

## THE CRYSTAL STRUCTURE OF KASOLITE

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In 1963 a paper [1] was published in Belgium on the determination of the crystal structure of kasolite  $\text{PbO} \cdot \text{UO}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ . In parallel with this, and quite independently, an attempt to decipher this structure was made in the Vernadskii Institute of Geochemistry and Analytical Chemistry, AN SSSR, Crystallochemistry Laboratory. Comparison of these investigations shows that in the Belgian version the  $\underline{y}$  coordinate of the Pb atom differed from that obtained by ourselves by half a period, which completely alters the coordination of the Pb atom. The coordinates of the remaining atoms differed insignificantly.

The structure determinations were made within the framework of the same space group  $C_{2h}^5 = P2_1/a$  (in the Belgian work  $P21/c$ ) for close elementary cell parameters:  $a = 13.28$ ,  $b = 6.96$ ,  $c = 6.74 \text{ \AA}$ ,  $\beta = 75^\circ 45'$ , and  $Z = 4$ . The fundamental experimental material in our investigation was the Weissenberg development of layer lines for rotation around the  $\underline{b}$  axis (in Cu radiation). In view of the fact that the crystals have the form of needles 0.02 to 0.05 mm thick, and that their linear absorption coefficient is  $\mu \approx 1500 \text{ cm}^{-1}$ , rotation about the other axes was hardly used at all.

The  $\underline{x}$  and  $\underline{z}$  coordinates of the U and Pb atoms were found from projections of the Patterson function  $P(xz)$  from the Belov-Mamedov theorem [2]. Furthermore, by means of the statistical Zacharisen equation, we determined the signs of the structure factors  $F_{h0l}$ ,  $F_{h1l}$ ,  $F_{h2l}$ , and  $F_{h3l}$ . The electron density synthesis  $\rho(xz)$  constructed with due allowance for these signs, confirmed the  $\underline{x}$  and  $\underline{z}$  coordinates of the heavy atoms. The third coordinate ( $\underline{y}$ ) of the U and Pb atoms were established from prickings of the three-dimensional syntheses of  $P(xyz)$  and  $\rho(xyz)$ . In both cases, identical values of  $\underline{y}$  were obtained. The  $\underline{y}$  coordinate of the Pb atom proved to be 0.570, whereas, in the Belgian investigation, the coordinate of this

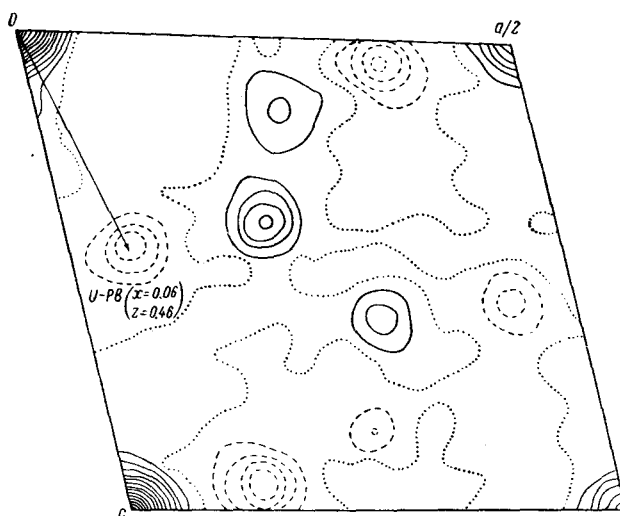


Fig. 1. Weighted projection of Patterson function  $P_1(xz)$ . Negative peaks shown dotted.

atom was 0.065. Our coordinate value was further confirmed by the weighted Patterson projection  $P_1(xz)$  (Fig. 1), in which the peak corresponding to the U - Pb distance is negative, whereas, for the Belgian U - Pb distance of 0.18 this should be positive.

The  $\rho(xz)$  synthesis gave no indication of the positions of the light atoms Si and O. In order to find these, we constructed a differential electron density projection on the  $xz$  plane, allowing for contributions from the U and Pb atoms, first introducing corrections into the structure factors  $F_{h0l}$  for absorption and temperature factor. The absorption corrections were determined by means of a graphical construction [3], but splitting the crystal cross section into a constant number of parts (in the present case, 128). The temperature constant B calculated after introducing the absorption corrections was 2.0. As a result of introducing the absorption corrections, the variance coef-

Coordinates of Basic Atoms in the Kasolite Structure

Atom	Author's coordinate			Belgian coordinate		
	x	y	z	x	y	z
U	0.180	0.246	0.526	0.171	0.250	0.523
Pb	0.117	0.570	0.073	0.115	0.065	0.074
Si	0.08	0.75	0.58	0.08	0.75	0.57
O <sub>Si1</sub>	0.03	0.75	0.83	0.03	0.75	0.82
O <sub>Si2</sub>	-0.01	0.75	0.45	-0.02	0.75	0.48
O <sub>Si3</sub>	0.16	0.94	0.51	0.15	0.94	0.50
O <sub>Si4</sub>	0.16	0.56	0.51	0.15	0.56	0.50
O <sub>U1</sub>	0.18	0.25	0.27	0.18	0.25	0.26
O <sub>U2</sub>	0.18	0.25	0.78	0.18	0.25	0.79

ficient calculated with respect to the U and Pb coordinates for  $h0l$  reflections fell from 0.23 to 0.19.

In the electron density projection  $\rho(xz)$ , as in analogous projections for uranophane [4] and sklodowskite [5], the U atoms are disposed in pairs, with intervening distances of about 1.7 Å in the plane of projection and 3.5 Å along the normal to this plane (half a  $b$  spacing). This analogy enabled us to interpret the differential projection and find the positions of the Si - O tetrahedron and the oxygen atoms of the uranyl group. The  $y$  coordinates of the light atoms were determined from geometrical and crystallochemical considerations. The position of the water molecule in the structure could not be ascertained. The coordinates of the atoms in the kasolite structure are given in the table, together with those of the Belgian authors.

Figure 2 shows the projection of the kasolite structure on the  $xz$  plane. The main structural characteristic, as in the case of uranophane and sklodowskite, is formed by the  $[(UO_2)_2(SiO_4)_2]^{-4}$  layers, consisting of heptahedra around the U atoms and  $SiO_4$  tetrahedra. The layers are linked together by  $Pb^{2+}$  cations. In contrast to the earlier structures, two Pb atoms belong to each  $[(UO_2)_2(SiO_4)_2]^{-4}$  group in the kasolite structure, i.e., the charge of the layer is completely compensated by the  $Pb^{2+}$  cations. Figure 2 shows the distances from the lead atom to the nearest oxygens. In the Belgian work, the Pb atom was disposed at the vertex of a triangular pyramid, the base of which was formed by three O atoms. In our structure, the lead atom is surrounded by eight oxygen atoms, forming a coordination polyhedron around the Pb in the form of a trihedral prism, one face and one base of which are centered. The U - O distances in the uranyl group are 1.7 Å.

The variance coefficient of the structure calculated with respect to the coordinates of all atoms found for reflections of the  $h0l$  zone ( $\sin \theta / \lambda \leq 0.6$ )

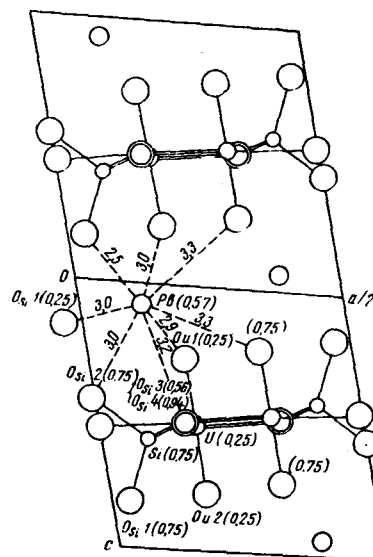


Fig. 2. Projection of the kasolite structure on the  $xz$ -plane.

was 0.15, whereas the value for the same reflections in the Belgian work was 0.26.

The formula of kasolite in accordance with its structure is  $Pb[(UO_2)_2(SiO_4)] \cdot H_2O$ , as given by Strunz [6].

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