

diagrams from sediments of similar absolute age at Totoket and Red Maple Swamp, Connecticut (13, 16, 17), there is no indication here of significant changes in the percentages of pine and spruce pollen within this zone. Zone T is overlain by a spruce pollen zone (A), which can be subdivided into a spruce-pine-oak subzone (A-2-3) and a spruce-fir-larch subzone (A-4). (Zone A-1 of Durham was not recognized here.) The increased frequencies of tree pollen and accompanying macrofossils of trees (at other sites) are generally interpreted as representing forest (13-15). The maximum percentage of oak and pine pollen in subzone A-2-3 throughout southern New England has been the ground for interpreting this subzone as warmer (mixed boreal and deciduous trees) than the overlying subzone A-4 (boreal trees); our corrected C<sup>14</sup>-dates, however, do not support the previous belief that the oak-pine maximum of A-2-3, the deposition of which ended 10,300 years ago, correlates with the Two Creeks time-interval ending 11,800 years ago (6, 13, 14, 17, 18).

When the pollen frequencies are expressed as accumulation rates, the resulting absolute pollen diagram (Fig. 3B) supports the previous interpretation of a major change in vegetation at the time of transition from zone T to subzone A-2-3. The increase in total pollen deposition from 1000 in zone T to 6000 per square centimeter per year in subzone A-2-3 results from a major increase in the number of grains of tree pollen reaching the sampling point, presumably because of the arrival or increase of trees which augmented the pollen productivity of the local vegetation. The implication of the percentage diagram (Fig. 3A), namely that incoming trees supplanted nonarboreal vegetation, is misleading; Fig. 3B shows that deposition of sedge pollen continued with little change in accumulation rate, while the rate for grass pollen actually increased on an absolute basis along with tree pollen. Within zone A, the major change shown by the absolute diagram, in contrast with the percentage diagram, is a continuing increase in the rate of accumulation of conifer pollen; this rate reaches maximum values in A-4, while the accumulation rate of oak pollen does not change very greatly. The characteristic drop in the percentage values for oak and pine pollen in A-4 has hitherto been considered to indicate a decrease in the abundance of oak and

pine trees in response to climatic cooling associated with the end of the Two Creeks interval. The data presented in Fig. 3B show, however, that at Rogers Lake the decrease in oak pollen is mainly an artifact of the presentation of data in the form of percentages. The number of grains of oak pollen reaching the sampling site in subzones A-2-3 and A-4 changed very little within the limits of accuracy of our assay; oak pollen makes up a smaller percentage of the total in A-4 largely because the total itself had increased from 6000 to 9000 per square centimeter per year. In a similar manner the percentage diagram masks the continuing increase in the rate of pine pollen accumulation through subzones A-2-3 and A-4. Our new data show further that the increased rate of accumulation of all types of tree pollen at the lower boundary of subzone A-2-3 was of far greater magnitude than is implied by the changes in percentages; in fact tree pollen is so scarce in zone T that changes in the ratios among the different types, indicated in percentage diagrams from Totoket and other sites and previously interpreted as evidence of climatic oscillations, may represent statistical artifacts rather than significant vegetational changes.

The amount of pollen deposited at one point on one lake bottom is not necessarily proportional to that deposited over the whole surface of the lake, nor is the latter necessarily related in any systematic way to the abundance and distribution of vegetation. The successful development of methods for studying the absolute pollen rain in the past, however, provides us with the first step toward more accurate use of the pollen record. The possibility that accumulation rates provide reliable indices of the absolute abundances of plants on the landscape is worth pursuing; it would allow a completely objective interpretation of results such as those from Rogers Lake (19).

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confidence limit  $ab =$   
 $ab \pm 2 (V_a b^2 + V_b a^2 + V_a V_b)^{1/2}$ ,  
where  $ab$  is the accumulation rate,  $a$  is the absolute pollen frequency,  $V_a$  is the variance of the absolute pollen frequency estimate,  $b$  is the sedimentation rate in centimeters per year, and  $V_b$  is the variance of estimate of the least-squares line.
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### Pentaborate Polyaniion in the Crystal Structure of Ulexite, NaCaB<sub>5</sub>O<sub>6</sub>(OH)<sub>6</sub>·5H<sub>2</sub>O

Abstract. *Triclinic ulexite crystals contain isolated borate polyaniions [B<sub>5</sub>O<sub>6</sub>(OH)<sub>6</sub>]<sup>5-</sup> related to the well known pentaborate polyaniion [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>3-</sup> by addition of two hydroxyl groups to two opposite B-O triangles. The isolated ulexite polyaniions form the [B<sub>5</sub>O<sub>6</sub>(OH)<sub>6</sub>]<sub>n</sub><sup>5n-</sup> chains previously found in crystals of the related mineral probertite, NaCaB<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>·3H<sub>2</sub>O.*

The pentaborate polyaniion [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>3-</sup> consists of a central borate tetrahedron and four BO<sub>2</sub>(OH) triangles, each sharing one corner with the tetrahedron and linked in pairs to produce two six-membered alternating B-O rings in approximately perpendicular planes. This polyaniion was found initially by Zachariasen (1) in the crystal structure of potassium pentaborate tetrahydrate; the structural formula [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>3-</sup> was proposed by Christ (2) and confirmed by Zachariasen and Plettinger (3) in their refinement of the structure.

Table 1. Atomic coordinates for ulexite,  $\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ . Triclinic,  $P1$ :  $a = 8.809 \pm 0.02$ ,  $b = 12.86 \pm 0.04$ ,  $c = 6.678 \pm 0.02$  Å,  $\alpha = 90^\circ 15' \pm 05'$ ,  $\beta = 109^\circ 10' \pm 05'$ ,  $\gamma = 105^\circ 05' \pm 05'$ , cell volume =  $687.0 \text{ \AA}^3$ ,  $Z = 2$ , density (calc.)  $1.959$  (obs.)  $1.955 \pm 0.001 \text{ g cm}^{-3}$  (4).

Atom	Coordinates (in fractions of cell edges)		
	x	y	z
B <sub>1</sub>	0.052	0.200	0.668
B <sub>2</sub>	.347	.270	.900
B <sub>3</sub>	-.189	.224	.783
B <sub>4</sub>	.235	.074	.782
B <sub>5</sub>	-.174	.269	.427
O <sub>1</sub>	.199	.289	.792
O <sub>2</sub>	.102	.106	.620
O <sub>3</sub>	-.029	.242	.466
O <sub>4</sub>	-.066	.167	.784
O <sub>5</sub>	.370	.169	.911
O <sub>6</sub>	-.260	.261	.565
O <sub>7</sub> (OH)	.299	.008	.670
O <sub>8</sub> (OH)	.159	.006	.929
O <sub>9</sub> (OH)	-.114	.324	.936
O <sub>10</sub> (OH)	-.318	.147	.836
O <sub>11</sub> (OH)	.478	.360	.002
O <sub>12</sub> (OH)	-.238	.313	.239
O <sub>13</sub> (H <sub>2</sub> O)	.144	.210	.222
O <sub>14</sub> (H <sub>2</sub> O)	.428	.102	.329
O <sub>15</sub> (H <sub>2</sub> O)	.472	.358	.488
O <sub>16</sub> (H <sub>2</sub> O)	.191	.479	.187
O <sub>17</sub> (H <sub>2</sub> O)	.224	.476	.610
Na	.477	.501	.244
Ca	.143	.026	.305

Modification of this polyanion by successive addition of hydroxyl groups to replace triangles by tetrahedra was postulated by Christ (2) who suggested in particular that the crystal structure of ulexite,  $\text{NaCaB}_5\text{O}_6 \cdot 8\text{H}_2\text{O}$ , would contain the polyanion  $[\text{B}_5\text{O}_6(\text{OH})_6]^{3-}$ , in which two pentaborate triangles are replaced by tetrahedra.

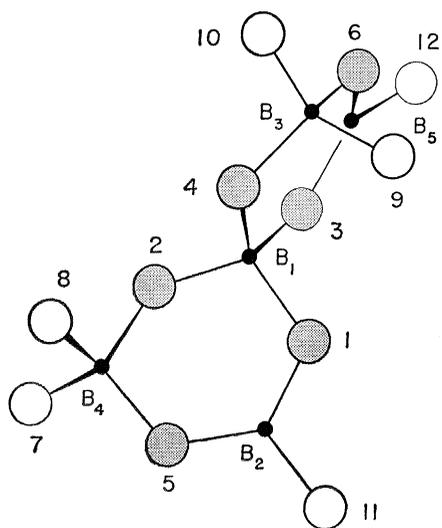


Fig. 1. The  $[\text{B}_5\text{O}_6(\text{OH})_6]^{3-}$  polyanion in ulexite viewed along the  $c$ -axis. Small black circles represent boron atoms; large shaded circles, oxygen anions; and large open circles, hydroxyl groups. Numbering of atoms conforms to Table 1.

The crystal structure of ulexite has now been solved and does contain the isolated polyanions (Fig. 1) proposed by Christ (2). The structure was determined by standard three-dimensional Patterson, and other, Fourier methods from about 9700 visually estimated data. The present residual factor is 0.16 for approximately  $4600 |F_{\text{obs}}| > 0$ , and the present atomic coordinates are listed in Table 1. The refinement is not expected to change the coordinates by more than  $\pm 0.005$ .

The average distances between B and O in the polyanion are 1.37 Å in the triangles and 1.48 Å in the tetrahedra. Each  $\text{Ca}^{2+}$  cation is surrounded by an irregular polyhedron of eight oxygen atoms, three of which are polyanion hydroxyls, and two, water molecules. The average distance between Ca and O is 2.48 Å. Each  $\text{Na}^+$  cation is coordinated by an octahedron of two hydroxyl oxygens and four water molecules at an average distance of 2.42 Å. Neighboring octahedra share edges to make a continuous chain parallel to  $c$ .

These three structural groups (borate polyanions, Ca-coordination polyhedra, and Na-coordination octahedra) are joined by hydrogen bonds into a three-dimensional network. The 16 distinct hydrogen bonds have an average value of 2.84 Å, the range being from 2.58 Å to 3.09 Å. All protons participate in the hydrogen-bonding scheme.

According to C. L. Christ's fourth rule (2), the ulexite polyanions may polymerize into chains by splitting out water. The  $[\text{B}_5\text{O}_7(\text{OH})_4]_n^{2n-}$  chains which have been described in the crystal structure of the related mineral probertite (5) exemplify this rule and confirm the prediction (2) that ulexite,  $\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ , and probertite,  $\text{NaCaB}_5\text{O}_7(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ , would contain the same polyanion. The shortest hydrogen bond (2.58 Å) in ulexite is between a triangle hydroxyl of one polyanion and a tetrahedron hydroxyl of the neighboring polyanion along  $c$ . The probertite chains extend along the  $c$  direction by linking a triangle of one polyanion to a tetrahedron of the next through a common oxygen. Both structurally and chemically, the relationships between the isolated polyanions of ulexite and the chains of probertite are analogous to those previously observed between two calcium borate minerals, meyerhofferite with isolated  $[\text{B}_5\text{O}_8(\text{OH})_5]^{2-}$  polyanions, and colemanite with  $[\text{B}_5\text{O}_{10}(\text{OH})_3]_n^{2n-}$  chains (6). The experimental

evidence therefore supports the transition mechanism embodied in C. L. Christ's fourth rule (2) and for ulexite and probertite, the following equation (7) applies:



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#### Kope Formation (Upper Ordovician): Ohio and Kentucky

Abstract. *Eden-like strata near Maysville, Kentucky, may be correlated with the Eden and lower Fairview formations of Cincinnati. To avoid the name Eden, which has stadial connotation, these rocks are included in the Kope formation, defined as medium-bedded limy shales (mean clastic ratio, 2.5 to 3.8) resting conformably between shaly Point Pleasant limestones (mean clastic ratio, 1.0) and unnamed shaly limestones (mean clastic ratio, 0.5).*

In the Maysville area of Kentucky and Ohio, Edenian and Maysvillian rocks (Upper Ordovician) are divisible into two intergradational lithic units. The lower, dominantly shale, has been correlated with the Eden and lower Fairview (Mount Hope) formations of Cincinnati; the upper, predominantly limestone, includes the lithic and faunal equivalents of the upper Fairview (Fairmount) and McMillan formations of Cincinnati (1). Thus the lower unit of the Maysville area is both Edenian and Maysvillian in age, whereas the upper formation is Maysvillian.