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ELECTRON MICROPROBE ANALYSES FOR PYROCHLORES FROM OKA, QUEBEC

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ABSTRACT

Thirteen electron microprobe analyses were performed on a uranpyrochlore and on three homogeneous, two zoned, and two uranium-rich pyrochlore grains from the Oka deposit, Quebec. The results, combined with reported compositional data, show that most Oka pyrochlores have a typical pyrochlore composition, but some are enriched in uranium, thorium and zirconium.

INTRODUCTION

A pyrochlore concentrate produced from the ore at Oka, Quebec, by St. Lawrence Columbium and Metals Corporation on October 4, 1974 was obtained by the Mineral Sciences Laboratories, Department of Energy, Mines and Resources, Ottawa. This concentrate was blended with a pyrochlore ore from the same deposit to prepare material for a chemically certified reference ore. To characterize the material, thirteen microprobe analyses were performed on eight pyrochlore grains from the concentrate. The analyses are presented here to supplement existing data on the mineral (Perrault 1968), and to further characterize the Oka pyrochlore.

METHOD OF ANALYSIS

A polished section was prepared from the pyrochlore concentrate and scanned with a

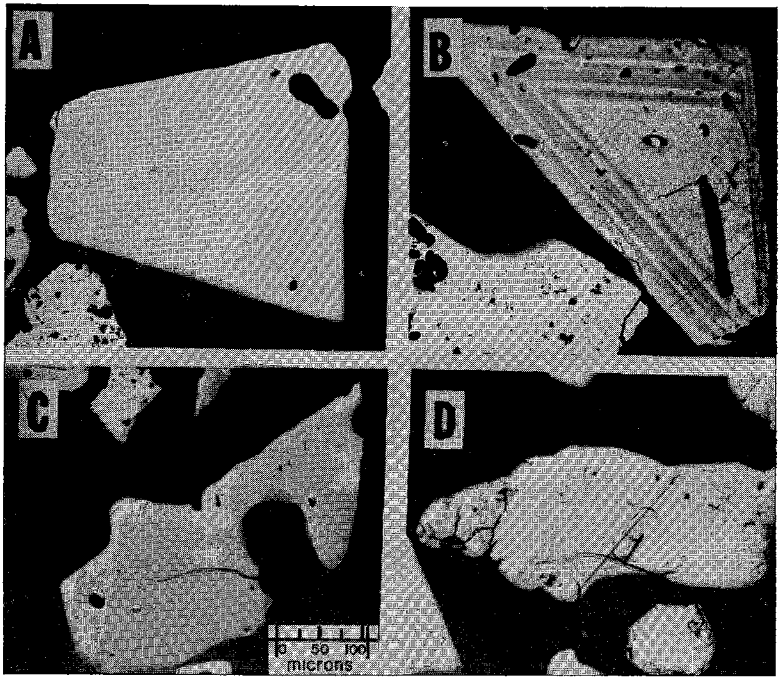

FIG. 1. Photomicrographs of grains in polished sections: (A) typical pyrochlore grain; (B) zoned pyrochlore grain; (C) uranian pyrochlore (grey) (grain x reported in Table 1) with a second U-rich phase (white); (D) uranpyrochlore (grey) (grain y reported in Table 2) with a second U-rich phase (white).

TABLE 1. MICROPROBE ANALYSES AND MOLECULAR COMPOSITIONS FOR OKA PYROCHLORES.

Oxide	Pyrochlore			Zoned Pyrochlores				Uranian Pyrochlore		Uranpyrochlore		Uranian Pyrochlore	
				A		B		X		Y		Z	
	C	D	K	Zone 1	Zone 2*	Zone 1	Zone 2*	Host	Second	Host	Second	Host	Second
Na_2O	6.01	3.69	5.76	6.37	6.11	5.38	5.67	4.68	1.68	1.11	0.00	5.82	0.99
CaO	17.05	18.29	15.19	15.06	14.87	17.06	15.58	14.17	6.12	6.33	5.06	12.86	9.19
MnO	0.07	0.24	0.21	0.10	0.06	0.04	0.03	0.11	0.51	0.15	0.23	0.13	0.10
SrO	0.68	0.27	0.44	0.48	0.61	0.72	0.73	0.61	0.99	0.21	1.18	0.35	0.78
FeO	0.66	1.38	1.21	1.10	0.37	1.09	0.69	2.28	2.34	2.75	3.00	1.45	2.01
U_3O_8	0.00	0.00	0.24	0.00	0.64	0.00	0.36	8.82	10.35	24.79	20.73	3.58	15.11
Ce_2O_3	3.28	6.47	6.17	5.11	4.02	2.56	4.87	5.51	6.35	3.01	3.49	7.82	4.53
Nd_2O_3	0.25	0.79	0.45	0.41	0.46	0.21	0.50	0.84	0.98	0.58	0.58	1.15	0.74
La_2O_3	0.69	0.97	1.08	0.97	0.96	0.67	0.92	1.15	1.41	0.77	0.79	1.64	1.14
Nb_2O_5	65.33	59.02	62.19	64.07	63.31	64.47	62.36	56.37	59.19	51.45	49.62	57.82	52.22
Ta_2O_5	0.12	0.16	0.45	0.37	0.56	0.39	0.39	2.23	2.67	3.46	3.88	3.08	4.11
TiO_2	4.21	5.57	3.84	3.26	4.08	3.41	4.68	3.57	3.98	5.00	5.14	4.44	6.33
ZrO_2	0.00	0.41	0.19	0.14	0.08	0.11	0.11	0.32	0.30	0.16	0.27	0.46	0.30
SiO_2	--	--	--	--	--	--	--	0.00	0.42	0.00	3.16	0.00	1.61
Total	98.35	97.26	97.43	97.44	96.33	96.11	96.39	100.67	97.27	99.78	97.14	100.61	99.15
Element						*Molecular Compositions*							
Na	0.71	.46	.71	0.77	0.74	.65	.69	.60	.21	.15	0.00	.73	.13
Ca	1.12	1.26	1.03	1.01	1.00	1.15	1.05	1.01	.43	.48	.39	.89	.66
Mn	0.004	.01	0.01	0.01	.004	.002	.002	.01	.03	.01	.01	.01	.004
Sr	0.02	.01	0.02	.02	.02	.03	.03	.02	.04	.01	.05	.01	.03
Fe^{2+}	0.03	.07	0.05	.04	.02	.06	.04	.05	.13	.16	.18	.06	.11
U	0.00	.00	0.004	.00	.01	.00	.004	.13	.15	.38	.34	.05	.22
Ce	0.07	.15	0.14	.12	.09	.06	.10	.13	.15	.08	.09	.18	.11
Nd	0.01	.02	0.01	.01	.01	.004	.01	.02	.02	.01	.01	.03	.02
La	0.01	.02	0.03	.02	.02	.02	.02	.03	.03	.02	.02	.04	.03
Total in *A*	1.98	2.00	2.00	2.00	1.91	1.96	1.98	2.00	1.19	1.30	1.09	2.00	1.31
Nb	1.80	1.71	1.79	1.82	1.80	1.83	1.77	1.69	1.75	1.66	1.63	1.69	1.59
Ta	0.01	.002	0.01	.01	.01	.01	.01	.04	.05	.06	.08	.05	.08
Ti	0.19	.27	0.17	.15	.19	.16	.22	.18	.19	.27	.28	.23	.32
Zr	0.00	.01	0.01	.004	.002	.004	.004	.02	.01	.01	.01	.01	.01
Fe^{3+}	0.00	.004	0.02	.02	.00	.00	0.00	.07	.00	0.00	.00	.02	.00
Total in *B*	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
O_6	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
O in (OH+F)	0.58	0.72	0.62	0.59	0.54	0.59	0.56	0.68	0.00	0.79	1.02	0.69	0.75
A/B	0.99	1.00	1.00	1.00	0.96	0.98	0.99	1.00	0.59	0.65	0.55	1.00	0.66

* Zone 2: narrow zones ThO_2, BaO, Al_2O_3, MgO, and Y_2O_3 looked for but not detected.   (OH+F) not determined.

Materials Analysis Company (MAC) electron microprobe to identify the typical and unusual varieties of pyrochlore. Selected areas were analyzed for Na, Ca, Fe, Mn, Sr, U, Ce, Nd, La, Nb, Ta, Ti, Zr, Th and Si by using the following standards: Mn, Zr, Ta, and Nb metals, sphene for Ca, Ti and Si, Fe_2O_3 for Fe, CeO_2 for Ce, $NaNbO_3$ for Na, $NdFeO_3$ for Nd, monazite for La, strontianite for Sr, pitchblende for U and uranothorite for Th. The data were processed with the computer program of Rucklidge & Gasparrini (1969).

CHEMICAL ANALYSIS AND MODAL COMPOSITIONS OF PYROCHLORE GRAINS

Three homogeneous grains (C, D, and K) two zoned grains (A, B, Fig. 1), two uranium-rich pyrochlore grains (X, Z) and a uranpyrochlore grain (Y) were analyzed. The uranium-rich grains and uranpyrochlore contain inclusions of a second U-rich phase and both were analyzed. The microprobe data are reported as oxides (Table 1) to be consistent with the manner of reporting pyrochlore analyses (Perrault 1968; Hogarth 1961; Vlasov 1966; Palache *et al.* 1944).

The general formula for pyrochlore is $A_{2-x}B_2O_6(OH,F)$ (Vlasov 1966) with *A* containing Na, Ca, Mn, Sr, Fe^{2+}, U, Ce, Nd and La, (as well as Y and Ba not found in Oka pyrochlore), and *B* containing Nb, Ta, Ti, Zr and Fe^{3+}. The main constituents in the *A* position in ideal pyrochlore are Na and Ca, and in the *B* position, Nb. These elements are replaced to varying degrees by the other elements. In published analyses of pyrochlore, Si is generally considered to be an impurity — a point of view accepted also in this study. Si was found only in the U-rich inclusions in uranian pyrochlore and uranpyrochlore; although no discrete Si-rich phase could be resolved with the microprobe, the Si is believed to be present as minute inclusions of a silicate. Molecular compositions were calculated from the chemical analyses by making the total mole content for Nb+Ta+Ti+Zr equal to 2 (*B* position) and calculating proportional values for the other elements (*A* position). Where the total for the *A*-position elements exceeded 2, Fe was redistributed among the two positions so that the mole content in each was equal to 2. Fe in the *B* position was then considered to be Fe^{3+}, and, in the *A* position, Fe^{2+} (Table 1). The amount of O_2 required to combine with the elements exceeded 6 for all grains except X_{second}. The excess O_2 was considered as being in the (OH, F) position. The OH and F contents were not determined.

DISCUSSION

The niobium contents (in atomic per cent) of the grains analyzed are significantly higher than tantalum, and values for (Nb+Ta)/Ti are larger than 6, hence all the grains belong to the pyrochlore group (Vlasov 1966). Further classification of the minerals within the group is currently under way by the IMA Commission on New Minerals and Mineral Names. In this paper the name pyrochlore will refer to a mineral in which no element other than Na and Ca exceeds 20% of the total atoms in the *A* position. Thus all the pyrochlore-group minerals found to date at Oka (Nickel 1962; Perrault 1968; this study), except Y_{host} and $Y_{sec.}$ (this study), are pyrochlores. Uranium accounts for more than 20% of the *A*-position atoms in Y_{host} and $Y_{sec.}$. The mineral is referred to as uranpyrochlore in this paper although the name hatchettolite has also been used for a mineral of this composition.

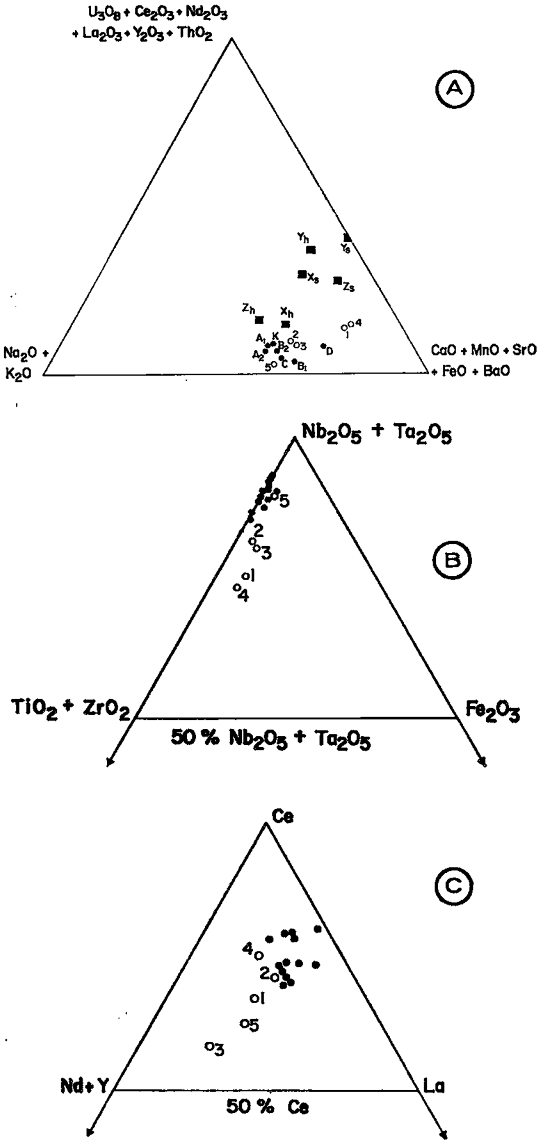

FIG. 2. Ternary diagrams for the distribution of elements in Oka pyrochlores: (A) elements in the *A* position; (B) elements in the *B* position; (C) rare-earth elements in the *A* position.
Open circles: pyrochlore (Perrault (1968); dots: pyrochlore (this study); solid squares: U-rich pyrochlore (this study).

Perrault (1968) classified the Oka pyrochlores on the basis of their colour, mode of occurrence, and composition as pyrochlores 1 to 5. This classification is adhered to in this study and expanded to accommodate new variants. To compare the pyrochlores of Perrault and this study, ternary diagrams for the distribution of elements were prepared from the pyrochlore data of these two investigations (Fig. 2). Figure 2 (*A* position) shows that pyrochlore C and zone 1 of pyrochlores A and B are similar to pyrochlore 5 of Perrault. Pyrochlore K and zone 2 of pyrochlores A and B are also similar to pyrochlore 5 but contain minor amounts of U_3O_8. Pyrochlore D may be similar to pyrochlore 2 of Perrault. Pyrochlores X and Z and the uranium-enriched secondary phases within them are uranium-rich pyrochlores.

On the basis of this study and other data, the Oka pyrochlores and pyrochlore-group minerals are divided as follows (Oka pyrochlores 1 to 5 were defined originally by Perrault 1968):

(1) Oka pyrochlore
  (a) pyrochlore 1, low-thorian and low-uranian pyrochlore, very fine-grained, red in thin section, (ThO_2=1.10 wt %, U_3O_8 =0.69 wt %)
  (b) pyrochlore 2, common Oka pyrochlore, coarse-grained, chocolate-brown in hand specimens, reddish-brown in thin section (pyrochlore D, this study).
  (c) pyrochlore 3, low thorian pyrochlore, medium-grained, amber in thin section (ThO_2 = 1.47 wt. %)
  (d) pyrochlore 4, zirconian pyrochlore, medium-grained, amber in thin section (ZrO_2 = 4.10 wt. %).
  (e) pyrochlore 5, common Oka pyrochlore, medium-grained, beige (pyrochlore C and zone 1 in pyrochlores A and B, this study).

(f) pyrochlore 6, low-uranium pyrochlore (pyrochlore K and zone 2 of pyrochlores A and B this study).

(g) pyrochlore 7, uranium pyrochlore (pyrochlore X_{host} Z_{host} $X_{sec.}$ and $Z_{sec.}$ this study).

(h) pyrochlore 8, thorian pyrochlore with about 8 wt. % ThO_2 (Nickel 1962).

(2) Uranpyrochlore (Y_{host} and $Y_{sec.}$ this study).

The compositional and physical variations of the pyrochlores may reflect pauses in the evolution of the carbonatite, where equilibrium was attained and specific types of pyrochlore crystallized in response to the thermodynamic and crystallochemical condition associated with the pauses. Existing data do not permit extensive interpretation to be made along this direction. However, the presence of zoned pyrochlore grains suggests that conditions for depositing the low-uranium pyrochlores of one zone (pyrochlore 6) alternated with the conditions for depositing the uranium-free pyrochlore (pyrochlore 5) of the other zone. It is possible that similar fluctuations existed for the deposition of the low-thorian pyrochlores (1 and 3) and pyrochlores 2 and 5. It is likely that different conditions existed for the deposition of the thorian and uranian pyrochlores (pyrochlores 7 and 8) and for the uranpyrochlore.

The A/B values are close to 1 for all Oka pyrochlores except the uranian pyrochlores ($X_{sec.}$ and $Y_{sec.}$) which contain more than 10.35 wt.% U_3O_8. The A/B values for X_{sec} and Y_{sec} and for the uranpyrochlore are between 0.55 and 0.66. Hogarth has shown that, for 63 pyrochlores analyzed previously, A/B varies from 0.33 to 1. Recalculation of 17 analyses reported by Vlasov suggests that A/B is close to 1 (0.77 to 1) for material analyzed as pyrochlore, and is much less (0.35 to 0.90) for the pyrochlore-group varieties enriched in U, Ce, Y, Ba and Sr in the A position. This corresponds with the data for the Oka pyrochlore-group minerals and suggests that A/B for pyrochlore is close to 1 and is less than 1 for the varieties enriched in heavy elements (U, Ce, Y, Ba and Sr) in the A position.

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