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A New Basic Copper Phosphate Mineral from Santa Rita, New Mexico

David B. Givens

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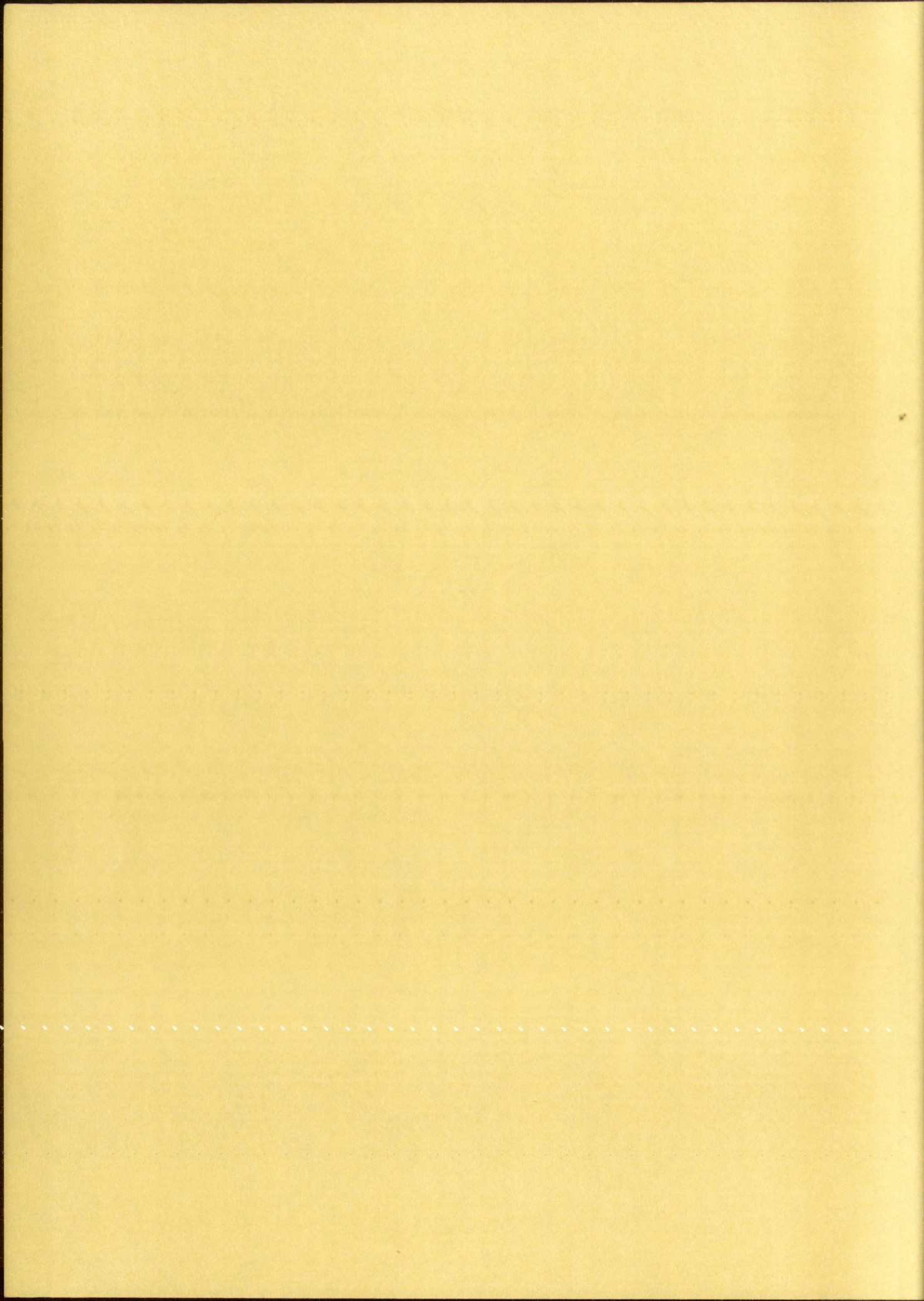


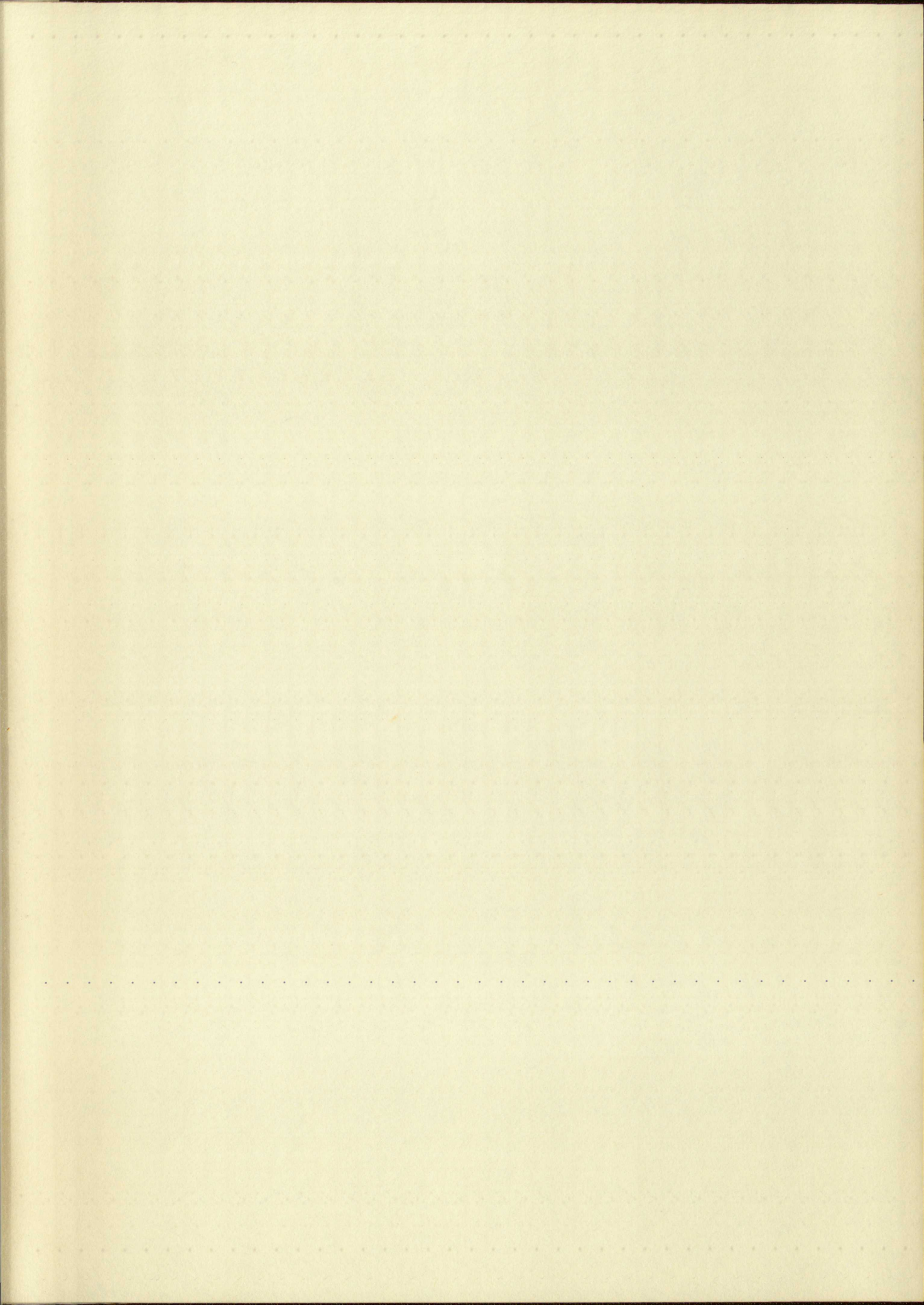
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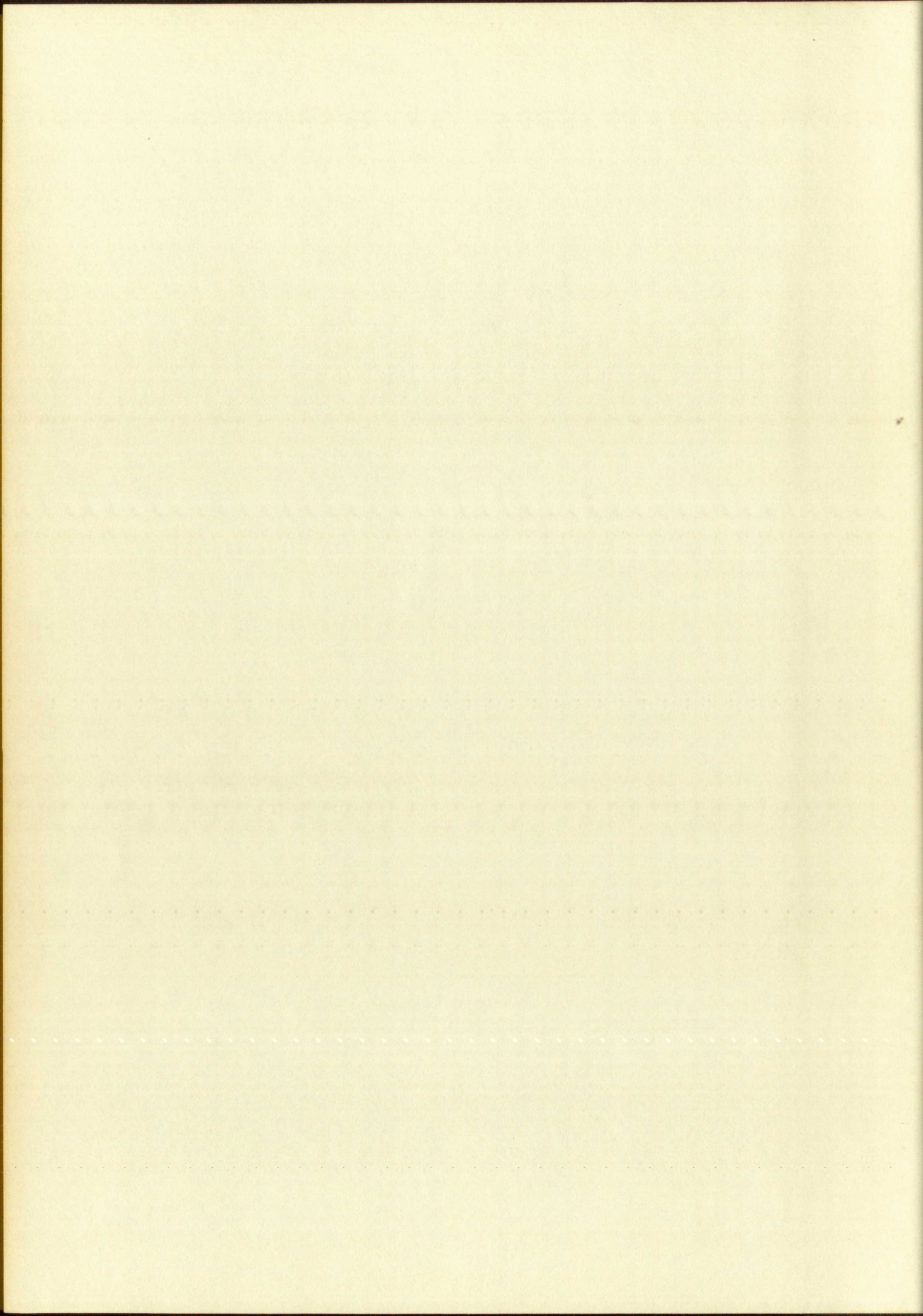
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A NEW BASIC COPPER PHOSPHATE MINERAL
FROM SANTA RITA, NEW MEXICO

By

David B. Givens

A Thesis

In partial fulfillment of the
Requirements for the Degree of
Master of Science in Geology

The University of New Mexico
1951



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NEW YORK

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This thesis, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

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A NEW BASIC COPPER PHOSPHATE MINERAL

FROM SANTA RITA, NEW MEXICO

By

David B. Givens

Thesis committee

Carl W. Beck
CHAIRMAN

V. G. Kelley

J. Paul Fitzsimmons

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This thesis directed and approved by the examining committee has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

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Since this thesis was presented to the University of New Mexico in partial fulfillment of the requirements for the degree of Master of Science the name CHINOITE has been accepted as appropriate for the new mineral described herein.

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Since this thesis was presented to the University of New South
in partial fulfillment of the requirements for the degree of Doctor
of Science the name UNIVERSITY OF NEW SOUTH WALES has been printed on
the new mineral described herein.

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A NEW BASIC COPPER PHOSPHATE MINERAL
FROM SANTA RITA, NEW MEXICO

Introduction

In the spring of 1950, through the courtesy of Mr. G. J. Ballmer, Superintendent of Mines, a dark emerald green, crystalline, encrusting, copper mineral from the Santa Rita open pit copper mine, Chino Division, Kennecott Copper Corporation, Hurley, New Mexico was given to the University of New Mexico for identification. The mineral was found by Mr. William Baltosser, Mine Engineer of the Santa Rita pit, in some fissures between two quartz monzonite dikes, 100 feet below the 6165 bench. This particular area of the pit is a highly altered section where the disseminated copper ore runs 0.5%-1.0%. Mr. Ballmer and Mr. Baltosser believed the mineral probably would be one of the more common supergene green copper minerals, such as atacamite, antlerite, or brochantite, and requested the mineralogy laboratory of the University to make the distinction.

Supergene minerals are not common, nor are they rare at Santa Rita. Kerr (1950,307) reports the presence of cuprite, melaconite, native copper, chrysocolla, malachite and azurite. There is also smithsonite present.

The physical appearance of the mineral, coupled with preliminary determinations of the indices of refraction, gave a rough correspondence with dihydrite (Larsen and Berman, 1934,135). However, enough discrepancy existed to warrant taking powder and Weissenberg X-ray pictures. From these it was evident immediately that the specimen was a new mineral species.

Acknowledgments

The writer is indebted to Dr. Carl W. Beck for suggesting the problem; to Dr. Beck and Dr. Dexter H. Reynolds for scientific aid and advice; to Dr. Vincent C. Kelley and Dr. J. Paul Fitzsimmons for helpful suggestions and critical reading of the manuscript. The writer is especially indebted to Mr. William Baltosser who generously donated specimens of this new mineral from his private collection.

Physical Properties

A specific gravity determination was made by means of a microchemical analytical balance, first weighing the crystal in air and then in carbon tetrachloride (CCl_4). This procedure was necessitated by the small size of the crystals and by the fact that not enough material could be sacrificed for a pycnometer determination. The largest crystal obtainable weighed 6.26 mg. in air, and 3.17 mg. in CCl_4 (specific gravity = 1.595). Using the formula:

$$d = \frac{\text{weight in air}}{\text{weight in air} - \text{weight in } \text{CCl}_4 \times \text{density } \text{CCl}_4}$$

$$d = \frac{6.26}{6.26 - 3.17 \times 1.595}, \quad d = 5.22$$

the density of the mineral was found to be 5.22, a close check with the theoretical value (page 8).

The cleavage of the mineral is perfect parallel to the prism (110); hardness, 5-6; luster, adamantine to vitreous; color, dark emerald green; diaphaneity, transparent to translucent; fracture, irregular.

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COLOR PHOTO OF NEW MINERAL

Introduction

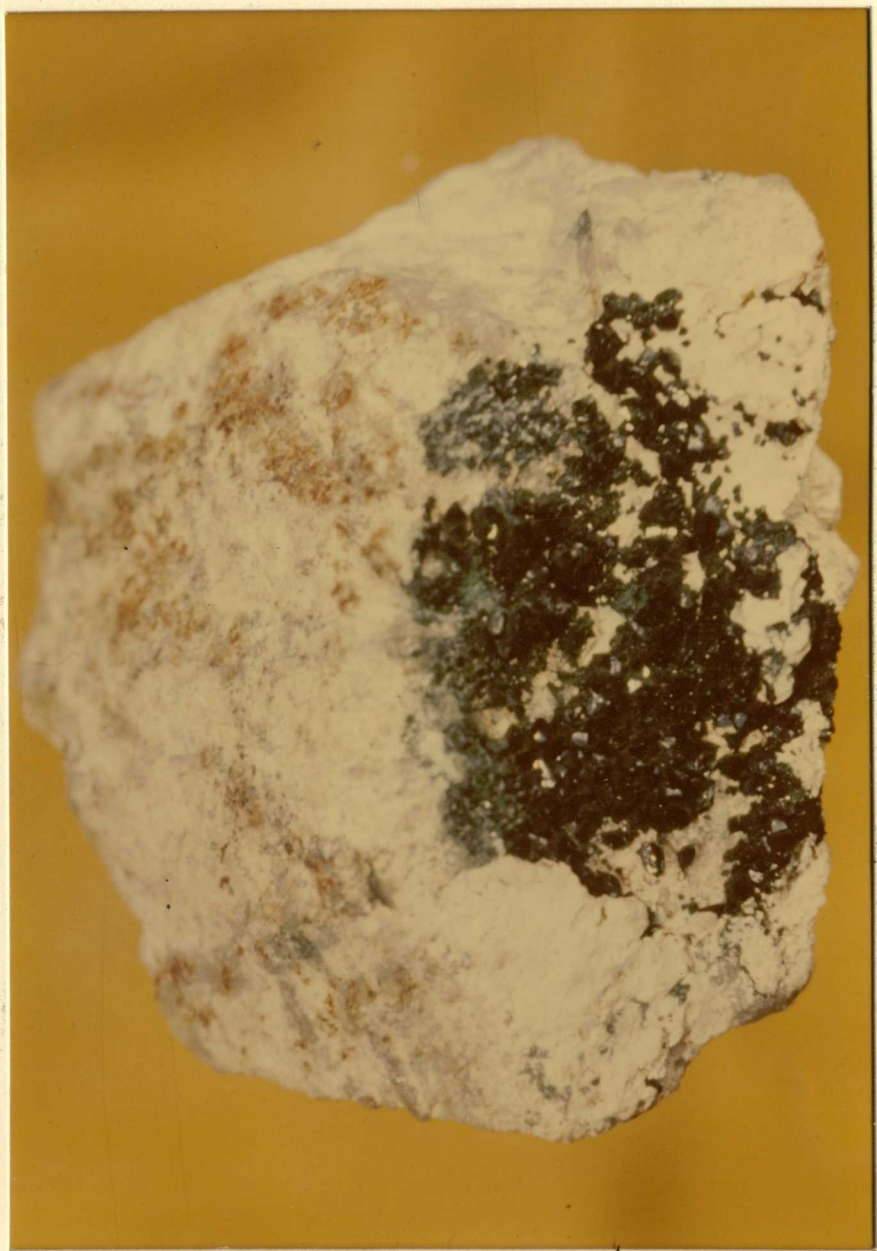
The first section of the report is devoted to a general description of the field work. It includes a description of the area, the methods used, and the results obtained. The second section is devoted to a detailed description of the mineral specimens collected. It includes a description of the specimens, their locations, and their characteristics.

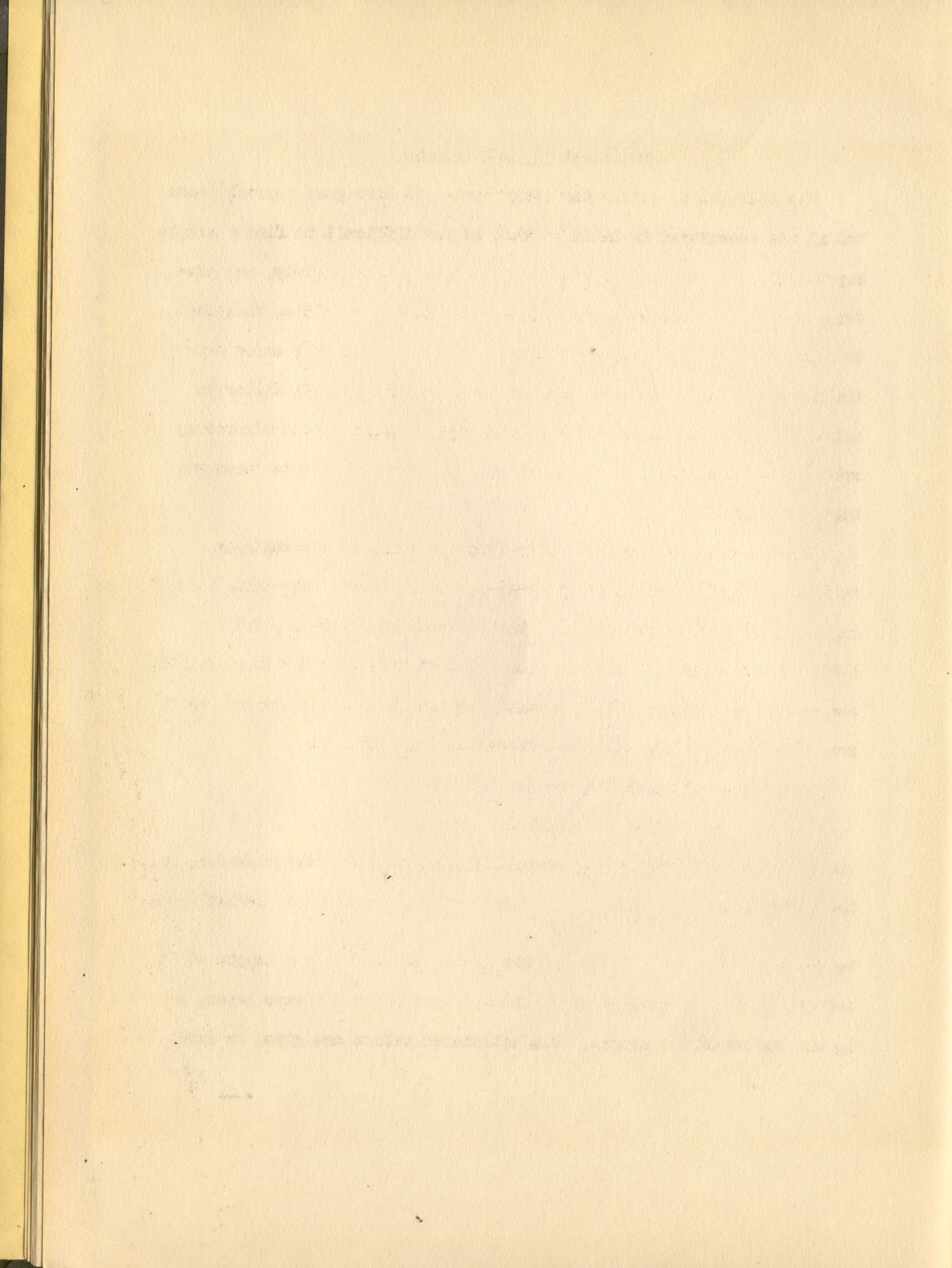
COLON PHOTO OF NEW MINERAL

The photograph shows a specimen of the new mineral, which is a colorless, transparent, prismatic crystal. It is composed of several small crystals, each of which is a single crystal. The crystals are prismatic, with a characteristic shape. The photograph is a color photograph, and the mineral is colorless.

Figure 1. Color photograph of the new mineral.

The photograph shows a specimen of the new mineral, which is a colorless, transparent, prismatic crystal. It is composed of several small crystals, each of which is a single crystal. The crystals are prismatic, with a characteristic shape. The photograph is a color photograph, and the mineral is colorless.





Structural Crystallography

The material available for study tended to have good crystal faces but it was encrusting in habit so that it was difficult to find a single crystal with all the form faces well developed. Fortunately, one perfect, doubly terminated crystal was found. It was possible, therefore, to take rotation and Weissenberg X-ray pictures around all three crystallographic axes. $\text{CuK}\alpha$ radiation was used through a Ni filter to eliminate $\text{CuK}\beta$ radiation. The Weissenberg films indicated rigorously orthorhombic symmetry as determined from the symmetry charts (Buerger, 1949, 482-483).

The observed Weissenberg diffractions conform to the following conditions: (hkl) present in all orders, $(h0l)$ present only with $h \neq k = 2n$, $(hk0)$ present in all orders, $(0kl)$ present only with $k \neq l = 2n$, $(h00)$ present only with $h = 2n$, $(0k0)$ present only with $k = 2n$, and $(00l)$ present in all orders; these criteria are characteristic for the space group $C_{2v}^{10}Pmn$. (Internationale Tabellen, 1944, 108-109)

The values obtained for the lattice dimensions are:

$$a = 7.47 \text{ \AA}, b = 8.31 \text{ \AA}, \text{ and } c = 5.83 \text{ \AA}$$

These values were obtained by measuring the rotation photographs and using the formula: $t = \frac{n \lambda}{\sin \tan^{-1}(y/r)}$ where t is the identity period (average to get d 's), n is the number of the layer, λ is the wave length of radiation, y is the distance of the n th layer from the zero layer, and r is the radius of the camera. The calculated values are given in Table I.

The material prepared in this manner is now subjected to
but it was essential to have a certain amount of
crystal size of the order of 1000 Å. The material
is subjected to a further treatment which is described
to some extent in the literature. The material is
dissolved in a suitable solvent and the solution
obtained is subjected to a further treatment which is
orthogonal to the one described in the literature.

The values obtained for the lattice constants are
the lattice constants of the material are
constant (100) Å. The lattice constants are
in (100) Å. The lattice constants are
(100) Å. The lattice constants are
present in all directions. These values are
given in Table I. (International Union of Pure and Applied Chemistry)

These values were obtained by measuring the X-ray diffraction and using
the formula $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ where d is the distance between
to get d_{100} a is the length of the lattice a in the direction of
reflection, h, k, l are the indices of the reflection, and d is the distance
is the value of the lattice constant. The estimated value of a is given in Table I.

Table I

Rotation Around a Axis

$$t_1 = \frac{1 \times 1.539}{\sin \tan^{-1}(5.4/26.85)} = 7.80 \text{ \AA}$$

$$t_2 = \frac{2 \times 1.539}{\sin \tan^{-1}(11.35/26.85)} = 7.91 \text{ \AA}$$

$$t_3 = \frac{3 \times 1.539}{\sin \tan^{-1}(18.95/26.85)} = 8.01 \text{ \AA}$$

$$t_4 = \frac{4 \times 1.539}{\sin \tan^{-1}(31.10/26.85)} = 8.13 \text{ \AA}$$

7.96 \AA is the measured a lattice dimension

Rotation Around b Axis

$$t_1 = \frac{1 \times 1.539}{\sin \tan^{-1}(5.50/26.85)} = 7.67 \text{ \AA}$$

$$t_2 = \frac{2 \times 1.539}{\sin \tan^{-1}(11.75/26.85)} = 7.68 \text{ \AA}$$

$$t_3 = \frac{3 \times 1.539}{\sin \tan^{-1}(19.90/26.85)} = 7.75 \text{ \AA}$$

$$t_4 = \frac{4 \times 1.539}{\sin \tan^{-1}(33.75/26.85)} = 7.87 \text{ \AA}$$

7.74 \AA is the measured b lattice dimension

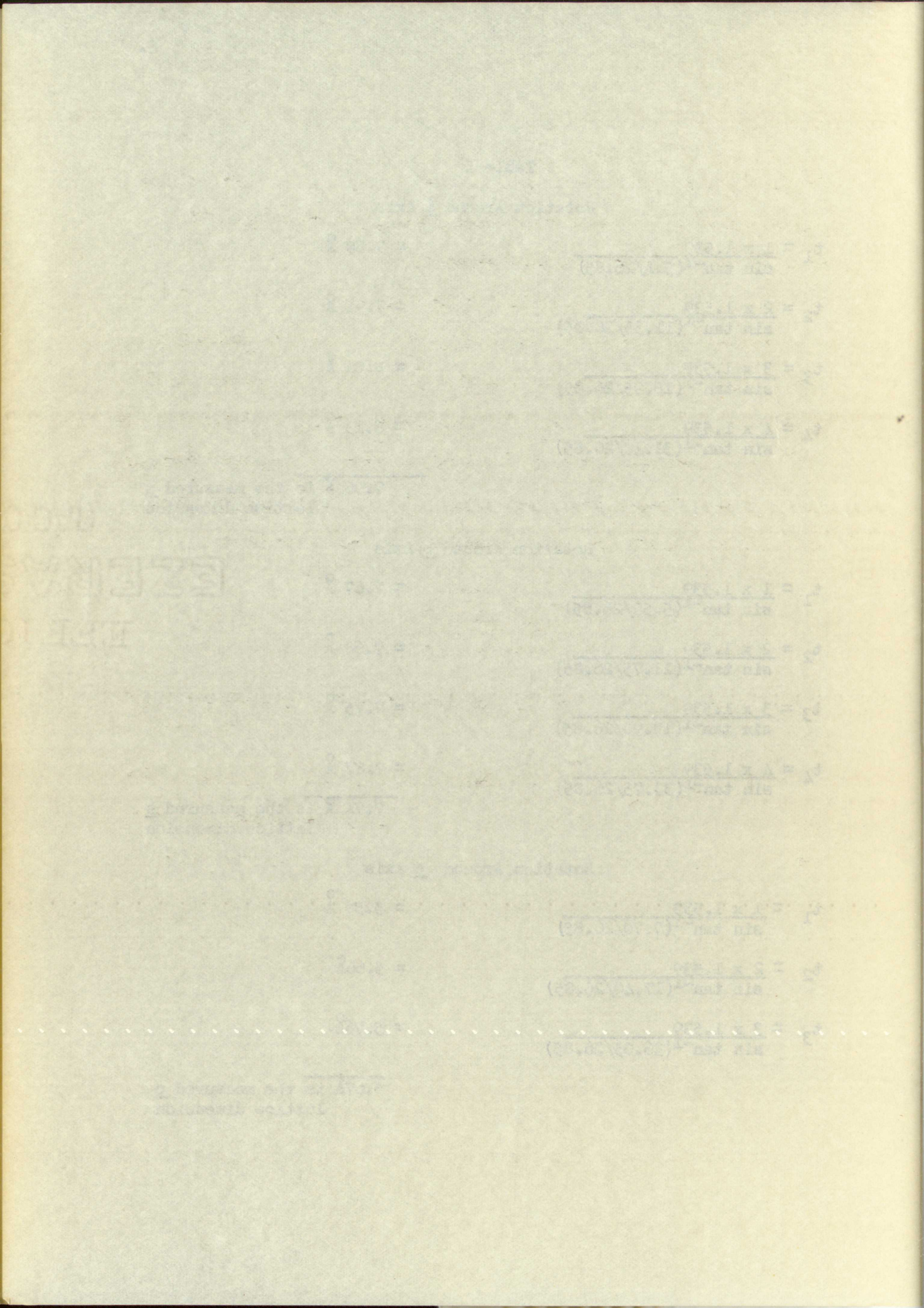
Rotation Around c Axis

$$t_1 = \frac{1 \times 1.539}{\sin \tan^{-1}(7.70/26.85)} = 5.58 \text{ \AA}$$

$$t_2 = \frac{2 \times 1.539}{\sin \tan^{-1}(17.40/26.85)} = 5.66 \text{ \AA}$$

$$t_3 = \frac{3 \times 1.539}{\sin \tan^{-1}(36.05/26.85)} = 5.76 \text{ \AA}$$

5.67 \AA is the measured c lattice dimension



The approximate cell dimensions as determined by rotation photographs and indicated in the above table were checked and determined accurately by use of the X-ray powder photographs.

X-ray Powder Pattern

By measuring the distances between the lines on the powder X-ray photographs, the distances between the crystallographic planes (d) were determined. These d 's proved that the powder pattern did not match any pattern of previously known minerals (Alphabetical and Grouped Numerical Index of X-ray Diffraction Data, 1950). The d 's and estimated intensities were checked from three films, and, by using the formula

$$d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

it was found that every line agreed with one or more theoretical values (Table II).

The powder pattern of pseudomalachite, the dimorphic form of the new mineral, is listed in Table III for comparison and contrast. The powder pattern of pseudomalachite was measured and calculated by Berry. (1950, 383).

The approximate cell dimensions of the material were determined by X-ray diffraction and are indicated in the next table. The material was prepared by the method described in the preceding paper.

X-ray diffraction patterns

In measuring the distance between the lines in the powder X-ray photographs, the distance between the regular crystal planes was determined. These data proved that the powder pattern was not a simple pattern of previously known systems (cubic, tetragonal, and orthorhombic). The d values were calculated from the Bragg equation, $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$, and the results are given in Table II.

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

It was found that every line appeared with the same intensity as the

(Table II)

The regular pattern of hexagonal cells, the distance d of the new mineral, is listed in Table III for comparison and contrast. The powder pattern of hexagonal cells was calculated and compared by using

(1957) 383-384

POWDER PHOTOGRAPHS OF
PSEUDOMALACHITE AND THE NEW MINERAL

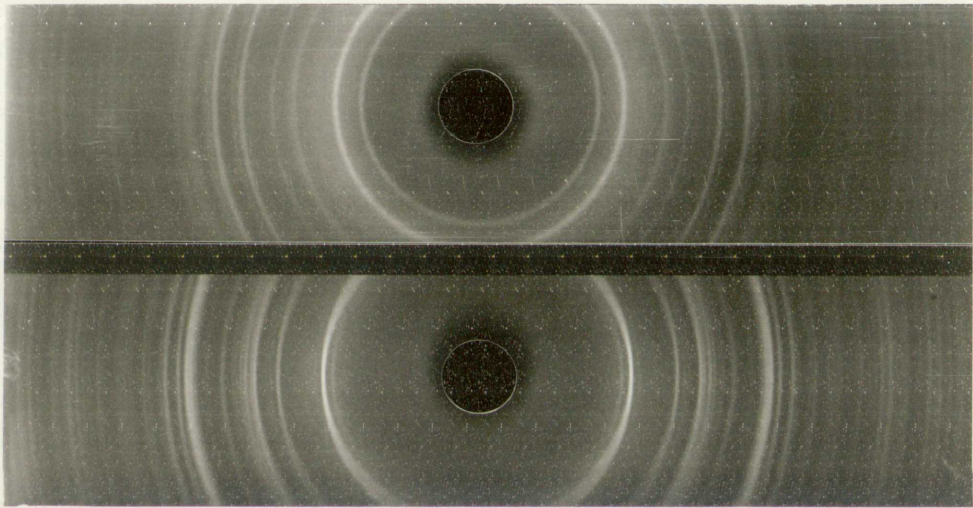
New Mineral

Pseudomalachite

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ACCOUNTS

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Table II

X-ray Powder Pattern

Orthorhombic, Fm $\bar{3}$; a = 7.47 Å, b = 8.31 Å, and c = 5.83 Å

I	θ	Cu	d(mess)	(hkl)	d(calc)	I	θ	Cu	d(mess)	(hkl)	d(calc)
8	7.59	5.83 Å	(001)	5.83 Å	1	31.35	1.51 Å	(341)	1.52 Å		
10	9.22	4.80	(011)	4.77				(421)	1.51		
1	10.66	4.16	(020)	4.16				(501)	1.54		
7	11.89	3.74	(200)	3.74				(250)	1.52		
8	15.32	2.91	(002)	2.92	1	31.90	1.48	(313)	1.49		
			(211)	2.88				(404)	1.49		
9	16.98	2.63	(130)	2.60	1	32.45	1.46	(431)	1.46		
3	17.59	2.55	(112)	2.57				(510)	1.47		
5	18.49	2.43	(022)	2.39				(251)	1.46		
4	19.42	2.31	(202)	2.30	1	33.92	1.43	(152)	1.42		
			(131)	2.36				(114)	1.41		
			(301)	2.29				(422)	1.44		
			(330)	2.33				(520)	1.43		
1	21.74	2.08	(231)	2.06	1	34.85	1.38	(143)	1.39		
			(040)	2.08				(511)	1.38		
2	23.60	1.92	(013)	1.89				(503)	1.40		
			(132)	1.94				(024)	1.37		
1	24.32	1.87	(113)	1.86				(440)	1.39		
			(400)	1.87	1	35.85	1.35	(214)	1.34		
			(141)	1.89				(124)	1.35		
1	25.25	1.80	(210)	1.82				(521)	1.33		
			(312)	1.81				(351)	1.33		
			(240)	1.82				(252)	1.34		
2	26.68	1.71	(123)	1.71	1	36.80	1.31	(441)	1.33		
			(411)	1.70				(333)	1.33		
			(331)	1.73				(413)	1.31		
			(241)	1.72				(530)	1.31		
			(042)	1.69				(260)	1.30		
			(420)	1.70	1	37.50	1.28	(155)	1.28		
2	27.46	1.67	(322)	1.70				(134)	1.27		
			(213)	1.68				(512)	1.28		
2	28.30	1.62	(142)	1.65				(224)	1.29		
			(051)	1.60				(204)	1.29		
			(150)	1.62				(053)	1.27		
2	29.12	1.58	(033)	1.59	1	38.45	1.24	(531)	1.25		
			(223)	1.58				(314)	1.24		
			(421)	1.59				(153)	1.24		
			(402)	1.57				(343)	1.22		

Table II Continued

I	θ	Cu	d(meas)	(hkl)	d(calc)	I	θ	Cu	d(meas)	(hkl)	d(calc)
2	29.72		1.55 $\overset{\circ}{\text{A}}$	(133)	1.56 $\overset{\circ}{\text{A}}$	1	38.45		1.24 $\overset{\circ}{\text{A}}$	(522)	1.24 $\overset{\circ}{\text{A}}$
				(151)	1.56					(062)	1.25
1	44.40		1.10	(460)	1.11					(035)	1.20
				(270)	1.13	1	45.50		1.08	(424)	1.09
				(414)	1.12					(551)	1.07
				(125)	1.11					(315)	1.04
				(215)	1.10					(135)	1.06
				(242)	1.13					(225)	1.07
				(602)	1.14					(701)	1.05
				(505)	1.11					(305)	1.06
				(370)	1.10					(710)	1.05
										(640)	1.07

Table III

Pseudomalachite X-ray Powder Pattern

Monoclinic, $P2_1/a$; $a = 17.06 \overset{\circ}{\text{A}}$, $b = 5.76 \overset{\circ}{\text{A}}$, $c = 4.49 \overset{\circ}{\text{A}}$

I	θ	Cu	d(meas)	(hkl)	d(calc)	I	θ	Cu	d(meas)	(hkl)	d(calc)
$\frac{1}{2}$	9.33		4.75 $\overset{\circ}{\text{A}}$	(210)	4.770 $\overset{\circ}{\text{A}}$	1	17.55		2.56 $\overset{\circ}{\text{A}}$	(320)	2.569 $\overset{\circ}{\text{A}}$
10	9.92		4.48	(001)	4.489					(610)	2.543
5	12.87		3.46	(111)	3.477	6	18.55		2.42	(021)	2.424
				(415)	3.425					(601)	2.421
$\frac{1}{2}$	13.64		3.27	(211)	3.254	8	18.85		2.39	(121)	2.397
2	14.29		3.12	(401)	3.120					(420)	2.388
4	14.43		3.09	(401)	3.164					(601)	2.382
2	14.69		3.04	(311)	3.025	5	19.38		2.32	(221)	2.337
4	15.03		2.97	(311)	2.987					(221)	2.325
3	15.24		2.93	(510)	2.933	5	20.19		2.23	(002)	2.245
1	15.71		2.85	(600)	2.843					(710)	2.243
				(120)	2.838					(321)	2.237
3	16.43		2.72	(220)	2.729					(611)	2.232
				(411)	2.705					(321)	2.221

Other values are given by Berry, but these are sufficient to show the difference between these dimorphous minerals. Figure 2 illustrates pictorially the differences in the powder patterns of pseudomalachite and the new mineral.

Table 1

Year	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960
...

Table 2

Year	1950	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960
...

Other values are given by hand, but have the same accuracy as those in the tables. For those between lines that are not given, the values are interpolated by the difference in the number of years between the two given values.

Morphological Crystallography

Three separate crystals, which could be mounted on a two-circle goniometer head, were used for the measurement of interfacial angles. Two of these crystals were mounted with the g axis parallel to the axis of the goniometer head and the third was successively mounted with each of the three crystallographic axes parallel to the axis of the head. The faces were macroscopically excellent but when subjected to optical reflection examination, appeared rough and gave multiple reflections. However, after the calculated angles were computed and compared with the measured angles, there was an excellent coincidence of data (Table IV).

The computation of the angles was accomplished by the use of simple trigonometric functions. The lengths of the axes are known from the powder pattern, and, therefore, the angles may be computed by finding the tangential relations of these values.

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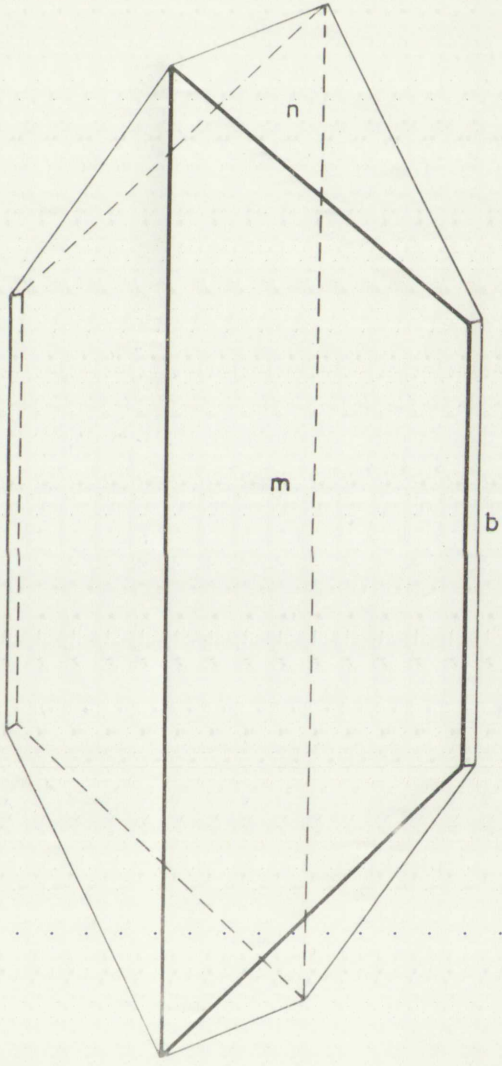
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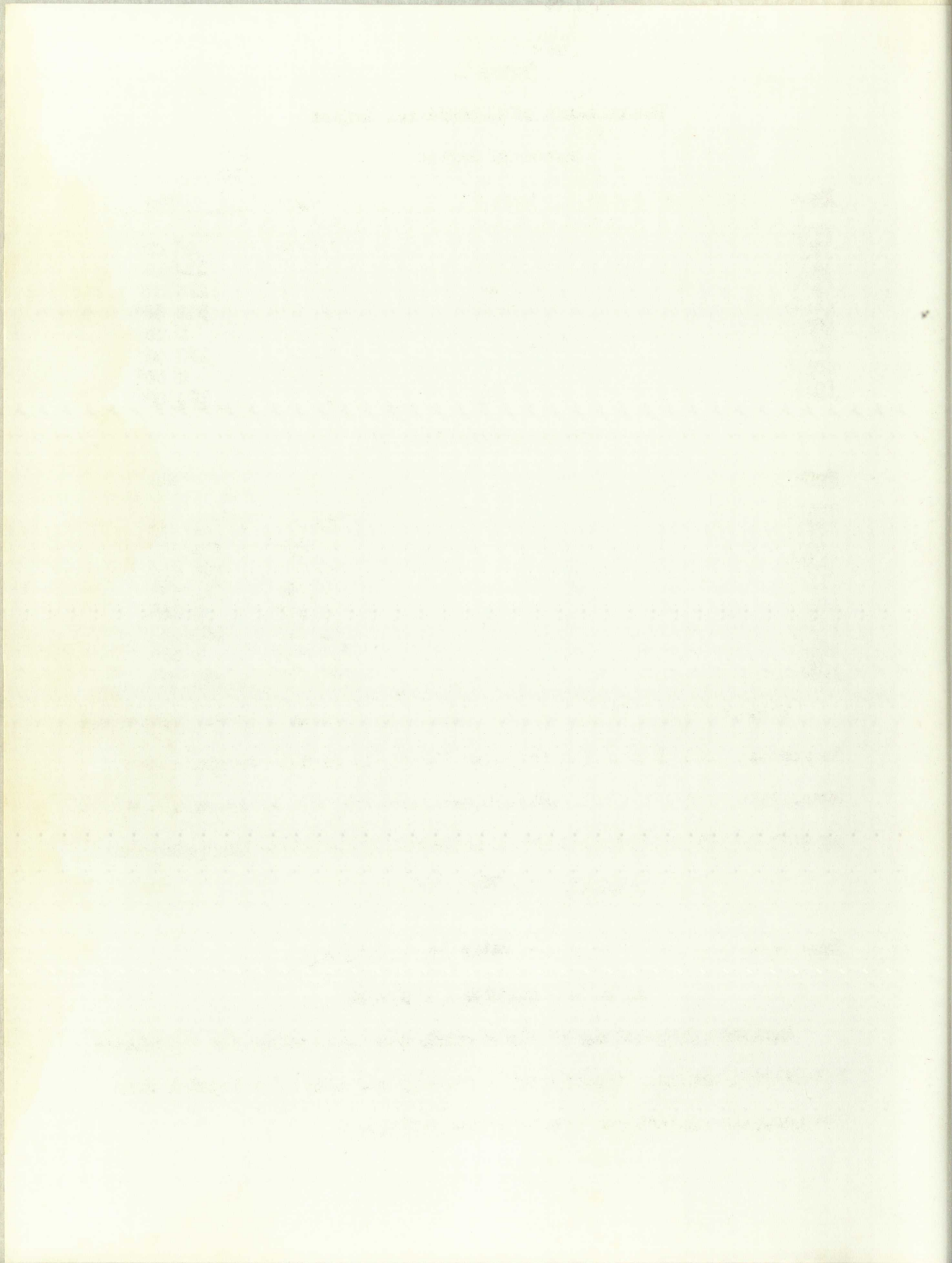


Table IV
Measurement of Interfacial Angles

Measured Angles				
Form	Number of Faces	Quality	Rho	Phi
($\bar{1}\bar{1}0$)	10	Poor to Fair	90° 00'	48° 07'
($\bar{1}\bar{1}0$)			90° 00'	132° 10'
($\bar{1}\bar{1}0$)			90° 00'	228° 07'
($\bar{1}\bar{1}0$)			90° 00'	312° 08'
(010)	2	Very Poor	90° 00'	0° 00'
(010)			90° 00'	180° 00'
(011)	6	Poor	35° 10'	0° 00'
(011)			35° 10'	180° 00'

Calculated Angles		
Form	Rho	Phi
($\bar{1}\bar{1}0$)	90° 00'	48° 03'
($\bar{1}\bar{1}0$)	90° 00'	131° 57'
($\bar{1}\bar{1}0$)	90° 00'	228° 03'
($\bar{1}\bar{1}0$)	90° 00'	311° 57'
(010)	90° 00'	0° 00'
(010)	90° 00'	180° 00'
(011)	35° 03'	0° 00'
(011)	35° 03'	180° 00'

Because only ($\bar{1}\bar{1}0$), ($\bar{1}\bar{1}1$), and (010) were present, it was impossible to measure good values for the polar elements, because terminal faces which intersect all three crystallographic axes must be present, or (101) as well as (011). However, it is possible to calculate the polar ratio;

$$p_o : q_o : r_o = 0.7803 : 0.7016 : 1$$

from which the following axial ratio is calculated;

$$a : b : c = 0.8989 : 1 : 0.7016$$

Gnomonic projections of the mineral were made using the calculated interfacial angles. A perspective drawing was made of a crystal from the gnomonic projection. It is shown in Plate 3.

TABLE I

Number of ...

...

Form	Number of
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(99)
(100)

...

...

TABLE II

Form	Number of
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(96)
(97)
(98)
(99)
(100)

Because ... (11) and (12) ...

to ...

which interest ...

as well as (10) ...

...

from which the following ...

...

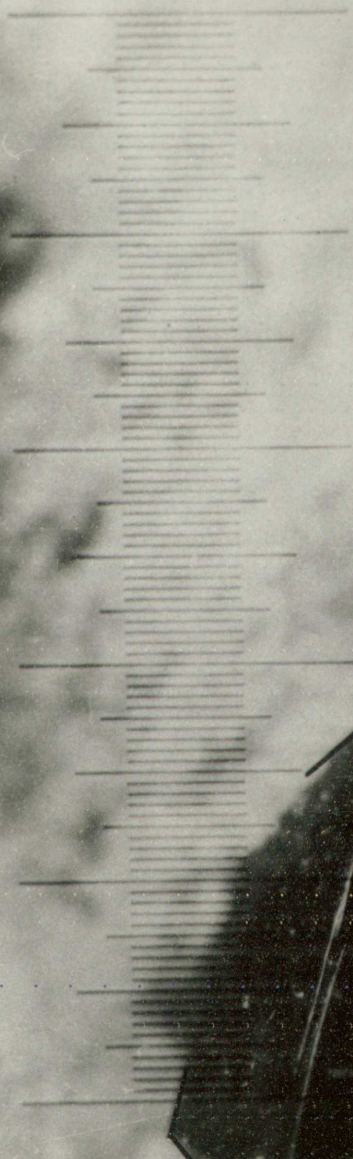
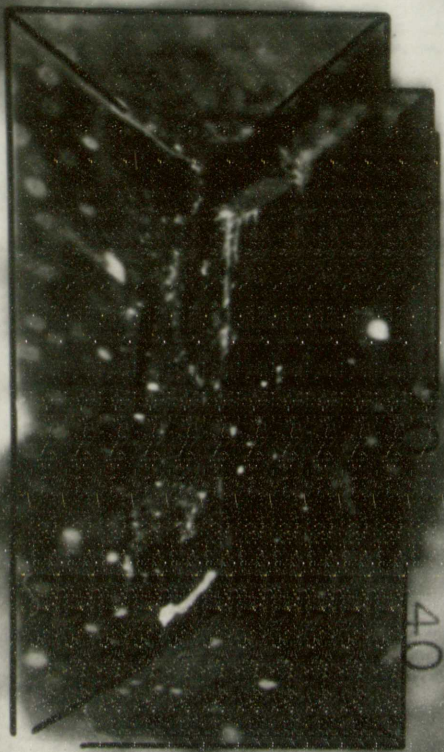
domestic ...

international ...

the domestic ...

PHOTOMICROGRAPH OF CRYSTALS
OF NEW MINERAL
(ENLARGEMENT APPROXIMATELY 100X)

PHOTOGRAPH OF CRYSTALS
OF NEW MINERAL
(ENRICHMENT APPROXIMATELY 100%)

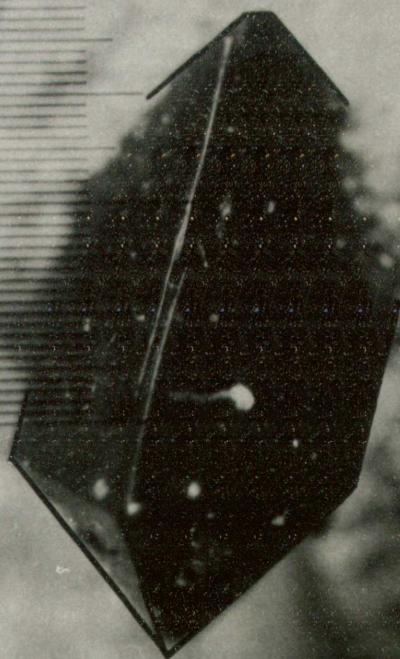


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60

80

100





PHOTOMICROGRAPH OF CRYSTALS
OF NEW MINERAL
(ENLARGEMENT APPROXIMATELY 40 X)



Composition and Cell Content

Only 0.2399 gm. of the mineral could be used for chemical analysis.

The results of this analysis are as follows:

<u>Constituent</u>	<u>Percent</u>
CuO.....	69.09
P ₂ O ₅	24.33
H ₂ O.....	06.57
Total.....	99.99

Table V

Determination of the Empirical Formula

	<u>Molecular Proportion</u>	<u>Molecular Ratio</u>
<u>Percent CuO</u> = $\frac{69.09}{79.57} = .8675$	$\frac{.8675}{.1716}$	5.025
<u>Percent P₂O₅</u> = $\frac{24.33}{141.96} = .1716$	$\frac{.1716}{.1716}$	1.000
<u>Percent H₂O</u> = $\frac{6.57}{18.00} = .3650$	$\frac{.3650}{.1716}$	2.068

The chemical analysis, by calculation shown in Table V, yields the empirical formula $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$ or $2\text{Cu}(\text{OH})_2 \cdot \text{Cu}_3(\text{PO}_4)_2$ for the mineral.

The structural lattice dimensions combined with the measured specific gravity (5.22) and the chemical analysis of the material gives the number of molecules in the unit cell:

$$\text{density} = \frac{\text{weight}}{\text{volume}}$$

$$d = \frac{nM \times 1.649 \times 10^{-24}}{a \times b \times c}$$

where M = mass of the chemical unit of which the crystal is composed

d = density

$a \times b \times c$ = volume of unit cell

n = number of molecules in the unit cell

1.649×10^{-24} = Avogadro's number which changes units of atomic weight into grams.

$$5.22 = \frac{n \times 1.649 \times 10^{-24}}{5.83 \times 7.47 \times 8.31}$$

In this formula n solves out to almost exactly 2 and inasmuch as n must be a whole number, the specific gravity of the mineral is 5.24 when 2 is substituted for n and d is calculated from the formula above.

Therefore, the structural formula for the mineral is $\text{Cu}_2(\text{PO}_4)_4(\text{OH})_8$ or $2(\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4)$ which makes the mineral dimorphous with pseudomalachite (Berry, 1950).

Optical Properties

The optical properties, as determined by immersion oils and the petrographic microscope are: $\alpha = 1.698$, $\beta = 1.745$, and $\gamma = 1.783$ (all ± 0.001); $2V = 90^\circ$; optically (\neq); $x = c$. The (110) cleavage of the mineral gives a somewhat preferred orientation (almost perfectly centered optic axis figure). This perfectly centered optic axis figure gives the full value of β . The full values of α and γ can also be obtained as the mineral is very brittle and fractures part of the time, with no preferred orientation.

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11 - 1000

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15 - 1000

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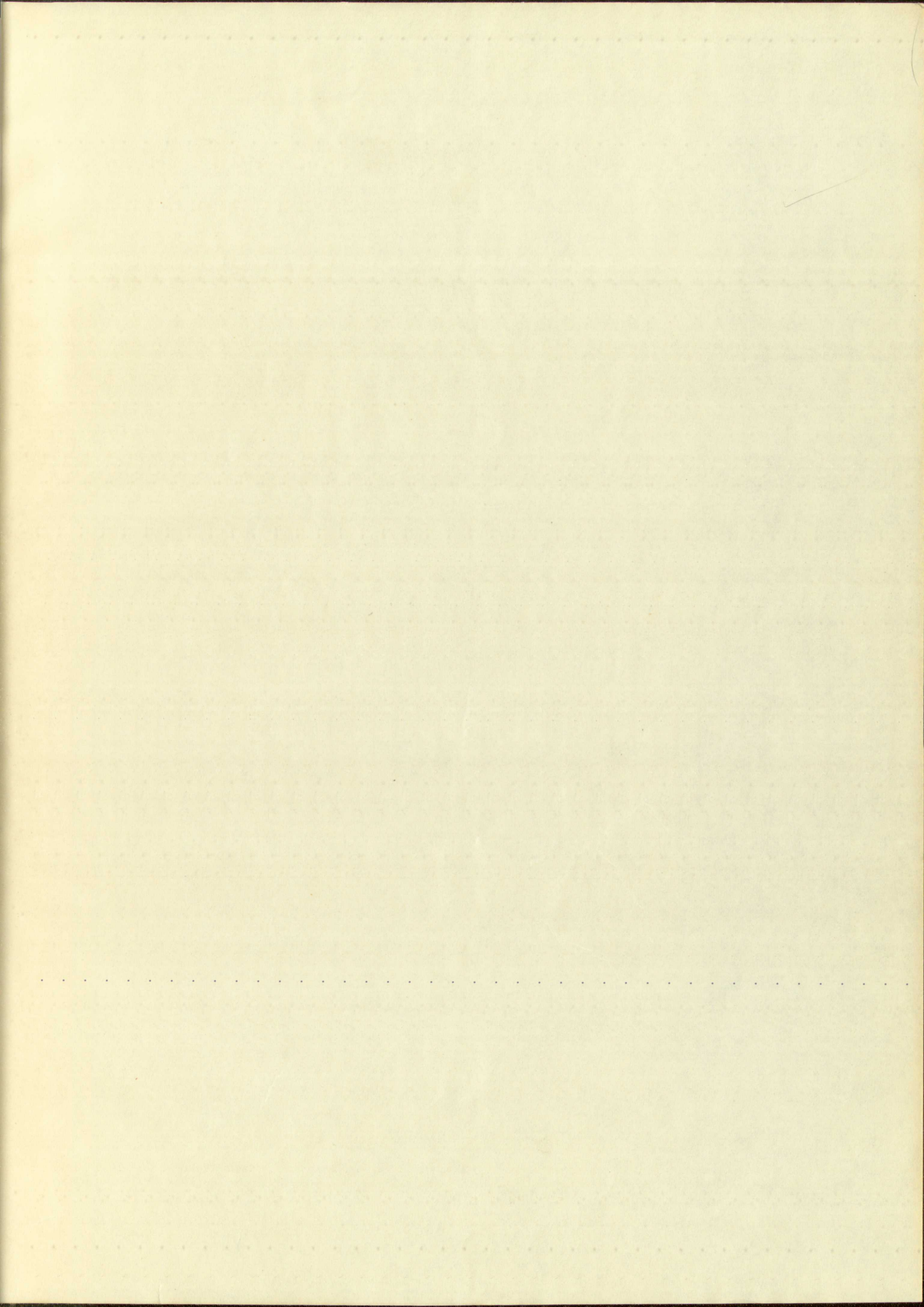
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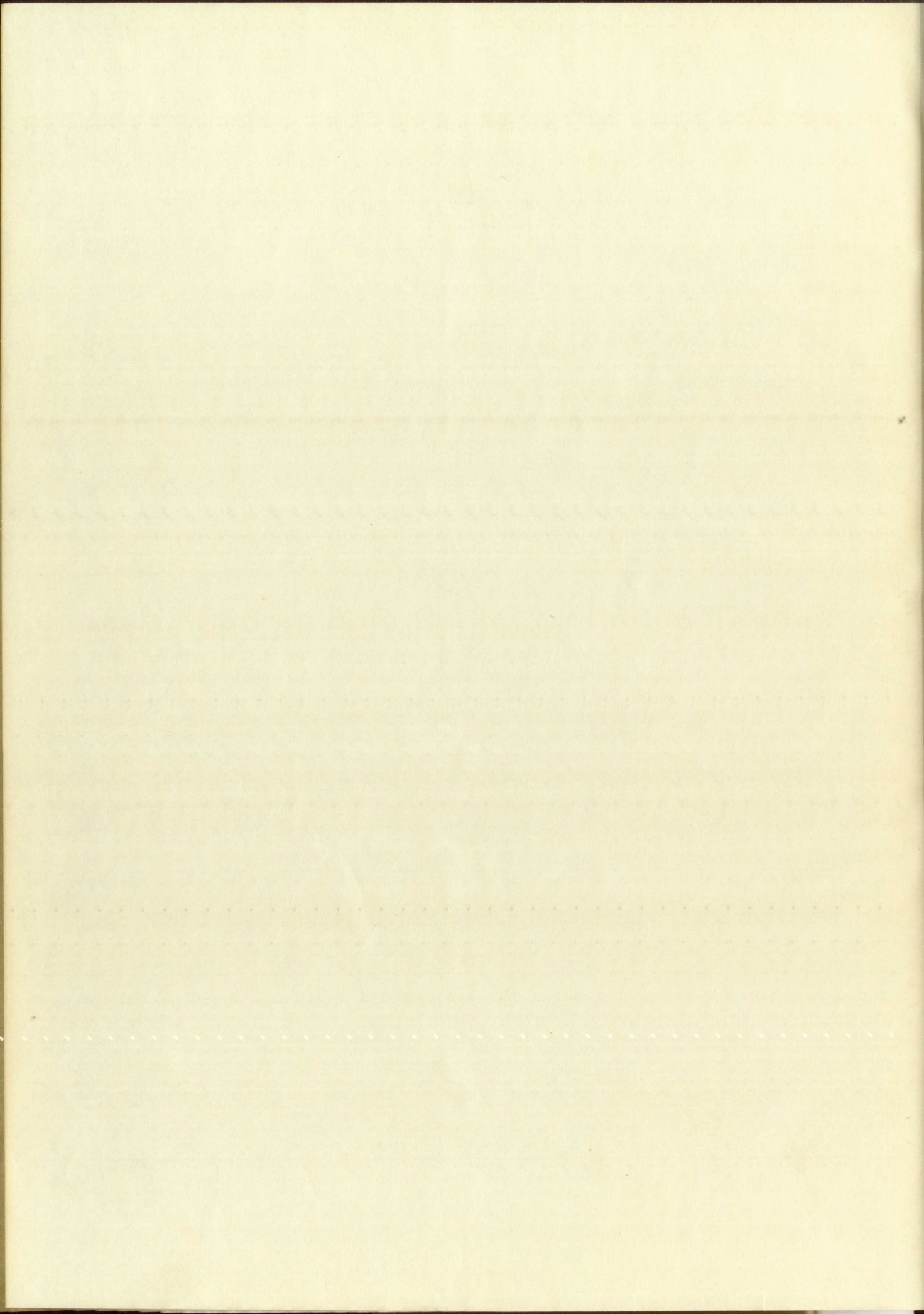
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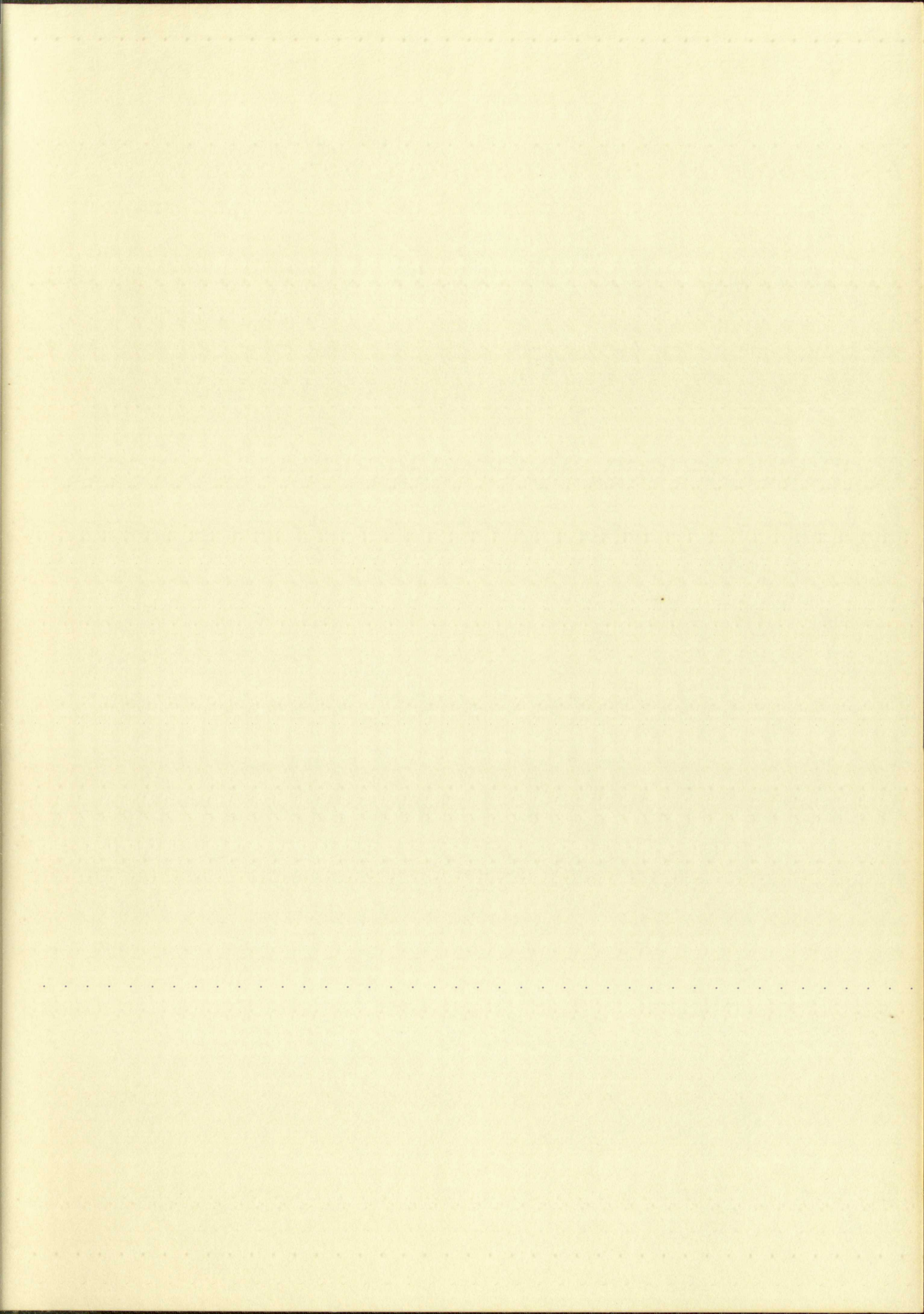
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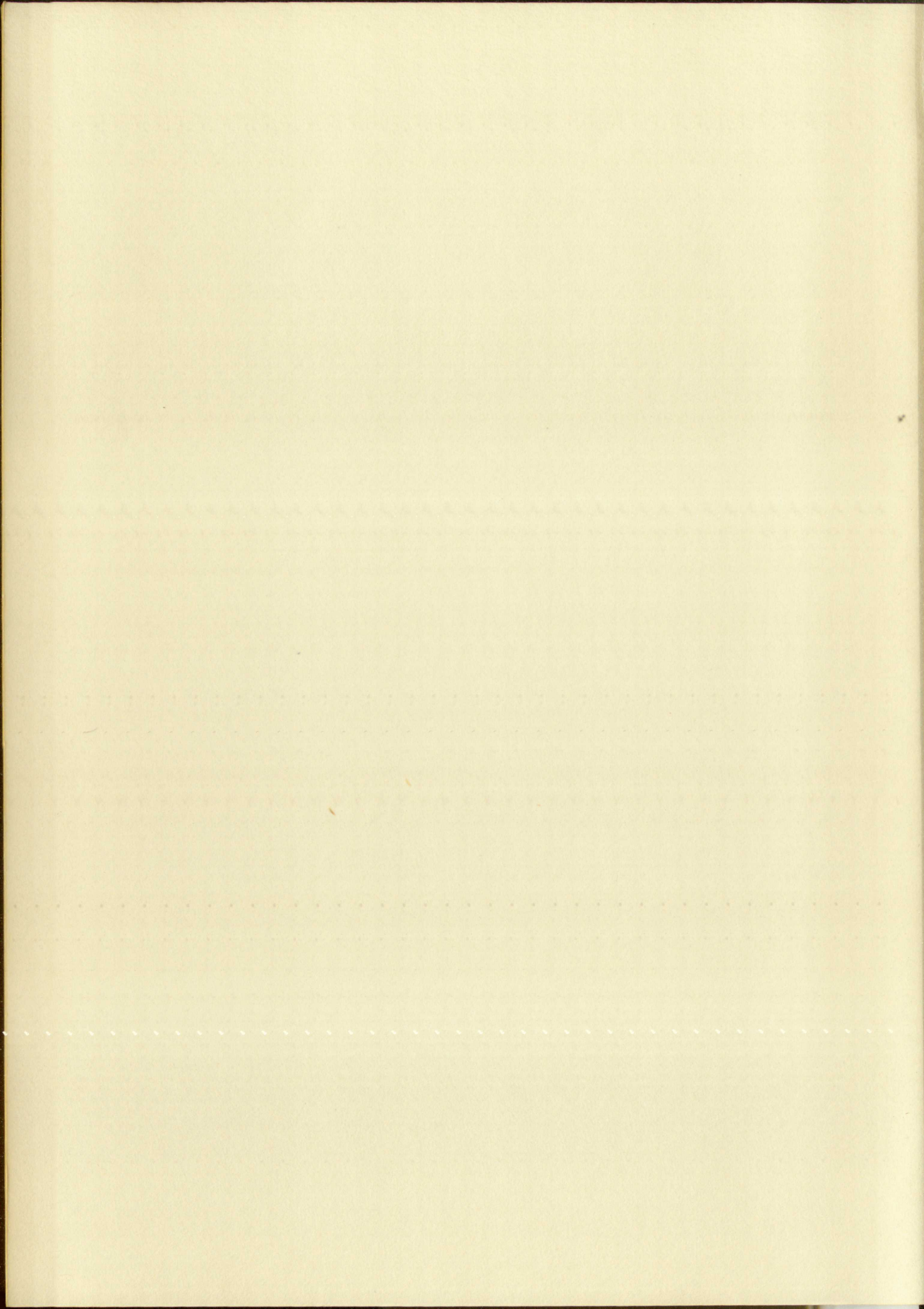


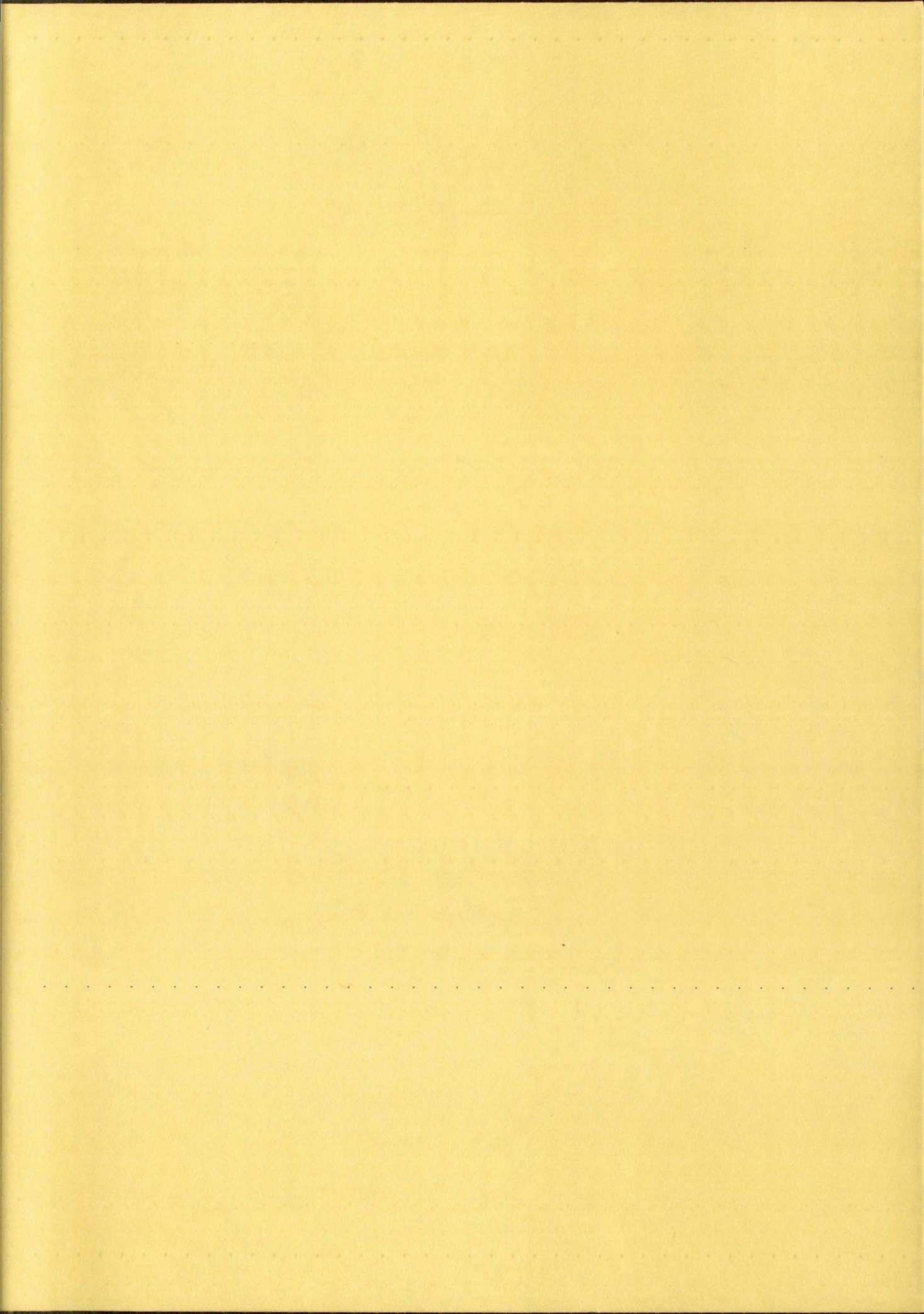
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