THE CRYSTAL STRUCTURE OF THE MINERAL POLLUCITE*

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Pollucite is a mineral whose chemical composition and structure are not clearly understood. Standard references[1,2] give compositions such as $CsAlSi_2O_6$ and $Cs_4Al_4Si_9O_{26} \cdot H_2O$. Náray-Szabó proposed a structure[3] based upon $CsAlSi_2O_6 \cdot xH_2O$.

Náray-Szabó's structure was suggested by the close similarity of the symmetry, cell dimensions, and composition of pollucite to those of analcite, whose structure had been solved by W. H. Taylor.[4] Both minerals have space group $Ia3d$, with cell edge $a = 13.7$ Å. Náray-Szabó retained the alumina-silicate framework of analcite, but placed the Cs in equipoint $16b$ rather than $24c$, where Taylor had placed the 16 Na atoms of the analcite cell. The water molecules were not specifically located, and Náray-Szabó also favored a tetragonal symmetry to accommodate the Al and Si atoms separately.

It is now recognized that pollucite contains Na as well as Cs. We were prompted to reinvestigate the structure of this mineral because a number of questions regarding it are still unanswered, especially: (1) Are these Na atoms located in the site of Taylor's Na or that of Náray-Szabó's Cs? (2) Is the symmetry of the crystal isometric or tetragonal? (3) Where are the water molecules located?

Material.—Our material was clear, colorless pollucite from Rumford, Maine. We found this to be optically isotropic and to have a specific gravity of 2.94. Foote's analysis[5] of this material, combined with our density and cell edge of $a = 13.69$ Å, yields a cell content of

$$Cs_{11.7} Na_{3.1}Li_{0.5}K_{0.4}Al_{15}Si_{33}O_{96.3} \cdot 4H_2O.$$
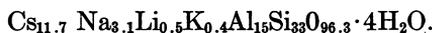
For purposes of computing intensities, we regarded this as approximately

$$Cs_{12}Na_4Al_{16}Si_{32}O_{96} \cdot 4H_2O.$$

We also confirmed the space group as $Ia3d$ from a complete set of precession photographs.

Structure determination: We used a clear pollucite sphere of radius 0.17 mm for measuring the intensities. Of the approximately 300 independent reflections in the $CuK\alpha$ sphere, 215 were accessible to our single-crystal diffractometer. The intensities were corrected for Lorentz, polarization, and absorption factors.

The three-dimensional Patterson function based upon these data was found to be consistent with the location of the heavy Cs atom in $16b$ at $^1/_8$ $^1/_8$ $^1/_8$. A Fourier synthesis phased on Cs revealed the (Si,Al) and O positions, which proved to be those of the analcite framework. We refined, by the method of least squares, the coordinates and isotropic thermal coefficients of the (Cs,Na), (Si,Al), and O atoms, but deliberately omitted the water molecules. The refinement reduced an initial value of the discrepancy index R from about 25 per cent to 9.7 per cent. Using the last values of the computed structure factors, we prepared an electron-density difference function, which showed that the omitted atoms occupied equipoint $24c$,

853

These atoms represented the four omitted water molecules. Because they have almost the same scattering powers, $4H_2O$ and $4Na$ could have been interchanged without affecting the result substantially.

Finally, we made corrections for anomalous scattering of all atoms, and introduced anisotropic thermal parameters for all atoms except the water molecules. With these changes we continued the least-squares refinement and reduced the discrepancy index, R, to 5.5 per cent.

TABLE 1

Description of the Crystal Structure of the Pollucite from Rumford, Maine

Space group: $I \frac{4}{a} \bar{3} \frac{2}{d}$.   Cell edge: $a = 13.69$ Å.

Atom	Equi-point	Occu-pancy	Representative coordinates			Parameters			Equivalent isotropic B
						x	y	z	
48 (Si, Al)	48g	1	x, $^1/_4 - x$, $^1/_8$			0.6624			0.235 Å²
96 O	96h	1	x	y	z	0.1037	0.1341	0.7202	1.665 Å²
16 (Cs, Na)	16b	1	$^1/_8$	$^1/_8$	$^1/_8$				1.972 Å²
4 H_2O	24c	$^1/_6$	$^1/_4$	$^1/_8$	0				1.750 Å²

Results.—The structure of pollucite resulting from our investigation is described in Table 1, except that we have transformed the anisotropic thermal parameters into equivalent isotropic values. The highlights of these results are as follows: The analcite-type framework proposed by Náray-Szabó as well as his nonanalcite-like location of the alkali atoms are confirmed. The 4 water molecules occur in equipoint 24c, but fill only a fraction of the 24 available sites. In view of the well-known isometric form development and the isotropic optics of pollucite, the low value of the discrepancy index of our refinement may be regarded as confirming the isometric symmetry of this mineral.

The alkali atoms occupy the largest voids of the framework. The water molecules occupy windows between these voids. Thus the water molecules lie between pairs of alkali atoms, whose distance apart is 4.8 Å. If the radius of the Cs ion in taken as 1.7 Å, the space between pairs of Cs ions is $4.8 - 2 \times 1.7 = 1.4$ Å. This space is much too small to be occupied by an Na ion, whose diameter is about 1.9 Å, even if the repulsion between ions is disregarded. This space is also too small to house a water molecule. On the other hand, if an Na ion occasionally replaces a Cs ion, the available space between Cs and Na ions is at least $4.8 - 1.7 - 0.9 = 2.2$ Å. It is even greater if the small Na atom is displaced a little from the center of its site, and this is enough to accommodate a water molecule. It is for this reason, apparently, that the location of the water molecule is in the window between pairs of alkali atoms when one or both happen to be occupied by the smaller Na ion. The aquisition of water supplements the coordination of the smaller ion.

[1] Dana, E. S., and W. E. Ford, *A Textbook of Mineralogy* (New York: John Wiley and Sons, Inc., 1932), 4th ed., p. 551.

[2] Deer, W. A., R. A. Howie, and J. Zussman, *Rock-Forming Minerals* (New York: Longmans, Green and Co. Ltd., 1963), vol. 4, *Framework Silicates*, p. 340.

[3] Náray-Szabó, St. v., "Die Struktur des Pollucits, $CsAlSi_2O_6 \cdot xH_2O$," *Z. Krist.*, **99**, 277–282 (1938).

[4] Taylor, W. H., "The structure of analcite ($NaAlSi_2O_6 \cdot H_2O$)," *Z. Krist.*, **74**, 1–19 (1930).

[5] Foote, H. W., "On the occurrence of pollucite, mangano-columbite and microlite at Rumford, Maine," *Am. J. Sci.*, **1**, 457–459 (1896).