis sample difficult and prevented accumulation of more than a minimal amount.

PHYSICAL PROPERTIES

Mourite occurs in spherulitic masses of purple bladed fibers, elongated parallel to the monoclinic b axis and flattened on $\{100\}$. Cleavage on $\{100\}$ is pronounced. Most of the matted masses are several millimeters in diameter, but individual crystals are of micron size. Some fibers are larger, up to 0.5 mm. along $[010]$, but these tend to be randomly oriented in the zone normal to the fiber axis. Mourite has an adamantine luster. The optical properties are incompletely known because the fibers decompose in the required index liquids, $n > 1.79$. Many of the grains ap-

pear to be opaque, but others of approximately the same size are pleochroic in shades of dark blue-violet and greenish blue-black. The extinction is parallel to the fiber axis in mourite from Texas. Kopchenova *et al.* (1962) report that mourite has inclined extinction ($\sim 10^\circ$) relative to the cleavage. We observed microscopic platelets of Russian mourite which were flattened on $\{100\}$, but elongated along $[001]$. In this orientation the reported extinction angle would be $Z \wedge c$, but as all the platelets examined were opaque, we were unable to confirm their extinction angle.

X-RAY CRYSTALLOGRAPHY

X-ray powder diffraction data for mourite are given in Table 1. Preliminary unit cell measurements obtained from Weissenberg and Buerger precession patterns were refined in stages by least squares analysis of X-ray diffraction powder data using the method of Evans *et al.*, 1963. In earlier cycles, the refinement was based upon a small pseudocell with $a \sim 12.22$ Å, $b \sim 3.59$, $c \sim 9.90$, $\beta \sim 102^\circ$, using all reflections in the powder diffraction pattern with intensities > 1 on a scale of 100, and limiting conditions of possible reflections to those consistent with space groups $C2$, Cm , or $C2/m$. In later cycles, the refinement included interplanar spacings for the remaining very weak reflections; the a and b axial lengths were doubled; concomitantly, the previously determined hkl were fixed as $2h.2k.l$ in the larger cell. For hkl with $k = 2n$, $2h + 2k = 4n$; for $k = 2n + 1$, no restrictions were placed on h . In rotation patterns from thick bundles of fibers taken along $[010]$ eighteen very weak $h1l$ reflections were observed, including (010) , (110) , and (210) , whereas only ten $h1l$ reflections are resolved in the powder pattern. The suggested space group for mourite is Pa or $P2/a$.

There are significant differences between the new interplanar spacings and those cited by Kopchenova *et al.* (1962); some, but not all, may be attributed to their use of unfiltered copper radiation. The interplanar spacing, $d = 12.77$ Å, reported by Kopchenova *et al.* (1962), was looked for, but not observed in patterns of mourite; the spacing $d(001) = 9.67$ Å found in our patterns, was not reported by them. If these interplanar spacings are basal spacings, respectively, of a more hydrated phase, and of a less hydrated phase, then the patterns of mourite should vary depending upon the water content of the sample at a given point in the hydration or dehydration process.

A variation in basal spacings with conditions of humidity in the atmosphere has been reported for the hydrous uranium molybdate, umohoite, $(UO_2)_2MoO_4 \cdot 2H_2O$ (Kamhi, 1959). In our study, the remarkable constancy of the unit cell parameters of mourite from two localities indicates that stable phases have formed with fixed volume requirements.

The interplanar spacings of mourite from Russia were obtained from clusters of crystals enclosed in a sealed glass capillary and X-rayed without either grinding or cementing into a spindle, whereas clusters of crystals and fibers of mourite from Texas were mounted on the open end of a glass rod for X-raying. A new chemical analysis of mourite from the U.S.S.R. shows that the sample that we have X-rayed has both the larger H₂O:Mo ratio, calculated elsewhere in this paper, and the smaller initial spacing, $d(001) = 9.67 \text{ \AA}$, thus excluding the 12.77 \AA interplanar spacing as a basal spacing of a more hydrated phase. Either the reflection is from an impurity or it represents a contamination of copper radiation by molybdenum radiation. The spacing 12.77 \AA , assuming $\lambda = 1.5418 \text{ \AA}$ and $2\theta = 6.92^\circ$, may be recalculated as $d(400) = 5.89 \text{ \AA}$, using $\lambda = 0.7107 \text{ \AA}$ and $2\theta = 6.92^\circ$.

CHEMISTRY

Chemical analyses of mourite are cited in Table 2. Kopchenova *et al.* (1962) calculated the reducing capacity of mourite to U⁴⁺ in order to avoid dividing the oxides of molybdenum into two valence states. They noted, however, that U⁴⁺ cannot be present together with Mo⁶⁺ in an acid medium; they also noted that the blue-violet color of mourite was characteristic of molybdenum in lower stages of oxidation.

Our analyses of mourite are calculated in two ways. The reducing capacity of the sample is ascribed to Mo⁵⁺ (Table 2, columns 4 and 6) and to U⁴⁺ (Table 2, columns 5 and 7). The evidence that the reducing capacity is due to Mo⁵⁺ is the blue-violet color of the mineral and the fact that Mo⁶⁺ would be reduced by U⁴⁺ in acid solutions, as noted above. The evidence that the reducing capacity of the sample is due to U⁴⁺ is that a UF₄ precipitate formed when the mineral was digested with HF solution. When we consider the additional fact that U⁴⁺ molybdate is insoluble in solutions of low acidity, this would change the acid potential of the U⁴⁺-U⁶⁺ couple so that the U⁴⁺ state is favored.

The reducing capacity was determined by decomposing the sample in 20 percent by volume hot sulfuric acid in the presence of excess potassium dichromate. Air was excluded by passing nitrogen through the solution during decomposition. Excess dichromate remaining in solution was determined by titration with standard ferrous iron.

The analysis of mourite from the U.S.S.R. (Kopchenova *et al.*, 1962) shows 93.19 percent hydrous uranium molybdenum oxides and 7.35 percent oxides of other cations (total 100.54 percent). The analysis was recalculated to its main components: "Rough approximate ratios of the oxides may be expressed in the form

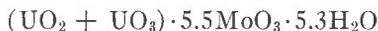


TABLE 1. X-RAY DIFFRACTION POWDER DATA FOR MOURITE

MOURITE

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Locality	U.S.S.R.				Karnes County, Texas			
	Kopchenova <i>et al.</i> , (1962) ^a	Present study			Present study			Cr/V, $\lambda = 2.2902 \text{ \AA}$
Radiation	Cu-unfiltered	Cu/Ni, $\lambda = 1.5418 \text{ \AA}$	Cu/Ni, $\lambda = 1.5418 \text{ \AA}$	Cu/Ni, $\lambda = 1.5418 \text{ \AA}$	Cr/V, $\lambda = 2.2902 \text{ \AA}$	Cr/V, $\lambda = 2.2902 \text{ \AA}$	Cr/V, $\lambda = 2.2902 \text{ \AA}$	
<i>a</i>		24.426 $\text{\AA} \pm 0.006 \text{ \AA}$	24.443 $\text{\AA} \pm 0.009 \text{ \AA}$	24.443 $\text{\AA} \pm 0.009 \text{ \AA}$				
<i>b</i>		7.185 ± 0.001	7.182 ± 0.001	7.182 ± 0.001				
<i>c</i>		9.895 ± 0.001	9.901 ± 0.002	9.901 ± 0.002				
β		102°10' $\pm 1'$	102°13' $\pm 2'$	102°13' $\pm 2'$				
Vol.		1698 \AA^3	1699 \AA^3	1699 \AA^3				
<i>I</i>	measured <i>d</i> (\AA)	calculated ^b <i>hkl</i> <i>d</i> (\AA)	measured ^c <i>I</i> <i>d</i> (\AA)	measured ^c <i>I</i> <i>d</i> (\AA)	calculated ^b <i>d</i> (\AA)	measured ^c <i>I</i> <i>d</i> (\AA)	measured ^c <i>I</i> <i>d</i> (\AA)	
90	12.77	001 9.673	12 9.67	13 9.66	9.677	mw 9.65		
10	6.80	110 6.880	<1 6.87	<1 6.87	6.878			
40	(6.41)							
40	6.10	210 6.156	100 5.97	100 5.98	5.972	s 5.97		
100	5.897	400 5.969	9 5.65	9 5.66	5.644	mw 5.65		
10	5.530	401 5.639			5.470			
		211 5.470			5.452			
		111 5.452			5.333			
		310 5.333			5.333			
		311 4.977			4.977			
		002 4.836			4.839			
		401 4.660			4.661			
		311 4.414			4.414			
		402 4.218			4.222			
		112 4.075			4.076			
		511 3.929			3.931			
		312 3.865			3.867			
		112 3.848			3.849			
		212 3.617			3.617			
10	(3.598)	020 3.592			3.591			
20	(3.528)	220 3.440			3.439			
10	(3.421)	402 3.421	7 3.424	4 3.426	3.422	vw 3.419		
70	3.285	221 3.305	25 3.302	17 3.306	3.305			
70	3.193	003 3.224	25 3.226	35 3.226	3.226	ms 3.225		
70	3.148	221 3.181	25 3.181	17 3.179	3.180			

(Continued on next page)

TABLE 1.—(Continued)

Locality Reference	U.S.S.R.			Karnes County, Texas			
	Kopchenova <i>et al.</i> , (1962) ^a	Present study		Present study			
	I measured d (Å)	calculated ^b d (Å)	I measured ^c d (Å)	calculated ^b d (Å)	I measured ^c d (Å)	measured ^e I d (Å)	
	50	3.095	403 711	18	3.130	21 3.132	m 3.130
			801 213	4	3.036	<1 3.114	w 3.038
	20	2.955	213 800	15	2.983	5 2.995	
	80	2.871	222 802	38	2.887	<1 2.986	m 2.984
	40	(2.710)	222 801	15	2.724	2.887 2.822	
			621 620			2.726 2.697	
	10	2.595	620 403	1	2.666	9 2.725	
			910 622	7	2.614	2.667 2.663	
	60	2.464	622 621	18	2.493 to 2.482	6 2.617	mw 2.616
			803 223			15B 2.485	
	10	2.407	223 404	2	2.426	2.482 2.467	
	10	2.311	404 802	4	2.330	2.428 2.427	
			131 223	1	2.300	2.419 2.414	
	10	(2.250)	514 114	2	2.279 2.246	3 2.427	mw 2.426
			623 622	3	2.204 to 2.196	5 2.330	mw 2.331
	10	2.198	622 331	<1	2.127	<1 2.284	
			913 531			2.248	
			332 11.1.1			2.240 2.215	
	10	2.100	804 404	3	2.109	1 2.211	
			224 12.0.1			2.207 2.201	
	60	2.024	224 332	12	2.037	2.193 2.133	
						2.123 2.122	
						2.111 2.094	
						1 2.113	mw 2.109
						15 2.038	mw 2.038
						2.037 2.025	

TABLE 2. CHEMICAL ANALYSES AND COMPOSITION OF MOURITE

	Analyses			Ratios						
	Calc. com- position	Previous data		Present study						
(1)	(2) U.S.S.R.	(3) U.S.S.R.	(4) U.S.S.R.	(5) U.S.S.R.	(6) Texas	(7) Texas	(8) U.S.S.R.	(9) U.S.S.R.	(10) Texas	(11) Texas
UO ₂	2.40	2.27	26.6	2.2	24.1		0.98	0.97	1.04	(Excluded)
UO ₃	19.38	21.65	40.7	23.0		22.8				
MoO ₃	63.67	64.47	23.2	65.3	33.4	57.6	5.00	5.00	5.00	
H ₂ O(+)	6.07	7.73	8.0	8.0	23.5	0.6	9.58	9.79		
H ₂ O(-)	1.67	1.12	0.8	0.8			1.38	0.98		
Total H ₂ O									10.00	
Na ₂ O	0.54	0.13	0.2	0.2	9.8	9.8				3.4
K ₂ O	0.58	0.46	0.1	0.1	1.0	1.0				0.4
CaO	2.09		<0.1	<0.1	1.9	1.9				0.45
MgO	0.49		<0.1	<0.1						0.8
Al ₂ O ₃	1.36	0.21	<0.1	<0.1						0.8
Fe ₂ O ₃	0.57	0.05	<0.1	<0.1	3.3	3.3	22.55	21.92	22.08	4.93
SiO ₂	1.72	0.82	<0.1	<0.1	3.9	3.9				
TiO ₂		0.06								
Tl ₂ O ₃		0.23								
PbO		0.09								
Total	100.54	99.29	99.7	99.7	100.9	100.9				
S.G.	>4.1		4.12		3.78					

1. Calculated composition for UO₂-5MoO₃-5H₂O.

2. Kopchenova *et al.* (1962); total originally given as 100.52. N. N. Kuznetsova, analyst. Ratios given as UO₂+UO₃-5.5MoO₃-5.3H₂O, where all the molybdenum is provisionally calculated as hexavalent.¹⁰ The oxides of light metals are considered admixtures of the enclosing rocks.

3. Skvortsova *et al.* (1969). T. A. Ukhina, analyst.

4. This study. J. Marinenko, analyst. Reducing power of sample ascribed to molybdenum.

5. Analysis of column 4, reducing power of the sample ascribed to uranium.

6. Impure sample, J. Marinenko, analyst. Reducing power of sample ascribed to molybdenum.

7. Analysis of column 6, with the reducing power of the sample ascribed to uranium.

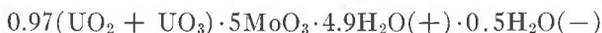
8. Ratios calculated to total Mo=5 for analysis of column 3; principal constituents only.

9. Ratios calculated to total Mo=5 for analysis of column 5; principal constituents only.

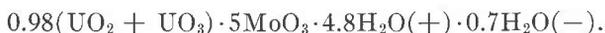
10, 11. Ratios calculated to total Mo=5 for analysis of column 7; suggested distribution of components between mourite, column 10, and excluded impurities, 11.

where all the molybdenum is provisionally calculated as hexavalent. Not excluded is the possibility that part of the CaO enters into the composition of the mineral. The other oxides shown in the analysis are evidently associated with the presence of admixtures of the enclosing rocks, which are very difficult to separate completely from the fine platy mineral." (Translation by M. Fleischer, U. S. Geological Survey, June 16, 1962.) A new analysis by Ukhina (in Skvortsova *et al.*, 1969) yielded 97.24 percent hydrous uranium molybdenum oxides and 2.05 percent oxides of other cations (total 99.29 percent). The analysis given in column 3, Table 2, establishes that calcium is not essential in mourite from Russia.

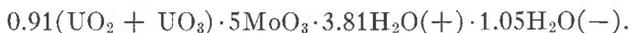
An analysis sample of Russian mourite was hand-picked by Smith. The sample contained 99.3 weight percent hydrous uranium molybdenum oxides (Table 2, columns 4 and 5). Certain oxides reported in the earlier analysis were present in greatly reduced quantities in the new analysis, thus supporting the exclusion of these oxides from the composition of mourite. We have calculated the new oxide ratios from Russian mourite on the basis of 5Mo^{6+} :



The oxide ratios for Russian mourite calculated to 5Mo^{6+} from the analysis of Ukhina in Skvortsova *et al.* (1969) are:

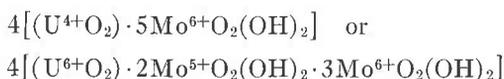


The $\text{H}_2\text{O}(+)$ in our analysis and in Ukhina's analysis is considered essential and is designated as (OH) in the ideal unit cell contents. It approximates the combined $\text{H}_2\text{O}(+)$ and $\text{H}_2\text{O}(-)$ in Kuznetsova's analysis in Kopchenova *et al.* (1962). The oxide ratios of Kopchenova *et al.* recalculated herein to 5Mo^{6+} are:



The sample of mourite from Texas consisted of dark blue-violet bundles of fibers penetrated by a white siliceous crust. This crust could not be removed without splintering the fibers into sizes too finely divided for recovery. The analysis of this material is given in columns 6 and 7 of Table 2. The interpretation of the distribution of components between mourite and impurities is given in columns 10 and 11 of Table 2, respectively. Oxides, including excess H_2O , present in greater proportions in the Texas sample than in the Russian sample, are allotted to the impurities. The mourite fraction, $1.04\text{UO}_2 \cdot 5\text{MoO}_3 \cdot 5\text{H}_2\text{O}$, calculates to 88.3 weight percent of the original sample; the impurities calculate to 2.5 weight percent excess H_2O and 10.1 weight percent other oxides (total 100.9).

We propose that the ideal unit cell contents of mourite may be expressed as:



depending upon whether the reducing power is ascribed to uranium or to molybdenum. The calculated density for the suggested unit cell contents, for a cell volume of 1699 Å³ is 4.22 gcm⁻³. The measured specific gravity of the bulk sample of mourite from Texas is 3.78; the weighted measured specific gravity of the mourite fraction is 4.17 after SiO₂, Al₂O₃, and excess H₂O are subtracted from the sample as halloysite. Approximate volume ratios,

$$\frac{1699}{4} \text{ \AA}^3 : \frac{468}{5} \text{ \AA}^3$$

are derived from the volumes occupied by one formula unit of mourite and 0.2 [Si₄Al₄O₁₀(OH)₈·4H₂O] calculated to halloysite with a $\rho \sim 2$. We have not identified an alkali-bearing alumino-silicate with a 1:1:1 ratio; therefore, the 0.85 Na+K is not deducted as a specific mineral in weighting the measured specific gravity for probable impurities.

It is hoped that the new data herein reported will lead to identification of mourite at other localities.

ACKNOWLEDGEMENTS

The authors especially wish to thank Professor G. P. Barsanov of the Fersman Mineralogical Museum in Moscow, U.S.S.R. for his courtesy in making available to us a sample of mourite from the type locality in Russia. Thanks are extended to S. R. Steinhauer of the U. S. Atomic Energy Commission who supplied us with samples of mourite from Texas, and with whom Weeks first visited the locality. We also wish to thank four of our colleagues in the U.S. Geological Survey; D. H. Eargle and A. H. Truesdell who have cooperated in the Texas Coastal Plain uranium studies, Daniel Appleman who refined the unit cell parameters from the powder diffraction data, and Michael Fleischer who translated for us the Russian article about mourite into English.

REFERENCES

- EARGLE, D. H. AND A. D. WEEKS (1968) Factors in the formation of uranium deposits Coastal Plain of Texas. *S. Texas Geol. Soc. Bull.* **9**, 3-13. (Paper presented Aug. 20, 1968 at 23rd International Geological Congress, Prague, Czech.).
- EVANS, H. T., JR., D. E. APPELMAN, AND D. S. HANDWENKER (1963) The least squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method [abstr.]. *Amer. Crystallogr. Assoc. Meet., Cambridge, Mass., 1963, Program abstr.*, p. 42-43.
- FRONDEL, C., AND A. D. WEEKS (1959) Recent progress in the descriptive mineralogy of uranium, Paper 2019, in Vol. 2, *Proc. Second U. N. Int. Conf. Peaceful Uses Atomic Energy, Geneva*, p. 277-285.

- KAMHI, S. R. (1959) X-ray study of umohoite. *Amer. Mineral.* **44**, 920-925.
- KOPCHENOVA, E. V., K. V. SKVORTSOVA, N. I. SILANTIEVA, G. A. SIDORENKO, AND L. V. MIKHAILOVA (1962) Mourite, a new supergene uranium-molybdenum mineral. *Zap. Vses. Mineral. Obshch.*, **91**, No. 1, 67-71. (In Russian.) [Translation by Michael Fleischer.]
- SKVORTSOVA, K. V., E. V. KOPCHENOVA, I. G. ZHIL'TSOVA, AND G. A. SIDORENKO (1969) Conditions of formation of uranium-molybdenum minerals in the zone of incomplete oxidation. *Zap. Vses. Mineral. Obshch.*, **98**, 29-40. (In Russian.)
- WEEKS, A. D., AND D. H. EARGLE (1963) Relation of diagenetic alteration and soil-forming processes to the uranium deposits of the southeast Texas Coastal Plain. *Clay Miner.* —*Proc. Nat. Conf.*, **10**, 1961 p. 23-41.

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