

Osbornite, meteoritic titanium nitride.

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[Read January 23, 1941.]

NEVIL STORY-MASKELYNE described in 1870 the mineral constituents of the Bustee meteorite, which was observed to fall in 1852 near Bustee about 45 miles west of Goruckpur, India.¹ The stone, weighing 1429 grams, now preserved in the British Museum collections, was found to consist chiefly of enstatite and diopside, and two constituents proved to be new minerals. Pale, chestnut-brown spherules of calcium sulphide, CaS, Story-Maskelyne named oldhamite² and golden-yellow octahedra found embedded chiefly in the oldhamite he named osbornite. One side of the meteorite has been ground to reveal the nodules of oldhamite and a coloured lithograph in W. Flight's book 'A chapter in the history of meteorites' reproduces the appearance of the chief mineral constituents very well.³ The minute octahedra of osbornite are easily visible with a lens in the meteorite itself.

Two chemical analyses of oldhamite, involving the solution of nearly a gram of that mineral in hydrochloric acid, left a residue of only 28 milligrams of the osbornite crystals, an amount too small in those days for a complete chemical analysis. Qualitative tests, however, seemed to have convinced Story-Maskelyne and Flight that osbornite contained calcium, sulphur, and titanium or zirconium, and they drew the rather odd conclusion that perhaps it was an oxysulphide of calcium, titanium, and/or zirconium. Story-Maskelyne was using the microscope for separating out the components of coarsely crushed meteorites, then a novel procedure, and sometimes yielding only very small samples of any one constituent for subsequent study. The manipulation of a few tiny crystals and minute precipitates seventy years ago was no mean achieve-

¹ N. Story-Maskelyne, Phil. Trans. Roy. Soc. London, 1870, vol. 160, p. 189; Proc. Roy. Soc. London, 1870, vol. 18, p. 146.

² N. Story-Maskelyne, Rep. Brit. Assoc. Adv. Sci., 1863, for 1862 (32nd meeting, Cambridge), Trans. of Sections, p. 190. Preliminary note on the Bustee meteorite, with the first mention of the name oldhamite.

³ W. Flight, London, 1887, p. 118; reprinted from Geol. Mag. London, 1875, dec. 2, vol. 2, p. 408, plate facing p. 401.

ment and mistakes were bound to occur. Probably Story-Maskelyne was not at all satisfied with his results for osbornite, but fortunately he refrained from using further material so rare and limited in supply. Since then osbornite has not been reported from any other meteorite and there can be only a minute amount in the Bustee stone itself.

In view of the difficulties which attended micro-chemical work in 1870 it would be unwise to show how the qualitative data published by Story-Maskelyne could have been differently interpreted. He did, however, publish two figures, the initial weight of osbornite analysed, viz. 28 milligrams and the weight 0.8 milligram of barium sulphate precipitated by barium chloride from the sublimate resulting from heating the crystals in a stream of chlorine. These figures correspond to only 4 % of sulphur so that sulphur can scarcely be one of the chief elements present. The same remark applies to calcium whether combined as sulphide or oxysulphide.

Story-Maskelyne had no difficulty in establishing the true symmetry of osbornite. He measured the interfacial angles of several crystals and found them all to be regular octahedra. It seemed to me probable that if the symmetry were cubic then an X-ray photograph might give additional information, perhaps a simple clue to the chemistry of the mineral. A crystal measuring $1/10$ mm. across was picked out from one of the oldhamite spherules and rotated about an octahedral edge. The patterns obtained from this and another crystal rotated about a [111] axis revealed that osbornite has a cubic face-centred lattice with cell-edge 4.235\AA . On consulting tabulated cell-edges of cubic substances¹ it seemed likely that artificial titanium 'cyanonitride' with rock-salt structure and cell-edge 4.24\AA . should yield the same type of X-ray photograph as osbornite. This was readily confirmed by photographing several specimens of so-called titanium 'cyanonitride' in the British Museum collections. This compound is found in slags and bears from blast furnaces either singly or in groups of sharp copper-coloured cubes up to several millimetres across in a matrix of green slag often with abundant graphite. Both osbornite and the titanium 'cyanonitride' have a metallic lustre and excepting the darker colour of the latter certainly show a marked resemblance as well as yielding closely similar X-ray patterns. Flight² himself knew of the existence and appearance of titanium 'cyanonitride' and it was unfortunate that his

¹ I. E. Knaggs and B. Karlik, Tables of cubic crystal structure of elements and compounds. London, 1932, p. 30. [M.A. 5-171.]

² Footnote on p. 120 of his book, but not in Geol. Mag. (loc. cit.).

own qualitative tests suggested zirconium rather than titanium as a constituent of osbornite.

Entirely satisfactory confirmation of the presence of titanium in osbornite was obtained by further X-ray and qualitative chemical tests. Titanium 'cyanonitride' is known to change to titanium dioxide when heated in air.¹ A crystal fragment of titanium 'cyanonitride' was first heated to about 850° C. The sharp cube edges and corners were found to be rounded after this treatment. Under the microscope the original cube faces were seen to be polycrystalline and the X-ray photograph showed that the compound had altered to oriented rutile. A crystal of osbornite was subjected to the same treatment. The tiny octahedron also lost its sharp edges and developed polycrystalline surfaces. Moreover, the metallic lustre and golden colour were replaced by a translucent pale yellow appearance. This altered crystal yielded a rutile pattern and when crushed in methylene iodide gave birefringent fragments with no trace of any other component. The specific gravity of the rutile pseudomorph is 4.10, very close to the lowest values for rutile, 4.123, given in L. J. Spencer's tables.² The X-ray pattern, specific gravity, and microscopic tests of the rutile pseudomorph after osbornite show that titanium is the chief metal present in the original mineral. Dr. M. H. Hey produced some equally convincing colour reactions for titanium from four crystals of osbornite and has further shown that neither calcium nor sulphur can be detected. It is not unlikely that both these elements found by Flight were due to contamination of the osbornite with a very small amount of oldhamite.

Since there is insufficient osbornite available for a complete chemical analysis, Dr. Hey hopes later to make an approximate micro-chemical analysis. In the absence of a direct determination of nitrogen and carbon the cell-edge measurement and colour identify osbornite almost certainly with titanium nitride. The identification depends upon a considerable amount of previous work which has been carried out upon titanium 'cyanonitride' and the two end-members of the series titanium nitride-titanium carbide, to which it belongs.

W. H. Wollaston,³ in 1823, published some interesting data on crystals from the slag of iron works at Merthyr Tydfil. He described them as cubes like pyrite with the lustre of burnished copper, specific gravity 5.3, which scratched quartz and possessed a high electrical conductivity.

¹ F. Wöhler, *Annalen der Chemie und Pharmacie*, 1850, vol. 73, p. 34.

² L. J. Spencer, *Min. Mag.*, 1927, vol. 21, pp. 356 and 364.

³ W. H. Wollaston, *Phil. Trans. Roy. Soc. London*, 1823, p. 17.

He was probably the first to recognize the metallic-like properties of the substance and for that reason he wrongly identified it as metallic titanium. F. Wöhler (1850, loc. cit.) first analysed similar material from a blast furnace in the Harz Mountains, and found that intimate intergrowth with graphite made complete separation from the latter difficult. His analysis in table I gives the content of carbon in titanium 'cyanonitride' as 3.64 % and he is responsible for the formula Ti_3CN_4 generally found in the literature. E. A. Rudge and F. Arnall¹ separated similar material from slag from a blast furnace converting Spanish haematite ore to pig-iron. They took especial care to free the titanium 'cyanonitride' from graphite by powdering finely in an agate mortar, passing through a 120-mesh sieve, then treatment with HCl to remove iron and HF to remove SiO_2 , after which the bulk of the graphite was removed by flotation in a heavy liquid of specific gravity 3. In this way they found that the carbon content was up to 1 % (see table I), whereas clean crystals of the 'cyanonitride' visibly free of graphite gave carbon contents up to 3.4 %. V. M. Goldschmidt² published the first X-ray measurements on titanium 'cyanonitride' (Wöhler's material) and showed that the substance possesses the rock-salt type of crystal-structure. This material gave the cell-edge dimension 4.243Å. Four specimens of titanium 'cyanonitride' from various blast-furnace slags now preserved in the British Museum collections have been X-rayed with a view to determining whether there is any appreciable variation in cell-edge dimensions. Three of the four specimens have a cell edge 4.24Å. and one gave 4.23Å. Since the error due to film shrinkage, &c. is approximately $\pm 0.01\text{Å}$, within these limits it can be said that specimens of titanium 'cyanonitride' from different slags have the same unit-cell dimensions.

Specimens of artificial titanium nitride and titanium carbide have also been photographed and give cell-edge values close to those reported by previous workers (tables II and III). The titanium nitride specimen prepared by A. E. van Arkel's method,³ in which titanium chloride and nitrogen interact and form a deposit on a thin tungsten filament, is a pale-golden polycrystalline rod $\frac{1}{2}$ mm. in diameter giving a 4.23Å., whereas a sample of black minutely crystalline titanium carbide gives a 4.31Å. It is probable, therefore, from Rudge and Arnall's work and

¹ E. A. Rudge and F. Arnall, Journ. Soc. Chem. Industry, Trans., 1928, vol. 47, p. 376.

² V. M. Goldschmidt, Nachrichten Gesell. Wiss. Göttingen, Math.-Physikal. Kl., 1927, p. 390.

³ A. E. van Arkel and J. H. de Boer, Zeits. Anorg. Chem., 1925, vol. 148, p. 345.

TABLE I. Chemical analyses of titanium 'cyanonitride', &c.

	1.	1a.	2.	2a.	3.	4.	4a.	5.
Ti ...	77.26	1.613	76.7	1.602	77.36	76.864	1.605	78.54
N ...	18.30	1.307	22.4	1.599	22.64	10.545	0.753	11.49
C ...	3.64	0.303	1.0	0.083	—	9.741	0.812	9.97
Graphite ...	0.92	—	—	—	—	1.550	—	—
Cell edge ...	4.243Å.	—	—	—	—	4.27Å.	—	—

1. Titanium 'cyanonitride' from an 80-lb. bear from a furnace in Rübeland, Harz Mts. F. Wöhler, 1850. Total 100.12.
- 1a. Calculated atomic proportions of no. 1. Molecular proportions of N and C add to 1.610 close to the titanium figure. This does not suggest that any graphite has been determined as combined carbon.
2. Titanium 'cyanonitride' = titanium nitride, from a blast furnace. E. A. Rudge and F. Arnall, 1928. Total 100.2, including Fe, Ca, Mg, 0.1.
- 2a. Calculated atomic proportions of no. 2, suggesting that either the nitrogen content is too high or that the carbon figure still includes graphite.
3. Theoretical composition of titanium nitride, TiN.
4. Cochranite = titanium carbonitride from Cleveland iron works. J. E. Stead, 1918. Total 98.927, including Fe 0.200, S 0.027, and Mn, Si traces.
- 4a. Calculated atomic proportions of no. 4, which suggest a deficit in N or C or both.
5. Theoretical composition of Ti₂CN.

from the X-ray measurements that titanium 'cyanonitride' is very close to pure titanium nitride and that although the carbon content may vary from one specimen to another it is not greater than 1 %.

Titanium nitride occurs not only in the slags and bears from blast furnaces, but has also been found in residues from acid solution of pig-iron and ferro-manganese. T. W. Hogg¹ described cubes and octahedra between 25 and 250 μ in size present in ferro-manganese and pointed out that although 1 c.c. of the metal contained about half a million crystals the maximum percentage by weight of the titanium compound was only 0.032. His description, however, does not provide any evidence for the existence of mixed crystals or solid solutions between titanium nitride and carbide. W. Hofmann and A. Schrader² who separated steel-grey cubes of titanium carbide from cast-iron bearing 5.1 % Ti noted particularly that they had not obtained a mixed carbide-nitride of titanium.

It is of some interest, therefore, that a re-examination of J. E. Stead's³ cochranite, now preserved in the British Museum collections,

¹ T. W. Hogg, Rep. Brit. Assoc. Adv. Sci., 1894, for 1893 (63rd meeting, Nottingham), p. 721.

² W. Hofmann and A. Schrader, Archiv für das Eisenhüttenwesen, 1936, vol. 10, p. 65. (See table II for their X-ray data.)

³ J. E. Stead, Journ. Iron and Steel Inst. London, 1918, vol. 97, p. 171. Min. Mag. 1919, vol. 18, p. 376. [M.A. 1-231.]

TABLE II. Cell-edge measurements of titanium nitride and carbide.

	1.	2.	3.	4.	5.	6.	7.	8.
TiN	4.40	4.23	—	—	—	—	4.225	4.23
Ti(N,C)	—	—	4.243	—	—	—	—	4.23 to 4.24
Ti ₂ CN	—	—	—	—	—	—	—	4.27
TiC	4.60	4.29	—	4.31	4.311	4.320	4.315	4.31

1. K. Becker and F. Ebert, *Zeits. Physik*, 1925, vol. 31, p. 268; their values are too high.
2. A. E. van Arkel, *Physica*, Eindhoven, 1924, vol. 4, p. 286.
3. V. M. Goldschmidt, 1927; F. Wöhler's titanium 'cyanonitride' (*loc. cit.*).
4. L. R. Brantley, *Zeits. Krist.*, 1931, vol. 77, p. 505. [M.A. 5-22.]
5. M. von Schwarz and O. Summa, *Zeits. Elektrochem.*, 1932, vol. 38, p. 743.
6. W. G. Burgers and J. C. M. Basart, *Zeits. Anorg. Chem.*, 1934, vol. 216, p. 209.
7. W. Hofmann and A. Schrader, 1936 (*loc. cit.*). They give 4.325Å. for TiC separated from cast-iron.
8. F. A. Bannister, 1941. Osbornite 4.235Å.

TABLE III. Physical data for Osbornite, TiN, TiC, &c.

	Osbornite.	TiN.	Ti(N,C).	Ti ₂ CN.	TiC.
Cell-edge <i>a</i>	4.235	4.23	4.23-4.24	4.27	4.31Å.
Colour	golden-yellow	golden-yellow	copper	blue	black
Hardness	—	8-9	8-8.5	>7	9-10
Melting-point	—	3200° C.	—	—	3400-3500° C.
Sp. gr. (calc.)	5.37	5.39	5.32*	5.14	4.93

* Calculated by V. M. Goldschmidt from the cell-edge and Wöhler's chemical analysis, the unit cell containing 4Ti(N,C).

together with his chemical analysis shows that under certain conditions a product is formed in blast-furnace bears that lies almost exactly midway between TiN and TiC. He first gives an interesting account of the mode of formation of a furnace bear 'sometimes called an old horse, a sow or salamander', terms used for the mass of metal, sometimes weighing from 50 to 800 tons, which is found below the hearth level of a blast furnace after the furnace has been blown out. Then follows a detailed account of the crystalline products found in bears from the Cleveland works. Cochranite was detected in a polished section of a mass from one of the furnaces. Dark-blue cubes up to 50 μ across embedded in a matrix of iron associated with graphite and manganese sulphide were separated for chemical analysis (table I). Although Stead assigned a wrong formula, calling it titanium dicyanide, his analysis shows that the blue cubes of cochranite must have a composition approximating to Ti₂CN. He mentions that his carbon figure may include a little associated graphite. Hence the blue crystals should be

called titanium carbonitride. The crystals when crushed yield a dark blue powder which gives an X-ray photograph of the same pattern as titanium nitride and titanium carbide and a cell edge of 4.27\AA . This measurement is confirmed by a single crystal photograph about a cube edge so that Stead's cochranite appears to be a uniform product. It would not be difficult to detect by X-ray measurements the existence of other mixed crystals in the series TiN-TiC , since the difference in the cell edges of the two end-members is 0.08\AA . So far no evidence exists that a complete series of mixed crystals is afforded by material from slags, bears, or cast metal.

This review of work on products related to osbornite together with the chemical and X-ray data collected in tables I, II, and III concludes the evidence for its probable identity with titanium nitride. I have also confirmed the identity of oldhamite with calcium sulphide and of the diopside and enstatite with the corresponding terrestrial minerals. X-ray photographs have been taken of specimens of all three minerals originally separated from the Bustee meteorite by Maskelyne and Flight. The cell edge of oldhamite 5.69\AA . is close to that of artificially prepared calcium sulphide 5.686\AA . measured by I. Oftedal.¹ Moreover, the nodules of oldhamite, measuring up to 4 mm. across, are single crystals showing cubic cleavage and are probably bigger than any yet found in meteorites or produced artificially. The X-ray identification of the enstatite and diopside calls for no comment. It should be noted, however, that Maskelyne used the mineral name augite for the Bustee diopside containing only 0.78 % iron oxide in the sense that we now use the name pyroxene.

The number of known titanium minerals is small. G. von Hevesy² states that the earth's crust contains 0.63 % Ti chiefly as rutile and ilmenite. The titanium content of the earth, including the core, he gives as 0.15 %, a little less than the average figure of 0.19 % for stony meteorites, but considerably greater than the content of 0.04 % for meteoritic irons. The occurrence of osbornite rather than rutile in the Bustee meteorite is in keeping with what little is known of the origin of meteorites but it is none the less a geochemical curiosity.

In conclusion, the formation of oriented rutile pseudomorphs after titanium nitride by oxidation (see page 38) merits attention as an interesting reaction in the solid state. Crystals not greater than $\frac{1}{2}$ mm. across change to rutile throughout in an hour at bright red-heat.

¹ I. Oftedal, *Zeits. Physikal. Chem.*, 1927, vol. 128, p. 154.

² G. von Hevesy, *Journ. Chem. Soc. London*, 1931, p. 1. [*M.A.* 4-514.]

Crushing the pseudomorph reveals no central core of titanium nitride, and as previously mentioned an octahedron of osbornite yields a pseudomorph of specific gravity 4.10. It is remarkable that the change from a single crystal of titanium nitride (melting-point 3200°C .)¹ to that of polycrystalline rutile (melting-point 1640°C .)² should take place at a temperature certainly lower than 1000°C . The expansion factor for this change is 1.64, so that the final specific gravity 4.10, although 3–4 % low for rutile, suggests that the reaction proceeded accompanied by expansion without the formation of large holes or gas-filled cavities. The orientation of the rutile crystallites on the pseudomorph is not unexpected in view of the close relationship between the titanium atom lattices of TiN and rutile. It was first of all noticed on the X-ray photograph of the rutile pseudomorph after osbornite. Accurate setting of the tiny, rounded octahedron after oxidation about an axis of the original crystal was not achieved, and no detailed study of the photograph for that reason has been attempted. A small cube of titanium 'cyanonitride' also loses its sharp edges during oxidation, but I found it relatively easy to set up along a cube edge after heating. The larger polycrystalline cube faces gave a general glitter in reflected light which proved most useful for setting purposes. The X-ray photograph of this pseudomorph showed at once that the (110) faces of the rutile crystallites fell nearly parallel to the cube faces. This is consistent with the obvious probability that the *c*-axes of the rutile crystallites (*a* 4.59, *c* 2.95 Å.) would fall along the cube diagonals of the crystal of TiN, *a* 4.23 Å. ($4.23/\sqrt{2} = 2.99$). This would also involve the superposition of the [110] axes of rutile and TiN, not so good a fit.

It is quite simple to calculate the positions of diffraction spots to be expected from the rotation of a rutile crystal about an axis inclined 45° to [001] and with two of its (110) faces vertical.³ Diffractions contributed from the two horizontal cube faces of the rutile pseudomorph must also be considered. These would be relatively weak diffractions due to the rotation of rutile about the [110] axis. The X-ray photograph actually obtained gave streaks which agreed fairly well with the theoretical photograph to be expected on the basis of the assumed orientation of the rutile crystallites. The spread of the streaks along the curves of constant θ (one-half the Bragg angle) may be due

¹ E. Friederich, *Zeits. Physik*, 1925, vol. 31, p. 813.

² O. Ruff, *Zeits. Anorg. Chem.*, 1913, vol. 82, p. 373.

³ J. D. Bernal, *Proc. Roy. Soc. London, Ser. A.*, 1926, vol. 113, p. 117.
[M.A. 3-333.]

to imperfection in the orientation and also to mis-setting the pseudomorph after its optically perfect cube faces were replaced by polycrystalline rutile. An attempt was made to increase the size of the rutile crystals by prolonged heating in a crucible over a Meker burner. It was not possible, however, to resolve the crystallites under the microscope sufficiently well to study the orientation over cube edges and corners, neither could I confirm Wöhler's description of sharp 'quadratoctahedra' with strong cross-stripping of the faces, a description which, incidentally, led him to think that they were anatase.

My thanks are due to Dr. M. H. Hey who carried out the qualitative micro-chemical tests on osbornite and to the Director of the Research Laboratories of the General Electric Company, Wembley, who provided the specimen of artificially prepared titanium nitride.
