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Effect of Tantalum on Coltan in Cassiterite Using Mathematical Modeling Approach with Respect to Gibbs Energy

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Abstract:

The objectives of this study were to evaluate the effect of tantalum on COLTAN in Cassiterite using mathematical modeling approach and how it controls the strength, cell size, magnetization, and density (grade), as well as electrical conductivity of COLTAN in Cassiterite. The effectiveness of COLTAN in Cassiterite in Extractive Industry depends on the ratio of tantalum to niobium in the solid solution during crystallization of magma with respect to Gibbs free energy and can be mathematically expressed as $Z[X_{n-x}Y_x]O_6$ as n ranges from 0 to 5 where x depends on 'n'. Mathematically, cassiterite consists of small ion lithophile elements, large ionic charge, with intermediate to greater ionic potential and these elements are partitioned along the aqueous phase, if both the aqueous phase and silicate phase coexist together during crystallization of magma. These trace elements include tin, iron; niobium, tantalum, and zircon are incompatible trace elements because of their inability to achieve a charge balance with silicate structure (SiO_4) in the silicate magma phase. These elements do not exist as free ions in the magma but form complexes with oxygen in the magma during crystallization. Methodologically, 20kg of cassiterite was crushed and pulverized in the laboratory mill machine for an hour, and was taken and sized by sieving into number of size fractions using the automatic sieve shaker for 15 minutes, after processing using high intensity magnetic separator and with the help of ordinary hand magnet of about 0.01Tesla, relative density measure, triaxial testing machine to measure the strength, the relationship between columbite and tantalite can be mathematically established using a COLTAN model. Findings have shown that, with increasing amount of tantalum atom on COLTAN, the COLTAN becomes more tantalized, and both are strong when subjected to shear modulus, electrical conductivity of COLATN also increases with increasing tantalum, but with its greater density, small cell size because of lanthanide contraction than the niobium, increasing the number of tantalum on COLTAN in cassiterite increases the quality of COLTAN in cassiterite, therefore we haveniobate type cassiterite, tantalized type cassiterite and coltan type cassiterite. In conclusion, the presence or absence of tantalum on COLTAN determines their genetic rock origin, in which the amount of tantalum on COLTAN increased from alkali rock with $\Delta G \geq 0$, e.g., nephelinesyenite to more silicic, with $\Delta G > 0$, e.g., granite pegmatite which gives the account that cassiterite rich in niobium is less dense than the cassiterite rich in tantalum. After comparative analyses between columbite and tantalite in cassiterite, concise valuable substantive empirical novel model was developed and can be employed to study COLTAN in cassiterite. This concise empirical novel model was, "COLTAN model designed with the aid of: Matrix equation, Oxidation and the Tantalization process, and can be recommended to study the effect of tantalum on COLTAN and the application can improve mineral processing in extractive Industry.

Keywords: Coltan, Niobate, tantalization, electrical conductivity, cell size, density

1. Introduction

1.1. Background to the Study

Mathematical model in Geology can also be termed "GEOMATHEMATICS" and is a system of model of computation of numerical values to chemical elements in their algebraic form to produce a material of a particular IUPAC nomenclature as was defined by Achuenu and Komolafe (2021), e.g., ferrohexasxonioabate (v) is the IUPAC name for columbite ($FeNb_2O_6$) and that of tantalite ($FeTa_2O_6$) is ferrohexasxotantalate (v).

Mathematical models involve the use of equations consisting of variables and constants according to Hubbert (1937). Geomathematics, in its broadest sense includes all applications of mathematics to studies of the earth's crust.

In geomathematical problems, one usually asks if there are theoretical reasons to assume the certain variables are related to one another and if theoretical geology can provide guidelines for statistical models to be fitted to the data. Generally, the geologist can observe and reconstruct only part of a very complicated process involving many variables that have taken place in the course of time under changing circumstances.

In practice, the resulting mathematical model may then consist of fitting to the data a few linear terms out of a Taylor expansion ([2.21]) for the mainly unknown geological process. Quantitative geologic considerations are indispensable, first for selection of the variables to be measured, for designing the mathematical model and later for interpretation and evaluation of the results.

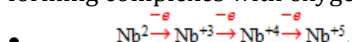
Modeling is process of representing a real-world object as set mathematical equations that is representing three dimensional objects especially in computer (ford, 2009). Mathematical models involve the use of equations consisting of variables and constants according to Hubbert (1937). Krumbein and Grayhill (1965) have distinguished three types of models in geology: (1) scale-models; (2) conceptual models; and (3) mathematical models. According to Nakayama and Vansiclen, (1981); Ungerer et al., (1984), deterministic models seek to identify and quantify all variables of the system and thus predict its behaviour by establishing values or limit for each system

Rocks contain thousands of tiny ferrimagnetic minerals grains. The compositions of ferrimagnetic minerals are mostly transition metals in which oxygen atoms fill the lattice space of the metal. These are iron (Fe), titanium (Ti), manganese (Mn), cobalt (Co) Nickel (Ni), Zircon (Zr), Niobium (Nb) and tantalum (Ta). These are magnetic elements, because of the presence of extra electrons in the d-orbital below the outer orbital, burns, Clark and Fyfe, (1964). The magnetic minerals to be modeled are: Columbite and Tantalite.

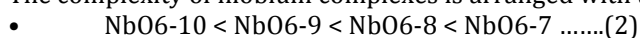
Niobium is often found in the minerals pyrochlore and columbite, hence the former name “Columbium”. Its name comes from the Greek mythology, specifically Niobe, who was the daughter of Tantalus, the namesake of Tantalum. The name reflects the great similarity between the two elements in their physical and chemical properties, making them difficult to distinguish. The element name comes from the Greek mythological character Tantalos. Niobe (Niobium) was the daughter of Tantalos. Ekeberg gave his new element the name Tantalum because it had been a tantalizing element to find. Tantalization in English word means to excite by exposing something desirable that remains or is made difficult or impossible to obtain. It also means strongly attractive to; excite the senses or desire of Niobium and tantalum occur in nature almost entirely as single isotopes (Nb93 and Ta181) and they commonly substituted for one another in minerals because they both have similar ionic radii and occur mostly in quinquevalent state. A great preponderance of one element over the other rarely occurs in certain types of rocks such as nephelinsyenite (niobium rich) or lithium-bearing pegmatite (tantalum rich). Columbite and Tantalite occur in most alkali rock such as nephelinsyenite, alkali ultramafic and mafic, carbonatite, sodic and alkaline granite. A greater amount of columbite, is recorded in nephelinsyenite with columbite to tantalite ratio of about 20 : 5 and tanalite in lithium pegmatite. Columbite dissolved and precipitates as hydrolysate, and some of them are carried to the ocean, where they crystalized as columbite while tantalites are more stable and found in marine clay. Columbite and Tantalite are the major sources of niobium and tantalum and their occurrences in rocks depend on magma type. They are concentrated in late differentiates and crystallates during fractionation process. They are both lithophilic, and enriched in the silicate crust of the earth. Univalent, divalent and some large ion trivalent exist as free ions in the magma and their crystallization can be satisfactory be defined in terms of ionic radii, ionic charge and electronegativity or its ionic potential according to Goldschmidt rule (1954). Ions with charges greater than three and some of the smaller trivalent ions form complexes with oxygen in the magma as shown in equation 2 and these complexes maintain their identity during the crystallization process. The higher the ionic potential of the elements, the more stable are the complexes formed. Niobium and tantalum have ionic potentials of intermediate values (Nb+5 and Ta+5), sufficiently high to form normally stable complexes, although they are also in the range where partial dissociation under certain conditions is possible. Niobium and tantalum probably form tetrahedral complexes (NbO₄)-3 and (TaO₄)-3 and octahedral complexes (NbO₆)-7 and (TaO₆)-7. The octahedral form is the one found in most niobium bearing minerals. Neither tetrahedral nor octahedral complexes of niobium and tantalum can be incorporated into the silicate structure (SiO₄) according to Ringwood (1955) and can be classified as incompatible trace element because of their inability to achieve a charge balance with this silicate structure. These elements tend to accumulate as complexes in the magma during crystallization until sufficiently concentrated to allow precipitation most likely as multiple oxide minerals or are scavenged during crystallization by accessory minerals of titanium or titanium and iron. Element with ionic potential less than 2.7, exists as a free ion in the magma, those between 2.7 and 4.8 are transitional, either exists as a free ion in the magma or forms complexes with oxygen and those greater than 4.8 form complexes with oxygen.

Niobium and tantalum are type of isomorphism that undergoes isovalent substitution, because of normal substitution of niobium for tantalum in solid solution during crystallization of magma. Both have the same charge and similar size with niobium has a size of 0.69 greater than tantalum with a size of 0.68 as shown in Table 1. The small size of tantalum is due to lanthanite contraction.

Because of presence of oxygen fugacity in the magma, niobium will undergo the following series of oxidation by forming complexes with oxygen, as shown in equation (1).



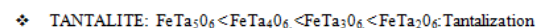
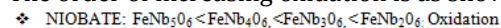
The complexity of niobium complexes is arranged with the following increasing stability as shown bellow



Equations (1, and 2) are called oxidation reaction series of COLTAN

The niobium ions at five oxidation states above are called niobium (ii) oxide, niobium (iii) oxide, and niobium (iv) oxide, and niobium (v) oxide. The niobium (ii), (iii) and (iv) oxide are unstable and transient and not found in natural compound. The oxides are in the form of columbite (FeNb₅O₆, FeNb₄O₆, FeNb₃O₆, FeNb₂O₆).

The order of increasing oxidation is as shown below;



The general formulas for COLTAN are as shown below;

- Coltan: $[X_{5-x}Y_x]O_6$: n = 5
- Coltan: $[X_{4-x}Y_x]O_6$: n = 4
- Coltan: $[X_{3-x}Y_x]O_6$: n = 3
- Coltan: $[X_{2-x}Y_x]O_6$: n = 2

These indicate that ionic replacement of one Nb⁵⁺ and for one Ta⁵⁺ ion can take place in solid-solution series according to Goldschmidt (1937) as shown in Figure 2.

1.2. Justification

The concept of this mathematical model is an empirical model that would be developed in this research to COLTAN in cassiterite and it is grouped according to Niobium to Tantalum ratio. It is a method developed to establish a relationship between columbite and tantalite in cassiterites to help students of mineralogy, petrology and other courses related to crystal geology as well as elementary science such as secondary school chemistry and Physics in order to understand the formation of COLTAN from ores originated from igneous and sedimentary rocks. It involves using mathematical equations, to calculate the empirical formula of each columbite and tantalite that formed during crystallization from the melt and sediment as shown in Figure 1. It also helps students to classify, name and understand genetic origin of the COLTAN in cassiterite. If niobium exceeds tantalum in COLTAN, it is called Columbite and if tantalum exceeds niobium in COLTAN, it is called Tantalite.

This research when completed would proffer a COLTAN model and would be one of the simplified models to study mineralogy, and petrology of CASSITERITE as well as its application to geochemistry and mineral exploration. Mendeleev classifies elements and arranged them according to their increasing atomic weight and they are independent of any conditions (condition independency). While this research uses two series of reactions with respect to niobium to tantalum ratio to classify COLTAN with increasing and decreasing magnetization, electrical conductivity strength, and density and they are condition dependency such as temperature, pressure and energy (Achuenu and Komolafe, 2021) as shown in Figure 3. The two series of reactions are Oxidation, and Tantalization reactions and these two series of reactions are used to design the conceptual frame work as shown in Figure 1.

1.3. Statement of the Problem

Goldschmidt classified elements according to the preferred host into a phase in the Periodic Table, but Mendeleev arranged these elements in the Periodic Table according to their increasing atomic number, without any change of conditions in which these elements formed. This means that, they do not depend on temperature and pressure as well as energy to form that is they are in their own physical and chemical states at all conditions in the planetary bodies. Conversely minerals depend on these conditions to form, but the problem is that, there are no proper mathematical documentations that explain the time of formation of these minerals with respect to these conditions.

In order to overcome or resolve this problem, mathematically;

- The temperature at which each mineral crystallizes, during crystallization from the melt and sediment must be mathematically documented
- The Pressure at which each mineral crystallizes, during crystallization from the melt and sediment must be mathematically documented
- The energy at which each mineral is at equilibrium after formation, during crystallization from the melt and sediment must be mathematically documented

This means that, COLTAN model depends on these conditions of change of temperature, pressure and energy of stabilization and the parameters used to establish this relationship are;

- Magnetization
- Strength
- Density
- Electrical conductivity
- Cell size

1.4. Aim and Objectives of the Study

The main aim of this research is the application of mathematical model to establish a relationship between the columbite and tantalite in cassiterite of Jos Plateau state using niobium to tantalum ratio with respect to thermodynamic principle and classify them according to niobium to tantalum ratio and the objectives are;

- Measuring magnetization of the ore in which its magnetic field is subjected to ordinary hand magnet of about 0.0T.
- Measuring the density of the ore using Archimedes' principle
- Measuring the strength of the ore using triaxial testing machine
- Using mathematical equations to ascertain the values measured from magnetization, density, strength and energy.

1.5. Conceptual Frame Work

The concept of this model indicates two series of reactions which are Oxidation (Niobate series), and Tantalization reactions series and this is shown in Figure 1. From Figure 1 the following deductions are made;

- Oxidation represents the horizontal axis and is called Niobate series while Tantalization represents the vertical axis and is called Tantalization series.
- Oxidation (Niobate series) is the reaction series that takes place in syenite.
- Tantalization series is the reaction series that takes place in pegmatite.
- The stability of minerals increases across the Figure from left to the right and increases down the Figure from top to bottom.
- The temperature of crystallization of minerals decreases across the Figure from left to the right and decreases down the Figure from top to bottom.
- Solid solution is the process of exchanging one ion to the other in molten form with respect to temperature.
- Minerals of Niobate series are niobium (ii) oxide, niobium (iii) oxide, niobium (iv) oxide, niobium (v) oxide
- Minerals that form during tantalization are tantalum (ii) oxide, tantalum (iii) oxide, tantalum (iv) oxide, tantalum (v) oxide

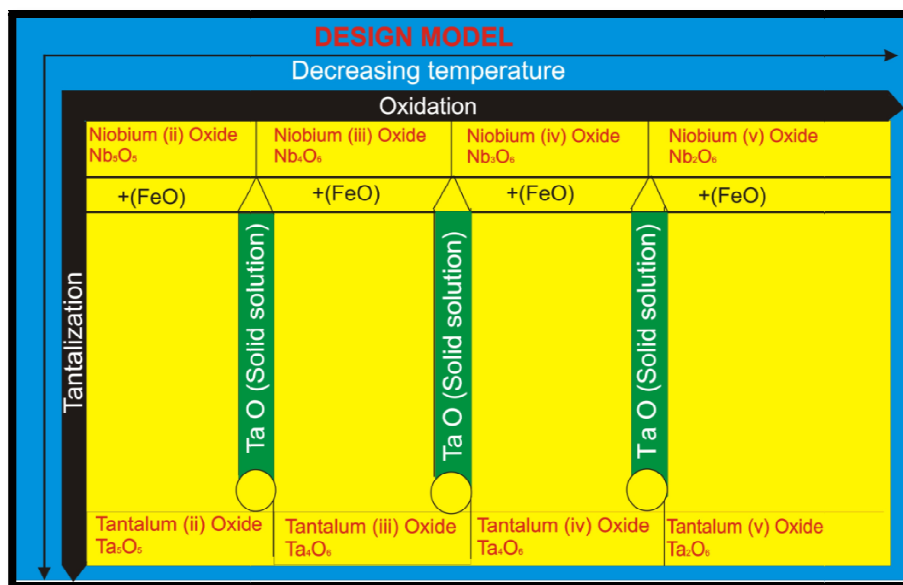


Figure 1: Design Model

1.5.1. Definition of Terms

- COLTAN: This is the ratio of columbite and tantalite in Cassiterite ore.
- MATRIX: Mathematical representation of rectangular array of minerals in rock (ore) arranged in rows and columns with respect to Gibbs free energy (Achuenu and Komolafe, 2021)
- OXIDATION: This is the addition of oxygen to the ores as temperature drops during crystallization of magma at a given Gibbs free energy with respect to temperature and pressure (Achuenu and Komolafe, 2021)
- TANTALIZATION: At a given Gibbs free energy with respect to temperature and pressure, Tantalization in this context is the process involving mathematical substitution of niobium by tantalum in equal proportion in solid solution during chemical process in the magma to produce a natural durable, high strength, heavy weight alloys of COLTAN that enhance the life of COLTAN in cassiterite which is desirable mineral that is rare, strongly attractive and almost out of reach, e.g., tantalite.
- "GEOMATHCHEMICAL MODELING as used in this research, is the system of model of computation of numerical values to chemical element in its algebraic form to produce a material of a particular IUPAC nomenclature (name)" e.g., iron ore according to Achuenu and komolafe, (2021).

NOTATIONS:

X = Nb

Y = Ta

Z = Fe

COLTAN = columbite and tantalite

IUPAC = International Union Pure and Applied Chemistry

T = tesla

N = number of mole

ΔG = change in Gibbs free energy.

2. Literature Review

2.1. Introduction

Krumbein and Grayhill (1965) have distinguished three types of models in geology: (1) scale-models; (2) conceptual models; and (3) mathematical models. Traditionally, geologists have been concerned with scale-models and conceptual models mainly.

Examples of scale-models are the geological map and cross-sections where the spatial variability of attributes is represented at a reduced scale for topographic surface and vertical planes, respectively. Geological processes also can be represented by scale-models. A classic discussion of this subject was given by Hubbert (1937). Conceptual models are mental images of variables and constants. They are statistical or deterministic depending on whether one or more random variables are used in the equation or systems of equations to express uncertainty. Mathematical equations generally can be represented geometrically by curves or surfaces.

The three types of models listed are not mutually exclusive. Scale-models can be based on mathematical criteria and conceptual models may be partly or entirely quantitative. Most mathematical models in geology have some important aspects of uncertainty and for this reason, are statistical. The problem may consist of eliminating the random variations from data so that a deterministic expression is retained representing the relationship between averages for assemblages of attribute rather than between single features. Statistical components or the uncertainty provide a way of expressing a range of different extrapolations for single features, all of which are possible, but with different probabilities of occurrence. This method replaces that of extrapolating a phenomenon with absolute certainty.

Geology differs from physics, chemistry and other sciences in that the possibility of doing controlled experiment is more limited. The observations are restricted to a record of past events, making geology a historical science. Generally, the final product of many interrelated processes is exposed at the surface of the earth in an imperfect manner. These mainly physical-chemical processes seldom reached a state

Younger igneous rocks, consisting largely of plutonic and volcanic components, form the Jurassic alkaline ring complexes of Jos Plateau, which are the major sources of the Nigerian tin and associated ores, iron ores (Macleod, et al. 1971). The bulk of the cassiterite was obtained from alluvial deposit on Jos Plateau general considered to be derived from the Jurassic biotite granites of the ring complexes. Only very few economic deposits of tin were known in the older basement rocks. The ore is currently being processed using magnetic and gravity methods. The presence of columbite and tantalite in cassiterite depends on the ratio niobium to tantalum and their genetic environment as shown in table 2. The geochemical behavior of niobium and tantalum in granitic rocks depends to a certain extent on the paragenesis of the titanium minerals. Monozite bearing granites containing ilmenite and rutile commonly niobium and tantalum in accessory biotite, whereas allanite – bearing granites containing sphene and magnetite commonly have niobium and tantalum are concentrated in sphene with only subordinate amounts in the biotite. In some granitic rocks, the niobium and tantalum in discrete accessory minerals of these element. Although exceptions occur, niobium and tantalum generally accumulate in the later differentiation during crystallization of granites and there is a tendency for tantalum to be concentrated relative to niobium in certain albitized or greisenized rocks. Separation of niobium from tantalum and the concentration of tantalum are attributed to change in alkalinity-acidity of the crystallizing medium and to the complexing of these elements with fluorine. High concentrations of niobium and tantalum occur in granitic pegmatite both as discrete niobium – tantalum minerals and as minor constituents in the lattices of mica, garnet, tourmaline, ilmenite, zircon and other minerals.

Nephelinesyenite is well known for its high concentration of niobium about 12:1 ratio of columbite to tantalite, as in Russia. Nephelinesyenites have been studied extensively by Russian geologists and Russian reports dominate the literature on these rocks. According to Es'kova (1960), nephelinesyenite comprises about one percent of the igneous rocks of USSR and more than thirty massifs of this type of rock are known to occur there. In eight prominent nephelinesyenite massifs the average niobium content ranges from 100 to 900ppm and the average tantalum content ranges from 8 to 70ppm.

As in granitic rocks, niobium and tantalum of nephelinesyenite are more highly concentrated in late phases of intrusive that is pegmatite, albitized zones and carbonite and hydrothermal veins such enrichment is several to tens of times the niobium and tantalum contents of parent rocks (Es'kova, 1969).

Niobium occurs in a wide variety of minerals in nephelinesyenite and other feature connected with them.

Tantalum was discovered by Anders G. Ekeberg in 1802 in Uppsalaa, Sweden, in the minerals tantalite from Finland and ytrotantalite from Sweden. Unfortunately for Ekeberg in 1809, the well-known English chemist, William

Wollaston said there had been no discovery and there was no new element. Granite pegmatites are also the only known commercial source of tantalum. Niobium and tantalum tend to be concentrated in the later products of crystallization of certain types of granite and the rocks tend to be enriched I tantalum with respect to niobium. In most granite, independent accessory minerals of niobium and tantalum are not found, but in pegmatite phases of such granites a wide variety of niobium and tantalum minerals is commonly formed. Niobium and tantalum enter also to a certain degree into the structure of other pegmatite minerals such as mica, garnet, tourmaline, ilmenite and zircon. Kuz'menko (1961) such that niobium is preferentially taken into the mica structure leaving tantalum to accumulates and form independent minerals of its own such as microlite and tantalite. The presence of lithium -bearing micas in pegmatite has significance in the formation of separate tantalum deposits. The content of tantalum with respect to niobium tends to increase from the earliest to the latest phases of pegmatite development. Such an increase in tantalum from wall zones to cores of pegmatite is reflected by the progressive increase in specific gravity in columbite- tantalite of the quartz.

Wollaston claimed, Ekeberg's new element was actually niobium, which had also been discovered in 1802. The scientific community came to believe Wollaston was right and that Ekeberg claim for new element had been a mistake.

Tantalum and niobium are in fact hard to separate from one another, which led to Wollaston error.

In 1846 German mineralogist Heinrich Rose finally proved beyond doubt that tantalum and niobium were different elements.

2.2. Modeling

A model is a simplified version of reality that is useful as a tool. There are primarily two types of models namely qualitative and quantitative models. Qualitative models are mostly descriptive and use of standard geological techniques of mapping and construction of cross-sections. The quantitative models are broadly of two types: deterministic and probabilistic models. According to Yukler and Welte, (1980); Welte and Yukler, (1981); Nakayama and Vansiclen, (1981); Ungerer et al., (1984), deterministic models seek to identify and quantify all variables of the system and thus predict its behavior by establishing values or limit for each system. They require large number of input data and therefore worthwhile only when extensive exploration has already been carried out. In probabilistic models, both input and output data are presented as probability distributions as according to Bishop et al., (1983); Sluijk and Nederlof, (1984).

A successful model strikes a balance between realism and practicality. Geologic maps constitute a familiar class of models. To map sedimentary section, a geologist collects data at certain outcrops. He casts his observations in terms of the local stratigraphy, which is itself a model that simplifies reality by allowing groups of sediments to be lumped together into formations. He then interpolates among his data point and projects beneath them to infer positions for formation contacts, faults and so on across his study area.

The first and most critical step in developing a geochemical model is conceptualizing the system or process of interest in a useful manner. By system, we simply mean the portion of the universe that we decide is relevant. The composition of a closed system is fixed, but mass can enter and leave an open system. A system has an extent, the amount of fluid and mineral considered in calculation.

The "art" of geochemical modeling is conceptualizing the model in a useful way as shown in Figure 6. This figure shows schematically the basis for constructing a geochemical model. The heart of the model is equilibrium system, which remains in some forms of chemical equilibrium, throughout the calculation. The equilibrium system contains an aqueous fluid and optionally one or more minerals. The temperature and composition of the equilibrium system are known at beginning of the model which shows the system's equilibrium state to be calculated. Pressure also affects the equilibrium state, but usually in a minor way under near-surface condition, (Helgeson, 1969 but also Hemley et.al, 1989), unless a gas phase is present.

In the simplest class of geochemical models, the equilibrium exists as a closed system at a known temperature. Such equilibrium models predict the distribution of mass among species and minerals as well as species activities, the fluid saturation state with respect to various minerals and fugacities of different gases that can exist in the chemical system. In this case the initial equilibrium system contributes the entire geochemical model.

Conceptualizing a geochemical model is a matter of defining:

- The nature of equilibrium to be maintained
- The initial composition and temperature of the equilibrium system.
- The mass transfer or temperature variation to occur over the course of the reaction process envisioned.

2.3. Equilibrium Modeling

According to Pitzer and Brewer, (1961), and Denbigh (1971), a system is in equilibrium when it occupies a specific region of space within which there is no spontaneous tendency for change to occur.

Geochemical models can be conceptualized in terms of certain false equilibrium states (Barton et.al, 1963; Helgeson, 1968). A system is in metastable equilibrium when one or more reactions proceed toward equilibrium at rates that are vanishingly small on the time scale of interest. Metastable equilibrium commonly Figure in geochemical model. In calculating the equilibrium state of natural water from a reliable chemical analysis, for example, we may find that the water is supersaturated with respect to one or more minerals. The calculation predicts that the reaction to precipitate these minerals have not progressed to equilibrium.

2.4. Classification of Elements in Periodic Table

Goldchmidt (1947), classifies chemical elements within the Earth according to their preferred host phases into lithophile (rock-loving), siderophile (iron-loving), chalcophile (ore-loving) and atmophile (gas-loving).

Mendeleev (1869) arranged 63 elements according to their increasing atomic number in several columns, noting recurring chemical properties across them.

Alexandre (1862), a geologist arranged elements in a spiral on a cylinder by order of increasing atomic weight. John (1866) noting that when the elements were listed in order of increasing atomic weight, similar physical and chemical properties recurred at intervals of eight.

Otto (1960) arranged them in a continuous spiral with hydrogen at the centre and transition metals, lanthanides and actinides occupying peninsulas.

Courtines periodic classification (1925), Wringley's system (1949), Giguere's Periodic helix (1965), Dufour Periodic Tree (1996), Stoewe's physicists Periodic Table (1989), Rayner-Canham's unruly inorganic chemists Periodic

Table (2002) which emphasizes trends and patterns and unusual chemical relationship and properties. Janet's left step Periodic Table (1928).

2.5. Thermodynamic Principle

In thermodynamic, the Gibbs energy (G) is the thermodynamic potential that is minimized when a system reaches chemical equilibrium at constant pressure and temperature. Gibbs energy is the energy available to do work (Gibbs, 1873). According to second law of thermodynamic, for systems reacting at standard conditions for temperature and pressure, there is a general natural tendency to achieve a minimum of the Gibbs free energy (Gibbs, 1873).

3. Theoretical Framework

Geomathematically and technically, *COLTAN* model is designed to classify *COLTAN* into groups according to niobium to tantalum ratio with respect to thermodynamic on the assumptions that

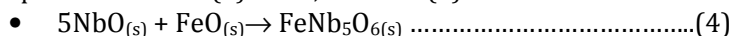
- Ions with charges greater than three and some of the smaller trivalent ions, however form complexes with oxygen and partitioned along the aqueous phase in preference to the silicate phase if both the silicate and aqueous phases coexist at equilibrium.
- Elements of the same charge and similar ionic radii must substitute for one another in crystal lattice of a mineral, equally (Goldschmidt, 1937) as in the case of niobium and tantalum and the substitution of this type is called *ISOVALENT isomorphism*.
- At equilibrium, all minerals must attain at least free Gibbs energy (ΔG) under certain control conditions of temperature and pressure.
- At an igneous condition niobium is present relative to tantalum at a controlled temperature under isobaric condition.
- At sedimentary condition niobium is absent; except that when the temperature of sedimentary rock is heated up to the igneous temperature that would precipitate niobium from the melt or sedimentary rock is the product of disintegration of igneous rock.

Igneous rocks solidify at temperature well above 1000°C (Bowens 1928). Both columbite and tantalite crystallize at above 900°C. Above 400°C, there is complete solid-solution between columbite and tantalite as in equations (8) and (9) respectively.

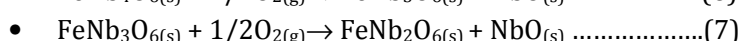
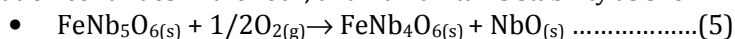


(Transient Niobium (ii) oxide)

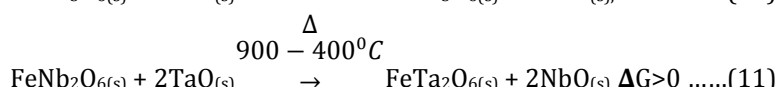
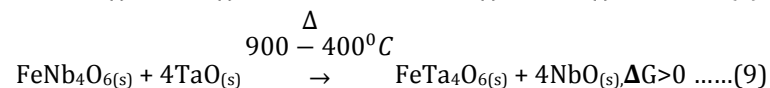
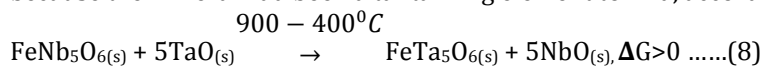
In the presence of iron (ii) oxide, niobium (ii) oxide oxides to form ferrohexaoxonioabate (ii) as shown in equation (4)



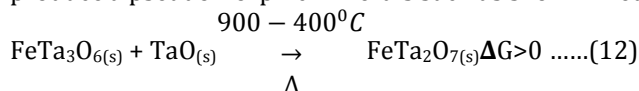
Oxidation continues in the rock, until it maintains stability as shown in equations (5), (6), and (7).

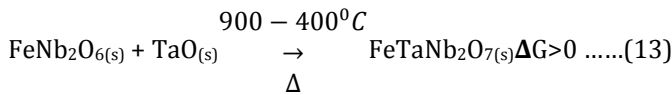


As the temperature of the syenite, to granite pegmatite continues to drop with $\Delta G < 0$, the rocks become richer in tantalum. At this temperature, the numbers of atoms of tantalum replace equal atoms of the niobium in the solid solution as shown in Figure 3. This continues so that at about 900°C - 400°C, (Kinnaird, 1984, Jackson, 1977), there is complete solid-solution between columbite and tantalite in the Granite and Mesozoic pegmatite rock with $\Delta G > 0$ and this process is known as *Tantalization* reaction of *COLTAN* in Cassiterite as shown in equations (8,9 and 10) below. This is the mathematical addition of tantalum to *COLTAN* in cassiterite to produce a more desirable mineral that is rare, strongly attractive and almost out of reach called tantalite as given by Ekeberg (1802). This means that tantalum improves the quality of *COLTAN* in cassiterite and the product is called tantalized coltan, and the tantalized coltan is called tantalite, because the mineral had been a tantalizing element to find, according to Ekeberg (1802)



The two minerals produced from equation 8, 9, 10 and 11 would react in unison with more tantalum (ii) oxide to produce a pseudomorphic minerals such as shown in equations (12 and 13),





3.1. Mathematical Expression for COLTAN

At rhyolitic and basaltic melt temperatures, magmas behave like weak electrolyte, especially on a microscopic scale and are applicable to principle of electroneutrality (Denbigh, 1971). The electrolytic value of magma increases as magma becomes more aqueous. High field strength, hydrophile and lithophile elements with intermediate ionic potential (I = 3 to 9.5) such as niobium and tantalum are partitioned along this aqueous phase and maintain equilibrium with silicate melt. Since they cannot be partitioned along the silicate phase, they are INCOMPATIBLE trace elements, because of their inability to achieve a charge balance with those elements that partitioned along the silicate phase with charge of +2 such as magnesium, calcium and barium if the crystal phase and aqueous phase coexist (Whittaker and Muntus, 1970). The precipitation of columbite from the aqueous phase is very much modified by the presence of water. Therefore, when silicate magma coexists with an aqueous fluid, niobium would be strongly partitioned in the aqueous phase. This affinity of water is almost certainly responsible for the concentration of niobium and its ore, columbite in pegmatite and hydrothermally altered rock. At an igneous temperature, there is a mobility of ions or atoms in the magma solution, since it behaves like a weak electrolyte under electrolytic condition according to Faraday second law of electrolysis, within the magma, so that ions or atoms with an ionic charge less than 3 tend to exist as free ions in the magma and then partition along the silicate phase but those with ionic charge greater than 3 and some of the smaller trivalent ions, will form a complexes with oxygen and then partitioned along the aqueous phase. These complexes maintain their identity during crystallization process. In this case under control condition of temperature, ions or atoms of the same charge or similar size must find themselves and occupy a lattice position to form crystals (Goldschmidt, 1937), which set in matrix (Cayley, 1895), to form rock of a particular composition. The rock formed would reduce to an ore whenever there is a weathering breakdown, such that high temperature minerals are more susceptible to weathering breakdown and would have gone into solution leaving behind low temperature minerals (Goldic 1988). Since niobium crystallizes at an igneous temperature in an aqueous phase, with respect to tantalum under electrolytic condition, there is always a solid solution between niobium and tantalum and can be mathematically expressed in the following equations below

Mathematical derivations of COLTAN are based on charge balance of the constituent species, according to Denbigh, (1971), which states that, the principle of electroneutrality requires that the ionic species in an electrolyte solution remains charge balanced on a microscopic scale. The electroneutrality condition of charge balanced among the species in solution, according to equation (14).

$$\sum Z_i M_i + \sum Z_j M_j = 0 \dots\dots\dots(14)$$

Where Z_i and Z_j are the ionic charges on basis and secondary species. It is useful to note, however, that electroneutrality as assured when the components in the basis are charge balanced.

Because at an igneous temperature condition, magma behaves like a weak electrolyte on a microscopic scale, application of Denbigh equation is necessary to solve the problem of rock forming ores and is expressed as follows;

In an aqueous phase, niobium (Nb), a small ion, lithophile element, of high ionic charge with ionic potential (I), approximately 7, would react with oxygen fugacity in the aqueous phase to produce series of oxides of niobium, called niobate oxide. Further decrease in temperature of the aqueous phase would lead to increase in oxygen fugacity of the melt, thereby oxidizes the oxides of niobium to more stable state as shown in equations below. At equilibrium, each of these oxides of niobium would be stable and maintain equilibrium with the silicate melt, crystallize as columbite with free Gibbs energy greater or equal to zero, numerically $\Delta G \geq 0$

- Oxygen (O) is a single anion with unit charge of (-2).

$$0 = -2 \\ = O^{2-}$$

- Cation with equivalent unit positive charge is needed to balance it, so that the algebraic sum is equal to zero.
- Let the cation be (X^{+2}) so that the formula becomes

$$n[(X^{+2}) (O^{2-})] = nXO \dots\dots\dots(15)$$

$$nXO + nZO = nZX_5O_6 \dots\dots\dots(16)$$

From equation (12), more electropositive element Y will replace some atoms of X in equal proportion so that the equation becomes

$$nXO = nX_{n-x}Y_xO \dots\dots\dots(17)$$

$$nX_{n-x}Y_xO + nZO = nZ[X_{n-x}Y_x]O_6 \dots\dots\dots(18)$$

$$nX_{1-x}Y_xO + nZO = nZ[X_{5-x}Y_x]O_6 \dots\dots\dots(19)$$

As temperature drops, there is an oxidation of nXO as shown equation (17).

$$nZX_5O_6 + 1/2O_2 = nZX_4O_6 + XO \dots\dots\dots(20)$$

$$nZX_4O_6 = nZ[X_{4-x}Y_x]O_6 \dots\dots\dots(21)$$

$$nZX_4O_6 + 1/2O_2 = nZX_3O_6 + XO \dots\dots\dots(22)$$

$$nZX_3O_6 = nZ[X_{3-x}Y_x]O_6 \dots\dots\dots(23)$$

$$nZX_3O_6 + 1/2O_2 = nZX_2O_6 + XO \dots\dots\dots(24)$$

$$nZX_2O_6 = nZ[X_{2-x}Y_x]O_6 \dots\dots\dots(25)$$

3.2. Sequence of Crystallization of COLTAN using Mathematical Expressions with Respect to Gibb's free Energy (ΔG)

According to second law of thermodynamic, for systems reacting at standard conditions for temperature and pressure, there is a general natural tendency to achieve a minimum of the Gibbs free energy (Gibbs, 1873).

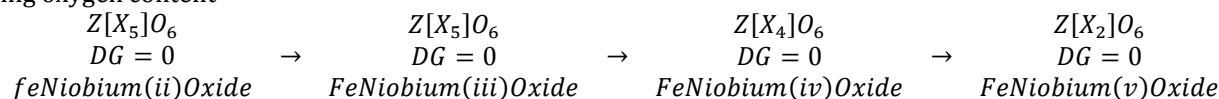
Geomathematically, during cooling of magma, the first COLTAN mineral to form is rich in niobium and is said to be in the state of chemical equilibrium with the melt, provided that temperature and pressure are kept constant, according to Gibbs (1873), numerically, $\Delta G = 0$. But with change in the condition of temperature under isobaric condition imposed on the system in a state of chemical equilibrium, free Gibbs energy will be negative (numerically, $\Delta G < 0$), so that the reaction would be spontaneous and equilibrium will shift to the point that favours crystallization, so as to annul the cooling effect by releasing more heat, according to Le-chaterlier principle (1898) as a result, the first niobium rich COLTAN to form oxidizes into another niobium COLTAN mineral, that is structurally different with distinct chemical composition. This process is called oxidation reaction in this research and the reaction is discontinuous, because oxygen is the only factor that determines the reaction, with less or no substitution of Niobium by Tantalum.

After oxidation, the surviving niobium rich COLTAN mineral would undergo series of reactions by substitutions of one element by another to produce crystals of the same structures, but with different chemical compositions, with free Gibbs energy, numerically less than zero ($\Delta G < 0$), but if the temperature imposed on the system remains the same, the crystals produced, would be at equilibrium with free minimum Gibb's energy, numerically, $\Delta G > 0$. This process is called solid solution and the reaction process is Tantalization reaction and is continuous because tantalum is only factor that determines the reaction as shown in Figure 3.

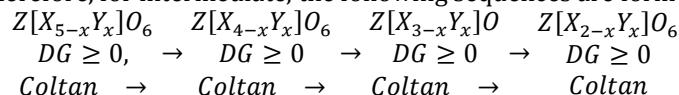
Geomathematically, as a result of these, two series of reactions are attributed to mathematical models of COLTAN; hence, Oxidation reaction series called the Niobate series and the Tantalization series called COLTAN series as shown in Figure 3.

Oxidation reactions series are series of equations that are discontinuous during cooling of magma and are required controlled addition of oxygen, to an already existing crystal that crystallizes from the melt, to form another crystal of different structure, but with distinct chemical composition and are called *Niobate series*.

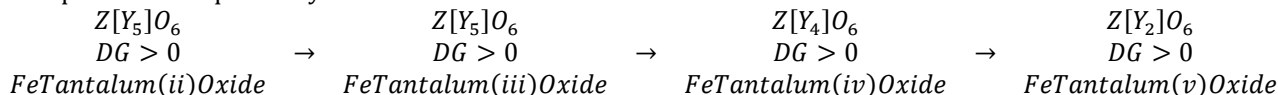
This progresses in sequence as temperature drops to produce sequence of crystallization and is given below in order of increasing oxygen content



Solid solution equations are series of equations that are continuous and they involve substitutions among the cations called (ionic substitution), to produce crystal of same structure but with different chemical compositions. Example, Tantalum substitutes for Niobium in solid solution to form crystals that are intermediates, both Tantalum and Niobium are present in equal proportion. Therefore, for intermediate, the following sequences are formed and are called COLTAN.



The complete substitution of Niobium by Tantalum will produce crystals that are wholly or partially Tantalum and are feebly magnetic and resistant to acid attack at room temperature, because they are stable in the presence of free tantalum and are represented sequentially below:



These minerals are formed sequentially until; it reaches the highest oxidation state which associates with other resistate minerals to produce an ore of tin called *CASSITERITE*. Cassiterite is an ore of tin that is mathematically and minerologically consists of tin, iron ore, columbite, tantalite, zircon, monazite and sand depending on the environment and the rock type in which the ore is being derived with respect to temperature of crystallization, if the Cassiterite source is syenite, granite-pegmatite, then the type of Coltan is COLUMBIT and therefore niobium is the dominant element, but if the source is pegmatite and hydrothermally altered rock, then the type of Coltan is tantalite. Cassiterite that contains more of tantalite is heavier than the one that contains columbite, because tantalum has a density with 8.0 higher than niobium with density of 5.2. Tantalite is in more stable with a minimum free Gibbs energy, numerically, $\Delta G > 0$, and therefore resists acid attack than columbite at room temperature

4. Research Methodology

Sample of fresh cassiterite was obtained from, Jos Plateau state. 20kg of cassiterite sample was obtained for the study. The sample of cassiterite was taken and broken manually with a sledge hammer to provide the required size acceptable to laboratory jaw crusher. The sample was crushed and pulverized, part of pulverized sample was weighed for sieve analysis and processing using magnetic separator. The procedure is as follows.

- 20kg of cassiterite was crushed and pulverized in the laboratory mill machine for an hour,
- Cassiterite was taken and sized by sieving into a number of size fraction using the automatic sieve shaker for 15 minutes.
- Cassiterite was gathered together and introduced into the laboratory mill machine and ground for 15 minutes.
- The cassiterite from the laboratory ball mill machine was sized and each sieve fractions were weighed and the value noted as the product or discharge.

- Sieve analysis. The ground samples were sieved into the following sieve size fractions; + 365 μm, 355 μm, +250 μm, -250 μm, +180 μm, -180 μm, +125 μm, -125 μm, +90 μm, -90 μm, +63 μm, -63 μm using automatic sieve shaker for 15 minutes.
- The discharged product of cassiterite was taken to magnetic separator for processing.
- Ordinary bar magnet of about 0.01 Tesla which produces 650 magnetic field lines is used to measure the magnetic property of the COLTAN in cassiterite obtained from the sources, that is cassiterite from Jos plateau state
- Relative densities of each of the minerals from the processed cassiterite were measured using Archimedes' principle and their specific gravities were calculated.

5. Expected Results and Discussion

5.1.Expected Results

The expected values measured from *magnetization*, electrical resistivity, *strength*, *density*, *cell size* and *matrix* equations according to tantalum to niobium ratio using Archimedes' principle, Magnet and Triaxial testing machine are presented in Table 1

Matrix	COLTAN		Numerical value of tantalum and niobium		Cell size	Electrical resistivity (nΩ)	Magnetization (0.01T)	Density (g/cm ³)	Strength	Rock TYPE
	Chemical formula	Mineral Name	Nb	Ta						
$\begin{pmatrix} 5, & 0 \\ 4, & 0 \end{pmatrix}$	$\begin{pmatrix} X_5O_6 \\ X_4O_6 \end{pmatrix}$	(Columbite) (Columbite)	5,4	0	0.69	152	Weakly magnetic by Hand magnet and paramagnetic	Less dense 8.57	Low 38	Nepeliesyenite
$\begin{pmatrix} 0, & 5 \\ 0, & 4 \end{pmatrix}$	$\begin{pmatrix} Y_5O_6 \\ Y_4O_6 \end{pmatrix}$	(Tantalite) (Tantalite)	0	5,4	0.68	131	Weakly Magnetic by Hand magnet	More dense 16.69	High 69	Lithium pegmatite
$\begin{pmatrix} 5, & 5 \\ 4, & 4 \end{pmatrix}$	$\begin{pmatrix} X_5Y_5O_8 \\ X_4Y_4O_6 \end{pmatrix}$	(Coltan) (Coltan)	5,4		Intermediate	Intermediate	Feebly magnetic by Hand magnet	Intermediate	6.0 – 6.5	Syenite - - pegmatite

Table1. Expected Values Measured from Electrical Resistivity, Magnetization, Density and Strength

5.1.1. Mathematical Modeling of COLTAN in Cassiterite

Consider COLTAN in Cassiterite, a weathering product of igneous rock, such as nepheliesyenite and lithium pegmatite given that tantalum is a distinguishing factor between cassiterite in syenite and pegmatite, therefore;

- Under syenitic condition, columbite is precipitated, with $\Delta G \geq 0$, because at this temperature columbite may or not in its minimum free Gibbs energy and can change to another form with an infinitesimal change in temperature and the columbite to tantalite ratio in nepeliesyenite is given as

Nb_2O_6 : Ta_2O_6 : = 4: 1, such that,
 Nb: Ta = 5:0

- Under pegmatitic condition, tantalum is present with $\Delta G >0$, because at this temperature tantalite is in its minimum free Gibbs energy and cannot change to another form even with change in temperature and the columbite to tantalite ratio in Lithium pegmatite is given as

Nb_2O_6 : Ta_2O_6 : = 1: 4, such that,
 Nb: Ta = 0:5

Based on these two assumptions, matrix equation is used to resolve the problem between *COLTAN* in syenite and *COLTAN* in pegmatite and the equations are mathematically expressed below;

From equation 6, $n [X_{1-x}Y_x] O \xrightarrow{n[ZO]} nZ[X_{5-x}Y_x]O_6$, we have that;

$[X_{5-x}Y_x]O_6 = 0$, where

5-x = x position

x = y position

Using factor theorem,

At x = 0

$$[X_{5-x}Y_x] O_6 = [X_5]O_6 \dots\dots\dots(26)$$

Such that, 5-x = x -position

5- x = 0

x = 5, and

x = y- position;

0 = y-position

y = 0

$$[x, y] [5, 0] = [X_5]O_6 \dots\dots\dots(27)$$

At x = 5

$[X_{5-x}Y_x]O_6 = [Y_5]O_6$, such that,

5-x = x position

5 - 5 = x

x-position = 0 and

x = y -position

5 = y-position

Y-position = 5

$$[x, y] [0, 5] = [Y_5]O_6 \dots\dots\dots(28)$$

$$[X_5]O_{6(s)} + [Y_5]O_5 = [5, 0] + [0, 5] \dots\dots(29)$$

$$[X_4]O_{6(s)} + [Y_4]O_5 = [4, 0] + [0, 4] \dots\dots(30)$$

$$[X_3]O_{6(s)} + [Y_3]O_5 = [3, 0] + [0, 3] \dots\dots(31)$$

$$[X_2]O_{6(s)} + [Y_2]O_5 = [2, 0] + [0, 2] \dots\dots(32)$$

$[XY]_5O_6 = \{5,5\}$

$[XY]_4O_6 = \{4,4\}$

$[XY]_3O_6 = \{3,3\}$

$[XY]_2O_6 = \{2,2\}$

Using matrices method, to represent numerical values assigned to chemical elements in its algebraic form to produce *COLTAN* of a particular IUPAC nomenclature, we have;

$$\begin{pmatrix} 5, & 0 \\ 4, & 0 \end{pmatrix} + \begin{pmatrix} 0, 5 \\ 0, 4 \end{pmatrix} = \begin{pmatrix} 5, 5 \\ 4, 4 \end{pmatrix} \dots\dots\dots(19).$$

$$\begin{pmatrix} X_5 O_6 \\ X_4 O_6 \end{pmatrix} + \begin{pmatrix} Y_5 O_6 \\ Y_4 O_6 \end{pmatrix} = \begin{pmatrix} X_5 Y_5 O_8 \\ X_4 Y_4 O_6 \end{pmatrix} \dots\dots\dots(33)$$

$$\begin{pmatrix} (Columbite) \\ (Columbite) \end{pmatrix} + \begin{pmatrix} (Tantalite) \\ (Tantalite) \end{pmatrix} = \begin{pmatrix} (Coltan) \\ (Coltan) \end{pmatrix} \dots\dots\dots(34)$$

$$[Syenite] + [Pegmatite] = [Syenite Pegmatite] \dots\dots\dots(35)$$

$$FeNb_5O_{6(s)} + FeTa_5O_6 = Fe[NbTa]_5O_6 \dots\dots\dots(36)$$

$$FeNb_4O_{6(s)} + FeTa_4O_6 = Fe[NbTa]_4O_6 \dots\dots\dots(37)$$

$$FeNb_3O_{6(s)} + FeTa_3O_6 = Fe[NbTa]_3O_6 \dots\dots\dots(38)$$

$$FeNb_2O_{6(s)} + FeTa_2O_6 = Fe[NbTa]_2O_6 \dots\dots\dots(39)$$

From equations (36), (37), (38) and (39), it means that weathering of syenite will give Cassiterite rich in Columbite that of Pegmatite will give Cassiterite rich in Tantalite and that of Syenite - Pegmatite will give Cassiterite rich in *COLTAN*

Equations (36), (37), (38) and (39), indicate that lithium pegmatite is a trace for tantalum and it affects the electrical conductivity, the cell size, magnetization, strength and density of COLTAN in cassiterite as shown in Table 1. Columbite $[\text{FeNb}_2]\text{O}_6$ responds weakly to magnetism by stationary hand magnet which is paramagnetic and is found in syenite as well as carbonatite.

Tantalite $[\text{FeTa}_5]\text{O}_6$, feebly responds to magnetism by rotating hand magnet, with the density more than the columbite and a greater tensile strength, which indicates the presence of tantalum and is mainly igneous like pegmatite. This means, the presence of tantalum in granite pegmatite affects the properties of COLTAN such as electrical conductivity, magnetization, strength and density and the amount of tantalum in coltan increased from the earliest phase e.g. syenite to latest phase e.g. pegmatite which gives the account that cassiterite rich in tantalum is of pegmatitic origin and more conductive, more dense, stronger strength than the cassiterite rich in niobium.

Using determinant matrix to classify COLTAN into Niobium rich Coltan and Tantalum rich Coltan groups;

Using determinant matrix to resolve equation (33) into equation (36)

$$\begin{pmatrix} 5, & 0 \\ 4, & 0 \end{pmatrix} + \begin{pmatrix} 0, 5 \\ 0, 4 \end{pmatrix} = \begin{pmatrix} 5, 5 \\ 5, 5 \end{pmatrix}$$

$$[0] + [0] = [0] \dots \dots \dots (40)$$

Therefore;

$$\begin{pmatrix} 5, & 0 \\ 4, & 0 \end{pmatrix} = \text{niobium rich coltan}$$

$$\begin{pmatrix} 0, & 5 \\ 0, & 4 \end{pmatrix} = \text{tantalum rich coltan}$$

$$\begin{pmatrix} 5, & 4 \\ 5, & 4 \end{pmatrix} = \text{coltan}$$

$$\begin{pmatrix} \text{columbite} \\ \text{columbite} \end{pmatrix} = \text{niobium rich coltan}$$

$$\begin{pmatrix} \text{tantalum} \\ \text{tantalum} \end{pmatrix} = \text{tantalum rich coltan}$$

$$\begin{pmatrix} \text{coltan} \\ \text{coltan} \end{pmatrix} = \text{coltan}$$

From equations (36), (37), (38) and (39),

- ❖ Coltan type cassiterite in syenite = columbite
- ❖ Coltan type cassiterite in pegmatite = tantalite
- ❖ Coltan type cassiterite in syenite-pegmatite = coltan

5.2. Discussion of Results

5.2.1. Coltan in Cassiterite

According to Mendeleev (1869), electrical conductivity, density and atomic radii of elements increase down the group of Periodic tables from top to bottom, but with decreasing ionic radii, this means that tantalum which is lower than niobium in group VB, of periodic table is stronger, denser, excellent electrical conductor and smaller in size than the niobium above it in the periodic table.

For all the oxides of niobium and tantalum, only the niobium (v) oxide and tantalum (v) oxide are stable, because they have the maximum oxidation states during crystallization of magma and form a more stable complex with oxygen in the magma, thereby attaining the minimum Gibbs free energy with $\Delta G > 0$

Geomathematically, for a COLTAN to be called columbite type, niobium must exceed tantalum in solid solution of COLTAN represented in cassiterite and tantalite type, if tantalum exceeds niobium in solid solution represented in cassiterite. Several experiments have shown that, in cassiterite ore, there must be at least, one type COLTAN in solid solution of COLTAN, either, coltan itself or columbite or tantalite depending on the genetic environment from which cassiterite is being derived from. The presence of tantalum oxide in cassiterite as shown in fig 1 indicates that there is always solid solution between tantalum and niobium at igneous temperature in form of $\text{Nb}_5\text{O}_6/\text{TaO}$. This means that tantalum forms at igneous temperature at about 400°C to 900°C . In sedimentary rock, the total absent or little amount of niobium and tantalum indicates that there is no solid solution (exsolution) between tantalum and niobium in the rocks at that particular igneous temperature, because the temperature requires for tantalum to precipitate from the melt is far above sedimentary temperature, unless the sedimentary material is heated up to igneous temperature that would precipitate niobium and tantalum from the melt. Based on this, a MODEL has been designed to classify COLTAN into groups according to tantalum to niobium ratio with respect to free Gibbs energy (ΔG) called COLTAN model as shown in Figure 3. Based on tantalum to niobium ratio, Cassiterite is placed either as niobium type coltan, tantalum type coltan or coltan itself.

From Figure 3, ferroniobium (ii) oxide crystallizes first with free energy, numerically less than zero ($\Delta G < 0$), and then with time and decreasing temperature, it oxidizes to ferroniobium (iii) oxide, ferroniobium (iv) oxide with free energy numerically equal to zero ($\Delta G = 0$) and ferroniobium (v) oxide, with free energy numerically greater than zero ($\Delta G > 0$) called oxidation reaction series as you are going across the Figure from left to right. As you are going down the Figure from top to bottom, the number of atoms of niobium decreases with increasing number of atoms of tantalum. The general molecular formula for the two series of COLTAN is $[\text{X}_{n-x}\text{Y}_x]\text{O}_6$, as n ranges from 2 to 5 and x depends on 'n'; the following minerals are obtained, and are subjected to a hand magnet of about $0.01T$, tensile strength, electrical conductivity and measurement of density. These minerals are columbite and tantalite.

Figure 3, indicates that niobium rich zone contains rock types such as nepheline, and carbonite with a general free Gibbs energy but not minimum, numerically $\Delta G \geq 0$ and the tantalum rich zone contains rock types such as granite, and lithium pegmatite with a general minimum free Gibbs energy numerically, $\Delta G > 0$.

The mineral in the upper part of Figure 3, such as columbite, is a lower density mineral, because niobium, which is a transition element placed in group VB, period five, has a density of 5.2, according to Mendeleev (1902). This makes cassiterite rich in niobium, lighter and is paramagnetic at room temperature because of some presence of its opposite and unequal spins magnetic moment, which is feebly magnetic when placed in magnetic field of about $0.01T$, as shown in Figure 3 and as such used to make alloy to increase the strength, ductility and corrosion resistance due to the formation of oxide film. The mineral in the lower part of Figure 3 such as tantalite is a rare, shiny gray dark metal and higher density mineral, because of complete replacement of niobium by tantalum in the solid solution which has a density higher than that of niobium, and hence it is an excellent conductor of heat and electricity which makes it good capacitors and high-power resistors. Because of its heavy in weight to density ratio, hard, shiny gray, as well as rust resistance, it is used to make alloy to increase the strength, ductility and as corrosion resistance, it is anti-ferromagnetic, at a low temperature, and paramagnetic at room temperature.

5.2.2. Coltan Model

Determinant matrix is used to construct *COLTAN* model in cassiterite according to tantalum to niobium ratio with respect to electrical conductivity, magnetization, strength, cell size and density in which tantalum is determinant factor and niobium is a constant variable and is expressed as follows from equations (33) and (42)

Using determinant matrix to resolve equation (33) into equation (41)

$$\begin{pmatrix} 5, & 0 \\ 4, & 0 \end{pmatrix} + \begin{pmatrix} 0, 5 \\ 0, 4 \end{pmatrix} = \begin{pmatrix} 5, 5 \\ 4, 4 \end{pmatrix}$$

$$[0] + [0] = [0] \dots \dots \dots (42)$$

Figure 3, shows that niobium-tantalum-oxide called COLTAN is grouped into three according to the ratio of niobium to tantalum, based on this research. These are Niobium rich Coltan, Coltan and Tantalum rich Coltan. Equation (42) indicates that there is a complete solid solution between columbite and tantalite, which means in each case the presence of one, is zero with respect to the other.

5.2.2.1. Niobium Rich Coltan

In this group, the amount of tantalum is zero, and niobium ion increases from +2 to +5 across the figure from left to right with a general Gibbs free energy numerically $\Delta G > 0$ and has not been affected by tantalum with ratio of niobium to tantalum to be 5:0. Minerals in this group are feebly magnetic, relatively high density and relative electrical conductivity and first weathered under weathering

- Condition when compared with tantalum rich coltan, according to Goldich (1988). Electrical conductivity increases down the figure from top to bottom with increasing tantalum in coltan, since tantalum is more conductive than niobium as described by Mendeleev periodic table of elements (Mendeleev 1902).
- Coltan: Minerals in this group have been affected by tantalum. In this group, the amount of tantalum atom increases down the group with decreasing number of atoms of niobium to the point where the atoms are equal in amount with the ratio of 5:5. In this case, they act as a single mineral entity and exhibit the same properties.
- Tantalum rich Coltan: In this group, the amount of tantalum atom increases down the group with decreasing number of atoms of niobium to the point where niobium is completely replaced by tantalum with the ratio of niobium to tantalum atom to be 0:5. Electrical conductivity and density of *COLTAN* increase with number of tantalums down the Figure with decreasing cell size because of lanthanide contraction. This means that tantalum improves the quality of Coltan in Cassiterite because of its higher electrical conductivity, tensile strength and density.

COLTAN MODEL

	Z(X _{2-x} Yx)O ₆	Z(X _{3-x} Yx)O ₆	Z(X _{4-x} Yx)O ₆	Z(X _{5-x} Yx)O ₆
1	(Fe)NbO ₆	(Fe)Nb ₂ O ₆	(Fe)Nb ₄ O ₆	(Fe)Nb ₅ O ₆
2	(Fe)Nb ₁₉ TaO ₆₀	(Fe)Nb ₂₉ TaO ₆₀	(Fe)Nb ₃₉ TaO ₆₀	(Fe)Nb ₄₉ TaO ₆₀
3	(Fe)Nb ₂ TaO ₃₀	(Fe)Nb ₁₄ TaO ₃₀	(Fe)Nb ₁₉ TaO ₃₀	(Fe)Nb ₂₄ TaO ₃₀
4	(Fe)Nb ₁₇ Ta ₃ O ₆₀	(Fe)Nb ₂₇ TaO ₃₀	(Fe)Nb ₃₇ Ta ₃ O ₆₀	(Fe)Nb ₄₇ Ta ₃ O ₆₀
5	(Fe) Nb ₄ Ta O ₃₀	(Fe) Nb ₁₃ Ta ₂ O ₃₀	(Fe) Nb ₉ Ta O ₃₀	(Fe) Nb ₂₃ Ta ₂ O ₃₀
6	(Fe) Nb ₃ Ta O ₁₂	(Fe) Nb ₅ Ta O ₁₂	(Fe) Nb ₇ Ta O ₁₂	(Fe) Nb ₉ Ta O ₁₂
7	(Fe) Nb ₇ Ta ₃ O ₃₀	(Fe) Nb ₄ Ta O ₁₀	(Fe) Nb ₁₇ Ta ₃ O ₃₀	(Fe) Nb ₂₂ Ta ₂ O ₃₀
8	(Fe) Nb ₁₃ Ta ₇ O ₃₀	(Fe) Nb ₂₃ Ta ₇ O ₆₀	(Fe) Nb ₃₃ Ta ₇ O ₆₀	(Fe) Nb ₄₃ Ta ₇ O ₆₀
9	(Fe) Nb ₃ Ta ₂ O ₁₅	(Fe) Nb ₁₁ Ta ₄ O ₃₀	(Fe) Nb ₈ Ta ₂ O ₁₅	(Fe) Nb ₂₁ Ta ₄ O ₃₀
10	(Fe) Nb ₁₁ Ta ₉ O ₆₀	(Fe) Nb ₂₁ Ta ₉ O ₆₀	(Fe) Nb ₃₁ Ta ₉ O ₆₀	(Fe) Nb ₄₁ Ta ₉ O ₆₀
11	(Fe) Nb Ta O ₆	(Fe) Nb ₇ Ta O ₆	(Fe) Nb ₃ Ta O ₆	(Fe) Nb ₄ Ta O ₆
12	(Fe) Nb ₉ Ta ₁₁ O ₆₀	(Fe) Nb ₁₉ Ta ₁₁ O ₆₀	(Fe) Nb ₂₉ Ta ₁₁ O ₆₀	(Fe) Nb ₃₉ Ta ₁₁ O ₆₀
13	(Fe) Nb ₂ Ta ₃ O ₁₅	(Fe) Nb ₃ Ta ₂ O ₁₅	(Fe) Nb ₇ Ta ₃ O ₁₅	(Fe) Nb ₁₉ Ta ₆ O ₃₀
14	(Fe) Nb ₁₇ Ta ₃ O ₆₀	(Fe) Nb ₁₇ Ta ₁₃ O ₆₀	(Fe) Nb ₂₇ Ta ₃ O ₆₀	(Fe) Nb ₃₇ Ta ₁₃ O ₆₀
15	(Fe) Nb ₃ Ta ₇ O ₃₀	(Fe) Nb ₈ Ta ₇ O ₃₀	(Fe) Nb ₁₃ Ta ₇ O ₃₀	(Fe) Nb ₁₈ Ta ₇ O ₃₀
16	(Fe) Nb Ta ₃ O ₁₂	(Fe) Nb ₃ Ta ₃ O ₁₂	(Fe) Nb ₅ Ta ₃ O ₁₂	(Fe) Nb ₇ Ta ₃ O ₁₂
17	(Fe) Nb ₂ Ta ₄ O ₁₅	(Fe) Nb ₇ Ta ₈ O ₃₀	(Fe) Nb ₆ Ta ₄ O ₁₅	(Fe) Nb ₁₇ Ta ₈ O ₃₀
18	(Fe) Nb ₃ Ta ₁₇ O ₆₀	(Fe) Nb ₁₃ Ta ₁₇ O ₆₀	(Fe) Nb ₂₃ Ta ₁₇ O ₆₀	(Fe) Nb ₃₃ Ta ₁₇ O ₆₀
19	(Fe) Nb Ta ₉ O ₃₀	(Fe) Nb ₂ Ta ₃ O ₁₀	(Fe) Nb ₁₁ Ta ₉ O ₃₀	(Fe) Nb ₁₆ Ta ₉ O ₃₀
20	(Fe) Nb Ta ₁₉ O ₆₀	(Fe) Nb ₁₁ Ta ₁₉ O ₆₀	(Fe) Nb ₂₁ Ta ₁₉ O ₆₀	(Fe) Nb ₃₁ Ta ₁₉ O ₆₀
21	(Fe) Ta ₂ O ₆	(Fe) Nb Ta ₂ O ₆	(Fe) Nb ₂ Ta ₂ O ₆	(Fe) Nb ₃ Ta ₂ O ₆
		(Fe) Nb ₉ Ta ₂₁ O ₆₀	(Fe) Nb ₁₉ Ta ₂₁ O ₆₀	(Fe) Nb ₂₉ Ta ₂₁ O ₆₀
		(Fe) Nb ₄ Ta ₁₁ O ₃₀	(Fe) Nb ₉ Ta ₁₁ O ₃₀	(Fe) Nb ₁₄ Ta ₁₁ O ₃₀
		(Fe) Nb ₇ Ta ₂₃ O ₆₀	(Fe) Nb ₁₇ Ta ₂₃ O ₆₀	(Fe) Nb ₂₇ Ta ₂₃ O ₆₀
		(Fe) Nb ₃ Ta ₄ O ₁₀	(Fe) Nb ₂ Ta ₃ O ₁₀	(Fe) Nb ₁₃ Ta ₄ O ₁₀
		(Fe) Nb Ta ₅ O ₁₂	(Fe) Nb ₂ Ta ₃ O ₁₀	(Fe) Nb ₅ Ta ₅ O ₁₂
		(Fe) Nb ₂ Ta ₁₃ O ₃₀	(Fe) Nb ₃ Ta ₅ O ₁₂	(Fe) Nb ₁₂ Ta ₁₃ O ₃₀
		(Fe) Nb Ta ₂₇ O ₆₀	(Fe) Nb ₇ Ta ₁₃ O ₃₀	(Fe) Nb ₂₃ Ta ₂₇ O ₆₀
		(Fe) Nb Ta ₁₄ O ₃₀	(Fe) Nb ₁₃ Ta ₂₇ O ₆₀	(Fe) Nb ₁₁ Ta ₁₄ O ₃₀
		(Fe) Nb Ta ₂₉ O ₆₀	(Fe) Nb ₃ Ta ₇ O ₁₅	(Fe) Nb ₂₁ Ta ₂₉ O ₆₀
		(Fe) Ta ₃ O ₆	(Fe) Nb ₁₁ Ta ₂₉ O ₆₀	(Fe) Nb ₂ Ta ₃ O ₆
			(Fe) Nb Ta ₃ O ₆	(Fe) Ta ₁₉ Ta ₃₁ O ₆₀
			(Fe) Nb ₉ Ta ₃₁ O ₆₀	(Fe) Ta ₉ Ta ₁₆ O ₃₀
			(Fe) Nb ₂ Ta ₃₁ O ₁₅	(Fe) Nb ₁₇ Ta ₃₃ O ₆₀
			(Fe) Nb ₇ Ta ₃₃ O ₆₀	(Fe) Nb ₈ Ta ₁₇ O ₃₀
			(Fe) Nb ₃ Ta ₁₇ O ₃₀	(Fe) Nb ₁₈ Ta ₇ O ₃₀
			(Fe) Nb ₁₃ Ta ₇ O ₃	(Fe) Nb ₁₂ Ta ₁₃ O ₃₀
			(Fe) Nb ₇ Ta ₁₃ O ₃₀	(Fe) Nb ₁₃ Ta ₃₇ O ₆₀
			(Fe) Nb ₃ Ta ₃₇ O ₆₀	(Fe) Nb ₆ Ta ₁₉ O ₃₀
			(Fe) Nb Ta ₁₉ O ₃₀	(Fe) Nb ₁₁ Ta ₃₉ O ₆₀
			(Fe) Nb Ta ₃₉ O ₆₀	(Fe) Nb ₉ Ta ₄₁ O ₆₀
			(Fe) Ta ₄ O ₆	(Fe) Nb ₄ Ta ₂₁ O ₃₀
				(Fe) Nb ₇ Ta ₄₃ O ₆₀
				(Fe) Nb ₃ Ta ₂₂ O ₃₀
				(Fe) Nb Ta ₉ O ₁₂
				(Fe) Nb ₃ Ta ₂₂ O ₃₀
				(Fe) Nb Ta ₉ O ₁₂
				(Fe) Nb ₂ Ta ₂₃ O ₃₀
				(Fe) Nb Ta ₂₄ O ₃₀
				(Fe) Nb Ta ₄₉ O ₆₀
				(Fe) Ta ₅ O ₆

Figure 2: Mathematical computation of coltan

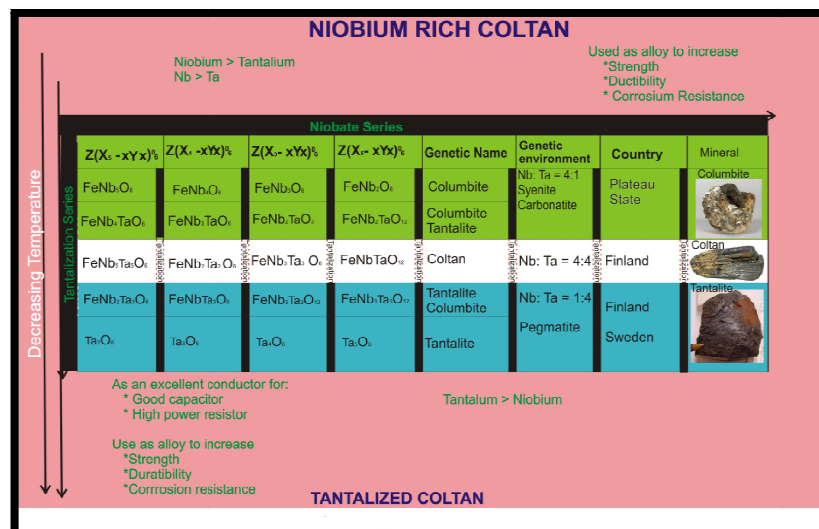


Figure 3: Coltan Model

6. Summary of Findings

The effect of tantalum on COTAN in cassiterite can be summarized in the following ways;

- The amount of columbite and tantalite in the silicate melt depend on the degree of an aqueous phase in the silicate melt which is furnished by the presence of water in the melt. This means that as the amount of water increases in the melt, the amount of columbite and tantalum also increase.
- Since columbite and tantalite have intermediate potential of 7.25 and 7.35, they both partitioned along the aqueous phase, and hence classed as incompatible trace element
- Drop in temperature in the melt, increases the water content of the melt. This means that water depresses the crystallization of anhydrous melt and increases the crystallization of a hydrous melt such as amphibole and mica.

For this reason, the concentration of columbite and tantalite is more in hydrous melt than in the anhydrous melt since water controls the concentration of both minerals

- There is an exsolution in the hydrous melt, because of presence of tantalum; therefore, there is ionic substitution of niobium by tantalum in the melt during solid solution.
- There is no exsolution in anhydrous melt, likewise the sedimentary rock, because the condition that favours the concentration of columbite and tantalite is limited in the melt.
- From Figure 3, there is an arithmetic progression of tantalum as you go from the top to bottom of the figure. This means there is a successive increment of tantalum and decrement of niobium from the top to bottom of the figure.
- The increment of tantalum and decrement of niobium from top to bottom affect the properties of niobium rich coltan such as its composition, its magnetism and the strength as well as its density and electrical conductivity.
- The effect of tantalum on coltan in cassiterite can be mathematically summarized through the following equation at the root of the equation [0, 5].

$$\sum_{x=0}^5 Z(X_{n-x}Y_x)O, Z(X_{n-x}Y_x)O_6 = 0, \text{ at the point of } (0, 5).$$

$$n = 0$$

$$x \leq n$$

If the summation of the equation is equal to zero and $x = 0$, then the Coltan type produced is Columbite and this is called niobium rich Coltan with the associated rock types such as nepheliesyenite and carbonatite. But at $x = 5$, the Coltan tantalized Coltan type called *tantalite*. This includes tantalite with the associated rocks such as granite and pegmatite.

7. Conclusion

Using mathematical modeling approach to appraise the effect of tantalum on COLTAN in cassiterite, it could be concluded that the presence of tantalum on COLTAN increases the electrical conductivity, magnetic property, density, with decrement in the cell size and high tensile strength of Niobium rich coltan. The grade of COLTAN is determined by more or less amount of tantalum it contains. Findings have shown that, both minerals can be single entity or can occur as separate entity, according Heinrich (1846), with the similar property of being used as alloy to increase strength, corrosion resistance, and ductility of a material, but with more electrical conductivity and higher density of tantalite, than the columbite, tantalites are used specially in electronics industry for capacitors and high power resistor, hence excellent conductor of heat and electricity making it more tantalizing mineral than columbite and rarely do they occur independently of the other, and the rocks origin are nepheliesyenite, biotite granite and lithium pegmatite. The ratio of columbite to tantalite in nepheliesyenite is 4:1, and columbite to tantalite ratio in lithium pegmatite is 1:4 according Goldschmidt (1954). Kuz'menko (1950) shows that the columbite to tantalite ratio in Jos Plateau state is about 4:1. In relation to COLTAN, columbite has a general Gibbs free energy numerically $\Delta G \geq 0$ and tantalite has general Gibbs free energy numerically $\Delta G > 0$. The weak magnetization of these two minerals makes them to be concentrated in the high intensity magnetic separator during mineral processing of cassiterite and paramagnetic at room temperature at 1atm. Finally, the presence or absence of tantalum on COLTAN in cassiterite determines their coltan type, either niobium rich type coltan, tantalum rich type coltan or coltan itself, as well as their genetic rock origin, in which the amount of tantalum on COLTAN increases from alkaline rock e.g. syenite to more silicic rock e.g. granite, such as pegmatite which gives the account that columbite is found in nepheliesyenite and tantalite is found in lithium pegmatite such that the weathering of syenite would give columbite and that of pegmatite would give tantalite.

Additionally, using matrix methods from equations (33), (34) and (35), COLTAN in cassiterite was modeled in which tantalum is a determinant factor, and COLTAN model was designed to classify them into groups, such that if niobium exceeds tantalum in coltan, it is called niobium rich coltan type and if tantalum exceeds niobium in coltan, it is called tantalum rich type, but if both the niobium and tantalum are equal in coltan it is coltan itself.

8. Innovation/Contribution to Knowledge

After comparative analyses between columbite and tantalite in cassiterite using, electrical conductivity, magnetism, strength, and density to appraise the COLTAN in cassiterite according to tantalum to niobium ratio, an expected concise valuable substantive empirical novel model would be developed and can be employed to study COLTAN in cassiterite. This concise empirical novel model was, "COLTAN model and can be outlined with the aid of the following:

- Because all minerals must be set in matrices to form rocks, "Matrix equations" would be used to resolve the problems between columbite and tantalite in cassiterite.
- Because minerals require temperature, pressure and energy to form, two series of reactions are used to establish these relationships, which are the *Oxidation called Niobate series* and the *Tantalization series* as shown in figure 1 and 3
- Because COLTAN is formed from two genetic environments of igneous rocks such as syenite and pegmatitic rocks, they are classified into a coltan groups using COLTAN model, as shown in figure 3.

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Appendix

A: Mathematical Expression of COLTAN and their IUPAC name. (X_n-xY_x)O₆

A1: Niobium Rich Coltan

Niobate series

- Ferrohexaoxonioabate (ii): FeNb₅O_{6(s)}
- Ferrohexaoxonioabate (iii): FeNb₄O_{6(s)}
- Ferrohexaoxonioabate (iv): FeNb₃O_{6(s)}
- Ferrohexaoxonioabate (v): FeNb₂O_{6(s)}

A2: Tantalized coltan:

Tantalization series :

- Ferrohexaoxotantalate (ii): FeTa₅O₆
- Ferrohexaoxotantalate (iii): FeTa₄O₆

- Ferrohexaoxotantalate (iv): FeTa_3O_6
- Ferrohexaoxotantalate (v): FeTa_2O_6

B: Chemical Classification of COLTAN with respect to Tantalum to Niobium ratio

B1: Niobium rich Coltan: Niobium is 100% present in the Coltan

1. Columbite: FeNb_2O_6

- Nb:Ta = 5:0

B2: Coltan: both Niobium and Tantalum are present partially or in equal amount.

2. Coltan: $\text{Fe}(\text{NbTa})_2\text{O}_6$

- Nb:Ta = 5:5

B3: Tantalized Coltan: Tantalum is 100% present in Coltan

3. Tantalite: FeTa_2O_6

- Nb:Ta = 0:5