THE AMERICAN MINERALOGIST, VOL. 45, SEPTEMBER-OCTOBER, 1960

RANQUILITE, A CALCIUM URANYL SILICATE

M. Jiménez de Abeledo, María Rodríguez de Benyacar
and Ernesto E. Galloni,

Comision Nacional de Energía Atômica, Buenos Aires, Argentina.

Abstract

A new uranium mineral, named ranquilite, has been found in Mendoza Province, Argentina. The probable formula is $1.5CaO \cdot 2UO_3 5SiO_2 \cdot 12H_2O$. The orthorhombic unit cell has $a_0 = 17.64$ Å, $b_0 = 14.28$ Å and $c_0 = 18.48$ Å. Z. = 8, G. = 3.32. Samples heated to 110–120° and to 130–140° C. show certain changes in the *x*-ray powder pattern suggesting two lower hydrates. After exposure to the air, the original pattern is again obtained.

Introduction

Late in 1957 the Geological Service Laboratory of the Argentine Atomic Energy Commission received samples from the Ranquil-C6 area, Portezuelo Hill, Malargüe Department, Mendoza Province, Argentina, consisting of gypsum associated with calcite and some limonite. Very small amounts of a fluorescent uranium mineral appeared in fissures in the gypsum. By hand picking it was possible to obtain about 20 mg. of this mineral with small amounts of gypsum. *X*-ray powder photographs and semi-quantitative spectrographic analysis indicated a new calcium uranyl silicate, that was named ranquilite from the occurrence (1, 2, 3).

The fine-grained character of the mineral precluded the measurement of any optical properties other than the mean index of refraction, which for analyzed material is 1.564. The density lies between 2.89 and 3.32. The mineral is easily soluble in acids, and yields a silica gel. It turns ocher-yellow on heating.

With the arrival of new samples it was possible to continue the study of the mineral. From 1.5 kg. of rock, about 2 gms. of relatively pure ranquilite were separated by hand. This was divided into several fractions according to the estimated proportions of gypsum. Several very pure grains were reserved for *x*-ray photographs, electron microscopy and electron diffraction. The chemical analyses and dehydration studies were performed on the fractions containing gypsum (amounts ranging from 1 to 10%).

Chemical Composition

Chemical analyses were performed on three different samples weighing 100 mg. or less each; the proportion of gypsum in those samples ranged from 6.3 to 1%. The results showed good agreement; data from one of the analyses are shown in Table I;* column (e) shows the chemi-

---

* Chemical Analyses by Enrique Garcia, General Chemistry Laboratory, Argentine Atomic Energy Commission.

Table I. Chemical Composition of Ranquilite

	Chemical composition of sample of ranquilite with gypsum impurity				Chemical composition of ranquilite
	On ignited sample		Data recalculated to sample as is		
	(a)	(b)	(c) (b)×.806	(d)	(e) (d)×100/96.72
SiO_2	31.9	31.9	25.71	25.71	26.6
U_3O_8	56.3	56.3	45.38	45.38	46 8
CaO	9.0	8.23	6.63	6.63	6.9
SO_3	1.1	—	—	—	—
H_2O (Loss on ignition on total sample.)	—	—	19.4	19.0	19.6
				96.72	99.9
$CaSO_4$	—	1.87	1.51	—	—
$CaSO_4 \cdot 2H_2O$	—	—	—	1.91	—
Total	98.3	98.3	98.63	98.63	99.9
H_2O^-%				8.1	
H_2O^+%			Loss on ignition	−11.5	
			Penfield method	−11.1	

(a) Results of analysis as made.
(b) SO_3 recalculated as $CaSO_4$
(c) and (d) Data recalculated to sample as is, on the basis of total water content, 19.4%.
(e) Results adjusted to 100% after deducting gypsum.

cal composition of ranquilite adjusted to 100% after deduction of gypsum. The probable formula, according to these analyses is:

$$1.5CaO \cdot 2UO_3 \cdot 5SiO_2 \cdot 12H_2O$$

Spectrographic semiquantitative analyses showed the presence of about 1% Al and 1% Mg, but those elements were not determined chemically.

The following elements were looked for, but not found, on the spectrographic plates: Ag, Tl, W, Ti, Sb, Sr, Li, Cr.

According to dehydration experiments, besides water lost at low temperature, (OH) groups are present in the mineral.

X-Ray Diffraction

Owing to the very small size of the crystals no single crystal pattern could be obtained. Table II shows data from a powder pattern taken in a 114.8 mm. diameter camera, with CuK_α radiation. Patterns taken with CoK_α radiation failed to show reflections with spacings larger than 9.3 Å.

From a small block three patterns were taken; the sample, kept stationary, was successively orientated in three directions at 90°. Powder patterns with lines of uniform intensity distribution were always obtained, showing that the sample consisted of microcrystals in random orientation.

Electron Diffraction and Electron Microscopy

Electron diffraction patterns and electron micrographs were obtained in a three stage Philips electron microscope. Many micrographs reveal a stacking of very thin, transparent plates, showing an excellent cleavage parallel to the largest face of the plates (Fig. 1).

The many single crystal electron patterns obtained were all very similar; the spots are arranged on an orthogonal net, and there is a very symmetrical distribution of intensities (Fig. 2). Colloidal graphite patterns, taken with the same settings of the microscope controls, were used for calibration.

Figure 2 shows a selected area diffraction pattern of ranquilite. Assuming it represents the $0a^*b^*$ plane of the reciprocal lattice, two directions at 90° were chosen for a^* and b^*. The values $a=17.6$ Å and $b=7.0$ Å result. Only $hk0$ reflections with $h+k=2n$ appear.

In many S.A.D. patterns, however, intermediate rows of faint spots

Table II. X-Ray Powder Pattern of the Natural Material from Ranquil-Có (Cu/Ni; $\lambda=1.4518$ Å; Film No. 83).

d (Å)	I	d (Å)	I	d (Å)	I
9.26	v s	2.508	v f	1.781	f
8.12	s	2.405	f	1.745	w
6.62	f	2.332	f	1.658	w
5.10	w	2.281	f	1.626	v f
4.63	m	2.222	w	1.600	f
4.47	v s	2.186	m	1.566	f
3.68	f	2.067	v f	1.535	v f
3.58	m	1.980	w	1.497	w
3.34	m	1.934	w	1.453	v f
3.21	m	1.892	w	1.351	f
3.03	v s	1.863	w	1.324	f
2.81	w	1.838	w	1.310	v f
2.63	w	1.811	w	1.294	v f

v s = very strong; s = strong; m = medium; w = weak; f = faint; v f = very faint.

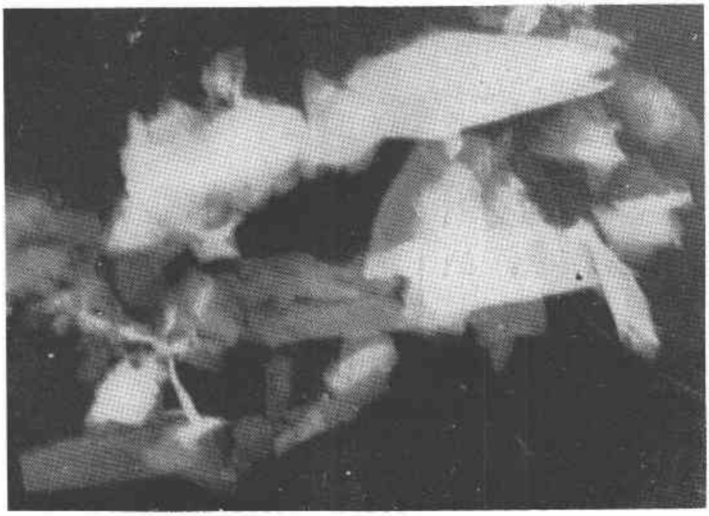

FIG. 1. Electron micrograph of ranquilite.

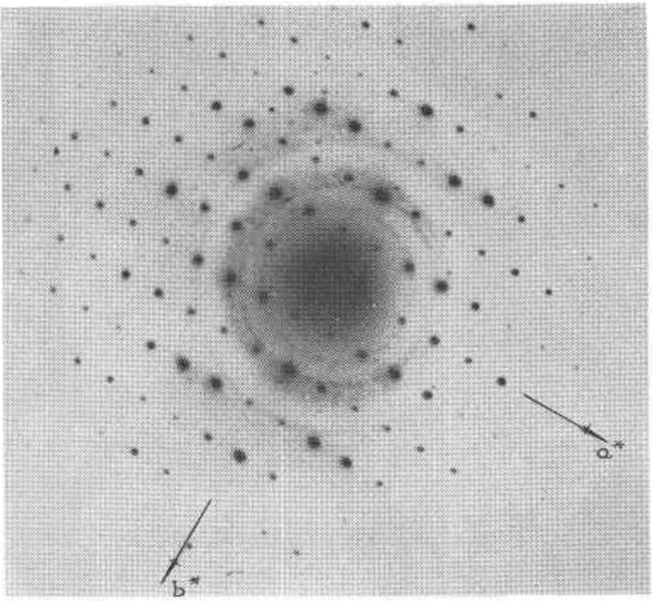

FIG. 2. Selected area electron diffraction pattern of ranquilite. Plane of the grid is approximately normal to the electron beam. 100 KV.

are clearly seen (Fig. 3). Those patterns may be supposed to belong to the thinnest crystals, since they show a larger central dark spot and a stronger blackening. The presence of the intermediate rows has to be accounted for by doubling b, giving 14 Å. With this value for b, and assuming that the faint spots belong to an upper level, only those $hk0$ reflections fulfilling the conditions $h=2n$ and $2h+k=4n$ are present. There are no limiting conditions for the hkl reflections.

Considering the easy dehydration of ranquilite (see later), some experiments were performed to determine whether the electron diffraction patterns belong to the natural material or to an alteration product resulting from exposure to high vacuum and electron beam bombardment. Data from powder patterns obtained in a Siemens Electron Microscope operated as a camera, and in a Metropolitan Vickers camera* both agree with x-ray powder diffraction and S.A.D patterns.

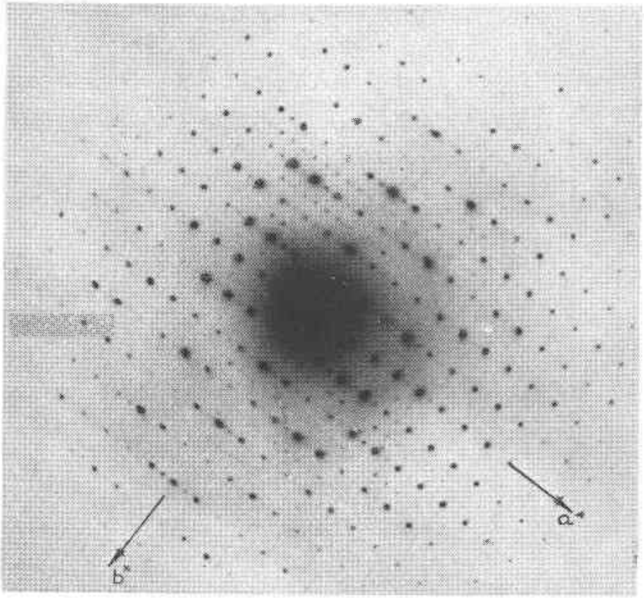

FIG. 3. Selected area electron diffraction pattern of ranquilite showing intermediate spots.

It seems that the spots of the S.A.D. patterns represent reflections that do not change while the mineral is exposed to high vacuum and electron beam bombardment.

---

* Both kindly taken Dr. Grünbaum, IDIEM Institute. Santiago de Chile.

DEHYDRATION STUDY

The changes suffered by the mineral on heating were followed by the changes in the *x*-ray powder patterns.

Samples contained in glass capillaries or mounted in the sample holders of the Philips wide range goniometer, were heated to different temperatures for periods ranging from 6 to 24 hours. Photographic patterns or goniometer records were taken immediately afterwards; the capillaries were heat-sealed prior to the taking of the patterns.

Some samples were exposed again to room conditions once the patterns were obtained; others were kept in chambers with known humidities. Later, *x*-ray photographs were taken again.

These experiments show that:

(*a*) There is a change in the diffraction pattern after heating the mineral to 110–120° C. On the photographs several lines shift to positions of smaller spacings; particularly the line $d=9.3$ Å changes to 8.2 Å and the line $d=4.62$ Å to 4.11 Å. The change coincides with the loss of water at 110–120° C. recorded by the chemical analyses.

(*b*) On two experiments the mineral was heated to 130–140° C. for 14 hours. The *x*-ray pattern showed a line with $d=7.3$ Å, while the lines with $d=8.2$ Å and $d=4.1$ Å were not present. A third "hydrate" is suggested.

(*c*) Samples that had been heated, if left for a time at room conditions, gave again the pattern of the "natural" material. Samples kept in chambers with 32, 50 and 75% relative humidities, gave also the original pattern. No intermediate steps could be detected.

(*d*) The goniometer records show that the intensity of some lines, already present in the "natural" pattern, are greatly enhanced after heating, while the intensity of other lines is much reduced (Fig. 4).

(*e*) Goniometer records taken after the dehydrated samples were kept at room conditions for a while, showed again the original spacings, and approximate intensity relationships.

From these results it was concluded that two forms with different amounts of water are present in our samples of ranquilite. On heating, Hydrate I changes to the less hydrated form (Hydrate II). Hydrate II rehydrates easily, by absorption of atmospheric moisture or when wetted, to give hydrate I.

CRYSTAL SYSTEM, UNIT CELL AND UNIT CELL CONTENTS

According to the dehydration experiments, lines belonging to two differently hydrated forms appear on the *x*-ray powder patterns of natural ranquilite. From the study of the lines that shift during dehydration and rehydration, it was concluded that the lines belonging to the form rich in water (hydrate I) are those listed in Table III.

The values $a_0=17.6$ Å and $b_0=14.0$ Å were obtained from electron

FIG. 4. *X*-ray diffraction goniometer traces of impure ranquilite.
a) Natural material from Ranquil-Có.
b) Sample heated to 110–120° C. for 13 hours.
c) Sample heated to 130–140° C. for 14 hours.
d) Sample wetted with water and kept 12 hours in a chamber with 100% relative humidity, after having been heated to 130–140° C.

The operating constants are: Radiation: Cu/Ni filtered; KVP: 36; MA 20; Divergence slit 1°; Receiving slit: 0.1 mm.; Scatter slit: 1°; Scale factor: 4; Multiplier: 1; Time constant: I seg.; Scanning speed: 0.5°/min.; Chart speed: 800 mm./hr.

diffraction patterns. A value for c_0 was obtained assuming that the lines that shift during dehydration represent $00l$ reflections. Taking the line with $d = 4.62$ Å as 004, we get $c_0 = 18.48$ Å. After having adjusted these values for a better agreement with *x*-ray data, we get:

$$a_0 = 17.64 \text{ Å} \qquad b_0 = 14.28 \text{ A} \qquad c_0 = 18.48 \text{ Å}$$

With these values for the unit cell, and assuming orthorhombic symmetry, it was possible to index all of the reflections in the ranquilite (hydrate I) pattern. As shown in Table III, for most of the spacings there were several choices of indices, so it is not possible to determine the space group.

The volume of the proposed unit cell is 4655 Å^3, and if $Z = 8$, the resulting theoretical density is 3.32. The actual density of ranquilite lies between 2.89 and 3.32.

Ranquilite shows a similarity with the mineral zeunerite (4) in its behaviour during dehydration-rehydration; by its *x*-ray diffraction pattern and chemical composition, it is closely related to the mineral named haiweeite by McBurney and Murdoch (5).

TABLE III. *X*-RAY POWDER PATTERN OF RANQUILITE (HYDRATE I)

I	d (Å) Measured	d (Å) calculated*	hkl
100.	9.30	9.241	002
0.4	6.63	6.618	120
		6.661	021
13.	5.07	5.050	203
43.	4.62	4.620	004
		4.610	031
		4.595	130
40.	4.47	4.469	104
		4.460	131
		4.509	123
8.	3.67	3.675	421
		3.683	133
		3.655	323
		3.695	005
20.	3.57	3.570	040
		3.578	015
		3.551	224
9.	3.40	3.408	205
		3.424	510
30.	3.34	3.330	042
		3.368	511
		3.315	215
		3.315	034
25.	3.21	3.210	512
		3.205	423
		3.228	125
		3.190	404
28.	3.037	3.035	106
		3.043	143
17.	2.814	2.814	523
		2.819	150
		2.823	051
		2.825	044
13.	2.63	2.633	425
		2.640	007
3.	2.508	2.509	540
		2.512	515
		2.501	630
7	2.405		
8	2.332		
8	2.281		
9	2.222		
10	2.186		
8	2.067		
13	1.98		
12	1.934		
18	1.892		
8	1.863		
6	1.838		
8	1.811		
9	1.781		
9	1.745		
5	1.658		

* Calculated for an orthorhombic cell with $a_0=17.64$, $b_0=14.28$ and $c_0=18.48$ Å.

Recently a new occurrence of ranquilite, associated with uranophane, has been reported in the San Sebastian Mine, Sañogasta area, Chilecito, La Rioja province, Argentina. Ranquilite has been identified by its *x*-ray diffraction pattern by Dr. Roberto O. Toubes* who is now studying the samples.

REFERENCES

1. PANDOLFI, C. L. DE, BENYACAR, M. RODRÍGUEZ DE, AND ABELEDO, M. JIMÉNEZ DE. On a new uranium mineral. Paper sent to the Second Conference on Pacific Uses of Atomic Energy. Geneva, September, 1958.
2. PANDOLFI, C. L. DE, BENYACAR, M. RODRÍGUEZ DE, AND ABELEDO, M. JIMÉNEZ DE. On a new uranium mineral from the Ranquil-Có area. Paper read at the 31 meeting of the Asociación Fisica Argentina, Buenos Aires, May 1958.
3. ABELEDO, M. JIMÉNEZ DE, BENYACAR, M. RODRÍGUEZ DE, AND GALLONI, ERNESTO E. Study of ranquilite, a new uranium mineral. Paper read at the fifth meeting of the Sesiones Químicas Rioplatenses Buenos Aires, July 29–31, 1959.
4. FRONDEL, C. Systematic Mineralogy of Uranium and Thorium. *Geological Survey Bulletin* **1064.**
5. MCBURNEY, T. C., AND MURDOCH, J. Haiweeite, a new uranium mineral from California. *Am. Mineral,* **44,** 839–843 (1959).

Manuscript received November 19, 1959.

---

* Geology Department, Atomic Energy Commission, Argentina.