Table 1. Atomic coordinates for ulexite, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$. Triclinic, $P1$: $a = 8.809 \pm 0.02$, $b = 12.86 \pm 0.04$, $c = 6.678 \pm 0.02$ Å, $\alpha = 90°15' \pm 05'$, $\beta = 109°10' \pm 05'$, $\gamma = 105°05' \pm 05'$, cell volume = 687.0 Å^3, $Z = 2$, density (calc.) 1.959 (obs.) 1.955 ± 0.001 g cm^{-3} (*4*).

Atom	Coordinates (in fractions of cell edges)		
	x	*y*	*z*
B_1	0.052	0.200	0.668
B_2	.347	.270	.900
B_3	−.189	.224	.783
B_4	.235	.074	.782
B_5	−.174	.269	.427
O_1	.199	.289	.792
O_2	.102	.106	.620
O_3	−.029	.242	.466
O_4	−.066	.167	.784
O_5	.370	.169	.911
O_6	−.260	.261	.565
$O_7(OH)$	.299	.008	.670
$O_8(OH)$	.159	.006	.929
$O_9(OH)$	−.114	.324	.936
$O_{10}(OH)$	−.318	.147	.836
$O_{11}(OH)$	.478	.360	.002
$O_{12}(OH)$	−.238	.313	.239
$O_{13}(H_2O)$	.144	.210	.222
$O_{14}(H_2O)$	.428	.102	.329
$O_{15}(H_2O)$	.472	.358	.488
$O_{16}(H_2O)$	.191	.479	.187
$O_{17}(H_2O)$	.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, $NaCaB_5O_9 \cdot 8H_2O$, would contain the polyanion $[B_5O_6(OH)_6]^{3-}$, in which two pentaborate triangles are replaced by tetrahedra.

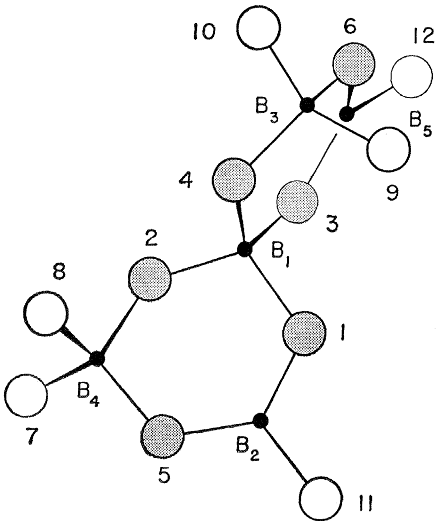

Fig. 1. The $[B_5O_6(OH)_6]^{3-}$ polyanion in ulexite viewed along the *c*-axis. Small black circles represent boron atoms; large shaded circles, oxygen anions; and large open circles, hydroxyl groups. Numbering of atoms conforms to Table 1.

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 $|F_{obs}| > 0$, and the present atomic coordinates are listed in Table 1. The refinement is not expected to change the coordinates by more than ± 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 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 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 $[B_5O_7(OH)_4]_n^{3n-}$ 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, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$, and probertite, $NaCaB_5O_7(OH)_4 \cdot 3H_2O$, 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 $[B_3O_3(OH)_5]^{2-}$ polyanions, and colemanite with $[B_3O_4(OH)_3]_n^{2n-}$ 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:

$$n[B_5O_6(OH)_6]^{3-} = [B_5O_7(OH)_4]_n^{3n-} + nH_2O.$$

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7. We thank W. T. Schaller who supplied crystals of ulexite from Boron, Calif., and C. L. Christ who suggested the study and made many valuable comments. Publication authorized by the director, U.S. Geological Survey.

25 June 1964

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.

Although it would probably be proper to map rocks of the lower formation as Eden in the Maysville area, there are problems in such a procedure that make it inadvisable. That is, the Eden formation of the Cincinnati area is the reference standard for a time-rock division, the Edenian stage, and extension of the name to its approximate lithic equivalent in the Maysville area would erroneously, but inevitably, imply an Edenian age for all the shaly rocks exposed there. Further, although these strata are grossly similar to the Eden formation of Cincinnati, they are somewhat thinner bedded and more calcareous than typical Eden strata.

We propose that the medium-bedded shales and limestones of the lower formation in the Maysville area, which lie beneath distinctly thinner-bedded more calcareous Fairmount and McMillan equivalents and above thin- to medium-bedded shaly limestones of the Point Pleasant formation, be included in the Kope formation. This formation, like other Upper Ordovician units in the Ohio Valley, consists of interbedded, highly fossiliferous gray limestones and shales. Limestones all fall within the classes described by Weiss and Norman (*2*); detrital rocks are mostly shale, but some siltstones and mudstones occur. Most of the shales are less fossiliferous than the limy beds.

The Kope formation is most sharply defined by recording (logging) its mass properties according to the method described by Weiss and Sweet (*3*) and more fully in Weiss *et al.* (*4*). The clastic ratio of the formation is compared with that of bounding units in Table 1 and illustrated in Fig. 1. The dominance of terrigenous detritus in the Kope is clearly expressed, as is the lateral persistence of variations within the formation.

Bedding indexes (*5*) of successive thin units of the upper Kope and superjacent beds are summarized in Table 2 and the right-hand curve of Fig. 1. By the nomenclature of Ingram (*6*) thin beds are 2.5 to 10 cm thick; medium beds, 10 to 30 cm; and thick beds, 30 cm and thicker. Table 2 and log *C′* of Fig. 1 show that the Point Pleasant formation is thin- and medium-bedded and invariably thinner bedded than the basal Kope; that the Kope is prevailingly medium-bedded, with some thin beds; and that beds above the Kope are characteristically thin-bedded. Bedding thickness is thus not

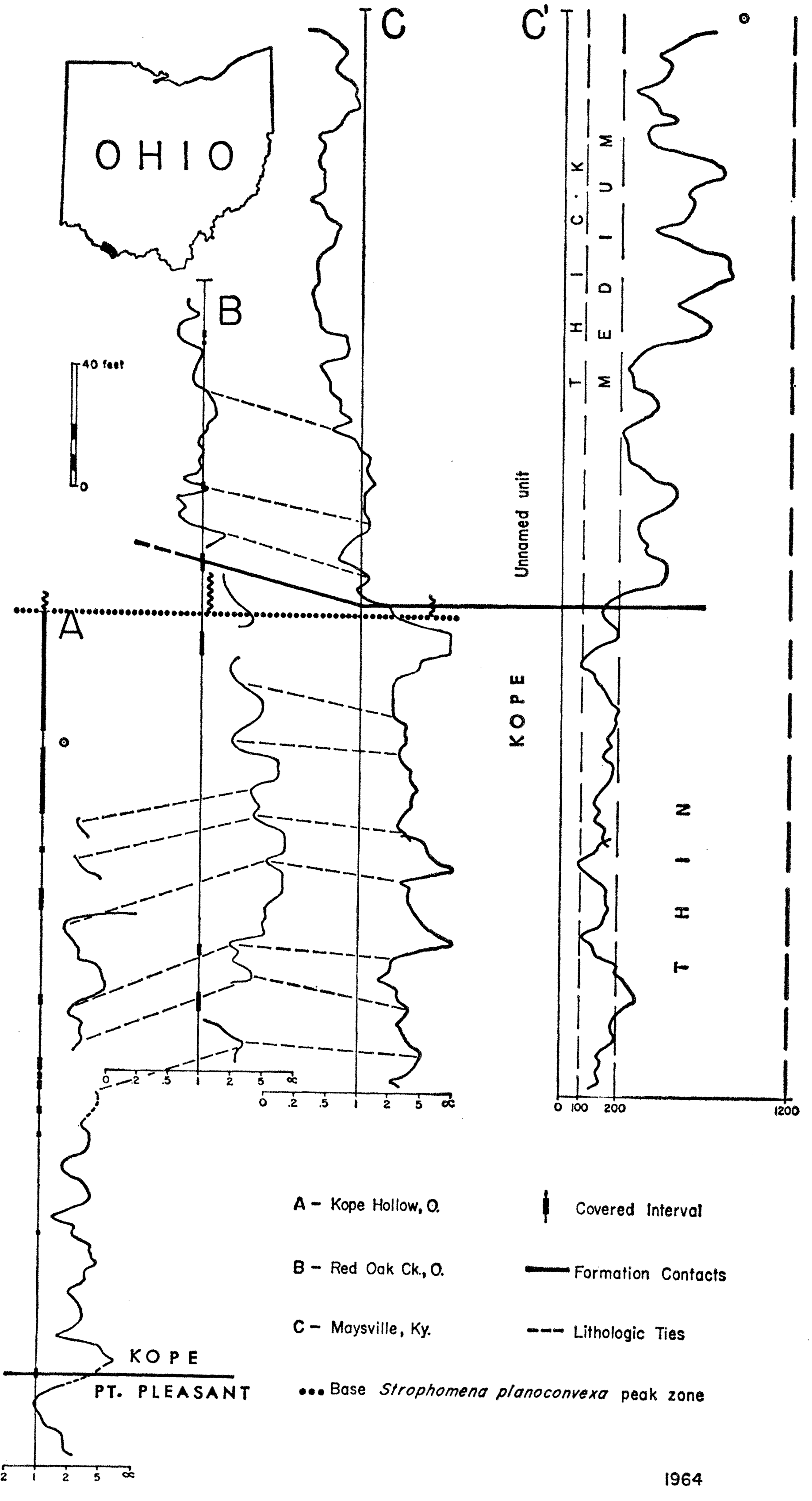

Fig. 1. Moving-average records (logs) of clastic ratios and one of bedding index for three sections, arrayed NW-SE with base of *Strophomena planoconvexa* peak zone as datum. Kope Hollow (log *A*) is at Levanna, Ohio; elevation of base, 151 m. Exposures in Red Oak Creek area (log *B*) are 3.2 km north of Ripley, Ohio; elevation of base, 175 m. Section at Maysville, Kentucky, (logs *C* and *C′*) is in cuts on highways 62 and 68 just south of town; elevation of base, 162 m. Airline distances between sections are: *A–B*, 4.5 km; *B–C*, 14.9 km.

critical for differentiating Kope from Point Pleasant, but it is diagnostic in distinguishing the Kope from beds above it. The smoothed curve of bedding indexes (log *C′*, Fig. 1) shows how sharp and persistent the difference between the two formations is.

The name Kope is taken from Kope Hollow, north of Levanna, Ohio, and largely on the Russellville 7.5-minute quadrangle in Brown County, Ohio. No continuous section of the entire formation is known, but the sections in Fig. 1 yield a composite thickness of 73.5 m and may be considered cotypical sections; the sections in Fig. 1 include both boundaries but are matched solely on lithic qualities. Many incomplete exposures in the area between Levanna (log *A*, Fig. 1) and Maysville (logs *C* and *C′*, Fig. 1) make it clear that the top of the formation slopes southeast from about 224 m above sea level at Levanna to about 209 m at Maysville.

In summary, the Kope formation is a conspicuous unit of Upper Ordovician shale and interbedded limestone in the Maysville area of Kentucky and Ohio; it lies between the Point Pleasant formation and shaly limestones equivalent to the Fairmount and McMillan formations of the Cincinnati section. The upper boundary of the Point Pleasant is conspicuous on clastic ratio logs (log *A*, Fig. 1) and is equally so on outcrop if adjacent beds are exposed. The upper boundary of the Kope is not sharp but is limited to a thin interval on both clastic-ratio and bedding-index logs. It is readily recognized in the field because lithic and bedding characters of the Kope and overlying beds are persistent for many tens of feet away from the contact interval (*7*).

Table 1. Clastic ratios (CR)* of Kope and bounding units.

Formation	Range	Mean
Supra-Kope beds	0.25–1.3 (mostly less than 1)	0.5
Kope: upper 3/5	2.0–∞	3.8
Kope: lower 2/5	1.3–11.0	2.5
Point Pleasant	0.0–2.0 (mostly close to 1)	1.0

* CR = (thickness of shale + mudstone) /thickness of limestone. It is computed for successive 0.9-m units.

Table 2. Bedding indexes (BI)* of Kope and bounding units.

Formation	Range	Mean
Supra-Kope beds	300–830	570
Kope: upper 3/5	100–400	230
Kope: lower 2/5	100–500	300
Point Pleasant	200–500†	300

* BI = (No. of beds per 0.9-m unit × 100)/3.
† Always higher than basal Kope.

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25 June 1964

Libration of Pluto-Neptune

Abstract. *Numerical integration of the orbits of the five outer planets over 120,000 years reveals that the distance between Pluto and Neptune at the closest approaches oscillates within a narrow range. The distance is never much less than the aphelion distance of Pluto from the orbit of Neptune. The near commensurability in the periods of Pluto and Neptune and the eccentricity of Pluto's orbit are responsible for the libratory motion.*

Because the radius of perihelion of Pluto is less than the radius of the orbit of Neptune, the usual Laplace expansion of the disturbing potential diverges. There is also the possibility of an indefinitely close approach. It was therefore proposed by Brouwer (*1*) that the orbit characteristics of Pluto be explored by numerical integration of the equation of motion of the five outer planets over an extended period of time. This has now been done at our laboratory, and almost immediately a remarkable regularity of the orbit of Pluto was revealed.

The integrations were performed on the Naval Ordnance Research Calculator (NORC), a 13-place computer. We used the data of Eckert *et al.* (*2*), and the method of integration that they employed. The integrations, which required about 100 hours of computer time, were run backward from the present to more than 120,000 years ago. This length of time represents some 750 revolutions for Neptune and approximately 500 revolutions for Pluto.

Some remarks are in order on the numerical strength of the results. Double precision accumulation of the first and second sums was used to enhance the precision of the computation. The energy and angular momentum were monitored and never differed from the value at epoch by more than two parts in 10^{10}. This corresponds to a theoretical standard deviation of 10^{-5} radians in the phase of Jupiter and of 10^{-10} radians in the phase of Pluto at the end of the integration. Methods of error analysis are given in (*2*) and (*3*).

It may be recalled that the orbit of Neptune is nearly circular with a radius of 30 AU (astronomical units), while the orbit of Pluto is rather eccentric, with a radius of perihelion of just under 30 AU and a radius of aphelion of 50 AU. The mass of Neptune is about 20 times that of Pluto. The orbit of Pluto is inclined 15 degrees to that of Neptune with the perihelion of Pluto 114 degrees in advance of the ascending node.

In the course of the integrations, the geometrical relations between Pluto and Neptune were observed. A libration of the relative positions of the two planets at the close approaches was observed which has a period of about 19,670 years. It is best described geometrically by considering the path of Pluto in a frame centered at the Sun and rotating with Neptune. This is shown in Fig. 1 for one synodic cycle. In that time Pluto passes through two perihelia and two aphelia. The path is almost periodic. At one extremum of the libration, Neptune is positioned with respect to the path as shown by one of the N's in Fig. 1. At the other extremum, it is positioned at the other N. In the course of the libration, Neptune moves with respect to the synodic path back and forth on the 76-degree arc between the two N's. The loops in the path of Pluto are due to the eccentricity of the orbit and to the consequently varying angular rate about the Sun. It is noted that in each synodic period there are three minima of the distance between Pluto and Neptune. Two are when Pluto is near each of the loops at the perihelia and the third is near one of the aphelia. In the course of the librations, the minima near the perihelia