noctilucent clouds observed by the authors, now amounting to seven over the past 6 months, would appear to be an unusual situation if the clouds were natural ones, even considering the unusual atmospheric transparency of the desert air of southern Arizona. Noctilucent clouds are normally rare phenomena restricted to the high latitudes during the summer months (*2*, *3*), and the occurrence of even a single one at low latitudes would be most unusual. It is interesting to note that the computed altitude of the noctilucent cloud of 15 June 1963 is 71 km, rather close to the average height of 82 km observed for natural noctilucent clouds (*2*) observed at the latitude of Oslo.

The association of these clouds with the vicinity of southern California provides a simple explanation for their appearance, as may be demonstrated by consideration of the cloud of 15 June 1963. On each day that a noctilucent cloud has appeared, including the day on which McDonald's ring cloud was seen, there has also been a launching of a space vehicle from the Pacific Missile Range at Vandenberg Air Force Base in southern California. The intensity of the other noctilucent clouds was not usually comparable with the one of 15 June 1963, but the launching during the afternoon of 15 June was of a solid-propellant "Scout" vehicle, which produces an exhaust cloud which is much more conspicuous than that produced by the more frequent Thor-Agena launches from that range. When coupled with the drift vector shown on Fig. 3, the cloud would appear to have originated from the approximate vicinity of the Pacific Missile Range about 5 hours before the time of occultation, which was at 8:51 P.M. M.S.T. We therefore feel that the intense noctilucent cloud of 15 June 1963 was the exhaust cloud from a Scout vehicle illuminated by sunlight after local sunset in Tucson.

As for the way in which these noctilucent clouds are produced, the altitude of 71 km indicates that they may be formed in the manner of natural noctilucent clouds, at the sharp thermal minimum that occurs in the atmosphere at the 80-km region. The formation of this cloud could have been caused by the injection from the Scout rocket exhaust of water vapor alone or in combination with solid particles. The additional water vapor could be sufficient to saturate the air at the thermal minimum and produce condensation upon the solid particles.

ADEN B. MEINEL
BARBARA MIDDLEHURST
EWEN WHITAKER
Steward Observatory and
Lunar and Planetary Laboratory,
University of Arizona, Tucson

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17 July 1963

Boron-Oxygen Polyanion in the Crystal Structure of Tunellite

Abstract. *The crystal structure of tunellite, $SrO \cdot 3B_2O_3 \cdot 4H_2O$, with infinite sheets of composition* $n[B_6O_9(OH)_2]^{2-}$, *has cations and water molecules in the spaces within the sheets. Adjacent sheets are held together by hydrogen bonding through the water molecules. The boron-oxygen polyanions provide the first example in hydrated borate crystals of one oxygen linked to three borons.*

A new kind of boron-oxygen polyanion (Fig. 1) has been found in the crystal structure of the mineral tunellite (*1*), $SrO \cdot 3B_2O_3 \cdot 4H_2O$. The polyanion is made up of three boron-oxygen tetrahedra and three triangles. These coordination polyhedra are joined by sharing corners so that one oxygen is common to all three tetrahedra and becomes the central point of three six-membered boron-oxygen rings, each ring constructed from two tetrahedra and one triangle. Considerable energetic stability must be associated with this kind of ring, first discovered in colemanite (*2*), $CaB_3O_4(OH)_3 \cdot H_2O$, and later found to be present in all members (*3*) of the series $2M^{2+}O \cdot 3B_2O_3 \cdot xH_2O$. In isolated form the present polyanion would have the formula $[B_6O_7(OH)_6]^{2-}$, but in tunellite individual polyanions are linked at corners to form infinite sheets of composition $n[B_6O_9(OH)_2]^{2-}$.

The polyanion provides the first example in any hydrated borate crystal structure of one oxygen linked to three boron atoms. Such a linkage was reported by Berger (*4*) for B_2O_3, in which each boron-oxygen tetrahedron shares each of three corners with two other tetrahedra, and a fourth corner with one other tetrahedron. The proposed structure was, however, determined from x-ray diffraction powder data only and has not been re-examined by modern techniques. The three B-O distances to the triply linked oxygen in the tunellite structure are 1.48, 1.51, and 1.54Å (all ± 0.04Å), slightly longer than the usual average tetrahedral B-O distance (*3*) 1.47Å. The average of three B-O-B angles around this oxygen is 119.7° compared with the usual average B-O-B ring angle (*3*) between tetrahedra, 121.9°.

Rules governing the nature of the polyanions in hydrated borates have been proposed by Christ (*5*) and by Edwards and Ross (*6*). The present polyanion is in accord with the four rules given by Christ, although it is not composed of one tetrahedron and two triangles as predicted by him for the $M^{2+}O \cdot 3B_2O_3 \cdot xH_2O$ compounds. However, the present polyanion contradicts the first postulate stated by Edwards and Ross. This postulate requires that the ratio of tetrahedral boron to total boron (3:6 in tunellite) be equivalent to the ratio of cation charge to total boron (2:6 in tunellite). Similar considerations have also been proposed by Krogh-Moe (*7*). Coordination of one oxygen to three borons invalidates this postulate, and the possibility of such coordination must be taken into account in future theories concerning borate structures.

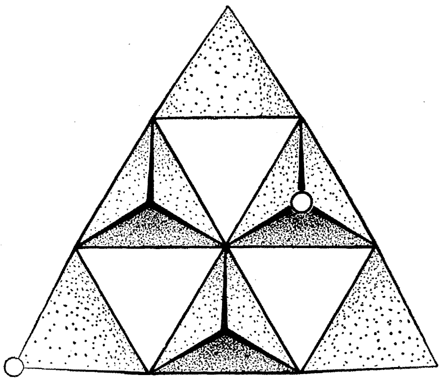

Fig. 1. An idealized view of the $[B_6O_9(OH)_2]^{2-}$ polyanion in tunellite, $SrO \cdot 3B_2O_3 \cdot 4H_2O$. Circles denote hydroxyl oxygens; all other oxygens are linked to more than one boron. If the polyanion occurred isolated, the terminal oxygens would each attach a proton, according to Christ's third rule (*5*), and the formula would become $[B_6O_7(OH)_6]^{2-}$.

Table 1. Crystallographic data (*1*) for tunellite monoclinic, $P2_1/a$: $a = 14.36 \pm 0.05$ Å; $b = 8.19_8 \pm 0.02$ Å; $c = 9.93_0 \pm 0.02$ Å; β (monoclinic angle) = 113° 55′ ± 10′; cell volume, 1068 Å^3; cell contents $Z = 4[SrO \cdot 3B_2O_3 \cdot 4H_2O]$; density, calc. 2.39 g cm^{-3}, obs. 2.40 ± 0.01.

Atom	Atomic coordinates		
	x/a	*y/b*	*z/c*
Sr	0.162	0.056	0.195
O_1	.194	.025	.952
O_2	.203	.038	.482
O_3 (OH, *)	.050	.681	.426
O_4 (H_2O)	.998	.168	.238
O_5 (OH)	.090	.536	.172
O_6	.242	.799	.399
O_7	.208	.341	.340
O_8	.238	.785	.081
O_9	.194	.350	.101
O_{10}	.089	.212	.773
O_{11}	.087	.210	.534
O_{12} (H_2O)	.021	.840	.068
O_{13} (H_2O)	.139	.580	.712
O_{14} (to 3 B)	.227	.083	.734
B_1	.194	.151	.849
B_2	.194	.156	.585
B_3 (*)	.043	.248	.625
B_4	.187	.455	.220
B_5 (*)	.253	.389	.486
B_6 (*)	.251	.388	.022

* Atom of B-O triangle.

A study of the crystal structure of tunellite is nearing completion. The crystallographic data and atomic coordinates are listed in Table 1. The residual factor is 0.11 for about 1200 three-dimensional data with $|F_{obs}| > 0$. The structural formula for tunellite is $SrB_6O_9(OH)_2 \cdot 3H_2O$, and the polyanion probably exists, either in the present form or modified according to Christ's rules, in other members of the $M^{2+}O \cdot 3B_2O_3 \cdot xH_2O$ series. In particular, nobleite (*8*), $CaO \cdot 3B_2O_3 \cdot 4H_2O$, is isostructural with tunellite and hence must be $CaB_6O_9(OH)_2 \cdot 3H_2O$ (*9*).

JOAN R. CLARK

U.S. Geological Survey,
Washington 25

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9. I thank my colleagues at the U.S. Geological Survey: R. C. Erd, for crystals of tunellite; D. E. Appleman, who gave much time to solution of associated computer problems and to discussion; M. Ross, who prepared Fig. 1; and C. L. Christ, who suggested the study. Publication was authorized by the director, U.S. Geological Survey.

8 August 1963

Apatite: Origin of Blue Color

Abstract. *The optical absorption and emission spectra of natural blue apatite are similar enough to spectra of synthetic compounds containing MnO_4^{-3} to conclude that the blue color of natural apatite results from the presence of this ion.*

The origin of the blue color in natural apatites has been the subject of investigation by chemical, optical, and electron-spin resonance techniques. None of this work has resulted in the unambiguous identification of the impurity or defect responsible for the blue color, which has been variously attributed to $O^=$ replacing two halide ions (*1*), to Mn^{+3} (*2*), or to an electron in a halide vacancy (*3*). In this report we present evidence that the blue color of apatite, obtained from the Hugo mine in Keystone, South Dakota, results from the presence of MnO_4^{-3}. The color of these samples is bleached at temperatures above 500°C as is the color in samples from other sources (*4*).

Prener and Kingsley (*5*) have recently found that single crystals of various calcium halophosphates (containing manganese) are blue when grown under suitable conditions. They grew single crystals of calcium chlorspodiosite (Ca_2PO_4Cl), calcium chlorapatite [$Ca_5(PO_4)_3Cl$], and fluorchlorapatite by slow cooling from a $CaCl_2$ melt containing $MnCl_2$ in an oxygen-containing atmosphere. Chemical analysis, optical absorption, and fluorescence studies showed that the blue color was due to the presence of MnO_4^{-3} ions, probably at PO_4^{-3} sites. Similar fluorescence was obtained from some light blue manganese-containing fluorapatite crystals grown by the Czochralski technique by P. D. Johnson (*6*). The optical absorption spectra of a number of materials containing MnO_4^{-3} are shown in Figs. 1 and 2. The marked similarity of the absorption spectra of MnO_4^{-3} in various environments to that of the blue natural apatite strongly suggests that MnO_4^{-3} ions are responsible for the blue color in the natural mineral. The very strong absorption in Fig. 1*a* at wavelengths below 3500 Å and the fact that the minimum at about 4500 Å does not go to zero is probably due to other impurities. The infrared fluorescence at 78°K observed by excitation in the visible absorption bands of the various compounds containing MnO_4^{-3} is compared with that observed in natural blue apatite in Fig. 3. Phosphors were excited by light from a tungsten lamp filtered by a $CuSO_4$ solution. The spectra are not corrected for sensitivity of the detection system. Again the similarity in the infrared fluorescence indicates the presence of MnO_4^{-3} in natural blue apatite. Assuming the same oscillator strength for the visible absorption band in the two cases shown in Figs. 1*a* and 2*b*, we calculate that the concentration of MnO_4^{-3} is ap-

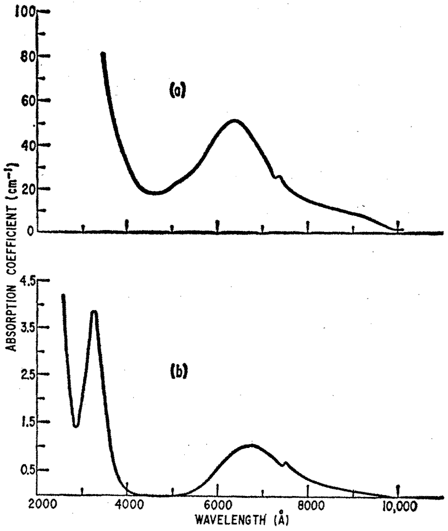

Fig. 1. Absorption spectra at 298°K. *a*, Blue apatite from Hugo mine in Keystone, South Dakota. *b*, Solution of MnO_4^{-3} in 12*M* KOH.

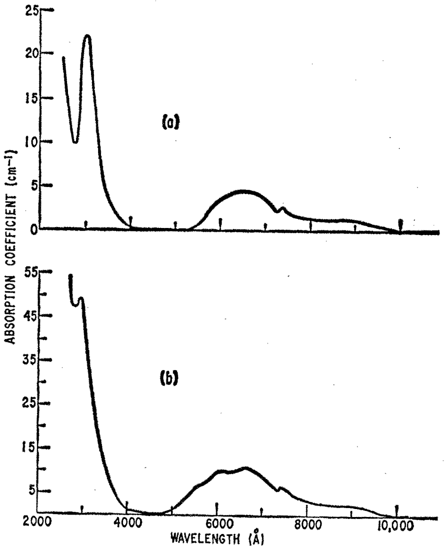

Fig. 2. Absorption spectra at 298°K. *a*, $Ca_5(PO_4)_3(Cl,F)$:MnO_4^{-3}. *b*, $Ca_5(PO_4)_3Cl$:MnO_4^{-3}; concentration of MnO_4^{-3} is 1.1×10^{19} cm^{-3}.