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Mathematical Modeling of Cassiterite Using Certain High Field Strength Elements (HFSE) with Respect to Thermodynamics Principle

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Abstract:

The main purpose of this study was to evaluate Cassiterite ore mathematically, using certain selected minerals of high field strength elements (HFSE) with respect to thermodynamic principle and how they control the formation of cassiterite during crystallization of magma. The effectiveness of Cassiterite ore in Extractive Industry depends on the properties of these minerals of HFSE that composed the Cassiterite during crystallization of magma and can be mathematically expressed as $Z[X_{n-x}Y_x]O_6$, $[X_{n-x}Y_x]O_4$ and $[X_{n-x}Y_x]O_3$ as n ranges from 0 to 5 where x depends on 'n'. These minerals contain HFSE and are those that essentially partitioned along the aqueous phase during cratallization magma. 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, the relationship between minerals of HFSE can be mathematically established using a Cassiterite model. Mathematically, findings have shown that, the minerals obtained from cassiterite during processing are mainly minerals of HFSE such as tin, ilmenite, columbite, tantalite, zircon, monazite and sand, and as such classified as, Ferri/Ferrous-Columbte, Ilmeno-Columbite Cassiterite type, and Ilmeno-tantalite types and chemical analysis using XRF revealed the following chemical compositions of cassiterite; SnO_2 , TiO_2 , Fe_2O_3/Fe_3O_4 , Nb_2O_6 , Ta_2O_6 , ZrO_2 . At a given chemical equilibrium under standard condition of temperature and pressure, these HFSE are partitioned along the aqueous phase and they set in matrices to form an Ore of these HFSE that is stable with minimum Gibbs free energy and is highly resistance to weathering during weathering breakdown, such as Cassiterite. In conclusion after the comparative analysis among the minerals of HFSE in cassiterite using matrix equations and certain measures such as density, magnetic susceptibility, and their electrical conductivity, it is observed that, the type of reactions that take place during the formation of Cassiterite are oxidized and isomorphous which include complex, isovalent and heterovalent reactions. This means that there was an oxidation of these complexes from one form to the other and substitution of one element to the other according to size and charge during the formation of cassiterite ore from magma. Presumably, if the reactions occur throughout the time of crystallization from the dry melt to an aqueous state with increasing particular trace elements over the others, then at a given chemical equilibrium with minimum Gibbs free energy, cassiterite can be processed in terms of ferrous/ferric – colubite cassiterite type Ilmeno-Columbite Cassiterite type and Ilmeno – tantalite cassiterite type. Finally, the presence or absence of HFSE over the other in cassiterite ore determine their genetic rock origin, in which the amount of titanium - tantalum in Cassiterite increased from alkali rock (magmatic) with $\Delta G \geq 0$, e.g. nepheline syenite to more silicic, with $\Delta G > 0$, e.g. granite pegmatite (hydrothermal) which gives the account that cassiterite rich in ferrous/ferric -niobium is less dense than the cassiterite rich in titanium-tantalum, therefore as result of this, concise valuable substantive empirical novel model was developed and can be employed to study cassiterite ore. This concise empirical novel model was, 'Cassiterite' model designed with the aid of: Matrix equation, Oxidation and the isomorphous process, and can be recommended to study the Cassiterite and the application can improve mineral processing in extractive Industry.

Keywords: HFSE, Cassiterite, Isovalent, Heterovalent, Complex

1. Introduction

1.1. Background to the Study.

Cassiterite is an ore of tin and mathematically, consists of HFSE, of 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. They are the major elements in Cassiterite ore and minor elements in the

source rock, e.g., Pegmatite These lithophile 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 (SiO₄) 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. Because cassiterite is a primary phase in pegmatite and can incorporate Nb, Ta, Zr, and Hf into its structure, it is expected that the Nb/Ta and Zr/Hf ratios of the cassiterite potentially reflect the Nb-Ta and Zr-Hf fractionation of the pegmatite melts as in this case. Cerny et al, also suggested that the compositional trend of cassiterite is from Nb-rich to Ta-rich cassiterite in lepidolite- subtype pegmatites.

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 Achueno and Komolafe (2021), e.g., ferrohexaoxonioate (v) is the IUPAC name for columbite (FeNb₂O₆) and that of tantalite (FeTa₂O₆) is ferrohexaoxotantalate (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

In this study, ICP-MS analyses show that the concentrations LILE, REE, Y, U, Th and Pb are extremely low in Cassiterite and do not show any distinct variation patterns. Therefore, we only focus on elements including Zr, Hf, Nb, Ta, W, Sn, Ti and Sc that are commonly present in cassiterite.

Lennen and Cuney, pointed out that such fractionation trends were likely due to different solubilities of the end-member phase in CGM and zircon respectively. According to their study, columbite and zircon have lower solubility than the tantalite and hafnon respectively, in metaluminous to peraluminous granite melts, the granite melts would be Ta- and Hf-rich with increasing fractionation degree. Recently, Van Lichtervelde et al, argued that isothermal Nb-Ta fractionation cannot be explained by solubility differences. Rather disequilibrium crystallization at supersaturation should be the reason for extreme of Ta enrichment in residual melts

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: Wustite (FeO), Rutile (TiO₂), Magnetite (Fe₃O₄), Haematite (Fe₂O₃), Ulvospinel (Fe₂TiO₄), Ilmenite and Coltan in cassiterite.

Because of presence of oxygen fugacity in the magma, iron will undergo the following series of oxidation, as shown in equation (1). $Fe^0 \xrightarrow{-e} Fe^{+} \xrightarrow{-e} Fe^{2+} \xrightarrow{-e} Fe^{3+} \dots \dots \dots (1)$

Equation (1) is called oxidation reaction series of iron ore.

The iron ions at three oxidation states above are called iron (i) oxide iron (ii) oxide, and iron (iii) oxide, the iron (i)oxide is unstable and transient and not found in natural compound. The oxides are in the forms of hematite (Fe₂O₃), magnetite (Fe₃O₄), wustite (FeO)

The order of increasing oxidation is as shown below;

Wustite (FeO) < magnetite (Fe₃O₄) < hematite (Fe₂O₃)

As noted from fundamental of Geophysics by William Lowrie, Reprinted (2004), Titanomagnetite – hematite is the name of the family of iron oxide minerals described by the general formula as shown below;

Magnetite: [X_{3-x}Y_x]O₄

Hematite: [X_{2-x}Y_x]O₃

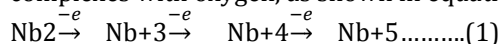
These indicate the ionic replacement of two Fe³⁺ by one Fe²⁺ and one Ti⁴⁺ ion can take place in solid-solution series according to Goldschmidt (1937) as shown in Table 2.

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.

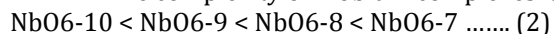
Niobium and tantalum occur in nature almost entirely as single isotopes (Nb93 and Ta181) and they commonly substituted for one another in minerals because they both have similar ionic radii and occur mostly in quinquevalent state. A great preponderance of one element over the other rarely occurs in certain types of rocks such as nepheline syenite (niobium rich) or lithium-bearing pegmatite (tantalum rich). Columbite and Tantalite occur in most alkali rock such as nepheline syenite, alkali ultramafic and mafic, carbonatite, sodic and alkaline granite. A greater amount of columbite, is recorded in nepheline syenite with columbite to tantalite ratio of about 20: 5 and tantalite in lithium pegmatite. Columbite dissolved and precipitates as hydrolysate, and some of them are carried to the ocean, where they crystallized 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 crystallites 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 lanthanide 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 below



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

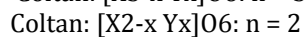
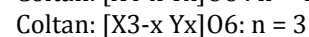
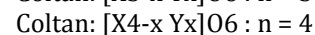
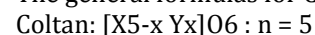
The niobium ions at five oxidation states above are called niobium (ii) oxide, niobium (iii) oxide, and niobium (iv) oxide, and niobium (v) oxide. The niobium (ii), (iii) and (iv) oxide are unstable and transient and not found in natural compound. The oxides are in the form of columbite (FeNb₅O₆, FeNb₄O₆,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

The order of increasing oxidation is as shown below;

NIOBATE: FeNb₅O₆ < FeNb₄O₆, <FeNb₃O₆, < FeNb₂O₆: Oxidation

TANTALITE: FeTa₅O₆ < FeTa₄O₆, <FeTa₃O₆, < FeTa₂O₆: Tantalization

The general formulas for COLTAN are as shown below;



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 cassiterite and it is grouped according to the ratio of HFSE in Cassiterite using matrix expressions. It is a method developed to establish relationships among minerals of HFSE in cassiterite 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 Cassiterite ore originated from granitic and lithium pegmatitic rocks. It involves using mathematical equations, to calculate the empirical formula of each minerals of HFSE in cassiterite that formed during crystallization from the magmatic melt and hydrothermal fluid as shown in Figure 1. It also helps students to classify, name and understand genetic origin of 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 cassiterite 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 HFSE ratio to classify Cassiterite according to its genetic origin using matrix expressions 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 Isomorphous 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, Cassiterite 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 appraise Cassiterite using certain HFSE with respect to thermodynamic principle and classify them according to their genetic origin 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 (complexes), and Isomorphous reactions series and this is shown in Figure 1. From Figure 1 the following deductions are made; Oxidation reaction represents the horizontal axis and is called Complex series while Isomorphous reaction represents the vertical axis and is called Isomorphous series.

- Oxidation (Complex series) is the reaction series that takes place in syenite.
- Isomorphous 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 Complex series are niobium (ii) oxide, niobium (iii) oxide, niobium (iv) oxide, niobium (v) oxide, ferrous and ferric oxide.
- Minerals that form during Isomorphous reaction are tantalum (ii) oxide, tantalum (iii) oxide, tantalum (iv) oxide, tantalum (v) oxide, titano-ferrous and ferric oxide.

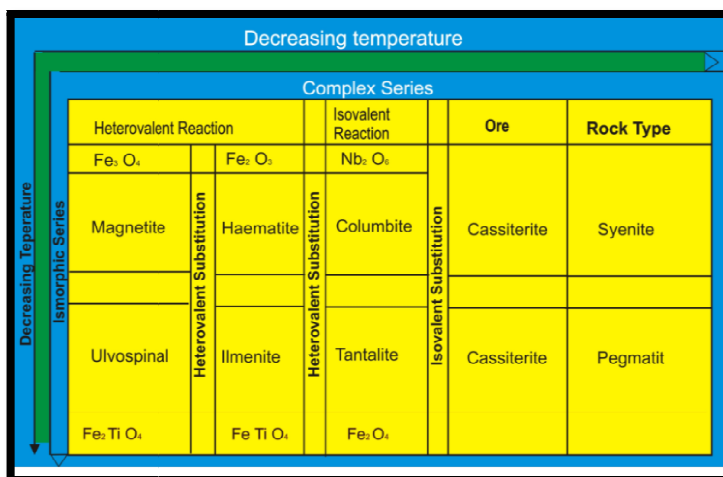


Figure 1: Design Model

1.5.1. Definition of Terms

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)

- **COMPLEX SERIES:** This is the addition of oxygen to the ores of HFSE as temperature drops during crystallization of magma at a given Gibbs free energy with respect to temperature and pressure.
- **ISOMORPHOUS SERIES:** At a given Gibbs free energy with respect to temperature and pressure, ISOMORPHOUS in this context is the process involving mathematical substitution of one element by another of similar size in equal proportion in solid solution during chemical process in the magma to produce a natural durable, high strength substance which enhances the life of given material possibly, cassiterite.
- **ISOVALEENT SUBSTTTUTION:** At a given Gibbs free energy with respect to temperature and pressure, ISOVALEENT in this context is the process involving mathematical substitution of one element by another of similar size with the same charge in equal proportion in solid solution during chemical process in the magma to produce a natural durable, high strength substance which enhances the life of given material possibly, COLTAN.
- **HETEROVALENT SUBSTITUTION:** At a given Gibbs free energy with respect to temperature and pressure, HETEROVALEENT in this context is the process involving mathematical substitution of one element by another of similar size but of different charge in equal proportion in solid solution during chemical process in the magma to produce a natural durable, high strength substance which enhances the life of given material possibly, iron such ilmenite and ulvospinel.
- '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:

HFSE = High Field Strength Elements

X = [Nb, Fe]

Y = [Ta, Ti]

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.

Nepheline syenite is well known for its high concentration of niobium about 12:1 ratio of columbite to tantalite, as in Russia. Nepheline syenites have been studied extensively by Russian geologists and Russian reports dominate the literature on these rocks. According to Es'kova (1960), nepheline syenite 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 nepheline syenite 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 nepheline syenite 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 nepheline syenite and other feature connected with them. Tantalum was discovered by Anders G. Ekeberg in 1802 in Uppsala, Sweden, in the minerals tantalite from Finland and yttritanalite 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 in 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 accumulate 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

Goldschmidt (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).

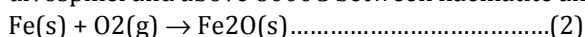
According to second law of thermodynamic, for systems reacting at standard conditions for temperature and pressure, there is a general natural tendency to achieve a minimum of the Gibbs free energy (Gibbs, 1873).

3. Theoretical Framework

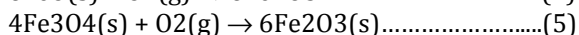
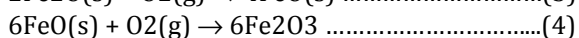
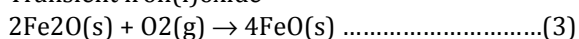
Geomathematically and technically, Cassiterite model is designed to classify Cassiterite into groups according to their genetic origin with respect to thermodynamics on the assumptions that

- 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 Gibb's energy (ΔG) under certain control conditions of temperature and pressure.
- At an igneous condition niobium and iron are present relative to tantalum and titanium at a controlled temperature under isobaric condition.
- At sedimentary condition niobium and titanium are 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.

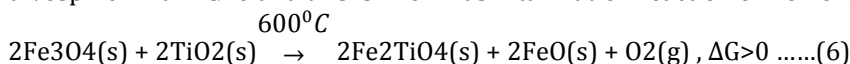
Igneous rocks solidify at temperature well above 10000C (Bowens 1928). Both titanomagnetite and hemoilmenites crystallize at above 13000C. Above 6000C, there is complete solid-solution between magnetite and ulvospinel and above 8000C between haematite and ilmenite as in equations (6) and (7) respectively.



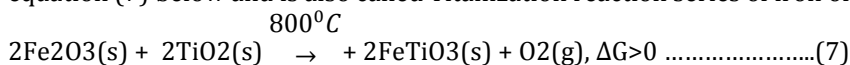
Transient iron(i)oxide



As the temperature of the igneous rock continues to drop with $\Delta G < 0$, the ferrimagnetic minerals become richer in titanium. At this temperature, the numbers of atoms of titanium replace equal atoms of the iron in the solid solution as shown in Table 2. This continues so that at about 6000C, there is complete solid-solution between magnetite and ulvospinel with $\Delta G > 0$ and this is known as Titanization reaction of iron ore as shown in equation (6) below.



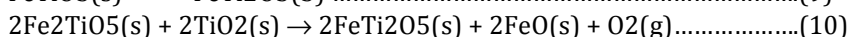
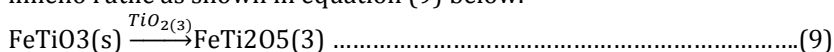
And above about 8000C, there is a complete solid-solution between haematite and ilmenite with $\Delta G > 0$ as shown in equation (7) below and is also called Titanization reaction series of iron ore.



The iron oxide, (Fe_2O_3), which is stable at above temperature of about 8000C reacts in unison with titanium oxide to produce a pseudo mineral called pseudo brookite [Fe_2TiO_5] as shown in equation (8) below.



Titanium replaces iron in equal proportion as the temperature of the rock continues to drop. This process continues so that at about above a temperature of 8000c, there is a complete solid-solution between pseudobrookite, and ilmeno rutile as shown in equation (9) below.

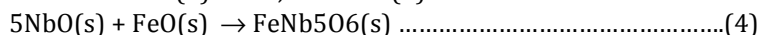


Conversely, both columbite and tantalite crystallize at above 9000C. Above 4000C, there is complete solid-solution between columbite and tantalite as in equations (8) and (9) respectively.

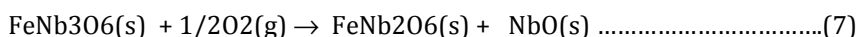
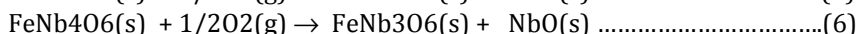
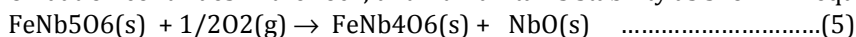


(Transient Niobium (ii) oxide)

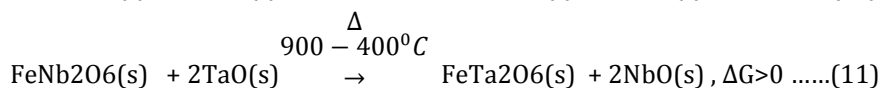
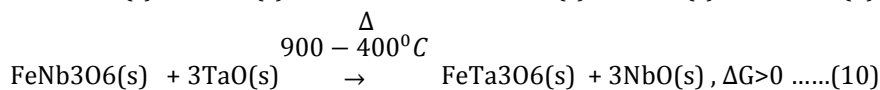
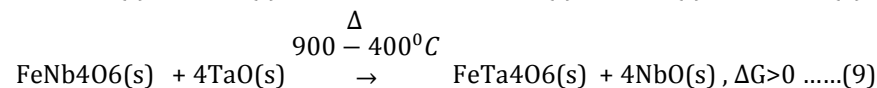
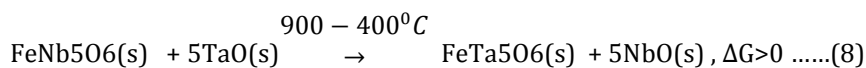
In the presence of iron (ii) oxide, niobium (ii) oxide oxides to form ferrohexaoxonioate (ii) as shown in equation (4)



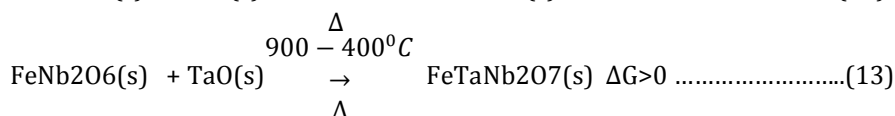
Oxidation continues in the rock, until it maintains stability as shown in equations (5), (6), and (7).



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 9000C - 4000C, (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 of Minerals of HFSE in Cassiterite

At rhyolitic and basaltic melt temperatures, magmas behave like weak electrolyte (Achuenu and Komolafe, 2021), 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, tantalum, tin, zircon, hafnium, titanium and iron 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), but incorporate into cassiterite structure as shown in equation 1. The precipitation of HFSE from the aqueous phase is very much modified by the presence of water making them hydrophilic elements. Therefore, when silicate magma coexists with an aqueous fluid, HFSE would be strongly partitioned in the aqueous phase. This affinity of water is almost certainly responsible for the concentration of HFSE and its ore, cassiterite in pegmatite and hydrothermally altered rock. At an igneous temperature, there is a mobility of ions or atoms in the molten magma, 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 HFSE crystallizes at an igneous temperature in an aqueous phase, under electrolytic condition, there is always a solid solution among the HFSE and can be mathematically expressed in the following equations below

Mathematical derivations of minerals of HFSE in Cassiterite 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 is 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;

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

$$O = -2$$

$$= O^{2-}$$

Cation with equivalent unit positive charge is needed to balance it, so that the algebraic sum is equal to zero.

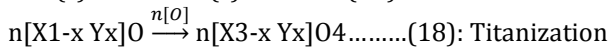
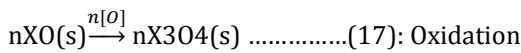
Let the cation be $(X+2)$ so that the formula becomes

$$n[(x+2) (O-2)] = nXO \dots\dots\dots(15)$$

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

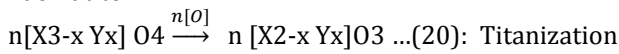
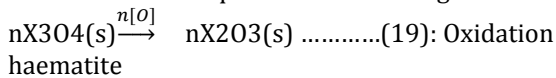
$$nXO = X_{1-x}Y_xO \dots\dots\dots(16)$$

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



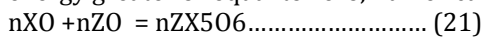
Equation (15) is used to calculate titano magnetite series as shown in Table 2.

The oxidation of equation nX_3O_4 will give more stable crystal as shown equation (19).

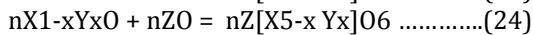
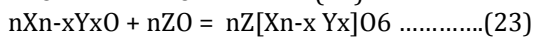
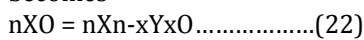


Equation (17) is used to calculate titano – haematite series shown in Table 2.

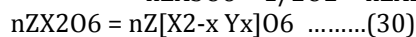
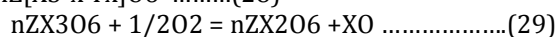
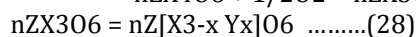
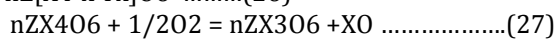
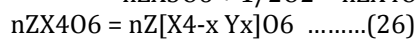
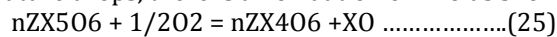
In an aqueous phase, niobium (Nb), a small ion, lithophile element, of high ionic charge with ionic potential (I), approximately 7, would react with oxygen fugacity in the aqueous phase to produce series of oxides of niobium, called niobate oxide. Further decrease in temperature of the aqueous phase 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 Gibb's energy greater or equal to zero, numerically $\Delta G \geq 0$



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



As temperature drops, there is an oxidation of nXO as shown equation (23).



3.2. Sequence of Crystallization of Minerals of HFSE 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). According to, Van Lichtervelde et al, isothermal Nb-Ta fractionation from cassiterite cannot be explained by solubility differences but rather disequilibrium crystallization at supersaturation and should be the reason for extreme of Ta enrichment in residual melts that lead to crystallization of cassiterite from lithium pegmatite.

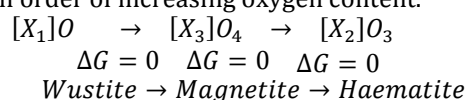
Mathematically, during cooling of magma, the first HFSE mineral to form is said to be in the state of chemical equilibrium with the melt, provided that temperature and pressure are kept constant, according to Gibbs (1873), numerically, $\Delta G = 0$. But with change in the condition of temperature under 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 HFSE mineral to form oxidizes into another HFSE mineral, that is structurally different with distinct chemical composition. This process is called oxidation reaction in this research and the reaction forms complex and discontinuous, because oxygen is the only factor that determines the reaction, with less or no substitution of iron by titanium or niobium by tantalum.

After oxidation, the surviving HFSE mineral would undergo series of isomorphic reactions by substitutions of elements by another to produce crystals of the same structures, but with different chemical compositions, with free Gibb's 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 is isomorphic and is continuous because titanium or tantalum is only factor that determines the reaction as shown in Table 2.

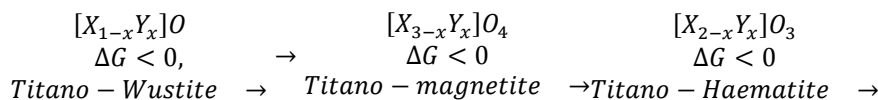
Mathematically as a result of these, two series of reactions are attributed to mathematical models of iron ore; hence, Oxidation reaction series called the Magneto- Haematite series and the Titanization series called Titano – Magneto – Haematite series and the type of isomorphic substitution that takes between titanium and iron in cassiterite ore is called Heterovalent substitution, because of involvement of ions similar size and different charge as shown in Table 2

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 complex crystal of different structure, but with distinct chemical composition and are called Magneto -Haematite complex series.

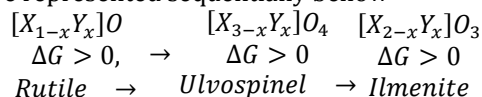
This progresses in sequence as temperature drops to produce sequence of crystallization with respect to free Gibb's energy (ΔG) and is given below in order of increasing oxygen content.



Solid solution equations are series of equations that are continuous and they involve substitutions among the cations called heterovalent substitution, to produce crystal of same structure but with different chemical compositions. Example, Titanium substitutes for iron in solid solution to form crystals that are intermediates in which both Titanium and iron are present in equal proportion. Therefore, for intermediate, the following sequence is formed and is called Tiatano - Magnetite.

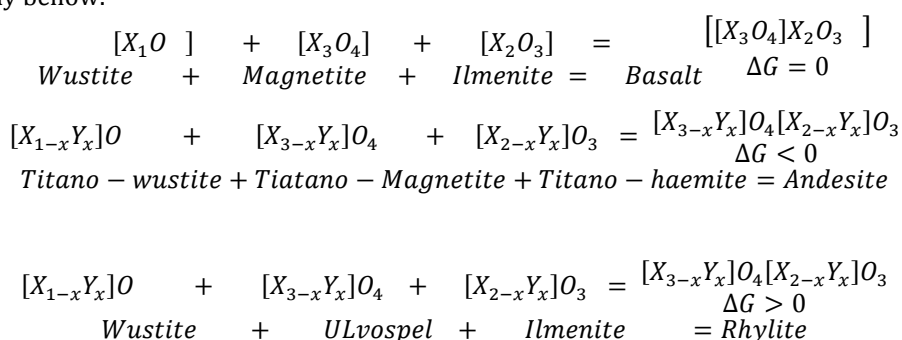


The complete or partial heterovalent substitution of Iron by Titanium would produce crystals that are wholly or partially titanium and are feebly magnetic, because they are stable in the presence of free titanium with minimum free Gibb's energy, numerically $\Delta G > 0$ and are represented sequentially bellow

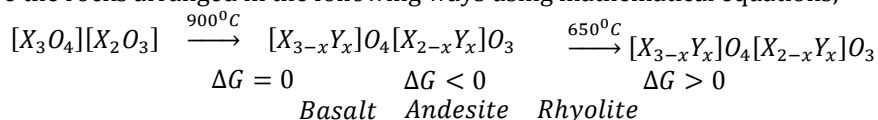


These minerals are formed sequentially to produce rocks of different compositions. Basalt is an igneous rock which mathematically and mineralogically consists of wustite, magnetite, haematite, depending on temperature of crystallization.

The probability of having any of these minerals in basalt depends on factor of temperature. The following minerals are presented sequentially bellow.



Sequentially, we have the rocks arranged in the following ways using mathematical equations;



Conversely at a given equilibrium, 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 richer in tantalum, provided that temperature and pressure are kept constant, 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 Gibb's energy will be negative

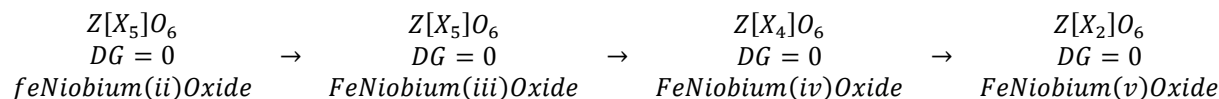
(Numerically, $\Delta G < 0$), so that the reaction would be spontaneous and equilibrium will shift to the side that favours crystallization, so as to annul the cooling effect by releasing more heat, according to Le-chaterlier principle (1898) as a result, the first niobium rich COLTAN to form oxidizes into another niobium rich 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 Gibb's 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 Isovalent substitution and the reaction process is Tantalization reaction and is continuous because tantalum is only factor that determines the reaction as shown in Figure 3.

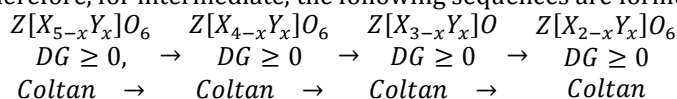
Geomathematically, as a result of these, two series of reactions are attributed to mathematical models of COLTAN; hence, Oxidation reaction series called the Complex series (Niobate series) and the Tantalization series called Isomorphic isovalent series (COLTAN series) as shown in Figure 3.

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 Complex series (Niobate series).

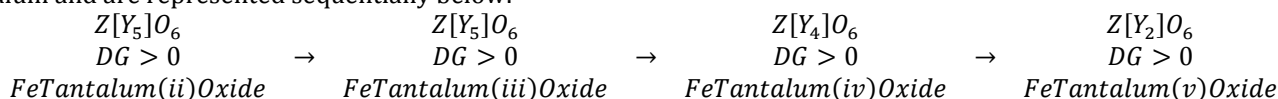
This progresses in sequence as temperature drops to produce sequence of crystallization and is given below in order of increasing oxygen content



Solid solution equations are series of equations that are continuous and they involve substitutions among the cations called Isovalent 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 of HFSE above are formed sequentially until; it reaches the highest oxidation state to produce an ore of tin called CASSITERITE. Cassiterite is an ore of tin that is mathematically and mineralogically consists of minerals of HFSE such as tin, iron, 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 cassiterite is Iron-Niobium rich cassiterite and therefore niobium and iron are the dominant elements, but if the source is lithium pegmatite and hydrothermally altered rock, then the type of cassiterite is Titanium-Tantalum rich cassiterite. 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 and titanium are 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. 50kg 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's 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

Ebikemefa (2020), noted that there is high concentration of tin(iv) oxide, niobium (vi) oxide, iron(iii) oxide and titanium (iv) oxide, but low concentration of tantalum (vi) oxide at Kuru-Jentar as shown in table 1. There is also a presence of zirconium (iv) oxide in high concentration but low Hafnium (iv) oxide. Mathematically, this shows that cassiterite in Table1 is expected to be ferro/ferri-niobate bearing Cassiterite, because, iron, niobium, and tin meet the percentage requirement for an ore of tin to form, therefore the rocks expected in area are Biotite granite and syenite which speak the geology of the area. Therefore, the minerals to be processed from the Cassiterite include; haematite, tin, columbite and other associated minerals like zircon, monazite and sand. In this case the Cassiterite type in Table1 is Ilmeno-columbite Cassiterite type as shown in Figure2.

The expected results from cassiterite during mineral processing are presented in the Table 3 and 4 below. The minerals processed from cassiterite were mainly minerals of HFSE which include tin, iron ore, columbite, zircon, monazite and sand and their chemical compositions are presented in Table 1. Their properties such as magnetization, electrical resistivity, strength, density, cell size is measured and how they set in matrix equations according to HFSE ratio as presented in Table 3 and 4 (Achuenu and Komolafe, 2021).

Oxide Composition %	CEB6		CEB8	CEB9	CEB10	
SiO ₂	ND	6.00	14.00	12.74	8.24	
Cl	ND	0.94	ND	ND	ND	
K ₂ O	0.99	0.94	ND	0.76	ND	
CaO	0.20	0.20	0.61	0.20	ND	
TiO ₂	17.00	15.20	13.80	15.90	14.70	
MnO	0.75	0.66	0.59	0.65	0.61	
Fe ₂ O ₃	16.67	15.81	14.22	17.02	15.57	
CuO	0.23	0.17	0.21	0.14	0.22	
ZnO	ND	ND	0.087	0.084	0.088	
SeO ₂	ND	ND	ND	0.004	ND	
Ga ₂ O ₃	0.070	ND	0.048	ND	ND	
As ₂ O ₃	0.028	0.008	ND	ND	0.02	
Y ₂ O ₃	0.832	0.653	0.696	0.832	0.738	
ZrO ₂	9.71	9.56	9.15	9.09	10.10	
Nb ₂ O ₅	11.20	10.60	10.20	9.42	11.00	
SnO ₂	32.20	30.00	30.44	24.00	28.20	
BaO	1.80	2.20	1.20	2.40	1.10	
CeO ₂	2.10	2.00	1.90	2.20	2.30	
Nd ₂ O ₃	0.26	0.40	0.20	0.51	0.19	
Eu ₂ O ₃	0.40	0.37	0.52	0.48	0.50	
HfO ₂	ND	0.41	0.26	0.40	0.39	
Ta ₂ O ₅	1.00	1.33	0.79	1.18	1.11	
WO ₃	ND	ND	0.22	ND	0.16	
PbO	0.13	0.15	0.26	0.17	0.590	
ThO ₂	1.53	1.44	ND	1.62	1.47	
LOI	2.90	0.90	0.60	0.20	2.70	

Table 1: Analyzed Cassiterite Sample
Source: Ebikemefa (2020)

Element	Atomic Number	Charge	Ionic Radius	Electronegativity	Ionic Potential
Aluminum	13	+3	0.51	1.5	5.88
Titanium	22	+4	0.68	1.6	5.88
Vanadium	23	+3	0.74	1.4	4.08
Iron	26	+2	0.74	1.7	2.71
Zirconium	40	+4	0.79	1.5	5.07
Niobium	41	+5	0.69	1.7	7.25
Tin	50	+4	0.71	1.8	5.64
Hafnium	72	+4	0.78	1.3	5.13
Tantalum	73	+5	0.68	1.5	7.35
Tungsten	74	+4	0.70	1.6	5.71
Molybdenum	42	+4	0.70	1.6	5.71

Table 2: Physical Constant of Some Elements
Source: Gordy and Thomas (1956)

Matrix	Iron ore		Numerical Value of Titanium	Group	Magnetization	Density	Strength	Rock
	Chemical formula	Mineral						
$\begin{pmatrix} 5, \\ 2, \\ 1 \end{pmatrix}$	$\begin{pmatrix} X_5Y_1O_8 \\ X_3Y_1O_6 \end{pmatrix}$	(Titanomag) (Titanohaem)	2	2	Feebly magnetic by Hand magnet	Intermediate	Intermediate	Andesite Diorite
$\begin{pmatrix} 2, \\ 1, \\ 1 \end{pmatrix}$	$\begin{pmatrix} X_2Y_1O_4 \\ X_1Y_1O_3 \end{pmatrix}$	(Ulvospinel) (Ilmenite)	1	1	Magnetic by Hand magnet	Low (light)	High	Granite Rhyolite
$\begin{pmatrix} 3, \\ 2, \\ 0 \end{pmatrix}$	$\begin{pmatrix} X_3O_4 \\ X_2O_3 \end{pmatrix}$	(Magnetite) (Haematite)	0	0	Highly magnetic by Hand magnet	High (heavy)	Low	Basalt, Sedimentary

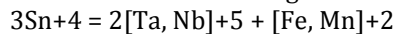
Table 3: Expected Values Measured from Magnetization, Density and Strength
Source: Achuen and Komolafe (2021)

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

Table 4: Expected Values Measured from Electrical Resistivity, Magnetization, Density and Strength
Source: Achuen and Komolafe (2021)

5.1.1. Mathematical Modeling of Cassiterite

Mathematically, cassiterite consists of minerals of HFSE, such as tin, iron ore, columbite, tantalite, zircon, monazite, and silica. Iron, manganese, tantalum, and niobium substitute for tin with a combination of divalent elements replacing the tetravalent tin following the relationship;



This substitution is in part responsible for the dark coloured cassiterite. In cassiterite, when there is an isovalent substitution of niobium by tantalum there is also a heterovalent simultaneous substitution of iron by manganese or titanium in solid solution during crystallization as shown in Figure 1 and 2. This process of simultaneous substitution in cassiterite is called isomorphous substitution.

As you are going across one of the periods in the periodic table from left to right, the substitution of elements is heterovalent because of the atoms of the same period but of different groups, but as you go down one of the groups from top to bottom of periodic table, the substitution of elements is isovalent, because of the atoms of the same group but of different periods. Across the period, there is a decrease in atomic size with increasing atomic number from left to right in the periodic table, because electrons are being added to the same electron shell. In group 1 and 2, electrons are being added to s and p – orbitals. In group 3 to 12, electrons are being added to penultimate shell below an outer orbital, so that the larger nuclear charge would attract all of the electrons more strongly, thereby contracting the atoms of heavier atomic nuclei, and then making the atomic radius of the atom to shrink in size, also there is a nuclear repulsion amongst the electrons as you go across the period from left to right of periodic table as a result elements become progressively more electronegative across the period from left to right. Therefore, as more electrons are added to the same electron shell, more nuclear attractions occur than the repulsive forces between the electrons, as you go across the period. Analogically, as you go across the period from left to right in the periodic table, titanium (+4) with the ionic size of (0.68Å) replaces iron (+2) with the ionic size of (0.74Å) in the solid solution during crystallization of magma to produce crystals of ulvospinel and ilmenite and this type of substitution is called heterovalent substitution because of substitution of atoms of different charges with similar size.

Down the group, there is an increase in atomic radius with increasing atomic number from top to bottom of the periodic table, because electrons are being added to different electron shells. As you are going down the group, there is sudden decrease in atomic size due to lanthanide contraction, especially amongst the transition elements. Analogically as you are going down one of the groups, tantalum (+5) with ionic size of (0.68Å) replaces niobium (+5) with ionic size of (0.69Å) in equal proportion in solid solution during crystallization of magma to produce crystal of tantalite, the small size of tantalum is due to lanthanide contraction and this type of substitution is called isovalent substitution because substitution of atoms of the same charge with similar size.

Cassiterite is typically found in high temperature hydrothermal veins and quartz porphyries where it is often associated with other oxides such as wolframite, columbite, tantalite, scheelite and haematite as shown in Figure 2.

At a given equilibrium under standard condition of temperature and pressure, cassiterites are formed on the assumption that HFSE undergo.

- Oxidation to form complex with oxygen
- Isovalent substitution during crystallization of cassiterite
- Heterovalent substitution during crystallization of cassiterite

Heterovalent Substitution in Cassiterite

HFSE that undergo heterovalent substitution during crystallization of cassiterite from nepheline syenite and granite are the iron and the titanium because of similar size and different charges. As you are going across the period in the periodic table of an element from left to right, the ionic size of an element decreases with increasing atomic number. Since the difference in ionic size between the iron and titanium is not more than 15% according to Goldschmidt (1937) and their electronegativity is not differed by 0.1 according to Ringwood (1955) as shown in Table 2, they can substitute each other even when they are of different ionic charge during crystallization of magma. This type substitution is called heterovalent substitution in cassiterite.

Consider that, iron ore is a product of sedimentary rock and a processing product of cassiterite from igneous rock, given that titanium is a distinguishing factor between iron ore in sedimentary and cassiterite from igneous rocks, therefore;

- Under sedimentary condition, there is no cassiterite because of the absence of HFSE, with $\Delta G \geq 0$
- Under igneous condition, cassiterite is present, because of the presence of HFSE with $\Delta G \geq 0$

Based on these two assumptions, matrix equation is used to resolve the genetic origin of cassiterite from igneous rocks (Achuenu and Komolafe, 2021) and the equations are mathematically expressed below;

From equation 6, $n [\text{X}_{3-x}\text{Y}_x] \text{O}_4 \xrightarrow{n[\text{O}]} n [\text{X}_{2-x}\text{Y}_x] \text{O}_3$, we have that;

$$[\text{X}_{3-x}\text{Y}_x] \text{O}_4 = 0, \text{ where}$$

$$3-x = x \text{ position}$$

$$x = y \text{ position}$$

Using factor theorem,

$$\text{At } x = 0$$

$$[\text{X}_{3-x}\text{Y}_x] \text{O}_4 = [\text{X}_3] \text{O}_4 \dots\dots\dots(31)$$

Such that, $3-x = x \text{ position}$

$$3-0 = 3$$

$$x = 3, \text{ and}$$

$$\begin{aligned}x &= y \text{ position;} \\ 0 &= y \\ y &= 0\end{aligned}$$

$$[x, y] [3, 0] = [X3]O4 \dots\dots\dots(32)$$

At x = 1

$$[X3-x Yx]O4 = [X2Y1]O4, \text{ such that,}$$

$$3-x = x \text{ position}$$

$$3 - 1 = x$$

$$x = 2 \text{ and}$$

$$x = y \text{ position}$$

$$1 = y$$

$$y = 1$$

$$[x, y] [2, 1] = [X2Y1]O4 \dots\dots\dots(34)$$

$$[X3]O4(s) + [X2Y1]O4 = [3, 0] + [2, 1] \dots\dots(35)$$

Also $[X2-x Yx] O3 = 0$, where;

$$2-x = x \text{ position}$$

$$x = y \text{ position}$$

Using factor theorem,

At x = 0

$$[X2-x Yx] O3 = [X2]O3 \dots\dots\dots(36)$$

Such that $2-x = x$ position

$$2-0 = x$$

$$[X2Y1]O4 \quad x = y \text{ position}$$

$$0 = y$$

$$Y = 0$$

$$[x, y] [2, 0] = [X2]O3 \dots\dots\dots(37)$$

At x=1

$$[X2-xYx] O3 = [X1Y1]O3, \dots\dots\dots(38)$$

Such that, $2-x = x$ position

$$2-1 = x$$

$$x = 1 \text{ and}$$

$$x = y \text{ position}$$

$$1 = y$$

$$Y = 1$$

$$[x, y], [1, 1] = [X1Y1]O3 \dots\dots\dots(39)$$

$$[X2]O3 + [X1Y1]O3 = [2, 0] + [1, 1] \dots\dots\dots(40)$$

$$[X3]O4 + [X2Y1]O4 = [X5Y1]O8 \dots\dots\dots(41)$$

$$[X2]O3 + [X1Y1]O3 = [X3Y1]O6 \dots\dots\dots(42)$$

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

$$\begin{pmatrix} 3 & 0 \\ 2 & 0 \end{pmatrix} + \begin{pmatrix} 2 & 1 \\ 1 & 1 \end{pmatrix} = \begin{pmatrix} 5 & 1 \\ 3 & 1 \end{pmatrix} \dots\dots\dots(43).$$

$$\begin{pmatrix} X_3O_4 \\ X_2O_3 \end{pmatrix} + \begin{pmatrix} X_2Y_1O_4 \\ X_1Y_1O_3 \end{pmatrix} = \begin{pmatrix} X_5Y_1O_8 \\ X_3Y_1O_6 \end{pmatrix} \dots\dots\dots(44)$$

$$\begin{pmatrix} \text{Magnetite} \\ \text{Haematite} \end{pmatrix} + \begin{pmatrix} \text{Ulvospinel} \\ \text{Ilmenite} \end{pmatrix} = \begin{pmatrix} \text{Titanomagnetite} \\ \text{Titanohaematite} \end{pmatrix} \dots\dots\dots(45)$$

$$Fe_3O_4(s), (\Delta G = 0) + [Fe_2Ti]O_4 (\Delta G > 0) = [Fe_5Ti]O_8 (\Delta G < 0) \dots\dots\dots(46)$$

$$[Fe_2]O_3(s) (\Delta G = 0) + [FeTi]O_3 (\Delta G > 0) = [Fe_3Ti]O_6 (\Delta G < 0) \dots\dots\dots(47)$$

$$[\text{Basalt}, \Delta G = 0] + [\text{Granite}, \Delta G > 0] = [\text{Andesite}, \Delta G < 0] \dots\dots\dots(48)$$

$$[\text{Sedimentary}, 0 < \Delta G < 0] + [\text{Granite}, \Delta G > 0] = [\text{Andesite}, \Delta G < 0] \dots\dots\dots(49)$$

5.1.2. Isovalent Substitution in Cassiterite

HFSE that undergo isovalent substitution during crystallization of cassiterite from lithium pegmatite and hydrothermal fluid are the niobium, zircon, hafnium and the tantalum because of similar size and the same charge. As you are going down the group in the periodic table of an element from top to bottom, the ionic size of an element increases with increasing atomic number, though the smaller size of both the hafnium and tantalum as you are going down the group is due to lanthanide contraction. Since they have similar ionic size provided that ionic size is not more than 15% and their electronegativity is not differed by 0.1 as shown in Table 2 and the same charge, they can substitute for one another during crystallization of magma. This type substitution is called Isovalent substitution in cassiterite.

Consider COLTAN, a weathering product of igneous rock, such as nepheline syenite and lithium pegmatite which consists of minerals of HFSE, given that tantalum is a distinguishing factor between cassiterite in syenite and pegmatite, therefore;

- Under syenitic condition, cassiterite rich in 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 cassiterite from nepeline syenite is given as;

$$\text{Nb}_2\text{O}_6: \text{Ta}_2\text{O}_6 = 4: 1, \text{ such that,}$$

$$\text{Nb: Ta} = 5: 0$$

- Under pegmatitic condition, cassiterite rich in tantalite is precipitated with $\Delta G > 0$, because at this temperature tantalite reaches its stability limit with 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;

$$\text{Nb}_2\text{O}_6: \text{Ta}_2\text{O}_6 = 1: 4, \text{ such that,}$$

$$\text{Nb: Ta} = 0: 5$$

Based on these two assumptions, matrix equation is used to resolve the genetic origin of Cassiterite in syenite and 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;

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

$$5-x = x \text{ position}$$

$$x = y \text{ position}$$

Using factor theorem,

$$\text{At } x = 0$$

$$[X_{5-x} Y_x] O_6 = [X_5]O_6 \dots\dots\dots(50)$$

Such that, $5-x = x$ -position

$$5-x = 0$$

$$x = 5, \text{ and}$$

$$x = y \text{ -position;}$$

$$0 = y\text{-position}$$

$$y = 0$$

$$[x, y] [5, 0] = [X_5]O_6 \dots\dots\dots(51)$$

At $x = 5$

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

$$5-x = x \text{ position}$$

$$5 - 5 = x$$

x -position = 0 and

$$x = y \text{ -position}$$

$$5 = y\text{-position}$$

$$Y\text{-position} = 5$$

$$[x, y] [0, 5] = [Y_5]O_6 \dots\dots\dots(52)$$

$$[X_5]O_6(s) + [Y_5]O_5 = [5, 0] + [0, 5] \dots\dots(53)$$

$$[X_4]O_6(s) + [Y_4]O_5 = [4, 0] + [0, 4] \dots\dots(54)$$

$$[X_3]O_6(s) + [Y_3]O_5 = [3, 0] + [0, 3] \dots\dots(55)$$

$$[X_2]O_6(s) + [Y_2]O_5 = [2, 0] + [0, 2] \dots\dots(56)$$

$$[XY]5O_6 = \{5,5\}$$

$$[XY]4O_6 = \{4,4\}$$

$$[XY]3O_6 = \{3,3\}$$

$$[XY]2O_6 = \{2,2\}$$

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

$$\begin{pmatrix} 5, & 0 \\ 4, & 0 \end{pmatrix} + \begin{pmatrix} 0, 5 \\ 0, 4 \end{pmatrix} = \begin{pmatrix} 5, 5 \\ 4, 4 \end{pmatrix} \dots\dots\dots(57).$$

$$\begin{pmatrix} X_5 O_6 \\ X_4 O_6 \end{pmatrix} + \begin{pmatrix} Y_5 O_6 \\ Y_4 O_6 \end{pmatrix} = \begin{pmatrix} X_5 Y_5 O_8 \\ X_4 Y_4 O_6 \end{pmatrix} \dots\dots\dots(58)$$

$$\begin{pmatrix} \text{Columbite} \\ \text{Columbite} \end{pmatrix} + \begin{pmatrix} \text{Tantalite} \\ \text{Tantalite} \end{pmatrix} = \begin{pmatrix} \text{Coltan} \\ \text{Coltan} \end{pmatrix} \dots\dots\dots(59)$$

$$[\text{Syenite}] + [\text{Pegmatite}] = [\text{Syenite Pegmatite}] \dots\dots(60)$$

$$\text{FeNb}506(s) + \text{FeTa}506 = \text{Fe}[\text{NbTa}]506 \dots\dots(61)$$

$$\text{FeNb}406(s) + \text{FeTa}406 = \text{Fe}[\text{NbTa}]406 \dots\dots(62)$$

$$\text{FeNb}306(s) + \text{FeTa}306 = \text{Fe}[\text{NbTa}]306 \dots\dots(63)$$



From equations (60) and (61), (62), (63), and (64) it means that weathering of basalt will give magnetite and haematite with no cassiterite because of absence of minerals of HFSE, that of granite and pegmatite will give cassiterite that contains minerals of HFSE such as ulvospinel, ilmenite, columbite and tantalite and that of andesite-syenite pegmatite will give titanomagnetite, titanohaematite and coltan.

Equations (48) and (49) indicate that granite and andesite are traces for HFSE and it affects the magnetization, strength and density of iron ores in cassiterite from granite as shown in table 3

Equations (59), (60), (61) and (62) 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 4.

5.2. Discussion of Results

5.2.1. HFSE in Cassiterite

The term HFSE is restricted to elements whose ions have a small radius and high charge, therefore high associated electric field, and high field strength: the definition of the field called ionic potential can be defined as the charge (Z), over ionic radius (r), (Z/r) and the importance of the field strength was first pointed out by Ahrens (1953). Ions with $Z/r > 2.0$ are generally thought to be high – field strength elements (HFSE) and include all trivalent and tetravalent ions as well as the rare earth elements, the platinum group elements, uranium and thorium. In geochemistry the term high field strength is mostly reserved for elements, such as Hf, Zr, Ti, Nb and Ta as a group and was mostly used in this research. The HFSE are used to discriminate between the tectonic settings of igneous rocks such as seen in nepheline syenite and in lithium pegmatite: Igneous from convergent plate boundaries are depleted in HFSE compared with those from divergent plate boundaries (Gill, 1980). This depletion in calc-alkaline rocks was noted for Ti (Chayes, 1965).

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 and hence undergoes isovalent substitution with niobium during crystallization of magma. Across the period, magnetization, electrical conductivity, density increase from left to right with decreases atomic radius, this means that iron which is in the middle of the first row of the periodic table as you go across the period is more magnetic, conductive, denser than the titanium which is at the beginning of the first row of periodic table and hence undergoes heterovalent substitution with titanium. Similarly, isovalent substitution also takes place between zircon and hafnium in cassiterite during crystallization of magma. Other elements in cassiterite that form complexes with oxygen include silicon, tin, wollastonite etc.

For all the oxides of HFSE, only the iron (iii) oxide, titanium (iv) oxide, tin (iv) oxide, zirconium oxide, 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 $\Delta G > 0$

Several experiments have shown that, in cassiterite ore, the maximum concentration of iron ore in cassiterite is 23.75% in composition and that of titanium oxide is 16.7% in composition as shown Table 1. Other magnetic minerals occur in trace. The presence of titanium oxide in cassiterite as analysed during chemical analysis as shown in the Table 1, according to Ebikemefa (2020), indicates that there is always solid solution between titanium and iron at igneous temperature in form of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ in which there is a heterovalent substitution of iron by titanium. This means that titanium forms at igneous temperature at about 6000C to 11000C. In iron ore from sedimentary rock, the total absent or little amount of HFSE indicates that there is no solid solution (exsolution) between HFSE and iron in the ore at sedimentary temperature, because the temperature requires for HFSE to precipitate from the melt is far above sedimentary temperature, unless the sedimentary material is heated up to igneous temperature that would precipitate HFSE from the melt according to Achueny and Komolafe (2021). Based on this, the origin of cassiterite can be traced to igneous rock because of the presence of HFSE in the cassiterite and is grouped into ferro-niobate cassiterite type and titanotantalate cassiterite type, therefore, a model has been designed to classify cassiterite into groups according to the ratio of one HFSE to another with respect to free Gibbs's energy (ΔG) called cassiterite model as shown in Figure 2.

From Figure 2, wustite and niobium (ii) oxide crystallized, first with free energy, numerically less than zero ($\Delta G \leq 0$), and then with time and decreasing temperature, they oxidized to magnetite and niobium (iii) oxide with free energy numerically equal to zero ($\Delta G \geq 0$) and then finally haematite and niobium (v) oxide, a more stable state of minerals of HFSE, with free energy numerically greater than zero ($\Delta G > 0$) called oxidation reaction series that form complex series as you are going across the table from left to right. As you are going down the table from top to bottom, the number of atoms of iron and niobium decrease with increasing number of atoms of titanium and tantalum. The general molecular formulas for the two series of solid solutions are $[\text{X}_n\text{-xY}_x]\text{O}_4$, $[\text{X}_n\text{-xY}_x]\text{O}_3$ and $[\text{X}_n\text{-xY}_x]\text{O}_6$ for Niobate - Titanomagnetite series and Tantalate - Titanohaematite series, as n ranges from 0 to 5 and x depends on n ; the following minerals are obtained, and can be subjected to a hand magnet of about 0.01T, tensile strength and measurement of density. These minerals are, Wustite, Magnetite, Haematite, Pseudo Brookite, Rutile, Ulvospinel, Ilmenite, columbite and tantalite.

Table 2, indicates that iron and niobium rich zone contains rock types such as basalt, dolerite, gabbro and nepheline syenite with a general free Gibbs energy numerically but not minimum, numerically $\Delta G \geq 0$ and the titanium and tantalum rich zone contains rock types such as granite, rhyolite and lithium pegmatite with a general minimum free Gibbs energy numerically, $\Delta G > 0$.

Cassiterite rich in the minerals shown in the upper part of Figure 2, such as magnetite, haematite and columbite, are less resistant to weathering breakdown than some minerals in the lower part of the Figure 2, e.g., tantalite and therefore can be carried from one geochemical environment to another. The minerals in the lower part of Table 2 such as ulvospinel, ilmenite and tantalite are hard, lustrous, and more resistant to weathering breakdown, because of isomorphic substitution of iron by titanium and niobium by tantalum in the solid solution which and therefore remains in their primary geochemical environment as a deposited of that ore. Because of its light in weight to density ratio, hard, lustrous, as well as rust resistance, it is used as a construction material for aircraft parts, artificial joints for humans and sporting equipment such as bicycle frames. It is anti-ferromagnetic, at a low temperature, and paramagnetic at room temperature.

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 Nb₅O₆/TaO. This means that tantalum forms at igneous temperature at about 4000C to 9000C. 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 Cassiterite into groups according to their genetic origin with respect to free Gibb's energy (ΔG) called Cassiterite model as shown in Figure 2. Based on tantalum to niobium ratio, Cassiterite is placed either as niobate – ferro/ferric cassiterite type and Gibb's ilmeno - tantalate cassiterite type.

5.2.2. Cassiterite Model

Cassiterite is an ore of tin that is stable at room temperature, not oxidized by air, not hydrolysed by water vapour and do not disproportionate or decomposed at normal temperature. Minerals of cassiterite contain HFSE that have ionic potentials greater than 3.5 and hence have similar stability limit. These HFSE are of higher oxidation states and formed stable complexes in cassiterite at normal temperature. They are small, highly charged ions and have vacant low energy orbitals to accept lone pairs of electrons donated by other groups or ligands and form complexes during crystallization of magma. These HFSE are called hard acids and their corresponding ligands or radicals are called hard bases.

Determinant matrix is used to construct Cassiterite model according to tantalum to niobium and titanium to iron ratio with respect to its genetic origin in which titanium and tantalum are determinant factors and niobium and iron are constant variables and are expressed as follow from equations (65) and (66). For isovalent substitution as shown in equation (66), the determinant matrix is always equal to zero, because there is always complete substitution of one HFSE to another in solid solution during crystallization of magma, which involves atoms of the same charge and similar size thereby making the two elements to be isomorphic and for heterovalent substitution as shown in equation (42), the determinant matrix is always equal to 2, because there is always partial substitution of one HFSE to another in solid solution during crystallization of magma, which involves atoms of different charges and similar size thereby making the two elements to be isomorphic

5.2.3. Determinant Matrix

Using determinant matrix to classify cassiterite according to its origin with respect to iron and titanium into groups;

Using determinant matrix to resolve equation (29) into equation (65)

$$\begin{pmatrix} 3, & 0 \\ 2, & 0 \end{pmatrix} + \begin{pmatrix} 2, 1 \\ 1, 1 \end{pmatrix} = \begin{pmatrix} 5, 1 \\ 3, 1 \end{pmatrix}$$

$$[0] + [1] = [2] \dots \dots \dots (51)$$

Therefore;

$$\begin{pmatrix} \text{Magnetite} \\ \text{Haematite} \end{pmatrix} = \begin{pmatrix} 3, 0 \\ 2, 0 \end{pmatrix} = \text{Sedimentary rock}$$

$$\begin{pmatrix} \text{Ulvospinel} \\ \text{Ilmenite} \end{pmatrix} = \begin{pmatrix} 2, 1 \\ 1, 1 \end{pmatrix} = \text{Igneous rock}$$

$$\begin{pmatrix} \text{Titanomagnetite} \\ \text{Titanohaematite} \end{pmatrix} = \begin{pmatrix} 2, 1 \\ 1, 1 \end{pmatrix} = \text{Igneous rock}$$

From equation (48) and (49);

- Iron ore in basalt = magnetite and haematite, no cassiterite
- Iron ore in sedimentary = magnetite and haematite, no cassiterite
- Iron ore in granite = ilmenite and ulvospinel in cassiterite
- Iron ore in andesite = titanite – maghaematite in cassiterite

From above statement, cassiterite is originated from magmatic melt, e.g., granite or syenite and hydrothermal fluid, e.g., lithium pegmatite but not sediment e.g., sedimentary rock. Because sedimentary rock does not contain most of these minerals of HFSE as igneous rock does, sedimentary rock does not host cassiterite, as igneous rock does.

Using determinant matrix to classify cassiterite according its origin into Niobium rich cassiterite and Tantalum rich cassiterite groups;

Using determinant matrix to resolve equation (65) into equation (66)

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

$$[0] + [0] = [0] \dots \dots \dots (66)$$

Therefore;

$$\begin{pmatrix} \text{columbite} \\ \text{columbite} \end{pmatrix} = \begin{pmatrix} 5, 0 \\ 4, 0 \end{pmatrix} = \text{syenite rich cassiterite}$$

$$\begin{pmatrix} \text{tantalum} \\ \text{tantalum} \end{pmatrix} = \begin{pmatrix} 0, 5 \\ 0, 4 \end{pmatrix} = \text{Pegmatite rich cassiterite}$$

$$\begin{pmatrix} \text{coltan} \\ \text{coltan} \end{pmatrix} = \begin{pmatrix} 5, 4 \\ 5, 4 \end{pmatrix} = \text{syenite-pegmatite rich cassiterite}$$

From equations (64), (65), and (67),

Coltan type cassiterite in syenite = columbite

Coltan type cassiterite in pegmatite = tantalite

Coltan type cassiterite in syenite-pegmatite = coltan

Isovalent Substitution using Determinant Matrix

For isovalent substitution, using determinant matrix

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

$[0] + [0] = [0]$ shows that there is a complete substitution of niobium by tantalum in solid solution during crystallization of magma

Heterovalent Substitution, using Determinant Matrix

$$\begin{pmatrix} 3, & 0 \\ 2, & 0 \end{pmatrix} + \begin{pmatrix} 2, 1 \\ 1, 1 \end{pmatrix} = \begin{pmatrix} 5, 1 \\ 3, 1 \end{pmatrix}$$

$[0] + [1] = [2]$ shows that there is a partial substitution of iron by titanium in solid solution during crystallization of magma.

Figure 2, has shown that Cassiterite is grouped into two according to its origin with respect to the ratio of niobium to tantalum and that of the ratio of tantalum to titanium. These are niobium – iron rich cassiterite, and tantalum - titanium rich Cassiterite and therefore formed the minerals in the upper part of the table such as the magnetite, haematite, hafnon and columbite and the minerals in the lower part of the table such as the ulvospinel, ilmenite, zircon and tantalite. The elements that formed complexes with oxygen formed minerals like monazite and sand.

- Niobium - iron rich Cassiterite: In this group, the amounts of tantalum and titanium atoms are zero, and niobium and iron atoms increase 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 and titanium with ratio of niobium to tantalum to be 5:0 and that of that of iron to titanium is 3:0 magnetite and 2:0 for haematite. Minerals in this group are relatively resistant to weathering during weathering breakdown and first weathered under weathering condition when compared with tantalum and titanium rich cassiterite, according to Goldich (1988). The rock types of this group of cassiterite are basalt and syenite.
- Tantalum – titanium rich Cassiterite: In this group, the amounts of tantalum and titanium atom increase down the group with decreasing number of atoms of niobium and iron to the point where niobium is completely replaced by tantalum with the ratio of niobium to tantalum atom to be 0:5 and iron is partially replaced by titanium with the ratio of iron to titanium to be 2:1 for ulvospinel and 1:1 for ilmenite. Minerals in this group are highly resistant to weathering during weathering breakdown and least weathered under weathering condition when compared with niobium and iron rich cassiterite, according to Goldich (1988). The rock types of this group of cassiterite are granite and pegmatite.

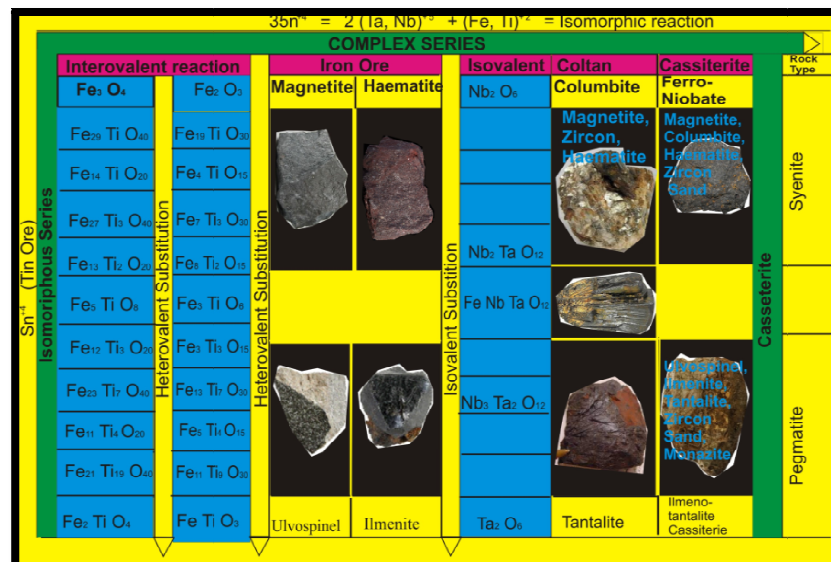


Figure 2: Cassiterite Model

5.2.3. Mineral Processing

The likely minerals obtained from cassiterite during mineral processing are tin, iron ore (which could be magnetite, haematite, or ilmenite), COLTAN (which could be columbite or tantalum), zircon sand, monazite and sand and were subjected to magnetism, shear stress, and density measurement using Archimede's principle and these properties determine the quality of cassiterite and its origin. They are processed according to these properties.

Magnetite, $[Fe_3]O_4$, product of sedimentary rock responds quickly to magnetism by stationary hand magnet which indicates the absence of other HFSE in sedimentary rock that is void of cassiterite as well as peridotite and dunite and even some basalt, therefore low intensity magnetic separator is used to separate these minerals from the gangue (chert) because they are ferromagnetic at room temperature. The ferromagnetic property of magnetite is due to the presence of partially filled d-orbital below an outer orbital which contribute to internal electric current in the material.

Ilmenite, $[FeTi]O_3$, product of igneous rock, feebly responds to magnetism by rotating hand magnet, with the density less than the magnetite and a greater tensile strength, which indicates the presence of titanium and is obtained during mineral processing of cassiterite from igneous like granite and pegmatite. This means, the presence of titanium in granite affects the properties of iron ores in cassiterite such as magnetization, strength and density and the amount of titanium in iron ore increased from Basic e.g. basalt with free Gibbs, not minimum numerically, $\Delta G = 0$ to more acidic e.g. granite with free minimum energy, numerically $\Delta G > 0$, which gives the account that oceanic basalt is more magnetic, more dense, weaker strength and less stable with void of cassiterite than the continental granite which contains cassiterite. The iron ore in cassiterite is paramagnetic at room temperature, because of partially substituted iron for titanium in solid solution during crystallization of magma, and concentrated in high magnetic separator during mineral processing of cassiterite.

Columbite $[FeNb_2]O_6$, product of syenitic rock, responds weakly to magnetism by rotating hand magnet and is paramagnetic at room temperature and is a processing product of cassiterite during mineral processing of cassiterite. The paramagnetic property of columbite is due to the presence of partially filled d-orbital with low unpaired spin magnetic moment and can be concentrated in low magnetic separator as ilmenite does.

Tantalite $[FeTa_5]O_6$, product of lithium pegmatite, 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 cassiterite such as electrical conductivity, magnetization, strength and density and the amount of tantalum in cassiterite increases 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. Just like niobium, the paramagnetic property of tantalite is due to the presence of partially filled d-orbital with low unpaired spin magnetic moment and can be concentrated in low magnetic separator as also does ilmenite.

Continental granite has a free Gibbs energy that is minimum, numerically greater ($\Delta G > 0$) and that of basalt has its free Gibbs energy but not minimum, numerically less or equal to zero ($\Delta G \leq 0$). Because of this, continental granite is generally more stable than oceanic basalt; this is because continental granite contains minerals of HFSE that are highly resistance to weathering during weathering breakdown. Therefore, the true source of Cassiterite is igneous rock such as syenite and pegmatite because of the presence of HFSEs. These HFSE include tin, iron, titanium, niobium, tantalum, zircon, monazite and silicon. They partitioned only along the aqueous phase and crystallized as minerals of HFSE at that phase if equilibrium is reached within their stability limit with minimum Gibbs free energy, numerically $\Delta G > 0$. The minerals of HFSE include tin, magnetite, haematite, ilmenite, columbite, tantalite, zircon sand, monazite and silica and processed according to their magnetic property. Therefore, in genetic orientation, cassiterite rich in tin, magnetite, haematite, niobium, zircon, monazite and sand is of syenitic origin and that rich in tin, ulvospinel, ilmenite, tantalite, monazite, zircon and sand is of pegmatitic origin as shown in Figure 2.

With the above reasons, cassiterite is processed using high intensity magnetic separator, this because atoms of these minerals of HFSE contain d-electrons, with low unpaired spin magnetic moment, and they are paramagnetic at room temperature.

5.2.4. Isomorphous Substitutions in Cassiterite Following the Goldschmidt and Ringwood Rules

When two ions that possess the same charge but different atomic radii compete for a lattice site, the ion with the smaller radius is preferentially incorporated.

'Mathematically, in substitution of these two ions during the formation of cassiterite from crystallization of magma, there is always a complete isovalent substitution of the ions of these elements as you are descending down the group from one period to the other, which implies atoms of the same charge with different ionic sizes provided that, the difference in ionic size would not be more than 15% according to Goldschmidt (1937) and the electronegative difference would not be more than 0.1, according to Ringwood (1955)' as shown in Table 3.

Analogically, from cassiterite model, as shown in Figure 2; tantalum (+5), with the size of 0.68Å, substitutes for niobium (+5) with the size of 0.69Å from top to bottom of the Figure and the substitution is isomorphous isovalent because of atoms of the same charge of similar size.

When two ions that possess similar radii but different charges compete for a lattice site, the ion with higher charge is preferentially incorporated.

'Mathematically, during substitution of these two ions, there is always a partial heterovalent substitution as you go across the period from one group to the other, which implies atoms of the similar ionic size with different ionic charges provided that, the difference in ionic size would not be more than 15% according to Goldschmidt (1937) and the electronegative difference would not be more than 0.1, according to Ringwood (1955)', as shown in Table 3.

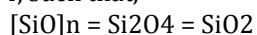
Analogically, from cassiterite model, as shown in Figure 2; titanium (+4), with the size of 0.68Å, substitutes for iron (+2) with the size of 0.74Å from top to bottom of the Figure and the substitution is isomorphous heterovalent because of atoms of the same charge of similar size.

Although, according to Ringwood (1955), these two rules are only applicable to atoms of the same electronegativity, therefore when atoms of different electronegativities compete for lattice site during crystallization of magma, the one with lower electronegativity would preferentially incorporate, because it forms a stronger and more ionic bond than the others as according to Ringwood (1955).

At a given chemical equilibrium under standard conditions during crystallization of magma, the element in a given complex has its oxidation state equal to number of oxygen molecule or atom in that given complex provided that, the algebraic sum the given species is equal to zero be it compound or radical. E.g.,

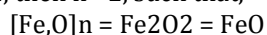
In [SiO]_n complex

If Si = +4, n = 4, such that,

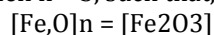


In [Fe₂O]_n complex

If Fe = +2, then n = 2, such that,



If Fe = +3, then n = 3, such that,



In conclusion, the substitution of elements down the group from one period to another during crystallization of magma, is isovalent, because the charges of both the ions of the elements are electrically neutral and the total determinant matrix amounts to zero as shown in equation (52) thereby making complete substitution of ion of one element to the other , while the substitution across the period from one group to another during crystallization of magma is heterovalent, because the charges of both ions are electrically unbalanced and the total determinant matrix is numerically expressed as a whole number or fraction as shown in equation (51), thereby making partial substitution of ion of one element to the other.

5.2.5. Application of Mathematical Model to Cassiterite Using Certain HFSE

Ebikemefa (2020) as shown in Table 1, observed that the concentration of certain selected oxides of HFSE such as iron oxide in cassiterite is about 16%, titanium oxide is 15%, niobium oxide is 11%, tantalum oxide is 1%, zirconium oxide is 9% and then the hafnium oxide is 0.4%. The above elements of these oxides except iron oxide have their ionic potential greater than 3, with their ionic charge greater 4. They have smaller ionic radius with larger atomic number than those of s and p block elements which make them HFSE with larger ionic charge. These oxides are represented empirically in Table 5, and their mathematical representations give them the IUPAC name, which is an expression of 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 according to Achuen and Komolafe (2021), e.g., ferrihexaoxonioate (v) is the IUPAC name for Columbite (FeNb₂O₆) and that of ferrihexaoxotantalate (v) is Tantalite (FeTa₂O₆) as well as iron (ii) and iron (iii) oxides for Haematite and Ilmenite.

Since [P:Q]O_n = [x:y] then,

[P:Q]O_n = [PxQy]O_n where x, and y are the mole ratio of P and Q and n is the number of molecules of oxygen in the complex.

Given that N is the sum of the mole ration of iron(x) and titanium (y) and n is the number of molecules of oxygen and is expressed as;

$x:y = N$, then,

$$N = x+y \dots\dots\dots (67)$$

$$\text{So that } x = N-y \dots\dots\dots (68)$$

$$\text{Therefore, } [P_xQ_y]O_n = [PN-yQy]O_n \dots\dots\dots (69)$$

Given that, the concentration of iron (iii) oxide in Kuru –Jentar cassiterite is 16% and that of titanium oxide is 15%, then, mathematically; comparing the ratio of iron to titanium in cassiterite, we have;

$$[\text{Fe}:\text{Ti}] = [x, y]$$

$$[16:15] \% = 16/55.85:15/47.90$$

$$[x:y] = 0.3:0.3$$

$$[x:y] = 1:1 \dots\dots\dots (70)$$

From $[x:y] = 1:1$, then $x = 1$ and $y = 1$

$$\text{Therefore } N = 1+1$$

$$N = 2$$

$$\text{Therefore, } [Fe_xTi_y]O_n = [Fe_{2-y}Ti_1]O_n$$

For $y=1$, then

$$[Fe_{N-y}Ti_1]O_n = [Fe_{2-1}Ti_1]O_n$$

$$[Fe_{2-1}Ti_1]O_n = [Fe_1Ti_1]O_n$$

, $[Fe_1Ti_1]O_n = [Fe_1Ti_1]O_3$ at $n = 3$, Since oxidation state of Fe is +3, then $n = 3$, then;

$$\{Fe:Ti\}O_3 = \{FeTi\}O_3$$

$$\{FeTi\}O_3 = \text{ilmenite}$$

2) Given that, the concentration of niobium oxide is 11% and that of tantalum oxide is 1%, then mathematically;

$$Nb = 92, Ta = 180.9$$

$$Nb = 11/92$$

$$Nb = 0.12$$

$$Ta = 1/180.9$$

$$Ta = 0.0055$$

Then the atomic ratio, $Nb:Ta = 0.12 : 0.0055$

If $Nb:Ta = x:y$, then

$$[Nb:Ta]O = [Nb_xTa_y]O_n \dots\dots\dots (71)$$

$$= 0.12/0.0068:0.0055/0.0055$$

$$x:y = 22:1$$

From $[x:y] = 22:1$, then $x = 2.2$ and $y = 0.1$

$$\text{Therefore } N = 2.2+0.1$$

$$N = 2.2$$

$$N \approx 2$$

Since the oxidation state of Nb = +5, then $n = 5$ and $N = 2$

Therefore, from equation (55), $[P_xQ_y]O_n = [PN-yQy]O_n$ such that $P = Nb$ and $Q = Ta$

$$[Nb_{2-x}Ta_x]O_5 = [Nb_{22}Ta]O_{50} \dots\dots\dots (72)$$

$$\{Nb:Ta\}O_5 = \{Nb_{22}Ta\}O_{50}$$

As $\{Nb_{22}Ta\}O_{50} \lim \rightarrow \{Nb_{22}\}O_{50}$, if $Ta \approx Nb$, since Ta is very small then,

$$Ta \approx 0$$

$$Nb_{20}O_5 = \text{columbite}$$

In the presence of iron oxide at minimum free Gibbs energy, numerically $\Delta G > 0$

$$Nb_{20}O_5 = FeNb_{20}O_6, \Delta G > 0$$

$$FeNb_{50}O_6 = \text{columbite}$$

3) Given that, the concentration of zirconium oxide is 9% and that of hafnium oxide is 0.292%, then mathematically;

$$Zr = 91.22, \text{ and } Hf = 178.49$$

$$Zr = 9/91.22$$

$$Zr = 0.099$$

$$Hf = 0.292/178.49$$

$$Hf = 0.0016$$

Therefore, mathematically, $[Zr_{1-x}Hf_x]O_n = \{Zr:Hf\}O_n$

Then the atomic ratio, $Zr:Hf = 0.1:0.002$

$$= 0.1/0.002:0.002/0.002$$

$$Zr:Hf = 50:1$$

$$\{Zr:Hf\}O = \{Zr_{50}Hf\}O_{100}$$

As $\{Zr_{50}Hf\}O_{100} \lim \rightarrow \{Zr\}O_2$, if $Hf \approx Zr$, since Hf is very small then;

$$Hf \approx 0$$

$$ZrO_2 = \text{Zircon}$$

4) Since the silica content of the Cassiterite in Table 1 is less than 40%, then there is no silica rich mineral such as sand (SiO_2) in the cassiterite.

Element	Iron Ore		Coltan		Zircon		Tin Oxide	Others
	Fe	Ti	Nb	Ta	Zr	Hf		
Percentage composition (%)	16	15	11	1	9	0.4	32	16
Atomic number	56	47	82	146	80	144	50	
Mole ratio	0.31	0.34	0.134	0.006	0.133	0.003		
Mole ratio/smallest	1	1	20	1	38	1		
Empirical formula	Fe	Ti	Nb ₂₀	Ta	Zr ₃₈	Hf		
Oxidation number	+3	+4	+5	+5	+4	+4	+4	
Number of oxygen atom	3	4	5	5	4	4	4	
Molecular oxygen formula	O ₃	O ₄	O ₅	O ₅	O ₄	O ₄	O ₄	
Chemical formula	FeTiO ₃		Nb ₂₀ TaO ₅₀		Zr ₃₈ HfO ₈₀		SnO ₂	
	FeTiO ₃		FeNb ₂₀ O ₆		ZrO ₂			
Genetic name	Ilmenite		Columbite		Zircon		Tin	

Table 5: Empirical Representation Of Cassiterite Obtained from Table 1

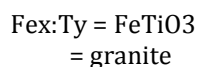
From the empirical expression in Table 5, the minerals obtained from cassiterite in Table 1 using mathematical method includes;

- Tin
- Columbite
- Tantalite
- Ilmenite
- Zircon

These are the minerals in Kuru-Jentar cassiterite that can be processed during mineral processing. Therefore, iron ore in granite, either in biotite or diorite rich cassiterite is ilmenite and is in group 1 iron ore according to Achuenu and Komolafe (2021) Table 3, as represented in equation (73), (74) and (75) below.

Since the mole ratio of iron to titanium is 1:1, therefore;

$x:y = 1:1$



If Granite = biotite or syenite, then from equation (73)

Haematite + Ilmenite = Titanohaemite (74)

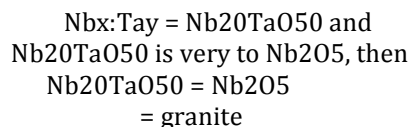
$\text{Fe}_2\text{O}_3(\text{s}) + \text{FeTiO}_3(\text{s}) = \text{Fe}_3\text{TiO}_6(\text{s})$ (75)

Basalt + Granite = Andesite (76)

Therefore, COLTAAN in granite, either in Nepheline Syenite or Lithium pegmatite rich cassiterite is columbite and is in Niobate group COLTAN according to Achuenu and Komolafe (2021) Table 3, as represented in equations (57), (58), and (59) below.

Since the ratio of niobium to tantalum is 20:1, therefore;

$x:y = 20:1$



From equation (45);

Columbite + tantalite = Coltan (77)

Granite + Pegmatite = Granite Pegmatite..... (78)

$\text{FeNb}_2\text{O}_6 + \text{FeTa}_2\text{O}_6 = \text{Fe}[\text{NbTa}]_2\text{O}_6$ (79)

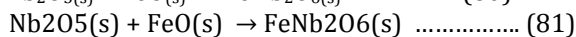
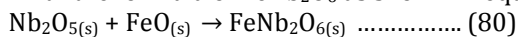
From equation (76), ilmenite is found in granitic rock which could be either biotite granite or syenitic granite

From equation (78), columbite is found in syenite granite or Diorite.

At a given Gibbs free energy, each of these minerals of HFSE maintains their highest oxidation states under standard conditions of temperature and pressure as shown in Table 5. From table 5, the following deductions were made;

1. Iron and Titanium have different oxidation states of +3 and +4. Hence undergo heterovalent substitution during crystallization of magma. Since the ratio of iron to titanium is 1:1, therefore the number of oxygen atoms would be 3, and then the molecular formula would be given as FeTiO_3 . At a given equilibrium, FeTiO_3 , would be stable, and has minimum free Gibb's energy, numerically $\Delta G > 0$, under standard conditions of temperature and pressure. Therefore, the type of iron ore in Kuru- Jentar cassiterite is ilmenite and it belongs to group 1 iron ore in periodic table of an iron ore according to Achuenu and Komolafe (2021).
2. The oxidation state of niobium and tantalum is +5, therefore the number of atoms oxygen in this case would be 5. Since the ratio of niobium to tantalum is 20:1, then the molecular formula would be $\text{Nb}_{20}\text{TaO}_{50}$. At a given free Gibb's energy, $\text{Nb}_{20}\text{TaO}_{50}$ is limiting to Nb_2O_5 , $\Delta G = 0$, this means that Nb_2O_5 is stable but not with minimum Gibbs

free energy under standard conditions. Therefore, further oxidation of Nb_2O_5 will produce a more stable crystal with the formula of FeNb_2O_6 as shown in equation (56).



Therefore, at equilibrium, Nb_2O_5 reacts with FeO in hydrothermally altered rock to produce FeNb_2O_6 as shown in equation (56). FeNb_2O_6 reaches its minimum Gibbs free energy under standard conditions of temperature and pressure, numerically $\Delta G > 0$.

Therefore, the type of COLTAN in Kuru-Jentar cassiterite is columbite and it belongs to Niobate –group COLTAN as shown in COLTAN model Table 2 according to Achuen and Komolafe (2021).

- The oxidation states of zirconium and hafnium is +4, therefore the number of oxygen atoms would be 4. Since the ratio of zirconium to hafnium is 38:1 as shown in Table5, then the molecular formula is $\text{Zr}_{38}\text{HfO}_{80}$. As the $\text{Zr}_{38}\text{HfO}_{80}$ is limiting to Zr_2O_4 , the free Gibbs energy of Zr_2O_4 is minimum under standard conditions. Therefore, the Kuru-Jentar cassiterite is a zircon – cassiterite type.

In conclusion, ilmeno-columbite rich cassiterite is granitic rock origin; therefore, this defines the geology of Kuru-Jentar of Jos Plateau. In this case, the geology of Kuru-Jentar of Jos Plateau is mainly Ilmeno- Columbite bearing Biotite and Syenite granite. Large commercial deposit of columbite-tantalite occurs in biotite granite (magmatic type) of Nigeria as well in placer (exogenic type) derived from such rocks and pegmatites (Kuz'menko1959, 60). Kuz'menko (1959) classified columbite of Jos Plateau state as Biotite granite and alkali granites with riebeckite and pyrochlore.

6. Summary of Findings

The appraisal of cassiterite using mathematical modeling approach with respect to minerals of HFSE can be summarized in the following ways;

1. At a given equilibrium, given that aqueous and silicate phases coexist together, HFSE partitioned along the aqueous phase while the LILE portioned along the silicate phase.
2. HFSE partitioned along the aqueous phase undergo series of isomorphous and oxidation reactions to produce minerals of HFSE within their stability limit in the aqueous phase
3. The isomorphous reactions in the aqueous phase include;
 - Isovalent substitution
 - Heterovalent substitution and then
 - Oxidation reaction
4. Isovalent substitution is the substitution that involves two ions of same charge of similar size, e.g., substitution of niobium with the ionic size of 0.69 by tantalum with the ionic size of 0.68, the smaller size of tantalum is due to lanthanide contraction and the heterovalent substitution is the substitution that involves two ions of different charges and similar size.
5. Oxidation reaction in an aqueous phase is the reaction in which single ion forms complex with oxygen during crystallization of magma.
6. Since HFSE have intermediate potentials of 3.5 and 9.5, they all partitioned along the aqueous phase, and hence classed as incompatible trace element.
7. 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 minerals of HFSE is more in hydrous melt than in the anhydrous melt since water controls the concentration of both minerals.
8. There is an exsolution in the hydrous melt, because of presence of titanium and tantalum; therefore, there is ionic substitution of niobium by tantalum and iron by titanium in the melt in solid solution during crystallization of the melt.
9. There is no exsolution in anhydrous melt, likewise the sedimentary rock, because the condition that favours the concentration of columbite, titanium and tantalite is limited in the dry melt.
10. From Figure 2, there is an arithmetic progression of titanium and tantalum as you go from the top to bottom of the figure. This means there is a successive increment of titanium and tantalum and decrement of iron and niobium from the top to bottom of the figure.
11. The increment of titanium and tantalum and decrement of iron and niobium from top to bottom affect genetic origin of cassiterite in which iron – niobium rich cassiterite is syenetic and titanium – tantalum rich cassiterite is pegmatitic.
12. The isomorphous substitution of one HFSE to another in cassiterite can be mathematically summarized through the following equation at the root of the equation [0, 5].

$$\sum_{x=0}^n Z(\text{X}_{n-x}\text{Y}_x)\text{O}_4 + Z(\text{X}_{n-x}\text{Y}_x)\text{O}_6 = 0, \text{ at the point of } (0, 5).$$

If the summation of the equation is equal to zero and $x = 0$ and $n = 5$, then the Cassiterite type is called niobium - iron rich Cassiterite with the associated rock types such as nepheline syenite and carbonatite. But at $x = 5, 1$, and $n = 0, 2$ then the Cassiterite type is called titanium - tantalum rich Cassiterite and the associated rocks such as granite and pegmatite.

7. Conclusion

Using mathematical modeling approach to appraise cassiterite with respect to HFSE, it could be concluded that the presence of HFSE in Cassiterite affirms the genetic origin of cassiterite from syenite to pegmatite, such that iron – niobium rich cassiterite is syenite as shown in Figure 2, Table 1 and 2 and titanium – tantalum rich cassiterite is pegmatite. The origin of cassiterite is determined by more or less amount of titanium and tantalum it contains. Findings have shown that, both HFSE elements undergo isomorphous substitution during crystallization of magma to produce crystals of haematite, magnetite, ilmenite, ulvospinel, columbite and tantalite that make up the cassiterite of a particular origin. Those that form complexes with oxygen to produce crystals of monazite, zircon and sand and because of durability and high strength of these minerals of HFSE, the cassiterite is relatively to highly resistant to weathering during weathering breakdown such that those rich in maghaematite – columbite are relatively resistant to weathering and can give room for weathering breakdown which can be later be recovered as alluvium deposit and the rock types are syenite and granite while those rich in ilmenite – tantalite are highly resistant to weathering and can be remained in situ as ore deposit and the rocks origin are, biotite granite and lithium pegmatite. The ratio of columbite to tantalite in nepheline syenite 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 cassiterite, maghaematite - columbite has a general Gibbs free energy numerically $\Delta G \geq 0$ and ilmenite - tantalite has general Gibbs free energy numerically $\Delta G > 0$ and these make cassiterite stable at room temperature. The weak magnetization of these 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 titanium and tantalum in cassiterite determines their cassiterite type, either ferro/ferric - niobium rich type cassiterite, or titanium - tantalum rich type cassiterite, as well as their genetic rock origin, in which the amount of titanium and tantalum in cassiterite increases from alkaline rock e.g. syenite to more silicic rock e.g. granite, such as pegmatite which gives the account that maghaematite and columbite are found in nepheline syenite and ulvospinel, ilmenite and tantalite are found in lithium pegmatite such that the weathering of syenite would give magnetite, haematite, and columbite and that of pegmatite would give tantalite.

Additionally, using matrix methods from equations (29), (30) and (43), cassiterite was modeled in which titanium and tantalum are determinant factors, and Cassiterite model was designed to classify them into groups, such that if niobium exceeds tantalum in cassiterite, it is called niobium rich cassiterite type and if tantalum exceeds niobium in cassiterite, it is called tantalum rich cassiterite type.

8. Innovation/Contribution to Knowledge

After appraisal of cassiterite using mathematical modeling approach with respect to minerals of HFSE, an expected concise valuable substantive empirical novel model would be developed and can be employed to study Cassiterite. This concise empirical novel model was, 'Cassiterite 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 of minerals of HFSE in cassiterite.

Because minerals require temperature, pressure and energy to form, two series of reactions are used to establish the relationships among the minerals of HFSE, which are the Oxidation called Complex series and the Isomorphous series called Isovalent and Heterovalent substitutions as shown in figure 1 and 2
Because Cassiterite is formed from two genetic environments of igneous rocks such as syenite and pegmatitic rocks, they are classified into cassiterite groups using Cassiterite model, and these are niobium – iron rich cassiterite, and tantalum - titanium rich Cassiterite as shown in figure 2.

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Appendix

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

A1: Niobium rich Coltan

(a) Niobate series

- I. Ferrohexaoxonioate (ii): FeNb₅O_{6(s)}
- II. Ferrohexaoxonioate (iii): FeNb₄O_{6(s)}
- III. Ferrohexaoxonioate (iv): FeNb₃O_{6(s)}
- IV. Ferrohexaoxonioate (v): FeNb₂O_{6(s)}

A2: Tantalized coltan:

(a) Tantalization series :

- I. Ferrohexaoxotantalate (ii): FeTa₅O₆
- II. Ferrohexaoxotantalate (iii): FeTa₄O₆
- III. Ferrohexaoxotantalate (iv): FeTa₃O₆
- IV. Ferrohexaoxotantalate (v): FeTa₂O₆

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: FeNb₂O₆
 - Nb:Ta = 5:0

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

2. Coltan: Fe(NbTa)₂O₆
 - Nb:Ta = 5:5

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

3. Tantalite: FeTa₂O₆
 - Nb:Ta = 0:5