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PYROCHLORE GROUP MINERALS IN CARBONATITES FROM LOE-SHILMAN, KHYBER AGENCY, N.W.F.P.

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ABSTRACT

Metamict, partially metamict and non metamict species of pyrochlore group minerals have been identified from a sheet like carbonatite complex in Loe-Shilman, Khyber Agency. Microscopy, X-ray diffractometry and partial chemical analyses are reported which indicate a chemical and structural variability between various species of pyrochlore. A multiplicity of intrusive activity is considered to be responsible for the variations described.

INTRODUCTION

Loe-Shilman is located at latitude 34°13′32″ N and 70°09′26″ E, about 40 miles north west of Peshawar (topo sheet No. 38 N/4). Carbonatite body exposed at Loe-Shilman is a sheet like intrusion (Fig. 1) in Palaeozoic metasediments in the north-western part of Khyber Agency N.W.F.P., Pakistan. This body is a part of an extensive alkaline igneous province extending from Warsak to Tarbela (Kempe and Jan 1970: Ashraf and Chaudhry 1977, Butt et al. 1980) where several centres of alkaline magmatism have so far been described. Radioactivity in the carbonatite of Khyber Agency was discovered in 1976 and some preliminary work suggested it to be due to pyrochlore (Syed 1975). Rahman (1980) interpreted the radioactive mineral to be betafite. This study provides additional data on radioactive minerals and attempts to propose a model for their genetic relation between carbonatite and the radioactive minerals.

Geological Setting

The Loe-Shilman Carbonatite makes the westernmost reported occurrence of a belt of alkaline rocks in Pakistan that extends up to southern bank of Tarbela in the East. Other occurrences of the alkaline rocks include Warsak (Kempe and Jan 1970), Malakand (Ashraf and Chaudhry 1977), Koga (Saddiqui et al., 1967). These rock are interpreted to be a part of the alkaline province around Peshawar plain and are considerd to have been associated with rifting (Jan et al., 1979, Butt et al., 1980).

Carbonatites

Carbonatites of the alkaline province are known only from three localities namely Malakand, Koga and Loe-Shilman.

The Loe-Shilman carbonatite exhibits extreme compositional variability which is a function of ratio of carbonate minerals to that of silicates. Carbonates include calcite and dolomite with varying proportions of other minerals such as apatite, strontianite, magnesio-arfvedsonite to magesio-reibeckite, biotite, phlogopite, sphene, aegirine-augite, alkali feldspar, quartz, pyrochlore, monazite and zircon.

METHODS OF INVESTIGATION

The radioactive minerals

Standard transmitted and reflected light microscopic techniques were employed for the study of radioactive minerals. In addition, selected carbonatite rock samples with high radioactivity were crushed and subjected to heavy liquid floatation to obtain heavy mineral suite of these rocks. Autoradiographic techniques were employed to identify radioactive grains in the concentrate. Binocular examination of autoradiographic emulsion plates revealed the following five colour varieties of radioactive minerals:

a) A vitreous black variety that gives a relatively high track density per unit exposure time on alpha sensative emulsion plates. These grains are generally in the form of octahedra with submetallic to vitreous lustre and subconchoidal to uneven fracture. The mineral has a hardness of about 5 and gives a pale yellow streak. Anhedral grains with similar character were also encountered.

b) A dark brown variety with a relatively high track density on alpha sensitive plate. Other physical properties are similar to those described above for the black variety.

c) A vitreous yellow variety with a relatively low track density on alpha sensitive plate. The mineral also forms relatively coarse octahedra with vitreous lustre, subconchoidal to uneven fracture, a hardness of about 5 and white streak.

d) A dull yellow variety with a relatively low track density. Other physical properties are similar to those described above for vitreous yellow variety.

e) A honey yellow variety with a relatively low track density. This mineral forms cubes, with resinous lustre and conchoidal fracture.

All the above varieties were separately hand picked under a binocular microscope and crushed to fine powder. These were exposed to Cu Kα radiation in capillary tubes mounted on a camera at 40 KV and 30 MA for 4 hours using a Ni filter. The X-ray powder data thus obtained are given in Table I Metamict and partially metamict varieties were subsequently heated at 1100° for one hour and the resulting product was X-rayed for powder diffraction data presented in Table II. Honey yellow mineral was identified to be monazite whereas all other varieties show an X-ray powder diffraction pattern of pyrochlore.

For the purpose of chemical analyses, the radioactive minerals were also hand picked under a binocular microscope. Since it was not possible to differentiate between metamict non-metamict and partially metamict grains under the microscope, these mineral grains were collected in two groups; yellow coloured grains and dark brown to black grains. The chemical data are given in Table III.

DISCUSSION AND CONCLUSIONS

X-ray powder diffraction data indicated the crystal structure of pyrochlore for two metamict, a partially metamict and a non-metamict mineral. Chemical data for each of these species could not be obtained. However partial chemical data on yellow varieties indicates a genrally lower uranium and higher Ti as compared to dark brown and black varieties (Table III). Data on Nb and Ta content of pyrochlore from Loe-Shilman was not obtained during this investigation but previously published data (Rahman 1980, Syed 1975) on dark brown varieties suggest that it contains 20.9 to 22% Nb, 6.4 to 7% Ta and as high as 35% U. Corresponding data for yellow varieties are not available.

In general, the composition of the minerals belonging to pyrochlore group resembles those of perovskite group, but invariably have as an additional anion, O, OH or F. The type formula for them is $A_{2-\times}$ B_2O_6 (O, OH, F), the most important members being microlite (Ca Na Ta_2O_6 (OH), pyrochlore (Ca Na Nb_2O_6 F) and betafite (Ca, U) (Nb, Ti_2) O_6 (OH). Ginsburg *et al.,* (1977) plotted the composition of pyrochlore group minerals (Fig. 2) for Nb, Ta and Ti (chief cations only) which shows a limited diadochy between Ti and Ta whereas a complete solid solution series seems to exist between Nb–Ta and Nb–Ti. Vlasov (1966) distinguished the pyrochlore and betafite minerals by the following chemical formulae.

Pyrochlore	$(Na, Ca)_{2-\times}$	Nb_2O_6 (OHF)
Betafite	$(U, Ca)_{2-\times}$	$(Nb, Ti, Ta)_2\ O_{6-\times}\ (OH)_{1+\times}$

It is obvious from the above formulae that the chief cation substitution occurs at the sites of Ti, Nb and Ta in the structure. Chemical composition of

TABLE I. X-RAY POWDER DIFFRACTION DATA ON THE RADIOACTIVE MINERALS

Vitreous black		Dark brown varieties		Vitreous yellow		Yellow		Pyrochlore standard		Betafite standard	
d A°	I/I	d A°	I/I	d A°	I/I	d A°	I/I	d A°	I/I	d A°	I/I
						5.98	10				
						3.45	1				
						3.35	1	5.99	10	4.05	60
						3.17	8	3.13	6	3.55	20
Totally		2.99	100	Totally		2.99	100	2.995	100	3.20	100
metamict		2.61	10	metamict		2.80	1	2.594	16	2.99	20
no lines				no line		2.70	1	1.996	6	2.81	10
obtained		1.84	60	obtained.		2.60	15	1.8338	40	2.61	10
		1.56	30			2.25	1	1.5637	30	2.50	80
						2.02	1	1.4968	8	2.02	20
						2.00	6	1.3500	2	1.83	50
						1.94	4	1.2961	4	1.71	30
						1.87	1	1.1894	12	1.67	30
		Partially				1.83	50	1.1590	8	1.59	10
		metamict.				1.79	2	1.0580	8	1.48	20
						1.75	1	0.9977	8	1.36	20
						1.58	1	0.9164	4	1.25	10

1.56	40	0.8764	12	1.20	10
1.50	10	0.8639	10	1.153	20
1.45	3	0.8196	8		
1.35	5				
1.30	5				
1.19	10				
1.16	10				
1.14	2				
1.09	2				
1.06	8				
1.00	8				
0.925	3				
0.91	2				
0.88	8				
0.87	8				
0.84	1				
0.825	5				
0.796	6				

TABLE II. X-RAY POWDER DIFFRACTION DATA ON HEAT TREATED PYROCHLORES

Vitreous black		Dark brown varieties		Vitreous yellow		Pyrochlore standard		Betafite standard	
d A°	I/I	d A°	I/I	d A°	I/I	d A°	I/I	d A°	I/I
5.84	5	5.84	5	5.98	10				
3.27	5	3.27	5	3.45	1				
3.09	5	3.09	5	3.35	1	5.99	10	4.05	60
				3.17	8	3.13	6	3.55	20
2.96	100	2.96	100	2.99	100	2.995	100	3.20	100
2.56	20	2.56	20	2.80	1	2.594	16	2.99	20
1.99	1	1.99	1	2.70	1	1.996	6	2.81	10
1.82	70	1.82	70	2.60	15	1.8338	40	2.61	10
1.56	40	1.56	40	2.25	1	1.5637	30	2.50	80
1.48	10	1.48	10	2.02	1	1.4968	8	2.02	20
1.45	1	1.45	1	2.00	6	1.3500	2	1.83	50
1.33	1	1.33	1	1.94	4	1.2961	4	1.71	30
1.28	5	1.28	5	1.87	1	1.1894	12	1.67	30
1.18	10	1.18	10	1.83	50	1.1590	8	1.59	10
1.15	10	1.15	10	1.79	1	1.0580	8	1.48	20

1.05	10	1.05	10	1.75	1	0.9977	8	1.36	20
0.99	4	0.99	4	1.56	40	0.9164	4	1.25	10
0.91	1	0.91	1	1.50	8	0.8764	12	1.20	10
0.879	1	0.879	1	1.45	3	0.8639	10	1.153	20
0.871	5	0.871	5	1.35	5	0.8196	8		
0.82	5	0.82	5	1.19	10				
					10				
					2				
					1				
					8				
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					8				
					8				
					1				
					3				
					6				
					6				

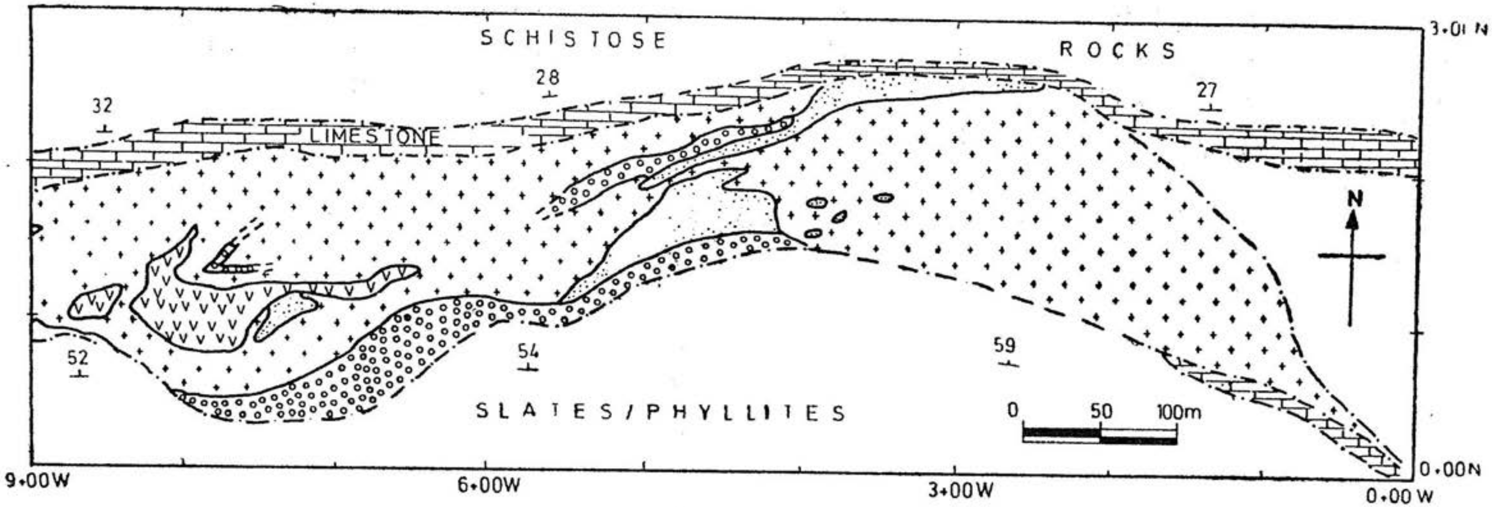

FIG 1. GEOLOGICAL MAP OF GARANG, LOE-SHILMAN KHYBER AGENCY

(After Qureshi et al, 1980)

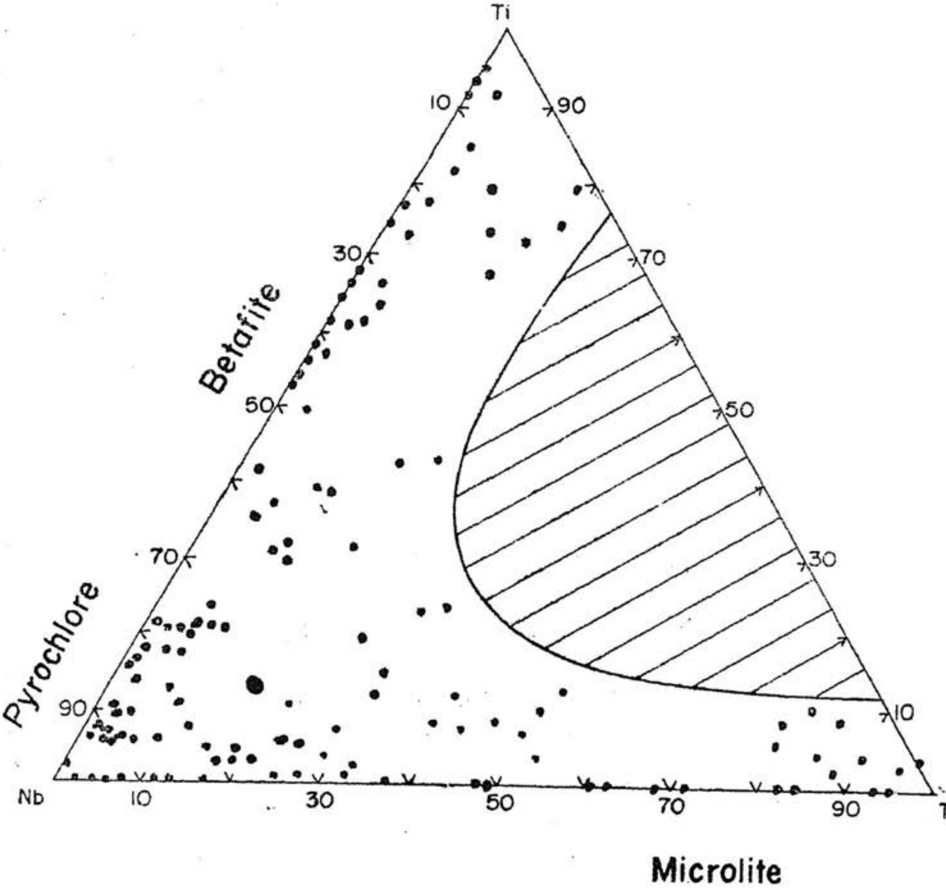

Fig. 2. Composition diagram (chief cations only) of the minerals in the pyrochlore group (Ginsburg *et al.*, 1977). Large dot indicates composition of Loe-Shilman pyrochlore.

natural pyrochlore group minerals suggests (Fig. 2) a complete solid solution series between pyrochlore – betafite and pyrochlore – microlite, and a limited solid solution between microlite and betafite. Ta does not seem to occur in natural betafite in amounts in excess of about 20% whereas titanian betafite is a member devoid of Nb. Natural pyrochlore-betafite compositions are dominantly a function of variability in Nb and Ti whereas the substitutional behaviour of Ta at this structural site is similar throughout the solid solution series. From the view point of chemical classification of betafite-pyrochlore group of minerals Ta content can be neglected since it remains constant for both pyrochlore and betafite. The ratio of Nb and Ti content should, therefore, define the limit. Vlasov's (1966) chemical classification of pyrochlore-betafite does not take Ti content of these minerals into consideration.

Instead, Nb and Ta contents are used to define the limits for pyrochlore and betafite (Table IV). Following the classification proposed by Vlasov (1966), Rahman (1980) argued that the dark brown radioactive mineral of Loe-Shilman carbonatite is betafite. Chemical data obtained during the present investigation shows that the Ti content of the mineral ranges from 2.78 to 6.46%. The titanium content of dark brown radioactive mineral combined with Nb and Ta values for the same mineral by Rahman (1980) and Syed (1975) plotted on composition diagram of the mineral (chief cation only) in the pyrochlore group (Ginsberg et al., 1977) falls close to pyrochlore composition (Fig. 2). The Ti content of yellow minerals is relatively higher but that too is too low to approach betafite composition. X-ray powder diffraction data obtained for these radioactive minerals also support a pyrochlore structure with wide departure from the structure of betafite. The disparity between the atomic structure and chemical composition of radioactive minerals from Khyber Agency (Rahman, 1980) also supports the chemical classification of pyrochlore and betafite based on Nb–Ti ratio rather than Nb–Ta ratio. Hogarth's (1961) classification of betafite being a member of pyrochlore group with 15 or more per cent uranium does not hold for the pyrochlores of Loe-Shilman (see Table III). The difference in X-ray powder diffraction patterns of pyrochlore and betafite seem to be a function of Ti–Nb ratio rather than Nb–Ta.

No detailed work has been done to establish the sequence of emplacement and relative ages of the carbonatites and related rocks in Loe-Shilman Khyber Agency. It is, however, unlikely that various rock types emplaced in a single sheet-like body (Fig. 1) are chronologically so apart to account for variability in the degree of metamictization. As described earlier, the pyrochlore ranging from totally metamict, through partially metamict to non-metamict species have been identified in Loe-Shilman Carbonatite. Field data (Qureshi et al., 1980) indicate that amphibole carbonatite was emplaced as the first phase followed by biotite carbonatite and subsequently the intrusion of strontranite-witherite carbonatite completed the carbonatite magmatism. Qureshi et al. (1980) reported that only amphibole carbonatite was pyrochlore bearing whereas Jan et al. (1979) reported a yellowish pyrochlore from strontianite-witherite carbonatite. Varying degree of metamictization has resulted due to post-amphibole carbonatite intrusions causing a reheating of metamict pyrochlore that crystallized from amphibole carbonatite magma. The lighter coloured varieties probably represent a re-equilibration of previously crystallized pyrochlore to the new P.T.C. conditions of late intrusions and hydothermal fluids. However, the possibility of crystallization of varying composition of pyrochlore with each intrusive pulse cannot be ruled out. Further work is required to establish the pyrochlore paragenesis with respect to the intrusive history of carbonatite.

Some conclusions of paragenetic significance are summarized as follows:

1. All colour varieties of pyrochlore from Loe-Shilman carbonatite crystallized independent of each other and the differences in the degree of metamictization are a result of their Uranium/Thorium contents or relative ages.

TABLE III. PARTIAL CHEMICAL ANALYSES OF RADIOACTIVE MINERALS

Sample No.	Colour Variety	Mineral name	U%	Ti%	Ca%	Nb%	Ta%
SN–1	Yellow	Pyrochlore	16.25	6.46	9.20	Nd	Nd
SN–2	"	"	10.51	7.50	10.80	Nd	Nd
SN–3	Dark brown to black	"	6.52	2.78	7.86	Nd	Nd
SN–4	"	"	2.05	2.88	14.17	Nd	Nd
1*	"	Betafite (?)	Nd	No	Nd	20.90	6.70
2*	"	Betafite (?)	Nd	Nd	Nd	21.4	6.40
3+	"	Pyrochlore	35.0	Nd	Nd	22.0	7.0

Nd – not determined, * data after Rahman (1980), + data after Syed (1975), SN 1–4 This study.

TAVLE IV. CHEMICAL CLASSIFICATION OF THE RADIOACTIVE MINERAL

	Nb_2O_5%	Ta_2O_5%
Pyrochlore	52 – 71	0.20 – 5.50
Betafite	21 – 35	1 – 14

2. The existence of two colour varieties of totally metamict pyrochlore within the same carbonatite complex suggests at least two stages of pyrochlore crystallization. Chronological contemporaneity or otherwise of these varieties can only be established through radiometric data or detailed chemical and field relation studies with respect to the distribution of these pyrochlores.
3. Partially metamict and non metamict varieties could have resulted from repeated reheating of pre-existing metamict pyrochlores due to continued carbonatite intrusive/extrusive activity along a structure that has allowed the emplacement/extrusion of carbonatite magma for an extended period.

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