# THE COMPLEXITY OF THE NIOBIUM DEPOSITS IN THE ALKALINE-ULTRAMAFIC INTRUSIONS CATALÃO I AND II - BRAZIL

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#### Abstract

This paper describes the geological and mineralogical differences between the Catalão I and II niobium deposits and the development work carried out by Mineração Catalão to improve the recovery and quality of its pyrochlore concentrate.

#### Introduction

The complexity of the niobium deposits of Catalão I and II, some geological differences between them and the different mica and pyrochlore contents made it necessary to introduce a pyrochlore reverse flotation process for silicates using a specific and selective silicates collector to obtain good separation of these minerals.

Without the silicate flotation, the pyrochlore concentrate obtained was not suitable for the production of a standard FeNb because the silicon content in the concentrate was much higher than the values allowed by the international specifications.

Extensive research was required to define the process route for pyrochlore recovery from the Catalão II deposit. The definitive process flowsheets are given in this paper.

#### **Regional Geology**

The Catalão I and II Ultramafic-Alkaline Complexes are part of a province of ultramaficalkaline intrusives that extends from the coast of the State of São Paulo to Ipameri in the State of Goiás and beyond. In the segment between Tapira (State of Minas Gerais) and Catalão (State of Goiás), this strip is characterised by the large ultramafic-alkaline complexes of Tapira, Araxá (Barreiro), Salitre I, Salitre II, Serra Negra, Catalão I, and Catalão II. In this portion of the belt, the complexes are intrusive in Proterozoic metasediments, with a predominance of schists and quartzites (Figure 1).

# Local Geology – Catalão I

The Catalão I Ultramafic-Alkaline Complex forms a subcircular plateau, with a diameter of about 6 km, standing out in the landscape, at an average altitude of 900 meters above sea level and a level difference of 100 meters in relation to the regional ground surface. The current relief is the result of the greater resistance to weathering of fenites that form the ring of the dome, supporting the plateau, and protecting the thick blanket of weathered material in the central part of the dome (Figure 2).

#### Weathered Material at the Deposits

The three deposits of niobium of Mineração Catalão (Figure 2) have developed over carbonatites intruded in the central portion of the complex. The ore is constituted by the weathered portions of the intrusives, in average reaching the depth of 80 meters, to a maximum of 120 meters. The weathered materials, which are made up of a lateritic cover and the underlying saprolite, result from the alteration of the rocks described in item Fresh Rocks underlying the deposits.

# Lateritic Cover

This zone constitutes the overburden to the mineralization and is made of a ferruginous and intensely weathered zone, where no relict structure of the primary rocks is recognisable. Its thickness is variable, in general not exceeding 25 meters. The dominant mineral is gorceixite, which confers to the basis of the horizon its ochre colour. Goethite, typical of laterites,

predominates at a depth of 17 to 20 meters. Quartz is found in round-shaped or fractured nodules. Pyrochlore, though always present, is generally fine-grained and, in most cases, stained with a film of iron hydroxides.



Figure 1: Location map.

# Saprolite Saprolite

This zone, which contains the economical mineralization of niobium, is made of weathered rocks in which relicts of the primary structures are still recognisable. Towards the base the saprolite grades into the underlying fresh rocks. At the contact it is characterized by a vermiculite horizon always above the fresh rocks. The saprolite is rich in apatite and anatase, although not evenly distributed.

The niobium mineralization occurs in variable form, both horizontally and vertically, reflecting the distribution of pyrochlore in the mother rocks, which appear as dikes and fracture-filling veins.

Large blocks and masses of supergene silexite are abundant in the saprolites and present a large mineralogical variety, with magnetite, barite, apatite, and secondary phosphates being always visible.



Figure 2: The dome of Catalão I.

# Fresh Rocks Underlying the Deposits

The Catalão I Ultramafic-Alkaline Complex is formed by an ultramafic phase, consisting of dunites and, subordinately, pyroxenites, that were intensely altered to phlogopitic rocks as a result of intense potassic metasomatism accompanying the multiple intrusions of carbonatitic phases. Only remnant relicts portions of the ultramafic rocks can be recognized among the dominant carbonatites and phlogopities. Following the phlogopitisation process, nelsonitic and carbonatitic intrusions occurred in successive events.

Nelsonite is a rock of the foscorite group containing pyrochlore. It is usually massive, but may also be banded, with variable shades of grey, and medium to coarse-grained. It occurs in the form of dikes and veins of centimetric to metric thickness, and is often cut by veins and dikes of other carbonatites. It is constituted essentially by magnetite, phlogopite, calcite and/or dolomite. Pyrochlore, apatite and sulfides are accessory minerals, even though they may locally

constitute essential minerals. Pyrrhotite predominates among the sulfides, and calcite among the carbonates. The dominant type of pyrochlore is a Na, Ca-pyrochlore, but a Pb-pyrochlore also occurs.

# Local Geology- Catalão II

The Catalão II Ultramafic-Akaline Complex is actually bicentric, with reentrant western and eastern borders, and a greater length in the NE - SW than in the SE - NW direction, measuring 5.0 and 2.7 km, respectively. According to Machado Junior, the external contour represents the structuring of the host rocks during the various magmatic pulses of the complex. The main lithologic groups that constitute this massif are briefly described below (Figure 3).

SCHEMATIC CROSS-SECTION SHOWING THE MAI CONTACT RELATIONSHIPS BETWEEN THE CATALAO II LITHOLOGIC TYPES



Figure 3: The main lithologic groups of Catalão II complex.

#### Pyroxenite Series

This group includes pyroxenites, magnetite pyroxenites, and biotite pyroxenites, often associated with rocks referred to as apatitites and with other rocks of metasomatic nature.

#### Syenite Series

Of localized occurrence, this series comprises a quartz syenite, which occurs in contact with quartzites, and a homogenous alkali feldspar syenite of a simple mineralogical composition.

#### Foscorites

These rocks represent the last silicate phase that preceded the carbonatitic manifestations. The group is composed of homogeneous and massive mafic rocks which, as the other rocks that preceded them, are extensively cut by veins and dikes of carbonatites.

<sup>&</sup>lt;sup>1</sup> Machado Júnior, D. L – Geologia e Aspectos Metalogenéticos do Complexo Alcalino-Carbonatítico de Catalão II . Thesis of Master's degree (unpublished).

From the economic point of view, nelsonite is the most important rock among the foscorites, as it is the host rock for the phyrochlore, in both the Catalão I and the Catalão II deposits. The nelsonites usually contain calcite and trace amounts of chalcopyrite and bornite.

#### Carbonatite Series

This series is characterized by the presence of carbonates as essential constituents. The carbonatites are clearly intrusives, occurring as dikes and veins cutting the ultramafic rocks.

Four successive stages have been defined, characterized by magmatic manifestations in the form of dikes that cut across the rocks described above. A clear differentiation is observed between these stages, from the initial terms, which are rich in silicates, oxides, sulfides and phosphates, to the final terms which are mainly composed of carbonate minerals.

#### Lamprophyre Series

This series comprises a group of undifferentiated melanocratic and ultramelanocratic rocks. They form narrow dikes that penetrate into cracks and faults within the complex.

# Metasomatites

Metasomatism mainly affected the pyroxenites, at the contact with dikes of carbonatites. The metasomatites are constituted by an association of Na-amphibole, Na-pyroxene, K-feldspar and carbonate. In general they are rich in phlogopite, which is the last mineral to be formed and the most stable in the series of metasomatic transformations.

In addition to these series, the quartzites and fenitised schists that occur at the border zone of the Complex should be mentioned.

As a result of the weathering of these lithologic types, a continuous blanket of weathered material was formed, in which there is ample predominance of ferruginous minerals, particularly hydroxides. This blanket also contains large quantities of mica group minerals - muscovite, biotite, and phlogopite –partially or totally altered to clay minerals and vermiculite. Also worth mentioning is the constant presence of silexites in the weathered zone, throughout the Complex.

The intense metasomatism that took place at Catalão II also gave rise to other rock types, which have high contents of sodium amphiboles and phlogopite.

The ore of Catalão II resulted from the supergenic action upon the entire package of rocks mentioned above, after the leaching of the most soluble components, particularly carbonates, and the residual concentration of the most resistant minerals, amongst which is pyrochlore. The ore is constituted predominantly of magnetite, fresh or weathered into martite, and by ferric hydroxides such as goethite and limonite, followed by ilmenite, micas, quartz and rare-earth minerals. Pyrochlore, which is almost always associated with magnetite, is easily observable near preserved nelsonite veins. The ore also contains clay minerals derived mostly from phlogopites and serpentine.

# **Mineral Resources and Ore Reserves**

Table I Lateritic soil - Mine I					
Category	Cut Off - Kg Nb <sub>2</sub> O <sub>5</sub> /t	T x 1000	% Nb <sub>2</sub> O <sub>5</sub>	Overall recovery %	Kg Nb <sub>2</sub> O <sub>5</sub> / t
Proved Reserve	3.4	1,256	0.85	65.7	5.58
Probable Reserve	-	-	-	-	-
Measured Resource	3.4	430	0.62	65.95	4.09
Inferred Resource	-	-	-	-	-
Total	3.4	1,686	0.79	65.71	5.20

The mineral resources and ore reserves for the various mining areas are given in Tables I to VI. Mines I and II and Boa Vista are currently in operation.

	Table II Lateritic soil - Mine II				
Category	Cut Off - Kg Nb <sub>2</sub> O <sub>5</sub> /t	t x 1000	% Nb <sub>2</sub> O <sub>5</sub>	Overall recovery %	Kg Nb <sub>2</sub> O <sub>5</sub> / t
Proved Reserve	3.4	747	1.09	56.40	6.15
Probable Reserve	-	-	-	-	-
Measured Resource	-	-	-	-	-
Inferred Resource	-	-	-	-	-
Total	3.4	747	1.09	56.40	6.15

Table III Lateritic soil – East area					
Category	Cut Off - Kg Nb <sub>2</sub> O <sub>5</sub> / t	T x 1000	% Nb <sub>2</sub> O <sub>5</sub>	Overall recovery %	$Kg Nb_2O_5 / t$
Proved Reserve	3.2	4,547	1.29	45.91	5.92
Probable Reserve	3.2	2,634	1.26	39.24	4.94
Measured Resource	-	-	-	-	-
Inferred Resource	3.2	51	1.22	36.73	4.48
Total	3.2	7,232	1.28	43.43	5.55

Table IV Lateritic soil – Boa Vista					
Category	Cut Off - Kg Nb <sub>2</sub> O <sub>5</sub> / t	t x 1000	% Nb <sub>2</sub> O <sub>5</sub>	Overall recovery %	Kg Nb <sub>2</sub> O <sub>5</sub> / t
Proved Reserve	-	-	-	-	-
Probable Reserve	3.4	2,837	1.67	51.33	8.57
Measured Resource	-	-	-	-	-
Inferred Resource	3.4	480	1.47	49.63	7.30
Total	3.4	3,317	1.64	51.10	8.39

Table V Lateritic soil – Summa	ary of recoverable Nb

		t Nb (Recoverable)						
Mines	Dome		Reserve			Resource		
		Proved	Probable	Total	Measured	Inferred	Total	
Mine I	Ι	4,899	-	4,899	1,229	-	1,229	
Mine II	Ι	3,211	-	3,211	-	-	-	
East Area	Ι	18,817	9,096	27,913	-	160	160	
Boa Vista	II	-	16,996	16,996	-	2,449	2,449	
Tota	al	26,927	26,092	53,019	1,229	2,609	3,838	

Life of mine (open-pit mining) – 18 years.

	Table VI (	Carbonatite – I	nferred resource	1	
Category	Cut Off - % Nb <sub>2</sub> O <sub>5</sub>	t x 1000	% Nb <sub>2</sub> O <sub>5</sub>	Overall recovery %	Kg Nb <sub>2</sub> O <sub>5</sub> / t
Inferred Resource	1.0	10,000	1.45	60	8.70

Life of mine (underground mining) -20 years.

## **Geological and Mineralogical Comparisons**

Table VII The main characteristics of the Catalão I and II domes, comparing their formation, mineralogy, and ore contents.

	Catalão I	Catalão II
	Geologica	al Aspects
Primary ultramafic phase composed essentially of dunites. Large volume of carbonatitic magma, responsible for intense metasomatism of the previous rocks, giving Intense phlogopitization.		Primary ultramafic phase composed essentially of pyroxenites, foscorites and syenites. Smaller volume of carbonatitic intrusions, with preservation of ultramafic rocks. Intense phlogopitization.
Nelsonitic and	carbonatitic intrusions, responsible for the mineralization.	Nelsonitic and carbonatitic intrusions, responsible for the mineralization.
	Mine	ralogy
Vermiculit Presen Presence of n Presence of mo Presence of Commo	e present in larger quantities as depth increases. ace of large quantities of apatite. noderate to large quantities of anatase (mainly in East Area). oderate to large quantities of manganese oxides and hydroxides. large quantities of rare-earth minerals. on sulfides: pyrite and pyrrhotite.	Large quantity of micas (mainly vermiculite; biotite; muscovite and phlogopite). Low apatite content. Presence of small quantity of anatase. Presence of small quantity of manganese oxides and hydroxides. Presence of large quantity of rare-earth minerals. Sulfides present: chalcopyrite, bornite, and pyrrhotite.
	Grad	es - %
Nb <sub>2</sub> O <sub>5</sub>	0.60	1.58
Fe <sub>2</sub> O <sub>3</sub>	33.73	26.86
SiO <sub>2</sub>	6.20	41.75

#### Processing

Due to the differences in mineralogical composition between the two deposits, with the ores of Catalão II containing more micaceous minerals, extensive research was required to define the process route for the ore from this deposit. Even though the final flow chart adopted was similar to that designed for the Catalão I deposit, the process variables differ substantially from one ore to the other.

As the Catalão II deposit is also characterized by small intrusive veins of magnetite-rich carbonatite cutting across the host schist rocks, a large portion of the run-of-mine ore is made

of blocks of schists that contains no pyrochlore, which permits the removal of the coarse fraction (+1'') as waste, during the initial crushing process.



#### Figure 4: Crushing flowsheet.

	1			C	
	% Mass	% Nb <sub>2</sub> O <sub>5</sub>	Dist. Nb <sub>2</sub> O <sub>5</sub> %	% SiO <sub>2</sub>	Dist. SiO <sub>2</sub> %
+ 1"	22	0.35	5.0	60.6	28.1
- 1"	88	1.65	95.0	38.8	71.9
Total	100	1.53	100.0	47.47	100.0

Table VIII Niobium and Silica balance

The metallurgical balance shows the enrichment of niobium and the reduction of silica in the fraction <1".

# Grinding - Magnetic Separation - Desliming

The fraction <1" is homogenized and then fed to the grinding circuit. No changes were made in this circuit to receive the ore from Catalão II.

There is also a significant difference in magnetite content between the two deposits, as illustrated in Table IX.

	Table IX N	lagnetite balance	Catalao I/II		
	Cat	alão I	Catalão II		
	% Mass	% Nb <sub>2</sub> O <sub>5</sub>	% Mass	% Nb <sub>2</sub> O <sub>5</sub>	
Magnetite	16.0	0.26	7.8	0.21	



Figure 5: Grinding – Magnetic Separation – Desliming flowsheet.

# Desliming

This is the most important process operation to ensure selectivity during the flotation stages.

When desliming is conducted in a laboratory all particles  $<\!\!10 \ \mu m$  are removed, always through two operations:

In the first operation, the undersize of a 65# screen is classified in a 40 mm cyclone, for separation of the natural ultrafines contained in the ore.

The fraction retained on the 65# screen is milled in a rod mill until it passes the 65# screen and this fraction also undergoes desliming as described above, for separation of the ultrafines obtained through grinding.

Table X shows the differences in size analysis between the ores from the two deposits.

	Table X Lab	oratory desliming ba	lance	
Dealimina	Cata	Catalão I Catalão II		
Desiming	% Mass	% Nb <sub>2</sub> O <sub>5</sub>	% Mass	% Nb <sub>2</sub> O <sub>5</sub>
Natural Slimes	8.7	0.70	15.3	0.90
Grinding Slimes	7.9	0.55	15.8	0.86
Total	16.6	0.63	31.1	0.88

In the industrial circuit, desliming is conducted using 4" and 1" cyclones, which generate three products:

Coarses:	particles between 100 and 15 $\mu$ m in size.
Fines:	particles between 15 and 5 µm in size.
Slimes:	particles of less than 5 $\mu$ m in size.

The slimes are fed to a thickener for settling and water recycling.

#### Silicate Pre-flotation

When the silicate (micaceous) minerals are not floated out the obtained concentrate is inadequate for the production of FeNb, as shown in the following table.

	%
$Nb_2O_5$	24.03
$Fe_2O_3$	9.34
$TiO_2$	1.86
$MnO_2$	0.35
$SiO_2$	41.68
$P_2O_5$	0.24
$Ta_2O_5$	0.01
BaO	8.27
PbO	0.16
$U_3O_8$	0.05
$Al_2O_3$	10.37
	96,36

Table XI – Pyrochlore Concentrate (Direct Flotation)

Several attempts were made to depress the micaceous minerals during pyrochlore flotation, all of which were unsuccessful. Thus, pre-flotation was adopted as an essential step to obtain a concentrate capable of meeting international specifications. This also applies to ores from deeper levels of Catalão I, in which vermiculite becomes an important mineral constituent.

Next, the coarse and fine fractions are conditioned with depressors and collectors before being fed to the flotation cells, where the silicates are floated.

For the coarse fraction the flowsheet includes roughing, scavenging and cleaning, whereas for the fines only roughing and scavenging are conducted.

In both cases, the rougher tails are deslimed prior to being fed to the scavenger.

	Coarses	s Circuit	Fines Circuit			
	Catalão I	Catalão II	Catalão I	Catalão II		
	%	%	%	%		
Flotation Feed	100.0	100.0	100.0	100.0		
Silicate Concentrate	15.4	49.0	11.2	87.0		
Flotation Tailings	84.6	51.0	88.8	13.0		

Table XII Mass Balance for Coarse and Fine Silicate Flotation for Catalão I and II



Figure 6: Flotation flowsheet.

A significant difference can be noted in the percentages extracted as silicates between the two deposits. In the fines circuit 87% of the mass of Catalão II is floated against 11% for Catalão I.

Also very different are the amounts of consumed depressors and collectors, as shown in Table XIII.

Table XIII Consumption of reagents (g/t)							
Reagents Catalão I Catalão II							
Starch	400	1,400					
Etheramine	50	280					

# **Pyrochlore Flotation**

Most of the pyrochlore reports to the scavenger cells tails which, after being dewatered for reagent removal, is ready to be fed to the pyrochlore flotation cells.

Up to this point separate flotation circuits are used for coarse and fine fractions with identical flow charts (roughing and cleaning), to obtain the final concentrate.

Significant differences in chemical composition are observed between the concentrates from the two ore bodies, as shown below on table XV.

Table XIV Metallurgical balance (Plant)								
		Catalão I		Catalão II				
	% Mass	% Nb <sub>2</sub> O <sub>5</sub>	% Recov.	% Mass	% Nb <sub>2</sub> O <sub>5</sub>	% Recov.		
ROM	100.00	0.89	100.00	100.00	1.53	100.00		
Magnetite Concentrate	16.00	0.26	4.69	7.77	0.21	1.07		
Slimes	18.73	0.77	16.26	38.58	0.69	17.31		
Silicate Concentrate	9.30	0.30	3.14	30.97	0.54	10.87		
Flotation Tailings	54.96	0.29	17.96	21.14	0.67	9.18		
Final Concentrate (FC)	1.01	50.90	57.95	1.54	61.13	61.57		
%SiO <sub>2</sub> (in FC)		2.76			2.72			

Table XV C	Table XV Chemical analysis of floated concentrate						
%	Catalão I	Catalão II					
Nb2O5	54.63	64.09					
$Fe_2O_3$	3.55	1.53					
$TiO_2$	3.74	3.72					
$MnO_2$	0.20	0.02					
$SiO_2$	2.76	2.72					
$P_2O_5$	0.66	0.30					
$Ta_2O_5$	0.29	0.13					
BaO	15.55	20.61					
PbO	5.65	0.28					
$U_3O_8$	0.35	0.02					
$Al_2O_3$	0.50	0.33					
	87,88	93,75					

## Leaching

The absence of apatite in the floated concentrate from Catalão II makes it unnecessary to use hydrochloric acid as a leaching agent. Leaching with caustic soda is sufficient not only to remove the small quantity of secondary phosphate that contaminates the concentrate, but also, if and when necessary, to adjust the sulphur content to international specifications.

Table XVI Chemical analysis – Final concentrate (Catalao II)

%	Leached
Nb <sub>2</sub> O <sub>5</sub>	63.70
$Fe_2O_3$	1.45
$TiO_2$	3.60
$MnO_2$	0.02
$SiO_2$	2.70
$P_2O_5$	0.15
$Ta_2O_5$	0.13
BaO	20.05
PbO	0.25
$U_3O_8$	0.02
$Al_2O_3$	0.30
	92,37



Figure 7: Leaching flowsheet.

#### Metallurgy

Regardless of the source of the concentrate, the metallurgical process used is an aluminothermal reduction, conducted in batch reactors.

The gases generated by the reaction are exhausted and scrubbed, before being discharged into the atmosphere.

After being crushed and screened, the obtained FeNb alloy shows no significant differences in its chemical composition, regardless of the origin of the ore, either Catalão I or Catalão II.

Model X vin Perto Anarysis Catalao I (Chapadao) and Catalao II (Boa vista)   %Nb %Al   %Nb %Al <th>%Mn</th>										%Mn	
Catalão I	66.20	0.39	0.48	0.06	0.13	0.10	0.09	0.06	2.48	0.15	0.15
Catalão II	66.10	0.34	0.10	0.06	0.13	0.48	0.03	0.04	2.43	0.12	0.18

Table XVII FeNb Analysis Catalão I (Chapadão) and Catalão II (Boa Vista)

After being crushed and sized according to client specifications, the FeNb alloy is stored in different types and sizes of packaging which range from big-bags holding 1 ton of FeNb alloy to small cans holding 10 lb of contained Nb.



Figure 8: Ferro Niobium flowsheet.