

RANQUILITE, A CALCIUM URANYL SILICATE

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ABSTRACT

A new uranium mineral, named ranquillite, has been found in Mendoza Province, Argentina. The probable formula is $1.5\text{CaO} \cdot 2\text{UO}_3 \cdot 5\text{SiO}_2 \cdot 12\text{H}_2\text{O}$. The orthorhombic unit cell has $a_0 = 17.64 \text{ \AA}$, $b_0 = 14.28 \text{ \AA}$ and $c_0 = 18.48 \text{ \AA}$. $Z = 8$, $G = 3.32$. Samples heated to $110\text{--}120^\circ$ and to $130\text{--}140^\circ \text{ C.}$ 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 ranquillite 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 ranquillite 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 ranquillite with gypsum impurity | | | | Chemical composition of ranquillite |
|------------------------------------------------------|--------------------------------------------------------------------|---------------------|-----------------------------------|------------------------|-------------------------------------|
| | On ignited sample | | Data recalculated to sample as is | | |
| | (a) | (b) | (c) (b) × .806 | (d) | |
| SiO ₂ | 31.9 | 31.9 | 25.71 | 25.71 | 26.6 |
| U ₃ O 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 ₂ O (Loss on ignition on total sample.) | — | — | 19.4 | 19.0 | 19.6 |
| CaSO ₄ | — | 1.87 | 1.51 | — | — |
| CaSO ₄ ·2H ₂ O | — | — | — | 1.91 | — |
| Total | 98.3 | 98.3 | 98.63 | 98.63 | 99.9 |
| | | H ₂ O-% | | 8.1 | |
| | | H ₂ O+-% | | Loss on ignition -11.5 | |
| | | | | Penfield method -11.1 | |

(a) Results of analysis as made.

(b) SO₃ recalculated as CaSO₄

(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 ranquillite adjusted to 100% after deduction of gypsum. The probable formula, according to these analyses is:



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 $\text{CuK}\alpha$ radiation. Patterns taken with $\text{CoK}\alpha$ 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 ranquillite. 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-C6 (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 ranquillite.

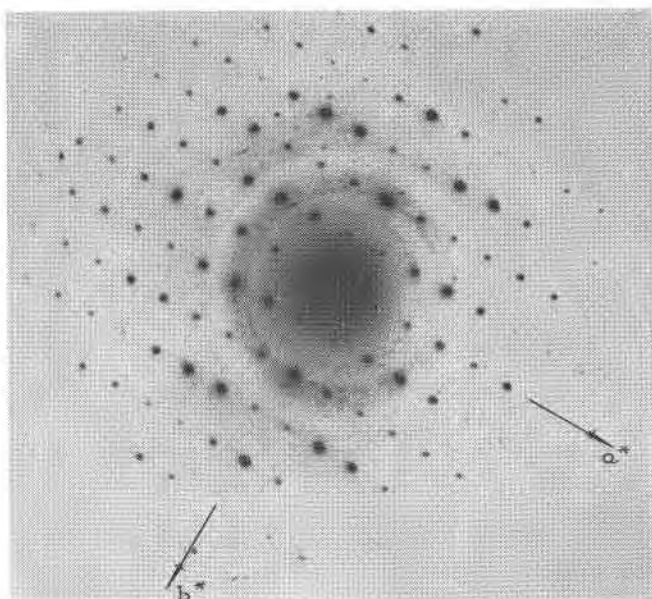


FIG. 2. Selected area electron diffraction pattern of ranquillite. Plane of the grid is approximately normal to the electron beam. 100 KV.

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

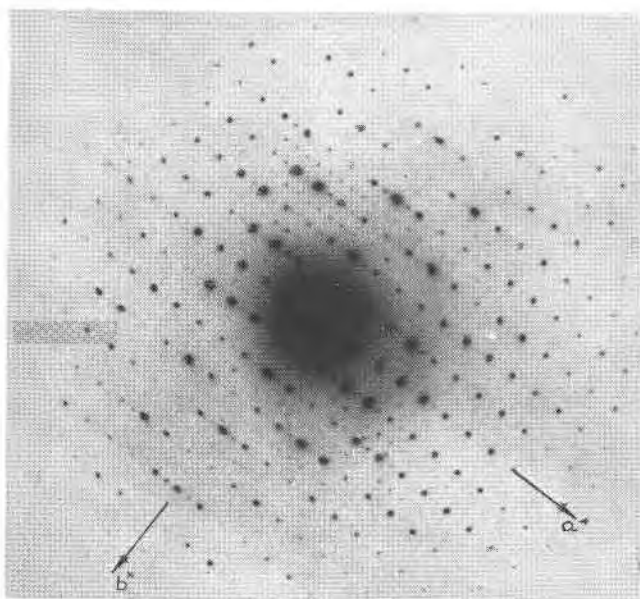


FIG. 3. Selected area electron diffraction pattern of ranquilite showing intermediate spots.

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.

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 ranquillite. 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 ranquillite. 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 ranquillite.

- Natural material from Ranquil-C6.
- Sample heated to 110–120° C. for 13 hours.
- Sample heated to 130–140° C. for 14 hours.
- 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: 1 sec.; 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 $d = 4.62 \text{ \AA}$ as 004 , we get $c_0 = 18.48 \text{ \AA}$. After having adjusted these values for a better agreement with x -ray data, we get:

$$a_0 = 17.64 \text{ \AA} \quad b_0 = 14.28 \text{ \AA} \quad c_0 = 18.48 \text{ \AA}$$

With these values for the unit cell, and assuming orthorhombic symmetry, it was possible to index all of the reflections in the ranquillite (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 \AA^3 , and if $Z = 8$, the resulting theoretical density is 3.32. The actual density of ranquillite lies between 2.89 and 3.32.

Ranquillite 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 | I | d Å measured |
|------|---------------------|------------------------|-------|----|-------------------|
| 100. | 9.30 | 9.241 | 002 | 7 | 2.405 |
| 0.4 | 6.63 | 6.618 | 120 | 8 | 2.332 |
| | | 6.661 | 021 | 8 | 2.281 |
| 13. | 5.07 | 5.050 | 203 | 9 | 2.222 |
| 43. | 4.62 | 4.620 | 004 | 10 | 2.186 |
| | | 4.610 | 031 | 8 | 2.067 |
| | | 4.595 | 130 | | |
| 40. | 4.47 | 4.469 | 104 | 13 | 1.98 |
| | | 4.460 | 131 | 12 | 1.934 |
| | | 4.509 | 123 | | |
| 8. | 3.67 | 3.675 | 421 | 18 | 1.892 |
| | | 3.683 | 133 | 8 | 1.863 |
| | | 3.655 | 323 | 6 | 1.838 |
| | | 3.695 | 005 | | |
| 20. | 3.57 | 3.570 | 040 | 8 | 1.811 |
| | | 3.578 | 015 | 9 | 1.781 |
| | | 3.551 | 224 | 9 | 1.745 |
| 9. | 3.40 | 3.408 | 205 | | |
| | | 3.424 | 510 | 5 | 1.658 |
| 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 | | |

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

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