Mining and Extraction

GEOLOGY AND MINERALOGY OF NIOBIUM DEPOSITS

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Abstract

Niobium is element no. 33 in the list of abundance in the crust of the Earth; it is less abundant than zinc, nickel, copper or tungsten but more abundant than cobalt, molybdenum or tantalum. Niobium makes 24 ppm of the crust but only 5 ppm of the whole Earth; it is enriched in the mantle and the crust but depleted in the core.

Pyrochlore is the most abundant mineral phase containing niobium: it corresponds to $A_{2-m}B_2O_6(O,OH,F)_{1-n} \cdot pH_2O$ where A is principally Na^+, Ca^{2+} and Ba^{2+} and B is principally Nb^{5+}. The most important commercial pyrochlores are bariopyrochlore from residually enriched carbonatite at Araxá, Brazil (Nb_2O_5 66, BaO 14 and H_2O 8%) and pyrochlore from primary carbonatite at St-Honoré, Quebec, Canada (Nb_2O_5 68, CaO 14 and Na_2O 5.8%). Columbite corresponds to $Fe\ Nb_2O_6$; it is derived by weathering of granites and concentration in placer deposits (Nigeria); Nigerian columbites contain 60 percent Nb_2O_5, 6.5 percent Ta_2O_5 and 15 percent FeO. Two different mineral species with a perovskite structure are known to contain niobium as a principal constitutent: lueshite $NaNbO_3$ and latrappite $(Ca,Na)(Nb,Ti,Fe)O_2$. Several other multiple oxide minerals contain Nb as principal element: fergusonite $(RE^{3+})NbO_4$, euxinite $Y(Nb,Ti)_2O_6$, aeschynite $La(Nb,Ti)_2O_6$ and stibiocolumbite $SbNbO_4$ occur in granites principally. Three silicate minerals are known to contain principal quantities of niobium: niocalite $Ca_7Nb\ Si_4O_{16}(O,Oh,F)$, nenadkevichite $Na_2NbSi_2O_6(OH) \cdot 2H_2O$ and niobophyllite $K_2Fe_6Nb_2Si_8(O,OH,F)_{38}$.

In all its minerals, niobium occurs in octahedral coordination with O^{2-} and Nb-O distances vary from 1.83 to 2.15 A; thus $r_{Nb^{5+}} \approx 0.58$ A. Carbonatites (magmatic rocks containing more than 50% carbonate minerals) are the principal rocks in which niobium deposits are formed. Three types are common: sövite (calcite rich), rauhaugite or dolomitite (dolimite rich) and ferro-

carbonatite (siderite, ankerite or ferroan dolomite rich). Soda carbonatite containing nyererite $Na_2Ca(CO_3)_2$ and thermonatrite Na_2CO_3, H_2O has been observed to issue forth as lava from modern volcanoes (e.g. Oldoinyo Lengai, Tanzania).

Silicate rocks are frequently associated with carbonatites; they are in general alkaline and contain 11 to 14 percent (Na_2O+K_2O). Principal intrusive ones are nepheline syenite, ijolite, urtite, while their extrusive equivalents are trachyte, phonolite and nephelinite. Some ultramafic varieties are also common: dunite, peridotite and pyroxenite. Carbonatites favor three assemblages: carbonatite-nephelinite, basalt-nephelinite and ultramafite-carbonatite.

Carbonatites occur along rift zones in the crust; these rift zones are located on tectonic lineaments in the Precambrian cratons reactivated at various times since late Precambrian. Mesozoic and Cenozoic carbonatites are the best documented geologically.

Two types of niobium ore deposits are known:

Primary: The host is carbonatite, the ore mineral is principally pyrochlore and the grade approximately 0.5 to 0.7 percent Nb_2O_5. The Niobec deposit (St-Honoré Quebec, Canada) and the Oka deposits (near Montreal, Quebec, Canada) are of this type.

Enriched by leaching: This type is probably derived from the former by the leaching out of carbonate minerals. The ore, thus, contains iron oxides, phosphate minerals, some barite, some quartz and bariopyrochlore: ore grade may be *2* to *10* times the grade of the primary carbonatite. The Araxá and Catalao deposits of Brazil are of this type.

Whereas columbite concentrates from placer deposits in Nigeria were important between *1950* and 1970, they now account for only *4* percent of the total niobium production.

Ore reserves at the various producing mines are considerable, e.g. *460* MT at *2.5* percent Nb_2O_5 at Araxá, Brazil and 16 MT at *0.68* percent Nb_2O_5 at St-Honoré, Quebec, Canada. Niobium resources in various manners of definition are also reported from many areas: Brazil (Tapira), Africa (Lueshe, Panda Hill, Chilwa Island, Kalubwe), Canada (James Bay, Nemegosenda, Lackner Lake, Manitou Islands, Oka). Proven reserves and indicated resources are sufficient to support columbium utilization at a level increased by one order of magnitude for the foreseeable future.

Niobium analyses in ores, concentrates and metallurgical processes are best done by X-ray fluorescence techniques. Precision attained is readily ± 0.02 Nb_2O_5 at the 1 percent Nb_2O_5 level. However, recent interlaboratory comparisons show much broader variations and indicate that accuracy in Nb_2O_5 measurements is still difficult to attain.

Introduction

Within the broader framework of Niobium *81*, we think that it is fitting to include a paper on the geology and mineralogy of niobium. Earth scientists and engineers are responsible for the search for niobium deposits and the principal part of our text (part *6*) embodies results to the present. On

the whole, we hope you will agree with our principal conclusion: niobium resources are plentiful on Planet Earth. They are sufficient to sustain a greatly increased rate of utilization for the foreseeable future.

Earth scientists and engineers interface with ore dressing engineers and metallurgists in the areas of mineralogy and crystallography. Hence the second part of our text, dealing with these subjects, is comprehensive; it includes all data useful to ore dressing experts and metallurgists especially on pyrochlore but also on other niobium minerals.

Niobium was discovered as an element in 1802 and was at that time named columbium. For a long time, it was a curiosity. Metallurgists have brought it out of that class and used it gainfully in many alloys; current principal useage is as a minor additive in microalloyed steels. In response, earth scientists and engineers in the period 1950 to 1960 searched for niobium resources and found all that was needed in carbonatite plugs, principally in Brazil, but also in Europe, Canada and Africa. The broad tectonic framework of areas where carbonatites occur in the Crust of the Earth is the object of part 5 of our text; it is necessarily sketchy and brief. We have tried to summarize, in about 20 pages, the knowledge acquired through an estimated two or three man-centuries! It became clear in the late 1950's that niobium was an abundant earth resource. Notwithstanding this fact, earth scientists have remained very interested in carbonatites and their associated alkaline and ultramafic rocks because these materials probably originate in the mantle of the Earth; carbonatites and their associated rocks thus deliver an important part of the knowledge on the mantle. It is reasonable to extrapolate that carbonatite research will continue unabated by the fact that our niobium resources are already guaranteed.

Finally, at the suggestion of D. G. Howden, conference coordinator, we have included as a last part in our text, some notes on the principal analytical technique used to measure Nb or Nb_2O_5 in ores and metallurgical products; namely X-ray fluorescence. Our first efforts on the application of XRF to measurement of niobium in ores and ore minerals goes back to 1956. The principal expertise gained from this method is summarized in the section "Niobium Analytical Chemistry".

Geochemistry

Niobium is a lithophile element; it favors an association with the principal constituents of the lithosphere, the silicate rocks. There are very few data on the cosmic abundance of niobium: from the value of 1.5 atoms Nb/10^6 atoms Si of Cameron (13), we can calculate a cosmic abundance of approximately 3 ppb (Table I). The lithophile character of Nb is apparent from its concentration to the level of 0.5 ppm (i.e. 150x its cosmic abundance) in the silicate meteorites, the chrondrites; it is much less abundant (0.03 ppm) in the iron meteorites.

From Table I, one would expect that Nb would be concentrated in the terrestrial planets of the solar system. This is certainly verified for the Earth (estimated to contain 5 ppm) and the Moon (5 to 60 ppm). Within the Earth, Nb is further concentrated in the crust (24 ppm) and, while we have no direct measurement on the nickel-iron core, it is reasonable to equate its Nb content with that of iron meteorites (0.03 ppm). The core is, thus, probably very low in Nb, the crust is enriched and the mantle is probably intermediate.

Table I. Distribution of Niobium in the Universe

Cosmic abundance (1)	3 ppb
Meteorites (2)	
Chrondrites	0.5 ppm
Irons	0.03 ppm
Moon (2)	
Estimated mean	5 ppm
Maria basalts	5 to 60 ppm
Highland anorthosites	2 to 7 ppm
Soil fines	12 to 60 ppm
Crust of the Earth (2)	24 ppm
Whole Earth	5 ppm

(1) From (13): 1.16 atoms Nb/10^6 atoms Si.

(2) From (93).

(3) From (57).

Niobium is concentrated in the two most abundant igneous rocks making up more than 90 percent of the crust: basalts contain 10 ppm and granites 22 ppm (Table II). Niobium is a relatively immobile element of igneous rocks: it is concentrated in the residual liquids of magmatic origin and is contained in the late differentiates. It is not appreciably affected by aqueous solution that frequently alters the chemical composition of igneous rocks. Amongst magmatic differentiates, niobium is concentrated in nepheline syenites (300 ppm) and most of all, in carbonatites (ca. 1900 ppm). Of course, this is where all commercial niobium production originates, directly (mines in carbonatite massifs) or indirectly (the rarer placer occurrences).

Table II. Distribution of Niobium in the Crust of the Earth Concentrated by Weathering in Placers and Laterites

IGENEOUS ROCKS	ppm	SEDIMENTARY ROCKS	ppm
Basalts	10	Clays	15
Granites	22	Limestone	0.3
Syenites	35	Sandstone	0.0
Nephiline syenites	300		
CARBQNATITES	1,900		

From Wedepohl (93).

Of all the elements in the crust of the Earth, niobium is number 33 in order of abundance (Table III). Tantalum is estimated to be about 10 times less abundant. Titanium another immobile element related in its behavior to niobium, is much more abundant (4,400 ppm). Gold is approximately 5000 times less abundant. The Earth has been bountiful with its niobium, concentrating it in ore deposits, 300 (Niobec) to 1200 (Araxá) times its crustal abundance. Few other ore deposits have been so concentrated in the crust: e.g. Al 4x, Fe 6x, Cu 100x, Zn 200x and Au 1 000x.

Table III. Selected Elements and Their Distribution in the Crust of the Earth (in order of abundance)

		ppm
1	Oxygen	466 000
	Silicon	277 200
	Aluminium	81 300
	Iron	50 000
5	Calcium	36 300
	Sodium	28 300
	Potassium	25 900
	Magnesium	20 900
9	Titanium	4 400
23	Zinc	132
	Nickel	80
	Copper	70
	Tungsten	69
33	NIOBIUM	24
	Cobalt	23
38	Molybdenum	15
54	Tantalum	2.1
73	Gold	0.005

After data from Mason (57).

Mineralogy and Crystallography

Niobium is an essential constituent of approximately fifteen natural mineral groups, mostly oxides and hydroxides, some silicates and one borate. In this brief review, we shall examine the following groups, most important for their columbium content:

1. pyrochlore
2. columbite-tantalite
3. perovskite-latrappite
4. other oxides
5. niocalite
6. nenadkevichite-labuntsovite
7. niobophyllite
8. others

Pyrochlore group

This is the most important from an economic point of view, because most ores of niobium are pyrochlore ores. It is well to begin consideration of the pyrochlore minerals by recognizing the latest rulings on nomenclature of the Commission on New minerals and Mineral Names of the International Mineralogical Association. This is reported in Hogarth (43).

Pyrochlore group minerals have a general formula as follows:

$$A_2B_2O_6F \qquad (1)$$

where A is principally Na^{+} and Ca^{2+}

B is principally Nb^{5+}, Ti^{4+} or Ta^{5+}

Detailed consideration of all world occurences reveal that:

1 - there are frequently replacements and vacancies in the A positions,

2 - fluorine may be replaced by O^{2-}, $(OH)^{-}$ or vacancies and

3 - some excess water is frequently present.

Thus, the more exact composition would be:

$$A_{2-m}B_2O_6(O,OH,F)_{1-n}\cdot pH_2O \qquad (2)$$

The nature and abundance of the B cation is a first argument for distinguishing sub-groups (Figure 1):

1 - the pyrochlore subgroup is characterized by Nb+Ta > 2Ti and Nb > Ti

2 - the microlite subgroup: Nb+Ta > 2Ti and Ta > Nb

3 - the betafite subgroup: 2Ti > Nb+Ta

The nature and abundance of the A cations is the second argument for distinguishing species: these distinctions are outlined in Figure 2. This leaves us with 16 valid species and *50* discredited mineral names, a very valid accomplishment in our opinion and a move towards easier international

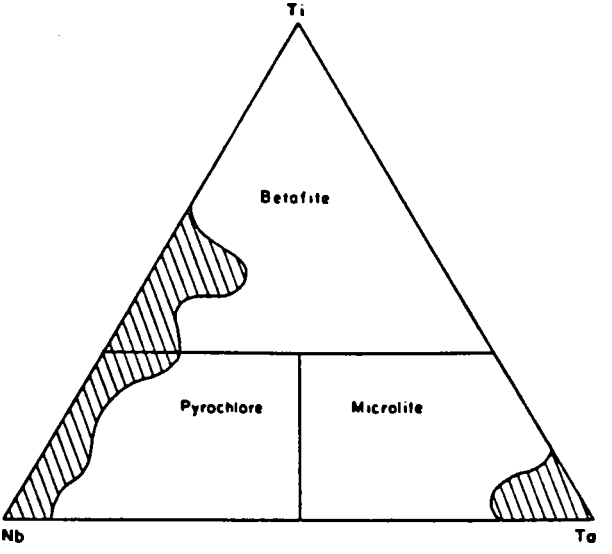


Figure 1. The occupation of B positions in pyrochlore, $A_2B_2O_6F$ by Nb, Ta and Ti. Crossed areas correspond to more frequent mineral compositions. After Hogarth (1977).

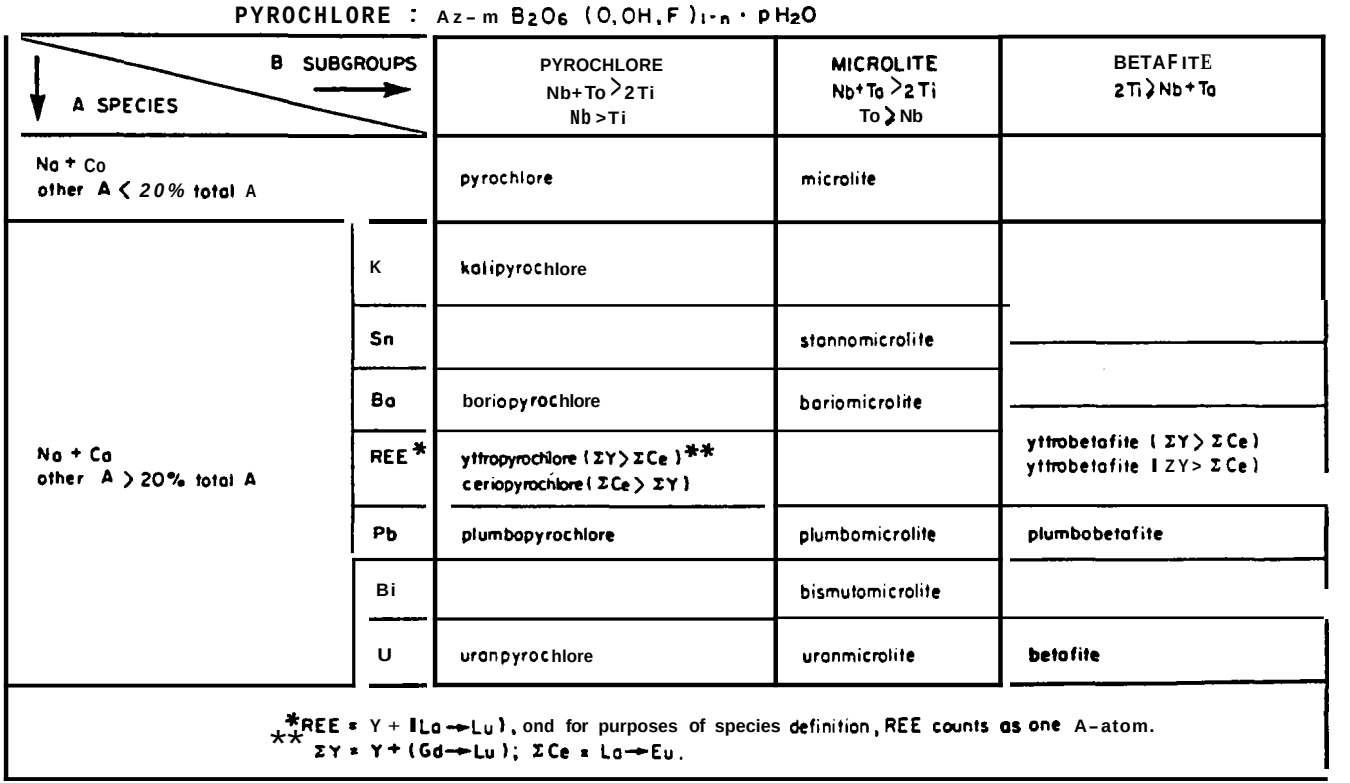


Figure 2. **Nomenclature of pyrochlore group minerals as approved by I.M.A. Commission on New Minerals and Mineral Names. After Hogarth (1977).**

communication and understanding in mineralogy. The retained species names are essentially pyrochlore, betafite and microlite with suitable chemical prefixes where necessary. Among the mineral name casualties, there is one regrettable one: pandaite, the name appled by Jager, Niggli and Van der Ven (45) to the bariopyrochlore from Panda Hill, Tanganyika and later used to designate the most important commercial pyrochlore from Araxá, Brazil. Finally, we should note also that the name pyrochlore applies

- to the group of minerals,
- to the subgroup with Nb+Ta > 2Ti and Nb > Ta
- to the species with Na^{+} and Ca^{2+} in the A position and no other A atoms greater than 20 percent of total A.

Pyrochlore group minerals are cubic: Fd3m, a 10.4 Å, Z = 8. The number of possible composition variables which relate to cell size is quite high and leaves little hope for using cell sizes to estimate chemical composition. Here are a few sample determinations of cell size in Angstroms:

pyrochlore	10.420	(no. 5, 73)
	10.395	(no. 4, 72)
	10.43	(no. 1, 72)
	10.40	(30)
	10.43	(42)
bariopyrochlore	10.56	(45)
kalipyrochlore	10.57	(91)
yttropyrochlore	10.36	(30)
uranpyrochlore	10.38	(42)
betafite	10.298	(8)
microlite	10.398	(48)

The most common crystal form for pyrochlore group minerals is the octohedron {111}, but sometimes the dodecahedron {110} modifies the edges of {111}. The cube {100} and the trisoatahedron {113} are rare.

The X-ray powder diffraction pattern is undoubtedly the most important single technique to identify pyrochlore group minerals. It is a necessary argument to positive identification and a sufficient argument to recognition of the structure type. Recognition of mineral species within the pyrochlore group requires identification of A and B cations and this is probably most easily done by X-ray fluorescence techniques. Uranian and/or thorian pyrochlores may be metamict (i.e. structurally damaged by radiation) in which case their X-ray powder difraction patterns are very poor: they may show only two or three peaks instead of the usual fifteen. This renders identification of the structure by X-ray diffraction difficult and uncertain; fortunately the quality of the structure can be restored by heat treatment (e.g. heating for 15 minutes at 700 C) and the X-ray powder pattern of the heated material is again very useful to identify structure type. Very little uranium (less than 1%) is necessary to render the X-ray powder patterns almost useless. Cell size variations in the pyrochlore group are small and they do not help much in the recognition of species within the group. (see Table IV).

The crystal structure is simple, yet difficult to visualize. It is completely defined by the coordinates of A, B, O and F (Table V). Coordinates of all atomic positions except one (the X coordinate for O^{2-}) are symmetry-fixed. We have best been able to visualize the structural arrangement by considering first, only the oxygen ions (Figure 3): these define

Table IV. X-Ray Diffraction Powder Pattern for Pyrochlore Group Minerals

hkl	1 (NATURAL) d	I/Io	(1 HEATED)		2 d	I/Io	3 d	I/Io
111	6.03	4LL	5.99	10	6.02	26	6.04	40
311			3.129	13	3.146	5	3.17	35
222	3.012	100	2.995	100	13.008	100	(3.034	100
400	2.611	15	2.594	16	2.605	7	2.632	15
331					2.391			
422					2.127	1		
333, 511			1.996	5	2.006	8	2.029	10
440	11.841	22	1.8338	41	11.8426	27	1.864	46
531					1.7621	2	1.783	10
533					1.5887	3	1.610	2
622	1.564	12	11.5637	28	1.5710	15	11.591	50
444			1.4968	8	1.5038	8	1.523	30
551, 711					1.4588	2	1.480	15
553, 731			1.3500	2	1.3564	3	1.377	15
800			1.2961	4	1.3018	2	1.321	25
822, 660					1.2276	1		
751, 555					1.2033	1		
662			1.1894	11	1.1952	6	1.211	40
840			1.1590	7	1.1650	4	1.180	40
911, 753					1.1438	1		
931					1.0925	1	1.108	1
844			1.0580	7	1.0634	4	1.078	30
933					1.0479	1	1.061	1
951					1.0071	1	1.019	25
10.2.2; 66b			0.99765	8	1.0027	5	1.016	35
10.4.2					0.95112	1		
11.1.1					0.93916	1		
880			0.91635	3	0.92114	3		
11.3.1					0.91065	1		
11.3.3					0.88429	1		
10.6.2			0.87638	12	0.88067	7		
12.0.1; 884			0.86394	9	0.86837	6		
11.5.3					0.83708	1		
12.4.0			0.81960	8	0.82373	4		
13.1.1					0.79687	1		
10.6.6			0.79044	12	0.79456	6		
12.4.4			0.78142	13	0.78559	6		

1 - Pyrochlore from Oka, metamict (72).
1 (heated) - Same pyrochlore, heated to 700 C for 15 min (72).
2 - Pyrochlore from Oka (72).
3 - Bariopyrochlore from Araxá, Brazil (99).

octahedral cages linked to one another along [1$\bar{1}$0] into a chain. At alternate levels, these chains are crossed-linked by similar chains in the [1$\bar{1}$0] direction (Figure 4). This provides the rigid network of the structure. Nb^{5+} are located in the centres of the octahedrae and Na^{+} and Ca^{2+} are distributed statistically in the larger holes of the structure (Figure 4). Fluorine ions complete the network of anions around the Na^{+}-Ca^{2+} position; coordination around Na-Ca^{2+} is eight-fold (6 O^{2-} and 2 F^{-}).

Physical properties of pyrochlore group minerals are:

- hardness 5 to 5-1/2
- density ca. 4 to 4.4
- luster: resinous
- color: quite variable, beige and reddish-brown common; green and other colors rare
- refractive index: 2.0 to 2.2
- reflectivity 12 to 19 percent

An impossible mineral to indentify positively from its physical properties!

Table V. Atomic Positions in the Pyrochlore Structure

ION	MULTIPLICITY	WYCKOFF NOTATION	FRACTIONAL COORDINATES
O^{2-}	48	f	0.316, 0, 0
Nb^{5+}	16	d	5/8, 5/8, 5/8
Ca^{2+}, Na^{+}	16	c	1/8, 1/8, 1/8
F^{-}	a	a	0, 0, 0

From Perrault (72)

The chemical composition is extremely variable. It is quite frequent to see fifteen elements present in excess of 1 percent each in any single occurence. We have gathered in Table VI a few analyses for most of the distinct species of the pyrochlore and betafite subgroups. Pyrochlore group minerals seem to be an exception to Dalton's law of simple proportions; crystal structure analysis has in recent years helped in the interpretation of chemical analyses. Here are some general rules useful in the interpretation of pyrochlore analyses:

1. The B-sites of the structure are probably fully occupied by Nb^{5+}, Ta^{5+}, Ti^{4+} and to a lesser extent, Zr^{4+}. This works out to 2.00 atoms per formula or 16.00 atoms per unit cell.

2. The A-sites are seldom completely filled; on the contrary, they may be predominently vacant (e.g. analyses 3 and 4, Table VII).

3. While F is nominally an essential constituent, partial replacement is the rule rather than the except. It is probable that $(OH)^{-}$ replaces for it. The site may also be vacant.

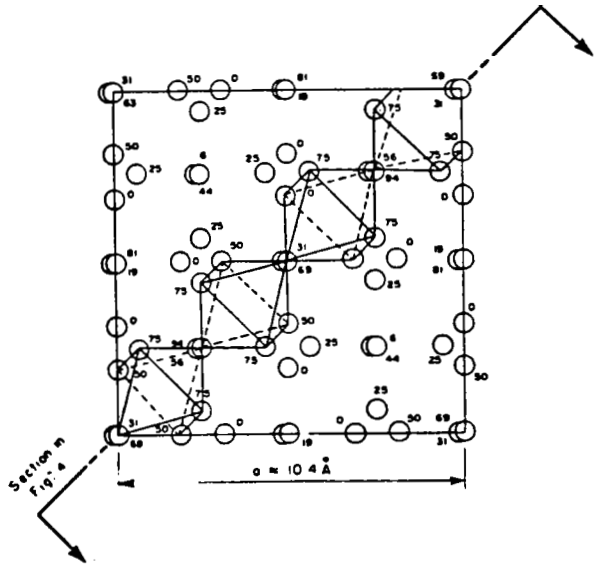


Figure 3. The oxygen positions in the pyrochlore structure. Numbers indicate elevation above base in 0.01 a. One chain of oxygen octahedrae is outlined.

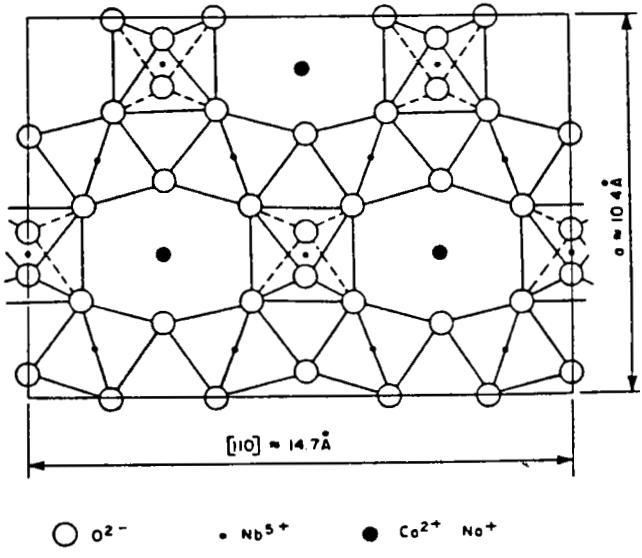


Figure 4. (110) view of the structure of pyrochlore.

Table VI. Chemical Composition of Pyrochlore Subgroup Minerals in wt. percent.

$A_{2-m}B_2O_6(O,OH,F)_{1-n}\cdot ph_2O$: Nb + Ta > 2Ti, Nb > Ti

	1	2	3	4	5	6	7	8
B								
Nb_2O_5	73.05	68.20	65.97	80.05	34.26	55.22	40.68	32.72
Ta_2O_5		0.13	0.07	**0.11**	7.50	5.86	3.58	14.26
TiO_2		2.65	4.74	0.033	4.11	2.88	0.81	8.87
ZrO_2		0.56	0.41	4.12	0.33	-	-	0.29
A								
Na_2O	8.52	5.75		0.58	0.40	2.52		
K_2O								
CaO	15.41	13.96	0.06	0.13	7.55	4.10	1.17	7.54
MnO			0.01	0.06	0.64			
FeO		1.04		0.07		0.02		1.23
SrO		1.55		1.73				0.50
BaO		0.05	14.21	0.38				
PbO			0.90	0.02			38.68	3.28
MgO			0.01	0.11	0.60	0.16		
Y_2O_3			0.03	0.022	12.30	5.07		
La_2O_3			0.21	0.13				
Ce_2O_3		0.58	1.41	0.25		13.33		0.16
Nd_2O_3		0.05		0.045				
Re_2O_3					9.55		4.07	
			1.19	0.06	6.05	0.50	2.87	
Sb_2O_3			0.04					
UO_2		0.04	0.08	0.08			1.82	23.76
ThO_2		0.35	1.65	0.17	0.50	0.20		
SnO_2			0.08	0.37			0.62	
F	5.22	2.74	0.02	0.11				
H_2O		1.00	8.26	8.37	10.73	6.40	4.28	8.30
Other		0.47			5.13	3.10		
Total	102.20	99.17	99.35	99.76	99.85	99.93	99.38	100.91
O ≡ F	2.20	**1.15**	0.01	0.05	-			
Total	100.00	98.02	99.34	99.71	99.85	99.93	98.38	100.91

1. Theoretical for Na Ca Nb_2O_6 F.
2. Pyrochlore from Niobec Mine, St-Honoré, Québec, Canada (73).
3. Bariopyrochlore (sic. pandaite) Araxa, Brazil (90).
4. Kalipyrochlore, Lueshe, Zaire (91).
5. Yttropyrochlore (sic. obruchevite), Lake Ladoga, U.S.S.R. (7).
6. Ceriopyrochlore (sic. marignacite), Wisconsin, U.S.A. (94).
7. Plumbopyrochlore. Urals, U.S.S.R. (85).
8. Uranpyrochlore, Crevier, Québec, Canada (52).

Table VII. Chemical Formulae of Pyrochlore Subgroup Minerals **of** Table **VI** in atomic percent.

$A_{2-m}B_2O_6(O,OH,F)_{1-n}\cdot pH_2O$: Nb + Ta > Ti, Nb > Ti

	1	2	3	4	5	6	7	8
B								
Nb^{5+}	2.00	1.86	1.78	1.82	1.48	1.74	1.84	1.17
Ta^{5+}		0.00	0.00		0.20	0.11	0.10	0.52
Ti^{4+}		0.12	0.21	0.16	0.29	0.15	0.06	0.30
Zr^{4+}		0.02	0.01	0.02	0.03			0.01
	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
A								
Na^{+}		0.67		*0.04*	0.01	0.34		
K^{+}				0.18		0.05		
Ca^{2+}	1.00	0.90		0.01	0.77	0.31	0.13	0.63
Fe^{2+}		0.05				0.01		0.08
Sr^{2+}		0.06		0.07				0.02
Ba^{2+}			0.33					0.07
Pb^{2+}			0.01				1.04	
Mg^{2+}						0.02		
Y^{3+}						0.19		
La^{3+}			0.01					
Ce^{3+}		0.01	0.03		0.24			
Nd^{3+}								
RE^{3+}							0.18	
Fe^{3+}			0.05			0.03	0.22	
$''^{4+}$				0.19			0.04	0.40
Th^{4+}			0.02					
	2.00	1.69	0.45	0.30	1.53	1.29	1.61	1.20
F								
F^{-}	1.00	0.52						
$(OH)^{-}$		0.23				0.60	0.36	1.39
O^{2-}							0.64	
	1.00	0.75				0.60	1.00	1.39
Q								
O^{2-}	6.00	5.83	4.82	4.20		6.00	6.00	
$(OH)^{-}$		0.17	1.18	1.80				
	6.00	6.00	6.00	6.00		6.00	6.00	6.00
$(H_2O)^{+}$	0.00	0.00	1.05	0.76		1.19	1.25	***1.48***

Table VIII. Chemical Composition and Formulae of Betafite Subgroup Minerals

$A_{2-m}B_2O_6(O,OH,F)_{1-n} \cdot p\,H_2O$: 2 Ti > Nb + Ta

	in wt. percent				in atomic percent		
	1	2	3		1	2	3
B							
Nb_2O_5	10.11	34.80	27.87	Nb^{5+}	0.28	0.99	0.96
Ta_2O_5	7.61	1.00	7.73	Ta^{5+}	0.13	0.02	0.17
TiO_2	34.22	16.20	15.20	Ti^{4+}	1.59	0.99	0.87
ZnO_2				Zn^{4+}	-	-	-
					2.00	2.00	2.00
A							
Na_2O			0.20	Na+	-		0.03
CaO	7.02	3.12	2.23	Ca^{2+}	0.46	0.29	0.18
MnO			0.75	Mn^{2+}	0.02		0.05
PbO	1.42		0.55	Pb^{2+}	-		0.01
MgO			0.09	Mg^{2+}			0.01
Y_2O_3			10.60	Y3+			0.43
Ce_2O_3		1.00	6.03	Ce^{3+}		0.03	0.17
RE_2O_3	3.30			RE^{3+}	0.07		
Fe_2O_3	6.96	0.50	4.30	Fe^{3+}	0.32	0.03	0.25
UO_3	20.20	27.15		V^{6+}	0.26	0.49	
UO_2			12.84	v4+			0.22
ThO_2	0.04	1.12	1.20	Th^{4+}	-	0.02	0.02
SnO_2		0.37		Sn^{4+}		0.01	
F			0.30		1.13	0.87	1.37
				F			
H_2O	7.45	12.50	4.47	F^-			0.07
				OH^-	0.10	0.83	0.93
Others	1.00	1.88	5.46	O^{2-}			
					0.10	0.83	1.00
				O			
				O^{2-}	6.00	6.00	6.00
Total	99.33	99.64	99.93				
O ≡ F			0.12	$(H_2O)^+$	1.48	3.18	1.13
Total	99.33	99.64	99.81				

I - Betafite from Tangen, Noway (8).
2 - Betafite from Ambalahazo, Madagascar (51).
3 - Yttrobetafite from Alakurtti vein, U.S.S.R (47).

4. Water in excess of that needed to fill the F-site is frequent, particularly when the A- sites are incompletely occupied or when both the A and F sites are essentially vacant.

Valence charge considerations lead to the conclusion that even the O-site may be incompletely filled by O^{2-}: there is always enough water in the analysis to complete occupation of O^{2-} sites with $(OH)^{-}$ if need be and this complete occupation seems necessary for the rigidity of the structure.

It is rarely possible to associate one chemical composition of pyrochlore with one locality; for instance, at Oka, Québec, Perrault (72) demonstrated the existence of at least five distinct pyrochlore composition at the St-Lawrence Columbium mine alone.

Pyrochlore crystals are frequently zoned. Electron microprobe measurements now make the measurement of these zonations possible. An example is given in Figure 5.

	1	2	3	4	5	6	7	8	9
Nb_2O_5	67.4	69.1	68.7	67.8	68.0	68.3	68.1	68.3	68.7
TiO_2	2.2	2.8	2.4	2.6	2.7	2.7	2.6	2.7	2.9
Na_2O	1.9	3.9	6.9	7.0	6.9	7.5	7.3	6.1	5.8
CaO	16.4	15.2	15.4	15.2	15.3	15.2	15.2	15.6	15.8
FeO	1.8	2.9	0.7	0.4	0.4	0.4	0.5	0.3	0.7
ThO_2	0.9	1.1	1.5	1.1	1.0	1.6	1.4	1.2	2.1
UO_2		0.4	0.3	0.1	0.3	0.1			
Total	90.6	95.4	95.9	94.2	94.6	95.8	95.1	94.2	96.0

Figure 5. Pyrochlore from St-Honoré, Québec, Canada. The periphery of the grain has a slightly higher reflectivity: microprobe analyses show a higher percentage of FeO and a lower content of Na_2O and CaO. Numbers on the micrograph correspond to microprobe analyses in the table.

Pyrochlore may occasionally be replaced by columbite: Figure 6 illustrates this point. Pyrochlore crystals in carbonatites frequently contain abundant inclusions; main inclusion minerals are apatite, biotite, dolomite, calcite and columbite (Figure 7). This makes correct analysis of pyrochlore an even more complex job.

Pyrochlore occurs principally in carbonatites and in pegmatites derived from alkalic rocks. Common associate minerals, in addition to the rock forming minerals (calcite and dolomite in carbonatites: nepheline, orthoclase and albite in alkalic rocks) are zircon, apatite and a number of other uncommon Zr, Ti, Nb and Ta minerals.

Alteration of pyrochlore is undoubtedly quite common, in witness to the multitude of pyrochlore species. Replacement by columbite has been mentioned above; alteration to fersmite, $(Ca,Ce)(Nb,Ti)_2(O,F)_6$ is also reported.

The columbite-tantalite group

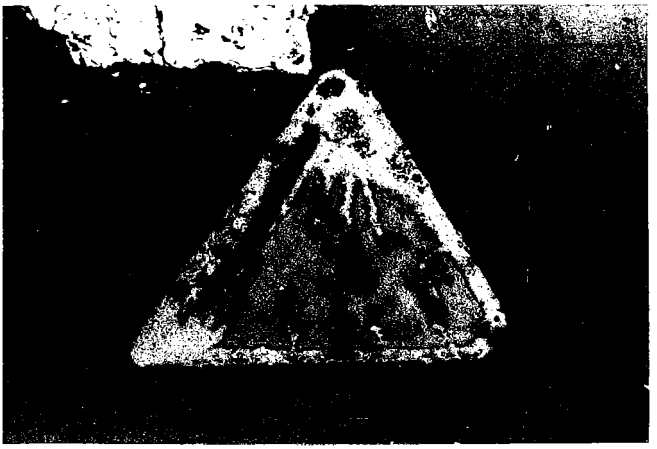
First important modern production of columbium was essentially derived from columbite; columbite concentrates were obtained as byproducts of tin (cassiterite) mining in Nigeria, Africa. The element columbium was discovered by Hatchett in 1802 (36) in a columbite specimen presented by John Winthrop to the British Museum in 1734 (68 years earlier!). The specimen may have been much older; it may have belonged to industrialist John Winthrop Jr. (1606–1676). It probably came from New London, Connecticut (see 70, p. 787). The name columbite has gained general acceptance by mineralogists to designate natural $Fe\ Nb_2O_6$.

Columbite, $Fe\ Nb_2O_6$, forms a pseudo-solid solution series with tantalite in naturally occurring specimens, we are calling it pseudo- because columbite is not rigorously isostructural with tantalite. Columbite is orthorhombic: Pcan, a 5.73, b 14.24 and c 5.08 A. Tantalite is tetragonal: $P\ 4_2/mnm$, a 4.57 and c 9.14 Å. The transformation composition, O ÷ T, is not known exactly.

Crystal forms are given in Figure 8. Crystals are tabular b {010}, short and prismatic with elongation along c {001}. Approximately a dozen distinct forms are known; c {001}, a {100}, g {130} and m {110} are the principal ones. Fine grained aggregates of columbites can also be pseudomorphic after pyrochlore (Figure 6).

The crystal structure of columbite was determined by Sturdivant (87) and refined from synthetic crystals by Weitzel (95). Data from Weitzel are given in Table IX and the structure is illustrated in Figure 9. Again the Nb^{5+} ion is in octahedral coordination. The octahedron is not quite regular; the mean Nb-O distance is 2.017 A and extremes are 1.835 and 2.194 A, while observed angles devlate up to 15° from regular octahedral angles.

The Fe^{2+} is also in octahedral coordination and somewhat more regular: the mean Fe-O distance is 2.112 and extremes are 2.090 and 2.125 Å while observed bond angles deviate up to 15° from regular octahedral angles.



(a)

(b)

Figure 6 (a). Pyrochlore and columbite from St–Honor&, Québec, Canada. the columbite forms the rim; the pyrochlore is the core.

(b). Pyrochlore grain from St–Honor&, Québec, Canada. The pyrochlore grain is invaded by a network of veins of columbite.

Figure 7. Pyrochlore from St-Honor@, Québec, Canada. The pyrochlore grain is chucked full of inclusions: apatite, biotite, dolomite, etc.

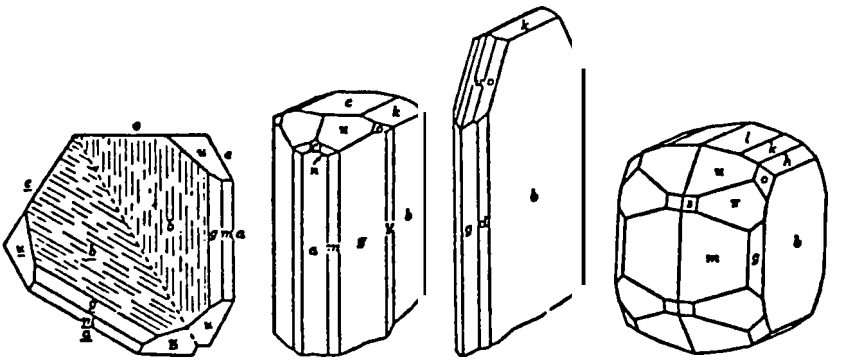


Figure 8. Columbite crystals. From Palache, Berman & Frondel (1944).

Table IX. Crystal Structure of Columbite (87)

Space group: Pcan

Cell: a 5.7288,
b 14.245
c 5.042

	WYCKOFF NOTATION	x	y	z
Fe	4c	0.1657	0	1/4
Nb	8d	0.1634	0.3814	0.7421
O(1)	8d	0.3908	0.0958	0.4321
O(2)	8d	0.1156	0.0808	0.9003
O(3)	8d	0.1144	0.2555	0.5879

THE Nb ATOM		THE Fe ATOM (r = 0.7708,)	
Nb - O(2)	1.835 Å	Fe - O(1)	2.090
Nb - O(3)	1.922	Fe - O(2)	2.125
Nb - O(1)	1.878	Fe - O(3)	2.120
Nb - O(3)	2.147		
Nb - O(1)	2.149		
Nb - O(3)	2.194		
MEAN	2.017	MEAN	2.112
O(2) - Nb - O(3)	103.2'	O(1) - Fe - O(1)	103.8'
O(2) - Nb - O(1)	100.0	O(1) - Fe - O(2)	95.4
O(3) - Nb - O(3)	94.0	O(1) - Fe - O(2)	94.2
O(2) - Nb - O(3)	96.1	O(1) - Fe - O(2)	87.6
O(1) - Nb - O(3)	98.5	O(1) - Fe - O(2)	168.6
O(2) - Nb - O(1)	90.6	O(2) - Fe - O(2)	164.5
O(3) - Nb - O(3)	88.1	O(2) - Fe - O(2)	84.3
O(1) - Nb - O(3)	163.2	O(2) - Fe - O(2)	84.0
O(2) - Nb - O(3)	168.6	O(2) - Fe - O(2)	81.1
O(1) - Nb - O(3)	156.8		
O(1) - Nb - O(1)	88.3		
O(3) - Nb - O(3)	82.2		
O(1) - Nb - O(3)	78.7		
O(1) - Nb - O(3)	74.8		
O(1) - Nb - O(3)	78.2		

The NbO_6 octahedrae form double layers, parallel to (010), that alternate with single layers of FeO_6 octahedrae. Within the layers, the NbO_6 octahedrae share edges; this contrasts with the NbO_6 octahedrae in pyrochlore who share apexes only. The 6-fold octahedral coordination of Fe^{2+} also contrasts with the 8-fold coordination of A ions in pyrochlore. All in all, the columbite structure is much more tightly bonded, leading to greater hardness and greater density than in pyrochlore.

X-ray diffraction patterns for columbite and tantalite are given in Table X. Careful interpretation of the powder pattern should permit the distinction between columbite and tantalite even though some of the more important lines are common to both. The distinction between columbite and pyrochlore is also straightforward; the principal lines of both are close (2.96 Å for columbite to 3.00 for pyrochlore) but there is still a difference of about 0.05 Å, a measurable difference. The 6.0 Å peak for pyrochlore is definately absent in columbite and should help to distinguish between the two. A complete interpretation of the film or diffractometer strip chart recording remains the most satisfactory manner of positive identification. Pyrochlore and columbite may be associated in specific deposits (e.g. Niobec ore, Figure 6 and also described in the Mbeya carbonatite, Tanzania, 46).

Physical properties of columbite are:

- cleavage along (010),
- hardness of 6,
- density of 5.2, increasing to 7.9 €or tantalite,
- color: black, brownish black,
- transparent in very thin splinters (n=2.4),
- reflectivity 20 to 25%, weakly anosotropic. The reflectivity is slightly higher than that of pyrochlore.

Chemical composition (Table XI) is easier to interpret because columbite is always stoichiometric and corresponds to AB_2O_6. The principal A cation is Fe^{2+}; there is always some Mn^{2+}. The principal B cation is Nb^{5+} for columbite and Ta^{5+} for tantalite. Substitution by other cations is minor in natural occurrences: Ti^{4+} is common; Sn^{4+} and W^{6+} have been observed.

Columbite is essentially a granite pegmatite mineral: it is reported from very many localities in P-, Li- and Sn- pegmatites. In carbonatites, columbite occurs principally as a fine grained replacement of pyrochlore. The question as to whether fersmite is a necessary intermediate product in this replacement is very much open to question (see 90 and 46).

The perovskite group

Perovskite is the name originally given to $CaTiO_3$. In nature, the various replacements observed led to recognition of other mineral species showing a similar stoichiometry and a similar crystal structure. These are:

- lueshite, $NaNbO_3$
- loparite, $(Na^{1+}_{0.5}\ RE^{3+}_{0.5})\ TiO_3$
- latrappite $(Ca,Na)\ (Nb,Ti,Fe^{3+})O_3$ with Nb > Ti

Perovskites are strongly pseudoisometric. Crystals are frequently cubes; microscopic examinations reveal that these cubes are never single crystals but rather an intricate intergrowth of twin lammellae parallel to cube faces (Figure 10). The pseudoisometric cell has the space group Pm3m and $a \approx 3.84$ Å. The true symmetry of perovskite remains an open question: McGaw (60) and Nickel and McAdam (65) proposed an orthorhombic cell, Roth (79) has proposed a tetragonal and a rhombobedral cell for some perovskite-type structures and finally, Zedlitz (100) suggested a monoclinic cell. Various cell symetries possibly apply to different chemical variants.

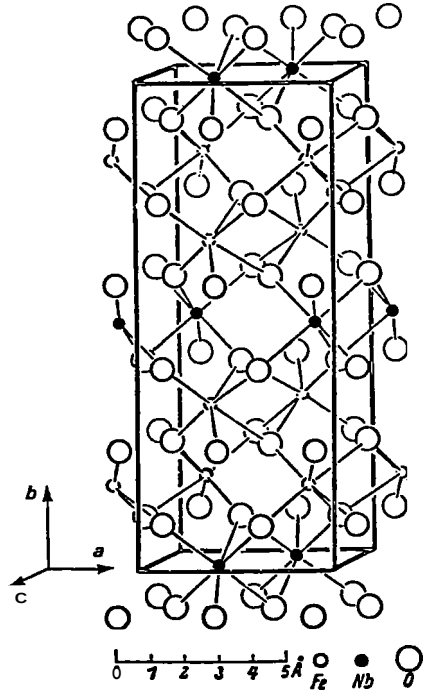


Figure 9. The structure of columbite after Structurbericht, 2.55.

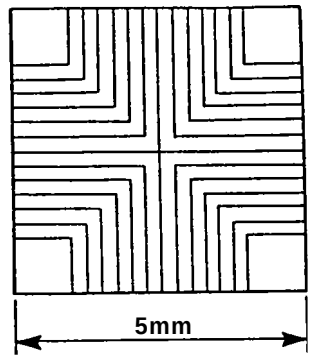


Figure 10. Twinning in perovskite. The form is a pseudo-cube; the twin lamellae are parallel to (001), (010) and (100).

Table X. X-Ray Powder Diffraction Data for Columbite and Tantalite

	COLUMBITES				TANTALITE	
	1		2		3	
hkl	d	I/Io	d	1/10	d	1/10
020	7.13	12	7.21	50	11.1	40
110	5.30	4	5.34	5	4.69	10
130, 111	3.66	50	3.68	100	3.79	20
040	3.57	10	3.60	35	2.95	70
131	2.96	100	2.98	100	2.88	20
200	2.86	10	2.87	35	2.76	20
220			2.67	5		
002	2.53	6	2.54	15	2.56	40
201	2.49	12	2.50	20	2.51	70
060	2.38	12	2.402	45	2.38	30
221			2.365	2		
151	2.279	2	2.299	2	2.275	10
032	2.236	4	2.244	5	2.21	50
231	2.207	4	2.220	10	2.12	30
132	2.084	6	2.092	10	2.099	40
240			2.074	2		
241	2.043	4	2.057	5	2.077	10
202	1.989	6	1.904	10	1.952	10
260	1.831	10	1.845	25	1.917	60
152, 171	1.796	4	1.810	5	1.835	50
330	1.772	14	1.782	35	1.780	80
062	1.735	12	1.745	35	1.743	70
261	1.721	20	1.734	50	1.723	70
331	1.672	2	1.683	5	1.609	20
-	1.608	2	1.543	5	1.560	60
133	1.534	8	1.539	15	1.540	50
190	1.516	2			1.504	20
262	1.484	4	1.492	10	1.480	30
203	1.465	14			1.468	100
191, 332	1.454	12	1.477	30	1.442	10
400	1.432	2			1.387	60
-	1.393	2				
401	1.380	2				

1 - Columbite from Tinton, S. Dakota, U.S.A.
a = 5.73, b = 14.24, c = 5.088, (67).

2 - Synthetic $MnNb_2O_5$, JCPDS, pattern 25-543.

3 - Tantalite, stannoan, JCPDS, pattern 16-147, (63).

Table XI. Chemical Compositions and Formulae for Columbite in wt. percent.

$A\,B_2\,O_6$

	1	2	3	4
B				
Nb_2O_5	78.88	72.74 %	55.91	47.95
Ta_2O_5			17.01	4.37
TiO_2		3.21	4.97	1.02
ZrO_2				
WO_3			3.65	
SnO_2			0.11	
A				
Na_2O		0.29		
FeO	10.63	16.80	14.98	
MnO	10.49	1.71	3.60	
CaO		1.39		
Sc_2O_3			0.80	
U_3O_8		0.09		
ThO_2		1.52		
Total	100.0	97.75	101.05	
	Formulae for B = 2.00 in atomic percent			
B				
Nb^{5+}	2.00	1.86	1.46	
Ta^{5+}			0.27	
Ti^{4+}		0.14	0.22	
Zr^{4+}			0.05	
W^{6+}	2.00	2.00	2.00	
A				
Na^{+}		0.03		
Fe^{2+}	0.50	0.80	0.72	
Mn^{2+}	0.50	0.08	0.18	
Ca^{2+}		0.08		
Sc^{3+}			0.04	
U^{4+}		0.00		
Th^{4+}				
	1.00	1.01	0.94	

1 - Theoretical for (Fe, Mn) Nb_2O_6 with Fe/Mn = 1.

2 - Columbite, St-Honoré, Quebec, Canada. Average of 71 micro-probe analyses (73).

3 - Columbite from St. Austell, Cornwall, England (41).

4 - Columbite from Nigeria, Standard I.G.S. no. 33. Partial Analysis (55).

Notwithstanding the preceding, the structure of perovskite has been resolved by Barth (4), at least for the cubic cell. This structure is represented in Figure 11. The same structural framework applies to lueshite $NaNbO_3$, loparite (Na, RE) TiO_3 or latrappite (Ca, Na) (Nb, Ti, Fe)O_3. Note in Figure 11 that Ti^{4+} or its substitute Nb^{5+} is in octahedral coordination; the central Ca^{2+} or its possible substitutes, Na^{+} and RE^{3+}, are in twelvefold coordination. Exact interatomic distances for these structures are not available but the following are approximately correct and agree with measurements on other niobate structures:

Nb - O ≈ 1.92 Å
(Ca, Na) - O ≈ 2.70 Å

X-ray powder diffraction patterns reflect the strong pseudoisometric character and also the departure from cubic symmetry. Lines on the diffraction films or the diffractometer strip chart recordings are closely grouped at the position indicated by the cubic symmetry and the 3.84 Å cell size. Careful examination, however, reveals that these peaks are not diffraction from cubic lattic planes but those of diffraction from less symmetric lattice planes with slightly different d spacings. Patterns for the four mineral species are given in Table XII; we have also indicated (hkl) indices for the simple cubic cell with a=3.84 Å to show the pseudoisometric character.

Physical properties of perovskite group minerals are:

- imperfect cubic cleavage {001},
- hardness of 5-1/2,
- density 4 to 4.5,
- luster adamantine to metallic,
- color: black to brownish black and gray streaked,
- refractive indices around 2.3,
- reflectivity around 17 percent (lower than for pyrochlore).

For the purpose of this paper, it is sufficient to locate perovskite chemical compositions in the field of perovskite, latrappite and lueshite. This can be done easily with an exploded tetrahedra (Figure 12). Seven typical analyses are given in Table XIII. There are many minor substitutions in these minerals, but there are few principal ones:

1 - Ti^{4+} and Nb^{5+} for the B part of the formula: latrappite is distinctly $Nb^{5+} > Ti^{4+}$ and Fe^{3+} is also a necessary substitute.

2 - Ca^{2+}, Na^{+} and RE^{3+} for the A part of the formula. Lueshite is characterized by predominance of Na^{+} and Nb^{5+}. Loparite is characterized by the importance of RE^{3+}; it could go to 0.5 occupation of A when the balance is occupied by Na^{+} but Ca^{2+} is important also. For loparite, $Ti^{4+} > Nb^{5+}$. Finally, for perovskite proper, it is characterized by preponderance of Ca^{2+} in A and Ti^{4+} in B.

Iron, when Fe^{3+}, seems to fit best in the B site while Fe^{2+} finds the A site more convenient; however, the determination of iron valency in these compounds is tricky and not always done. This makes the interpretation of analyses somewhat difficult.

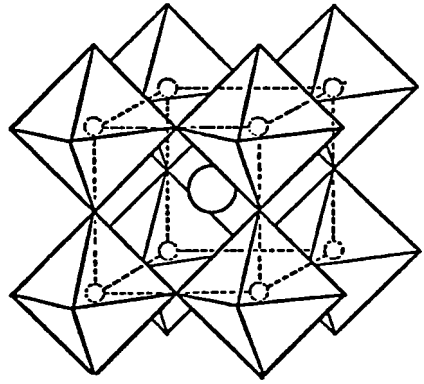


Figure 11. Idealized structure of perovskite. From Bragg and Claringbull (1965. Ca atom at the center of the cube and the $Ti-O_6$ octahedrae are shown diagrammatically.

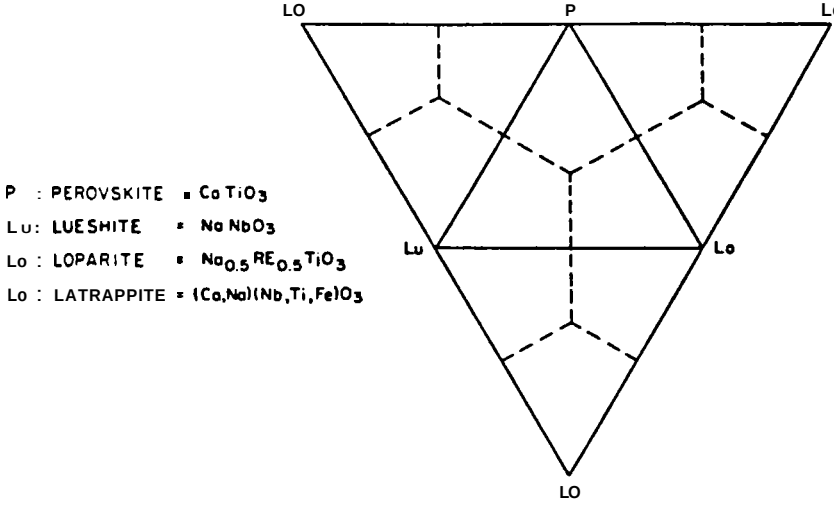


Figure 12. Composition of perovskite type minerals in an exploded tetrahedra.

Table XII. X-Ray Powder Diffraction Patterns for Perovskite, Lueshite and Latrappite

1 d	1 I/Io	2 d	2 I/Io	3 d	3 I/Io	4 d	4 I/Io	5 d	5 I/Io	hkl (6)
						3.898	4			
3.90	10	3.80	20	3.90	85	3.860	45	3.887	79	100
3.50	10					3.440	10	3.471	5	
								3.319	< 1	
								3.125	< 1	
						3.010	20	3.005	2	
						2.861	10			
						2.754	25	2.773	30	} 110
2.752	100	2.690	100	2.76	100	2.734	100	2.744	100	
						2.717	25			
						2.581	5	2.608	< 1	
						2.432	10	2.421	< 1	
2.243	20	2.299	10			2.322	8	2.339	4	} 111
		2.213	10			2.235	10	2.281	< 1	
								2.207	< 1	
						2.138	20	2.152	< 1	
						2.065	20	2.079	< 1	
						1.984	5			
1.934	65	1.9135	80	1.949	70	11.932	90	11.942	57	200
								1.915	< 1	
						1.8685	10	1.888	< 1	
								1.835	< 1	
1.743	10					1.7313	50	1.750	4	
				1.746	35	1.7265	50	1.737	9	} 210
						1.6945	20	1.707	2	
								1.631	< 1	
						1.5845	10	1.595	14	
1.583	55	1.5680	30	1.594	70	1.5810	15	1.579	25	} 211
		1.5590	40			1.5705	20			
						1.5083	3	1.500	< 1	
						1.4360	3	1.448	< 1	
						1.3760	20	1.386	< 1	
1.372	30	1.361	10	1.379	25	1.3653	40	1.374	9	} 220
		1.354	30			1.3564	20	1.363	< 1	
						1.3060	5	1.301	< 1	
1.294	5			1.302	12	1.2927	10	1.289	< 1	} 300
						1.2820	5			
								1.236	< 1	
1.228	25	1.211	30	1.235	15	1.2213	60	1.229	7	310
1.172	10									311
1.080	5	1.0260	5							
1.039	30	1.0218	10	1.044	15					
		1.0197	7							

1 - Loparite JCPDS 20-272 (54).
2 - Perovskite, Oka, Quebec. Perrault, personal files.
3 - Lueshite, J.C.P.D.S. (71).
4 - Niobium perovskite, Oka, Quebec. Perrault, personal files.
5 - Latrappite, Oka, Quebec (65).
6 - Based on pseudoisometric cell; a ≈ 3.84.

Perovskite minerals approach formula stoichiometry, but where important differences are noted (analyses 4 and 6, Table XIII), there is room for interpretation. Definitive analyses are a difficult task.

Of the four principal types of niobium minerals, perovskite is certainly the most widespread in occurence.

It has been reported to occur:

- in Kimberlite (Yakuty, USSR; Perrynkn N.W.T., Canada; S.W. Greenland: Argentina; Colorado, U.S.A.),

- in carbonaites and alkaline intrusives (Oka, Quebec, Canada; Alnö Sweden; S.W. Greenland),

- in skarns,

- in basaltic rocks,

- in ultrabsic rocks and

- in basalts from the Moon.

Latrappite is reported only from carbonatites at Oka, Quebec, Canada.

Lueshite is reported from carbonatites and alkaline intrusives from Lueshe, Goma, Congo (80); it has also been observed in Greenland and in the Koodor massif of U.S.S.R.

Loparite is known to occur in nepheline syenites of Siberia.

Other oxides

There are numerous mineral names applied to oxides of Nb, Ta and Ti with rare earth elements, uranium and thorium. These are frequently a "mineralogical headache":

- their chemical composition is complex,
- these minerals are generally metamict, and
- they are frequently altered.

These minerals generally occur in granite pegmatites and placers derived from them. They do not generally occur in carbonatites and therefore, they are of less importance in a study of niobium ore deposits. Most of them can be identified positively only through determination of their chemical composition (by microprobe for instance) and of their X-ray powder diffraction patterns both natural and heated. We include herewith principal data for the most abundant of these minerals.

Fergusonite corresponds to ABO_4 with $A=Y^{3+}$ and the heavy rare earths (Gd to Lu)$^{3+}$ and $B=Nb^{5+}$, Ta^{5+}, Ti^{4+}. It is translucent and brown in thin sections ($n \approx 2.1$), dark brown and vitreous with a hardness of 6 and a density of 5.7. It is very difficult to identify positively: the X-ray diffraction patterns on both natural and heated specimens and a microprobe analysis are generally necessary (Tables XIV and XV). The mineral formanite corresponds to the tantalum end of this series.

Table XIII. Chemical Composition of Perovskite, Latrappite and Lueshite in wt. percent.

	A B O_3						
	1	2	3	4	5	6	7
B							
TiO_2	58.76	51.2	43.55	38.70	25.0	10.05	6.35
Nb_2O_5		0.69	5.80	25.99	27.6	43.90	67.95
Ta_2O_3		0.07	1.95		2.79		0.36
Fe_2O_3		2.84			6.38	8.74	
ZrO_2		0.13			0.95		0.06
A							
Na_2O		0.31	8.73	1.72	3.75	4.03	14.90
K_2O		0.23		0.44	0.22	0.03	0.49
CaO	41.24	38.2	7.63	23.51	28.7	25.95	4.19
MnO		Tr.	2.78		0.10	0.77	
SrO		0.35			0.65		
MgO		0.12				2.20	0.13
FeO			1.12	5.69			
Ce_2O_3		1.60		3.08	2.04		
La_2O_3		0.80			0.94		
Nd_2O_3		0.23			0.30		
RE_2O_3			27.45			2.03	1.48
Fe_2O_3							1.38
ThO_2		0.17			0.04		
SmO_2			0.86				
$(H_2O)^+$		1.44			0.90		
Other							
Total	100.00	98.22	100.23	100.58	100.36	99.70	100.34

Chemical Formulae of Perovskite, Latrappite and Lueshite in atomic percent.

Formulae, B = 1.00

	1	2	3	4	5	6	7
B							
Ti^{4+}	1.00	0.95	0.92	0.71	0.51	0.24	0.13
Nb^{5+}		0.00	0.07	0.29	0.33	0.57	0.86
Ta^{5+}		0.00	0.01		0.02		0.01
Fe^{3+}		0.05			0.14	0.19	
Zr^{4+}		0.00			0.00		
	1.00	1.00	1.00	1.00	1.00	1.00	1.00
A							
Na^{+}			0.47	0.08	0.20	0.23	0.81
K^{+}				0.01	0.01	0.00	0.02
Ca^{2+}	1.00	0.97	0.23	0.62	0.83	0.80	0.13
Mn^{2+}			0.07		0.00	0.02	
Sr^{2+}			0.07		0.01		
Mg^{2+}						0.09	
Fe^{2+}			0.03	0.12			
Ce^{3+}		0.01		0.03	0.02		
La^{3+}					0.01		
Nd^{3+}					0.00		
RE^{3+}			0.28			0.02	0.02
Fe^{3+}							0.03
Th					0.00		
	1.00	0.98	1.08	0.86	1.08	1.16	1.01

1 - Theoretical for $CaTiO_3$.
2 - Perovskite, Oka, Quebec, Perrault, unpublished analysis.
3 - Loparite, USSR, (84).
4 - Niobium perovskite, Kaiserstuhl, Germany, (62).
5 - Niobium perovskite, Oka, Quebec, Perrault, unpublished analysis.
6 - Latrappite, Oka, Quebec, (65) and (64).
7 - Lueshite, carbonatite in Siberia, (3).

Table XIV. X-Ray Diffraction Patterns for Miscellaneous Nb-Oxide Minerals

FERGUSONITE (1)				EUXENITE (2)		AESCHYNITE (3)		STIBIO-COLUMBITE (4)	
Natural		Heated		Heated					
d	1/10	d	1/10	d	1/10	d	I/Io	d	1/10
5.32	6	5.45	5	7.28	16	5.48	25	5.9	20
4.09	9	4.05	7	13.66	40	4.841	6	4.55	30
3.12	50	3.116	100	3.37	20	4.431	25	3.52	50
3.030	100			3.28	10	4.390	10	3.11	100
2.971	25	2.952	78	12.99	100	4.075	14	2.95	60
2.749	30	2.732	38	12.95	40	3.847	4	2.79	10
2.650	30	2.635	18	2.78	25	3.773	6	2.71	50
2.460	30	2.516	16	2.63	10	3.427	4	2.46	30
		2.154	7	2.60	30	3.106	35	2.27	20
		2.009	7	2.55	20	3.024	80	2.21	10
1.909	30	1.896	41	2.52	6	2.975	100	2.10	5
1.863	40	1.854	27	2.45	16	2.808	20	2.02	20
1.752	10	1.752	10	2.43	20	2.698	30	1.985	20
		1.642	12	2.31	18	2.574	10	1.945	5
		1.620	18	2.21	14	2.474	8	1.892	40
1.572	10	1.571	10	2.19	14	2.443	8	1.821	40
		1.563	7	2.12	20	2.306	10	1.737	70
		1.555	14	2.08	4	2.283	8	1.707	10
		1.507	8	2.04	6	2.278	10	1.670	30
		1.499	6	1.979	10	2.215	10	1.629	10
1.478	20	1.475	7	1.940	14	2.170	8	1.590	5
				1.897	25	2.085	8	1.561	10
				1.880	4	2.037	25	1.523	30
				1.830	30	2.031	20	1.495	10
				1.806	20	1.961	25	1.478	5
				1.774	25	1.933	12	1.451	5
				1.731	25	1.922	6	1.402	20
				1.727	30	1.885	20	1.349	30
				1.704	4	1.862	10	1.332	5
				1.683	4	1.852	10	1.313	20
				1.643	25			1.268	30
								1.245	10
						1.712	20	1.232	30
								1.208	5
								1.186	30

1 - Fergusonite from Walker Lake, Quebec. Data from McCann, personal communication. The specimen was heated to 1300 C for 3 hours.

2 - From Riso, Norway, J.C.P.D.S., 9-442. Sample heated in air to about 1200 C.

3 - Synthetic $CeTiNbO_6$. Nat. Bur. Standards, U.S.A. (1964). In JCPDS, data card no. 15-864.

4 - Stibiocolumbite, J.C.P.D.S., 11-111.

Table XV. Chemical Composition of Miscellaneous Nb-Oxide Minerals in wt. percent.

	FERGUSONITE (1)	EUXENITE (2)	AESCHYNITE (3)	STIBIO COLUMBITE (4)
	$A\,B\,O_4$	$A\,B_2\,O_6$	$A\,B_2\,O_6$	$A\,B\,O_4$
B				
Nb_2O_5	**47.22 %**	**28.62 %**	**30.93 %**	**37.30**
Ta_2O_5	0.78	2.65		13.00
TiO_2	0.23	**22.96**	**23.88**	
Fe_2O_3		2.07		
A				
Y_2O_3	**26.88**	**24.31**	0.98	
$(Gd\text{-}Lu)_2O_3$	16.61			
$(La\text{-}Eu)_2O_3$	2.15	0.44	**26.50**	
Sb_2O_3				**49.28**
Bi_2O_3				0.53
CaO	0.56	1.92	2.34	
FeO	0.22		2.20	
UO_2	0.62	8.81		
ThO_2	1.83	3.94	11.27	
$(H_2O)^+$	3.60	2.23		
Others		2.34	1.17	
	100.92	100.29	99.27	100.11

Chemical Formulae of Miscellaneous of Nb-Oxide Minerals in atomic percent.

	Formulae			
B				
Nb^{5+}	0.92	0.80	0.88	0.83
Ta^{5+}	0.01	0.04		0.17
Ti^{4+}	0.01	1.06	1.12	
Fe^{3+}		0.10		
	1.01	2.00	2.00	1.00
A				
Y^{3+}	0.66	0.80	0.03	
$(Gd-Lu)^{3+}$	0.24			
$(La-Eu)^{3+}$	0.04		0.61	
Sb^{3+}				1.00
U^{4+}	0.01	0.12		
Th^{4+}	0.02	0.06	0.16	
Ca^{2+}	0.03	0.13	0.16	
Fe^{2+}	0.01		0.11	
	1.01	1.11	1.07	1.00

1 - Data from J. McCann, personal communication.
2 - From Sabine Tp., Ont (24).
3 - From Urals, U.S.S.R. (15).
4 - From Mesa Grande, California, U.S.A. In Palache, Berman & Frondel (1944).

Euxenite corresponds roughly to $YNbTiO_6$; however, there are many possible substitutions: Y can be replaced by Ce, Ca, U and Th and Nb and Ti can be replaced by Ta and Fe. It resembles fergusonite in physical properties. Euxenite may be isostructural with columbite. The name polycrase has been given to the titanium end of the series (Ti>4Nb). A typical composition and an X-ray powder pattern are given in Table XIV and XV.

Aeschynite comes close to $CeNbTiO_6$. The Ce is frequently partly replaced by Ca^{2+}, Fe^{2+} and Th^{4+}. It is generally metamict and physically resembles the two preceding minerals. It can be distinguished only by chemical analysis and X-ray powder photographs.

Stibiocolumbite is a rare mineral so far observed only at Mesa Grande, California in granite pegmatites. It corresponds to $SbNbO_4$ with some Ta^{5+} replacing Nb^{5+}.

Mossite approximates $Fe(Nb,Ta)_2O_6$. It is similar to columbite in chemical composition but differs in crystal form. We know of no reliable X-ray data for this mineral.

Polymignite is a complex ABO_4 compound with A=Ca, Fe, Y, Re, Zr, Th and B = Nb, Ti, Ta. We know of no reliable X-ray data for this mineral.

Niocalite

Niocalite corresponds approximately to $NbCa_7Si_4O_8$ (OH, F). It is monoclinic P2/a; a=10.83, b=10.42, c=7.38 Å and β=109°40'. Its X-ray powder pattern is given in Table XVI and its chemical composition and formula in Table XVII.

Niocalite occurs as coarse, prismatic crystals up to one centimeter in length in carbonatites at Oka, Québec, Canada; it has a vitreous lustre and a lemon-yellow color. Hardness is 6 and specific gravity is 3.32. We know of no other locality for this mineral.

Nenadkevichite - labuntsonite

Nenadkevichite corresponds roughly to $Na_2NbSi_2O_6(OH)$. $2H_2O$. There is a quasi-solid solution series extending to $KTiSi_2O_7$, $2H_2O$, labuntsovite. Both of these minerals are found in hydrothermal veins within alkaline intrusive massifs. Crystals are prismatic, variously terminated; they are clear to pinkish white. Chemical composition and X-ray diffraction pattern for nenadkevichite are given in Tables XVI and XVII.

Niobophyllite

Niobophyllite is the niobium analogue of astrophyllite. Its formula is approximately $K_2Fe_6Nb_2Si_8(O, OH, F)_{32}$. It occurs in paragneiss from the Seal Lake area, Labrador, Canada. It is a micaceous mineral of chocolate-brown color: perfect (001) cleavage, specific gravity of 3.42.

Table XVI. X-Ray Powder Patterns for Nb Silicates

NIOCALITE (1)		NENADKEVICHITE (2)		NIOBOPHYLLITE (3)	
d	I/I_o	d	I/I_o	d	I/I_o
7.31	30	7.15	100	10.52	90
6.97	10	6.59	32	9.68	30
5.77	20	5.04	33	6.15	5
5.015	10	4.86	2	5.76	20
4.677	10	4.17	1	5.26	10
4.595	10	3.995	5	5.15	5
4.535	10	3.583	2	4.696	10
4.174	20	(3.290	60	4.42	30
3.473	10	3.185	78	4.363	
3.395	10	3.143	5	4.20	5
3.240	50	2.982	9	4.059	30
3.117	10	2.921	6	3.87	5
3.012	100	2.698	1	3.741	40
2.891	60	2.656	24	3.506	100
12.852	60	2.566	25	3.40	5
2.613	10	2.518	22	3.258	50
2.557	30	2.407	1	3.12	5
2.528	10	2.387	1	3.071	10
2.493	10	2.310	1	3.019	60
2.460	10	2.256	25	2.977	10
2.433	30	2.195	2	2.859	30
2.292	20	2.131	1	2.82	5
2.268	20	2.083	16	2.778	80
2.130	20	1.975	14	2.72	5
2.031	30	1.914	4	2.662	10
2.006	20	1.853	9	2.636	30
1.949	10	1.784	19	2.574	70
1.901	20	1.742	25	2.475	40
1.844	40	1.727	5		

1 - From Oka. Québec, Canada (66).
2 - From St-Hilaire, Québec, Canada. Perrault, personal files.
3 - From Seal Lake, Labrador, Canada(68).

Table XVII. Chemical Composition of Principal Nb Silicates in wt. percer

	NIOCALITE (1)	NENADKEVICHITE (2)	NIOBOPHYLLITE (3)
Nb_2O_5	16.56	29.9	14.76
Ta_2O_5			0.52
TiO_2	0.22	7.45	2.94
SiO_2	29.70	37.7	33.40
Al_2O_3	1.31	Tr	0.89
RE_2O_3			1.59
CaO	47.50	0.57	0.72
Fe_2O_3			
FeO	0.49	0.46	23.74
MnO	1.28	0.25	9.83
MgO	0.28		0.16
Na_2O	0.78	11.3	2.49
K_2O		1.10	5.51
$(H_2O)^+$	0.16	11.7	3.64
F	1.7		0.46
Others	0.62		0.08
	100.60		100.64
O ≡ F	0.71		0.19
	99.89	100.48	100.45

Chemical Formulae of Principal Nb Silicates in atomic percent.

	Formulae		
Nb^{5+}	1.92	2.76	1.49
Ta^{5+}			0.03
Ti^{4+}	0.04	1.18	0.49
	1.96	3.94	2.01
Si^{4+}	7.60	8.00	7.47
Al^{3+}	0.40		0.23
	8.00		7.70
Re^{3+}			0.12
Ca^{2+}	13.03	0.11	0.17
Fe^{2+}	0.10		4.44
Mn^{2+}	0.05	0.03	1.86
Mg^{2+}	0.11		0.05
Na^{+}	0.39	3.76	1.08
K^{+}		0.24	1.57
	13.68	4.14	9.29
F^{-}	1.38		0.32
OH-	0.27	1.20	5.43
O^{2-}	33.34	26.80	25.25
	34.99	28.00	31.00
H_2O		8.00	

1 - From Oka, Québec, Canada (66).
2 - From St-Hilaire, Québec, Canada (74).
3 - From Seal Lake, Labrador, Canada (68).

Others

There are many other minerals containing 5 to 15 percent Nb_2O_5. For a list of these, the reader is referred to Wedepohl (93), particularly pp. 41-D-6 to 41-D-11) and to Fleischer (27); the latter reference is very good to establish synonyms and to have correct nomenclature.

In the above minerals, Nb^{5+} is preponderant in at least one site in the structure of the mineral. Thus, all Nb_2O_5 rich naturally occurring compounds are included.

There is an additional group of 35 mineral species reported to contain between 1 and 5 percent Nb_2O_5 (see Wedepohl (93), particularly p. 41-D-10).

Petrology

Carbonatites are the principal rocks in which niobium deposits are formed. Carbonatites are associated in their occurence in the crust with alkaline silicate rocks and kimberlites. In the following, we propose to define the chemical and mineralogical composition of carbonatites; this may serve the purpose of ore dressing engineers. In addition, we will briefly define principal petrologic terms for associated rocks; the object of this latter exercise is to render intelligible the discussion to follow on the occurence and genesis of carbonatite massifs.

Petrographic nomenclature is somewhat more complex than mineralogical nomenclature because rocks are not single phases but mixtures; thus, it behooves the petrologist to set limits based on the mineral and/or chemical composition to define rock types. This is further complicated by the fact that petrologists generally like to attach a genetic significance to rock names; this adds an uncertain element to the definition because the origin of rocks is seldom directly observed. Carbonatites are good examples of this uncertainty. Bragger (12) first considered Alnöo carbonatites, which he called sövites, to be intrusive; Bowen (10) considered the same rocks to be replacement bodies. Shand (83) and most scientists since have come back to an intrusive origin for carbonatites. We now know from direct observations (18); Oldoinyo Lengai volcano) that some carbonatites are extrusive (volcanic) and this certainly adds weight to the existance of carbonatite magmas and to an intrusive origin from those coarser-grained carbonatites presumably crystallized under rock cover. Finally, whereas mineralogists effectively agree on an International Commission on Nomenclature, petrologists lack such an international agreement. As a result, finding what is the correct usage of specific petrologic names remains an essentially tricky business. In the following, we present our perception of most generally accepted rock names associated with carbonatites along with characteristic chemical and mineralogical composition under three headings:

1 - carbonatites,
2 - associated silicate rocks, and
3 - kimberlites

Carbonatites

The name carbonatites is quite generally applied to rocks containing 50 percent or more carbonate minerals of apparent magmatic origin (intrusive or extrusive). One can distinguish between carbonatites by the principal mineral contained:

Calcite carbonatites are known as sövites (12). The term calcitite has also been used and is certainly not ambiguous. Sometimes other important mineral names are used as qualifiers: e.g. biotite, sövite, apatite sövite, etc. Rodbergite is a hematite sövite.

Dolomite carbonatites are termed rauhaugites (12). The name dolimitite is also used. The name beforsite (92) also still has its users: some beforsites contain a ferroan dolomite [$Ca(Mg, Fe)(CO_3)_2$] incorrectly termed ankerite by many petrologists: the name ankerite should be reserved to dolomite-type minerals where Fe > Mg in Ca $(Fe, Mg)(CO_3)_2$. We know of no carbonatite where the dominant carbonatite mineral is ankerite, but there are many where ferroan dolomite is the principal carbonate mineral. The niobium-rich Araxa, Brazil carbonatites are intensively weathered; carbonate minerals have been leached out and the residuum (niobium ore) now contains very little CO_2. Fresh carbonatites cut in drill holes have been termed beforsites by da Silva et al. (17); ferroan dolomite is likely the principal carbonate mineral.

Siderite carbonatites have been observed at Seis Lagos, Amazone, Brazil (44); it is capped by a thick mantle of laterite but drill holes into the fresh material have cut a "ferrugionous carbonatitic breccia" containing principally siderite. The author has also observed it in drill cores from the James Bay area, Quebec. The name ferrocarbonatite might cover it although that also includes ferroan dolomite carbonatites.

Sodium carbonatite lavas from Oldoinyo Lengai, Tanzania, have not yet received a special name. They contain phenocrysts of a new mineral, $Na_2Ca(CO_3)_2$, nyererite (61) set in a matrix of thermonatrite, Na_2CO_3, H_2O. The designation soda carbonatite is of frequent usage to designate these lavas and it is certainly not confusing.

Typical carbonatite chemical compositions are given in Table XVIII.

Associated silicate rocks

The silicate rocks associated with carbonatites are generally alkaline, rich in soda and potash and relatively poor in magnesia and undersaturated with respect to silica. Most of the silicate rocks are magmatic and both intrusive and extrusive types are frequent; some are metasomatic (fenites).

The silicate minerals of alkaline rocks belong to solid solution series; determining exact compositions (for instance by microprobe techniques) of coexisting phases may give important information on magmatic conditions at crystallization (e.g. (31)). For the sake of simplicity, we have left out of our text, data of this type and we give hereafter approximate mean compositions of the most frequently encountered silicate phases of alkaline rocks:

Table XVIII. Carbonatites: Chemical Composition in wt. percent.

	1	2	3	4	5
SiO_2	1.40	3.36	1.85	1.51	Tr
Al_2O_4	1.80	1.69	0.32	0.26	0.08
Fe_2O_3	8.44	6.13	9.88	0.92	0.26
FeO	17.60	2.99	2.47	0.78	
MnO	1.08	0.31	1.11	0.94	0.04
MgO	14.50	3.10	12.40	1.83	0.49
CaO	9.20	44.35		48.09	12.14
BaO	1.95	0.10	0.42	0.22	0.95
SrO	0.59		0.21	0.75	1.24
RE_2O_3					
Ce_2O_3	0.42				
La_2O_3	0.16		0.03		
Na_2O	0.14	0.04	0.10	0.23	29.53
K_2O	0.42	0.50	0.15	0.12	7.58
Cr_2O_3	0.01				
ZrO_2	0.02				
TiO_2	2.30	0.30	0.42	0.06	0.10
Nb_2O_5	0.72	0.80	0.61	0.36	
P_2O_5	0.69	3.26	6.88	1.10	0.83
SO_3	1.95	0.06	0.30	0.73	2.00
L.O.I.					
CO_2		32.80	32.80		31.75
F	0.07	0.28	0.56	0.12	2.69
H_2O		0.30	0.83	0.07	8.59
Other	0.48				3.86
	99.73	100.85	100.44	99.93	102.73
F, Cl = 0	0.03	0.13	0.22	0.05	2.00
	99.70	100.72	100.22	99.88	100.73

1 - Beforsite Araxá Brazil, (17).
2 - Sövite, Alno Island, Sweden, (5).
3 - Dolomitite, St-Honoré, Québec, (89).
4 - Carbonatite, Oka, Québec (33).
5 - Soda carbonatite, Oldoinyo Lengai, (18).

Alkali feldspars

orthoclase	$KAlSi_3O_8$
albite	$NaAlSi_3O_8$
Nepheline	$(Na_{0.8}K_{0.2})\ (AlSiO_4)$
Mica	
biotite	$(K_{1.6}Na_{0.4})\ (Fe^{+2}_{2.9}\ Fe^{+3}_{1.1}Mg_{1.6}Ti_{0.4})\ [Al_2Si_6O_{20}](OH)_4$
phlogopite	$K_2[MgFe^{2+}]6\ (Al_2Si_6O_{20})\ (OH)4$
Amphibole	
richterite	$Na_2Ca(Mg,Fe,Al)Si_8O_{22}(OH)_2$
Pyroxenes	
aegirine-augite	$(Na_{0.9}Ca_{0.1})\ (Fe^{+2}_{0.1}\ Fe^{+3}_{0.7}\ Al^{+3}_{0.2})\ Si_2O_6$
diopside	$Ca\ MgSi_2O_6$
titan-augite	$Ca(Ti_{0.2}Fe^{+3}_{0.1}Fe^{+2}_{0.3}Mg_{0.4})\ (Al_{0.3}Si_{1.7}O_6)$
Garnet	
melanite	$(Ca_{2.7}Fe^{+2}_{0.3})\ (Fe^{+3}_{1.5}Al^{+3}_{0.3}Ti_{0.2})\ Si_3O_{12}$
Wollastonite	$CaSiO_3$
Pectolite	$Ca_2NaHSi_3O_9$
Olivine	$(Mg,Fe)SiO_4$

Nomenclature of the alkaline intrusive rocks associated with carbonatites is best referenced to the ternary diagram of alkali feldspar-nepheline-pyroxene (Figure 13). Broadly speaking, five groups can be distinguished:

- syenites,
- nepheline syenites,
- feldspathic ijolites,
- urtites and ijolites and
- pyroxenites.

The syenites are generally composed of alkali feldspar (principally $KAlSi_3O_8$) 50 to 80 percent, pyroxene 15 to 50 percent, and accessory minerals (apatite, calcite) 5 percent. Usage of the names pulaskite and lusitanite requires knowledge of exact mineral abundances and thus, rests on microscopic examination.

The nepheline syenites by definition contain more than 10 percent nepheline. Typical mineral abundances in nepheline syenites associated with carbonatites are:

nepheline	12 to 40%
alkali feldspar	20 to 40
aegirine-augite	15 to 50
calcite	0 to 3
apatite	0 to 2
sphene	0 to 5
melanite	0 to 15

Usage of the names juvite, foyaite and malignite requires exact knowledge of mineral abundances, not readily established in the field.

Ijolites and urtites essentially contain nepheline and a pyroxene (aegirine-augite)

nepheline	30 to 100%
alkali feldspar	0 to 10
aegirine-augite	5 to 60
melanite	0 to 40
biotite	0 to 7
wollastonite	0 to 20
pectoite	0 to 10
apatite	0 to 15
calcite	0 to 25
Fe-TI oxides	0 to 5
sphene	0 to 5

In Figure 13, these rocks are grouped under the name foidalite. Since abundance of aaegirine-augite (a dark mineral) and nepheline (a light-colored mineral) is the argument for distinguishing between urtite and ijolite, appreciation of the color of the rock in the field generally permits this distinction, hence the name foidalite is infrequently used.

Feldspathic ijolites are intermediate in mineral composition between urtite-ijolite and nepheline syenites.

Pyroxenites contain essentially pyroxene. Aegirine-augite is the most common: pyroxenites containing this mineral are termed alkali pyroxenites. Diopside pyroxenites are plain pyroxenites. Acmite pyroxenites are also found in association with carbonatites. Jacupirangite is a name reserved for titan-augite pyroxenites. Pyroxenites generally contain more accessory minerals; amphibole, melanite, biotite, calcite, apatite and Fe-Ti oxides. Typical mineral compositions are:

pyroxene	60 to 80%
plagioclase	0 to 20
nepheline	0 to 20
melanite	0 to 15
olivine	0 to 15
biotite	0 to 10
amphibole	0 to 25
perovskite	0 to 10
apatite	0 to 10
Fe-Ti oxides	5 to 20

Typical chemical and mineral compositions of silicate rocks associated with carbonatites are given in Table XIX.

Table XIX. Chemical Composition of Coarse Grained Alkaline Rocks Associated with Carbonatites in wt. percent.

	1	2	3	4	5	6
SiO_2	64.79	59.36	43.75	47.71	40.50	33.53
Al_2O_3	17.78	15.50	15.77	17.35	18.95	13.20
Fe_2P_3	2.05	2.43	5.58	4.91	3.53	7.27
FeO	0.88	2.24	3.77	4.73	3.70	3.41
MgO	0.40	1.00	0.29	1.85	3.46	8.66
CaO	2.21	4.43	11.73	7.54	12.21	19.14
Na_2O	8.42	3.59	7.36	8.18	8.64	2.45
K_2O	3.19	9.17	4.17	4.44	3.41	2.16
H_2O	0.33	0.33	0.32	0.92	0.44	1.73
CO_2			3.41	0.42	1.66	2.34
TiO_2	0.43	0.41	1.48	0.72	1.94	3.44
P_2O_5	0.19	0.25	1.38	0.43	0.71	2.37
MnO	0.09	0.09	0.25	0.19	0.20	0.40
Others					1.09	0.60
	100.76	100.51	99.85	99.39	100.44	100.70

Normative compositions:

Quartz	0.7			
Orthoclase	18.8	34.3	26.4	
Albite	70.9	21.3	6.3	
Anorthite	1.5	4.0		
Nepheline		4.6	31.5	
Acmite			4.0	
Diopside	2.2	8.3	19.1	
Wollastonite	2.4	2.7	3.8	
Magnetite	1.9	3.5	5.2	
Hematite	0.8			
Ilmenite	0.8	0.8	1.4	
Apatite	0.3	0.5	1.1	
Calcite			0.9	
	100.3	100.0	99.7	

1 - Syenitic fenite, Budela complex, Eastern Uganda, *(49)*.
2 - Potash syenitic fenite, Budela complex, Eastern Uganda, *(49)*.
3 - Maligaite, Fen Norway. **(12)**.
4 - Nepheline syenite (foyaite), Budela complex, Eastern Uganda, *(49)*.
5 - Ijolite, Fen, Norway, (12),
6 - Jacupirangite, Oka, Quebec, *(33)*.

Nomenclature of the alkaline extrusive rocks associated with carbonatites is best referenced to a ternary diagram with the same minerals as those used for the alkaline intrusive rocks, i.e. an alkali feldspar-nepheline-pyroxene diagram (Figure 14). The extrusive rocks are not exact mineral equivalents of the coarser-grained intrusive (?) rocks; this is probably due to the fact that an important portion of the coarse-grained rocks are in fact metasomatic (fenites). Syenites, nepheline syenites and feldspathic ijolites are particularly suspected to be of metasomatic origin when associated with carbonatites. There are three principal volcanic rocks associated with carbonatites: trachyte, phonolite and nephelinite. Formal recognition of rock type for these volcanic rocks is best done by chemical analysis; Table XX gives typical chemical and normative compositions.

Kimberlites

Kimberlites are minor intrusives frequently associated with alkaline rocks and carbonatites. There is general agreement that kimberlites provide the deepest samples of the earth's mantle intruded into the crust; their association with carbonatites makes a mantle origin for the latter very probable.

Essentially, kimberlites are composed of a peridotite matrix and numerous xenoliths: the xenoliths comprise deep mantle rocks (peridotites, pyroxenites, eclogites) and diverse rocks plucked from the walls of the conduit (shale, sandstone, limestone, gneisses, granite, etc.). Some Kimberlites are diamantiferous. In general, kimberlites occur in small pipes (100 to 1000 m in d.) or as dikes. Many kimberlites also contain magmatic carbonate minerals.

Broad Tectonic Setting of Carbonatite

In the early years of observations on carbonatites (1920-50), they were regarded as petrologic curiosities and even their intrusive nature was questioned throughout most of the period. During the period 1950-60, a few of these carbonatites became important sources of economic minerals (niobium, phosphates, rare earths). This sparked interest in them and many new carbonatite bodies were found. In the period 1960-80, carbonatites and the alkaline intrusive rocks with them came to be recognized as of great scientific interest: carbonatites are revealing important information on intracontinental tectonics and geological processes effective in the Earth's mantle (e.g. silicate-carbonate liquid immiscibiity, alkaline magmatism and metasomatism, rare-element fractionation, etc.). Heinrich (39) estimates that around 500 carbonatite occurrences are now on record for the world on all continents.

In the brief summary to follow, we propose to focus on the essential tectonic features of carbonatites by examining principal occurrences in Brazil, Africa, Canada, U.S.A. and U.S.S.R.

Brazil

Principal carbonatites and alkaline'rock occurrences of Southern Brazil are located in Figure 15. Essentially, these are intruded into the Precambrian basement rocks; they are from 50 to 90 My old in the northwest and somewhat older (ca. 120 My B.P.) in the southeast.

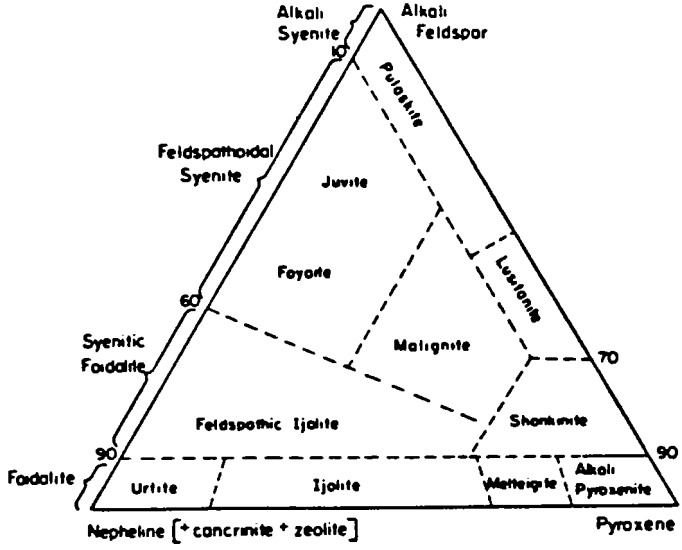


Figure 13. Mineral compositions of alkaline intrusive rocks associated with carbonatites.

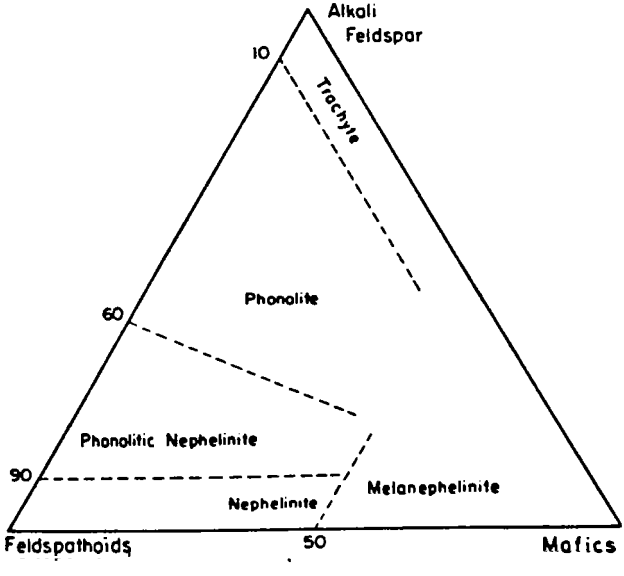


Figure 14. Mineral composition of alkaline extrusive rocks associated with carbonatites.

Table XX. Chemical Composition of Extrusive Alkaline Rocks Associated with Carbonatites in wt. percent.

	1	2	3
SiO_2	53.46	58.43	39.36
Al_2O_3	19.31	17.84	10.88
Fe_2O_3	3.25	5.09	11.65
FeO	1.31		6.08
MgO	0.61	0.43	6.38
CaO	2.39	0.80	12.86
Na_2O	10.09	0.38	5.81
K_2O	4.25	13.90	2.76
$(H_2O)^+$	4.95	1.05	
$(H_2O)^-$		0.11	
CO_2			
TiO_2	0.41	0.34	2.50
P_2O_5	0.05	0.35	0.90
MnO	0.21	0.42	0.27
BaO		0.18	
	99.45	99.32	99.45
	Normative compositions:		
Quartz		0.5	
Orthoclase	25.1	82.3	
Albite	24.7	3.1	
Anorthite		4.2	
Kaliophilite			9.5
Nepheline	27.5	0.6	23.0
Acmite	8.6		5.5
Diopside	6.1		37.5
Wollastonite	1.7		4.4
Hypersthene		1.1	
Magnetite	0.4	0.5	1.07
Hematite		4.8	2.2
Ilmenite	0.8	0.6	4.7
Apatite	0.1	0.7	2.0
	95.0	98.4	100.0

1 - Phonolite, Toror, Eastern Uganda, *(49)*.
2 - Trachyte. Toror, Eastern Uganda, *(49)*.
3 - Nephelinite, Napak, Eastern Uganda, *(49)*.

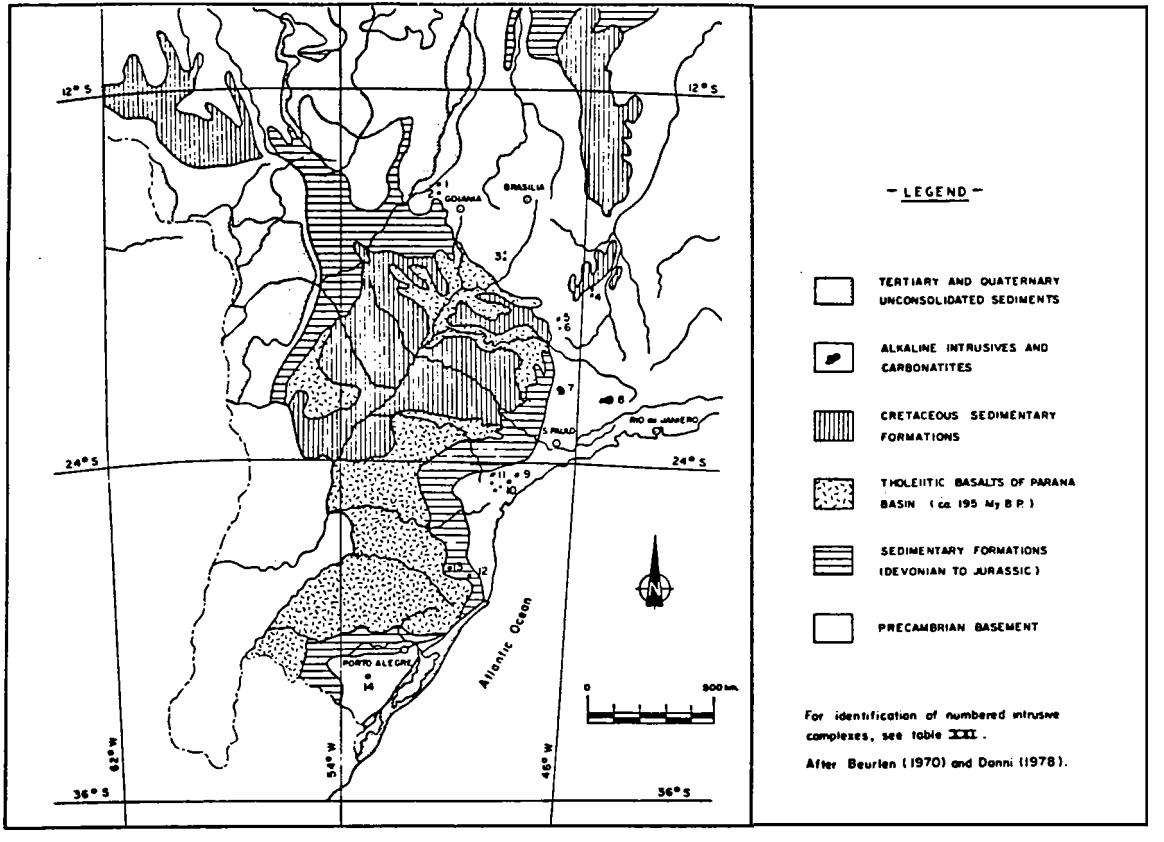


Figure 15. Geology of Southern Brazil.

All these intrusive and volcanic alkaline masses border on the vast Parana basin of tholeiitic basalt flows. The Parana basin basalts are of Triassic to Jurassic age (150 to 120 My B.P.); they are vast outpourings of basalt covering approximately 1.2 x 10^6 km^2 and locally reach a thickness of 2 km. Estimated total volume of Parana basalts is 1.0 x 10^6 km^3. These basalts were probably erupted through long fissures formed at the opening of the Atlantic Ocean. It is believed (Danni 1978) that the alkaline and carbonatite intrusive and extrusive masses formed at the margin of the Parana basin and more particularly in regions of arching. Exact location may depend on reactivated old (Precambrian) tectonic lineaments (faults).

The pretrographic types encountered in these alkaline rocks are quite diverse (Table XXI). They stretch all the way from dunites to carbonatites; pyroxenites, gabbros, syenites, nepheline syenites, urtites, ijolites, jacupirangites and carbonatites (many calcitic and some dolomitic). Cosanguinity is certainly indicated for all the silicate rocks; as for the carbonatites, they are intimately associated with the alkaline silicate rocks at most localities. The experimental work of Wyllie (98) supports the idea of immiscibility between Ca-Na carbonatite magmas and nepheline-bearing silicate magmas. Carbonatite intrusions are likely late products of alkaline magmatism; the latter in turn, may be magmatism residual to Parana basin tholeiitic magmatism.

A mantle origin is certianly indicated for the vast outpourings of tholeiitic Parana basalts. It is also likely for the associated alkaline magmatism.

Africa

More than 150 carbonatite occurrences are known in Africa. In addition, alkaline magmatism is widespread in and around the great East African rift zones. We have located principal areas of carbonatite magmatism on the McConnell (59) tectonic map of southeast Africa (Figure 16); in addition, Table XXII gives principal petrographic features and economic geology notes on columbium mineralization for the most important carbonatites.

The first obvious feature, clearly apparent in Figure 16, is that carbonatite masses in Africa are located in and immediately adjacent to the great post-Karoo rift valleys (carbonatite masses 3 to 11 incl. on Figure 16). Rift faults creating these valleys were principally active in the Cenozoic (67 to 0 My B.P.); there are, however, many indications from geological mapping that these faults are localized along ancient mobile belts in the Precambrian shield and that there may have been as many as seven major orogenic cycles affecting the pre-Silurian (440 My B.P.) rock assemblages (59). Thus, the rifted belts of East Africa are interpreted as produced by mantle mechanism and repeated activation along fault lineaments in the Precambrian basement.

The Mrima Hill carbonatite, about 80 km southwest of Mombassa in Kenya is a somewhat isolated and intensely weathered carbonatite, intruded into basement sediments. It is of interest both for niobium and rare earth contents, and is reported by Deans (21) to contain 55 Mt of 0.7 percent Nb_2O_5. In 1979 the Rhone Poulenc group began development of the deposit to produce and recover the rare earth content.

Three principal petrographic associations can be recognized in the alkaline magnatism of the East African rift zones:

Table XXI. Principal Carbonatite and Alkaline Rock Occurrences of Southern Brazil.

No. on Fig. 15	Locality (state)	Description	Age My B.P.
1	Morro do Macaco (Goias)	Domes of dunite and pyroxenites. some syenites. No carbonatite observed.	81-75
2	Corrego dos Bois (Gois)	Dunitic domes; cores of wehrlite pyroxenite, gabbro and minor nepheline syenite. No carbonatite observed.	81-75
3	Catalao I S II (Goias)	Ultramafic complex with extensive fenitized quartzites and schists, nepheline syenites, silicocarbonate rocks and carbonatites (sovite).	83
4	Serra Negra (Minas Gerais)	No carbonatite but eluvial pyrochlore deposits. Alkaline rocks comprise jacupirangites serpentized dunite, tuffs and agglomerates.	82
5	Araxa (Minas Gerais)	Carbonatites (sovite & beforsite) app. 5 km^2. Associated phlogopite schists. Deeply weathered and poorly exposed.	91
6	Tapira (Minas Gerais)	Carbonatites app. 1.5 km^2 90% of exposed rocks are alkaline rocks. 13.7 mt at 0.51% Nb_2O_5 reported.	70
7	Pocas de Caldas (Minas Gerais)	No carbonatite exposed. Essentially alkaline volcanic (tinguaites and phonolites and intrusive (nepheline syenite) rocks.	87-52
8	Itatiaia (Rio de Janeiro)	Carbonatites and alkaline rocks.	66
9	Morro de Serrote (Sao Paulo)	Carbonatites, ca. 5 km^2 (sovite and dolomite). Associated nepheline syenite, peridotites, pyroxenites and ijolites make up 20 km^2.	127
10	Jacupiranga (Sao Paulo)	Carbonatites (ca. 0.3 km^2 sovite) in core of alkaline pipe is a late intrusive. Rocks associated are ijolites, jacupirangite, periodotite and dunite; they aggregate some 40 km^2.	140
11	Itapirapua (Sao Paulo)	Carbonatite (ca. 0.3 km^2 sovite) in alkaline stock of foyaite and tinguaite.	103
12	Anitapolis (Sao Paulo)	Small carbonatite asses in pyroxenites and nepheline syenites.	115-90
13	Lajes (Santa Catarina)	Small carbonatized pipe, breccias and carbonatite dikes (beforsite) in small alkaline pipes (nepheline syenites and olivine mellilitites).	115-90
14	Rio Grande do Sul	No carbonatites. A dozen small trachyte and phonolite pipes.	100

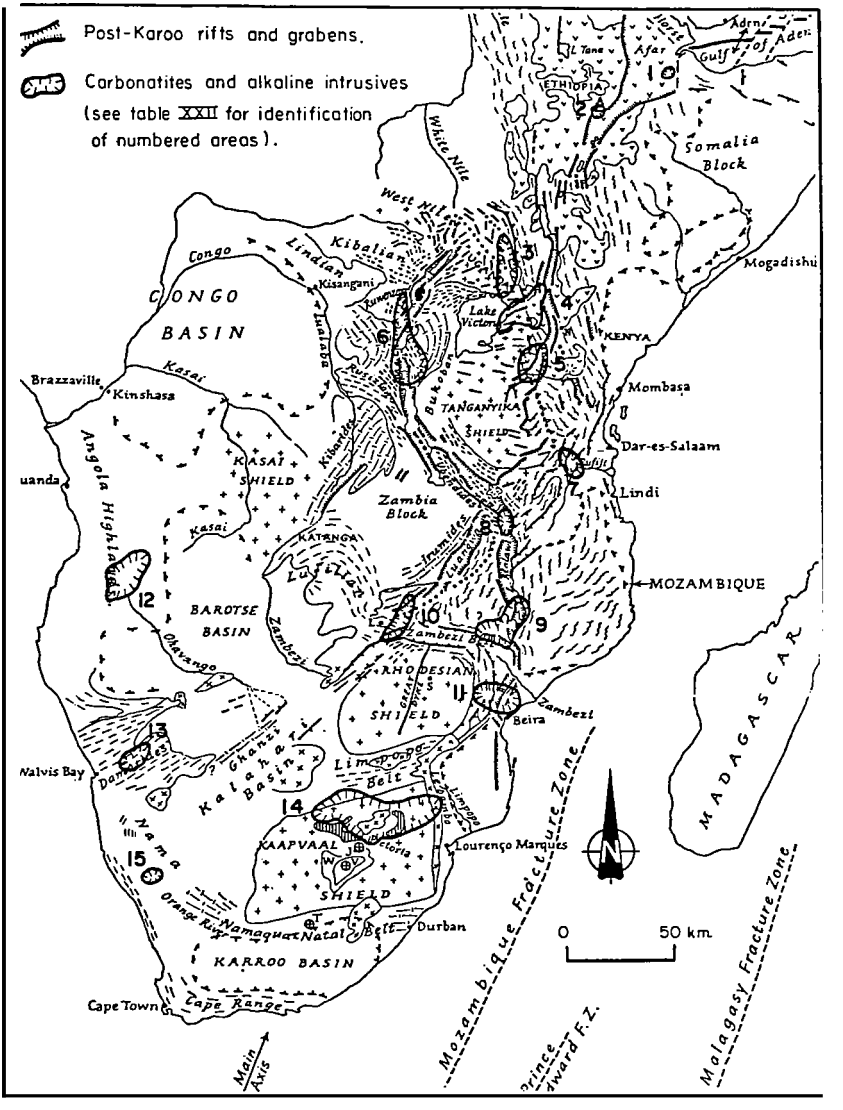


Figure 16. Tectonic map of Southeastern Africa after McConnel (1972). Areas of carbonatites and alkaline intrusives added.

Table XXII. Principal Carbonatites of Africa.

No. on Fig. 16	Locality	summary Description	Age My B.P.
1	Somali Darkainle	Alkaline rocks and minor carbonatite.	
2	Ethiopia Bishoftu	Explosion crater possibly related to carbonate vulcanism.	
3	Uganda Sukulu	Smite and Smite breccia; some fenite breccia.	
	Napak	Remnant of volcano. Ijolite with central carbonatite plug.	
	Toror	King intrusion of carbonatite in phonolitic lavas.	
	Toraro	Carbonatite intruded in syenitic fenites, nepheline syenites and ijolites. Possible recovery of some pyrochlore as by-product of phosphate.	
4	Kenya Homa	Sovite, alvikite and ferrocarbonatite intrusions with ijolites. Syenitic fenites. Phonolite and nephelinite volcanics.	13-1
	Sokolo	Sovite, alvikite. ferrocarbonatite and late carbonatite in that order. Some phonolites.	10-5
	Ruri	Sovite. alvikite and ferrocarbonatite accompanied with tuffs. agglomerates and breccias.	15-5
	Wasaki	Phonolite lavas and plugs. Sovite. alvikite, ferrocarbonatites and late carbonatites.	3
	Kisingiri	Ijolite followed by carbonatites. Nephelinite and agglomerate followed by pyroclastics and carbonatites.	38-11
5	Tanzania Oldoinyo Lengai	Ijolite tuffs and agglomerates, nephelinite tuffs and agglomertes, melanephelinite extrusives mixed carbonatites and soda carbonatite in that order.	0
	Mosonik	Nephelinite and phonolite volcano. Sovite plug in the crater.	
	Oldoinyo Dili Essimingor Basatu	Sovite and nephelinite. phonolite, ijolite. Recent volcanism.	
6	Zaire Lueshe	Smite, rauhaugite and syenite plug in fenitized basement schist. Reported 30 Mt of 1.35% Nb_2O_5.	
	Nyiragongo	Leucitite and nephelinite volcanism, calcite in groundmass.	0
	Burundi Karonge	Bastnaesite vein deposit related to a carbonatite parent.	
7	Tanzania Wigu Hill Maji Ya Weta Luhombero	Carbonatite dikes and breccia pipes.	
8	Sangu	Carbonatite (dolomite and calcite) sill in basement complex.	
	Panda Hill	Sovite plug in fenitized precambrian basement complex. Reported 125 Mt of 0.3% Nb_2O_5.	
	Nackendazwaya	Carbonatite, ijolite and foyaite. Reported small lenses of urampyrochlore ore.	

Table XXII. Principal Carbonatites of Africa. continued.

No. on Map	Locality	Summary Description	Age My B.P.
9	**Malawi** Malombe	Feldspathic agglomerate. volcanic vents with carbonatired phonolite plugs.	
	Kangankumde	Ankerite-strontianite carbonatite vlth associated fenitized gneisses.	
	Chilwa Island	Sovite, ankeritic sovite and siderite carbonatite in breccia zone. Some columbium ore reserves have been outlined.	(140)
	Mozmbique Muambe Hill	Central core of carbonatite in agglomerate in Karoo metasediments.	
10	Zambia Kalubwe	Fragmental sovite conformable with Karoo sediments; large potential for low grade pyrochlore ore.	(10)
	Nkombusa	Superficially altered carbonatite (ankeritic) plug in Karoo sediments.	
	Mwambuto	Carbonatite plug and carbonatite volcanics in Karoo sediments.	
	Chasweta	Sovite and sovite breccia, tuff and agglomerate in Karoo sediments.	
11	Rhodesia Dorawa	Syenite and syenite fenites vlth central area of ijolite and foyaite. Small carbonatite pluge.	(200)
	Chishanya	Carbonatite. minor ijolite and nepheline syenite in fenitized granite.	(200)
	Mozambique Ziluvo	Central plug of carbonatice in outer ring of volcanic breccias.	
12	Angola Longonjo	Carbonatite ring complex.	
	Coola	Carbonatite and trachyandesite breccia.	
	Chianga	Nepheline syenite complex with central core of ferrocarbonite.	
	Bailondo	Dolomitite core in dolomitie breccia: outer ring of syenite.	
	Capuia	Carbonatite and carbonatite breccia plug.	
13	S W. Africa Ondurakorume	King structure: rauhaugite breccia. sovite, foyaite and syenite.	
	Kalkfeld	Carbonatite in syenite and foyaite. Fenitized country rocks.	
	Cape Cross Messum Doros Okonjeje	Differentiated basic complexes related by lineament to the above carbonatite masses.	
14	South Africa Palabora	Double intrusion of pyroxenite. Ring structure. Some syenite. Carbonatite core in "phoscorite" containing magnetite, apatite. carbonates. olivine and serpentine. An important Cu producer.	2060
	Spitskop	Dolomitite, beforsite and sovite in foyaite and ijolite.	
	Kruidfontein	Sovite and beforsite core in carbonated pyroclastic breccia.	
	Premier	Kimberlite pipe cut by carbonatite dikes; an important producer of diamonds.	
15	S W. Africa Brukkaros	Eroded ultrabasic volcano carbonatite likes on lineament with numerous kimberlite pipes.	130-112
	Chamais	Small carbonatite plug.	

Ages in peranthesis derived from stratigraphic consideration.

1 - Gittins (1966).
2 - Deans (1966).
3 - Le Bas (1977).
4 - Dawson (1966).
5 - Prins (1978).
6 - Marsh (1973).
7 - Dawson (1980).

1. A carbonatite-nephelinite assemblage: this is characterized by abundance of carbonatites, development of ijolites, nephelinitites, phonolites, syenites and important and widespread fenitization (alteration of host rocks). We believe carbonatites of areas **9** (Malawi-Mozambique), **10** (Zambia) and **11** (Rhodesia-Mozambique) are of this type. These alkaline rock complexes are all approximately Jurassic to Lower Cretaceous (ca. 200 to **100** My B.P.).

2. A basalt-nephelinite assemblage: this is characterized by abundance of mafic rocks, development of nephelinite generally containing olivine as the mafic mineral, scarcity of carbonatites, ijolite and urtites. Rock assemblages of this type are common in the Kenya and the Ethiopian Rifts. Our Figure **16** emphasizes carbonatite occurrences; alkali basalt magmatism has not been noted since carbonatites are rare therein. Nevertheless, areas **1** (Somali), 2 (Ethiopia), **3** (Uganda), 4 (Kenya) and 7 (Tanzania) should probably be related to this assemblage. These rock assemblages and the associated carbonatites are for the most part Cenozoic **(67** to 0 My B.P.).

3. Mixed basalt-nephelinite and carbonatite-nephelinite assemblages: areas **5** (Tanzania), **6** (Zaire and Burundi) and **8** (Southern Tanzania) show characteristics of both associations and are presumed to represent a zone where both forms of magmatism were effective. Most of the carbonatites of these areas are recent (the last **5** My).

Kimberlites are frequent associates of the carbonatite-nephelinite assemblages. In this respect the following rules of observation seem to hold:

- Kimberlites are rarely in close proximity to nephenilitic rocks: they tend to form different pipes,
- Ijolite and kimberlite are similarly mutually exclusive,
- Carbonatites provide the link between alkaline silicate rocks and kimberlites: kimberlites can be carbonatitic and carbonatites are otherwise frequently associated with ijolite and nephelinite. South African carbonatites and kimberlites are Proterozoic (e.g. Premier at **1500** My B.P.) or Cretaceous (e.g. the Kimberley-Pretoria carbonatites and kimberlites, Palabora, Kruidfontein, etc.),

The carbonatites **of** Damaraland **(13** on Figure **16)** and those of Southwest Africa (Namibia) have been related to Brazilian and Uruguayan carbonatites (Figure **17,** from **58);** presumably these were formed along the same lineaments before the opening of the Atlantic Ocean.

Canada

In their **1966** memoir, Tuttle and Gittins **(88)** reported on 20 carbonatite occurences in Canada, since that time, an estimated 20 more have been found. Principal ones, located in Eastern Canada, are indicated in Figure **18** and essential data are summarized in Table XXIII.

Canadian carbonatites occur in four age groups: **1750** to **1550, 1100** to **850, 600** to **300** and **125** to **90** My B.P. They can generally be seen to cut the Precambrian basement gneiss or greenstone complexes. Carbonatites of the two older groups are distributed along or near the Kapuskasing High, a lineament extending from Lake Huron to James Bay showing gravity and magnetic highs. Carbonatites of the two younger groups are essentially in or near the St-Lawrence rift system.

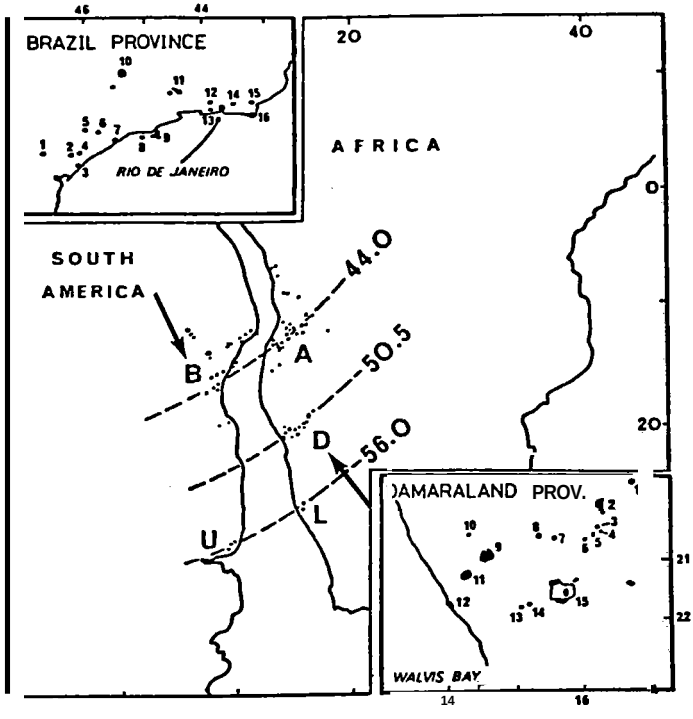


Figure 17. The South Atlantic 140 My B.P. showing the distribution of alkaline complexes in Africa South America. Dashed arcs are portions of small circles centered on the Cretaceous pole of rotation and their distance from this pole is given in degrees. Reprinted by permission from Marsh (1973).

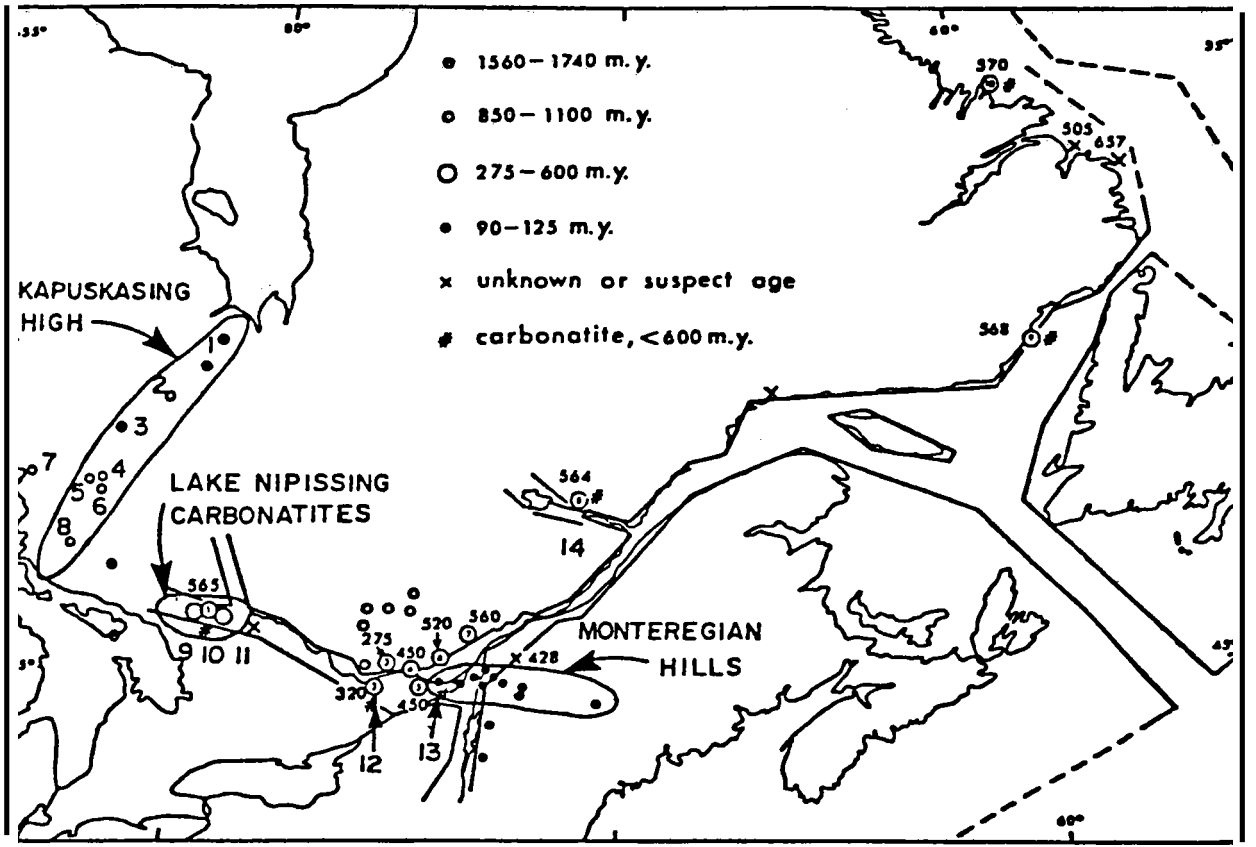


Figure 18. Carbonatites and alkaline intrusives in Eastern Canada. After Doig (1970). For the designation of numbered plutons, see Table XXIII.

Table XXIII. Principal Carbonatites of Eastern Canada.

No. on Pig. 16	Locality	Summary Description	Age My BP.
	Kapuskasing Lineament		
1	James Bay	Pyroxenite-carbonatite complex intruded in Precambrian hornblende gneiss complex 62 Mt at 0.52% Nb_2O_5 proven.	1655
2	Clay Tp.	Aegirine syenite and carbonatite circular complex.	1010
3	Cargill	Aeromagnetic high on poorly exposed pyroxenite cut by carbonatite dikes.	
4	Nemegosenda	Alkaline syenite, syenite breccia, fenites, minor carbonatites, nittudes in Precambrian granite gneisses. Ore reserves estimted at 20 Mt at 0.47% Nb_2O_5.	1740–1560
5	Borden	Prominent circular magnetic high.	
6	Lackner L.	A circular complex of nepheline syenite, ijolite, malignite and minor carbonatite. 80 MT at 0.25% Nb_2O_5 plus magnetite and apatite.	1100-850
7	Firesand	Circular complex of sovite and rauhaugite intruded into Precambrian greenstones.	1100-850
8	Seabrook Lake	Circular intrusion of mafic breccia and ijolite with central core of sovite.	1100–850
	Lake Nipissing		
9	Iron Island	Probable carbonatite.	
10	Manitou Islands	Ring complex of alkaline rocks, carbonatite and fenites intruded into Precambrian hornblende granite gneiss. Newan deposit: 2.7 Mt at 0.69% Nb_2O_5. ~~and 0.4% U_3O_8.~~	565
11	Calander Bay	Principally nepheline syenite cutting Precambrian gneisses.	
	Ottawa		
12	Eastviev	Alkanite syenite complex	
	Monteregian Hills		
13	Oka	Carbonatite. sovite. ijolite, fenite, alnofte complex intruding Precambrian gneisses. See also p. 110.	95
14	~~St-Honore~~	Central carbonatite (dolomite) plug in syenite, foyaite and ijolite ring, intruding Precambrian gneisses and anorthosites. Extensive fenitization See also p. 110.	560

(1) Stockford 1972
(2) Tuttle & Gittins 1966
(3) Doig 1970
(4) Heinrich 1966
(5) Perguson 1971
(6) Vallee & Dubuc 1970

The two older groups are not well documented because they are poorly exposed. The 1100 to 850 My B.P. carbonatites are possibly to be related to nepheline syenite magmatism of the Grenville province (e.g. Haliburton-Bancroft area).

Many of the 600 to 300 My B.P. carbonatites have been observed in and around the St-Lawrence rift system which is associated with the opening of the Atlantic Ocean some 200 My B.P. Reconstruction of the continents to their pre-200 My B.P. configuration (Figure 19) shows in fact that the Scandinavian, Greenland and Canadian carbonatites of the 600 to 30 My B.P. occur in one long zone (one exception, the North Greenland carbonatite). Thus, St-Lawrence River rift system may represent the reactivation of a much older tectonic zone. The St-Honor@ carbonatite (Niobec mine) belongs to this group.

The Oka carbonatite is Cretaceous (ca. 95 My B.P.). It is spatially and petrographically related to Monteregian magmatism (nepheline syenite and gabbro: see pp. 110).

A number of carbonatites are known in Western Canada although these have generally not been well-explored. A placer deposit with significant niobium content is located in the Bugaboo area of British Columbia.

The currently most significant of these is located in the Northwest territory, about 5 km north of the Hearne Channel of the Great Slave Lake. The area is locally identified as Thor Lake. Aerial photographs show an annular structure approximately 19 km in diameter. The strucutre is a syenite complex, surrounded by alkalic granite, Rotherham (78). Altered and mineralized zones occur within the syenite complex.

The mineralization is columbite with some tantalite. Rare earth minerals, including allanite, monazite and bastnaesite are also present. One mineralized zone has been defined over an area of about 1.2 by 1.8 km, and exploration to date has indicated approximate grades of 0.4 percent Nb_2O_5 together with 0.03 percent Ta_2O_5.

It seems probable that further exploration will reveal numerous other carbonatites in Northwestern Canada.

United States of America

Carbonatites are not as numerous in the U.S.A. as they are in Canada. Four are given in Table XXIV. The four age groups known in Canada are also observed in U.S.A.

1 - Obson & Pray (69).
2 - Heinrich (38).
3 - Tuttle & Gittins (88).
4 - LeBas (53).
5 - Heinrich et al (40).

Weyll (96) makes an interesting case of the "38th parallel lineament", an east-trending fault zone containing numerous alkaline intrusions and cryptovolcanic structures; this basement lineament may have been tectonically active since late Precambrian. This lineament lies approximately 300 km north of the Magnet Cove-Gem Park-Iron Hill carbonatites and the link between carbonatites and this lineament is at best tenuous.

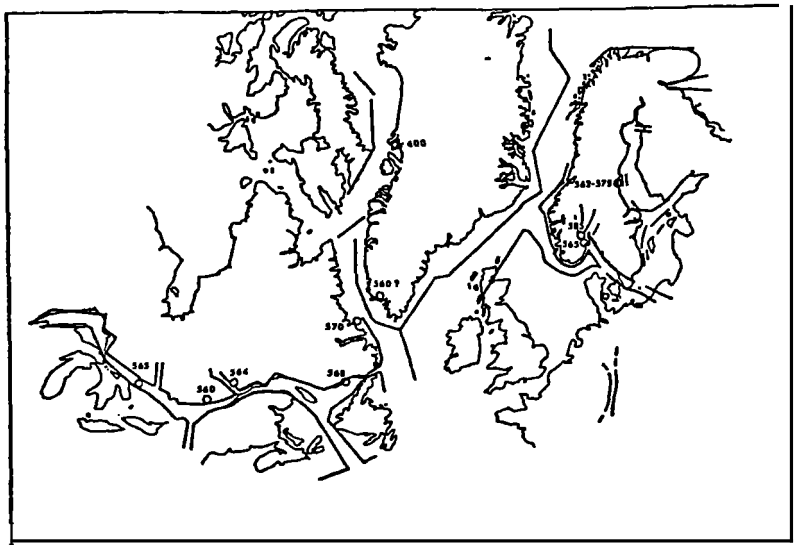


Figure 19. Reconstruction of the North-Atlantic region on which the carbonatltes representing the 565 My B.P. lineament have been superposed. Reprinted by permission from Dolg (1970).

Table XXIV. Principal Carbonatites of the U.S.A.

No. on Fig. 16	Locality	Summary Description	Age My B.P.
1	Mountain Pass (California)	Carbonatite and syenite mass intrusive in Precambrian gneisses. Important bastnaeslte (rare earths) mineralization.	1400
2	Magnet Cove (Arkansas)	Core of carbonatlte and ljolite in trachyte, phonollte, nepheline syenlte and jacuplrangite.	95
3	Gen Park & McClure Mtn. (Colorado)	Pyroxenites, gabbros, syenltes, lamprophyles cut by carbonatlte dikes and sills.	700
4	Powderhorn, Ironhill (Colorado)	Carbonatlte in nepheline syenlte, pyroxenite, ijollte and fenlte complex. Injected in Precambrian granite. Some niobium mineralization.	580-520

(1) Obson & Pray (1954).
(2) Heinrich (1966).
(3) Trittle & Gittins (1966).
(4) LeBas (1977).
(5) Heinrich et al (1978).

U.S.S.R

A brief overview of alkaline-ultramafic and carbonatite provinces of the U.S.S.R. was presented at the Pocas de Caldas symposium by Borodin in 1976; the following account is largely taken from the publication that appeared shortly thereafter, **(9)**.

Figure 20 shows the broad tectonic setting. Carbonatites occur principally in the Kola peninsula, the Maimecha-Kotin province of Polar Siberia, the East Alden area and the Eastern Sayan area. In addition, alkaline magmatism is extensive along deep-seated lineaments where tectonic activity has been recurrent since late Precambrian.

The ultramafic and carbonatite complexes fall into two age groups: pre-Phanerozoic, ca. **700** to 600 My B.P. and Paleozoic, ca. *400* .to 200 My B.P. Alkaline basalts are more generally *400* to 300 and 100 to 0 My B.P. Nepheline syenite magmatism has extended from 600 to 100 My B.P. with a climax between 300 and 200 My B.P.

The ultramafic and carbonatite complexes show the following sequence of formation: ultramafic rocks, ijolite, melteigite, nepheline syenite and carbonatites. Alkali metasomatism (fenitization) is widespread; many ultramafic rocks are transformed into ijolite-melteigite rocks. Carbonatite is generally sovite at the start, dolomitic later on and frequently ferrocarbonatitic in the last stages.

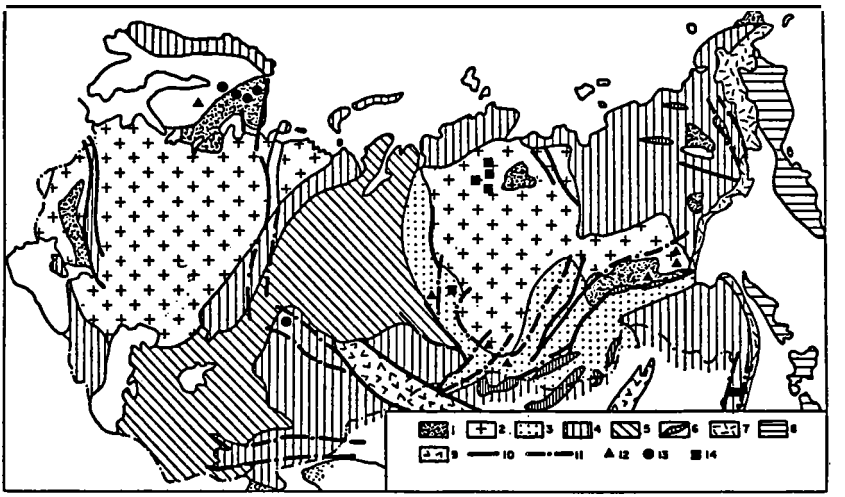


Figure 20. Alkaline provinces of the U.S.S.R. 1 and **2**, ancient platforms and shields; **3** to 9 folded belts, **3** rifieides, *4* Lower Paleozoic, 5 and 6 Paleozoic-Mesozoic belts on the continental crust, 7 Pacific Ocean volcanic belts, 8 Recent volcanic belts, *9* folded belts on the oceanic crust. 10 and **11** faults and boundaries. **12**, 13 and 14 alkaline ultramafic rocks and carbonatites, **12** pre-Phanerozoic, 13 Paleozoic, 14 Mesozoic. After Borodin **(1978).**

Current (1980) production of niobium for the world outside communist areas is estimated as follows, (56).

	1980 10^3 t Nb_2O_5
Araxá, Minas Gerais, Brazil	15.9
St-Honoré, Québec, Canada	3.2
Catalão, Goias, Brazil	2.3
Nigeria	0.9
Total	22.3

We present hereafter brief descriptions of these four producing areas. We have also added a description of the Oka mine, once an important producer. Together, these five descriptions contain essential data on the manner of occurrence, grade, and reserves to allow an understanding of the mineralization. in yet other districts and a reasonable projection as to future supply.

Araxá

The Araxá carbonatite is a roughly circular complex approximately 4 km in diameter centered about 6 km south of the city of Araxá, state of Minas Gerais, Brazil: the latter lies approximately 550 km northwest from Rio de Janeiro. The Araxá carbonatite belongs to a northwest trending group of carbonatite complexes extending from Tapira, through Araxá.

Salitre, and Serro Negra to Catalão, a distance of some 600 km (Figure 15). These complexes have been intruded into folded Precambrian belts of the Araxl, Canastra and Bambiu groups along old fault zones during Late Cretaceous time (83 to 70 My B.P.). The northern edge of the very extensive Parana basin (tholeiitic basalts) is just 50 km southwest of Araxl and the later melteigic tuffs of the Planalto da Mata Corda occupy some few tens of km^2, some 20 km to the northeast.

The Araxá carbonatite gives rise to a clear magnetic high and to an important radiometric anomaly (up to 20 times background). It comes to surface in only one small outcrop; the rest of the complex is intensively weathered and forms a lateritic soil up to 300 m thick.

The Araxá niobium deposit occurs in the central part of the carbonatite plug. It is mined by C.B.M.M. (Cia. Brasileira de Metalurgia e Mineracao). Our principal references on this deposit are da Silva et al. (17) and Guimaraes (35); the former gives a list of approximately fifteen other references on Araxá. The geological map of the complex (Figure 21 after da Silva et al. 17) has primarily been derived from study of drill cores.

The country rocks are

1 - quartzite and interbedded schists, 100 to 600 m thick, overlain by

2 - biotite–muscovite schists.

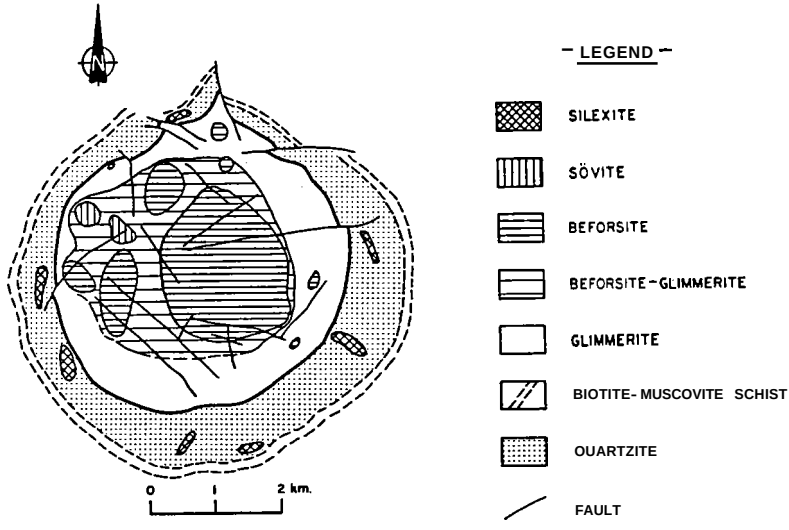


Figure 21. Geology of the Araxá carbonatite. After da Silva et al. (1979).

Near the eastern contact with the intrusive, the quartzite is in a nearly vertical position (dip of approximately 60° east). The country rocks are cut by numerous dikes (sbvite, apatite sbvite, lamprophyre) both radially and concentrically. Fenitization is extensive: in the eastern part of the complex it extends up to 2.5 km from the contact.

This fenitization takes the form of addition of certain minerals: soda-amphibole, K-feldspar, apatite, dolomite, acmite and pyroxene. Outlines of fenitized country rocks are quite irregular; they show some control by fractures. The silicate bodies occurring in the quartzite band are believed to be hydrothermal; they consist of chalcedony and quartz, with lesser quantities of magnetite, barite, apatite and bariopyrochlore.

The carbonatite intrusives are

1 - principally beforsite: it contains dolomite and ankerite, magnetite, barite, apatite, pyrite and bariopyrochlore. These rocks are coarse to medium grained,

2 - sbvite (two masses in the northwest quadrant): calcite is the principal carbonate mineral and the rock also contains magnetite and barite,

3 - glimmerites: these contain phylogopite with subordinate dolomite and magnetite. Locally the glimmerite also contains diopside and olivine,

4 - beforsite-glimmerite: these rocks are essentially mixtures by brecciation and diking.

The composition of one beforsite is given in Table XXV, column 1.

Table XXV. Chemical and Mineral Composition of Araxa Carbonatites in wt. percent.

	1	2
SiO_2	1.40%	2.86
Al_2O_3	1.80	1.19
Fe_2O_3	8.14	44.00
FeO	17.60	1.00
MgO	14.50	0.43
CaO	9.20	0.33
TiO_2	2.30	3.30
Na_2O	0.14	
K_2O	0.42	
SO_3	1.95	8.46
F	0.07	
P_2O_5	0.69	3.33
Cr_2O_3	0.01	
NiO	Tr.	
MnO	1.08	1.21
BaO	1.95	17.50
SrO	0.59	
Nb_2O_5	0.72	3.50
CeO_2	0.42	1.62
La_2O_3	0.16	2.46
ZrO_2	0.02	0.14
L.O.I.	(34.93)	
CO_2	33.00	2.06
ThO_2		0.14
U_3O_8		< 0.01
H_2O^+		6.07

Mineral compositions calculated from 1 and 2

	1 primary rock	2 weathered ore
Dolomite	31	5
Magnesite (1)	30	
Siderite	12	
Magnetite	12	2
Phlogopite	5	
Ilmenite	4	1
Barite	3	24
Bariopyrochlore	1	5.3
Pyrite	1	
Monazite	1	6
Goyazite	1	5
Coethite		46
Rutile		2.8
Quartz		2.8
Zircon		0.2
	101	100.1

(1) A mineral obtained by the calculations but not one that is observed,

1 - Beforsite (ankerite), E part. da Silva et al. (1979).
2 - Bariopyrochlore ore in no. 1 adit, Araxa. Grossi Sad & Torres (1978), p. 310.

The lateritic cover of the carbonatite renders mapping of the structural features of the complex nearly impossible. This cover is 40 to 60 m deep in the northwest portion of the complex and 160 to 300 m deep in the center and southern portions. The formation of this cover is essentially the result of weathering in a lateritic climate. Special features of the carbonatite rocks may have been important in accelerating the leaching process; brecciation and faulting in the complex provided channelways for leaching solutions and the presence of pyrite in the primary carbonatite may have rendered the solutions more active in the leaching of carbonates through the formation of sulphuric acid. Most important of all, leaching of the carbonatite provided a first step in the concentration of the pyrochlore.

The ore is essentially composed of goethite, barite, monazite, goyazite, some residual ferroan dolomite and bariopyrochlore with subordinate amounts of magnetite, rutile, quartz, ilmenite and zircon. Recalculation of mineral compositions from the chemical compositions permits some definition of the leaching process; it seems to involve principally:

- dissolution of most of the carbonate minerals (from 73% to 5%),
- concentration of insoluble minerals (bariopyrochlore, barite, monazite, goyazite) by a factor of about 5,
- production of goethite by the transformation of iron carbonates,
- quartz, a thermodynamically unstable phase in the primary rock is probably obtained by the leaching of the phlogopite.

Ore reserves at Araxd are currently estimated at 460 Mt at 2.5 percent Nb_2O_5.

At the current level of production (ca. 1Mt/y.), this yields a value of many centuries for the productive life.

The Araxá carbonatite also sustains some phosphate production and also has both rare earths and uranium production potential.

Catalao I

The Catalão I complex is a plug of ultramafic, alkaline and carbonatitic rocks located approximately 10 km east of the city of Catalao, in the state of Goias, Brazil. The plug is approximately 6 km in diameter. Our principal reference on this complex is de Carvalho (22).

General geology of this complex is illustrated in Figure 22. The country rocks are Precambrian mica schists, quartzites and occasional amphibolites of the Araxd group, generally striking NW-SE and dipping to the SW. Fenitization is extensive in the immediate neighborhood of the complex; it extends irregularly up to 2 km from the contact.

Principal rocks of the complex are dated at 83 My B.P. and comprise:

- silicocarbonatites: de Carvalho (22) has regrouped various petrographic types under this name. They contain essentially phlogopite (30 to 70%) and calcite (10 to 60%) with numerous relict and alteration minerals: apatite, serpentine, barite, amphibole, pyroxene, feldspars, zircon and pyrochlore. These are believed to be alteration and metasomatic products of ultramafic rocks (dunites and pyroxenites).

- smites: they are essentially calcitic (60 to 95% in calcite). Minor constituents are apatite, phlogopite, serpentine, magnetite, pyrite and pyrochlore.

- glimmerites: these are the phlogopite-rich rocks (70 to 80%).

- silexites: these are not shown on the map. They are widespread throughout the complex especially at its periphery. These rocks are essentially composed of chalcedony and quartz (80 to 95%)with the same accessory minerals as those contained in the other rocks of the complex.

Lateritization is important throughout the complex. It has given rise to various "cangas" or crusts of residual material: magnetite "cangas" and limonite conglomerate are principal amongst those.

Ore zones are essentially residual carbonatites. The ore mineral may be a certain pyrochlore formerly known as koppite, and bariopyrochlore.

Ore reserves are given as 25 Mt at more than 1 percent Nb_2O_5 for the Mineraçao Catalao de Goias (Brasimet) property. Other properties on this complex may bring the total potential of Catalao complex to 40 Mt at more than 1 percent Nb_2O_5.

The Catalao carbonatite is also a producer of phosphates, and potentially, vermiculite and ilmenite.

St-Honoré

The St-Honoré complex in plan is a roughly circular area of approximately 25 km^2. It is located 5 km west of the village of St-Honoré and some 13 km north of Chicoutimi, Quebec. Tectonically, it borders the Saguenay graben, which in turn is part of the St-Lawrence Rift system (Figure 18). It has been dated at 560 My B.P. 89) and 650 My B.P., (89).

The St-Honoré complex shows up clearly on airborne geophysical surveys: it gives a clear radiometric high and distint magnetic high associated with a magnetic low. Ground gravity surveys also show some slight positive Bouguer anomalies centered on the complex.

The country rocks are Precambrian gneisses and anorthosite of the Grenville subprovince (Figure 23). These include magnetite diorite, hypersthene syenite, anorthosite and biotite-pyroxene gneisses. Fenitization around the carbonatite core may be extensive; it is apparent by the development of veinlets of sodic amphibole, aegirine and carbonate minerals in the enclosing magnetite diorite and syenites. It may be that some of these enclosing syenites are principally fenitization products. The carbonatite is overlain unconformably by the Trenton limestone of Ordovician age over half of its area; the rest of it is covered with Pleistocene glacial clays; thus, geological information on the complex rocks was essentially derived from a few outcrops some trenches, some diamond drilling, and mine workings.

The carbonatite complex comprises

- a central nucleus of dolomitic and ankeritic carbonatite locally rich in rare earths,

- numerous ring dikes and cone sheets of dolimitite (not shown in Figure 23),

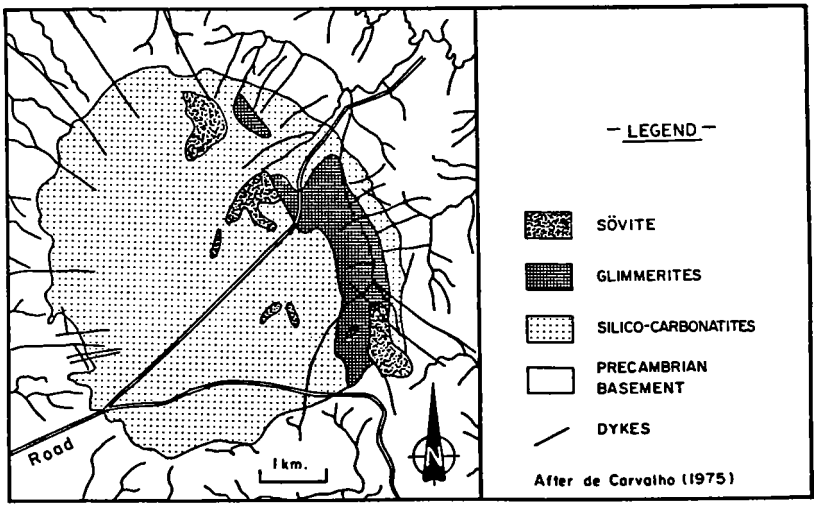


Figure 22. Geological map of Catalão - 1.

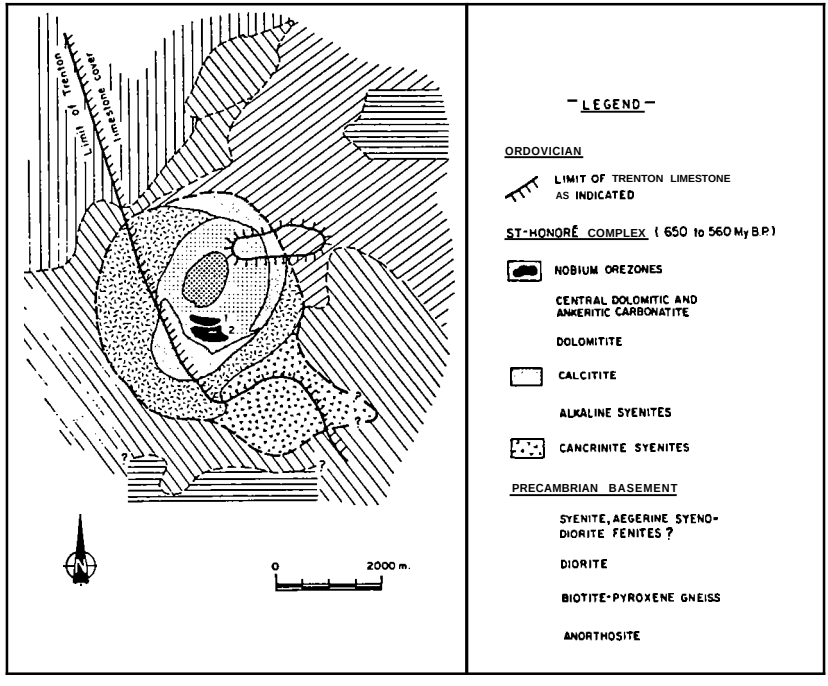


Figure 23. Geology of St-Honorè complex. After Gagnon (1979) and Vallée & Dubuc (1970).

- an annular mass of dolomitic and calcitic carbonatite locally rich in Nb_2O_5; ore zones 1 and 2 are contained in this ring,

- an exterior, nearly complete ring of alkaline syenites, feldspathoidal syenites, ijolites and urtites, and

- a triangular area, contiguous to the main complex and to the southeast of it, consisting of cancrinite syenites.

The ore zones are composed of numerous mineralized lenses with Nb_2O_5 contents greater than 0.5 percent. Ore zones no. 1 comprises six of these lenses. These lenses are arcuate structures, dipping steeply (ca. 65°) towards the center of the complex (north). The ore is essentially a dolomitic carbonatite with the following average mineral composition: dolomite 63 percent, apatite 12, magnetite and hematite 13, calcite 5, biotite 3, chlorite 2, pyrite 1, pyrochlore 0.8 and columbite 0.2 percent. Locally the ore contains a small quantity of coal like material. Ore zone no. 2 comprises ten mineralized lenses; it differs from ore zone no. 1 by the fact that pyrochlore is the only niobium-bearing mineral phase; the carbonatite is essentially calcitic, contains more biotite and less combined magnetite and hematite. The carbonatite of orezone no. 2 also contains fragments of lamprophyre (pyroxene, biotite, chlorite, calcite); these may be mineralized. Chemical compositions of the pyrochlore and columbite have been given in Table VI (col. 2) and Table XI (col. 2).

Ore reserves are estimated at 16 Mt at 0.69 percent Nb_2O_5 in ore zones no. 1 and 2.

Rare earth concentrations in the dolomitic core may eventually be further explored, and apatite in the two ore zones may eventually be recovered as by-product of the pyrochlore concentration.

Oka

The Oka carbonatite was the first niobium deposit to be mined in Canada. It was mined by St-Lawrence Columbium and Metals Corp.; during its productive life (1961 to 1976), this mine produced approximately 20,000 t of Nb_2O_5 from 6.3 Mt of ore. The operation was terminated in 1976 because of economic difficulties. Many other companies explored the Oka carbonatite complex and found niobium resources (see below).

The Oka carbonatite is probably one of the best exposed in the world; it is also one of the more extensively drilled with more than 100 km of core drilling on the more important mineral properties.

The Oka complex belongs to the Monteregian petrographic province which extends in an east-west direction from Oka in the west to Mount Megantic in the east, a distance of some 300 km. Ten visible monadnocks (Figure 18) stand out in the St-Lawrence River Lowlands and another six plutons are indicated by magnetic anomalies, but are covered with Paleozoic sediments. The Monteregian plutons are composed of alkaline and ultramafic intrusives: peridotite, pyroxenite, gabbro, nepheline diorite, nepheline syenite and carbonatite (Oka). The Monteregian arc lies across the St-Lawrence Rift system. It is tempting to suggest some form of magmatic differentiation along the Monteregian arc; the most easterly intrusive is granodioritic while the most westerly (Oka) is carbonatitic. All these intrusives including the Oka carbonatite are dated at approximately 110 My B.P. (32).

Structurally, the Oka complex is a double circle having the form of a distorted Figure 8 (Figure 24). It is intruded in Precambrian quartz-feldsparbiotite gneiss and anorthosite of the Grenville sub-province. The rocks of the complex define essentially concentric lithostructural units; in the southern ring, dips are everywhere outwards and increase towards the margin, while in the northern ring, inward dips prevail in the central part and outward dips near the margin.

The rocks of the complex comprise

- carbonatites (sövite) in the central part of both rings, some dolomitites have been observed in the northwestern part of the north ring,

- okaite; a rare alkaline rock essentially composed of melilite (70%), nepheline (20%), haüyne and accessories (apatite, perovskite, magnetite, biotite).

- ijolites and urtites and

- alnoite and alnoite breccia: olivine, augite and biotite phenocrysts in a matrix of magnetite, melilite, calcite and apatite. The breccia contains diverse fragments of the enclosing rocks.

The ore zones are composed of lenses of mineralized sövite. The ore mineral is pyrochlore containing 55 to 66 percent Nb_2O_5, Perrault (72). The ore lenses generally have a nearly vertical dip.

Resources in Nb_2O_5 of the Oka area are abundant, (14):

	Mt	% Nb_2O_5
St-Lawrence Columbium & Metals	62	0.40
Columbium Mining Products Ltd.	30	0.40
Quebec Columbium Ltd.	30	0.60

A large part of the complex remains unexplored.

Nigeria

Some columbite concentrates have been produced in Nigeria in the last three decades. In fact, prior to 1962, the Western World's columbium production was almost totally Nigerian. These come from the Plateau Province near Jós, in Central Nigeria; tin is also produced from this area.

The deposits are placer deposits produced by erosion of weathered granites and concentrated by alluvial processes. The Rayfield-Gona phase of the granite intrusion is one of the richest in columbite. Cassiterite and columbite are present in all deposits, but the tin to columbium ratio is highly variable (1:10 to 0.5:1). There were twenty-four mining companies producing columbite concentrates in 1970, but four mines produced more than 90 percent of the total.

Reserves of principal producers are of the order of 10,000 t of contained Nb_2O_5.

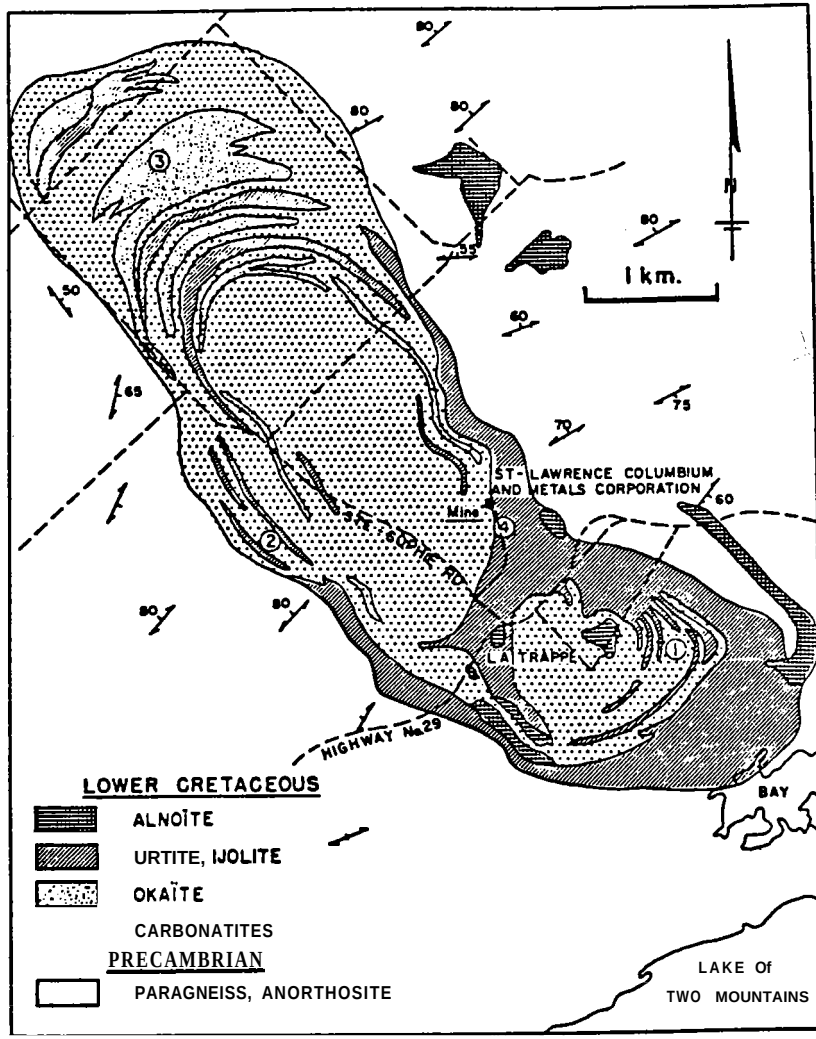


Figure 24. The Oka carbonatite, near Montreal, Canada. After Gold (1969).

Niobium Analytical Chemistry

Reliable analyses for niobium are fundamental to the search for ores, to their mining, to process control within the ore dressing plant and to marketing of concentrates; they are also necessary for quality control of metallurgical processes. A survey of analytical techniques used in the analysis of International Geoscience Standard no. **33,** Lister **(55)** reveals that X-ray fluorescence techniques were used for 48 percent of the total determinations, gravimetric for **38** percent and colorimetric for *14* percent. In our opinion, gravimetric analyses are too time-consuming for industrial control; as for colorimetric techniques, they are not as readily reliable. For the last **25** years, we have used X-ray fluorescence techniques almost exclusively for Nb determinations; hence we will report on the latter only.

Industrial X-ray fluorescence units have now been available for 30 years. During that time, we have found that they will give accurate and precise niobium determinations provided suitable techniques are used in sample preparation, valid calibration materials are available and X-ray fluorescence units are used correctly.

Sample preparation is probably the most important step. Various factors affect the intensity of the characteristic niobium line used for the determination. When analyzing a mineral powder, the following three factors should always be borne in mind:

1. Grain size: the fluorescence yield varies with grain size. Coarse powders **(>100μm)** will yield a different intensity per per cent contained element; the effect tends to become negligible in powders crushed to particles less than **5** μm D. There is no suitable mathematical model to correct for this effect; even if there were, a granulometric analysis would have to precede each niobium analysis.

2. Nature of bonding of the element analyzed: the same quantity of niobium in pyrochlore will not give the same intensity of Nb K a as if it were contained in columbite. The effect is complex and we do not have satisfactory models to correct for it.

3. Matrix effects: these are of two types. Absorption effects are due to the different absorbing power of the matrix on the Nb K a line. Enhancement effects are caused by other elements in the specimens with important characteristic lines slightly more energetic that Nb K a. There are mathematical models to correct for these effects, e.g. Lachance & Traill **(50).** To apply them, one must determine all elements in a specimen and this restricts their usefulness to research specimens.

The importance of these various influences on the critical X-ray fluorescence line can be rendered close to negligible. Grain size can be eliminated by a fusion technique. Borax or lithium tetraborate are very popular fluxes for this purpose: fused samples can be cast in the form of glass discs (ca. **2.5** cm D.) and used directly as is, in the X-ray fluorescence unit. The bonding of niobium disappears in the fused glass. As for matrix effects, they can also be rendered negligible by dilution and addition of a highly absorbing material (e.g. barium oxide). The following formulae have been used with success in our laboratory:

for ore samples:
- 1 g sample
- 5 g lithium tetraborate ($Li_2B_4O_7$)

for pyrochlore concentrate samples:
- 0.200 g sample
- 5 g borax ($Na_2B_4O_7$)
- 1 g barium oxide (BaO_2)

for ferrocolumbium:
- dissolve and heat to dryness, then treat as pyrochlore concentrate.

Standard samples have to be prepared with spectrographically pure oxides using the same fusion technique. In time, we have established that individual ore sample analyses (0.1 to 2.0% Nb_2O_5) could be analyzed to ∓ 0.02 percent Nb_2O_5 and that ferrocolumbium (50 to 60% Nb) could be analyzed to ∓ 0.2 percent Nb.

As for X-ray fluorescence instruments, two types are currently available industrially:

Wave-length dispersive systems - Crystals are used to separate the various parts of the spectrum, following Bragg's Law ($n\lambda = 2d \sin\theta$). A LiF crystal gives very good separation for niobium determinations.

Energy dispersive systems - Solid state detectors (e.g. Si(Li) or Ge) are used to disperse the characteristic radiation according to its energy. This works well with niobium using Nb L α (energy of 2.166 KeV).

We still favor wave-length dispersive systems because they are more accurate with light elements (e.g. Al, Si) but we have obtained satisfactory results with energy dispersive systems for the analysis of ores and concentrates. Energy dispersive systems are gaining in popularity for use in microprobe systems.

The analysis of IGS.33 (columbite) reported in Lister (55) is informative as to the accuracy of Nb_2O_5 determinations:

number of participating laboratories	55
Nb_2O_5 content of Nigerian columbite:	
- mean value	47.95% Nb_2O_5
- median value	47.928
- standard deviation	0.597
- recommended value	47.93
- confidence limits: lower	47.77
higher	48.07

It seems clear to us that while precision may be quite good in any particular laboratory (e.g. ∓ 0.2% Nb_2O_5), discrepancies that show up in interlaboratory comparisons may be much higher; this points to the fact that accuracy of Nb_2O_5 determinations is still not generally available.

We conclude with the unavoidable truism: good analyses depend on good analysts.

Acknowledgments

We are thankful to the organizers of Niobium 81 for the invitation to present this note, and especially for the occasion to participate in the Conference; from the list of papers, the conference does seem to cover the entire story of niobium. We are content that on returning home, we will be more useful to the cause for having shared this experience.

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References

1. Alves, B. P., Distrito niob - titanifero de Tapira Brasil Dept. Nac. Fomento Prod. Mineral Bol. **103, 1960.**

2. Amaral, G., Potassium-argon age studies on the Jacupiranga Alkaline districts, state of Sao Paulo, Brazil. In de Andrade Ramos, **20, 297-301, 1978.**

3. Bagdasaroo, Y. A. Gaydukova, V. S. Ruznetsooa, N. N. & Sidorenko, G. A., Lueshite from the carbonatites of Siberia. Dokl. Acad, Sci. U.S.S.R. Earth Sci. Section, **147, 157-159** in the English translation, **1964.**

4. Barth, T., Norsk. Geol. Tidsskrift, **8, 201,** As cited in Bragg & Claring-bull **(11), 100, 1925.**

5. Barth, T. F. W. & Ramberg, I. B., The Fen Circular Complex. In Tuttle & Gittins **(88), 225-257, 1966.**

6. Beurlen, K., Geologie von Brasilien, Gebrinder Borntraeger, Berlin, **1970.**

7. Beus, A. A. & Kalita, A. P., New data on so-called wiikite. Dokl. Acad, Sci. U.S.S.R., Earth Sci. Sect., **141, 1278-1280, 1963.**

8. Bjorlykke, H., Ein Betafit-mineral von angen, bei Kragerφ. Norsk. Geol. Tidskr, **12, 73, 1931.**

9. Borodin, L. S., Alkaline-ultramafic and carbonatite provinces of the U.S.S.R. In de Andrade Ramos **20, 223-226, 1978.**

10. Bowen, N. L., The Fen area in Telemark, Norway. Am. Journ. Sci., **8, 1-11, 1924.**

11. Bragg, W. L. & Claringbul, G. F., Crystal structures of minerals. Cornell University Press. Ithaca, New York, **1965.**

12. Brögger, W. C., Die Eruptivgesteine des Kristianiagebietes, IV, Das Fengebiet in Telemark, Norwegen. Norsk. Vidensk. Selsk. Skifter, I, Math. Naturv, kl., **(1920),** No Θ, pp. **1-408, 1921.**

13. Cameron, A. G. W., A new table of abundances of the elements in the solar system. In ahrens, L.H.I.O.J. Origin and distribution of the elements. Oxford, Permagon Press, 1968.

14. Carbonneau, C., Mining fresh carbonatite rocks for production of pyrochlore concentrates. Preprint of paper read at A.I.M.E. annual meeting. Feb 1964, New York, 1964.

15. Chernik, J. Russ. Phys.-Chim. Geo. Abt. 61, 735 in Palache, Berman and Frondel (70), 796, 1930.

16. Danni, J. C. M., Magmatic differentiation of the alkaline ultrabasic intrusion of the Ipora region, South Wet Goias, Brazil. In de Andrade Ramos (20), 149-167, 1978.

17. Da Silva, A. B., Marchetto, M. & De Souza, O. M., Geology of the Araxá (Barreiro) Carbonatite. C.B.M.M. Report. Paper read at G. A. C. annual meeting, Quebec, 1979, 1979.

18. Dawson, J. B., Oldoinyo Lengai. - an Active Volcano with Sodium Carbonatite Lava Flows. In Tuttle & Gittins (88), pp. 155-168, 1966.

19. Dawson, J. B., Kimberlites and their Xenoliths. Springer Verlag, Berlin, 1980.

20. De Andrade Ramos, J. R., Proceedings of the First International Symposium on Carbonatites. Republica federativa do Brasil, Ministerio das Minas e Energia, Dept. National do Produçao Mineral, Brazil, 1978.

21. Deans, T., Economic Mineralogy of African Carbonatites. In Tuttle & Gittins (88), 385-413, 1966.

22. De Carvalho, N. T., Aspectos geologicas e petrogiaficos do complexo ultramafico-alcalino de Catalao I, Geologia, 107-141, 165184. Preprint, 1975.

23. Doig, R., An alkaline rock province linking Europe and North America. Can. Journ. Earth Sciences, 7, 22-28, 1970.

24. Ellsworth, Am. Min. 12, 215. As cited in Palache et al (70), 792, 1927.

25. Felicissimo, J., An abridged report on the history of the first carbonatite complex identified in Brazil. In de Andrade Ramos (20), 263-274, 1978.

26. Ferguson, S. A., Colombium (Niobium) Deposits of Ontario. Ontario Dept. of Mines, Toronto. Mineral Resources Circular 14, 1971.

27. Fleischer, M. Clossary .of mineral species. Published by the Mineralogical Record, P. O. Box 783, Bowie, Maryland 20715, U.S.A., 1975.

28. Gagnon, G., La complexe de carbonatite de St-Honoré et ses depots de Niobium. Preprint of paper read at annual meeting of the Geological Association of Canada. Quebec, May, 1979.

29. Gaspar, J. C., Aspects petrográficos e mineralogicos dos carbonatitos de Catalao, Goias. Unpublished report, 1975.

30. Ginzburg, A. I. Ghorzhevskaya, S. A. Erofeeva, E. A. & Sidorenko, G. A., The chemical composition of isometric titanium, tantalum niobates. Geochemistry, Engl. Transl., no. 5, 615-636, 1958.

31. Gittins, J., Some observations on the present status of carbonatite studies. In de Andrade Ramos (20), pp. 107-115, 1978.

32. Gold, D. P., Alkaline ultrabasic rocks in the Montreal area. In Wyilie (99), 288-302, 1967.

33. Gold, D. P., The Oka Carbonatite and Alkaline Complex. In Pouliot (76), 43-62, 1969.

34. Grossi Sad, J. H. & Torres, N: Geology and mineral resources of the Barreiro Complex, Araxá, Minas Gerais. In de Andrade Ramos (20), 307-312, 1978.

35. Guimaraes, D., Relatorio sobre a jazida de pirocloro de Barreiro, Araxá, Minas Gerais. Dep. Nac. Prod. Min. Bol. 103, Rio de Janeiro, 1957.

36. Hatchett, As cited in Palache et al. (70), 1802.

37. Hasui, Y. & Cordani, U. G., Idades Potassio-argonio de rochas Eruptivas Mesozoicas do Oeste Mineiro e Sul de Goias. An XXII Cong. Bras. Geol., 1, 139-143, 1968.

38. Heinrich, E. Wm., The geology of carbonatites. Rand McNally, Chicago, 1966.

39. Heinrich, E. Wm., Contrasts in the Anatomy of Neighboring Alkalic Carbonatitic Complexes. In de Andrade Ramos (20), 22-36, 1978.

40. Heinrich, E. Wm. Giardini, A. A., Melton, C. E. & Gupta, S. K., Gases in the alkalic rocks from McClure Mountain, Colorado. In de Andrade Ramos (20), 257-260, 1978.

41. Hodkinson, I. P. & Clark, A. M., Columbite from St. Austell, Cornwall. Min. Mag., 41, 131-132, 1977.

42. Hogarth, D. D., A study of pyrochlore and betafite. Canadian Mineralogist, 6, 610-633, 1959.

43. Hogarth, D. D., Classification and nomenclature of the pyrochlore group. American Mineralogist, 62, 403-411, 1977.

44. Issler, R. S., The Seis Lagos carbonatite complex. In de Andrade Ramos (20), 233-240, 1978.

45. Jager, E., Niggli, E. & van der Veen, A. H., A hydrated bariumstrontium pyrochlore in a biotite rock from Panda Hill, Tanganyika. Min. Mag., 32, 10-35, 1959.

46. James, T. C. & McKie, D., The alteration of pyrochlore to columbite in carbonatites in Tanganyika. Min. Mag., 31, 889-900, 1958.

47. Kalita, A. P., New data on some minerals in the Alakurtti vein, nr. 1. Trudy Inst. Miner. Geokhim. i. Kristallokhim. Redkikh Element, Voprosy Miner. Geokhim. i. Genezisa Mestorozhdenii Redkikh. Element nr. 2, 164-172 (Chem. Abstr. 19602, 54, 19317 d/i), 1959.

48. Kerr, P. F. & Holmes, R. J., X-ray study of the tantalum mineral simpsonite. Bull. G. S. A., vol. 56, 1945.

49. King, B. C. & Sutherland, D. S., The carbonatite complexes of Eastern Uganda. In Tuttle & Gittins (19661, 73-126, 1966.

50. Lachance, G. R. & Traill, R. J., A practical solution to the Matrix Problem in X-ray Analysis. Can. Spectroscopy, 11, 43-49, 63-72, 1966.

51. Lacroix, A., Minéralogie de la France et de ses colonies. Vol. 1, pp. 379 et sq., 1912.

52. Laplante, R., Etude de la minéralisation en Nb-Ta-U du complexe igné alcalin du canton Crevier, Comté Roberval, Lac St-Jean, P. Q. These M. Sc. A., Ecole Polytechnique, 1980.

53. Le Bas, M. J., Carbonatite-nephelinite volcanism. John Wiley & Sons, New York, 1977.

54. Leonov, Piryutko & Keler, Bull Acad. Sci. (Div. of Chem. Sci.) 5, 756-60. As cited on J.C.P.D.S. card no 20-272, 1966.

55. Lister, B., The preparation of twenty one standards, IGS 20 39. Preliminary work and assessment of Data. Geostandards Newsletter, 2, 157-186, 1978.

56. Manker, E., Columbium-an outlook. Paper presented at 83rd annual general meeting, C.I.M., Calgary, Alberta, May 3-6, 1981 to be published in C.I.M. Bulletin, 74, no. 832, 93, 1981.

57. Mason, B., Principles of geochemistry. John Wiley & Sons, New York, 1952.

58. Marsh, J. S., Relationships between Transform Directions and Alkaline Igneous Rock Lineaments in Africa and South America. Earth and Plan. Sci. Letters, 18, 317-323, 1973.

59. Mc Connell, R. B., Geological Development of the Rift system of Eastern Africa. Bull. G.S.A., 83, 2549-2572, 1972.

60. Mc Gaw, H., Crystal structure of double oxides of the perovskite type. Proc. Phys. Soc., 58, 133-152, 1946.

61. Mc Kie, D. & Francis, E. J., Nyererite a new volcanic carbonate mineral from Oldoinyo Lengai, Tanzania. Z. Krist, 145, 73-95, 1977.

62. Meigan & Hugel, As cited in Palache et al (70), 735, 1913.

63. Nickel, E. H., Wodginite - a new tin-manganese tantalate from Wodgina, Australia and Bernic Lake, Manitoba. Can Mineralogist, 7, 390-402, 1963.

64. Nickel, E. H., Latrappite, a proposed new name for the perovskite-type calcium niobate mineral from the Oka area, Quebec. Can. Min., 8, 121-122, 1964.

65. Nickel, E. H. & McAdam, R. C., Niobium perovskite from Oka, Quebec: a new classification for minerals of th perovskite group. Can. Min., 7, 683-697, 1963.

66. Nickel, E. H., Rowland, J. F. & Maxwel, J. A., The composition and crystallography of Niocalite. Can. Min., 6, 264-272, 1960.

67. Nickel, E. H., Rowland, J. F. & Mc Adam, R. C., Ixiolite, a columbite substructure. Am. Mineralogist, 48, 961-979, 1963.

68. Nickel, E. H., Rowland J. F. & Charette, D. J., Niobophyllite the niobium analogue of astrophyllite; a new mineral from Seal Lake, Labrador. Can. Mineralogist, 8, 40-52, 1964.

69. Olson, J. C. & Pray, L. C., The Mountain Pass Rare Earth Deposit. Bull. California Div. Mines and Geology, 170, 23-29, 1954.

70. Palache, C., Berman, H. & Frondel, C., The system of mineralogy of J. D. Dana and E. S. Dana. 7th edition, Volume 1, J. Wiley & Sons, New York, 1944.

71. Parker, Adama & Hildebrand, U.S.G.S., Paper 450C, 4-6. As cited on JCPDS card, 1962.

72. Perrault, G., La composition chimique et la structure cristalline du pyrochlore d'Oka, P. Q. Canadian Mineralogist, 9, 383-402, 1968.

73. Perrault, G., Composition minéralogique des souches metallurgiques 72 à 91. minerai de columbium de St-Honoré Qué. Private report to Niobec Mines Ltd., IREM/IMERI no. 78-3, 1978.

74. Perrault, G., Boucher, C., Canillo, E. & Rossi G., Structure cristalline du nenadkevichite. Act. Cryst., B-29, 1432-1438, 1973.

75. Prins, P., Geochemical Aspects of the Alkaline Carbonatite complexes of Damaraland, South West Africa. In de Andrade Ramos (1978), 179-188, 1978.

76. Pouliot, G., Geology of the Monteregian Hills. Guide Book, GAC-MAC (19691, Montreal.

77. Ribeiro, M., Structural setting of some alkaline pipes in the Rio Grande do Sul Shield. In de Andrade Ramos (20), 171-175, 1978.

78. Rotherham, D.C. (1981): Private communication.

79. Roth, R. S., Classification of perovskite and other ABO_3-type compounds. Journ. Research, N.B.S., 58, 75-88, 1957.

80. Safiannikov, A., Gisement de pyrochlore de Lueshe. Bull, Soc., Geol. Belgique, 90, B461-486, 1966.

81. Safiannikoff, A. & Van Wambeke, L., Sur un terme plombifére du groupe pyrochlore-microlite. Bull. Soc. Franc. Min. Crist., 84, 382-384, 1961.

82. Scheibe, L. F., Fazenda varela carbonatite, Lajes, Santa Catarina, Brazil. In de Andrade Ramos (20), 137-146, 1978.

83. Shand, S. J., The Eruptive Rocks. Thomas Murby & Co., London, 1950.

84. Sitnin, A. A. & Leonova, T. N., Loparite, a new accessory mineral of albitized and geisenized granites. Dokl. Acad, Sci. U.S.S.R. Earth Sci. Section, English translation, 140, 1090-1093, 1963.

85. Skorobogatova, N. V., Sidorenko, G. A. Dorofeeva, K. A. & Stolyarova, T. I., On plurnbopyrochlore. Geol. mestorozh. redikh elementov, I zd. "Nedra", 30, 84-95. In MA. 9-226, 1966.

86. Stockford, H. R., The James Bay Pyrochlore Deposit. Bull. C.I.M., June 1972, pp. 1-9, 1972.

a7. Sturdivant, J. H., Zeit Kristall, 75, 88-108. As cited in Weitzel (95), 1930.

88. Tuttle, O. F. & Gittins, J., Carbonatites. Interscience Publishers, New York, 1966.

89. Vallée, M. & Dubuc, F., The St-Honoré Carbonatite Complex, Quebec. Trans. C.I.M., LXXIII, 346-356, 1970.

90. Van der Veen, A. H., A study of pyrochlore. Geol. serie, deel 22, Verhandelingen van het Koninklyk Nederlands geologish mijnbonwkundig genootschap, Mijnbonwstrast 20. Delft (Holland), 1963.

91. Van Wambeke, L., Kalipyrochlore, a new mineral of the pyrochlore group. Amer. Min. 63, 528-530, 1978.

92. Von Eckerman, H., The alkaline district of Alnö Island. Sveriges Geol. Undersök. 5er Ca., 36, 1948.

93. Wedepohl, H. K., Handbook of Geochemistry. Springer-Verlag, Berlin, 1978.

94. Weidman 6 Lenher, Am. Journ. Sci., 23, 287. As cited in Palache et al. (70), 1907.

95. Weitzel, H., Kristallstrukturverfeinerung von Wolframiten und Columbiten. Zert. Kristall., 144, 238-258, 1976.

96. Weyll, A. V., The 38th Parallel Lineament and its Relationship to Ore Deposits. Econ. Geol. 67, 879-894, 1972.

97. White, M. G., Niobium (columbium) and tantalum Resources of Brazil. Unpublished professional report, 1975.

98. Wyllie, P. J., Silicate - carbonate systems with bearing on the origin and crystallization of carbonatites. In de Andrade Ramos (20),61-78, 1978.

99. Wyllie, P. J., Ultramafic and related rocks. John Wiley & Sons, New York, 1967.

100. Zedlitz, Der Perowskit, Mineralogische und rmntgenographische. Untersuchugen an Perowskit, Uhligit und Dysanolyte. Jb. Min., Beil. Bd., 75, 245-296, 1939.