Physico-chemical and mineralogical characterization of coltan ores from the Tanganyika province in the Democratic Republic of Congo.

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Abstract
The physico-chemical, mineralogical and radioactive characterization of coltan ores has the advantage of facilitating the prediction of the various hydrometallurgical methods to be implemented to produce tantalum and niobium in their pure state, taking into account the content of their oxides and that of accompanying impurities. At the end of this investigation, we noted that the coltan ores collected from the four mining sites in Tanganyika province did not have the same mineralogy or the same chemical composition in terms of tantalum and niobium oxides and accompanying impurities. These ores contain a mineralogy that looks like either struëverite, euxènité, colombo-tantalite or tantalite. Moreover, the coltan from this province presented no risk of exposure to ionizing radiation, given the radioactivity values found by the dosimeter and whose average value in milli-Sieverts per year remained well below the threshold set in the regulations in force in DR Congo. We found an average value of 0.143 mSv/year versus 20 mSv/year featured in the law of March 29, 2005 and promulgated in the official gazette of country.

Keywords: Characteristics, physico-chemistry, mineralogy, coltan from Tanganyika, DRC.

I. INTRODUCTION

Niobium and tantalum are two strategic metals whose growing demand has revolutionized advanced technology for over two decades now, in fields such as aerospace, telecommunications, optics and nuclear power [6, 7]. These two metals are generally found together in the same type of deposits, rare element pegmatites, and a few specialized granites. Another part is found in niobium-rich carbonatites, but also in tin smelting residues or minerals with similar characteristics [1, 22]. DR Congo is the leading producer of tantalum and ores containing these two oxides are mined in four of the country's 26 provinces [8]: Maniema, North Kivu, South Kivu and Tanganyika. Tanganyika Province comprises six territories: Kalemie, Kongolo, Moba, Nyunzu, Manono and Kabalo [2,3]. In this province, coltan comes mainly from the mines at Kahendwa, Mayi-baridi, Kisengo (Nyunzu and Kalemie) and Mukubu in the Manono territory [2,4]. Tantalum and niobium exist in ore in different mineralogies dictated by the chemical composition...
of the ores [2,3]. From the chemical analysis of each ore, different tantalum and niobium minerals can be identified according to their respective concentrations and the nature of the impurities that accompany them. These include columbite and tantalite (Fe,Mn) (Nb,Ta)O6, pyrochlore (Ce,Na,Y2 (Nb,Ta)2O8(OH,F), microlite (Na,Ca)TaO6(OH,F), 5-Morseite (Ce,Na,Ca)2(Ti,Nb)O6, euxenite (Y,Ca,Fe,U,Do,Nb,Ta)2O6, enderbyite (Ti,Nb,Sn,V)2O6, simpsonite Al4(Nb,Ta)3O12(OH), thoreaulite SnTa2O6, struëverite (Ti,Ta,Fe3+)3O6, fergusonite (Re3+,Nb,Ta)O4, sumarskite (Fe,Ca,Sn,Ta,O)2O6 and tapiolite (Fe,Mn)(Nb,Ta,Ti)2O6 [18]. The metallurgy required to obtain tantalum and niobium in their pure state involves the processing of their ores, whose physicochemical and mineralogical characteristics need to be known in advance to guide the choice of metallurgical method to be used in the extraction and purification processes for these two valuable metals [5]. It has been shown, for example, that the presence of impurities such as silicon and titanium in the solution resulting from the leaching of coltan ore has a direct influence on the solvent extraction of tantalum and niobium during their purification using tributylphosphate as an extractant; the increase in the concentration of silicon and titanium in such a leaching solution favors the extraction of tantalum to the detriment of niobium in a hydrofluoric acid medium [19].

The above illustration shows how important it is to be able to identify and determine the physico-chemical and mineralogical characteristics of the coltan ores extracted from the various quarries (deposits) in Tanganyika province. This characterization will enable researchers interested in the metallurgy of these two metals to predict the metallurgical methods (pyrometallurgical and/or hydrometallurgical) to be implemented for the extraction and subsequent transformation of tantalum and niobium into high-purity products. The aim of this research is to identify the mineralogy and physico-chemical characteristics of various coltan ores extracted from mines or quarries in the Tanganyika province of DR Congo, with a view to providing a better understanding of these properties to researchers interested in the metallurgy of tantalum and niobium. The major mining sites supplying coltan ore in this province are: Kahendwa and Kisengo (in Nyunzu), Mayi-baridi (in Kalemie) and Mukubu (in Manono).

II. MATERIALS AND METHODS

II.1. MATERIALS

For this study, we used: (Duran Germany, iso 4788) graduated test tubes for bulk density determination [9]; Boeco, Germany analytical balance. Six of the Brand Univesal (Jayant Scientific ind) granulometoric sieves with apertures of 50 µm; 100 µm; 212 µm; 425 µm; 850 µm and 1200 µm [10]. A vibro-tamiseur, brand Univesal (Jayant Scientific ind). Two chemical analysis instruments, X-ray Fluorescence (XRF) of the brand Thermo-scientific, Niton XL3t and Induction Plasma Optical Emission Spectrometer (ICP-OES) of the Brand Spectro-Arcos. Two mineralogical analysis instruments, an Alltion optical microscope for mineralogical analysis and an X-ray diffractometer (DRX). Sinsmart systems oven of the Brand, Sinsmart systems vibro-grinder. The coltan ores were collected at four sites (Mayi-baridi; Kahendwa, Kisengo and Mukubu) in Tanganyika province, respectively in the territories of Kalemie and Nyunzu for the first three quarries, and Manono for the Mukubu quarry.

II.2. METHODS

The experimental tests were carried out in three stages: the first was physical characterization, which
consisted in identifying the physical appearance (color, apparent density, and size of mineral particles by determining the granulochemical distribution) of each coltan ore per site studied. The second stage consisted in carrying out chemical analyses of each type of coltan ore at each site; and finally, the third stage involved mineralogical analysis to determine the mineralogy of each coltan site from the various quarry in Tanganyika province. It should be emphasized that the samples used in this study were collected and purchased from the hands of several diggers from the four targeted mines, to obtain a representative sample from each site.

II.2.1. Sample Origin

![Figure 1. Map of the DRC's administrative provinces and coltan sample collection area.](image)

II.2.2. Physical appearance of samples

![Kahendwa coltan ore](image)  ![Kisengo coltan ore](image)  ![Mayi-baridi coltan ore](image)  ![Mukubu coltan ore](image)

Figure 2. Images of coltan from the four study sites

The second figure below shows the physical and granular appearance of coltan from various mines in the Tanganyika province of DR Congo. Direct observation of the site images associated with the alphabetical letters shows that the coltan collected from the Kahendwa quarry in Nyunzu has more or less
coarse particles and a greyish appearance blending in with the earth; on the other hand, coltan from Kisengo in Nyunzu and Mayi-baridi in Kalemie has the same granular appearance, with a blackish color for the Mayi-baridi coltan and a less blackish color for the Kisengo quarry. Coltan from Mukubu in Manono has an appearance that is between red and grey. This information is important for an area where mining is almost entirely artisanal. Artisanal miners are the main exploiters, under cover of certain businessmen working in the sector; this situation is often at the root of armed conflicts [3,11].

Table 1. Granulochemical distribution of tantalum and niobium from Tanganyika province

<table>
<thead>
<tr>
<th>Particle size ranges</th>
<th>Coltan from Mayi-baridi Distribution (%)</th>
<th>Coltan from Kisengo Distribution (%)</th>
<th>Coltan from Kahenwa Distribution (%)</th>
<th>Coltan from Mukubu Distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ta₂O₅</td>
<td>Nb₂O₅</td>
<td>Ta₂O₅</td>
<td>Nb₂O₅</td>
</tr>
<tr>
<td>1200 µm</td>
<td>15,30</td>
<td>14,18</td>
<td>15,58</td>
<td>14,94</td>
</tr>
<tr>
<td>850 µm</td>
<td>18,38</td>
<td>20,04</td>
<td>23,84</td>
<td>26,25</td>
</tr>
<tr>
<td>425 µm</td>
<td>22,92</td>
<td>22,32</td>
<td>15,71</td>
<td>14,69</td>
</tr>
<tr>
<td>212 µm</td>
<td>11,73</td>
<td>12,84</td>
<td>14,62</td>
<td>13,67</td>
</tr>
<tr>
<td>100 µm</td>
<td>7,53</td>
<td>7,74</td>
<td>11,94</td>
<td>12,36</td>
</tr>
<tr>
<td>50 µm</td>
<td>10,38</td>
<td>9,84</td>
<td>10,69</td>
<td>10,44</td>
</tr>
<tr>
<td>50 µm</td>
<td>13,76</td>
<td>13,04</td>
<td>7,63</td>
<td>7,65</td>
</tr>
<tr>
<td>Total</td>
<td>100,00</td>
<td>100,00</td>
<td>100,00</td>
<td>100,00</td>
</tr>
</tbody>
</table>

Table 1. Granulochemical distribution of tantalum and niobium from Tanganyika province

II.2.3. Granulochemical analysis results

The results of the granulochemical distribution were obtained after the chemical analysis of the rejects from each sieve. The masses and distribution of tantalum and niobium on the different slices were calculated from the weight in grams of rejects from each sieve using formulas 1 and 2:

\[
\text{Weight of oxide (in grams) } = \frac{\% \text{ of oxide } \times \text{ weight in grams of reject on sieve}}{100} \quad \text{F1}
\]

\[
\text{Distribution (\%) } = \frac{M(\text{Mass of oxide on a given fraction } \times 100)}{\text{Total mass of oxide on all sieve fraction}} \quad \text{F2}
\]
III. RESULTS AND DISCUSSION

III.1. RESULTS OF PARTICLE SIZE DISTRIBUTION.

Figure 3. Granulometric distribution of tantalum and niobium from Tanganyika Province, DRC.

Figure 3 above shows that coltan from these four mining sites has different particle sizes. At the Kehendwa quarry in Nyunzu, tantalum and niobium particles have a particle size greater than 1200 µm; those at Mukubi in Manono and Kisengo in Nyunzu have a particle size greater than 425 µm. At the Mayibaridi quarry in Kalemie, the grain size was over 850 µm. These observations show that, overall, coltan from Tanganyika province is not coarse insofar as most mineral particles do not exceed 1200 µm [12]. In our opinion, these results can be explained, on the one hand, by the fact that coltan mining in the eastern part of the Democratic Republic of the Congo is carried out on an artisanal basis, and that diggers tend to manually discriminate between large, sterile particles that do not contain tantalum and niobium. Moreover, the geology, mineralogy and geochemistry of this region have revealed that tantalum and niobium are contained in granitic pegmatites, and that during the extraction of these two metals in mining quarries, diggers use sharp objects to fragment these rocks, thus imposing any granulometry on them [20,23].

III.2. CHEMICAL ANALYSIS RESULTS

The results of chemical analysis by X-ray Fluorescence and ICP-OES were obtained by analyzing representative samples from each site, and the average values for tantalum and niobium oxides with their major impurities are reported in Table 2 below.
Table 2. Results of chemical characterization of coltan from mining sites in Tanganyika province

<table>
<thead>
<tr>
<th>Mining site</th>
<th>Concentration of tantalum and niobium with their impurities (%)</th>
<th>Apparente density</th>
<th>Radioactivity Hits per minute</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ta₂O₅</td>
<td>Nb₂O₅</td>
<td>Fe</td>
</tr>
<tr>
<td>Mayi-baridi quarry</td>
<td>23.93</td>
<td>19.89</td>
<td>7.84</td>
</tr>
<tr>
<td>Kisengo quarry</td>
<td>32.75</td>
<td>43.97</td>
<td>5.88</td>
</tr>
<tr>
<td>Kahendwa quarry</td>
<td>37.10</td>
<td>41.29</td>
<td>4.84</td>
</tr>
<tr>
<td>Mukubu quarry</td>
<td>49.88</td>
<td>21.79</td>
<td>3.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mining site</th>
<th>Concentration of tantalum and niobium with their impurities (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>Mayi-baridi quarry</td>
<td>0.28</td>
</tr>
<tr>
<td>Kisengo quarry</td>
<td>0.79</td>
</tr>
<tr>
<td>Kahendwa quarry</td>
<td>0.26</td>
</tr>
<tr>
<td>Mukubu quarry</td>
<td>0.29</td>
</tr>
</tbody>
</table>

This table shows that the various coltan mines in Tanganyika province do not have the same chemical composition in terms of tantalum and niobium oxide, impurities and bulk density, while the radioactivity values have remained close to or even constant. It is already possible to predict the ore mineralogy of each of these different mines from their chemical composition [14,4]. We found that Mayi-baridi coltan was comparable to trüverite due to the presence of titanium in high concentrations and a tantalum and niobium oxide value close to and not exceeding 24%; this hypothesis seems to be verified by the color of the ore collected, which is blackish, as demonstrated by Prigogine's studies on coltan from DR Congo in 1956 [4,15]. Kisengo coltan, for its part, would be assimilated to euxenite, with tantalum and niobium concentrations ranging from 0-47% and 4-47% respectively [5,16]; Kahendwa coltan has been associated with colombo-tantalite in view of its manganese and iron concentration, as revealed by other researchers [4,17].

Coltan from Mukubu to Manono, on the other hand, is a tantalite [15] with a majority tantalum concentration and manganese and iron as the major impurities. It should also be noted that the density of these different coltan ores is also a function of tantalum concentration. We noted a high bulk density of 6.58 for ores from the Mukubu quarry, where tantalum is dominant, followed by ores from the Kahendwa quarry with a bulk density of 5.74, those from Kisengo with 5.68 and ores from Mayi-baridi with a bulk density of around 5.44. The results for apparent density as determined in this research appear to be close to, but slightly lower than, those obtained by Prigogine in 1956 [4]. The small difference observed in apparent density is due to the fact that the high demand for tantalum ores in the Great Lakes region has led to a decrease in tantalum and niobium concentration, to the point where we are increasingly encountering ores no longer exceeding 50% in these two oxides concentration. Whereas in the above-mentioned work, these two oxides could reach a concentration of 60 to 70% in some places in the eastern part of the Democratic Republic of Congo, especially after physical concentration [21].

As for the analysis of radioactivity, it showed that all the samples from the four sites under examination had average values not exceeding 60 counts per minute CPM or hits per minute, whereas the reference standard value was 51.57 counts per minute (value to be considered as dosimeter background); i.e., an average value of 0.143 mSv/year. Referring to article 11 of decree no. 05/022 of March 29, 2005,
regulating protection against the dangers of ionizing radiation, we found that samples with an average radioactive activity of 57.20 CPM, i.e., 0.143 mSv/year, are not at risk of occupational exposure, as the average effective dose limit is 20 mSv/year over a period of 5 consecutive years [24].

To confirm the mineralogy of tantalum and niobium at each site, we used optical microscopy and X-ray diffraction (XRD) to analyze the various samples.

### III.3. RESULTS OF MINERALOGICAL ANALYSIS USING AN OPTICAL MICROSCOPE

The results of the mineralogical analysis were obtained after analysis under the transmitted and reflected light optical microscope of the Faculty of Sciences, Department of Geology, University of Lubumbashi. They are presented in figures 4 a, b, c and d below for the Mayi-baridi, Kisengo, Kahendwa and Mukubu quarries respectively.

![Images of optical microscopic mineralogical analysis of coltan ore from Mayi-baridi (a), Kisengo (b), Kahendwa (c) and Mukubu (d) quarry.](image)

Analysis of these four optical microscopy images shows that coltan from various quarries in Tanganyika province displays tantalum and niobium in colors ranging from red to opaque, while rutile (TiO$_2$) has similar characteristics to coltan, but is slightly darker, yellowish-brown cassiterite, pyrolusite (MnO$_2$), a blackish mineral with a siliceous gangue, quartz (SiO$_2$) associated with pyroxenes, iron and magnesium minerals associated with silica, with the general formula (Mg,Fe,Ti,Al)(Si,Al)$_2$O$_6$, whose color on the images ranges from opaque gray to light gray. Overall, these mineralogical analysis results show that coltan from the Tanganyika province of the Democratic Republic of Congo has almost identical mineralogical characteristics at the four target sites.

### III.4. X-RAY DIFFRACTOMETER (XRD) MINERALOGICAL ANALYSIS RESULTS

The results of the X-ray Diffractometer analysis were obtained in South Africa at Wits University using 2-theta-theta coupling. The XRD spectra of the samples from the sites under examination are shown in Figure 5, with the designations a, b, c and d for the sample from the mayi-baridi quarry (Kalemie), Kisengo, Kahendwa (Nyunzu) and Mukubu (Manono) respectively.
Detailed analysis of Figure 5a, b, c and d show that the results obtained by X-ray Diffraction are consistent with chemical analysis by X-ray Fluorescence and ICP-OES and mineralogical analysis by optical microscope in transmitted and reflected polarized light. For the sample from the Mayi-baridi site (DRX spectrum 5a), peaks of NbO$_2$, Ta$_2$O$_5$, NbFeO$_4$ and Ti$_5$O$_9$ were identified, and peak summation confirmed the presence of strüverite containing tantalum, niobium, titanium, and iron. For the Kisengo sample, we identified peaks of Nb$_4$Ta$_2$O$_{15}$, Nb$_{2}$O$_6$, Ta$_2$O$_5$, NbFeO$_4$ and TiO$_2$, which are the constituent oxides of euxenite, compared with the tantalum and niobium oxide contents found after chemical analysis. The DRX spectrum of the Kahendwa sample revealed peaks of Nb$_2$O$_5$, Ta$_2$O$_5$, Sn$_2$O$_3$, (Mn, Fe)(Ta, Nb)$_2$O$_6$ and TiO$_2$, which are characteristic of Colombo-tantalite, while the Mukubu sample showed DRX peaks of Nb$_2$O$_5$, Ta$_2$O$_5$, Sn$_2$O$_3$, (Mn, Fe)(Ta, Nb)$_2$O$_6$ and TiO$_2$, which are characteristic of tantalite. The various oxides identified on the DRX spectra are similar to those found in Kahendwa ore, but the difference lies in the intensity of the peaks, which is high in Colombo-tantalite from Kahendwa and lower in tantalite from various mining sites in Tanganyika province.
Mukubu. This information proves that coltan ores from Tanganyika Province are generally accompanied by titanium, iron, manganese, tin and silicon as major impurities [5,15].

**IV. CONCLUSION**

To predict the methods of a hydrometallurgical process to be set up for the production of tantalum and niobium in their pure state, it was opportune to know the physico-chemical, radioactive and mineralogical characteristics of coltan from different quarries in the Tanganyika Province in the Democratic Republic of Congo. The various parameters analyzed during this study showed that tantalum and niobium ores can be found in the Tanganyika Province, with mineralogy matching that of strüverite (Mayi-baridi site in Kalemie) with titanium as a major impurity, euxènite with relatively low impurities (Kisengo site in Nyunzu), Colombo-tantalite or tantalite with iron and manganese as major impurities for the Kahendwa site in Nyunzu and Mukubu site in Manono respectively. The average bulk density of these various samples was around 6.16, and the average radioactivity of the samples was around 0.143 mSv/year, compared with the 20 mSv/year stipulated by Congolese regulations on the subject. This showed that coltan ores from Tanganyika present no danger in terms of radioactivity for those handling them.

All the information provided during the course of this research enabled us to note that knowledge of the mineralogy of Tanganyika coltan will enable metallurgists and chemists to effectively choose the hydrometallurgical processing methods to be implemented to produce pure tantalum and niobium, since all the impurities revealed during chemical and mineralogical analysis will certainly have a direct impact on the solution and purification process (especially during the solvent extraction stage).

**REFERENCES**


[23]. Journal official de la Présidence de la RDC, décret n°05/22 du 29 Mars 2005 portant réglementation de la protection contre les dangers des rayonnements ionisants à son article 11.