SOME ASPECTS OF THE MINERALOGY OF CBMM NIOBIUM DEPOSIT AND MINING AND PYROCHLORE ORE PROCESSING – ARAXÁ, MG – BRAZIL

Abrahão Issa Filho, Bruno Fernando Riffel and Clovis Antônio de Faria Sousa

CBMM - Companhia Brasileira de Metalurgia e Mineração
Córrego da Mata s/n – P.O. Box 08
38.183-970 - Araxá, MG, Brazil

Abstract

Aspects of the mineralogical composition and of the distribution of the principal chemical elements in the minerals of the mine ore are presented. Amongst the topics treated are the chemical alteration of the primary ore mineral, the probably mixed origin of barite in the residual enrichment zone and other transformations which occur there, the mining of the secondary ore, and some features of the floatation concentrate and its preparation.

Geology of the Araxá Mine

Country Rocks

The Araxá Group, which hosts the Barreiro carbonatite complex, is mainly composed of deep-water and shelf sediments along with contemporaneous volcanic rocks that were then intruded by syn-orogenic plutons and were metamorphosed and strongly deformed. It is therefore difficult to establish the original stratigraphic sequence.

The Barreiro Carbonatite Complex

The Barreiro Carbonatite Complex is situated some 6 km south of the city of Araxá, in the state of Minas Gerais (Figure 1). The complex is roughly circular with a surface diameter of 5 km. About 90 million years ago its intrusion into quartzites and schists of the Araxá Group caused arching which gave rise to a domed structure with concentric and radial fractures in the country rocks, as well as intense shattering of the quartzites. The complex has magnetic and radioactive anomalies, especially at the center.

Figure 1: The location of Araxá City, Minas Gerais state, Brazil.

The complex is predominantly formed by dolomite carbonatite with subordinate calcite carbonatite, phlogopite glimmerite and the primary ore. The latter is present in fresh plutonic carbonatite forming the core of the structure, and consists of cumulates containing magnetite with exsolved ilmenite, phlogopite, pyrochlore and ilmenite with associated apatite. The cumulates are cut by thin veins of different widths and grain sizes composed of various mineral assemblages, including the major components dolomite+magnetite+phlogopite, dolomite+magnetite, and dolomite+Fe-Cu sulphide minerals+barium carbonate (norsethite). The presence of barium carbonate in carbonatite is unusual, but may be a consequence of the presence of an unusual Ba-rich mantle below southeastern Brazil, reflected by high Ba contents in many Neoproterozoic, Mesozoic and Tertiary igneous rocks in the region (1,2). Drill cores to depths of 844 m register the presence of mineralized rock, which may still be present at even greater depths. Apart from the minerals already mentioned and pyrochlore, the presence of barite, monazite, and baddeleyite, amongst others, have been noted.

The glimmerite contains rare relict pyroxene and olivine, and was produced by metasomatism of ultramafic igneous rocks, probably peridotite and pyroxenite. The metasomatism may have occurred during the magmatic, alkaline-carbonatite stage involving the necessary alkali-rich fluids (3). Fenitization occurred at the contact zone in the form of veins and veinlets mainly composed of Na-amphibole cutting the host quartzites. Few quartz-feldspathic fenites have been found.

The carbonatites and primary ores present evidence for the action of low-temperature deformation. Anastosomosing faults with fault breccias are present in the carbonatites, while some crystals in primary ore are fractured, and phlogopite crystals frequently have kink bands.
Although no volcanic rocks are associated with the Barreiro Complex, there is an evidence that it may be cogenetic with kamafugites of the Late Cretaceous Alto Parnaíba Igneous Province, which borders the Paraná basin (2).

Niobium Resources

Study Methods

Besides conventional microscopy, a large part of the studies of rocks, ores and weathering products was undertaken using back-scattered electron images (BSEI) acquired using a scanning electron microscope (SEM). Mineral identification was aided by energy dispersion X-ray analysis (EDS) and x-ray diffraction (XRD). A very rich bariopyrochlore concentrate processed at CBMM Laboratories was analysed at Lakefield Geolab – Belo Horizonte/Brazil, mainly by X-ray fluorescence (XRF).

Overburden

Two main types of sterile overburden are visually distinguished by their colors. The sterile yellow overburden mainly contains kaolinite and goethite, in association with subordinate gorceixite. The red overburden contains gibbsite and kaolinite, with subordinate gorceixite, goethite and hematite.

Niobium Ores

Two types of niobium ores are found in Araxá: the primary ore already described with a mean grade of 1.5% Nb_2O_5, and a maximum grade of 8% Nb_2O_5, and the residual ore with a mean concentration of 2.5% Nb_2O_5. Only the latter is exploited by open-pit mining. The alteration and decomposition leading to the formation of the friable residual ore, simplify mining procedures. The following information on the secondary ore is the result of observations made by Riffel and Issa Filho over a number of years, during CBMM's research into the nature of the ores.

Weathering caused relative enrichment of the niobium ore mineral, which was physically preserved but chemically modified during leaching, as well as alterations in the other minerals present. Samples collected from brecciated zones show that pyrochlore *s.s.* is progressively transformed into bariopyrochlore along fractures and at grain boundaries by the substitution of calcium and sodium by barium (Figures 2 – 4), probably due to the action of meteoric waters.

Norsethite is present in the primary ore (Figures 5, 6), which together with barite represent the main barium bearing minerals. Sulphides are restricted to the primary ore. When fractured, the sulphides developed oxidized borders (Figure 7).

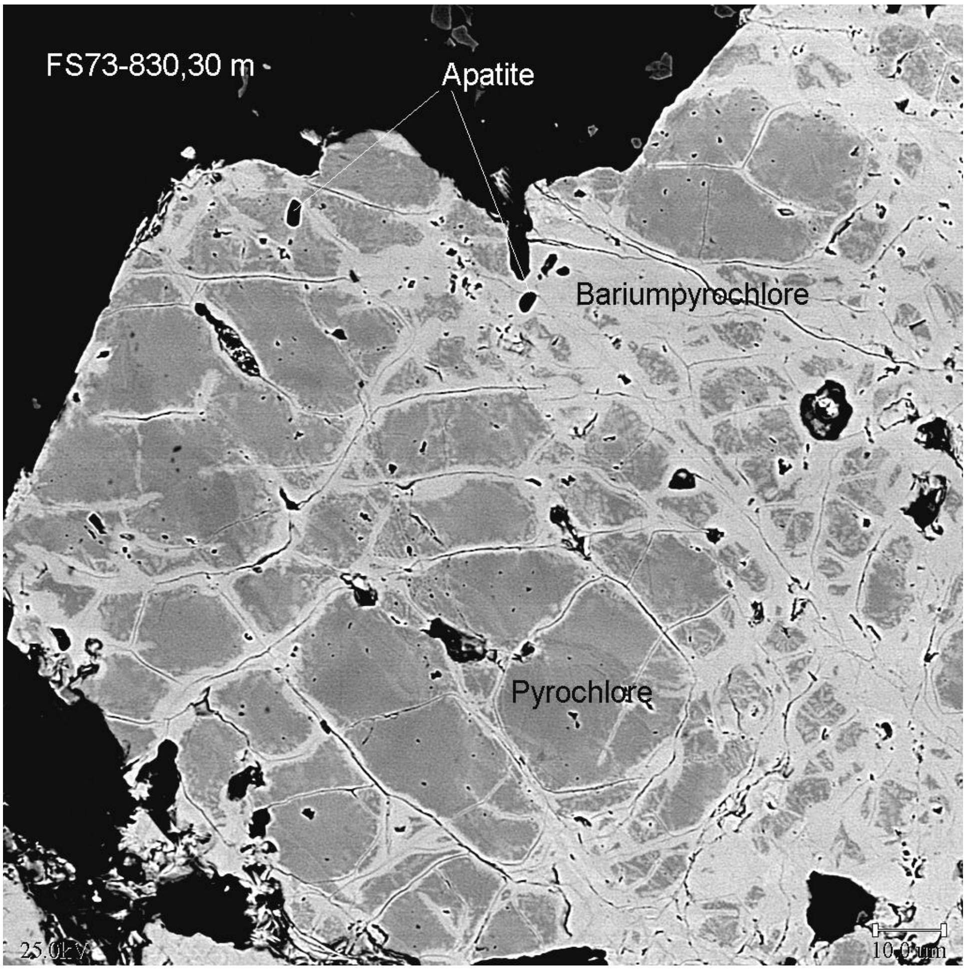

Figure 2: BSEI of fractured primary ore, showing transformation of pyrochlore (dark areas; see Fig.3) into bariopyrochlore (light areas; see Fig. 4).

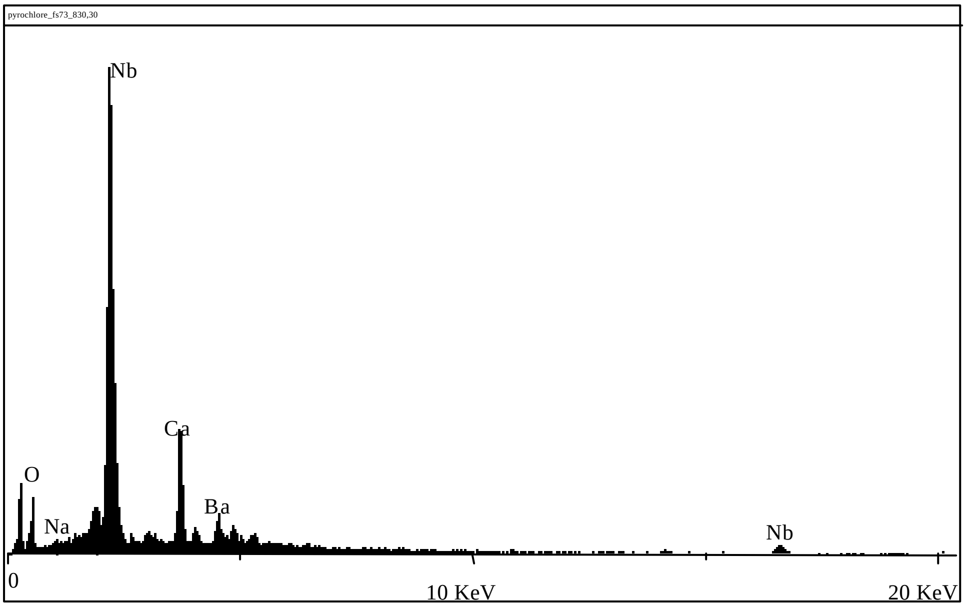

Figure 3: Spot EDS analysis on dark pyrochlore *s.s* (dark areas).

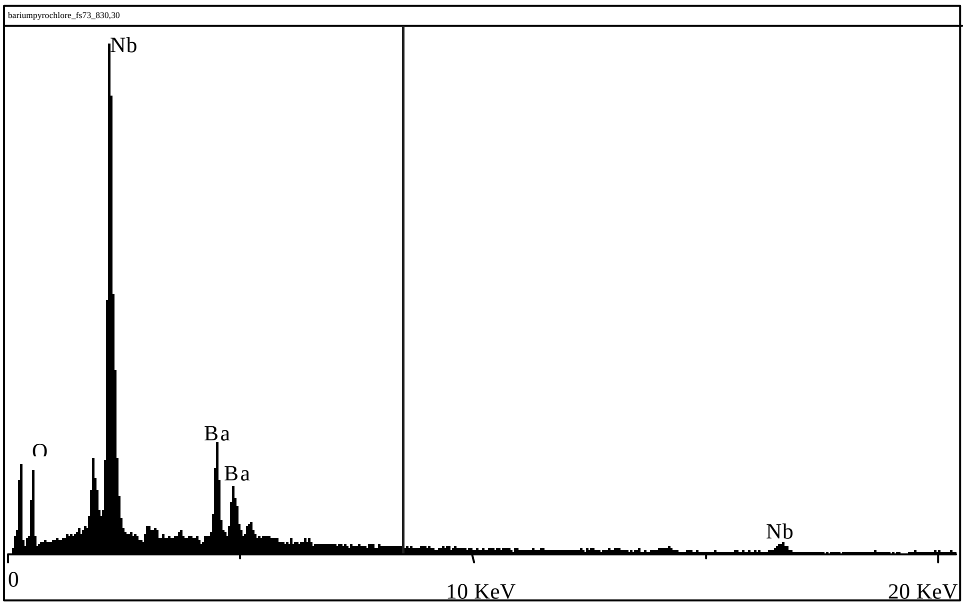

Figure 4: Spot EDS analysis on light pyrochlore: bariopyrochlore.

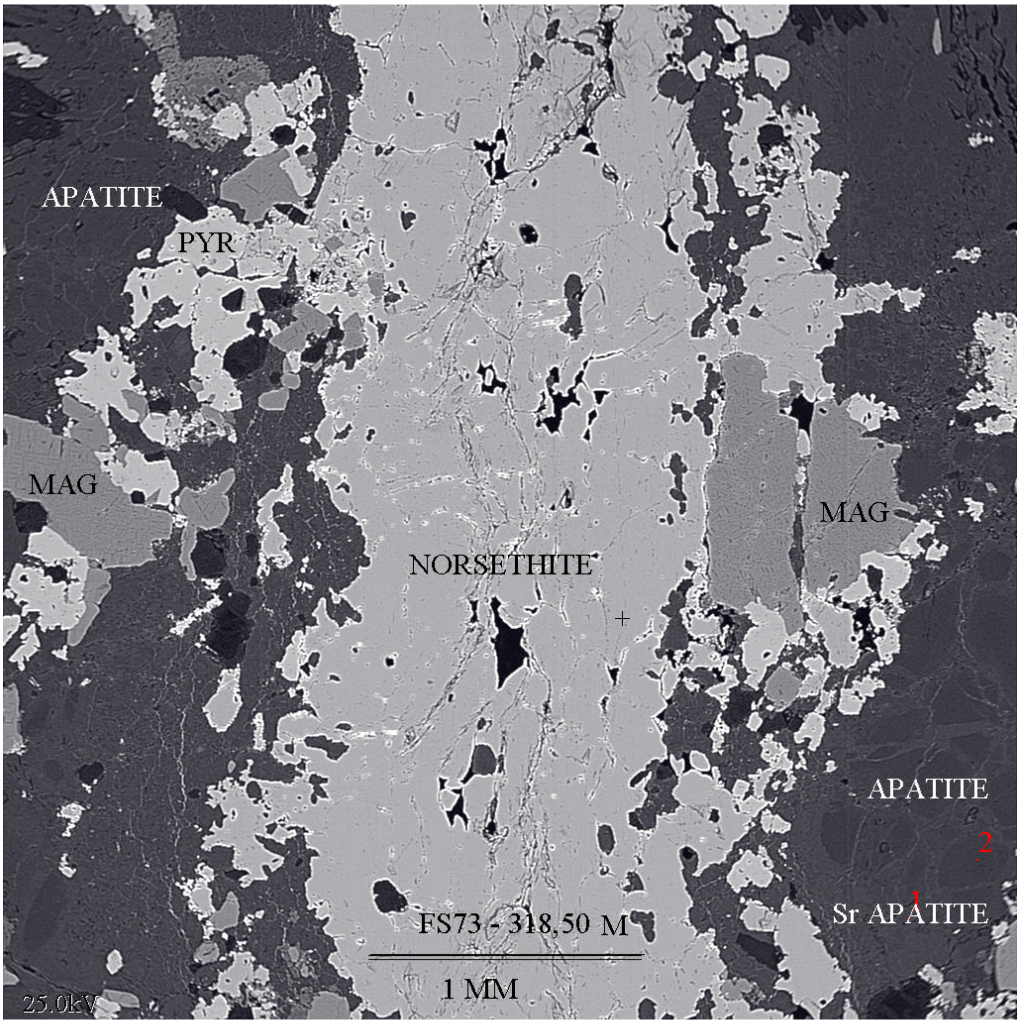

Figure 5: BSEI of the rock from drillhole FS-73- 318,50 m, showing barium carbonate (norsethite; EDS in Fig.6), pyrochlore, magnetite, apatite and late strontium-apatite.

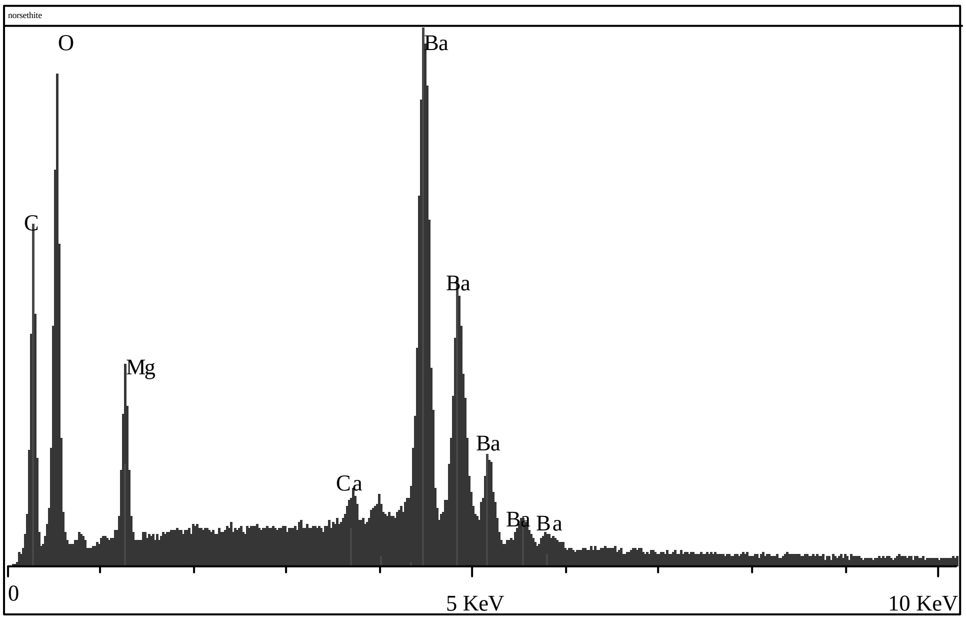

Figure 6: EDS spectrum of barium carbonate – norsethite: $BaMg(CO_3)_2$.

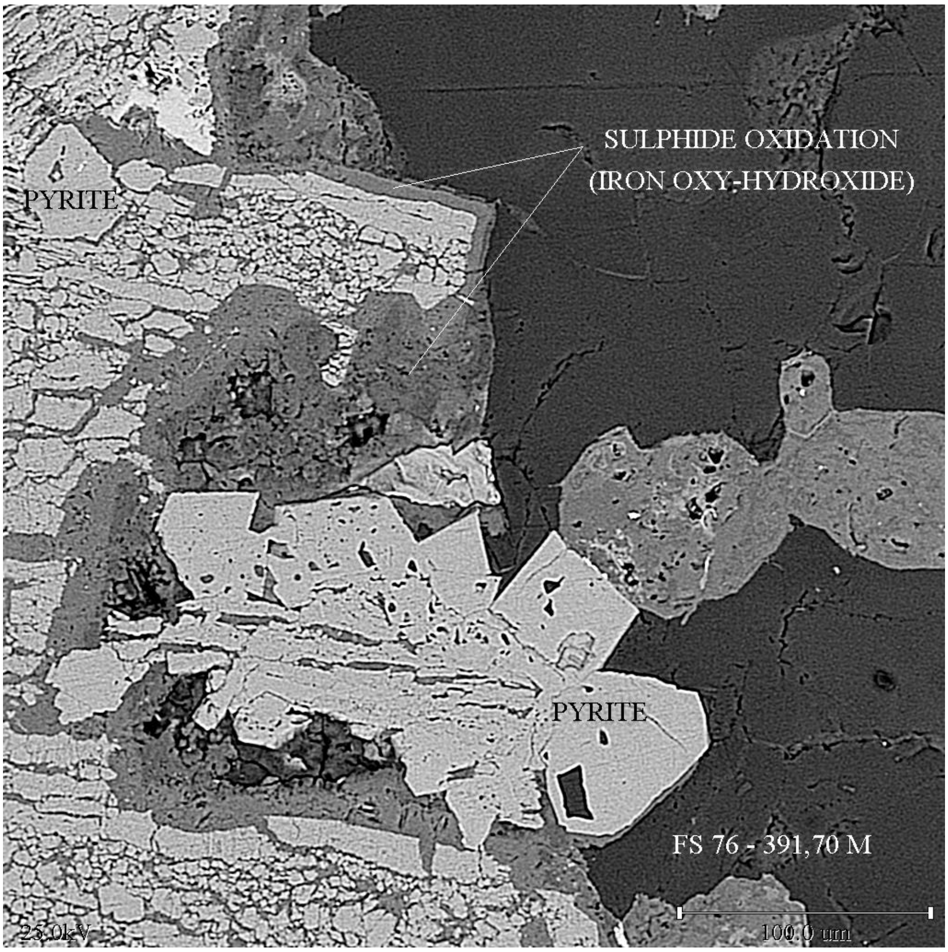

Figure 7: BSEI of a rock from drillhole 76 – 391,70 m, showing oxidation of pyrite to iron oxy-hydroxide.

The Residual Ore

Weathered material derived from primary ore, now being mined, contains about 4% bariopyrochlore, the principal niobium mineral present in the residual ore. The average mineralogical composition of the Araxá residual niobium ore is shown in Table I, its chemical composition in association with the bariopyrochlore chemical composition is given in Table II.

The 450 million tons of residual ore are sufficient to satisfy current world demand for centuries. The ore mined in open pits which feeds the plants has a grade of 2.5 % Nb_2O_5, and it is up to 250 m thick. New drilling performed in 2001 revealed zones with 4.6 to 7 % Nb_2O_5, which must therefore contain about 10% bariopyrochlore.

Figure 8: Panoramic view of the mine.

Table I Average mineralogical composition of Araxá residual ore

Mineral	%
Bariopyrochlore	4
Limonite, goethite (Includes silica in the plasma)	36
Barite	20
Magnetite (Includes exsolved ilmenite and inicial oxidation products – martite)	16
Gorceixite	6
Monazite	4
Ilmenite	5
Quartz	4
Others	5
Total	100

Table II Chemical composition of residual ore and of bariopyrochlore – Araxá

Sample	1	2	3	4
Component	%	%	%	%
Fe_2O_3(*)	45.0	1.19	-	0.92 (**)
FeO(*)	-	-	2.37	0.28
BaO	16.0	14.21	16.51	10.9
SO_3	7.0	-	-	-
TiO_2	4.0	4.74	2.3	4.3
SiO_2	5.3	-	-	-
P_2O_5	3.7	-	-	-
$(RE)_2O_3$(***)	3.2	1.62 (****)	3.29	4.0
Nb_2O_5	2.5	65.97	63.42	66.0
Al_2O_3	2.0	-	-	-
MnO	0.9	0.01	0.16	0.01
MgO	0.3	0.01	-	0.2
CaO	0.4	0.06	0.44	0.02
PbO	Trace	0.90	0.42	0.63
K_2O	Trace	-	-	0.04
Ta_2O_5	Trace	0.07	0.15	0.14
SrO	-	-	-	0.07
ThO2	Trace	1.65	2.34	2.7
SnO_2	Trace	0.08	0.10	0.06
ZrO2	-	0.41	-	0.18
UO2	-	0.08	-	0.05
LOI	6.5	-	-	-
H_2O	-	8.26	8.50	7.83
Total	96.8	99.26	100	98.33

[1] Residual ore; [2] Bariopyrochlore (4); [3] Bariopyrochlore (4); [4] Bariopyrochlore – composition adjusted from analysis of high purity concentrate containing micro inclusions of gorceixite. (*) Total iron reported in the most appropriate oxidation state; (**) Fe_2O_3 determined by difference between total Fe and FeO; (***) Total of analysed rare earth elements (RE); (****) La_2O_3 + Ce_2O_3; (-) not determined.

Mining Operation

Due to the altered and decomposed nature of the overburden and ore, drilling and blasting are not necessary in the stripping and mining operations. The equipment used in the mine comprises D8R and D6R Caterpillar bulldozers, L 120 C Volvo front-end loaders, and MB2638 dump trucks. The bulldozers cut the ore in a down hill mode. The front-end loaders then load the trucks, which transport the ore about 500 m to the feed station of a 3.2 km long conveyor belt. The belt transports the ore to the mill, which has a capacity of 4,000 t/day.

A computerized mining plan was introduced in June, 2000. The block model was developed based on historical data acquired during geological surveys performed in the past and also based on historical database generated during the operation along the last 40 years of operation. New data will be store in the database after a new set of geological survey planned for the next year. This plan allows CBMM to improve its mining operation based on a correlation between the quality of the ore and its behavior during the concentration process.

Concentration Process

The pyrochlore concentration process was recently up-graded, including computerized process control, and duplication of the grinding and desliming circuit. The present capacity is 84,000 tons per year. The steps used in pyrochlore concentration are the following:

Crushing and Grinding

Normally the ore is completely disaggregated and decomposed, and does not require heavy crushing. The crushing facilities consist of an apron feeder, which delivers the ore to a roll crusher. The crushed ore is stored in two 4,500 ton capacity silos, each one feeding a separate grinding circuit.

Bariopyrochlore crystals of the Araxá ore are very small, seldom exceeding 1 mm in size. Optimum liberation is achieved after grinding to 95 per cent minus 104 microns (-150#). A 3.7 m x 4.9 m (12‘ x 16‘) ball mill and another, 3.7 m x 5.33 m (12’ x 17’6”) compose the grinding circuit. The discharge from each ball mill passes to a specific magnetic separation section.

Magnetic Separation

The Araxá ore contains 15 to 30 per cent magnetite that is removed by low intensity (800 – 900 Gauss) double-drum magnetic separators. The magnetic concentrate is pumped to a tailings pond. The non-magnetic slurry is classified in 508 mm (20”) hydro-cyclones. The overflow goes to the desliming and the underflow returns to the grinding circuit.

Desliming

The floatation of Araxa pyrochlore is very sensitive to the presence of slimes. The lateritic nature of the ore implies the existence of considerable amounts of natural –5µm slimes, in addition to the slimes generated during the grinding, and therefore desliming is mandatory. For this reason, three-stage desliming is used at 381 mm (15”), 102 mm (4”) and 50 mm (2”).

Floatation Circuit and Filtering

The concentration of the bariopyrochlore crystals is by selective froth floatation. Deslimed slurry is conditioned with an amine type cationic collector. The floatation circuit is acidified with hydrochloric acid and the pH is controlled at 2.5 to 3.5. Rougher floatation consists of a bank of eleven 8.5 m^3 (300 ft^3) floatation cells. Rougher concentrates, together with second cleaner tailings, are sent to first cleaner. Cleaner floatation consists of four cleaning stages, each one in closed circuit with the previous stage. The first cleaner consists of a bank of seven 8.5 m^3 (300 ft^3) cells; second cleaners use six 4.8 m^3 (170 ft^3) cells and third and fourth cleaners have six 1.7 m^3 (70 ft^3) cells. Floated concentrates are thickened in 30 m (100 ft) diameter thickener and filtered in a 2.4 m x 1.8 m (8´x 6‘) filter. Floated concentrates having 11 per cent moisture are ready for refining via leaching or by the pyrometallurgical process.

After milling, magnetic separation, desliming and floatation the bariopyrochlore concentrates contain 0.2% S and >10% H_2O (constituent water and moisture, represented as loss on ignition).

Figure 9: Floatation concentrate: bariopyrochlore retained on 200# Tyler sieve.

Trace Impurity Minerals in the Concentrate

A number of minerals have been identified in the floatation concentrate mostly by SEM/EDS. The main minerals which occur as inclusions in, or as components of compound grains with bariopyrochlore, are gorceixite (Fig. 10 and Fig 11), ilmenite, martite with ilmenite exsolution lamellae, goethite and limonite. The overgrowth/intergrowth relationships between bariopyrochlore and gorceixite are observed at all scales down to a few microns. Barite, ilmenite, niobian ilmenorutile or rutile, martite, goethite, limonite and quartz form rare associations. Quartz and kaolinite may form a small part of the Fe oxy-hydroxide plasma grains.

While most of the Pb present in the concentrate occurs in solid solution in bariopyrochlore, plumbopyrochlore is sometimes detected.

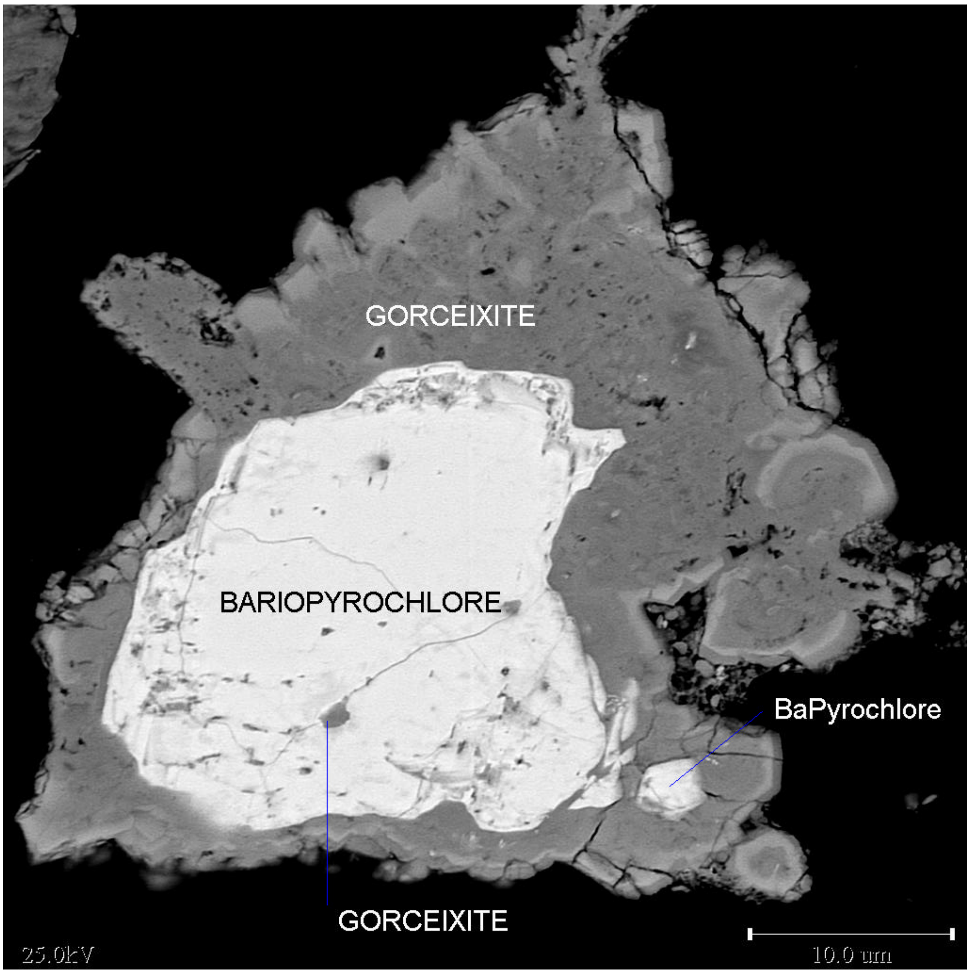

Figure 10: BSEI of bariopyrochlore and gorceixite.

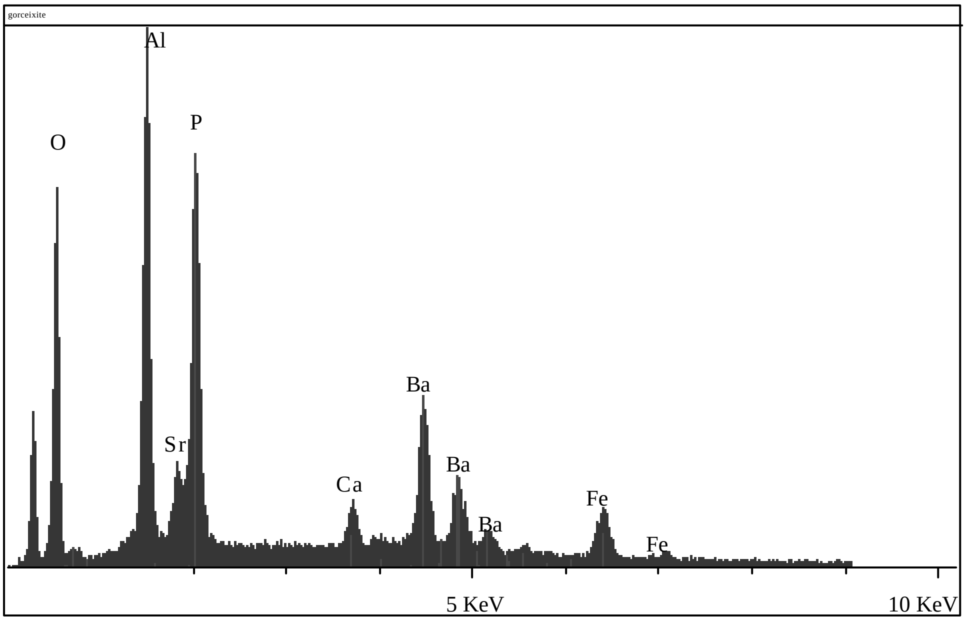

Figure 11: Spot EDS of gorceixite.

Genesis of the Residual Ore

The interpretations of paragenetic relationships between the minerals are based on their main mode of occurrence, whether exclusively in the primary, “fresh” rocks or ore, in the residual weathered ore, or in both environments. In addition, textural relationships between minerals already described for the residual ore and the floatation concentrate were used.

The supergene alteration processes which act on the primary Nb ore result in volume reduction and relative Nb enrichment. They include leaching of carbonate minerals, transformation of primary silicate minerals into clays, substitution of original phosphates by minerals of the crandalite group, partial to total oxidation and hydration of magnetite with formation of martite or iron hydroxide, and oxidation of sulphides. In a general way, the concentrations of the alkalis and light alkaline earth elements undergo large reductions. Although most primary oreminerals are modified or decomposed during supergene alteration, some minerals (e.g. baddeleyite) seem to be conserved.

Primary apatite and late-formed strontium apatite are restricted to the primary ore. The main phosphate-bearing mineral in the residual ore is very fine-grained neoformed gorceixite. Gorceixite is believed to be formed at the cost of apatite, which supplies P, as well as part of the Ca and RE; tetraferriphlogopite (supplying Al and some Ba) and carbonate minerals (Ca, Sr, RE and some Ba).

In one form of occurrence of barite in the residual ore, it comprises the fine-grained matrix of blocks containing dark nodules formed by Fe-oxy-hydroxides and gorceixite, while in the other type of occurrence it forms veins with quartz which cut nodules of intergrown quartz and Fe-oxy-hydroxides. Barite in the residual ore sometimes contains inclusions of silica and gorceixite, and this generation of barite is therefore also thought to be secondary, formed by the encounter of Ba-rich solutions formed by the decomposition of norsethite with SO_4^2 – rich solutions formed by the oxidation of sulphides. No method of distinguishing between primary and secondary barite has so far been found, but the concentration of primary barite in the rock is clearly insufficient to produce residual ore with high concentrations of barite.

Acknowledgements

The authors gratefully acknowledge the help of Dr. Ian McReath with the translation of the text into English, and for his suggestions and comments.

References

(1) Wiedemann-Leonardos, “Further signs of enriched mantle source under the Neoproterozoic Aracuí-Ribeira Mobile Belt” Revista Brasileira de Geosciências, 30(2000), 95-98).

(2) J.A Brod, S.A. Gibson, R.N. Thompson, T.C. Junqueira Brod., J.H. Seer, L.C. Moraes and G.R. Boaventura, “The Kamafugite-Carbonatite association in the Alto Paranaíba Igneous Province (APIP) - Revista Brasileira de Geosciências, 30(3)(2000), 404-408.

(3) A. Issa Filho, P.R.A. Lima.and O. M. Souza, “Aspects Of Geology of the Barreiro Carbonatitic Complex, Araxá, MG, Brazil”, Carbonatitic Complexes of Brazil (São Paulo, Brazil: CBMM, 1984).

(4) G. Perrault and E.A. Manker, “Geology and Mineralogy of Niobium Deposits”, Niobium, ed. H.Stuart (Warrendale, PA: TMS-AIME, 1984), 3.

(5) O.S. Paraiso and R. de Fuccio, “Mining, Ore Preparation and Ferro-niobium Production at CBMM”, Niobium, ed. H.Stuart (Warrendale, PA: TMS-AIME, 1984), 113.