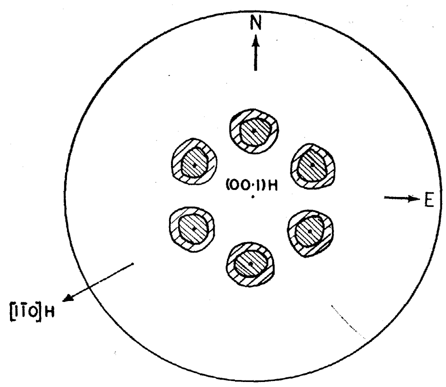

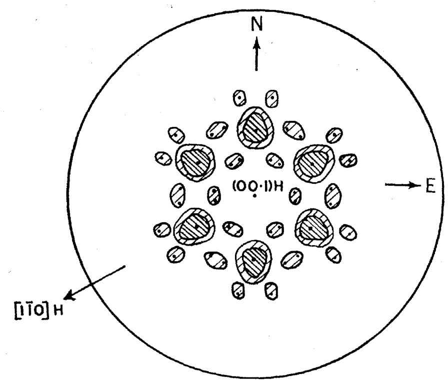

Fig. 1 (left). (210) Pole figure of magnetite on the basal plane of hematite reduced by thermal dissociation. Points represent ideal (210) pole positions. The actual measurements in both figures were limited to the area bounded by the longitudes 72°W and 18°E and by the latitudes 50°N and 34°S. The remainder of each figure was constructed from symmetry. Fig. 2 (right). (210) Pole figure of magnetite on the basal plane of hematite reduced by carbon monoxide. Points represent ideal (210) pole positions. See legend to Fig. 1.

In orientation II, the close-packed oxygen layers of magnetite are thought to be derived from highly distorted versions of close-packed oxygen layers which are perpendicular to the directions [100], [010], and [1̄1̄0] in hematite.

We believe that the double orientation observed on the second crystal has an important bearing on the kinetics of the reduction of iron oxide ores to metallic iron. Starting with hematite, the steps in the reduction, for temperatures above 570°C, are:

$$\underset{\alpha\text{-}Fe_2O_3}{\text{Hematite}} \longrightarrow \underset{Fe_3O_4}{\text{Magnetite}} \longrightarrow \underset{FeO}{\text{Wüstite}} \longrightarrow \text{Fe.}$$

Since, compared to hematite, magnetite is already partially reduced, it is somewhat surprising that hematite ores generally become reduced to metallic iron more rapidly than magnetic ores. Bitsianes and Joseph (*6*), in commenting on this apparent contradiction, have pointed out, among other possible factors, the importance of "grain refinement" (grain size diminution) which accompanies the conversion of hematite to magnetite. According to them, grain refinement would be enhanced by the relatively drastic rearrangement in the crystal structure that must take place in the transition from the hexagonally close-packed oxygen arrangement in hematite to the cubic close-packed arrangement in magnetite. There would, of course, be a similar mechanism operating during the conversion of magnetite to wüstite. However, since the wüstite structure is also based on a cubic close-packed oxygen framework, the rearrangement in the crystal structure is not so drastic and the degree of grain refinement would be expected to be much less. The larger surface area accompanying grain refinement increases the overall reaction rate by increasing the frequency factor in the Arrhenius expression.

The two orientations of magnetite reported here provide a definite mechanism for grain refinement. Neighboring magnetite crystallites growing in different orientations would meet and be mutually terminated over structurally incompatible surfaces. On the other hand, if only one orientation were possible, neighboring crystallites could join over compatible surfaces and grow into a single larger crystal.

We cannot say that our failure to observe orientation II in the crystal reduced by thermal dissociation is proof that the double orientation does not exist in this case. The very thin layer of magnetite may simply contain too little of orientation II to be observed (*7*).

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2. The structure of hematite is referred to hexagonal axes in this paper. The direction [*uvw*] in the hexagonal system is the direction of the vector $u\vec{a}_1 + v\vec{a}_2 + w\vec{c}$.
3. J. W. Gruner, *Econ. Geol.* **21**, 375 (1926).
4. The crystals were from the O'Keefe Lake area, Quebec.
5. See for example: H. S. Peiser, H. P. Rooksby, A. J. C. Wilson, *X-ray Diffraction by Polycrystalline Materials* (Institute of Physics, London, 1955), chap. 21.
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7. Supported by the Institute of Mineral Research at the Michigan College of Mining and Technology. We thank M. E. Volin, director of the institute, for acquainting us with this problem and for his aid and advice. We thank W. A. Hocking for carrying out the reductions and for many valuable suggestions.

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5 July 1963

Low-Latitude Noctilucent Cloud of 15 June 1963

Abstract. *A bright noctilucent cloud was observed and photographed northwest of Tucson on 15 June 1963. Results of computations indicate that the cloud was at a height of 71 kilometers. The cloud appears to have resulted from the launching of a Scout space vehicle.*

Sun-illuminated clouds have reportedly been seen near the end of twilight in the northwesterly direction from Tucson, Arizona, upon a number of occasions and by numerous persons, including the authors. In particular, the ring-shaped cloud reported by McDonald (*1*) has been the most spectacular of the group up to date. Since the term "noctilucent cloud" has evolved to refer to a rare type of natural cloud observed only at high latitudes, we wish to extend the use of this term to any cloud that remains illuminated by the sun near the end of astronomical twilight, regardless of latitude or possible origin of the cloud.

On the evening of 15 June 1963, another unusually bright noctilucent cloud appeared in the northwestern sky (Figs. 1 and 2). The cloud persisted in full sunlight until 8:37 P.M. Mountain Standard Time (M.S.T.) and was fully occulted by sunset at 8:51 ± 0.5 minutes M.S.T. as noted by Middlehurst. The correction to local time to give mean solar time is +24 minutes at Tucson and the equation of time is negligible on 15 June so that the meridian passage of the center of the sun's disk occurred at 12:24 M.S.T. The angle to the cloud above the horizon at occultation was 4.5 degrees apparent angle. These parameters, after correction for refraction by the terrestrial atmosphere, yield a height of 71 km (44 miles) for the cloud and a range of 555 km (345 miles) in a direction 40 degrees north of west from Tucson. The location of the cloud is shown in

Fig. 3. No reports of clouds at normal altitudes over the Pacific have been obtained and meteorological conditions over California at this time of year generally are consistent with complete absence of cloud, other than ocean fog, for at least 1000 miles over the ocean. Consequently, we have not corrected the time of sunset either for the presence of a cloud layer or for atmospheric screening, both of which would tend to slightly increase the height of the cloud.

The orientation of the cloud in azimuth was deduced from the appearance of the cloud at occultation. The first portion of the cloud to dim was the southern end of the well-defined streak, followed by the lower diffuse region. If the cloud were at a constant elevation for the upper streak, and if the cloud were oriented in a north to south direction, then the southern portion would dim much sooner than the northern, since the azimuth of the sun was 50 degrees north of west. If the azimuth of the streak were normal to the solar azimuth then the entire length would have dimmed at about the same time; in fact, the southern end began to fade out at 8:37 P.M., 14 minutes before the time of total disappearance of the cloud. We therefore feel that the orientation shown in Fig. 3 is a reasonable assumption based upon these observations, although the assumption of a constant height of the streak may not be valid. In the event of the southern end of the streak being at a higher altitude than the northern end, then the azimuth of the cloud would move into closer alignment with the north to south direction.

Visibility of the cloud was noted from about 8:05 P.M. The cloud was not visible earlier in twilight since Meinel, only a few minutes before 8 P.M., had noted the excellent clarity of the western horizon and the complete absence of clouds or haze streaks. He was therefore rather surprised to see the conspicuous cloud upon looking at the sky again at 8:05 P.M. We therefore conclude that the cloud had a low surface brightness and was only made conspicuous by contrast with the increasing darkness of the twilight sky.

Photographs of the cloud were taken on Kodachrome film; two were obtained by Whitaker and four by Meinel. Those taken by Meinel were measured for the velocity of the apparent drift. The fact that the cloud was drifting eastward was noted by the authors when the photographs were made. Measurement by Meinel yielded a velocity of angular drift in the direction of the zenith of 0.016 rad/hr and parallel to the horizon of 0.026 rad/hr. We used the height and range, derived by Middlehurst from the occultation time, to find that the velocity components at the point measured (shown by the position of the vector in Fig. 3) were 22 km/hr northward and 66 km/hr eastward. The direction of the velocity vector is well determined, while our measurement of the actual speed depends critically on the times at which the photographs were taken and these are known only to a few minutes accuracy.

The frequency of occurrence of

Fig. 1 (top left). Southern portion of the noctilucent cloud of 15 June 1963, photographed from Tucson, Arizona, by Ewen Whitaker.

Fig. 2 (top right). Central and northern portions of the noctilucent cloud after onset of occultation of the southern end, photographed by A. B. Meinel. Doubling of images is due to errors in pointing of the camera during exposure.

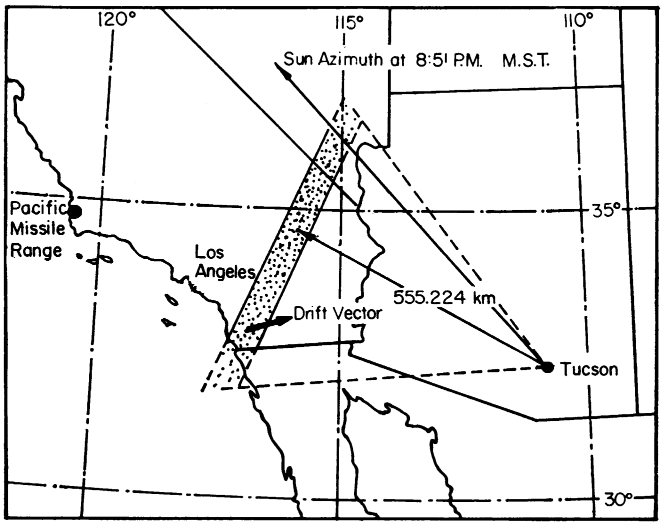

Fig. 3 (right). Apparent location of the low-latitude noctilucent cloud of 15 June 1963 observed by Meinel, Middlehurst, and Whitaker.

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.

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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.

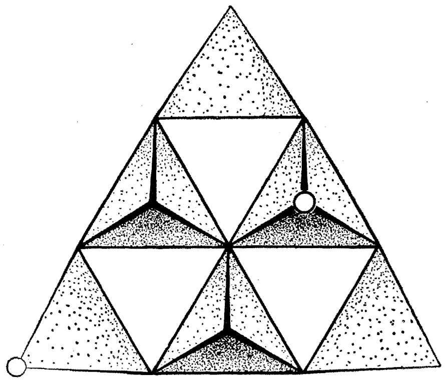

Fig. 1. An idealized view of the $[B_6O_9(OH)_2]^{2-}$ polyanion in tunellite, $SrO\cdot 3B_2O_3\cdot 4H_2O$. Circles denote hydroxyl oxygens; all other oxygens are linked to more than one boron. If the polyanion occurred isolated, the terminal oxygens would each attach a proton, according to Christ's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