

## RARE-EARTH-ELEMENT MINERALOGY OF GRANITIC PEGMATITES IN THE TROUT CREEK PASS DISTRICT, CHAFFEE COUNTY, COLORADO

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### ABSTRACT

Numerous bodies of granitic pegmatite are associated with the 1.7 Ga Denny Creek Granodiorite in the Trout Creek Pass pegmatite district in Chaffee County, Colorado. They range in size from several meters to approximately 85 meters in maximum dimension. Four of the larger pegmatites are well zoned and notably enriched in REE, Nb, and Ti, and depleted in fluorine. All exhibit a distinct spatial as well as a chemical separation of the REE into LREE- and HREE-enriched mineral phases. In the absence of abundant fluorine as a potential complexing agent, we suggest that crystallochemical constraints and mineral fractionation are primarily responsible for the observed LREE-HREE separation. The proposed three-stage crystallization sequence for REE-mineral formation is: 1) during crystallization of the wall zone and early stages of core crystallization, all of the REE, Y, Nb, and Ti were selectively partitioned into the residual melt; 2) during the later stages of core crystallization LREE and P were incorporated into allanite-(Ce) and monazite-(Ce), selectively removing these elements from the residual melt; 3) the remaining HREE-, Nb-, and Ti-enriched fluid eventually corroded and replaced earlier-formed core minerals and ultimately formed albite-rich replacement units containing polycrase-(Y) or aeschynite-(Y). The formation of polycrase-(Y) or aeschynite-(Y) as a late-stage pegmatite mineral requires the rare combination of Ti, Nb, Y, and HREE enrichment coupled with low concentration of fluorine in the final stages of pegmatite formation.

**Keywords:** pegmatite, rare-earth element, polycrase-(Y), aeschynite-(Y), allanite-(Ce), monazite-(Ce), Trout Creek Pass, Colorado.

### SOMMAIRE

De nombreuses venues de pegmatite granitique sont associées avec la granodiorite de Denny Creek (1.7 Ga), dans le district pegmatitique de Trout Creek Pass, dans le comté de Chaffee, au Colorado. Elles vont de quelques mètres à environ 85 mètres en dimensions maximales. Quatre des massifs les plus puissants sont zonés et définitivement enrichis en terres rares, Nb et Ti, et appauvris en fluor. Tous font preuve d'une forte zonation spatiale et chimique des terres rares, logées dans des minéraux enrichis en terres rares, soit légères, soit lourdes. En l'absence du fluor qui aurait pu effectuer la complexation nécessaire, nous pensons que ce sont les contraintes cristallochimiques et le fractionnement des minéraux qui étaient surtout responsables de la séparation efficace des terres rares. Nous proposons une séquence de cristallisation en trois stades: 1) au cours de la cristallisation de la paroi externe et au stade précoce de la formation du coeur, toutes les terres rares, ainsi que Y, Nb et Ti, ont préféré le liquide silicaté résiduel; 2) lors des stades plus avancés de la cristallisation du coeur, les terres rares légères et le P ont servi à la cristallisation de l'allanite-(Ce) et de la monazite-(Ce), ce qui les a appauvris dans le bain fondu résiduel; 3) une phase fluide, dans laquelle les terres rares lourdes qui restaient, ainsi que le Nb et le Ti, ont été concentrés, a éventuellement attaqué et remplacé les minéraux précoces du coeur pour former des zones de remplacement riches en albite et contenant polycrase-(Y) ou aeschynite-(Y). La formation de ces phases accessoires au stade ultime de cristallisation d'une pegmatite granitique requiert la combinaison assez rare d'un enrichissement en Ti, Nb, Y et terres rares lourdes, et d'une faible teneur en fluor.

(Traduit par la Rédaction)

**Mots-clés:** pegmatite granitique, terres rares, polycrase-(Y), aeschynite-(Y), allanite-(Ce), monazite-(Ce), Trout Creek Pass, Colorado.

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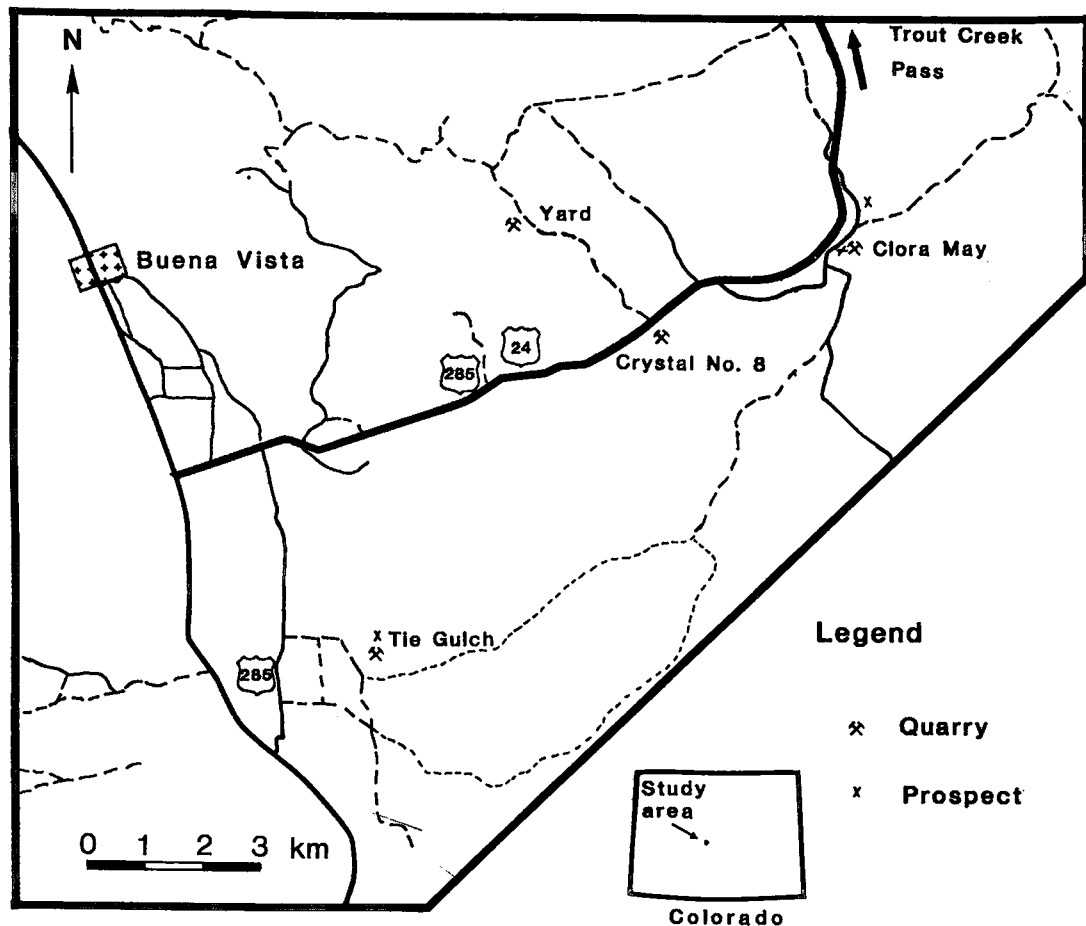


FIG. 1. Location map of the Trout Creek Pass pegmatite bodies showing the location of the Yard, Crystal No. 8, Clora May and Tie Gulch pegmatites.

#### INTRODUCTION

The Trout Creek Pass pegmatite district is located in the Mosquito Range near Buena Vista, in Chaffee County, Colorado (Fig. 1). Numerous bodies of granitic pegmatite are associated with the Denny Creek Granodiorite. These pegmatites range in size from several meters to approximately 85 meters in maximum dimension, are poorly exposed, and have not been extensively quarried. Only four of the larger pegmatites, the Yard, the Clora May, the Crystal No. 8, and one informally named the Tie Gulch pegmatite, exhibit well-developed internal zonation consisting of a thin, discontinuous border zone, a wall zone, and a composite quartz-microcline core with superimposed albite-rich replacement units. These four also are characterized by strong *REE*-mineral enrichments and are the only pegmatites investigated in this study.

The Trout Creek Pass pegmatites contain notable concentrations of *REE*, Nb, and Ti, and are conspicuously fluorine-poor. There are distinct spatial and chemical separations of the *REE* into light-*REE*-enriched and heavy-*REE*-enriched mineral phases. Allanite-(Ce) and monazite-(Ce), the dominant *LREE*-enriched phases, are found in association with the core, whereas polycrase-(Y) or aeschnite-(Y), the dominant *HREE*-enriched phase, is restricted in its occurrence to late-stage replacement units. A similar separation of *REE* into distinct *HREE*- and *LREE*-mineral suites in the fluorine-enriched pegmatites of the South Platte pegmatite district, Jefferson County, Colorado, has been attributed to fluorine complexing (Simmons *et al.* 1987, Simmons & Hanson 1988, 1991). The Trout Creek Pass pegmatites provide an opportunity to examine *REE* behavior in a fluorine-depleted, *REE*-enriched pegmatite suite.

## GENERAL GEOLOGY

*Host pluton*

The Trout Creek Pass pegmatite district is located within the Denny Creek Granodiorite, a member of the synorogenic Routt Plutonic Suite. Plutons of this suite are foliated to various degrees and concordant with their metamorphic country-rocks (Tweto 1987). The Denny Creek Granodiorite is a cluster of intrusive bodies ranging in composition from quartz monzonite to quartz diorite (Tweto 1987). In the Trout Creek Pass pegmatite district, the dominant rock-type is a foliated biotite granite, close to quartz monzonite in composition.

The name Trout Creek Augen Gneiss was originally applied to the Denny Creek Granodiorite in the Mosquito Range by Hutchinson & Hedge (1967) and Hutchinson (1972). However, as these rocks are no more foliated than other units of the Routt Plutonic Suite, Tweto (1977, Table 1) revised the name Trout Creek Augen Gneiss to the Denny Creek Granodiorite. The Trout Creek Augen Gneiss of Hutchinson & Hedge (1967, Fig. 8) is approximately 1.7 Ga based on Rb-Sr age determinations. Thus, the host Denny Creek Granodiorite is related to the Boulder Creek orogenic event.

*Pegmatites*

The four REE-enriched pegmatites investigated in this study are internally zoned, ellipsoidal bodies consisting of a thin discontinuous border zone, a graphic granite wall zone, and a composite quartz-microcline core with superimposed albite-rich replacement units. Pegmatites typically have elliptical horizontal cross-sections. Dips of the pegmatite - host rock contacts, as well as contacts between the internal zones of the pegmatite, range from either gently outward or steeply outward in the upper portion of the pegmatite, to steeply inward in the lower portion. Replacement units (pods) are larger and more abundant in the upper portions of the pegmatites. Although the true "replacement pods" are generally restricted to the outer core, secondary albitization occurs in both the core and wall zones.

Wall zones of the pegmatite bodies range in thickness from 1 to 15 m, with an average thickness of 3 to 4 m, and completely enclose the composite core. Wall-zone rocks are composed primarily of a graphic intergrowth of pink microcline perthite and quartz. In general, graphic granite in the wall zone gradually increases in grain size toward the core. In some places, microcline perthite of the graphic granite has been partially or completely corroded and replaced by white albite, which was subsequently sericitized.

The composite quartz-microcline core is volumetrically the largest portion of the pegmatites. The core consists primarily of microcline perthite and quartz, with lesser amounts of both primary and secondary, highly sericitized plagioclase, and minor amounts of biotite. Microcline, either pink or white in color, has an average grain-size of approximately 0.6 m. The plagioclase is generally only slightly smaller in size. Electron-microprobe analyses reveal that the primary plagioclase is oligoclase ranging from An<sub>12.7</sub> to An<sub>29.6</sub>. The secondary plagioclase is nearly pure albite. Quartz occurs as masses of "bull" quartz that range in size from several cm to several meters across. Large books of biotite, up to one meter in maximum dimension, are generally restricted to thin discontinuous zones, which are located along the core - wall-zone boundary near the top of the pegmatite bodies. Biotite also occurs in minor amounts along the core - wall-zone boundary as smaller grains 1 to 2 cm across. Muscovite, 1 to 2 cm across, occurs as a fracture-related phase in the core. In addition to these principal minerals, lesser amounts of monazite-(Ce) and allanite-(Ce) are associated with the core. A single gadolinite-(Y) crystal was found on the mine dump from the Clora May pegmatite (P. Modreski, pers. comm.). From the associated minerals, it appears most likely that the gadolinite-(Y) also formed in the quartz-microcline core.

Replacement units are typically located along the core - wall-zone margin. They range in size from 0.5 to 2 m in diameter and are characterized by aggregates of anhedral quartz grains, from 0.5 to 2 cm in maximum dimension, which are either partly or completely surrounded by a secondary, highly sericitized, white albite. In some instances, the quartz in these aggregates is smoky. Other minerals occurring in replacement units are magnetite and polycrase-(Y) or aeschynite-(Y). Magnetite occurs as subhedral to euhedral masses up to 2 cm across. Polycrase-(Y) or aeschynite-(Y) typically occur as anhedral masses up to five cm across and as rare, crudely formed crystals in the Yard and Clora May pegmatites and as 1 to 2 mm grains in the Crystal No. 8 and Tie Gulch pegmatites.

## ANALYTICAL METHODS

All REE-bearing minerals were analyzed in the wavelength-dispersion (WD) mode on the ARL electron microprobe at the University of New Orleans, with an accelerating voltage of 15 kV, a sample current of 22 nA measured on brass, and a beam diameter of 1  $\mu$ m. Data were collected at 150,000 preset beam counts (approximately 31-second counting times).  $L\alpha$  peak positions were used for all REE determinations. For each mineral,

background positions were carefully selected from WD scans in order to avoid interfering peaks. *REE* peak-overlap interferences were corrected for by applying spectrometer and crystal-specific empirical correction-factors determined by Wayne (1986). The *REE* corrections were calculated and applied to the raw data using REECOR, a program developed at the University of New Orleans. Corrected data were reduced using PDQ, a modified 30-element, IBM-PC version of EMPADR (Rucklidge 1967). The following standards were used for the *REE*: synthetic *REE*-bearing glasses (Drake & Weill 1972), synthetic *REE* fluorides (Wayne 1986), and synthetic *REE*-Ga garnets (U. S. National Museum numbers: S-65, S-67, S-69, S-87, S-90, S-92, and S-529). The limits of detectability for the *REE* are between 0.1 to 0.05 oxide wt.%, with the exception of Pr, Tb, Dy, Ho, Er, and Yb, which have large corrections due to overlap and are essentially eliminated as concentration levels fall below about 1.0 to 0.1 oxide wt.%, depending on the concentration of the interfering element. Other standards used were tanzanite, albite, thorianite, rutile, pyrope, uraninite, fluorapatite, synthetic Ba-Cl-bearing apatite, ferrosilite, manganotantalite, and synthetic Y niobate, Y-Al garnet, and Zr oxide (Hanson 1990).

X-ray-diffraction analyses of polycrase-(Y) and aeschynite-(Y) were carried out using a Scintag XDS-2000 X-ray diffractometer, and analyses of allanite-(Ce) and monazite-(Ce) were conducted using a Norelco XRG-5000 X-ray diffractometer. Samples were run with an operating voltage of 35 kV and a current of 15 mA, using  $\text{CuK}\alpha$  radiation

(graphite-monochromated for the Norelco instrument), and a scan rate of  $2^\circ 2\theta$  per minute. Synthetic corundum and quartz were used as standards for instrument calibration. Unit-cell dimensions were calculated from X-ray powder-diffraction data using 11 to 23 reflections between  $10^\circ$  and  $60^\circ 2\theta$  and CELL, a modified IBM-PC version of the least squares unit cell refinement program of Appleman & Evans (1973).

#### POLYCRASE-(Y) AND AESCHYNITE-(Y)

Strongly radioactive, black, vitreous, anhedral masses and euhedral crystal fragments a few mm to ten cm across occur with quartz-albite aggregates in replacement units from the Yard, Clora May, Tie Gulch and Crystal No. 8 pegmatites. Samples are optically isotropic in thin section and show no X-ray-diffraction peaks, indicating complete metamictization of this material. Material from the Yard pegmatite was previously identified as "euxenite" by Hanley *et al.* (1950).

The general formula for minerals of the euxenite group of complex orthorhombic Nb-Ta-Ti oxides is  $\text{AB}_2\text{O}_6$ , in which *A* represents Y, *REE*,  $\text{Fe}^{2+}$ , Mn, Ca, Th, U, Pb, and Sc, and *B* represents Nb, Ta, Ti,  $\text{Fe}^{3+}$ , W, Sn, and Zr (Ewing 1976). The dominant cation in the *B* site is Nb in euxenite, Ta in tautauxenite, and Ti in polycrase-(Y) (Fig. 2a). These minerals are almost always metamict and generally altered; thus their crystal structure is poorly understood.

Further complicating the classification of euxenite-group minerals is their close chemical and

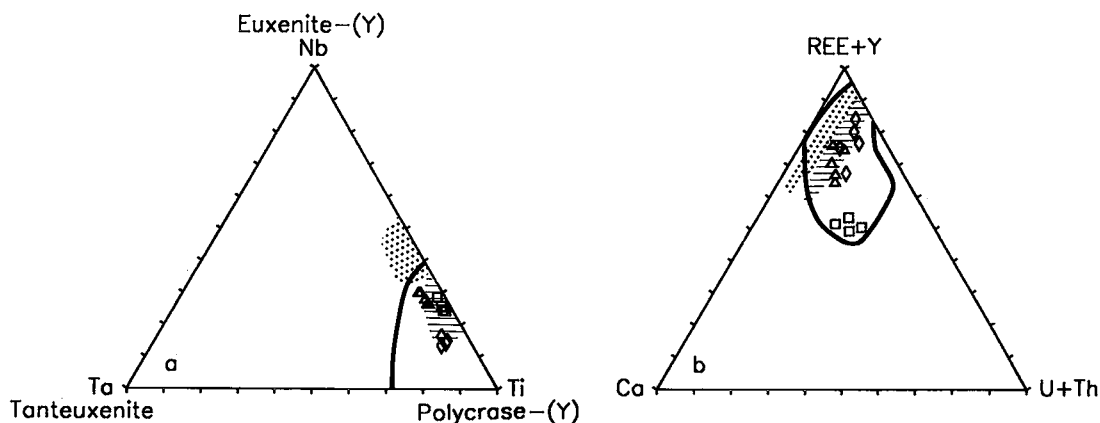


FIG. 2. Triangular plots of Trout Creek Pass Nb-Ta-Ti oxides: (a) major *B*-site cations (Nb, Ta and Ti) with euxenite-group mineral names; and (b) major *A*-site cations (*REE* + Y, U + Th, and Ca). The fields of "polycrase" (within the dark outlined area), "priorite" (stippled area), and "blomstrandine" (horizontal-ruled area), of Cerný & Ercit (1989) are shown for comparison. Symbols for pegmatite samples are as follows: squares: Yard, triangles: Crystal No. 8, diamonds: Clora May.

structural relationship to aeschynite-group minerals (Černý & Ercit 1989). Aeschynite-group minerals [including aeschynite-(Ce), aeschynite-(Y), "priorite", and "blomstrandine"] have the same general  $AB_2O_6$  formula as euxenite-group minerals. In most aeschynite-group minerals, Ti is the dominant B-site cation and LREE are the dominant A-site cations. Thus, in older literature "aeschynite" typically refers to aeschynite-(Ce). "Priorite" and "blomstrandine" are the names previously applied to the HREE-Ti-dominant aeschynite-group minerals and are now both considered equivalent to aeschynite-(Y). "Blomstrandine" was considered to be a Ti-rich variety of "priorite" (Komkov 1963). Thus, aeschynite-(Y), "blomstrandine" and "priorite" are all chemically equivalent to the euxenite-group mineral polycrase-(Y).

The difficulty of chemically differentiating Nb-Ta-Ti oxides was addressed by Ewing (1976), who employed a method of canonical discriminant analysis to distinguish between euxenite- and aeschynite-group minerals. He suggested that the sum of uranium oxides ("ΣU") and ThO<sub>2</sub> content may be critical in discriminating between "euxenite" [euxenite-(Y)] and "priorite" [aeschynite-(Y)]. By inference, as polycrase-(Y) is a euxenite-group mineral, the abundance of U and Th could possibly be used to discriminate between polycrase-(Y) and aeschynite-(Y). For example, a Ti-dominant  $AB_2O_6$  oxide with the sum of uranium

oxides ("ΣU") greater than ThO<sub>2</sub> should be called polycrase-(Y). Alternatively, if the sum of uranium oxides is less than ThO<sub>2</sub>, the nomenclature is ambiguous (Ewing 1976).

### Analytical results

Tables 1 and 2 show the electron-microprobe analytical results and calculated chemical formulas for the Trout Creek Pass pegmatite district Nb-Ta-Ti oxides. Formulas were calculated on the basis of three cations total. Iron is reported as all Fe<sub>2</sub>O<sub>3</sub> with the exception of Clora May samples, where 50% of the iron was converted to FeO to compensate for high totals in the B site and low totals in the A site. Although the valence state of uranium is unknown, all uranium is reported as U<sub>3</sub>O<sub>8</sub>, which yields better analytical totals than UO<sub>2</sub>. UO<sub>3</sub> would yield even higher totals, but it is considered unlikely that all of the uranium is present as U<sup>6+</sup>. All of the microprobe analyses yield low analytical totals. As the ratio of the sum of A-site cations to the sum of B-site cations is close to the stoichiometric ratio of 1:2, the low analytical totals are believed to be attributable to absorbed molecular water, a common feature of metamict minerals (Ewing 1975).

The dominant B-site cation in Trout Creek Pass pegmatite district Nb-Ta-Ti oxides is Ti. Y and REE are the dominant A-site cations (Figs. 2a, b). The overlap of the "polycrase", "priorite", and

TABLE 1. CHEMICAL COMPOSITION OF TROUT CREEK PASS POLYCRASE-(Y) AND AESCHYNITE-(Y)

OXIDE	POLYCRASE-(Y)										AESCHYNITE-(Y)			
	YD-1	YD-2	YD-3	YD-4	XL-1	XL-2	XL-3	XL-4	XL-5	CM-1	CM-2	CM-3	CM-5	
Nb <sub>2</sub> O <sub>5</sub>	18.22	15.57	17.94	15.65	16.37	16.88	19.42	19.32	17.95	9.73	9.35	10.09	10.58	
Ta <sub>2</sub> O <sub>5</sub>	2.51	2.04	2.23	2.80	5.57	5.56	6.65	6.19	5.83	6.93	6.89	6.89	6.64	
TiO <sub>2</sub>	27.32	28.38	26.06	28.13	24.82	25.89	24.39	24.55	25.39	27.45	32.44	31.97	32.82	
ThO <sub>2</sub>	3.25	2.41	2.51	3.12	2.08	2.89	2.06	2.17	2.41	6.12	4.56	6.43	4.66	
U <sub>3</sub> O <sub>8</sub>	19.29	13.49	16.64	18.06	9.28	7.48	4.46	6.44	6.79	3.96	2.60	4.26	4.01	
La <sub>2</sub> O <sub>3</sub>	0.03	n.d.	n.d.	0.07	0.05	0.04	0.03	0.04	0.03	0.02	0.02	0.04	0.03	
Ce <sub>2</sub> O <sub>3</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	0.04	0.10	n.d.	
Nd <sub>2</sub> O <sub>3</sub>	0.35	0.41	0.49	0.43	0.10	0.26	0.23	0.32	0.25	0.69	0.74	0.63	0.40	
Sm <sub>2</sub> O <sub>3</sub>	0.55	0.49	0.64	0.63	0.36	0.39	0.40	0.42	0.48	0.72	0.88	0.83	0.62	
Eu <sub>2</sub> O <sub>3</sub>	0.06	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	0.07	n.d.	0.05	0.08	n.d.	
Gd <sub>2</sub> O <sub>3</sub>	1.02	1.15	1.27	1.13	0.85	0.99	1.17	1.11	1.16	1.88	2.00	1.93	1.68	
Tb <sub>2</sub> O <sub>3</sub>	0.40	0.15	0.33	0.26	0.24	0.14	0.30	0.33	0.28	0.43	0.44	0.47	0.42	
Dy <sub>2</sub> O <sub>3</sub>	2.14	1.80	2.12	2.15	2.52	2.29	2.75	2.58	2.72	2.90	3.13	3.33	3.14	
Ho <sub>2</sub> O <sub>3</sub>	0.33	0.28	0.25	0.43	0.49	0.47	0.59	0.48	0.62	0.06	0.12	0.29	0.22	
Er <sub>2</sub> O <sub>3</sub>	1.48	1.45	1.65	1.55	1.70	1.48	1.78	1.83	1.92	1.72	1.31	1.61	1.89	
Tm <sub>2</sub> O <sub>3</sub>	0.27	0.18	0.24	0.48	0.39	0.39	0.54	0.44	0.46	0.19	0.14	0.20	0.30	
Yb <sub>2</sub> O <sub>3</sub>	1.89	1.59	1.67	1.85	1.63	1.45	1.65	1.94	1.97	0.68	0.69	1.19	1.39	
Lu <sub>2</sub> O <sub>3</sub>	0.33	0.21	0.37	0.82	0.63	0.62	0.49	0.58	0.62	0.23	0.11	0.24	0.20	
Y <sub>2</sub> O <sub>3</sub>	10.09	9.84	11.30	9.88	14.32	15.12	17.40	16.17	16.10	10.78	16.74	15.08	16.49	
ZrO <sub>2</sub>	0.48	0.28	0.57	0.47	0.40	0.45	0.42	0.40	0.44	0.58	0.48	0.39	0.44	
MnO	0.57	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	
ZrO <sub>2</sub>	2.98	3.57	3.38	3.71	2.97	2.76	2.22	2.77	1.83	1.90	0.82	1.03	0.98	
CaO	0.15	0.10	0.09	0.08	0.10	0.09	0.12	0.09	0.14	n.d.	0.06	0.05	0.05	
Sc <sub>2</sub> O <sub>3</sub>	0.06	0.04	0.05	0.03	0.24	0.25	0.17	0.12	0.15	n.d.	0.21	0.09	0.07	
PbO	1.84	0.83	0.48	0.73	0.35	0.39	0.62	0.17	1.26	n.d.	n.d.	0.20	0.04	
WO <sub>3</sub>	0.36	0.19	0.05	0.30	2.06	1.72	1.89	2.52	2.49	4.61	4.61	5.39	4.05	
Fe <sub>2</sub> O <sub>3</sub>	3.00	2.48	3.82	2.98	4.37	4.45	2.84	4.55	2.92	1.60	1.26	0.75	1.05	
FeO										1.44	1.13	0.67	0.85	
TOTAL	97.07	87.04	94.07	95.48	91.87	92.45	92.17	95.51	94.30	94.99	93.36	94.33	93.12	

Pr analyzed for but not detected; n. d. = not detected

TABLE 2. CHEMICAL FORMULAS OF TROUT CREEK PASS POLYCRASE-(Y) AND AESCHYNITE-(Y)

	POLYCRASE-(Y)									AESCHYNITE-(Y)			
	YD-1	YD-2	YD-3	YD-4	XL-1	XL-2	XL-3	XL-4	XL-5	CM-1	CM-2	CM-3	CM-5
Th	0.048	0.035	0.035	0.044	0.030	0.040	0.029	0.029	0.034	0.095	0.063	0.090	0.065
U	0.255	0.186	0.221	0.238	0.124	0.098	0.059	0.082	0.090	0.057	0.034	0.057	0.052
La	0.001			0.001	0.001	0.001	0.001	0.001	0.001			0.001	0.001
Ce										0.002	0.001	0.002	
Nd	0.008	0.009	0.011	0.010	0.002	0.006	0.005	0.007	0.006	0.014	0.016	0.014	0.009
Sm	0.012	0.011	0.014	0.013	0.007	0.006	0.009	0.009	0.010	0.017	0.018	0.018	0.013
Eu	0.002			0.001				0.001	0.001			0.001	0.001
Gd	0.021	0.026	0.026	0.023	0.020	0.020	0.024	0.022	0.024	0.042	0.040	0.040	0.034
Tb	0.008	0.003	0.007	0.005	0.005	0.003	0.006	0.006	0.006	0.009	0.009	0.010	0.008
Dy	0.042	0.040	0.042	0.042	0.051	0.045	0.055	0.050	0.054	0.063	0.061	0.066	0.061
Ho	0.006	0.005	0.005	0.008	0.010	0.009	0.011	0.009	0.012	0.001	0.002	0.005	0.004
Er	0.029	0.029	0.032	0.030	0.033	0.029	0.034	0.034	0.037	0.037	0.026	0.031	0.036
Tm	0.005	0.003	0.005	0.009	0.007	0.007	0.010	0.008	0.009	0.004	0.003	0.004	0.006
Yb	0.037	0.031	0.035	0.035	0.031	0.027	0.027	0.035	0.037	0.018	0.013	0.022	0.026
Lu	0.006	0.004	0.007	0.017	0.010	0.011	0.009	0.010	0.011	0.005	0.002	0.004	0.004
Y	0.332	0.338	0.373	0.317	0.475	0.492	0.575	0.515	0.531	0.588	0.543	0.496	0.532
Mn	0.026	0.016	0.019	0.025	0.021	0.023	0.022	0.020	0.023	0.033	0.025	0.021	0.023
Ca	0.197	0.247	0.224	0.244	0.198	0.161	0.149	0.178	0.121	0.139	0.040	0.098	0.064
Sc	0.006	0.006	0.005	0.003	0.006	0.006	0.007	0.005	0.007		0.003	0.003	0.003
Pb	0.031	0.014	0.009	0.012	0.006	0.006	0.010	0.003	0.021			0.003	0.001
Fe <sup>2+</sup>										0.061	0.058	0.035	0.048
SUM A	1.071	1.002	1.069	1.077	1.037	1.011	1.041	1.024	1.035	1.005	0.957	0.991	0.990
Nb	0.453	0.455	0.499	0.435	0.461	0.467	0.546	0.523	0.533	0.299	0.259	0.282	0.290
Ta	0.042	0.038	0.038	0.044	0.094	0.093	0.112	0.101	0.098	0.129	0.160	0.110	0.110
Ti	1.268	1.379	1.215	1.300	1.163	1.191	1.141	1.105	1.182	1.401	1.488	1.486	1.487
Fe <sup>3+</sup>	0.140	0.120	0.178	0.138	0.205	0.205	0.124	0.205	0.195	0.081	0.058	0.035	0.049
W	0.006	0.003	0.001	0.005	0.033	0.027	0.031	0.039	0.040	0.065	0.073	0.067	0.064
Sn	0.002	0.001	0.001	0.001	0.006	0.006	0.004	0.003	0.004		0.005	0.002	0.002
Zr	0.019	0.003							0.001				
SUM B	1.930	1.997	1.832	1.923	1.962	1.989	1.959	1.976	1.964	1.994	2.042	2.008	2.011

Formulas based on three total cations

“blomstrandine” fields of Černý & Ercit (1989) for *B*-site cations in Nb-Ta-Ti oxides is shown in Figure 2a. The Trout Creek Pass samples overlap the “polycrase” and “blomstrandine” fields. The diagram showing *A*-site occupancy (Fig. 2b) suggests that samples from the Yard are “polycrase”, whereas samples from the Clora May and Crystal No. 8 fall within the area of overlap between the “blomstrandine” and “polycrase” fields. Thus they are not clearly either “polycrase” [polycrase-(Y)] or “blomstrandine” [aeschynite-(Y)]. However, samples from the Yard and the Crystal No. 8 pegmatites have U<sub>3</sub>O<sub>8</sub> in excess of ThO<sub>2</sub>, suggesting that they are polycrase-(Y), whereas those from the Clora May pegmatite have U<sub>3</sub>O<sub>8</sub> less than ThO<sub>2</sub>, which does not unambiguously categorize them as either polycrase-(Y) or aeschynite-(Y).

A plot of the major *A*-site cations ( $\Sigma LREE$ ,  $\Sigma HREE + Y$ , and Ca) shows the extreme *LREE* depletion of the Nb-Ta-Ti oxides (Fig. 3c). Chondrite-normalized plots (Fig. 4) for these oxides show that the *HREE* and *Y* are enriched over the *LREE* by almost two orders of magnitude.

#### *X-ray diffractometry*

Heating experiments of metamict, complex Nb-Ta-Ti oxides by Ewing & Ehlmann (1975) show that upon heating, an aeschynite-type phase forms

first at low temperatures and then is converted to a euxenite-type structure at high temperatures. They reported the transition to occur between 550 and 750°C for *Y*-rich compositions, and between 900 and 1000°C for *Ce*-rich compositions.

Only the Yard and Clora May pegmatites yielded sufficient material for recrystallization experiments. Samples were heated in air at 400, 500, 600, 700, 900, 1000, and 1100°C for 24 hours (Fig. 5). All samples recrystallized between 500 and 600°C. Samples from the Yard pegmatite recrystallized to a euxenite-type structure, and diffraction patterns correspond closely with that of a heated euxenite-(Y) (PDF 9-442); the Yard samples have slightly smaller *d*-values (Hanson 1990). These samples retained the euxenite-type structure from 600 to 1000°C (Fig. 5a). Samples from the Clora May pegmatite recrystallized first with an aeschynite-type structure, with a diffraction pattern corresponding closely to that of a synthetic aeschynite-(Y) (PDF 20-1401) (Hanson 1990). This structure was retained up to 1000°C and then converted to the euxenite-type structure between 1000 and 1100°C (Fig. 5b).

Thus, based on the heating experiments, both polycrase-(Y) and aeschynite-(Y) are present within the Trout Creek Pass pegmatite district. However, the annealing results are different from those reported by Ewing & Ehlmann (1975) in that the Yard polycrase-(Y) recrystallizes directly to a

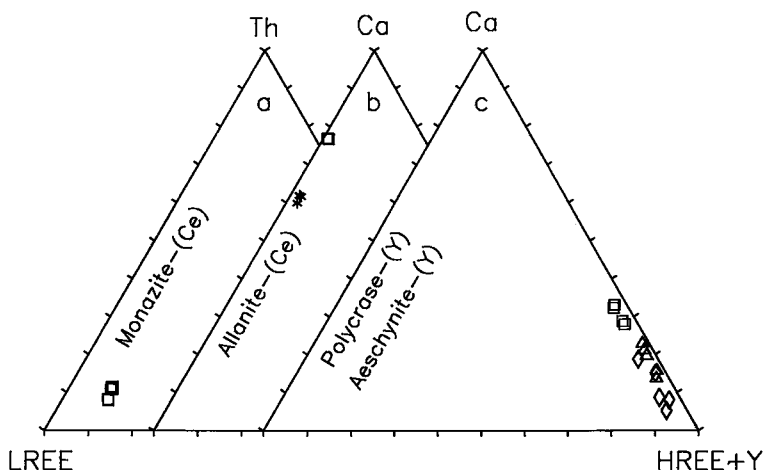


FIG. 3. Triangular plot of major A-site cations for Trout Creek Pass minerals: (a) monazite-(Ce), (b) allanite-(Ce), and (c) polycrase-(Y) and aeschnite-(Y). Symbols for pegmatite samples are as follows: squares: Yard, triangles: Crystal No. 8, diamonds: Clora May, stars: Tie Gulch.

euxenite-type structure with no intermediate aeschnite-type structure. Furthermore, the transition from an aeschnite-type structure to a euxenite-type structure for Clora May samples occurs between 1000 to 1100°C, which is higher than the transitions reported by Ewing & Ehlmann (1975).

Cell parameters calculated for recrystallized polycrase-(Y) from the Yard pegmatite are:  $a$  5.534(1),  $b$  14.424(5), and  $c$  5.178(1) Å. Cell parameters calculated for recrystallized aeschnite-(Y) from the Clora May pegmatite are:  $a$  5.181(3),  $b$  10.901(7), and  $c$  7.382(3) Å.

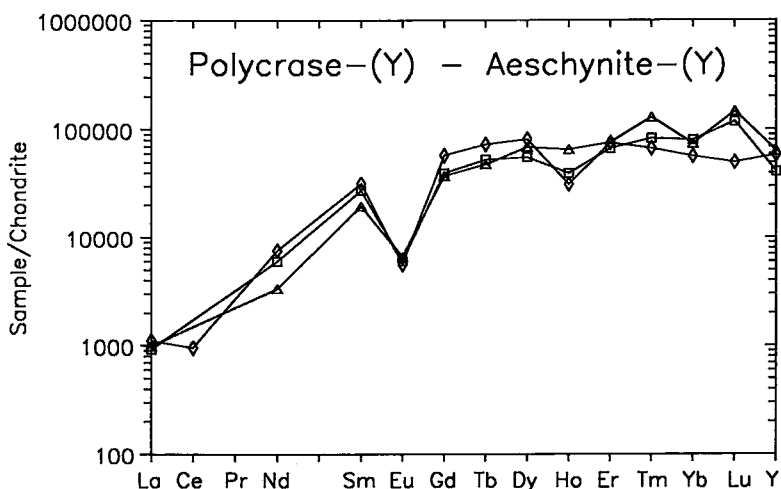


FIG. 4. Chondrite-normalized REE plot for Trout Creek Pass polycrase-(Y) and aeschnite-(Y). Symbols as in Figure 2.

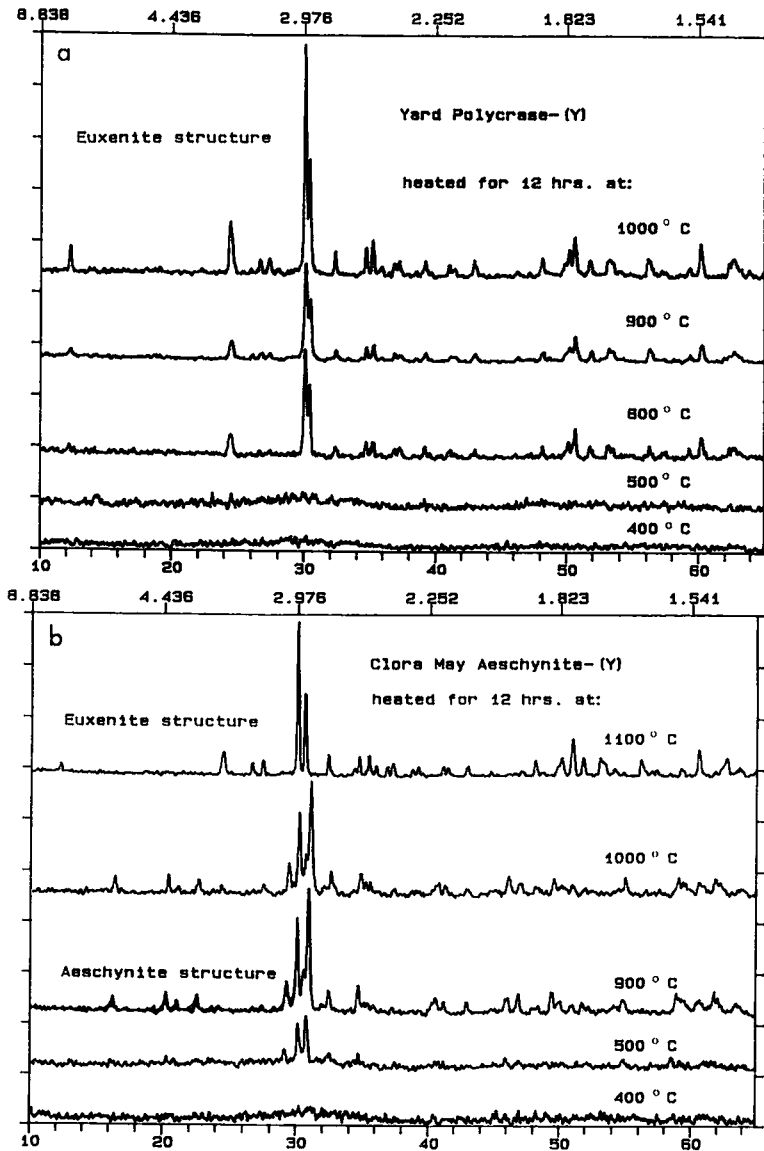


FIG. 5. X-ray-diffraction patterns showing the recrystallization history of metamict Nb-Ta-Ti oxides: (a) Yard samples recrystallized with a "euxenite" structure, which was retained through 1000°C; (b) Clora May samples recrystallized first with an "aeschynite" structure, which was retained up to 1000°C before conversion to a "euxenite" structure above 1000°C.

#### ALLANITE-(Ce)

Allanite-group minerals are members of the epidote group, represented by the general formula  $A_2M_3Si_3O_{13}H$ , where  $A$  represents large, high-coordination-number cations such as Ca, Sr, REE, etc., and  $M$  represents octahedrally coordinated Al,  $Fe^{3+}$ ,  $Mn^{3+}$ ,  $Fe^{2+}$ , Mg, etc. (Dollase 1971).

Allanite-group minerals are related to epidote through the coupled substitution:  $REE^{3+} + Fe^{2+} = Ca^{2+} + Fe^{3+}$  (Dollase 1971, Deer *et al.* 1962, Exley 1980).

Allanite-(Ce) occurs as anhedral, black masses up to 2 cm in size in the Yard and the Tie Gulch pegmatites. Although no allanite-(Ce) was found in the Clora May or the Crystal No. 8 pegmatites



in this study, it is reported to occur in both of these pegmatites, with allanite-(Ce) from the Crystal No. 8 occurring as long straight crystals up to one cm across and fifteen cm long (Hanley *et al.* 1950). Allanite-(Ce) is always associated with microcline perthite of the core rather than with quartz-albite aggregates of replacement units.

### Analytical results

Representative results of electron-microprobe analyses and calculated formulas are given in Tables 3 and 4. Formulas were calculated on the basis of three Si cations, as the epidote-group minerals characteristically show little replacement of Si by Al in the tetrahedral sites (Deer *et al.* 1962). The sum of the *M* sites is slightly high, and the sum of the *A* sites is somewhat low. Total iron was partitioned into ferrous and ferric iron on the basis of 25 total charges. OH was calculated by stoichiometry on the basis of one (OH, Cl, F).

Allanite-(Ce) from the Trout Creek Pass pegmatite district is *LREE*-enriched, with Ce as the dominant *REE* (Table 3). Allanite-(Ce) from the Yard pegmatite has higher total *REE* than that from the Tie Gulch pegmatite. Figure 3b shows the *LREE* enrichment of allanite-(Ce) on a triangular plot of major *A*-site cations. Ce is approximately twice as abundant as either La or Nd on a weight basis. The relative proportions of Ce, La and Nd are shown in Figure 6b. Allanite-(Ce) samples from the Yard are somewhat enriched in Nd compared to Tie Gulch samples. Chondrite-normalized plots (Fig. 7) of allanite-(Ce) show the extreme *LREE* enrichment relative to Y.

TABLE 3. CHEMICAL COMPOSITION OF TROUT CREEK PASS ALLANITE-(Ce)

OXIDE	YD-B	YD-C	TG-A	TG-B
SiO <sub>2</sub>	33.00	33.74	33.61	34.43
Al <sub>2</sub> O <sub>3</sub>	21.99	22.55	20.82	22.16
CaO	11.15	11.63	15.13	15.00
Ce <sub>2</sub> O <sub>3</sub>	10.15	9.32	8.88	7.04
La <sub>2</sub> O <sub>3</sub>	4.89	4.24	3.47	3.51
Nd <sub>2</sub> O <sub>3</sub>	4.41	4.90	2.17	2.90
Sm <sub>2</sub> O <sub>3</sub>	1.28	1.38	0.32	0.30
Gd <sub>2</sub> O <sub>3</sub>	0.88	0.95	0.39	0.39
Yb <sub>2</sub> O <sub>3</sub>	0.14	0.14	n.d.	n.d.
Lu <sub>2</sub> O <sub>3</sub>	0.25	0.13	0.14	n.d.
Y <sub>2</sub> O <sub>3</sub>	0.17	0.22	0.21	0.11
TiO <sub>2</sub>	0.13	0.05	0.32	0.30
MnO	0.25	0.18	0.22	0.22
ThO <sub>2</sub>	n.d.	n.d.	0.81	0.97
MgO	0.30	0.21	0.03	n.d.
FeO	10.51	9.77	10.78	12.28
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.51	1.83	0.54
Cl	0.28	0.29	0.38	0.32
SUM	99.78	100.11	97.48	99.57
O=Cl	0.06	0.07	0.09	0.07
SUM	99.72	100.04	97.39	99.50

Elements analyzed for but not detected include: Na, U, F, Pr, Eu, Th, Dy, Ho, Er and Tm  
n. d. = not detected;

TABLE 4. CHEMICAL FORMULAS OF TROUT CREEK PASS ALLANITE-(Ce)

	YD-B	YD-C	TG-A	TG-B
Si	3.000	3.000	3.000	3.000
Ca	1.088	1.099	1.447	1.400
Ce	0.338	0.304	0.224	0.225
La	0.164	0.139	0.114	0.113
Nd	0.143	0.156	0.059	0.062
Sm	0.040	0.042	0.010	0.009
Gd	0.027	0.028	0.011	0.011
Yb	0.004	0.004		
Lu	0.007	0.004	0.004	
Y	0.008	0.011	0.010	0.005
Mn	0.019	0.014	0.016	0.016
Th			0.017	0.019
SUM A	1.836	1.901	1.922	1.860
Al	2.356	2.383	2.190	2.275
Fe <sup>2+</sup>	0.789	0.726	0.805	0.895
Fe <sup>3+</sup>		0.034	0.123	0.036
Ti	0.008	0.003	0.021	0.020
Mg	0.041	0.027	0.003	0.003
SUM M	3.204	3.163	3.142	3.229
Cl	0.043	0.043	0.057	0.047
OH	0.957	0.957	0.943	0.953

OH determined by stoichiometry

### X-ray diffractometry

X-ray-diffraction analysis reveals that Trout Creek Pass allanite-(Ce) is only partially metamict, as XRD patterns yield most of the major characteristic peaks of allanite-(Ce), yet show none of the smaller peaks (Hanson 1990). Cell parameters were calculated for samples from both the Yard and the Tie Gulch pegmatite. Cell dimensions for Yard material are: *a* 8.892(1), *b* 5.706(4), and *c* 10.136(2) Å, with  $\beta$  115.27°. The Tie Gulch allanite-(Ce) yielded the cell dimensions *a* 8.955(2), *b* 5.701(4), *c* 10.187(2) Å, and  $\beta$  115.48°. These values are slightly different from values given by Černý *et al.* (1972) (PDF 25-169) for a non-metamict allanite-(Ce): *a* 8.932, *b* 5.770, *c* 10.1575 Å, and  $\beta$  114.69°. The slight differences in these values are likely related to slight differences in composition and the partially metamict nature of allanite-(Ce) from the Yard and Tie Gulch pegmatites.

### MONAZITE-(Ce)

Monazite-(Ce) is the least abundant *REE* mineral in Trout Creek Pass pegmatites. In this study, it was found only in the Yard pegmatite, where it occurs sporadically as brick-red euhedral to subhedral crystals up to 20 cm across. Like allanite-(Ce), monazite-(Ce) occurs in the core and is not associated with the albite-rich replacement units.

The general formula for monazite-(Ce) is  $ABO_4$ , where *A* represents *REE*, Th, U, and Ca, and *B* represents P and Si. Monazite-(Ce), (Ce,La,Nd,Th)PO<sub>4</sub>, is a member of an isostructural series of

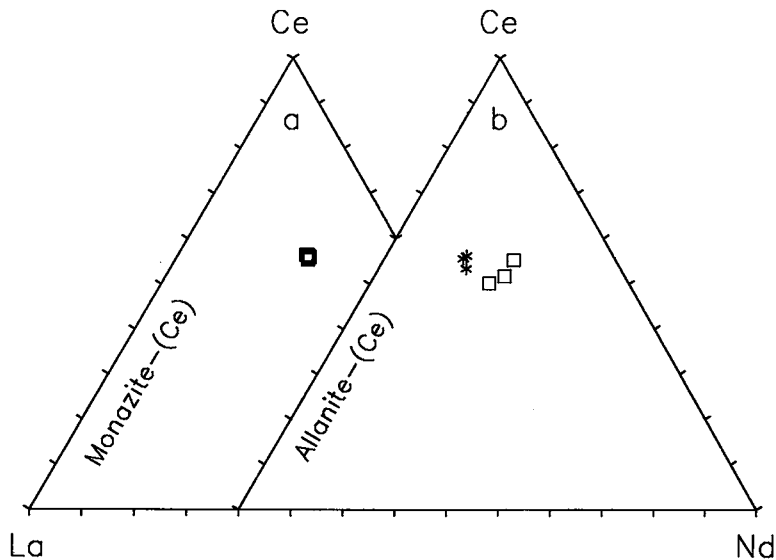


FIG. 6. Triangular plot of major rare-earth elements, Ce, La and Nd, for Trout Creek Pass minerals: (a) monazite-(Ce) from the Yard pegmatite (squares), and (b) allanite-(Ce) from the Yard (squares) and Tie Gulch (stars) pegmatites.

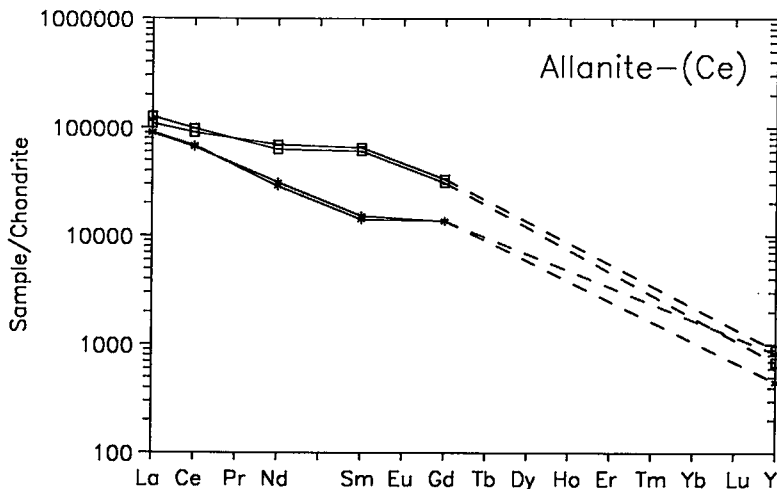


FIG. 7. Chondrite-normalized REE plot for Trout Creek Pass allanite-(Ce) from the Yard (squares) and Tie Gulch (stars) pegmatites. The dashed lines are extrapolated across the HREE to Y as the HREE abundances in allanite-(Ce) are at or below the limits of detection.

monoclinic minerals including cheralite,  $(\text{Ca,Ce,Th})(\text{P,Si})\text{O}_4$ , and huttonite,  $\text{ThSiO}_4$  (Bowles *et al.* 1980, Fleischer 1987).

#### Analytical results

Tables 5 and 6 show representative results of

electron-microprobe analyses and calculated chemical formulas for monazite-(Ce) from the Yard pegmatite. The formulas were calculated on the basis of four oxygen atoms. The sum of *A*-site cations is slightly low, and the sum of *B*-site cations is somewhat high. Monazite-(Ce) is *LREE*-enriched, with Ce as the dominant *A*-site cation (Fig. 3a).

TABLE 6. CHEMICAL ANALYSES OF TROUT CREEK PASS MONAZITE-(Ce)

OXIDE	M-1B	M-3	M-4A	M-5A	M-5B	M-6
P <sub>2</sub> O <sub>5</sub>	30.80	29.79	29.66	31.10	30.54	29.48
SiO <sub>2</sub>	2.16	2.67	2.61	2.29	2.20	3.02
La <sub>2</sub> O <sub>3</sub>	9.03	8.48	8.45	8.81	8.85	8.73
Ce <sub>2</sub> O <sub>3</sub>	24.69	24.43	24.48	24.94	24.90	24.07
Pr <sub>2</sub> O <sub>3</sub>	1.84	1.54	1.61	1.68	1.69	1.49
Nd <sub>2</sub> O <sub>3</sub>	11.82	11.10	11.28	11.99	12.25	11.20
Sm <sub>2</sub> O <sub>3</sub>	3.33	3.52	3.40	3.36	3.54	3.31
Eu <sub>2</sub> O <sub>3</sub>	0.60	0.55	0.50	0.49	0.40	0.49
Gd <sub>2</sub> O <sub>3</sub>	3.00	3.01	2.94	3.08	3.09	2.72
Dy <sub>2</sub> O <sub>3</sub>	0.55	0.53	0.50	0.48	0.51	0.49
Y <sub>2</sub> O <sub>3</sub>	2.58	1.87	2.06	2.25	2.11	2.07
ThO <sub>2</sub>	8.40	10.67	10.92	8.18	8.17	11.33
CaO	0.74	0.87	0.86	0.78	0.75	0.82
PbO	0.78	0.98	0.94	0.72	0.82	0.90
SUM	100.02	100.01	100.21	100.12	99.82	100.12

Elements analyzed for but not detected include: Fe, U, Tb, Ho, Er, Tm, Yb and Lu; n. d. = not detected

TABLE 6. CHEMICAL FORMULAS OF TROUT CREEK PASS MONAZITE-(Ce)

	M-1B	M-3	M-4A	M-5A	M-5B	M-6
P	0.989	0.968	0.965	0.993	0.986	0.956
Si	0.082	0.103	0.100	0.086	0.084	0.116
SUM B	1.071	1.071	1.065	1.079	1.070	1.072
La	0.126	0.120	0.120	0.123	0.125	0.123
Ce	0.341	0.343	0.344	0.344	0.348	0.338
Pr	0.023	0.022	0.023	0.023	0.024	0.021
Nd	0.160	0.152	0.155	0.161	0.167	0.153
Sm	0.043	0.047	0.045	0.044	0.047	0.044
Eu	0.008	0.007	0.007	0.006	0.005	0.006
Gd	0.038	0.038	0.038	0.038	0.039	0.035
Dy	0.007	0.007	0.006	0.006	0.006	0.006
Y	0.052	0.042	0.042	0.045	0.043	0.042
Th	0.072	0.096	0.098	0.070	0.071	0.099
Ca	0.030	0.036	0.035	0.031	0.031	0.034
Pb	0.008	0.010	0.010	0.007	0.008	0.009
SUM A	0.908	0.919	0.921	0.898	0.914	0.910

Formulas based on four oxygen atoms

TABLE 7. UNIT-CELL DATA FOR MONAZITE-(Ce) AND SOME SYNTHETIC END-MEMBER PHOSPHATES

	a (Å)	b (Å)	c (Å)	B (°)
Yard	6.783(1)	7.003(1)	6.478(1)	103.75
Magnet Cove *	6.796	7.006	6.466	103.95
LaPO <sub>4</sub> **	6.89	7.05	6.48	104.57
CePO <sub>4</sub> ***	6.777	6.993	6.445	103.5
CaTh(PO <sub>4</sub> ) <sub>2</sub> ****	6.69	6.93	6.38	104.4

\* Carron *et al.* (1958); (PDF #11-556)

\*\* Semenov (1963)

\*\*\* Boatner *et al.* (1980)

\*\*\*\* Bowie & Horne (1953)

The relative proportions of Ce, La and Nd are shown in Figure 6a. The monazite-(Ce) in the Trout Creek Pass pegmatites is enriched in Nd relative to La. It is interesting to note that the relative proportions of La, Ce and Nd in monazite-(Ce) are very similar to those of allanite-(Ce) (Fig. 6b). Chondrite-normalized plots of monazite-(Ce) show the strong and relatively uniform enrichment of LREE (Fig. 8).

X-ray diffractometry

X-ray-diffraction patterns of Trout Creek Pass monazite-(Ce) correspond almost perfectly to that of Carron *et al.* (1958; PDF 11-556) and can be found in Hanson (1990). Calculated unit-cell dimensions for monazite-(Ce) from the Yard pegmatite are shown in Table 7. The table shows the relationship between the cell dimensions of monazite-(Ce) from the Yard pegmatite, that in PDF 11-556, and other synthetic monazite-structure phosphates.

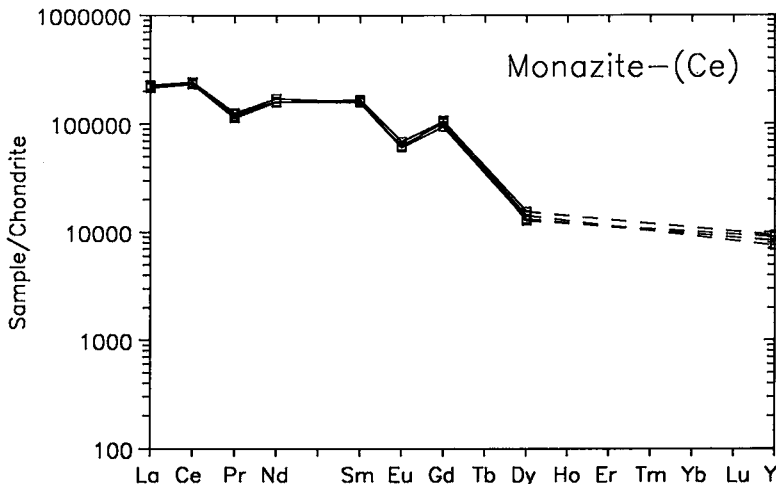


FIG. 8. Chondrite-normalized REE plot for Trout Creek Pass monazite-(Ce) from the Yard pegmatite (squares). The dashed lines are extrapolated across the HREE to Y as the HREE abundances in monazite-(Ce) are at or below the limits of detection.

## DISCUSSION

The Trout Creek Pass pegmatites display a distinct chemical, as well as a spatial separation of the light *versus* the heavy rare-earths. Chemically, polycrase-(Y) or aeschnite-(Y) is the only *HREE*-enriched phase present, and allanite-(Ce) and monazite-(Ce) are the only *LREE*-enriched phases. Within the pegmatites, the *LREE* minerals, allanite-(Ce) and monazite-(Ce), are spatially restricted to the core or core margin, whereas the *HREE* mineral, polycrase-(Y) or aeschnite-(Y), is always associated with late-stage, albite-rich replacement units.

Similar separations between early-forming *LREE* minerals and late-stage *HREE* minerals have been reported by Mineyev (1963). Two arguments have been suggested to explain the separation of light from heavy rare-earths. One view holds that *REE* separation can be achieved by crystal chemistry alone. According to the other view, *REE* separation can be explained by geochemical factors, in particular the stronger tendency for the *HREE* to form complexes.

According to the crystallochemical model, *REE* separation is a direct result of crystal-structure requirements such as ionic radius and coordination. Semenov (1958) suggested that lanthanide selectivity is related to coordination number (CN). Minerals with high-CN elements are *LREE*-selective, those with low-CN elements are *HREE*-selective, and those with intermediate-CN elements are nonselective. Semenov classified "euxenite" as being Y-selective, "allanite" as nonselective, and "monazite" as Ce-selective.

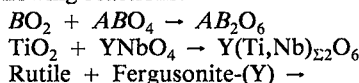
On the other hand, Mineyev (1963) suggested that *HREE-LREE* separation may be explained in terms of geochemical differences. He suggested that the *HREE* have a tendency to form complexes more readily than the *LREE*, particularly with fluorine and chlorine, thus allowing the *HREE* to undergo more pronounced differentiation.

In pegmatites of the South Platte district, Colorado, Simmons *et al.* (1987) observed a chemical zonation of F, Nb, Th, U, and *REE* between groups of pegmatites. They reported a direct correlation between high concentrations of fluorine and *HREE* mineralization. Pegmatites containing abundant fluorite are enriched in the *HREE* and yttrian phases, samarskite-(Y), *HREE*-enriched zircon and yttrian fluorite. Pegmatites with sparse or no fluorite are characterized by the *LREE* phase allanite-(Ce). They suggested that fluoride complexing was primarily responsible for the *REE* separation in South Platte pegmatites.

However, in the Trout Creek Pass pegmatites, no fluorine- or chlorine-bearing minerals are present in the late-stage replacement units. As

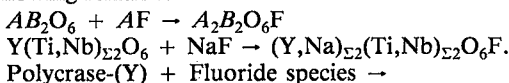
fluoride or chloride ions were unavailable for the formation of *HREE* complexes, the observed *HREE-LREE* separation must be the result of some process other than fluoride or chloride complexing. It appears likely that in the Trout Creek Pass pegmatite district, the sequence of mineral formation and crystallochemical factors are responsible for the observed *HREE-LREE* separation. The separation of the *LREE* occurred first, with the crystallization of monazite-(Ce) and allanite-(Ce) along the core - wall-zone margin. The euhedral to subhedral nature of the monazite-(Ce) crystals is further evidence that they are primary and not the result of the later replacement phase of crystallization. The *HREE* were consequently partitioned into the residual fluid, which subsequently formed the late-stage replacement units containing polycrase-(Y) or aeschnite-(Y).

Several questions arise related to the mineralogy of the replacement units. First, why does polycrase-(Y), a rare mineral, form as the Nb-Ta-Ti oxide, and second, why does rutile not crystallize from this titanium-rich residual fluid. Burt (1989) suggested that simple combinations of *A-B* oxides may be used to define oxide reactions. For the Trout Creek Pass pegmatites, we propose the following reactions:



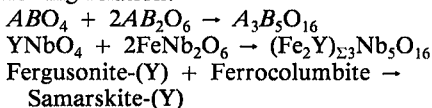
Polycrase-(Y) or Aeschnite-(Y).

This reaction suggests that the association rutile + fergusonite is unstable if polycrase-(Y) or aeschnite-(Y) is stable. Polycrase-(Y) or aeschnite-(Y) may coexist with either rutile or fergusonite-(Y), but not both. In addition, the following relation:



Pyrochlore-group mineral

demonstrates that an  $AB_2O_6$  oxide such as polycrase-(Y) or aeschnite-(Y) is stable only in a fluorine-depleted environment. Hence, the absence of fluorine in the Trout Creek Pass pegmatites is, at least in part, responsible for the formation of these minerals. However, in the presence of fluorine, the following relation:



may explain the presence of samarskite-(Y) in the South Platte pegmatites (Simmons *et al.* 1990, Simmons & Hanson 1991).

Thus, the formation of polycrase-(Y) or aeschnite-(Y) as a late-stage mineral in the pegmatite bodies requires the rare combination of fluorine

depletion, coupled with Ti, Nb, Y, and *HREE* enrichment in the residual fluid, a relationship that accounts for the scarcity of the mineral.

## ACKNOWLEDGEMENTS

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