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NINGYOITE, A NEW URANOUS PHOSPHATE MINERAL FROM JAPAN*

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ABSTRACT

Ningyoite, $U_{1-x}Ca_{1-x}R.E._{.2x}(PO_4)_2 \cdot 1\text{–}2H_2O$, where x is about 0.1 to 0.2, is a new uranous mineral which occurs in an unoxidized zone of the Ningyo-toge mine, Tottori Prefecture, Japan. It coats pyrite and other minerals, or fills cavities and cracks in the ore. Ningyoite is acicular or elongated lozenge-shaped, and is very fine grained. The color is brownish green or brown in transmitted light, and faint pleochroism, darker in the Z direction, is observed. Extinction is parallel with positive elongation. The index of refraction varies and is about 1.64. Double refraction seems to be low. The x-ray pattern of the mineral resembles that of rhabdophane, $R.E.PO_4 \cdot H_2O$, but whereas rhabdophane has hexagonal symmetry, ningyoite is pseudohexagonal, orthorhombic, and the space group is probably $P222$ (D_2^1). The unit cell has dimensions $a = 6.78 \pm 0.03$ Å, $b = 12.10 \pm 0.05$ Å, and $c = 6.38 \pm 0.03$ Å, and contains 3 formula weights.

A similar compound, $UCa(PO_4)_2 \cdot 1.5H_2O$, was synthesized from slurries composed of uranous phosphate and calcium phosphate in sealed glass tubes at 150° C., and 185° C. at pH 1.4 to 4.8. The synthetic compound was not obtained at 100° C. and 130° C., nor when the HCl concentration was greater than (1+10). The synthesized acicular crystals are green in transmitted light. Pleochroism is Z = green and X = pale green. Extinction is parallel, elongation positive. α is between 1.69 and 1.70, and γ is between 1.70 and 1.71, but they are variable. The x-ray powder diffraction patterns of the samples of the synthetic compound are almost the same as that of the natural ningyoite, except for slight differences in line spacings. The cell dimensions are $a = 6.73 \pm 0.03$ Å, $b = 12.13 \pm 0.05$ Å, and $c = 6.36 \pm 0.03$ Å.

Upon heating at 800° to 900° C. in argon, both the natural mineral and the synthetic compound changed to a monazite-type structure which has a smaller cell size than that of natural monazite and is close to that of cheralite.

The properties of ningyoite and the synthetic mineral are compared and the effect of the presence of rare earths on the properties of the former are discussed.

The mineral was named for the locality.

INTRODUCTION

The uranium deposit in Ningyo Pass, Tottori Prefecture, Japan, was found in November 1955, by the carborne radiometric survey of the Geological Survey of Japan. Since the discovery, the area has been explored by the Atomic Fuel Corporation, Japan, and it is now the biggest uranium mine in Japan. Originally, only autunite was known as the ore mineral, but in March 1957, a more radioactive black ore was found in the

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unoxidized zone by members of the Atomic Fuel Corporation, Japan.

After the discovery of this black ore, Tadashi Muto and Toru Murano were assigned to study the mineralogy of the black ore, and found that the uranium in the ore was not in known minerals. The nature of the new mineral, however, could not then be determined because of the extreme fineness of the crystals and the difficulty of obtaining a pure sample of this mineral.

In March 1958, Muto was sent to the U. S. Geological Survey where he and members of the U. S. Geological Survey resumed the study of this mineral after a purer sample was prepared. Subsequent *x*-ray, spectrographic, and microchemical analysis revealed the nature of the mineral. However, as a pure fraction of the mineral could not be separated, synthesis of the mineral was undertaken.

The new mineral, ningyoite, is named for the locality, Ningyo Pass.

OCCURRENCE OF NINGYOITE

The geology of the Ningyo-toge mine was described by Katayama and Sato (1957), and Sato (1958). The Tertiary conglomerate where ningyoite occurs is called the Ningyo-toge formation, and overlies the eroded surface of Cretaceous granite. The pebbles are mainly granite and andesitic rocks. Ningyoite occurs in the unoxidized zone, usually as a thin coating on pyrite and apatite or filling cavities, especially in the matrices of the conglomerate or on the surface and along the cracks of the pebbles. Minerals associated with ningyoite are pyrite, marcasite, sphalerite, apatite, chlorite, gypsum, quartz, feldspar, hypersthene, biotite, rutile, calcite, kaolinite, montmorillonite, and traces of unidentified minerals. At least the first six minerals seem to have been brought in after the sedimentation along with ningyoite, which is apparently the last phase except for gypsum. A photomicrograph of a thin section of the ore is shown in Fig. 1.

PHYSICAL AND OPTICAL PROPERTIES OF NINGYOITE

The ore containing ningyoite is black or gray, and is very friable. Cavities are abundant. Because of its extreme fineness and contamination with other minerals the specific gravity and hardness of the mineral cannot be measured. It sinks in methylene iodide.

Ningyoite is acicular or elongated lozenge-shaped. The color is brownish green to brown, and slight pleochroism was observed, the color being paler in the X direction. Extinction is parallel, elongation positive. The crystals are so small (about 5μ) that the index of refraction cannot be measured exactly, but it is estimated to be about 1.64, and seems to vary a little from crystal to crystal. The double refraction seems to be low.

SEPARATION

Ningyoite is very difficult to separate because of its extremely small crystal size and intimate association with pyrite, clay minerals, and other contaminants. Radioactivity is higher in the finer-grained part than in the coarser-grained part of the ore. The ore was crushed in a ball mill for about one minute, and then passed through a 40-mesh sieve. The coarser part was discarded. The finer fraction was ground again in a ball mill for about 15 minutes, and the −100 mesh fraction was treated several times on a Wilfley table. The more radioactive black material was concentrated in the intermediate portion between pyrite and felsic minerals. The ultrasonic separator was used to remove clays from the black material. Flotation, centrifuging in methylene iodide, and magnetic separation were used repeatedly and alternately. Most of the pyrite was removed by flotation using the Mayeda cell. Quartz, calcite, and feldspar were removed by bromoform. Most of the apatite went to the nonmagnetic side of the Frantz isodynamic separator at the intensity 0.5 ampere. The final concentrate (sample no. C-1-M) seemed to be about 60 to 70 per cent ningyoite, and the remainder was found to be mostly hypersthene and organic material, but still contained very small amounts of pyrite, rutile, quartz, feldspar, and probably various phosphates of calcium, manganese, aluminum, and iron, including apatite.

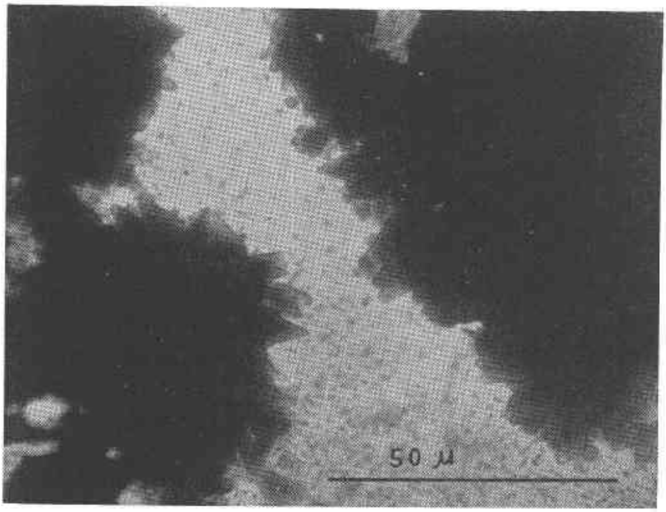

FIG. 1. Photomicrograph of a thin section of a ningyoite ore. Pyrite (black mass) is coated by ningyoite growing towards a cavity.

CHEMISTRY

As ningyoite could not be purified sufficiently, a preliminary leaching was made on a sample (sample no. N-2-W), a lower concentrate (about 30 per cent) of ore taken from another place in the mine. About 200 mg. of the sample, whose radioactivity was 1,574 counts per minute as measured by a Geiger-Müller counter, was treated with cold (1+1) HCl. After 10 minutes the green solution was filtered. The radioactivity of the residue was 96 counts per minute. By measuring the intensities of the characteristic *x*-ray diffraction lines of the contaminating minerals using an *x*-ray diffractometer, before and after the leaching, it was shown that most of these minerals were not dissolved although the ningyoite went into solution. The semiquantitative spectrographic analysis of the residue, after evaporation, of the (1+1) HCl soluble portion is shown in Table 1. It shows that the rare earths such as Y and Ce are present together with the major constituents Ca, U, and P of the dissolved fraction.

TABLE 1. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF A RESIDUE, AFTER EVAPORATION, OF THE (1+1) HCl SOLUBLE PORTION OF A CONCENTRATE OF NINGYOITE (SAMPLE NO. N-2-W)

Analyst: J. C. Hamilton, U. S. Geological Survey

Per cent[1]	Elements
>10	Ca U
7	P
3	Fe
1.5	Ce Y
0.7	La Nd
0.3	Ba Dy Er Gd Mo Pr Sr
0.15	Al Mn Pb Sc Si Sm Yb
0.07	Mg Zr
0.03	Cu
0.015	Be
0.003	Cr

[1] Figures are reported to the nearest number in the series 7, 3, 1.5, 0.7, 0.3, 0.15, etc., in per cent. These numbers represent midpoints of group data on a geometric scale.

Comparisons of this type of semiquantitative results with data obtained by quantitative method, either chemical or spectrographic, show that the assigned group includes the quantitative value about 60 per cent of the time.

The purest concentrate, C-1-M, was dried at 110° C. for about a week, in order to remove adsorbed water, before the infrared analysis The dried sample was inserted between two sodium chloride plates with a mineral oil. The curve is shown in Fig. 2. Peaks appearing at 3.4, 6.8, 7.2, and 13.8 μ are caused by the oil. Peaks at 3.0 and 6.1 μ represent water

(Hunt and others, 1950). A broad depression from 8 to 12 μ having a peak at 9.5 μ seems to indicate the presence of phosphate. There is no indication of the presence of the uranyl radical which should appear sharply at 10.6 μ (R. G. Milkey, U. S. Geological Survey, oral communication, 1958). This strongly suggests that ningyoite is a quadrivalent hydrous uranium mineral because all known sexivalent uranium minerals contain the uranyl radical.

Synthesis of Ningyoite

Various procedures for the synthesis were tried. The method by which a comparatively pure sample was obtained will be described in detail.

Fifty milliliters of a 0.5 M solution of UO_2Cl_2 was reduced in a Jones reductor to UCl_4 in the presence of excess HCl. Phosphoric acid (0.05 M) was added and the gelatinous precipitate was washed with water several times, $Ca(H_2PO_4)_2 \cdot H_2O$ (6.3 g) and water were added and mixed well. The resulting slurry was divided into three equal parts. To each of two parts were added 2.1 g. and 6.3 g. of $Ca(H_2PO_4)_2 \cdot H_2O$, none was added to the third. The resulting mixtures have U:Ca atomic ratios of 1:2, 1:4, and 1:1, respectively. Glucose (0.015 g.) was added to each part as an antioxidant. Approximately 10-ml. portions of slurry were sealed in 20-ml. glass tubes under nitrogen. Portions have the same U:Ca ratio were run in quadruplicate, two being heated at 150° C. and two at 185° C. After 18 days at 150° C. and 7 or 15 days for 185° C., the tubes were opened and the precipitates were filtered on a glass filter and washed with (1+5) HCl and then with water to remove excess calcium phosphate and uranium salts. This acid concentration was selected to minimize the solution of the synthetic compound and to remove the contaminants as completely as possible.

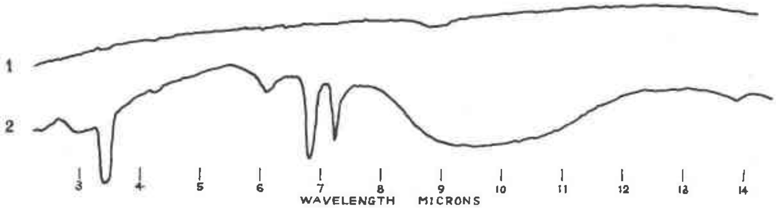

FIG. 2. Infrared analysis curve of ningyoite. 1. Blank. 2. Ningyoite with oil.

The pH of each solution before and after heating is shown in Table 2. The grayish-green precipitates were checked with an x-ray diffractometer for the major lines of ningyoite. These lines were almost identical with those for the natural ningyoite except for slight shifts of 2θ. Differences in temperature and pressure during synthesis did not seem to affect the *x*-ray patterns, but differences in composition of the original slurries did affect the positions and the intensity ratios of the peaks. The sample with U:Ca ratio of 1:2, formed at 150° C. (sample no. Cup-E2-150), appeared to be most similar to the natural material.

A similar procedure, in which a 1:1 U:Ca ratio was used with an initial pH of 4.8 and maintained at 100° or 130° C., failed to produce ningyoite. Under the same experimental conditions, the synthesis, however, was successful at 150° C. The precipitate formed at 100° C. was almost amorphous; that at 130° C. gave an *x*-ray diffraction pattern but not that of ningyoite. Ningyoite could not be synthesized using solutions containing 1:1 HCl. Under the same experimental conditions, uranyl phosphate with glucose at pH 1.4 resulted in the formation of ningyoite, but did not if the original slurry was dissolved in 1:10 HCl. In both runs, uraninite was also detected.

TABLE 2. EFFECT OF HEATING ON PH OF SLURRIES USED IN SYNTHESIS

Temperature (° C.)	Heating time (days)	pH[1]		
		U:Ca=1:1 (Cup-E1)	U:Ca=1:2 (Cup-E2)	U:Ca=1:4 (Cup-E3)
Unheated	0	1.6	1.8	2.1
185	7	1.5	1.5	1.7
185	15	1.3	1.3	1.4
150	18	1.2	1.2	1.3

[1] Measured at room temperature.

The synthesized compound is grayish green and extremely fine grained. Its specific gravity was not determined because of the extreme fineness of the material. Under the microscope, it is acicular crystalline, and green in color. Extinction is parallel, elongation positive. Pleochroism is recognized with Z=green, and X=pale green. The indices of refraction vary, but α seems to be between 1.69 and 1.70 and γ between 1.70 and 1.71. The *x*-ray pattern of the compound did not change after heating in air to 160° C., but the average index of refraction dropped to 1.66. This effect can be explained by the existence of zeolitic water as in rhabdophane (Mooney, 1950). The difference in the indices of refraction between natural and synthesized ningyoite seems to be caused by the presence of rare earths in the natural mineral, and probably also by the variation in the amount of zeolitic water.

ANALYTICAL PROCEDURES

The selection of the methods used for the chemical analysis of the natural material and the synthetic compound was guided by the qualitative spectrographic analyses of the samples by K. V. Hazel and H. W. Worthing, U. S. Geological Survey. Micro- and semimicro chemical procedures were used for the various determinations. Approximately 50 mg. of the final concentrate of the natural material and 125 mg. of the synthetic compound was available for chemical analysis. Both samples were analyzed by essentially similar methods.

One portion of each sample was used for the total water and carbon determinations, another for the $H_2O(-)$, (1+1) HNO_3 insoluble, total uranium, P_2O_5, CaO, and FeO determinations, and a third portion for the UO_2 determination.

The first portion, approximately 25 mg. for each sample, was dried to constant weight at 110° C. and then boiled with acid to determine the insoluble residue. An Emich microbeaker and sintered glass filter stick was used for the separation of the insoluble residue which was dried to constant weight at 110° C. The synthetic compound was boiled with (1+1) HNO_3 and the residue was washed with dilute nitric acid and water before drying to constant weight. The insoluble residue in the synthetic material was found to be silica, which seems to come from glass filters used in the synthesis.

To minimize the solution of pyrite during the decomposition of the natural material for the subsequent determination of the major constituents of the mineral, the natural material was boiled with (1+3) HCl instead of (1+1) HCl as was done in the preliminary leaching experiment described above. The appearance of the insoluble material remaining after boiling with (1+1) HCl did not seem to differ greatly from the appearance of the natural material before boiling. The solution was light yellow. To insure the solution of most of the ningyoite present, concentrated HNO_3 was added and the mixture boiled again. The boiling was continued until most of the black material was decomposed. The solution was now dark yellow and the residue contained some black dense material but the major part of the residue appeared to be fluffy and brown. The residue was mostly noncrystalline silica; hypersthene, quartz, and pyrite were present. The residue was washed with dilute nitric acid and water before drying to constant weight.

Aliquots of the filtrate from the acid insoluble determination were used for the total uranium, P_2O_5, FeO (total iron), and CaO determinations.

Total uranium was determined spectrophotometrically by the ammonium thiocyanate procedure in acetone-water medium. P_2O_5 was determined spectrophotometrically as molybdovanadophosphoric acid. A standard curve was made using known P_2O_5 solutions containing approximately the same concentration of uranium present in the aliquot of sample solution taken for the determination of P_2O_5. Total iron was determined spectrophotometrically by the o-phenanthroline procedure. CaO was determined by flame photometry (wavelength = 554 mμ). The solution was compared to standard calcium solutions containing approximately the same concentrations of uranium and phosphorus as present in the solution analyzed.

The UO_2 was determined volumetrically after solution of an 18-mg. portion of the synthetic compound in boiling (1+3) H_2SO_4. The dissolved sample was titrated with approximately 0.03 N. standard $KMnO_4$; UO_3 was calculated by difference. Carbon and total water were determined by use of a modified microcombustion train of the type used for the determination of carbon and hydrogen in organic compounds; 30 mg. synthetic compound and 20 mg. of natural material were decomposed by ignition at 900° C. in a stream of oxygen.

ANALYTICAL RESULTS

Table 3 shows the results of spectrographic analysis of the purest concentrate of natural material, the acid soluble portion (approximately 70 per cent of original), and the acid insoluble portion. One-milligram samples were used. Table 4 shows the results of the microchemical analysis of the natural material and the synthetic compound. These results indicate that the chemical formula of the synthetic compound is $CaU(PO_4)_2 \cdot 1.5H_2O$.

From Table 3 it appears that all the phosphorus, yttrium, barium, boron, and ytterbium, and most of the calcium go into solution along with the uranium. As most of the rare earths shown in Table 1 were not detected in sample C-1-M by qualitative spectrographic analysis (Table 3) owing to the smallness of the sample and the limitations of the method (Stich, 1953), an *x*-ray fluorescence analysis was made by J. M. Axelrod, U. S. Geological Survey, on the acid soluble part of a specimen less concentrated than C-1-M. Minor amounts of Y, La, Ce, Nd, Er, Sr, Pb, Mn, and Cr, and possible minor amounts of Zn, Cu, and Gd were detected together with major amounts of U, Ca, and Fe. The total amount of rare earths seemed to be a few per cent.

It is impossible to get the exact chemical formula of ningyoite from the analysis shown in Table 4 because of the impurities. However, as discussed below, the *x*-ray data indicate a similarity of structure of ningyoite, the synthetic compound, and rhabdophane which has the ideal formula $R.E.(PO_4) \cdot H_2O$ (Palache and others, 1951). This suggests that

TABLE 3. QUALITATIVE SPECTROGRAPHIC ANALYSES (IN PER CENT) OF CONCENTRATE OF NINGYOITE
(SAMPLE NO. C-1-M)

Analyst: K. V. Hazel, U. S. Geological Survey

Substance	Elements														
	Si	P	U	Ca	Fe	Mg	Mn	Ti	Al	Na	Pb	Y	Ba	B	Yb
Original	>10	5–10	5–10	1–5	1–5	1–5	0.5–1.0	0.5–1.0	0.5–1.0	0.1–0.5	0.1–0.5	—	—	—	—
Acid soluble	0.1–0.5	>10	5–10	5–10	1–5	0.1–0.5	0.1–0.5	—	1–5	—	—	0.5–1.0	0.1–0.5	0.05–0.1	0.05–0.1
Acid insoluble	>10	—	—	0.1–0.5	1–5	0.5–1.0	0.1–0.5	0.5–1.0	0.1–0.5	—	0.05–0.1	—	—	—	—

— indicates that the element was either absent or its concentration was below the limits of detection of the procedure (Stich, 1953, p. 7). Other elements were looked for but not found. Because purified material was scarce, these qualitative analyses were performed on 1-mg. samples mostly for detection of major constituents. The per cent values shown are rough estimates and cannot be compared with those in Table 1 which were derived from an extract of a 200-mg. sample.

TABLE 4. MICROCHEMICAL ANALYSES OF CONCENTRATE OF NINGYOITE (C-1-M) AND SYNTHESIZED COMPOUND (Cup-E2-150)

Analyst: Robert Meyrowitz, U. S. Geological Survey

Constituent	C-1-M	Molecular ratio	Cup-E2-150	Molecular ratio
CaO	6.1[1]	0.92	11.5	0.99
UO_2	23.3[1,2]	0.73	50.8	0.92
UO_3	N.D.[3]		0.7	
P_2O_5	16.8[1]	1.00	29.4	1.00
FeO	4.8[1,4]	0.56	N.D.[3]	
Rare earths	N.D.[3]		N.D.[3]	
Acid insoluble	30.9		1.0	
H_2O (total)	9.3	4.37	5.4	1.45
Total	91.2		98.8	
$H_2O(-)$	1.9		1.2	
C	2.3		0.1	

[1] Acid soluble.
[2] Total uranium as UO_2.
[3] Not determined.
[4] Total iron as FeO.

ningyoite has a formula close to $CaU(PO_4)_2 \cdot 2H_2O$, in which the rare earths of rhabdophane are substituted for by equivalent amounts of calcium and quadrivalent uranium.

In interpreting the results in Table 4, excess calcium may come from the contaminating apatite and calcite. Iron seems to come mostly from pyrite and hypersthene and partly from the soluble phosphate minerals.

Although one cannot calculate the molecular ratio of the rare earths from the available spectrographic data, it may be estimated that the mineral contained a few per cent rare earths. This would be equivalent to a molecular ratio of a few tenths or less. Hence, excess phosphorus can be accounted for by rare earths, apatite, and possibly other soluble phosphate minerals. The high content of water seems to be derived from the organic material in which hydrogen has been oxidized to water.

There is no direct proof showing that uranium and calcium coexist with rare earths in the same mineral, but this seems reasonable, when we consider the deviations of the unit cell of the natural ningyoite and the synthetic compound from the hexagonal unit cell of rhabdophane. The comparison will be described later.

The chemical formula of ningyoite can be presented as

$$Ca_{1-x}U_{1-x}R.E._{2x}(PO_4)_2 \cdot 1\text{–}2H_2O,$$

where x is about 0.1–0.2.

X-Ray Powder Diffraction Patterns

X-ray powder diffraction films were made on the final concentrate of ningyoite (C-1-M) and on the synthetic compound (Cup-E2-150). They resemble that of rhabdophane, a hexagonal hydrous rare earth phosphate (Hildebrand and others, 1957). Figure 3 shows films of rhabdophane (from Salisbury, Conn.), ningyoite, and the synthetic compound. The diffraction lines of the ningyoite and the synthetic compound are so broad that their crystallinity seems to be poor.

It was necessary to assume orthorhombic symmetry to index the patterns of ningyoite and the synthetic compound, though they are pseudohexagonal. The indices by the orthorhombic system for major lines were transformed from those by the hexagonal system to which rhabdophane belongs, and fairly good coincidence between the observed and the calculated *d* values were obtained as shown in Table 5. It is shown in the table that ningyoite and the synthetic mineral belong to a simple lattice as indicated by the existence of the lines such as 120, 011, etc., instead of a *C*-face centered lattice which would be that of rhabdophane, if it were regarded as of an orthorhombic system. The space group of ningyoite is presumed to be *P*222 ($D_2{}^1$), because this is the only orthorhombic space group consistent with that of rhabdophane, $P6_222$ ($D_6{}^4$). It is known that ningyoite has 3 molecules in the unit cell from the analogy with rhabdophane which has 3[R.E.$PO_4 \cdot H_2O$] in the unit cell of the hexagonal system (Mooney, 1950). The deviation from the hexagonal symmetry appears also in the ratio *a*:*b* which is 0.577 in the

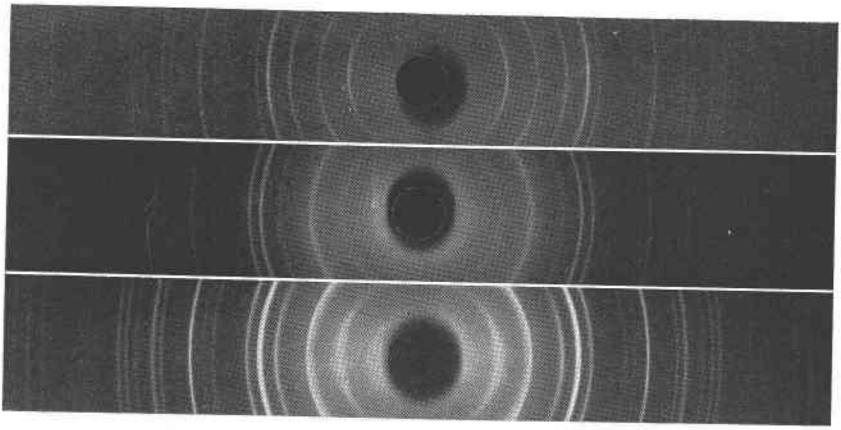

Fig. 3. *X*-ray powder diffraction patterns of rhabdophane, ningyoite, and synthetic compound. Camera diameter 114.6 mm., CuKα radiation. *Top:* Rhabdophane, Salisbury, Conn. *Middle:* Ningyoite (C-1-M). *Bottom:* Synthetic compound (Cup-E2-150).

TABLE 5. *X*-RAY POWDER DIFFRACTION DATA, IN Å, FOR RHABDOPHANE, NINGYOITE, AND THE SYNTHETIC COMPOUND

Rhabdophane (Salisbury, Conn.)				Ningyoite (C-1-M)				Synthetic compound (Cup-E2-150)		
d(obs.)[1]	I	*d*(calc.)	*hk.l*[2]	*hkl*[3]	*d*(obs.)[4]	I	*d*(calc.)	*d*(obs.)[4]	I	*d*(calc.)
				010	12	f	12.10	12	f	12.13
				100	6.8	f	6.78	6.8	f	6.73
				001	6.35	vw	6.38	6.33	f	6.36
6.07	m	6.05	10.0	020	5.99	wb	6.05	6.03	wb	6.07
				110			5.92			5.89
				011	5.65	vw	5.64	5.68	vw	5.64
				120	4.49	vw	4.51	4.48	vw	4.50
4.40	s	4.39	10.1	021			4.39			4.39
				111	4.33	m	4.34	4.30	s	4.32
				030	4.02	f	4.03	4.04	f	4.03
3.49	m	3.49	11.0	130	3.45	w	3.47	3.46	vw	3.47
				200	3.38	mb	3.39	3.36	mb	3.36
				002	3.19	f	3.19	3.18	f	3.18
		3.06	11.1	131			3.05			3.03
				201	3.02	vsb	3.00	3.02	vsb	2.97
3.02	vsb	3.02	20.0	040			3.02			3.03
				220			2.96			2.92
2.83	s	2.82	10.2	022			2.82			2.82
				112	2.81	s	2.81	2.80	s	2.80
		2.73	20.1	041	2.73	vw	2.73			2.74
				221	2.69	vw	2.69			2.63
2.36	w	2.36	11.2	132	2.35	w	2.35	2.35	vw	2.34
				202	2.33	f	2.32	2.30	f	2.31

Order of decreasing intensities: vs, s, m, w, vw, f; b = broad.

[1] Measured on *x*-ray powder diffraction film, camera diameter 114.6 mm. CuKα radiation, $\lambda = 1.5418$ Å; d(obs.) cut-off at 12 Å.

[2] Indices of the hexagonal system.

[3] Indices of the orthorhombic system.

[4] Measured with *x*-ray diffractometer, using CuKα radiation, $\lambda = 1.5418$ Å, 1°/min., time constant 4 sec., scale factor 2.

(Continued on next page)

TABLE 5 (*continued*)

Rhabdophane (Salisbury, Conn.)				Ningyoite (C-1-M)				Synthetic compound (Cup-E2-150)		
d(obs.)[1]	I	*d*(calc.)	*hk.l*[2]	*hkl*[3]	*d*(obs.)[4]	I	*d*(calc.)	*d*(obs.)[4]	I	*d*(calc.)
				150			2.28			2.28
2.28	vw	2.29	21.0	240	2.26	f	2.26	2.25	f	2.25
				310	2.22	f	2.22			2.20
				151			2.15			2.15
2.15	s	2.15	21.1	241	2.13	s	2.13	2.12	s	2.12
				311			2.10	2.08	f	2.08
		2.13	00.3	003			2.13			2.12
2.02	f	2.02	30.0	060	2.01	f	2.02	2.01	f	2.02
				330			1.973			1.961
1.920	w	1.923	30.1	061	1.926	f	1.923	1.926	f	1.926
				331	1.903	vw	1.885	1.899	vw	1.875
				152			1.853			1.844
1.859	m	1.859	21.2	242	1.845	wb	1.842	1.842	wb	1.838
				312			1.824			1.814
1.743	vwb	1.741	20.3	043	1.740	w	1.739	1.740	vw	1.737
				223	1.728	f	1.727	1.722	f	1.720
		1.746	22.0	260			1.733			1.733
				400	1.692	w	1.696	1.688	w	1.682
1.704	vw	1.705	30.2	062			1.704			1.706
				332	1.681	vw	1.678	1.669	f	1.669
				170			1.675			1.678
1.675	vw	1.678	31.0	350	1.653	vw	1.652	1.647	vw	1.646
				420	1.634	f	1.633			1.621
					1.547	vw		1.542	f	
					1.505	f		1.506	f	
					1.451	f		1.449	f	
					1.343	vw		1.346	vw	
					1.307	vw		1.304	vw	
					1.262	f		1.262	f	
					1.247	f		1.246	f	

ideal hexagonal system. Table 6 shows that the deviation of the ratio is greater in the synthetic mineral than in ningyoite.

PHASE CHANGES ON HEATING

Both ningyoite and the synthetic compound were heated at various temperatures. Ningyoite ignited at 800° C. for 15 minutes and the synthetic compound ignited at 900° C. for 10 minutes (both in argon) changed to a monazite-type structure as indicated by their *x*-ray powder patterns. Table 7 shows their *x*-ray diffraction patterns together with those of natural monazite and the synthetic cheralite, $CaTh(PO_4)_2$, one of the monazite-type minerals (Bowie and Horne, 1953). Very weak lines of uraninite in the film of the ignited ningyoite and a few additional lines presumably of an unknown phase, are omitted in Table 7.

TABLE 6. CELL DIMENSIONS OF RHABDOPHANE, NINGYOITE, AND THE SYNTHETIC COMPOUND

CuKα radiation, $\lambda = 1.5418$ Å

Rhabdophane (Salisbury, Conn.) $R.E.PO_4 \cdot H_2O$ (generalized formula) Hexagonal unit cell	Ningyoite (C-1-M) $Ca_{1-x}U_{1-x}R.E._{2x}(PO_4)_2 \cdot 1\text{–}2H_2O$ Orthorhombic unit cell	Synthetic compound (Cup-E2-150) $CaU(PO_4)_2 \cdot 1.5H_2O$ Orthorhombic unit cell
$a = 6.98 \pm 0.03$ Å $(b = 12.10 \pm 0.05$ Å$)$* $c = 6.39 \pm 0.03$ Å $(a:b:c = 0.577:1:0.528)$* $V = 269.4$ Å^3, $(539.7$ Å$^3)$*	$a = 6.78 \pm 0.03$ Å $b = 12.10 \pm 0.05$ Å $c = 6.38 \pm 0.03$ Å $a:b:c = 0.560:1:0.527$ $V = 523.4$ Å^3	$a = 6.73 \pm 0.03$ Å $b = 12.13 \pm 0.05$ Å $c = 6.36 \pm 0.03$ Å $a:b:c = 0.555:1:0.524$ $V = 519.2$ Å^3 Sp. gr. (calc.) $= 4.75$

* The figures in parentheses show those of the orthorhombic lattice which were transformed from the hexagonal lattice.

The cell size of synthetic cheralite is most similar to that of the ignited ningyoite among the minerals having a monazite-type structure. The cheralite cell is slightly larger than the cell of the ignited ningyoite. This seems to be a result of the ionic radii of the elements involved, given in Table 8. The ionic radii of U^{+4}, Th^{+4}, Ca^{+2}, and rare earths are given in Table 8. The fairly good similarity of the *x*-ray patterns of the ignited ningyoite and synthetic compound may indicate that the average ionic radius of the rare earths contained in natural ningyoite approaches the average ionic radius of quadrivalent uranium and calcium, where as natural cheralite from Travancore, South India, has a larger cell size than that of the synthetic cheralite because natural cheralite has large

TABLE 7. *X*-RAY POWDER DIFFRACTION DATA, IN Å, OF MONAZITE, A SYNTHETIC CHERALITE, IGNITED NINGYOITE, AND IGNITED SYNTHETIC COMPOUND

CuKα radiation, $\lambda = 1.5418$ Å, camera diameter = 114.6 mm; *d*(obs.) cut-off at 12 Å

	Monazite[1] (from Magnet Cove, Ark.)		Synthetic cheralite[2] ($CaTh(PO_4)_2$)		Ignited ningyoite (C-1-M)		Ignited synthetic compound (Cup-E2-150)	
hkl	*d*(obs.)	I	*d*(obs.)	I[3]	*d*(obs.)	I[4]	*d*(obs.)	I[4]
$\bar{1}01$	5.20	13	5.18	vvw	5.18	f	5.16	vw
110	4.82	6	4.67	vw	4.75	f	4.75	vw
011	4.66	18			4.62	vwb	4.62	w
111	4.17	25	4.12	mw	4.15	m	4.13	m
101	4.08	9			4.02	f	4.04	w
$\bar{1}11$	3.51	25	3.47	w	3.45	vwb	3.47	wb
200	3.30	50	3.24	s	3.25	s	3.25	s
120	3.09	100	3.05	vs	3.04	vs	3.04	vs
210	2.99	18	2.94	vvw	2.93	fb	2.94	vw
$\bar{1}12$, 012	2.87	71	2.83	vs	2.82	vs	2.83	s
$\bar{2}02$	2.61	18	2.58	w	2.59	vw	2.58	w
211	2.44	18	2.41	w	2.41	w	2.42	m
$\bar{2}12$, 112	2.40	4			2.36	f	2.36	vw
	2.34	4			2.31	f	2.32	f
	2.25	2					2.22	f
	2.19	18	2.16	v	2.15	w	2.16	m
	2.15	25	2.11	mb	2.11	w	2.12	m
	2.13	25			2.08	w	2.08	m
	2.02	2					1.989	fb
	1.961	25	1.941	ms	1.933	s	1.929	s
	1.933	6					1.907	f
	1.895	13	1.872	vvw	1.870	f	1.870	w
	1.870	18	1.846	msb	1.841	wb	1.845	m
	1.859	18					1.834	m
	1.797	9	1.778	vw	1.774	f	1.774	vw
	1.762	18	1.740	vw	1.740	vw	1.743	w
	1.737	25	1.718	ms	1.710	w	1.713	m
	1.689	13	1.667	mw	1.658	vw	1.664	w
	1.645	6	1.629	vvw	1.603	f	1.608	vw
	1.600	6	1.583	vvw	1.578	f	1.580	vw
			1.556	vvw				
	1.535	13	1.517	mw	1.517	vw	1.519	w
	1.463	4					1.444	f
	1.386	3						
	1.368	4			1.347	f	1.347	fb
	1.339	9			1.323	f	1.323	vw
	1.329	9			1.313	vw	1.313	w
	1.307	2						
	1.280	6					1.268	f
	1.261	2			1.254	f	1.259	vw
	1.245	3					1.232	f
	1.233	9			1.217	f	1.216	vwb
	1.189	3					1.172	fb
	1.168	6					1.151	f
	1.153	3					1.133	f

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[1] From Carron and others, 1958, p. 264–265.
[2] From Bowie and Horne, 1953, p. 97.
[3] Order of decreasing intensities: vs, s, ms, m, mw, w, vw, vvw; b = broad.
[4] Order of decreasing intensities: vs, s, m, w, vw, f; b = broad.

TABLE 8. IONIC RADII, IN Å, OF U^{+4}, Th^{+4}, Ca^{+2}, AND RARE EARTHS, INCLUDING AVERAGE IONIC RADII IN NINGYOITE AND CHERALITE

	Ahrens (1952, p. 168–169)	Goldschmidt (1954, p. 89)		Ahrens (1952, p. 168–169)	Gold schmidt (1954, p. 89)
Elements			Er[2]	0.89	1.03
U	0.97	1.05	Tm[2]	0.87	1.01
Th	1.02	1.10	Yb[2]	0.86	1.00
Ca	0.99	1.06	Lu[2]	0.85	0.99
La[1]	1.14	1.22			
Ce[1]	1.07	1.18	Minerals		
Pr[1]	1.06	1.16	Ningyoite		
Nd[1]	1.04	1.15	$\left(\frac{U+Ca}{2}\right)$[1]	0.98[3]	1.06[4]
Sm[1]	1.00	1.13			
Eu[1]	0.98	1.12			
Gd[1]	0.97	1.11	Cheralite		
Tb	0.93	1.09	$\left(\frac{Th+Ca}{2}\right)$[1]	1.01[3]	1.08[4]
Dy[2]	0.92	1.07			
Ho[2]	0.91	1.05			

[1] Forms the monazite structure on heating (Carron and others, 1958).

[2] Forms the xenotime structure on heating (Carron and others, 1958).

[3] $>$Tb$=0.93$ (Ahrens, 1952). Should form monazite structure. Agrees with experiment.

[4] $<$Tb$=1.09$ (Goldschmidt, 1954). Should form xenotime structure. Does not agree with experiment.

amounts of rare earths such as lanthanum and cerium, which have comparatively larger ionic radii.

The similarity between rhabdophane and ningyoite is demonstrated in the fact that rhabdophane (from Salisbury, Conn.) was converted to monazite by sealing the mineral in a silver crucible containing water and heating at 300° C. for 5 days (Carron and others, 1958, p. 273). Carron and others (1958, pp. 263–269) have also shown that the rare earths having ionic radii larger than that of terbium form the monazite structure when they react with phosphate in a sealed glass ampoule or silver crucible, and those having ionic radii smaller than that of terbium form the xenotime structure. This principle is applicable for cheralite and the ignited ningyoite when Ahrens' data (1952) are taken, but is not if Goldschmidt's data (1954) are taken, as shown in Table 8.

Ningyoite ignited at 950° C. for 15 minutes in argon gave the *x*-ray patterns of uraninite and a small amount of monazite. The uraninite pattern of the ignited ningyoite seems to indicate the decomposition of the phosphate. There is no line of uraninite in the ignited synthetic ningyoite at 900° C., indicating that the rare earths in natural ningyoite possibly lowered the temperature of the decomposition of the monazite-type structure.

The synthetic ningyoite ignited at 600° C. in air for 5–10 minutes still retained the original orthorhombic structure without measurable change of the cell size. Both the ningyoite and the synthetic compound when ignited at 900° C. in oxygen changed in color and gave unidentified *x*-ray patterns which are different from each other. They seem to have been oxidized.

COMPARISON WITH LERMONTOVITE

Ningyoite resembles lermontovite, $(U,Ca,R.E.)_3(PO_4)_4 \cdot 6H_2O$, (Soboleva and Pudovkina, 1956, pp. 181–182) in color, chemical components, and some optical properties, but differs in the ratio of the elements and birefringence. Lermontovite has a U:Ca ratio of 10:1, whereas ningyoite has 1:1. The ratio of cations to phosphorus is 3:4 in the former and 1:1 in the latter. The birefringence of lermontovite is described as 0.14–0.15 and is much greater than that of natural ningyoite. No *x*-ray data are available for lermontovite.

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REFERENCES

AHRENS, L. H. (1952), The use of ionization potentials. Part 1, Ionic radii of the elements: *Geochim. et Cosmochim. Acta*, 2, 168–169.

BOWIE, S. H. U. AND HORNE, J. E. T. (1953), Cheralite, a new mineral of monazite group: *Mineralog. Mag.*, **30,** 97.

CARRON, M. K., NAESER, C. R., ROSE, H. J., JR., AND HILDEBRAND, F. A. (1958), Fractional precipitation of rare earths with phosphoric acid: *U. S. Geol. Survey Bull.* **1036-N,** 253–275.

GOLDSCHMIDT, V. M. (1954), Geochemistry: London, Oxford Univ. Press.

HILDEBRAND, F. A., CARRON, M. K., AND ROSE, H. J. (1957), Re-examination of rhabdophane (scovillite) from Salisbury, Connecticut (abs.): *Geol. Soc. America Bull.*, **68,** 1744.

HUNT, J. M., WISHERD, M. P., AND BONHAM, L. C. (1950), Infrared absorption spectra of minerals and other inorganic compounds: *Anal. Chem.*, **22,** 1487.

KATAYAMA, N., AND SATO, Y. (1957), Sedimentary environment of the uraniferous bed of the Ningyo Pass: *Sci. Papers College of General Education, Univ. Tokyo,* **7,** 131–144.

MOONEY, R. C. L. (1950), *X*-ray diffraction study of cerous phosphate and related crystals. I. Hexagonal modification: *Acta Cryst.*, **3,** 337–340.

PALACHE, C., BERMAN, H., AND FRONDEL, C. (1951), Dana's system of mineralogy, 7th ed., v. 2: New York, John Wiley and Sons, Inc., 774.

SATO, MOTOO (1958), On the results of prospecting for the promising uranium deposits of Japan: Presented at the Second International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, September 1–13, 1958.

SOBOLEVA, M. V., AND PUDOVKINA, I. A. (1956), Mineraly Urana, Spravochnik (Uranium Minerals Handbook), Moscow, from *Am. Mineral.*, **43,** 379 (1958).

STICH, J. N. (1953), Spectrographic identification of mineral grains: *U. S. Geol. Survey Circ.* **234.**

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