THE AMERICAN MINERALOGIST, VOL. 46, JULY–AUGUST, 1961

X-RAY STUDY OF AUTUNITE

YUKIO TAKANO, *Institute of Earth Science, College of General Education, University of Tokyo, Tokyo, Japan.*

ABSTRACT

The autunite-meta-autunite I—meta-autunite II series was studied by *x*-ray diffraction. In America and Europe, autunite is usually found as the meta-autunite I phase, whereas in Japan it occurs as autunite. By studying the process by which autunite is dried and heated until it finally forms a high temperature phase, the writer has determined the diffraction pattern of each phase. Single crystals were analyzed by the Weissenberg method, and the lattice constants and space groups were determined. The large cell proposed by Donnay and Brichard for meta-autunite was not found. Meta-autunite II is orthorhombic, with $a_0=6.55$, $b_0=7.05$ and $c_0=8.16$ Å. This c_0 value is smaller than the c_0 of meta-autunite I, contrary to the values hitherto reported.

INTRODUCTION

The first *x*-ray study of autunite was attempted in 1938 by J. Beintema, who found it to be tetragonal. *X*-ray study of this mineral has been active since 1955, and reports have been published by G. Donnay and J. D. H. Donnay (1955); C. Frondel, D. Riska and J. W. Frondel (1956); P. B. Gechebe (1957); and H. Brichard and H. Brasseur (1958), and others, One of the latest is A. Volborth (1959), who studied strontian meta-autunite. Table 1 summarizes the *x*-ray data on the autunite series.

The crystal structures of the members of the autunite series have not yet been determined, and the views on the hydration state of each phase are varied. Most of the research since 1955 has been concentrated on meta-autunite, which is regarded as the most stable mineral in this series, and very little data on autunite and meta-autunite II have been pub-

TABLE 1. SPACE GROUP AND CELL DIMENSIONS OF AUTUNITE SERIES

Name		Autunite	Meta-autunite I	Meta-autunite II
Chemical formula		$Ca(UO_2)_2(PO_4)_2 10\sim 12H_2O$	$Ca(UO_2)_2(PO_4)_2 2\sim 6H_2O$	$Ca(UO_2)_2(PO_4)_2 O\sim 2H_2O$
Crystal system		Tetragonal	Tetragonal	Orthorhombic
Space group		*I4/mmm*	*P4/nmm*	*P mmm*
Cell dimensions	a_0	6.989	6.972	6.45
	b_0	—	—	6.97
	c_0	20.63	8.47	8.65

lished since Beintema's work. Hence, the writer's study was focussed on these lesser-known minerals.

TRANSITIONAL RELATION

The samples used in the present study are from Ningyō Pass, on the border between Okayama and Tottori Prefectures, Japan, and from the Daybreak Mine, Washington, U.S.A. The samples are all micaceous, tetragonal platy crystals. Those from Ningyō Pass are light greenish yellow and transparent, or yellow and translucent, mostly 4 mm. in the maximum diameter, having tetragonal outlines, whereas those from Daybreak are yellow to dark green or greenish black and many of them are rectangular and platy, occasionally as large as 1 cm. or more in diameter. Of the Daybreak mine specimens, only the yellow portions were selected and used in the experiments. From these samples, pure thin flakes of crystals were separated under petrographic and binocular microscopes. The flakes were ground in a mortar, and *x*-rayed with a diffractometer operated as follows: Cu/Ni, 35 K.V., 15 M.A., and scanning speed 1° per 1′. The results (lower part of Fig. 1) disclose that almost all the samples from both Ningyō Pass and Daybreak are autunite. According to Volborth (1959), most of the autunites occurring in nature are supposed to be meta-autunite, but the writer has found that the samples from Ningyō Pass in humid Japan are autunite, and contain almost no meta-autunite. Moreover, the Daybreak samples, collected at the same locality as those by Volborth, gave more diffraction patterns of autunite than of meta-autunite, when the samples were examined in Japan. Hence the geographical situation of Japan is favorable for this kind of experiment. Accordingly the writer has carried out various experiments in order to obtain diffraction patterns of pure autunite. Figure 1 shows the results of one of these experiments, in which a powdered sample was placed in a holder, water was then added, and gradually allowed to dry up. In this experiment, the samples from both localities, when soaked in water, first showed diffraction patterns of low temperature type autunite, but gradually changed into meta-autunite I, beginning with a dried part. This fact indicates that autunite, which remains relatively stable in Japan, becomes meta-autunite I without being heated when it is pulverized and soaked in water. The samples that have gone through this transitional process become autunite again if water is added, but as they dry up the transition from autunite to meta-autunite I takes place at a faster rate than before. On the other hand, if autunite samples were not soaked in water they would remain stable for more than a year, even after they were pulverized. When a sample that has transitionally altered to meta-autunite I is placed in the air bath at 110° C. to

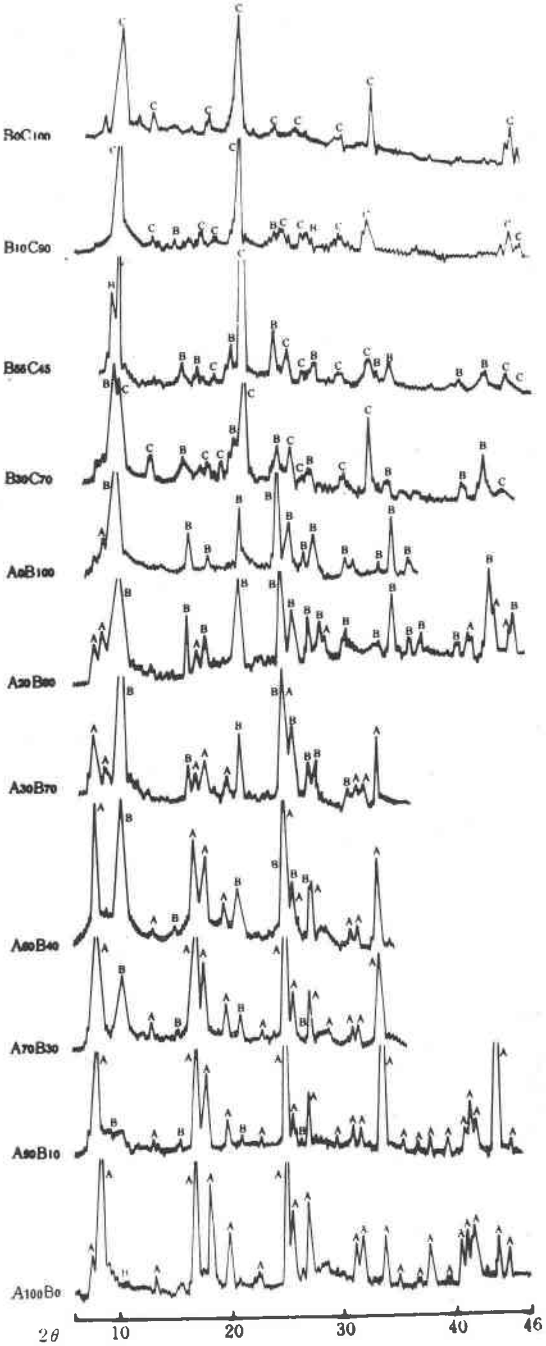

FIG. 1. *X*-ray diffractometer traces of transition in the autunite series. Samples from Ningyō-Pass.

A—autunite; B—meta-autunite I; C—meta-autunite II.

TABLE 2. *X*-RAY DATA FOR AUTUNITE

I4/mmm
$a_0=6.969$ Å $c_0=20.76$ Å (Ningyō-Pass)
$a_0=6.872$ Å $c_0=20.73$ Å (Daybreak Mine)

Calculated values		Ningyō-Pass		Daybreak Mine		Mt. Spokane	
hkl	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)
002	10.37	100	10.48	100	10.31	160	10.4
101	6.61	6	6.74	4b	6.52	10	6.67
004	5.19	86	5.19	36	5.21	84	5.19
110	4.92	35	4.91	30	4.93	39	4.96
103	4.91						
112	4.45	15	4.46	9	4.46	29	4.48
105	3.567	83	3.565	53	3.574	70	3.58
200	3.486	18	3.495	29	3.495	31	3.51
202	3.304	22	3.317	18	3.315	28	3.33
204	2.893	8	2.899	5b	2.915	8	2.91
213	2.842	13	2.861	6	2.854	12	2.86
107	2.729	16	2.727	10	2.722	17	2.73
008	2.598	5	2.596	—	—	3	2.60
215	2.492	3	2.495	4b	2.492	5	2.50
220	2.464	5	2.440	6	2.454	5	2.48
206	2.454						
222	2.397	7b	2.418	5	2.411	8	2.41
118	2.299	9	2.299	—	—	5	2.30
224	2.225	14	2.219	6	2.214	8	2.22
310	2.203	26	2.193	11	2.203	10	2.19
109	2.187	22	2.181	11	2.177	9	2.17
312	2.157	16	2.161	10	2.146	12	2.15
217	2.146	17	2.143				
208	2.080	45	2.080	15	2.072	24	2.08
0·0·10	2.076						
314	2.028	9	2.033	7	2.033	9	2.039
305	2.028						
1·1·10	1.914	10	1.917	5	1.910	7	1.918
219	1.854	5b	1.857	—	—	—	—
307	1.829	5b	1.835	4	1.828	2	1.834
1.0.11	1.822	4b	1.820	—	—	—	—
2.0.10	1.784	5b	1.785	—	—	4	1.787
325	1.755	4b	1.754	5	1.751	4	1.761

be heated intermittently for short periods, and then cooled, the resulting *x*-ray diffraction pattern gradually shows the phase of meta-autunite II. The transitional process, as shown in the left side in Fig. 1, was determined by assuming that the samples used in the experiment are admixtures of the three phases, and by calculating the mixing ratio by the

TABLE 3. *X*-RAY DATA FOR META-AUTUNITE I

*P*4/*nmm* a_0=6.972 Å c_0=8.47 Å (Volborth)

Small cell	Calculated values†	Takano (1959)		Volborth (1959)		Brichard (1958)			Frondel (1956)		Large cell‡	Gechebe (1957)	
						Synthetic		Natural					
hkl	*d* (Å)	I	*d* (Å) meas.	I	*d* (Å) meas.	I	*d* (Å) meas.	*d* (Å) I	I	*d* (Å) meas.	*HKL*	I	*d* (Å) meas.
001	8.47	100	8.54	100	8.47	s	8.465	8.52	10	8.51	001	10	5.98
101	5.38	32	5.37	44	5.38	s	5.39	5.41	7	5.39	221	2	5.35
110	4.93	14	4.93	21	4.93	s	4.92	4.95	5	4.96	040	0.5	4.84
111	4.26	16	4.28	—	—	vf	4.42	—	—	—	240*	—	—
002	4.24	30	4.25	69	4.23	m	4.25	4.26	6	4.28	002	2	4.12
102	3.62	86	3.62	85	3.61	m	3.64	3.64	8	3.63	222	10	3.56
200	3.49	28	3.50	31	3.48	s	3.48	3.51	9	3.50	440	5	3.44
201	3.22	18	3.24	23	3.22	—	—	—	—	—	—	—	—
112	3.21	10	3.20	—	—	s	3.23	3.24	8	3.24	042	5	3.19
211	2.93	11	2.93	15	2.93	m	2.93	2.94	4	2.94	621	4	2.98
003	2.82	—	—	—	—	—	—	—	—	—	—	—	—
202	2.69	—	—	—	—	vf	2.70	2.705	1	2.68	213*	—	—
103	2.62	48	2.62	35	2.61	—	—	2.62	3	2.61	—	—	—
212	2.51	7	2.51	6	2.51	f	2.52	2.52	2	2.51	323*	5	2.58
220	2.47	—	—	4	2.47	w	2.47	2.48	2	2.47	—	—	—
113	2.45	9	2.45	4	2.45	—	—	—	—	—	—	—	—
221	2.37	3	2.38	8	2.37	w	2.38	2.38	3	2.38	423*	—	—
301	2.24	4	2.25	5	2.24	w	2.24	2.25	2	2.25	523*	—	—
310	2.21	7	2.21	10	2.21	m	2.21	2.215	3	2.21	480	2	2.19
203	2.19	6	2.19	—	—	—	—	—	—	—	—	—	—
311.222	2.13	—	—	—	—	w	2.13	2.14	3	2.14	613*	—	—
004	2.12	63	2.11	71	2.11	—	—	—	—	—	—	—	—
213	2.09	18	2.095	—	2.04	f	2.10	2.10	3	2.10	623	7	2.08
302	2.04	8	2.037	9	2.04	w	2.05	2.05	3	2.04	633*	2	2.01
104	2.03	17	2.020	14	2.02	—	—	—	—	—	—	—	—
114	1.946	22	1.943	14	1.943	—	—	—	2	1.941	—	4	1.92

* Where Brichard's indexing does not agree with Volborth's, the *HKL* indices are marked with an asterisk.

† In this table all calculated *d* values larger than 2.00 Å for small cell are given.

‡ Large cell, a_0=19.72, c_0=8.47; by the transformation $\bar{2}20/220/001$.

Alexander Klug method. Unlike single crystals, transition of powder samples occurs sporadically, beginning with scattered grains within the holder, and continues as water escapes, until the transition is completed.

The above-mentioned experiments were repeated and diffraction patterns of the respective phases were separated, as shown by Tables 2, 3 and 4. In the *x*-ray data hitherto reported, autunite diffraction patterns were generally commingled with several meta-autunite patterns, and meta-autunite patterns contained some of autunite lines. Consequently, there may have been many cases where the diffraction pattern of one phase was erroneously indexed as the other phase, so that the resultant calculated values became identical incidentally. Therefore, even about the phase of meta-autunite I which has been studied best of all in this series, discussions are still going on whether or not the a_0 value should be

TABLE 4. X-RAY DATA FOR META-AUTUNITE II

Pmmm

$a_0=6.55_1$ Å $b_0=7.05_3$ Å $c_0=8.16_4$ Å (Ningyō-Pass)

Calculated values		Ningyō-Pass		Mt. Spokane		U.S.S.R.	
hkl	*d*	I	*d*	I	*d*	I	*d*
001	8.16	100	8.17	150	8.21	10	7.90
100	6.55	6	6.57	9	6.58	—	—
011	5.35	5	5.30	9	5.33	2	5.25
110	4.80_5	9	4.81	11	4.81	2	4.42
111	4.14	32	4.14	—	—	—	—
002	4.08	57	4.08	70	4.08	10	4.03
—	—	—	—	5	3.60	—	—
020	3.53_5	13	3.51	17	3.53	5	3.50
200	3.28	6	3.28	8	3.27	—	—
—	—	—	—	6	3.21	4	3.21
112	3.11	4	3.10	2b	3.12	—	—
210	2.972	8	2.963	10	2.97	4	2.94
121	2.907	5	2.926	—	—	—	—
003	2.722	14	2.718	16	2.72	7	2.69
202	2.555	4	2.556	2	2.58	—	—
013	2.539	4	2.542	—	—	—	—
103	2.220	5	2.205	5	2.21	1	2.19
300	2.182	4	2.179	—	—	—	—
033	2.157	4	2.156	—	—	—	—
004	2.041	10	2.040	7	2.04	7	2.02
213	2.008	6	2.007	—	—	—	—
230	1.914	3	1.916	2	1.90	2	1.87
—	—	—	—	—	—	1	1.84
040	1.768	3	1.778	—	—	1	1.74
005	1.633	8	1.630	5	1.63	1	1.63
401	1.605	8	1.601	3	1.61	—	—
025	1.482	4	1.480	3	1.48	2	1.47

$2\sqrt{2}$ times as great. The writer's experiments by *x*-ray diffraction may give a fairly precise answer to the above question.

AUTUNITE

Detailed numerical data on autunite have been very few since the study of Beintema (1938). It is probably because of the fact that autunite seldom occurs in nature as it easily alters to meta-autunite II. Unless the region where autunite occurs is moist and relatively cool, like Japan and Soviet Russia, experiments on natural autunite at room temperature are difficult.

Table 2 shows the *x*-ray diffraction patterns of autunite obtained from the above-mentioned experiments. The experiments reveal that the samples from Ningyō Pass have slightly larger c_0 values than those from Daybreak. At room temperature in Japan, each of the samples showed the (001) peak of meta-autunite I on the outer side of (002). This phenomenon was especially noticeable in the Daybreak samples. Nevertheless, in the experiments on the samples fully soaked in water (Fig. 1 *b*-2), this peak disappeared, and it coincided with the diffraction pattern of meta-autunite I. Thus, it has been confirmed that the peak does not belong to the autunite phase.

Small flakes of autunite were separated from the Ningyō Pass samples and more than sixty flakes were tested by *x*-ray oscillation photographs. Autunite flakes, no matter how thin, are considered to consist of aggregation of parallel crystals with interspaces parallel to (001). It is, therefore, very difficult to obtain specimens suitable for single crystal tests. The writer was able to find seven such autunite flakes, and made *a*- and *c*-axis Weissenberg photographs. The cell dimensions of autunite were confirmed as $a_0=6.97$, $c_0=20.76$ Å. Only reflections with $h+k+l=2n$ were found. Hence the space group is $I4/mmm$, and the indexing of the powder patterns was confirmed. Figure 2 shows the 0-level Weissenberg photograph with rotation around the *a* axis.

META-AUTUNITE I

Table 3 shows the experimental values obtained by the writer from the Ningyō Pass samples and the values converted from the calculated values of Volborth (1959). With a marked increase of data on meta-autunite I, two different theories concerning the value of a_0 are being advocated; one is represented by Beintema and Volborth who maintain that a_0 is 6.97 Å, while the other is supported by Donnay and Brichard who insist that a_0 is 19.8 Å, which is $2\sqrt{2}$ times the former. However, the present experiments were convenient for studying this problem, for the writer was observing the transitional stages of autunite. The experiments revealed, as indicated in Table 3, that the index (B) of large cell of meta-autunite I reported by Donnay, Brichard and others corresponds to index (A) of autunite, *i.e.*, B(240) is Å(112), B(213) is A(107), B(613) is A(217) and A(312), and B(633) is A(0·0·10) and B(302). As the diffraction patterns representing large cells are all weak, it may be appropriate to think that autunite phase is included there, and the small cell theory of Volborth seems to be right. The samples from Ningyō Pass even showed (111), (112), (203) and (213) lines which do not occur among the experimental values by Volborth although they are found among his calculated values. In addition, almost all diffraction lines which did not disappear, were those of the space group P4/*nmm*, whereas no diffrac-

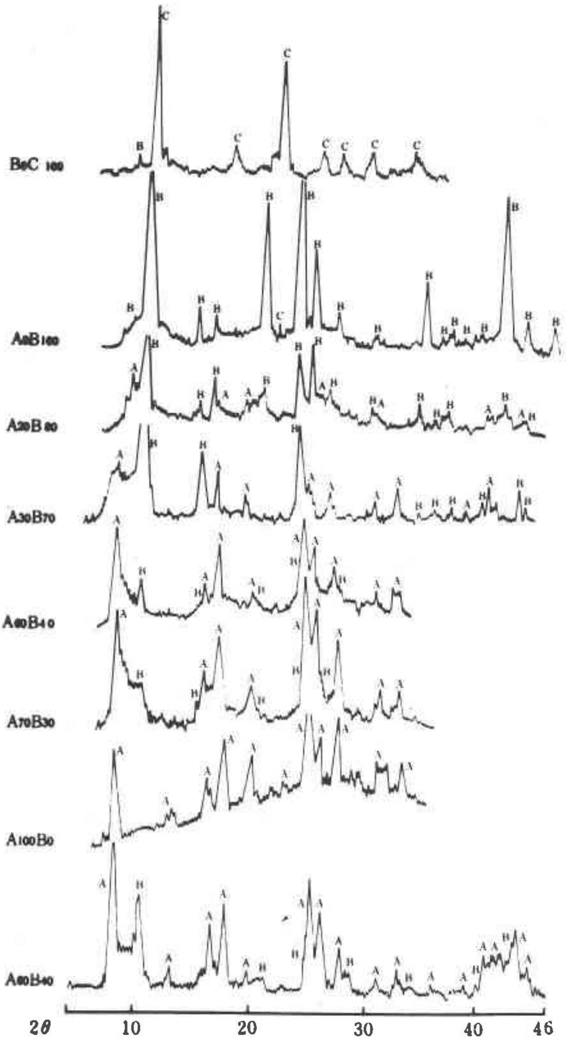

FIG. 2. *X*-ray diffractometer traces of transition in the autunite series. Samples from Daybreak Mine.

A—autunite; B—meta-autunite I; C—meta-autunite II.

tion lines supporting the large cell theory of Donnay and others were found.

META-AUTUNITE II

Important new data on meta-autunite II have been contributed by a recent study by Leo (1960). Since he did not index the powder photographs, the present writer has carried out the indexing. The results are

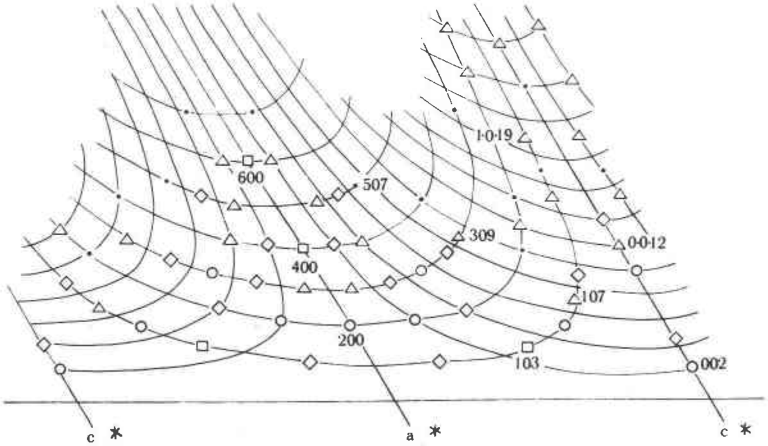

FIG. 3. Weissenberg photograph of autunite; 0-level, rotation around *a* axis. Symbols: ○-very strong; □—strong, ◇—medium; △—weak; ●—faint.

shown in Table 4, along with the new data obtained in this paper. The cell dimensions obtained $a_0=6.55$, $b_0=7.05$, and $c_0=8.16$ Å; space group *Pmmm*. According to Crystal Data (Donnay and others, 1954), $a_0=6.97$, $b_0=8.65$, and $c_0=6.45$ Å, while Beintema reported $a_0=6.45$, $b_0=6.97$, and $c_0=8.65$ Å. However, in the writer's precise experiments, the basal reflection (001) of meta-autunite II appeared as one of the double lines on the outer side of (001) of meta-autunite I. It has become clear, therefore, that c_0 of meta-autunite II should have a smaller value than $c_0=8.47$ Å of meta-autunite I. Thus, c_0 of meta-autunite II becomes 8.16 Å, instead of 8.65 Å.

Using the lattice constants of meta-autunite II obtained in the present experiments, indices cannot be assigned to 3.60 and 2.31 A of Leo's data. However, (102) and (201) of meta-autunite I are fairly strong reflections, and roughly correspond to the two above-mentioned values, so it is possible that Leo's data resulted from the mis-indexing of these reflections.

When meta-autunite II is measured at high temperatures, diffraction patterns of a different lattice having 7.6 to 8.0 Å basal reflections can be obtained. This cell is probably an orthorhombic cell in which $a_0=5.58$, $b_0=6.36$ and $c_0=7.95$ Å. Its lattice constant becomes shorter with increase in temperature, and when cooled it returns to the initial state of meta-autunite II.

DISCUSSION

As *x*-ray study of single crystals of autunite has been limited, in many cases reflections have been assigned indices impossible for an I lattice.

In powder data for fully hydrated autunite by Leo (1960, Table 6), the reported indices (009), (140) and (029) are an example. In the writer's experiments (1959) using Buerger's precession camera, it seemed that the (hk0) reflections appeared with $h+k+1=2n+1$. However, when (hk1) and hk2 levels were obtained, it was found that reflections from more than one level were being recorded. An autunite plate may look like a single crystal because of the very perfect cleavage, but in fact it is an aggregation of several pseudo parallel-grown crystals with markedly large dimensions of c_0. Consequently, reciprocal lattice points of different levels of other slightly inclined crystals give such effect as mentioned above.

Previously the writer made precise measurements of the crystal structure, morphology and optical character of xanthophyllite, and found that pseudo-hexagonal plates of the mineral consists of many-sectored structures of varied orientation (Takano and Takano, 1958, Fig. 4). Then, in micaceous autunite having such structures, he unraveled a similar relation from precession photographs (Takano and Takano, 1959*b*, Figs. 3, 4). These results have been practically verified by Leo's detailed optical measurements (Leo, 1960, Fig. 3*a*). That the space group of autunite is *I*4/*mmm* has been confirmed by the recent analysis of the Weissenberg photographs.

It is important, but very difficult, to determine quantitatively the degree of hydration at each stage of the autunite series, because the minerals of this series change easily under nearly normal temperature and humidity. Besides, as is known from the writer's experiments, separation of quite pure specimens of the respective minerals is almost impossible. It is anticipated also that in the transition experiments under temperature of little variance, some portion of the specimen may remain unaffected on account of the fact that a plate is usually composed of several flakes due to cleavage and sectoral structure. For example, calculated values of hydration of autunite would become smaller than the theoretical value 12 H_2O, as a result of intermixture of some meta-autunite I. The writer has entrusted M. Tsuboi and K. Takano with the measurement of the hydration state of autunite by infrared absorption, so the result will be reported in the near future.

ACKNOWLEDGMENTS

The present writer is greatly indebted to Professor Nobuo Katayama of College of General Education, University of Tokyo, for his valuable suggestions during this study of autunite, as well as for his criticism on the manuscript. In the *x*-ray work and related calculations, much help and advice were given by Mrs. Kotoyo Takano of Chemical Institute, Science Department, University of Tokyo, to whom the writer's thanks are due.

The writer also wishes to express his sincere thanks to Dr. Kichinosuke Henmi of Okayama University for his discussion throughout the study, and to Dr. Akiho Miyashiro of Geological Institute, Science Department, University of Tokyo, for his cordial offer of a sample of autunite from the Daybreak Mine.

References

Beintema, J. (1938), On the composition and the crystallography of autunite and the meta-autunites: *Rec. Travaux Chim. Pays-Bas*, **57,** 155–175.

Brichard, H., and Brasseur, H. (1958), Sur les autunites naturelles et synthetiques: *Bull. Soc. Franç. Miner. Crist.*, **81,** 4–10.

Donnay, G., and Donnay, J. D. H. (1955), Contribution to the crystallography of uranium minerals: *U.S.A.E.C. Tech. Inf. Serv., Oak Ridge, TEI*-**507,** 42.

Frondel, C., Riska, D., and Frondel, J. W. (1956), *X*-ray powder data for uranium and thorium minerals: *U. S. Geol. Survey Bull.*, **1036-G,** 91–153.

Gechebe, P. B. (1957), Pykobogcmbo no onepegelehubo ypahobeix nuheparob: Bonpocor reolomu yparea, Mockba, 143.

Heinrich, E. W. (1958), Mineralogy and geology of radioactive raw materials: McGraw-Hill Book Company, Inc., New York, 654 p.

Katayama, N., and Sato, Y. (1957), The sedimentary environment of the uraniferous bed of the Ningyo-pass: *Sci. Pap. Coll. Gen. Educ. Univ. Tokyo,* **7,** 131–144.

Leo, G. W. (1960), Autunite from Mt. Spokane, Washington: *Am. Mineral.*, **45,** 99–128.

Nuffield, E. W., and Milne, I. H. (1953), Studies of radioactive compounds: VI. Meta-uranocircite: *Am. Mineral.*, **38,** 476–488.

Palache, C., Berman, H., and Frondel, C. (1951), The System of Mineralogy, 7th ed., vol. 2: John Wiley and Sons, Inc., New York, 1124 p.

Soma, T. (1957), Autunite from the Ningyo-pass on the boundary between Tottori and Okayama prefectures, Japan: *Jour. Miner. Soc. Japan,* **3,** 214–217.

Takano, Y., and Takano, K. (1958), Apparent polytypism and apparent cleavage in micas: *Jour. Miner. Soc. Japan,* **3,** 674–692.

Takano, Y., and Takano, K. (1959a), The relation between optical anomaly and crystal structure: *Jour. Geol. Soc. Japan,* **65,** 236–247.

Takano, Y., and Takano, K. (1959b), The problem of the stability of the reciprocal main axis in polysynthetic twin: *Jour. Jap. Ass. Miner. Petro. Econ. Geol.*, **43,** 194–202.

Volborth, A. (1959), Strontian meta-autunite from the Daybreak mine, Mt. Spokane, Washington: *Am. Mineral.*, **44,** 702–711.