# THE OCCURRENCE, PROPERTIES, DETECTION, ESTIMATION AND SEARCH FOR COLUMBITE

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## ABSTRACT

Niobium is used in the construction of jet engines and at the present time columbite is the only mineral from which it is obtained in large amounts, but other potential sources are noted.

The physical properties of columbite, its occurrence, and the minerals with which it is associated are briefly indicated.

Chemical methods of detecting niobium in minerals, and further physical and chemical methods of recognising columbite and obtaining semi-quantitative data concerning the occurrence of the mineral in soil, alluvial, rock and mill samples are described.


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## Introduction

The term columbite is used to denote a member of the isomorphous series (Fe, Mn)$Nb_2O_6$ - (Fe, Mn)$Ta_2O_6$ in which niobium greatly exceeds tantalum, whilst a member exceedingly rich in tantalum is called tantalite. The prefix manganois added to denote varieties in which manganese preponderates greatly over iron.

Within the past decade, and largely as a result of the development of the jet-engine, certain niobium-containing alloys have become of paramount importance because they neither creep when subjected to high temperatures, nor succumb to the attack of hot gases.

Consequently, columbite, which occurs in considerable and readily available quantities in certain of the secondary cassiterite-bearing deposits of Nigeria, and which was only of nuisance value in the past, rapidly assumed considerable economic importance. At present columbite is the only important source of niobium, but it is possible that it may be also obtained from other minerals in the future: these are discussed briefly below.

## Potential Sources of Niobium Other Than Columbite-Tantalite.

Many niobium-containing mineral species are known but most of them are rare and are confined to certain pegmatites. Apart from columbite-tantalite, the only species likely to be used as commercially important sources of niobium in the not-too-distant future are ilmenorutile and pyrochlore.

A few other niobium-bearing minerals have been mined from time to time on a small scale; thus fergusonite - essentially a meta-columbite and -tantalite of certain rare earths and containing uranium - has been obtained in commercial quantities, for example, at Barringer Hill, Texas. (De Ment, J. and Dake, H.C., 1946, p.150).

### (i) Ilmenorutile.

This consists essentially of titanium dioxide together with up to sixty per cent of iron niobate (and a little tantalate). It is black, and although often possessing an appreciably higher specific gravity than ilmenite, is likely to be mistaken for the latter, when it is water-worn. A test which enables rapid differentiation to be made between these species is described below.

### (ii) Pyrochlore.

Pyrochlore is essentially a fluo-niobate of calcium, sodium and cerium but may contain several per cent. of $ThO_2$ and $U_3O_8$. According to Hey (1950, p. 206) its formula is 8 [(Ca, Na, Ce) (Cb, Ti, Ta)$_2$ (O, OH, F)$_7$] but Greenwood (see Mackay, R.A., Greenwood, R. and Rockingham, J.E., 1949, p. 80) proposes the fol-

lowing formula for a Nigerian variety:- $(Na, Ca, Pb, Ce)_2 (Nb, Ti)_2 O_5F$. The species usually displays an octahedral habit and is brown, dark reddish-brown, blackish-brown or yellow in colour. Although it was formerly regarded solely as a rare pegmatite-mineral it occurs as an accessory mineral in several albite-riebeckite-granite masses in Nigeria; and the granite at Kaffo contains, according to Mackay's estimate (1952, p. 17), 0·26 per cent. $(Nb, Ta)_2O_5$ and 0·012 per cent. $U_3O_8$ because of the presence of pyrochlore (together with 2 - 4 per cent of the commercially valuable mineral cryolite). On account of the fact that Nigerian pyrochlore is radioactive, radiometric surveys have been employed by Mackay (1952) to evaluate some of the Nigerian deposits.

In East Africa, pyrochlore, together with apatite, occurs as an accessory mineral in carbonatites, and these deposits are being investigated.

Research into economic methods of making pyrochlore concentrates from Nigerian and East African material is being carried out. (See, for example, Ore Dress. Invest. Univ. Melb. no. 462, Melbourne, October 19, 1953).

(iii) Other possible sources of niobium.

In due course niobium may be extracted from bauxite derived from the breakdown of alkalic rocks: Arkansas bauxite, for example, contains an average of 0·05 per cent. of niobium which is chiefly present in ilmenite (Fleischer, M. and others, 1952).

Some varieties of tin, tungsten and zirconium minerals also contain appreciable quantities of niobium which might be extracted economically.

Columbite-tantalite.

Physical Characteristics.

The physical characteristics of members of the columbite-tantalite series may be summarized as follows:

Colour:- Usually iron-black, greyish or brownish-black.

Streak:- This varies from dark to pale brown and may resemble that of the softer mineral wolframite. As the streak of ilmenite is black, application of a streak test, or powder examination, enables ready differentiation to be made between it and columbite-tantalite.

Lustre:- Sub-metallic: often very brilliant. This greatly assists differentiation under the microscope between small columbite crystals and the duller, but sometimes not otherwise obviously dissimilar, crystals of ilmenite.

Hardness:- 6

Crystal System and Habit:- Orthorhombic. Both prismatic and tabular habits are displayed and twinning sometimes occurs.

Cleavage:- The species possesses two cleavages, but the more pronounced is much less marked than that of wolframite.

Specific Gravity:- This increases with the tantalum content from 5·3 to 7·3 and its determination enables the $Nb_2O_5$ content of a given specimen to be obtained to within $\pm$ 10 per cent. of the assay value. (Jacobson, R.R.E., Cawley, A. and Macleod, W.N., 1951, Fig. 1.)

Occurrence

Columbite-tantalite occurs in granite pegmatites in many localities throughout the world and the whole of the marketed tantalite is either obtained directly from these bodies or from the eluvials and alluvials derived from them. The annual production of columbite-tantalite from these sources is not great and the percentage occurring in any given pegmatite is small although the body may contain rich pockets of this material.

At the present time the demand for columbite is almost entirely satisfied by the Nigerian output which is almost wholly derived from alluvials and eluvials associated with certain of the Younger Biotite-Granites in which columbite occurs

as an accessory mineral. Some columbite has, however, been obtained recently from the granites themselves.

The columbite of these granites rarely exceeds 10-mesh and often 20 per cent, or more, of the total in a given volume of rock is minus 200-mesh. Ilmenite, zircon, malacon, monazite and thorite are common associates, and sometimes the radioactivity of the columbite-rich granite is considerably higher than the granites with which it is spatially related so that its outcrop may be readily determined by means of a radiometric survey.

As a result of the weathering of these granites and the associated cassiterite-bearing lodes, alluvials and eluvials have developed which are composed of an interesting mineral assemblage which includes columbite, "normal" and magnetic cassiterite, zircon and the altered variety malacon, ilmenite, magnetite, monazite and thorite.

Some of the Nigerian alluvials are covered with basalt, and it is possible that some of these "deep leads" may contain economically important concentrations of columbite.

The Identification of Columbite and the Detection of Niobium and Tantalum.

A consideration of the colour, hardness, streak, crystal characteristics and specific gravity of large crystals of columbite-tantalite usually enables them to be identified with comparative ease. Furthermore, as stated earlier, a reasonably accurate specific gravity determination will permit the percentage of $Nb_2O_5$ (or niobium) to be determined approximately.

With experience, small columbite crystals occurring in a sample of Nigerian alluvial material or in a gravity concentrate made from "columbite-granite" can usually be identified by examination under the microscope in reflected light provided that they are neither markedly water-worn nor pitted as a result of attack by mineralising agents during the development of the associated lodes. This comparative ease of detection is due to the characteristic habits and colour of the crystals and especially to the high reflectivity which they display. However, when columbite crystals are water-worn or corroded, and consequently comparatively dull, visual differentiation between them and ilmenite crystals is often extremely difficult. For this reason Mackay (1950-51, pp. 129 - 131) developed the following procedure for detecting columbite grains in composite Nigerian samples:

Sufficient flux (the composition of which is noted below) is fused in a flat nickel dish of 2 to 3 inches diameter to just cover the bottom when molten. During this stage the dish is tilted slightly so that most of the bottom is only covered with a thin veneer of melt. When the melt has cooled the grains to be examined are sprinkled over it and heating is resumed until the flux melts, and then for a further 30 seconds. After cooling the dish to room-temperature it is examined in a dark-room under either long- or short-wave ultraviolet light. Under these conditions columbite grains are surrounded by pale yellow haloes whilst intense yellow haloes encircle thorite grains. Any grains of monazite which may be present are surrounded by very weak yellow haloes, but these do not lead to confusion when testing for columbite as monazite grains are never black.

The flux employed in the above test has the following composition:

| | |
|---|---|
| Sodium bisulphate | 2 per cent by weight. |
| Sodium fluoride | 5 per cent by weight. |
| Sodium carbonate<br>Potassium carbonate | Balance in equal parts. |

In order to discover whether the above test was equally well-suited to the identification of columbite from fields other than Nigeria, Horne (see Mackay, R.A., 1950-51, pp. 250 - 251) applied it to eighteen members of the columbite-tantalite series and also assessed the radioactivity of each one. The results of these tests led him to make the following conclusions: "First, the test did not permit a distinction to be made between columbite and tantalite; secondly, by means of the test —— columbites and tantalites could not be distinguished with any certainty from minerals containing uranium but no niobium. All one could

say was that very bright fluorescence usually denoted at least a few per cent. $U_3O_8$, to which columbite and tantalite rarely attained; that bright fluorescence denoted anything down to a small but appreciable amount of uranium, which was not infrequently present in columbites and tantalites; and that faint or very faint fluorescence denoted either a trace of uranium, or the presence of niobium as a major constituent, or both those factors."

Methods of detecting niobium and tantalum

The following two tests are particularly useful for detecting appreciable quantities (say not less than 5 per cent.) of niobium/tantalum in most monomineralic and composite samples in which the elements are likely to occur.

(i) The tartaric acid hydrolysis test.

The test - originally described by Schoeller and Powell (1940, p. 161) - is conducted as follows:

About 0·5g. of the finely-powdered sample is fused with potassium bisulphate in a silica crucible. The cooled melt is leached with hot 20 per cent. tartaric acid and the resultant solution is filtered. The filtrate is boiled with about a quarter of its volume of concentrated HCl. The development of a white precipitate - which usually appears after boiling for a few minutes, but which occasionally may not be apparent until the solution has been boiled for an hour - is a certain indication of the presence of niobium and/or tantalum.

Under the conditions of the test, tungsten - the only interfering element - causes the development of a yellow precipitate, the colour of which is masked when the sample contains only a few per cent. of $WO_3$ and 60 to 70 per cent. of $Nb_2O_5/Ta_2O_5$.

As the solution in which the precipitate develops is yellow because of the presence of iron, the colour of the precipitate can only be evaluated after the latter has been removed by filtration and washed, or after the colour of the solution has been destroyed by dilution with water. However, the development of a precipitate is normally reliable evidence of the presence of niobium/tantalum when Nigerian products are subjected to the above test, as there is comparatively little tungsten mineralisation in the country.

When a considerable quantity of niobium/tantalum is present in the sample the writer has found that the test may be carried out quite adequately by conducting the fusion and the subsequent acid treatments in a single hard-glass test tube.

(ii) The reduction test.

Under appropriate conditions the following well known test enables niobium, tantalum, titanium and tungsten to be detected. It is most useful when examining a specimen of a single mineral which contains a considerable quantity of one (or in certain instances of two or three) of the above-mentioned elements, but in the absence of tungsten it may be generally applied with advantage to the detection of niobium and/or tantalum in composite samples provided that the components sought represent at least 5 to 10 per cent. of the sample.

About 0·25g. of the finely-powdered sample is fused in a silica crucible with potassium bisulphate. (A "primus" or blow lamp may be used as the source of heat in the field). The melt is dissolved by boiling it in a boiling tube with concentrated HCl. A white precipitate (or cloudy suspension) at this stage indicates the presence of niobium and/or tantalum. After sufficient 5 N. HCl has been added to increase the volume of solution to about 20 ml. the latter is warmed and a few fragments of either zinc or tin are added. Under these conditions titanium gives a violet solution and both niobium and tungsten yield blue solutions: tantalum causes the development of a white precipitate.

It is pertinent to make the following comments on this test:

(a) Tin reacts much slower than zinc with the acid, but the writer prefers the former as the slower reduction occasioned by its use enables subsequent changes in the colour of the test-solution to be much more readily aapreciated. Thus, when tin is employed, a solution rich in tungsten rapidly

becomes inky-blue, whereas a niobium-rich solution becomes sky-blue, and a solution derived from the treatment of tantalite develops a white precipitate which may show little or no "niobium-blue" until an hour has elapsed.

(b) The presence of niobium in a Nigerian columbite/ilmenite sample which contains as little as 7 per cent. columbite can be detected by the above tin-reduction test. Under such circumstances the presence of titanium is indicated by the development of a clear violet solution and that of niobium by a strong blue colour which is associated with the undissolved tin and which can be best seen by looking through the bottom of the tube.

(c) The tin-reduction test has proved to be a suitable means of differentiating between ilmenite and ilmenorutile. Whilst ilmenite results solely in a violet solution, ilmenorutile causes the production of a violet solution together with a white precipitate with a "niobium-blue" base.

Prospecting for Columbite and Methods of Determining the Columbite Content in Prospectors' Samples.

(i) Alluvial and eluvial deposits.

In essence, the procedures adopted for prospecting alluvial and eluvial deposits for columbite are the same as those employed when examining similar types of deposit for cassiterite, and involve pitting and/or Banka drilling the ground on a grid, taking samples from various horizons to bed-rock and examining them quantitatively in order to determine the distribution and amount of the sought-after mineral.

Methods employed in Nigeria for determining the percentage of columbite in a given sample vary, but with experience a useful result may be obtained by making a "crude" concentrate by panning or calabashing a known quantity of sample, separating the concentrate into a magnetic and a non-magnetic fraction, weighing both fractions, obtaining the specific gravity of the magnetic fraction by a displacement method, estimating the percentage of cassiterite in the magnetic fraction after "tinning" the species by treatment with zinc and dilute HCl in order to facilitate recognition, determing the percentage of columbite in the magnetic fraction by applying the formula below, and finally calculating the percentage (and lbs. per cubic yard) of columbite in the original sample.

The formula applied to obtain the percentage of columbite (x) in the magnetic fraction is as follows:

$$\frac{\%SnO_2}{7} + \frac{100 - \%SnO_2 - x}{4{\cdot}5} + \frac{x}{5{\cdot}5} = \frac{100}{S}$$

S is the specific gravity of the magnetic fraction and $\%\ SnO_2$ is the estimated percentage of cassiterite in the fraction.

A much more reliable indication of the amount of columbite in the sample can be obtained by subjecting the crude concentrate to a quick assay which is based on the tartaric acid hydrolysis test described above and which is discussed and described in another paper in this series by Polkinghorne.

The value of promising ground may also be confirmed by subjecting appropriate samples to small-scale mill-tests.

(ii) Columbite-bearing granite.

Prospecting for primary deposits of columbite involves the search for columbite-rich granite outcrops and when one is discovered the mapping of its outcrop and subsequently the determination of the quantity of columbite available in the superficial, decomposed - and therefore readily mined - portions of the mass.

Up to the present the discovery of columbite-rich granite outcrops has resulted from the examination of samples of the granites in the vicinity of rich secondary columbite deposits by a variety of methods. Having proved the existence of such granite in a given area its lateral extent may be established by determining the columbite content in samples obtained by drilling on a grid. Sometimes mineralogical differences between a given columbite-rich granite and the granites adjacent to it may make the mapping of the former comparatively easy. Thus the writer was able to determine the extent of a certain columbite-

rich granite in Nigeria because it, unlike the granites with which it was spatially related, was characterised by the presence of doubly-terminated quartz crystals. So, whenever the soil contained an abundance of these crystals it was reasonably safe to assume that it was, for all practical purposes, overlying the columbite-rich granite. The same granite also contained considerably more thorite and malacon than the adjacent granites and was, consequently, considerably more radioactive. Thus its outcrop could be established by a radiometric survey. It is possible that radiometric methods might be usefully employed to locate columbite-rich granites elsewhere in Nigeria.

It is probable that columbite-rich granite could be located, and its outcropping portion delineated, by employing geochemical methods of prospecting. (Such methods might also enable deep-leads of columbite to be located beneath the basalt flows in Nigeria). In essence such methods involve the taking of small samples of soil from an appropriate horizon and at pre-determined points on the ground, and then subjecting these samples to rapid semi-quantitative analysis in order to locate any points where the niobium content of the soil is unusually high. A colorimetric and a chromatographic method of determining niobium in soils have been developed and these are described briefly below. It must be stressed, however, that although these analytical methods are comparatively simple, geochemical prospecting programmes should only be undertaken by those who have given considerable time to the study of the subject.

(a) A colorimetric method of determining niobium in soils.

(See Ward, F. N. and Marranzino, A. P. Determination of Microgram Quantities of Niobium in Rocks. U.S. Geol. Surv.)

This method depends on the fact that niobium reacts with the thiocyanate ion in a hydrochloric acid solution of stannous chloride forming a yellow product. If tartaric acid is also added and then the solution is shaken with ether, interference due to iron, uranium, titanium, vanadium, molybdenum and tungsten is largely eliminated and the niobium compound reports in the ether layer. The ether layer is separated from the aqueous phase and its colour is compared with those of standard solutions. The quantity of niobium in samples which contain from 250 to 1,000 p.p.m. of the element can be determined by this method and an experienced person can carry out from 30 to 40 estimations per day. The niobium is brought into solution initially by fusing a known quantity of the soil sample with sodium bisulphate in a test tube and extracting the melt with tartaric acid.

(b) A chromatographic method of determining niobium in soils,

(See Williams and Burstall. Analyst, 1952, 77, 983), depends on digesting a small but known quantity of the soil sample with hydrofluoric acid, placing a drop of the solution near one of the shorter edges of a rectangle of Whatmans No. 1 filter-paper, and after drying the spot in air standing the paper in a covered 600 ml. polythene beaker containing a 15 : 85 mixture of hydrofluoric acid and methyl ethyl ketone. As the liquid mixture ascends the paper the niobium in the test spot is separated from other components, transported some distance up the paper, and concentrated in a band. When the liquid front has almost reached the top of the paper the latter is removed, dried in air, exposed to ammonia vapour and sprayed with tannic acid. The niobium band then becomes yellow, and the intensity of the colour and width of the band varies with the niobium content: thus, by comparing the chromatogram with standards the niobium content in the soil sample can be determined.

By this method as little as 4 p.p.m. of niobium can be detected. The method is, therefore, considerably more sensitive than the colorimetric one described above, but suffers from the disadvantage of employing highly toxic hydrofluoric acid.

Determination of the Amount of Columbite in Samples of Columbite-rich Granite.

Columbite-rich granite is unlikely to contain more than about 3 lbs. of columbite per ton and it may often contain considerably smaller amounts. As no quick, and at the same time reasonably accurate and simple method exists for determining the small amounts of Nb/Ta encountered in such material, and as it is of paramount importance to evaluate these granites with respect to their columbite content, the following method which was employed in Nigeria by Jones (1953, pp. 8 - 9) to achieve this end should, in its original, or in an appropriately modified form, prove to be of the utmost value:-

Details of the method employed by Jones for determining the columbite content of certain Nigerian granites.

Pan a known volume of rock (previously crushed to minus 30- mesh if not decomposed) until a large, dirty concentrate is obtained.

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Subject concentrate to an ordinary hand-magnet

| Magnetics | "Non-magnetics" |
|---|---|
| Magnetite | Columbite, ilmenite, cassiterite, thorite, zircon, monazite, wolframite, iron oxides, biotite, felspar, quartz |

↓

Subject to an "Eclipse" magnet (i.e., a powerful hand-magnet)

| Magnetics | Non-magnetics |
|---|---|
| Columbite, ilmenite, cassiterite, thorite zircon, monazite, wolframite, iron oxides, biatite. | Cassiterite, zircon, quartz felspar. |

↓

Digest with conc. HCl for c. 24 hours. Wash, dry and subject to an Eclipse magnet.

| Magnetics | Non-magnetics |
|---|---|
| Columbite, cassiterite, monazite | Thorite, zircon, biotite. |

↓

Heat in a crucible for 90 minutes at about 1,000 °C. Cool, and subject to an Eclipse magnet.

| Magnetics | Non-magnetics |
|---|---|
| Columbite and monazite | Cassiterite |

↓

Pick out the black Columbite and weigh it. Knowing the average density of the granite, calculate the lbs. of columbite per ton.

Determination of the Grade of a Columbite Concentrate.

The grade of a columbite concentrate is usually determined in the mill by employing a specific gravity test which for its effectiveness depends on the assumption that columbite possesses a specific gravity of 5·3 whereas that of any impurities is 4·5. Normally a 100 g. of the concentrate is placed in a burette containing about 50 ml. of petrol and the displacement of the liquid is recorded. Some operators, at least, regard the concentrate as being of shipping grade if a 100 g. effects a displacement of from 18·2 to 18·6 ml.

Although this simple method is fairly reliable, it is the writer's opinion that whenever it is possible the results obtained by its use should be supplemented to some extent by those gained by conducting rapid chemical assays.

Evaluation of Tributers' "Crude" Concentrates.

Methods of evaluating "crude" concentrates submitted for sale by native tributers vary somewhat, but most, if not all, depend - largely or entirely - on visual examination (with or without the aid of a hand-lens) and direct or indirect consideration of the specific gravity of the material. Although such methods may appear to be very primitive they normally give sufficient information to an experienced buyer to enable him to purchase wisely.

Conclusion.

In conclusion it is hoped that this paper will supply answers - or indicate where the answers may be found - to certain constantly reiterated questions concerning the occurrence, properties, detection, estimation and search for columbite. If it succeeds in this it will have achieved its purpose.

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