

DEHYDRATION OF POLLUCITE

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ABSTRACT

Samples of pollucite from two localities have been studied under the microscope and by means of x -rays before and after dehydration. This study is further evidence that the water present in the mineral is not an essential part of the crystal lattice. The shape of the dehydration curve is not, in this case at least, a reliable means of deciding the role of water in a mineral.

Pollucite still remains, nearly a hundred years after its discovery by Breithaupt in 1846, the only mineral which contains the rare alkali cesium as an essential constituent, the Cs_2O content being as high as 36 per cent. Although pollucite has been considered to be of very rare occurrence, there is good reason to believe that it will be found at many more localities than the ten from which it has so far been reported: Hebron, Rumford, Buckfield, Greenwood, Mt. Mica and Newry in Maine; Leominster, Mass.; Tin Mountain, South Dakota; San Piero on the isle of Elba; and Varuträsk, Sweden. Massive pollucite is extremely difficult to distinguish from quartz in the field. It has no cleavage and has nearly the same hardness and luster as quartz. Under the microscope, however, it is readily distinguished, being isotropic. It is of considerable interest to the geochemist that at all the localities listed above, pollucite occurs in pegmatites rich in lithium minerals, although pollucite itself contains very little lithium. In other lithium-bearing pegmatites, its presence has probably been overlooked.**

Pollucite was long thought to be of fixed composition, but recently Richmond and Gonyer (5) showed that the composition is variable, and suggested the formula $(\text{Cs}, \text{Na})_{14+x}\text{Al}_{14+x}\text{Si}_{34-x}\text{O}_{96} \cdot n \text{H}_2\text{O}$, with $x=0, 1,$ or 2 , and with n variable between 4 and 9. The observed water content, which varies from 1.5 to 3.8 per cent, increases as sodium replaces cesium in the mineral. The dehydration of pollucite was studied in 1936 by Strunz (6), who considered that the dehydration curve (reproduced in Fig. 1) obtained by him on material from Elba was that of a typical zeolite, indicating that the water present (2.6 per cent in his sample) was not bound in the crystal lattice. He confirmed this by the observation that an x -ray powder photograph of material dehydrated at 500° was identical with that taken on the original sample. He found, how-

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** Dr. W. T. Schaller informs us that pollucite, in very small amount, has been identified from Pala and Mesa Grande, California. Here, as in the other pegmatites, it is associated with beryl containing cesium and with lithium minerals.

ever, that the mineral, unlike typical zeolites, did not, after dehydration, take up water on exposure to air saturated with water vapor.

The dehydration of pollucite seemed worthy of further study, since Strunz's results are in disagreement with observations by Wells (7), who reported that material from Hebron lost only 0.01 to 0.03 per cent at 170°. We have carried out dehydration experiments on two samples of pollucite, one from Hebron, Maine, and one from Elba, and have studied the product of dehydration under the microscope and by *x*-rays. The sample from Hebron (No. 2677 of the Brush Collection of Yale University) was part of the material analyzed by Wells. It was fresh and

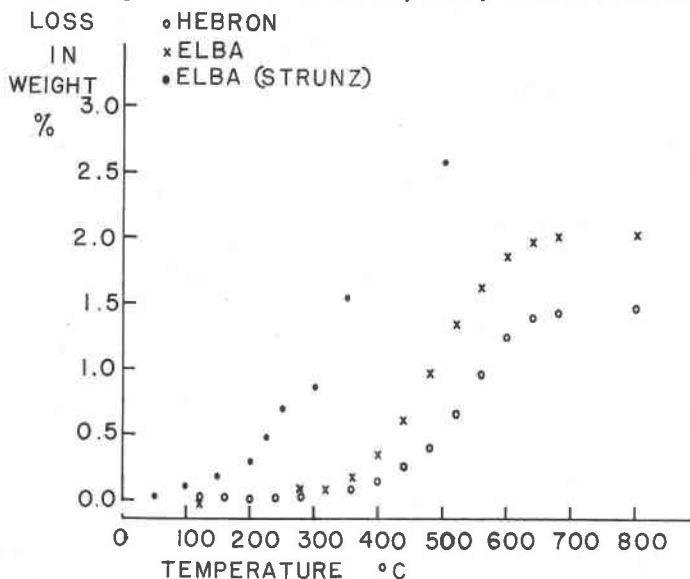


FIG. 1. Dehydration curve of pollucite.

transparent and of ideal purity. The sample from Elba (No. R2952 of the U. S. National Museum) was also transparent but contained a small amount of very fine grained material present along cracks. The sample was easily purified by floating off the foreign material in bromoform, and was then dried at 110°.

In the dehydration experiments, a weighed amount of the powdered mineral was placed in a platinum crucible and heated in an electric furnace, the temperature being held constant to $\pm 5^\circ$. When the loss in weight was less than 0.02 per cent over a 24-hour period, the temperature was raised.

Our results are given in Table 1 and Fig. 1, Strunz's results being also given for comparison. Both samples we studied showed practically no

loss in weight below 300° and were completely dehydrated at 640°. In the temperature range 300–640°, most of the loss in weight at each temperature occurred in the first twenty-four hours, but the sample continued to lose weight slowly. It seems probable that pollucite could be dehydrated completely at 450° or lower, but that a long time would be required. We cannot account for the difference between our results and those of Strunz, especially since he used a very short period of heating at each temperature.

TABLE 1. Dehydration of pollucite

Temp. °C.	Total loss wt. % (Hebron, F-K)	Hours at temp. (Hebron, F-K)	Total loss wt. % (Elba, F-K)	Hours at temp. (Elba, F-K)	Total loss wt. % (Elba, Strunz)	Hours at temp.
50	—	—	—	—	0.04	8
100	—	—	—	—	0.11	8
120	0.01	50	0.00	72	—	—
150	—	—	—	—	0.18	8
160	0.01	26	—	—	—	—
200	0.01	24	0.01	42	0.30	8
225	—	—	—	—	0.49	8
240	0.01	28	—	—	—	—
250	—	—	—	—	0.70	4
280	0.02	48	0.07	42	—	—
300	—	—	—	—	0.86	4
320	—	—	0.10	48	—	—
350	—	—	—	—	1.55	4
360	0.07	40	0.19	46	—	—
400	0.15	27	0.35	77	—	—
440	0.26	48	0.61	67	—	—
480	0.41	50	0.97	74	—	—
500	—	—	—	—	2.58	4
520	0.66	54	1.35	74	—	—
560	0.96	68	1.63	71	—	—
600	1.25	72	1.87	72	—	—
640	1.40	52	1.98	56	—	—
680	1.44	48	2.01	48	—	—
800	1.46	48	2.03	48	—	—
1520	1.46	24	—	—	—	—

The dehydration curves of Fig. 1 seem at first sight to indicate that the water in pollucite is “bound” or “combined” water. Certainly the course of dehydration is not what would be expected of a typical zeolite. Nevertheless, the optical and *x*-ray studies show that the water may be expelled without appreciably changing the surrounding lattice. The refractive index of the mineral is lowered by dehydration—from 1.523 to

1.513 for the Hebron material, and from 1.520 to 1.506 for the Elba material. This lowering of refractive index is most easily explained by assuming that the water in pollucite occupies interstitial space in the crystal lattice. When the mineral is dehydrated, the water is replaced by air, and the refractive index of the mineral is lowered. The change in refractive index is greater for the Elba pollucite, as would be expected from the higher water content.

Rotation powder spectrum photographs of dehydrated samples of pollucite from Hebron and from Elba were found to be identical with those of the original material and with each other, and also with that obtained from a crystal of pollucite from Greenwood, Maine. This was a portion of the material studied by Richmond and Gonyer (5). The same lines are present in each powder photograph, and no change in the intensities or in the spacings of the lines could be detected.

Changes of the crystal lattice have been observed when some zeolites are dehydrated, but no such effects were observed with pollucite. The length of the cell edge calculated from the measurements of the lines of the powder spectrum photographs is $13.69_6 \pm 0.005 \text{ \AA}$. Previously, others have reported 13.68 (2), 13.71 (6), 13.66 (1), 13.74 (3) and 13.65 (5).

For future identification of pollucite by the *x*-ray powder method, the planar spacings d/n and the relative intensities of the lines are recorded in Table 2. Strunz (6) has recorded intensities of the powder spectrum lines, but his table is incomplete.

According to the *x*-ray work by Strunz (6) and by Naray-Szabo (3), the structure of pollucite is very close to that of analcime. Pollucite is, then, zeolite-like in structure in that the water is not an integral part of the crystal lattice. It differs somewhat from most zeolites in (1) the very low water content, (2) the difficulty of dehydration, and (3) the difficulty of rehydration. This last point is rather interesting. We have kept a sample of pollucite, which had been dehydrated at 500° , in contact with water vapor at room temperature for over six weeks. In agreement with Strunz's result, there was only a very slight gain in weight, which was lost on heating at 110° . No change in refractive index was observed.

It seemed possible, however, that water might be put back into the mineral under pressure. We have carried out experiments in which the dehydrated mineral was heated at $400\text{--}500^\circ$ with water in a bomb. As we had hoped, the pollucite was partly rehydrated by this treatment. It had been thought by us that the mineral might be partly decomposed with the formation of claylike alteration products, similar to those which have been observed at Tin Mountain and at Varuträsk. No such decomposition was observed in our experiments, the pollucite remaining

TABLE 2

Planar spacings and relative intensities of the x-ray diffraction lines of pollucite taken with filtered Cu-K radiation. (These are from our measurements on samples of pollucite from Hebron, Elba and Greenwood, which gave identical values.) The specimen was rotated during the exposure, and a circular camera, calibrated with NaCl, and having a radius of 57.22 mm., was used. Estimated intensities of the diffraction lines are based on a scale of ten, ten being the intensity of the strongest line.

Lines	Intensity	d/n	Indices*
1	2	5.64	112
2	3	4.90	022
3	3	4.17	113
4	4	3.67	123
5	10	3.43	004
6	8	2.925	233
7	2	2.620	134, 015
8	6	2.424	044
9	4	2.224	116, 235
10	1+	2.019	136
11	1+	1.977	444
12	2	1.899	046
13	5	1.863	127, 255, 336
14	1	1.830	246
15	7	1.740	156, 237
16	2	1.713	008
17	1+	1.686	118, 147, 455
18	1	1.637	356
19	2+	1.592	057, 138, 347
20	2+	1.551	257
21	2+	1.531	048
22	2	1.477	129, 167, 556
23	1	1.444	039, 158, 457
24	3+	1.413	239, 367
25	4	1.356	1 1 10, 277
26	3	1.306	1 3 10, 259, 567
27	2	1.282	178, 477, 558
28	2	1.260	169, 3 3 10
29	3+	1.219	1 2 11, 1 5 10, 369
30	3+	1.182	2 3 11, 279, 3 5 10, 677
31	1+	1.164	1 4 11, 578
32	1	1.140	2 6 10
33	3	1.117	1 7 10, 2 5 11, 5 5 10
34	1	1.088	1 6 11, 3 7 10
35	1+	1.062	299, 3 6 11, 679
36	2	1.036	1 2 13, 2 7 11, 5 7 10
37	2	1.016	1 9 10, 2 3 13, 5 6 11
38	2	1.004	1 4 13, 1 8 11, 4 7 11

* Indices based on a cubic lattice.

transparent and isotropic. The refractive index of the material rose with increasing hydration. Recently, Norton (4) has reported a single experiment in which pollucite was heated in a bomb with water and carbon dioxide. No change was observed by him, but as the refractive index of the material was not determined, it is possible that some dehydration occurred in his experiment.

The two most interesting of our experiments, summarized in Table 3, were carried out to test the reversibility of the dehydration. The pro-

TABLE 3. Rehydration experiments

	H ₂ O content wt. %	<i>n</i>
<i>Elba pollucite</i>		
<i>At start of bomb experiment</i>		
Sample A (dehydrated at 500°)	0.28	1.510
Sample B (fresh material)	2.03	1.520
<i>After heating in bomb at 500° for 24 hrs. with 2.2 g. H₂O (approx. 300 atm. pressure)</i>		
Sample A	1.29	1.516
Sample B	1.44	1.516
<i>Hebron pollucite*</i>		
<i>At start of bomb experiment</i>		
Sample C (dehydrated at 460°)	0.35	1.516
Sample D (fresh material)	1.46	1.523
<i>After heating in bomb at 493° for 36 hrs. with 3.0 g. H₂O (approx. 380 atm. pressure)</i>		
Sample C	1.12	1.521
Sample D	1.06	1.521

* This experiment was kindly carried out for us by Dr. Earl Ingerson of the Geophysical Laboratory.

cedure used was to place two small platinum crucibles, one containing a known weight of partially dehydrated pollucite, the other containing a known weight of fresh pollucite, side by side in a small bomb with water. After the bomb had been heated at the desired temperature, it was cooled, the crucibles were removed, dried at 110°, and reweighed, and the refractive indices of the samples were determined.

It seems probable from the data in Table 3 that the hydration experiments represent equilibrium conditions. Nevertheless, it is somewhat puzzling that such high pressures are required for partial rehydration of the mineral at 500°. Assuming that the experiments in Table 3 do represent equilibrium conditions, the two samples of pollucite studied require a pressure of at least 400 atmospheres to rehydrate them to their original

condition at 500°. One might reasonably expect that if these samples were placed at 500° under atmospheric pressure, the dehydration would be extremely rapid, even explosive. Actually, dehydration proceeds rather slowly and no decrepitation was noticed.

The rehydrated material does seem to lose its water somewhat more rapidly than the original material. Sample A of Table 3 showed the following loss in weight when heated (24 hours at each temperature): 120° 0.00, 220° 0.06, 300° 0.23, 420° 0.89, 530° 1.29, 620° 1.36 per cent.

The differences in behavior between pollucite and analcime are probably largely due to the fact that the very large cesium ion occupies much of the "free" space in the pollucite structure. This steric effect would account for the low water content and for the difficulty of dehydration. The increase in water content of pollucite as sodium replaces cesium is in accord with this idea. One would expect that the samples with high sodium content would be dehydrated more readily. Unfortunately, none of the samples available to us had over 2 per cent water. Dehydration experiments on material with 3.5–4 per cent water would be of great interest.

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