Uranocircite from Ogitsubo, Iida City, Nagano Prefecture

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Abstract

Uranocircite, a hydrated phase of barium and hexavalent uranium, $Ba(UO_2)_2 \cdot (PO_4)_2 \cdot 8H_2O$, was identified in the oxidation zone of Ogitsubo in the "Iida radio-activeanomlous area" in 1968. This yellow green mineral occurred in fine arkosic silt and white fissure clay (montmorillonite) which were deposited in the basal part of Miocene sediments just above the unconformity.

Uranocircite, a sort of uranium mica minerals, is rarely found in ordinary uranium deposits, because barium in the mineral is easily replaced by such an element as calcium. Basement granite of this area contains abnormally rich thorium, while a relatively large amount of monazite, $(La, Ce, Th, Y) \cdot PO_4$, is found in several localities of this district.

Around the crystals of monazite included in biotite intense pleochroic haloes are observed under the microscope. Perhaps these environmental conditions led the generation of the barium-bearing uranophosphate mineral as secondary ore.

1 Introduction

The raidoactive anomaly in the Iida district, Nagano Prefecture, was found in January 1967 during the survey made by the Power Reaction and Nuclear Fuel Development Corporation. Since the discovery the radioactive areas, especially the areas of the Miocene sediments, have been widely explored over the southern part of Nagano Prefecture.

But uranocircite is the only mineral that has hitherto been identified as the ore mineral (Figure 1).

Uranocircite was first described as a secondary mineral in quartz veins by WEISBACH from Bergen near Falkenstein in Voigtland, Saxony, Germany in 1877 (WEISBACH, 1877). Later, however, it was proved to be isostructural with the meta I phase of the minerals of meta-torbernite group. As a result, the name uranocircite is given to the fully hydrated phase isostructural with the torbernite
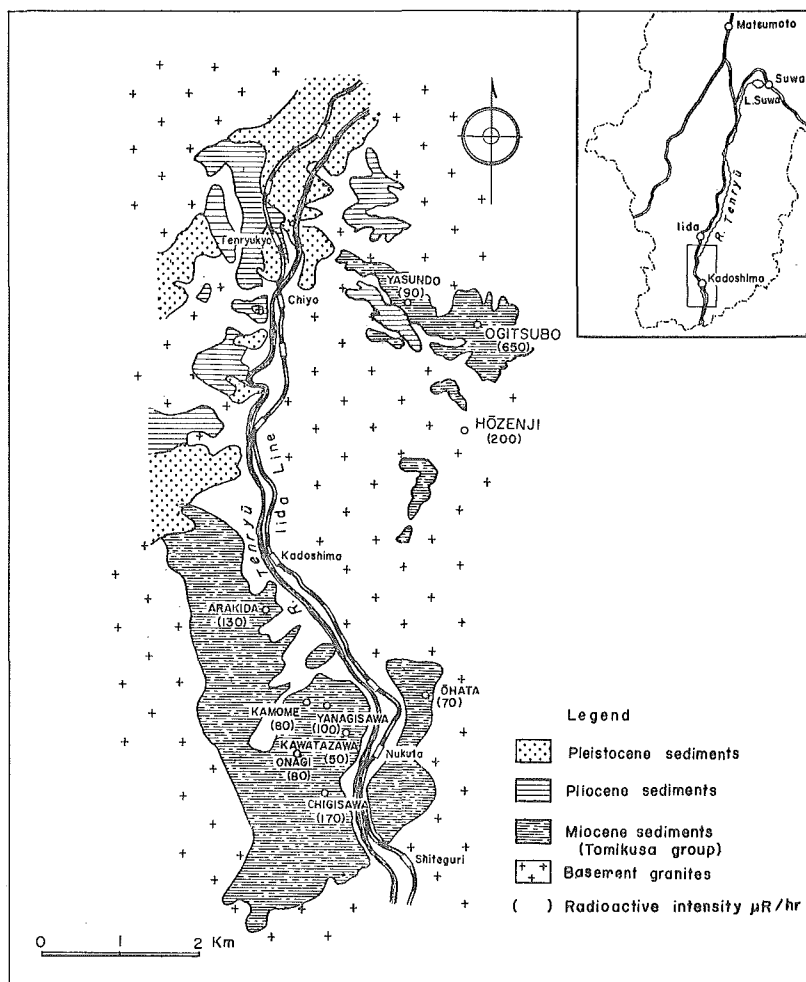
Fig. 1 Geological map and radioactive anomaly areas

group and occurring normally in nature (NUFFIELD and MILNE, 1953).   But the convention of using the term uranocircite without qualification is adopted throughout this paper to denote hydrous calcium uranyl phosphate in any state of hydration.   Wherever the precise hydration state is germane to the discussion, the terms, fully hydrated uranocircite, meta I phase uranocircite and meta II phase uranocircite will be used.

In Japan the first discovery of this mineral was made by HAYASHI from the Toki uranium deposits, Gifu Prefecture in 1965 (HAYASHI, 1965).   Uranocircite of Ogitsubo was first confirmed by HIRONO in 1968, which was the second discovery in Japan (HIRONO, 1968).

Members of the uran mica group have the layer structures of the general composition $A(UO_2)_2 \cdot (XO_4)_2 \cdot nH_2O$, where A=H, Ni, Mg, Ca, Cu, Na etc., and X=P, As. Many of these are synthetic products in which base replacement takes place rapidly. Thus a large number of uran mica mineral groups can be made. Synthetic uranocircite was made either by a cation exchange of autunite using barium chloride solutions or by a reaction of phosphoric acid with a mixed solution of barium chloride and uranyl nitrate (NUFFIELD and MILNE, 1953; HENMI, 1961). But the mineral uranocircite is rarely found in nature, especially in sedimentary uranium deposits. The rare occurrence is due probably to the minor abundance of barium and to the readiness of its cation exchange.

In uranocircite the value of n varies zeolitically with temperature and vapor pressure in the phase, roughly from 2 to 6 in the meta II phase, from 6 to 10 in the meta I phase, and from 10 to 12 in the fully hydrated phase (NUFFIELD and MILNE, 1953). Actually the X-ray powder spacing data of the uranocircite from Ogitsubo suggest several different phases that are obviously the reflections of the delicate changes of conditions in the laboratory.

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2 Occurrence

The Iida district is composed of various kinds of granitic rocks, as it is called the Ryôke granitic rocks. They are correlated to the Permian or Triassic by a group of geologists, but are regarded as of the late Mesozoic by another. In any case, they are divided into two groups, namely the Older Ryôke granites and the Younger Ryôke granites (YAMADA, 1967). Hornblende biotite granites belonging to the older group are widely distributed in this area (Tenryūkyô granite). But the granite constituting the basement of the Ogitsubo area in the southern part of Iida City and the neighbouring highly radioactive granite are classified into the younger intrusive type of the Ryôke granites (Ikuta granite). These younger granites are composed mainly of coarse- or medium-grained biotite granite remarkably rich in monazite especially at the highly radioactive localities.

Uranocircite was found from only one locality of Ogitsubo, where it occurs in siltstone and weathered white clay of lacustrine sediments. In this locality, the

basement granite is in contact with a mineralized zone. The mineralization was caused probably by a fault running from north to south and dipping steeply to the east.   The stratigraphical study of this district has been made by various authors, and the mother rock containing the mineral has been correlated to the upper Miocene formation of the Tomikusa group (SHIKAMA, 1954).
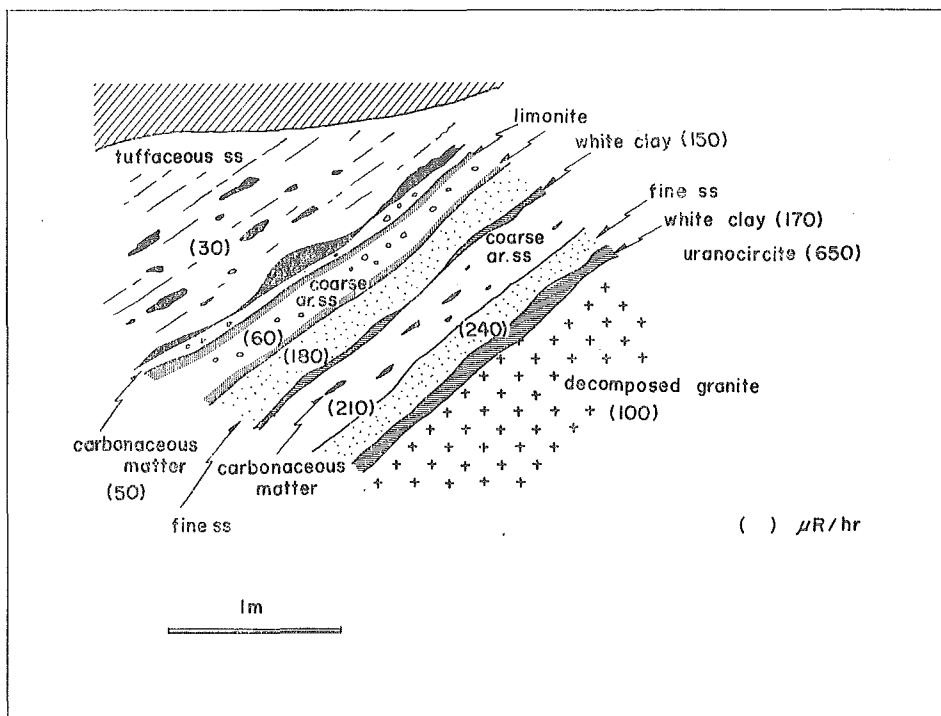

Fig. 2 Sketch of the outcrop where the specimens of uranocircite were collected

    The uranocircite is recognized within a bed of arkosic siltstone which overlies the eroded surface of Ikuta granite. A sketch of the outcrop where the specimens were collected is shown in Figure 2.   The uranocircite occurs as aggregates of minute flakes in the oxidation zone, filling fissures or thinly coating siltstones. In the latter case it is altered secondarily into montmorillonite.

    Tuffaceous sandstones in the higher horizon are separated by a bed of fine limonite from the lower coarse arkosic sandstone, and the former have been left in reduced condition especially around the carbonaceous matter. Radioactive anomaly is evident as shown in Figure 2, in which a tendency of increasing intensity from the upper to the lower beds is obvious. Also there are many other localities of radioactive anomaly, which are found both in the Ryôke granites and

the Miocene sediments of the Tomikusa group in the Iida district (Figure 1).

3 Mineralogical Data

a) Microscopic Observation and Examination

Uranocircite of Ogitsubo occurs as small transparent flakes of light greenish yellow which closely resemble the other uranium mica minerals, especially autunite. The larger flakes of the specimens are more than 5 mm in diameter and have distinct pinacoidal cleavage which is reasonably assumed to be (001). The massive grains can be scratched with a needle, but the mineral exists generally as very fine-grained aggregates. Its strong fluorescence is light green in ultraviolet light. The hardness, as far as it can be ascertained, is from 2 to 3 as expressed on the Mohs' scale. The specific gravity is nearly 3.6 by means of Clerici solution method.

Under the microscope, every specimen shows fibrous aggregates in which crystals are generally from 0.05 to 0.25 mm in length. Usually the crystals are positively elongated with straight extinction. The colour is pale grass-green yellow or colourless, and distinct cleavage is parallel with the fibrous form of the crystals (Plate 1).

Pleochroism is colourless or faintly pale yellow-green. Birefringence is high, n_0 being 1.622 and n_X 1.610.

b) X-ray Powder Spacing Data

The X-ray powder spacing data are given in Tables 1 and 2. The so-called meta I phase uranocircite containing $8H_2O$ at ordinary conditions is recognized in this locality. This specimen does not change into fully hydrated phase even under water-saturated condition at room temperature. It suggests that the fully hydrated phase is very unstable in nature. This fact coincides with the common knowledge about uranocircite mineral group and the nomenclature derived from these relations. But the X-ray spacing data for humid condition show slight expansion at large d spacing, for the values of 10.35 Å and 10.20 Å are obtained. So far as these two d spacing data are recognized, the values almost coincide with that of fully hydrated phase uranocircite. Perhaps, in uranocircite, the absorbed water behaves as interlayer water as it is in montmorillonite. According to these data, the mineral is tetragonal with the following cell dimensions, i.e. $a_0 = 6.93$ Å, $c_0 = 17.86$ Å, and $a_0 : c_0 = 1 : 2.577$. On heating treatment, d spacing varies slightly with water content in their respective ranges of stability. A particularly interesting fact concerning meta I phase is that the specimen heated at 30°C for 1 hour does not change into meta II phase. At 50°C a lower hydrated meta II phase with 2 to 6 H_2O is formed. At over 100°C meta II phase changes into an unstable phase. But this phase is reversible to meta II phase if it is kept

Table 1   X-ray data for meta I uranocircite

1		2		3		4	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
10.39	10	10.35	10 br			10.25	15
		10.20	8				
8.93	100	8.93	100	8.83	100	8.91	90
		8.50	8				
		6.50	6	6.50	5	6.49	10
5.47	2	5.47	14	5.47	20	5.47	40
5.21	7					5.12	15
4.90	2	4.92	8	4.92	10	4.93	30
		4.74	2	4.74	6	4.75	10
4.44	70	4.43	50	4.43	55	4.42	50
		4.30	8	4.30	10	4.31	45
						4.12	10
3.72	9	3.72	65	3.72	70	3.73	100
		3.60	3				
		3.48	13	3.48	15	3.48	35
3.41	1	3.41	5	3.41	8	3.41	20
						3.34	25
		3.23	10	3.23	15	3.24	40
3.15	1	3.15	5	3.15	10	3.15	15
						3.06	5
2.99	1	2.99	2	2.99	5	2.99	10
2.94	2	2.94	8	2.94	8	2.93	20
		2.74	4	2.74	3		
2.70	6	2.71	30	2.71	40	2.71	40
				2.54	3	2.54	10
						2.46	10
		2.43	2 br	2.43	2	2.44	10
				2.37	5	2.37	15
		2.34	4	2.34	2	2.33	10
2.20	25	2.20	24	2.20	30	2.20	35
						2.18	15
2.13	4	2.13	8	2.13	10	2.14	25
2.08	3	2.10	16	2.10	20	2.10	25
2.05	2	2.05	2	2.05	5	2.06	15
2.01	2	2.01	8	2.01	10	2.01	15

1 : Ogitsubo, Nagano Pref.

2 : Ogitsubo, Nagano Pref. (Water saturated condition)

3 : Ogitsubo, Nagano Pref. (Air drying condition)

4 : Toki, Gifu Pref., by HAYASHI (1965)

br : Broad line

Table 2   X-ray data for meta II uranocircite

5		6	
d ($\overset{\circ}{A}$)	I	d ($\overset{\circ}{A}$)	I
8.47	100	8.47	100
6.46	7 br		
5.37	40	5.36	40
4.92	12	4.92	20
4.23	60	4.23	30
3.62	80	3.61	70
3.48	20	3.48	35
3.22	30	3.21	30
2.93	8 br	2.92	15
2.69	4 br	2.68	5
2.61	50	2.61	20
2.51	5	2.51	10
2.44	10	2.46	8
		2.36	8
		2.24	5
2.19	5 br	2.21	8
		2.13	8
2.11	70	2.11	15
2.09	12	2.09	15
2.03	12	2.03	10
2.02	25	2.02	8

5 : Ogitsubo, Nagano Pref. (Treatment : heated for 1 hour at 50°C)
6 : Cameron, Arizona, U.S.A., by HAYASHI (1964)
br : Broad line

Table 3   Chemical composition of meta I uranocircite

	1		2
Ba	11.06 %	BaO	12.42 %
U	39.09 %	UO_3	46.97 %
P	5.60 %	P_2O_5	12.84 %
		H_2O	27.77 %

1 : Analyzed value
2 : Calculated value as oxides
Analyst : Power Reaction and Nuclear Fuel Development Corporation

at room temperature and in that humidity for about 8 minutes. Also the change from meta II phase into meta I phase is easily reversible, and so meta II phase does not commonly exist in nature. Thus meta I phase uranocircite is undoubtedly stable under the temperature and the humidity of the mineral deposits in this area.

c) Chemical Composition

The results of chemical analyses of carefully purified uranocircite are recorded in Table 3. From the present analyses the chemical composition of the mineral, in calculating formula, is

$$Ba (UO_2)_{2.037} (PO_4)_{2.248} \cdot 7.3H_2O.$$

This is approximately close to the formula,

$$Ba (UO_2)_2 (PO_4)_2 \cdot 8H_2O,$$
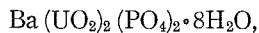
meta I phase uranocircite. These two formulas coincide very well with each other, except accidental errors. The X-ray fluorescent analyses of the present specimen of uranocircite show, besides the main elements, the existence of Zr, Sr and Fe.

d) Differential Thermal Analysis and Thermal Gravimetric Analysis

DTA and TGA curves for the specimen are shown in Figure 3. The DTA curve has characteristic endothermic peaks at 45°C and 72°C, due to dehydration of zeolitic water. Probably each peak corresponds to the converted reaction of meta II phase and unstable phase uranocircite. Between about 72°C and 680°C no remarkable reaction is discernible from the curve. Perhaps the unstable phase is held in this wide range. The curve also shows a gradual endothermic reaction at about 680°C, which suggests a change of heat capacity in the specimen.

To ascertain the nature of progressive dehydration of uranocircite an additional experiment of thermo-gravimetric analysis was carried out. The curve
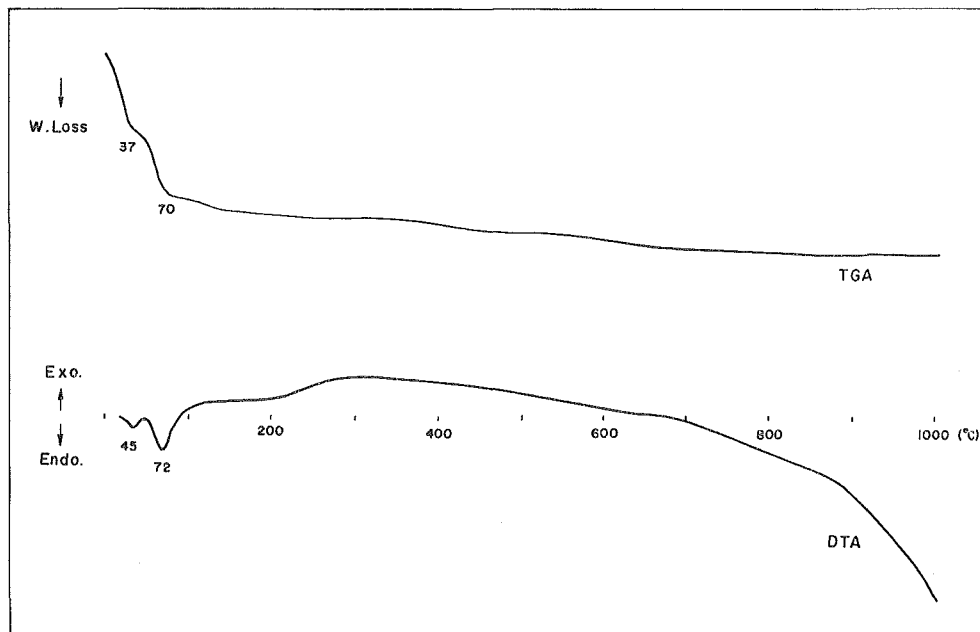

Fig. 3   DTA and TGA curves of the uranocircite

thus obtained, showing remarkable weight loss at 37°C and 70°C, corresponds well to the DTA curve. The weight loss continues very slowly from about 100°C, where the weight of the specimen becomes almost constant. At 1000°C the weight loss comes up to about 30% compared with the original specimen at room temperature.

e) *Infrared Absorption*

Infrared absorption spectrum of dried specimen is shown in Figure 4. The specimen was inserted between two plates of sodium chloride with Nujol oil. Peaks appearing at 2940, 2850, 1450 and 1370 cm^{-1} are caused by the Nujol oil. Zeolitic water in the specimen gives rise to a broad depression around 3400 cm^{-1} and another around 1640 cm^{-1}. Also a broad band from 1200 to 900 cm^{-1} is due to the presence of phosphate. Overlapping with phosphate absorption, the band at 980 cm^{-1} seems to indicate the presence of uranyl radical. Each of these absorption spectrum suggests that the uranium mineral has existed as hydro-urano-phosphate.

4 Geochemical Consideration and Discussion

Two problems are taken up in the following lines. The first is that of the sequence of uranium migration and the formation of hydrophosphate of barium and uranium namely uranocircite. First, the Younger Ryôke granites and the overlying Miocene sediments are unquestionably the fundamental conditions of the ultimate formation of the mineral deposits. It explains probably the mechanism of migration of uranium solution, and must be considered in comparison with other "groundwater type uranium deposits". From the field evidence and also from the chemical characters both of the mineral and granites, it is safely infered that uranium and barium are derived from Ikuta granite. The results of the X-ray fluorescence examination on representative samples are summarized in Table 4. According to these data, the high content of uranium, thorium and barium in the Ikuta granite produced apparently the radioactive anomaly of this area, while the mutual relations between the three elements are significant for explanation of their mode of migration. Generally the Th/U ratio in ordinary granites ranges from 3 to 6, and is quite constant. But it is clearly seen from Table 4 that the Th/U ratio of the Ikuta granite in the radioactive anomaly areas is very high. What is evident from these data is that uranium that behaves as a resistate against weathering was almost reached out from the mother rocks, while thorium and rare-earth elements were left behind. The fact that the thorium contents show positive and linear correlation with such rare-earth element as yttrium may suggest a genetic relation between them. Also, the microscopic observations and the autographic examinations reveal that the counts are

high in the Ikuta granite, and pleochroic haloes are distinct around the monazite crystals. It suggests that radioactive elements had affected more severely in the Ikuta granite than in other types of granite (Plates 1 and 2). These evidences mentioned above suggest that at least uranium and barium in the deposits had a common source. In its ionic radius barium is too large to replace calcium or sodium, and the only major element of comparable ionic size is potassium. Therefore barium is to be captured in biotite or potash feldspar on account of its higher charge. On the other hand, uranium and thorium are characterized by the tendency of being concentrated in residual magmas. These elements behave, in the magmas, chiefly as ions U^{+4} and Th^{+4} with radii of 1.05 Å and 1.10 Å respectively. Because of the above fact and also because of their relatively large ionic size, these ions, despite of their high charge, probably behave freely in the

Table 4   Minor chemical composition of granites (mean value)

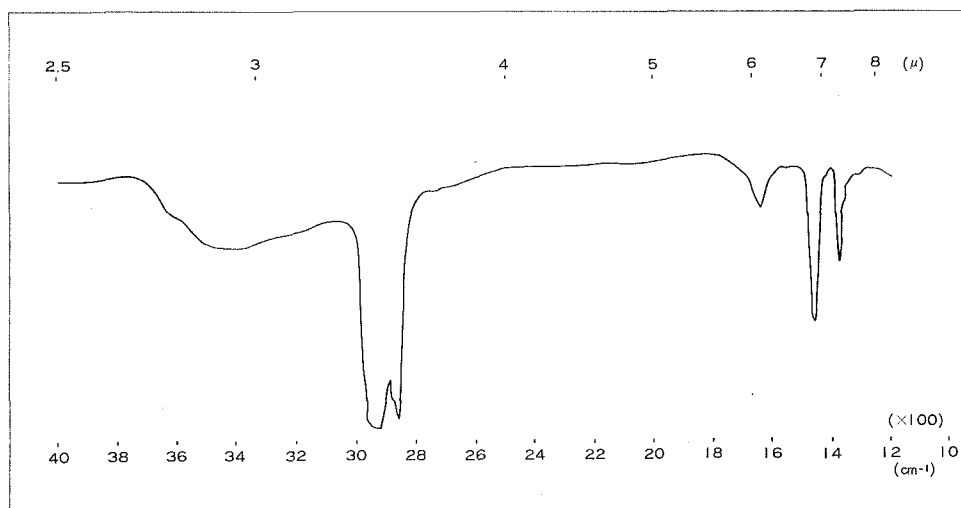|	N	U	Th	Th/U	Y	Zr	Sr	Rb	Ba
Tenryûkyô Gr.	3	1	–	–	58	272	392	292	–
Ikuta Gr.	2	1	–	–	56	430	398	280	–
RA 1 (Ikuta Gr.)	1	2	420	210	89	170	465	315	2000
RA 2 (Ikuta Gr.)	1	5	595	119	325	350	350	425	2300

(ppm)

N : Numbers of analyzed specimens

– : Below the limit of sensitivity

RA 1 : Radioactiveanomalous specimen (Mitsuzawabashi

RA 2 : Radioactiveanomalous specimen (Hôzenji)

Fig. 4   Infrared absorption spectrum of the uranocircite

magmas. During the cycle of weathering and erosion barium in rocks would easily be removed into solution together with other alkali and alkaline-earth ions.   But the extraction of uranium from weathering granite would occur gene-rally in forms of complex carbonate ions like in the case of sedimentary uranium deposits. If dissolved uranium is brought into contact with calcium, magnesium, or sodium bicarbonate solutions, tricarbonate ion $UO_2(CO_3)^{-4}$ could result (GRUNER, 1956).   This radical can carry the metal like uranium for long distances along the erosion surface especially along a "channel". On the way, the water carrying uranium discharges the element at the contact with organic matter, where reducing condition prevails. For carbonaceous matter is the best reducing agent, and it has a function to absorb uranyl ions.

During the deposition of the Miocene sediments in Ogitsubo reducing conditions were prevailing as suggested by the abundance of carbonized remains.   When, however, oxidizing environments happened to be realized along the fault or the shear zone, reducing precipitates would be redissolved and carried away into other stable places.   An environment, in which dissolved uranium solution is generally and gradually enriched and oxidizing conditions appear temporarily or intermit-tently, is probably the minimum necessary condition for the Ogitsubo deposits. Perhaps the minor fissure along the shear zone had retained an impermeable closed condition, and then argillization might have proceeded to generate the secondary uranium mineral.

The second problem concerns with that of hydration and the matter of cation replaciability. Uranocircite has the three phases according to water content, and

8   9   10   11 (μ)

(×100)

13   12   11   10   9   8
(cm·¹)
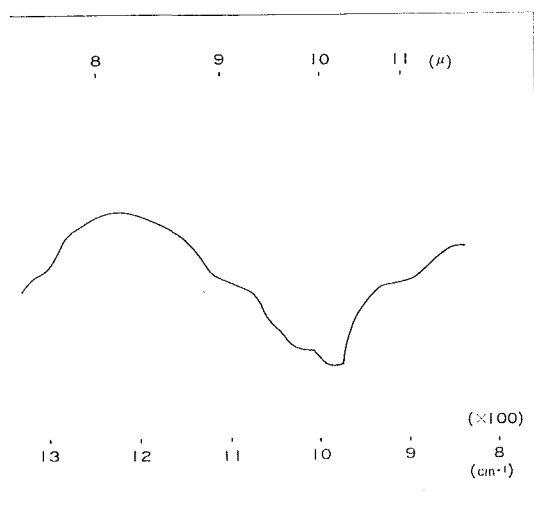
the established theory that hydrous phase does not occur in nature had been accepted (NUFFIELD and MILNE, 1953). Uranocircite found in the Toki district was recognized in forms of three phases in the labo-ratory, so the new doctrine was advocated by HAYASHI that the uranocircite of every three phases can exist in nature according to the condition of humidity. So far as the Ogits-ubo deposits are concerned, however, fully hydrated phase is not recognized and only the

meta I phase is found in nature. Minerals with the uran mica structure but with a smaller cation, for example saleeite (Mg-uran mica), are stable only in the fully hydrated phase under the ordinary condition.   When intermediate metal cation occupied this structure as in autunite (Ca-uran mica), it is thought to give rise to the approximately equal stability both in the meta I phase and in the fully hydrated phase. Uranocircite with such a larger cation as barium seems to exist stably as meta I phase in nature, and the fact coincides well with the field occurrence so far as this district is concerned.   On the other hand, the problem of cation replaciability is of great importance, for it is closely related with hydration status of this mineral. In general replacing power of cation is Ca<Ba, which means that barium will easily replace calcium. But according to KILLY, there is little difference between these two cations because of their similar replacing powers (KILLY, 1948).   In synthetic base exchange mentioned before, uranocircite is made by the treatment of Ca-uran mica with a strong solution of barium chloride. In this way uranocircite was easily produced. Also treating uranocircite with calcium chloride it is readily changed into Ca-uran mica, autunite.   In conclusion the stability relation between uranocircite and such common uran mica as autunite is greatly influenced by the relative abundance of the two cations at the spot of the deposits.

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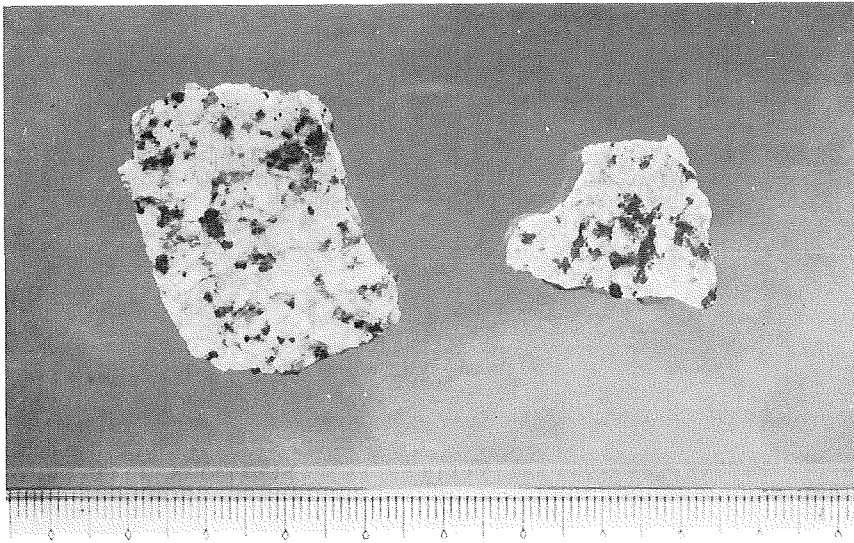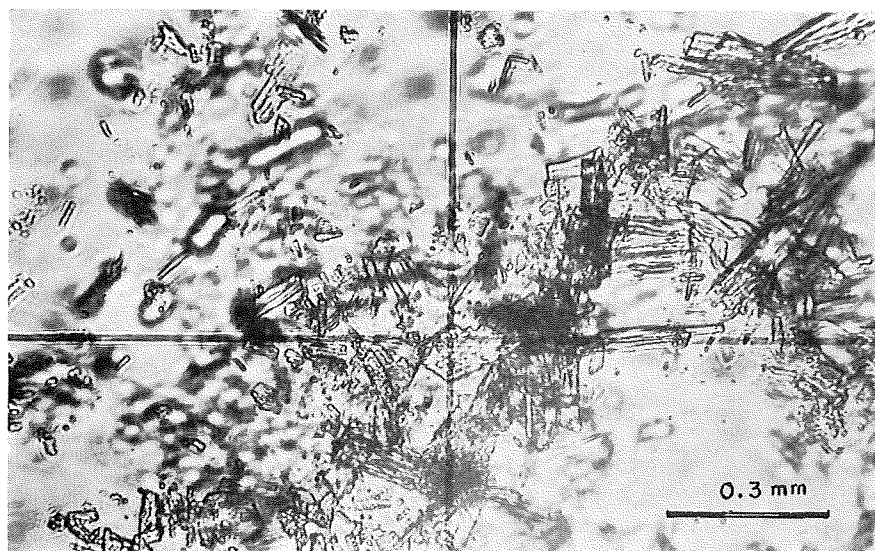
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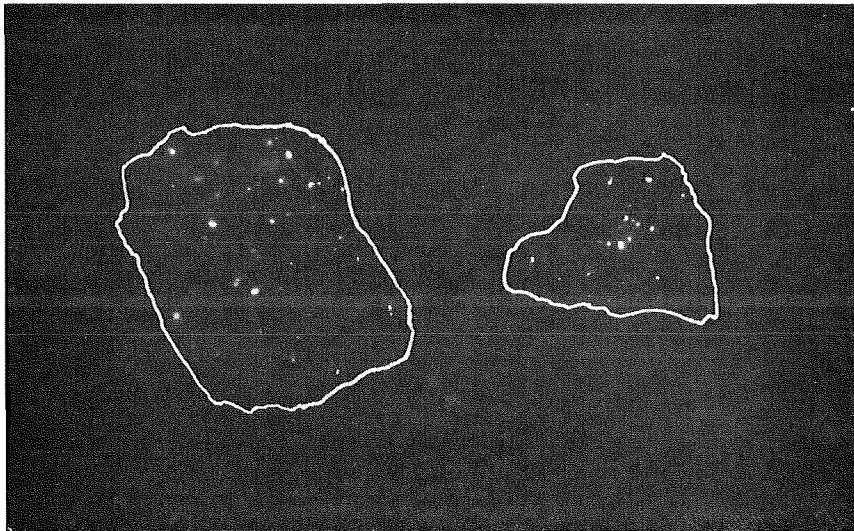
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Plate 1

1 : Radioactiveanomalous specimens of the Ikuta granite (Hòzenji)
2 : Autoradiograph of the same specimens (Exposed for 21 days)

0.3 mm

1

M

B

0.3mm

2

Plate 2

3 : Microscopic photograph of the uranocircite (Open nicol)
4 : Microscopic photograph of the Ikuta granite (Hôzenji, open nicol)
M : Monazite   B : Biotite