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THORTVEITITE AND ASSOCIATED Sc-BEARING MINERALS FROM RAVALLI COUNTY, MONTANA

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ABSTRACT

The rare Sc mineral thortveitite, $(Sc,Y)_2Si_2O_7$, occurs as µm- to mm-sized crystals in fluorite-bearing granitic pegmatites and the host melagabbro within the Crystal Mountain fluorite deposit, Ravalli County, Montana. Thortveitite is found as colorless and clear to smoky and translucent, subhedral to euhedral prisms up to 3 mm in length in the massive fluorite, as mm-sized anhedra to subhedra in diopside and edenite, and as µm-sized droplet-like crystals in actinolite. Micrometric textures suggest that some thortveitite exsolved from actinolite, which contains between 1.2 and 2.9 wt.% Sc_2O_3. Associated ferroan diopside contains as much as 4.8, edenite as much as 2.1, actinolite as much as 2.0, allanite as much as 0.5 and titanite as much as 0.4 wt.% Sc_2O_3, respectively. The source of the Sc is believed to be magmatic, rather than from assimilation and extraction of Sc from adjacent amphibolite xenoliths. Indices of refraction, determined using spindle-stage techniques, are: α 1.752, β 1.780, γ 1.804, all ±0.003, $\gamma - \alpha = 0.052$. The mineral is biaxial negative, $2V_{\text{meas.}} = 70°$, $2V_{\text{calc.}} = 84°$. The empirical formula derived on the basis of 7 atoms of oxygen from electron-microprobe and laser-ICP analyses is $(Sc_{1.83}Y_{0.05}Fe^{3+}_{0.05}R_{0.07})_{\Sigma 2.00}(Si_{1.97}Al_{0.04})_{\Sigma 2.00}O_7$ where *R* represents Mn, Ca, Mg, Ti, Na, K, Nb, Sn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U, Hf, Zr, P, Li, Be, B, V, Cr, Co, Ni, Cu, Ba, Ga, Ge, As, Rb, Sr, and In. $D_M = 3.50$, $D_C = 3.50$ g cm^{-3}. The mineral contains $\Sigma REE = 4.63$ wt.% and is enriched in the heavy rare-earth elements. Cell dimensions are: *a* 6.5304(4), *b* 8.5208(4), *c* 4.6806(5) Å, β 102.630(7)°, V 254.1(1) Å^3, $Z = 2$, space group *C2/m*. The unit-cell volume is smaller than that of thortveitite from most other localities because of its Sc enrichment. Similarly, the metal–oxygen distances (2.088 to 2.199 Å) are smaller than those for most natural specimens of thortveitite.

Keywords: thortveitite, scandium silicate, rare-earth mineral, fluorite, actinolite, diopside, granitic pegmatite, X-ray data, crystal-structure refinement, Crystal Mountain mine, Ravalli County, Montana.

SOMMAIRE

Nous avons trouvé la thortveitite, $(Sc,Y)_2Si_2O_7$, minéral rare de Sc, en cristaux de taille micrométrique à millimétrique dans des pegmatites granitiques à fluorite et dans leur encaissant mélagabbroïque du gisement de fluorite de Crystal Mountain, comté de Ravalli, au Montana. Elle forme des prismes sub-idiomorphes à idiomorphes, incolores et transparents à fumés et translucides, jusqu'à 3 mm en longueur dans la fluorite massive, en cristaux millimétriques xénomorphes ou sub-idiomorphes dans la diopside et l'édenite, et en cristaux micrométriques en forme de goutelette dans l'actinolite. Les textures à l'échelle micrométrique font penser qu'il s'agit d'une origine par exsolution à partir de l'actinolite, qui contient entre 1.2 et 2.9% de Sc_2O_3 en poids. La diopside ferreuse associée en contient jusqu'à 4.8%, l'édenite, jusqu'à 2.1%, l'actinolite, jusqu'à 2.0%, l'allanite, jusqu'à 0.5%, et la titanite, jusqu'à 0.4%. L'enrichissement en Sc serait primaire (magmatique) plutôt que due à l'assimilation et à l'extraction du Sc des xénolithes d'amphibolite associés. Les indices de réfraction, déterminés avec platine munie d'une aiguille, sont: α 1.752, β 1.780, γ 1.804, avec dans chaque cas, et $\gamma - \alpha = 0.052$. C'est un minéral biaxe négatif, $2V_{mes.}$ 70°, $2V_{calc.}$ 84°. Les données obtenues par microsonde électronique et par plasma à couplage inductif avec laser, mènent à la formule empirique suivante, pour sept atomes d'oxygène, $(Sc_{1.83}Y_{0.05}Fe^{3+}_{0.05}R_{0.07})_{\Sigma 2.00}(Si_{1.97}Al_{0.04})_{\Sigma 2.00}O_7$. Ici, R représente Mn, Ca, Mg, Ti, Na, K, Nb, Sn, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U, Hf, Zr, P, Li, Be, B, V, Cr, Co, Ni, Cu, Ba, Ga, Ge, As, Rb, Sr et In. La densité mesurée est de 3.50, et la densité calculée, 3.50. La thortveitite contient 4.63% en poids de terres rares, et montre un enrichissement en terres rares lourdes. Les dimensions de la maille élémentaire sont: a 6.5304(4), b 8.5208(4), c 4.6806(5) Å, β 102.630(7)°, V 254.1(1) $Å^3$, $Z = 2$, groupe spatial $C2/m$. Le volume de la maille élémentaire, plus petit que ce qui a été documenté dans la plupart des autres exemples connus, serait dû à l'enrichissement en Sc dans ce cas. De même, les distances entre métal et oxygène (2.088 à 2.199 Å) sont plus courtes que dans la plupart des autres exemples de ce minéral.

(Traduit par la Rédaction)

Mots-clés: thortveitite, silicate de scandium, minéral de terres rares, fluorite, actinolite, diopside, pegmatite granitique, données de diffraction X, affinement de la structure cristalline, mine de Crystal Mountain, comté de Ravalli, Montana.

INTRODUCTION

The occurrence of the rare Sc mineral thortveitite, $(Sc,Y)_2Si_2O_7$, in the Crystal Mountain fluorite deposit of Ravalli County, Montana (Fig. 1), was first reported by Parker & Havens (1963). Fluorite was extracted from the deposit from 1952 to 1973 (Taber 1952), but no additional data were obtained on the thortveitite until the deposit was evaluated in 1984 as a potential Sc resource (Birmingham, unpubl. data, 1984). This occurrence, in the southern Sapphire Mountains, is the only one reported for North America, and one of fewer than a dozen areas in the world where thortveitite has been positively identified (Voloshin *et al.* 1991, Bianchi *et al.* 1988, Yamada *et al.* 1980, Åmli 1977, Kainov 1973, Mathiesen 1970, Oftedal 1969, Krol *et al.* 1969, Phan *et al.* 1967, Sakurai *et al.* 1962, Neumann 1961). This paper presents new data on the thortveitite and associated Sc-bearing minerals at Crystal Mountain. Samples used in this study were provided by Boulder Scientific Company, the present owner of the deposits.

OCCURRENCE

Thortveitite at Crystal Mountain is dispersed over a 1 km^2 area in several tabular bodies of fluorite cut by many minor faults of small displacement, and in small bodies of intrusive melagabbro. The fluorite bodies, now mostly removed by open-pit mining, extended downward to less than 200 m below the surface; only a small exposure of the melagabbro is preserved at Crystal Point (Fig. 1).

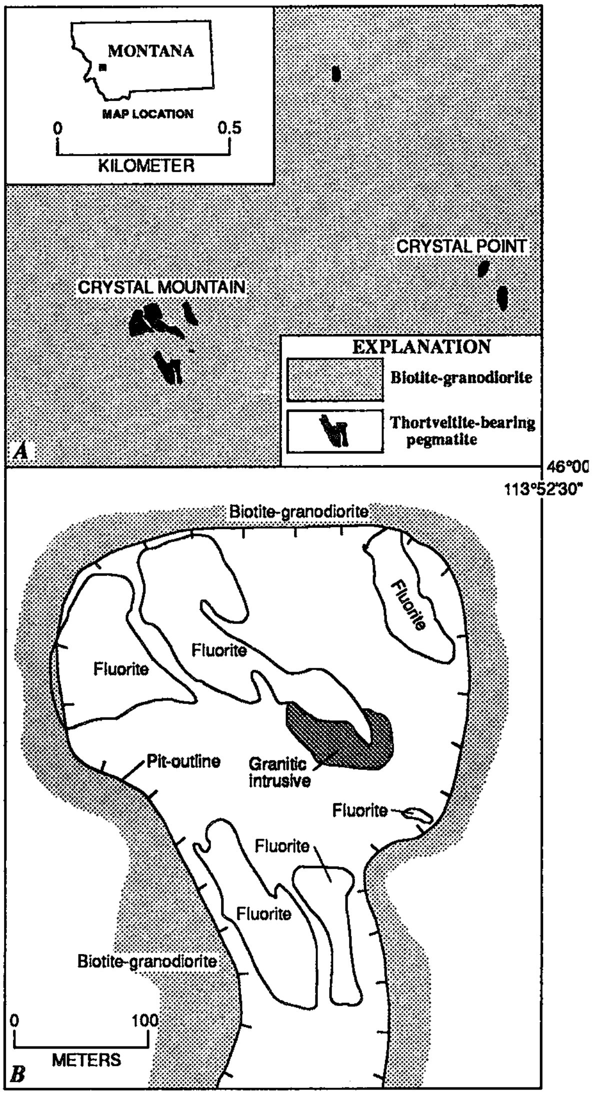

FIG. 1. (A) Index map and simplified geological map of the Crystal Mountain thortveitite deposits. (B) Simplified geological map showing fluorite deposits as of 1952 (now mostly removed), and an intrusive body of granite in the pit floor approximately 100 m below the 1952 surface. Adapted in part from Taber (1952).

The fluorite and thortveitite at this locality are believed to be related 1) to hypidiomorphic-granular granitic pegmatites consisting primarily of quartz, biotite, plagioclase, and microcline, and 2) to associated thortveitite-bearing melagabbro. The granitic rocks are poor in Sc; the thortveitite occurs primarily within areas of the fluorite bodies that are enriched in biotite, magnetite, fergusonite, allanite-(Ce), epidote, xenotime, clinopyroxene (ferroan diopside), and amphibole (actinolite and calcic edenite). Other minerals identified in the fluorite bodies are: apatite, chalcopyrite, spessartine–almandine, pyrite, titanite, rutile, zircon, thorite, uranothorite, molybdenite, and possible thorianite. The melagabbro associated with the fluorite-bearing granite pegmatites contains edenite – edenitic hornblende, quartz, titanite, magnetite, biotite, and thortveitite. The diopside, edenite – edenitic hornblende, actinolite, allanite-(Ce) and titanite contain variable amounts of Sc.

The area surrounding the Crystal Mountain fluorite pegmatites is composed primarily of a biotite granodiorite pluton of Tertiary to Cretaceous age that is presumed to be related to the Bitterroot lobe of the Idaho batholith (Wallace *et al.* 1982). This pluton contains large foliated xenoliths of biotite – quartz – plagioclase gneiss and hornblende–plagioclase gneiss that resemble the thortveitite-bearing melagabbro, but are poor in Sc. Dikes of similar age consisting primarily of microcline and quartz, and hornblende gabbro dikes are known to the east in the Sapphire Wilderness Study Area, and may be cogenetic with the Crystal Mountain pegmatites. However, they are not known to contain fluorite and also are poor in Sc: the hornblende gabbro dikes typically contain about 30 ppm Sc, and the microcline–quartz pegmatites, about 15 ppm (Campbell *et al.* 1983). Crystal Mountain is adjacent to the Late Cretaceous Sapphire batholith, an epizonal complex of six comagmatic peraluminous intermediate plutons. Wallace *et al.* (1982) reported that monzogranite and granodiorite in the western part of Sapphire Wilderness Study Area contain high concentrations of Sc and the rare earths, but thortveitite has not been identified in this area; whole-rock analytical results presented by Campbell *et al.* (1983) show ≤50 ppm Sc and, in most cases, <10 ppm. Several other fluorite-bearing deposits occur along the eastern margin of the Idaho batholith in Mineral, Missoula, and Ravalli counties, Montana (Ekambaram *et al.* 1986), but thortveitite has not been identified at any of these localities, and they show no anomalous concentrations of Sc (Birmingham, unpubl. data, 1984). Rocks of the Idaho batholith may generally be slightly enriched in Sc; some batholith-derived heavy-mineral placers in central Idaho reportedly contain 200–1,500 ppm Sc, mainly in tantalite, columbite, euxenite, and ilmenite (Sondermayer 1976, Parker & Adams 1973).

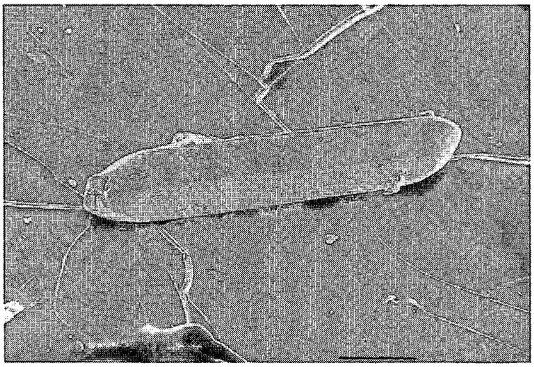

FIG. 2. Photomicrograph of thortveitite. Scale bar represents 100 µm. Substrate is double-sticky tape.

PHYSICAL AND OPTICAL PROPERTIES

Thortveitite in the massive fluorite bodies is found as subhedral to euhedral prisms up to 3 mm long. They range from colorless and clear to smoky and translucent. Some crystals have well-developed {110} prisms, but well-developed pyramids are uncommon; the {110} cleavage is indistinct (Fig. 2). Some crystals exhibit polysynthetic twinning, with {110} as the composition plane. The optical properties of thortveitite from Crystal Mountain were determined in blue-filtered white light. The indices of refraction, determined using spindle-stage techniques, are as follows: α 1.752, β 1.780, γ 1.804, all ± 0.003, $\gamma - \alpha = 0.052$. The mineral is biaxial negative, $2V_{meas.} = 70° \pm 2°$, $\pm 2V_{calc.} = 84°$. The mineral is colorless and shows no pleochroism. Dispersion $r > v$ is distinct. The optical orientation scheme is: $X \Lambda c = -6°$, $Y = b$. $D_M = 3.50$, $D_C = 3.50$ g cm^{-3}. The thortveitite is commonly enclosed by fluorite, and may envelop small (up to 100 µm) crystals, mainly of thorite and uranothorite, but also purple fluorite, amphibole, clinopyroxene, and titanite. The inclusions are commonly very numerous, evenly distributed, and randomly oriented. Thortveitite in the melagabbro occurs as anhedral to subhedral crystals up to 2 mm across within edenite, and contains the same inclusions found in thortveitite from the fluorite deposits. In some of the melagabbro, thortveitite is found as small, droplet-like anhedral crystals (<10 µm across) within actinolite that may be a result of exsolution (Fig. 3).

EXPERIMENTAL PROCEDURE

Chemical analyses

Electron probe microanalyses were carried out on polished grain-mounts using ARL–SEMQ instruments at the Italian National Research Council (C.N.R.) at the Centro di Studio per la Stratigrafia e la Petrografia delle Alpi Centrali, Milan, at the Department of Geological

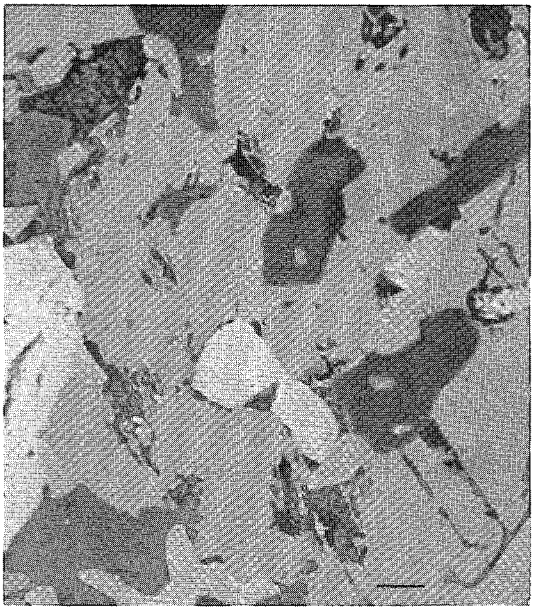

FIG. 3. Photomicrograph of thortveitite-amphibole intergrowth. White: calcite, light grey: thortveitite, medium grey: actinolite, and dark grey: quartz. Scale bar in lower right corner is 10 µm.

Sciences at the University of Texas at Austin, and at the U.S. Geological Survey in Denver, Colorado. Standard operating conditions were as follows: accelerating voltage from 15 to 20 kV; sample current on brass of 0.01 µA; beam spot diameter of 5 or 15 µm; 10- or 20-second count time at peak position, and 10- or 20-second count times on background positions, respectively. PET, LiF, TAP, and RAP spectrometer crystals were used. A combination of natural minerals and synthetic compounds, as described in Jarosewich *et al.* (1980), Ingamells (1978), and Mannucci *et al.* (1986), were used as standards. Data were reduced using MAGIC IV and MAGIC V programs (Colby 1968).

This study also utilized a VG PlasmaQuad PQ+ inductively coupled plasma mass spectrometer equipped with a Spectrum Laser Systems pulsed Nd/YAG laser operated at the primary frequency of 1.068 µm (Arrowsmith 1987). A single mm-sized crystal of the mineral was ablated using the Q-switched mode of the laser operated at 158 mJoules/pulse and pulsed at 10 Hz for a 33-second integration. All masses except m/z = 40 were integrated. Calibration of the instrument was accomplished using an internal reference-standard glass GSE (Myers *et al.* 1976). Composite results of analyses of thortveitite, diopside, edenite, actinolite, allanite, and titanite using several different crystals and both analytical techniques (EPMA and ICP–MS) are presented in Table 1.

Crystal-structure refinement

A crystal measuring 0.10 × 0.12 × 0.20 mm, from a heavy-mineral concentrate from the fluorite-processing mill at Crystal Mountain, was mounted on an Enraf-Nonius CAD-4 diffractometer, and twenty-five intense reflections having a 2θ value in the range 12.03–37.48° were centered using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). The diffracted intensities [1618 with $I > 3\sigma(I)$] were collected at room temperature with variable scan speed (maximum scan-time for each reflection: 90 s) by exploring the hemisphere of the reciprocal lattice with $0 \leq h \leq 11$, $-15 \leq k \leq 15$, and $-8 \leq l \leq 8$, out to a maximum 2θ angle of 80°. The diffracted intensities were corrected for Lorentz, polarization and background effects. The data and other pertinent information are presented in Tables 2–5.

An empirical absorption correction was applied by performing a psi-scan correction (North *et al.* 1968), followed by a DIFABS correction (Walker & Stuart 1983), according to the procedure already described in Demartin *et al.* (1991). After averaging the symmetry-related data, whose agreement was 0.8% on an F_o basis, 825 independent reflections were obtained; of these, 797 with $I > 3\sigma(I)$ were considered for the structure refinement. Scattering factors for neutral atoms and anomalous dispersion correction factors were taken from Cromer & Waber (1974) and Cromer (1974), respectively. The structure was refined, starting from the atomic positions reported in Bianchi *et al.* (1988), by full-matrix least-squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Weights assigned to individual observations were $1/\sigma^2(F_o)$, where $\sigma(F_o) = [\sigma^2(I) + (kI)^2]^{1/2}/2F_oLp$, $\sigma^2(I)$ is the standard deviation for each reflection as derived from counting statistics, k (=0.04) is a coefficient for improving the goodness of fit, and Lp is the Lorentz–polarization factor. Anisotropic displacement parameters were assigned to all the atoms. The refined extinction coefficient was 1.59×10^{-5}. The occupancy of Sc was refined to the value of 1.12, thus confirming partial replacement of this element by Y and heavy lanthanides. All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package (Frenz *et al.* 1980). We found the maximum residual in the final difference Fourier synthesis to be 0.4 e/Å^3. The final *R* (unweighted) and R_w indices were 0.015 and 0.029, respectively.

DISCUSSION

The behavior of Sc^{3+} in igneous systems cannot be readily explained in terms of simple diadochic substitution. Although some correlations may be possible with Fe^{2+}, Fe^{3+}, Mg^{2+} and Al^{3+}, a stronger relationship may be found with total Fe because the relative proportions of Fe^{3+} and Fe^{2+} determined in whole-rock analyses may

TABLE 1. CHEMICAL COMPOSITION OF THORTVEITITE, FERROAN DIOPSIDE, EDENITE, ACTINOLITE, ALLANITE-(Ce) AND TITANITE

	Mill conc. Thortveitite***		Mill conc. Ferroan diopside				CM-18-2 Ferroan diopside		CM-18-2 Edenite**		CM-18-1 Edenite**		Mill conc. Edenite**		Mill conc. Actinolite**		Mill conc. Allanite-(Ce)**	Mill conc. Titanite**		CM-18-2 Titanite**
			Sc-rich		Sc-poor		–		Crystal Point		–									Crystal Point
	Wt. %	Stoich.	Wt. %	Stoich.	Wt. %	Stoich.	Wt. %	Stoich.	Wt. %	Stoich.	Wt. %	Stoich.	Wt. %	Stoich.	Wt. %	Stoich.	Wt. %	Wt. %	Stoich.	Wt. %
SiO_2	44.60^{++}	1.966	52.5	1.99	52.0	1.99	52.9	2.00	43.3	6.69	44.4	6.86	44.5	7.03	55.0	7.82	32.5	31.0	1.01	31.0
Al_2O_3	0.81^{++}	0.042	1.1	0.05	1.1	0.05	1.25	0.06	9.4	1.71	8.5	1.55	8.6	1.60	1.8	0.30	14.8	6.0	0.23	5.7
FeO	¢1.48^{++}	0.049	9.3	0.29	11.6	0.37	11.4	0.36	16.1	2.08	14.2	1.84	15.7	2.07	9.7	1.15	14.8	¢3.2	0.08	¢2.6
MgO	0.06^{++}	0.004	9.1	0.51	10.3	0.59	10.1	0.57	11.5	2.65	12.9	2.97	11.5	2.71	17.1	3.62	0.6	0.2	0.01	0.2
CaO	0.10^{++}	0.005	19.7	0.80	22.6	0.93	21.5	0.87	11.5	1.90	11.4	1.89	11.3	1.91	11.7	1.78	14.5	27.2	0.95	27.0
MnO	0.03^{++}	0.001	0.4	0.01	0.5	0.02	0.45	0.01	0.4	0.05	0.4	0.05	0.4	0.05	0.2	0.02	0.2	0.0	0.0	0.0
K_2O	0.18^{++}	0.010	0.0	–	0.0	–	0.0	–	1.7	0.34	1.6	0.32	1.4	0.28	0.3	0.05	0.0	0.0	0.0	0.0
Na_2O	0.03^{++}	0.003	2.5	0.18	0.9	0.07	1.5	0.11	1.9	0.57	1.8	0.54	1.9	0.58	0.7	0.19	0.0	0.0	0.0	0.0
TiO_2	0.30^{++}	0.010	0.1	0.00	0.1	0.00	0.0	–	<0.1	0.00	<0.1	0.00	0.15	0.02	<0.1	0.00	0.5	27.9	0.68	28.0
Sc_2O_3	47.66^{++}	1.831	4.8	0.16	0.3	0.01	0.85	0.03	1.7	0.23	1.6	0.22	1.6	0.22	2.0	0.25	0.5	0.4	0.01	0.4
P_2O_5	0.03^{++}	0.001	–	–	–	–	–	–	<0.1	0.00	<0.1	0.00	<0.1	0.00	<0.1	0.00	–	–	–	–
F	–	–	–	–	–	–	–	–	1.7	0.83	2.2	1.08	–	–	0.7	0.32	0.7	2.8	0.29	2.75
H_2O^+	–	–	0.57*	–	0.57*	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
TOTAL	99.718[1]		100.07		99.97		99.95		99.2		99.0		97.05		99.2		79.1	100.00[2]		97.65
O=F	–		–		–		–		0.72		0.93		–		0.29		0.29	1.18		1.15
TOTAL	99.718		100.07		99.97		99.95		98.48		98.07		97.05		98.91		78.8	98.82		96.50
Analytical method:	EPMA and ICP-MS		EPMA		EPMA		EPMA		EPMA		EPMA		EPMA		EPMA		EPMA	EPMA and ICP-MS		EPMA

NOTES - ¢ Fe expressed as Fe_2O_3.

* Water determined on 35 mg of purified concentrate by Karl Fisher titration by L.L. Jackson (USGS).

** Averages given are those for grains with maximum Sc_2O_3 contents. Other grains contain lesser amounts of Sc_2O_3.

*** Weighted average of analyses for two grain populations. + - value from ICP-MS, ++ - value from EPMA.

[1] Total also includes 0.13^{+} (0.001) Nb_2O_5, 0.07^{+} (0.001) SnO_2, 0.02^{+} (0.000) La_2O_3, 0.08^{+} (0.001) Ce_2O_3, 0.02^{+} (0.000) Pr_2O_3, 0.12^{+} (0.002) Nd_2O_3, 0.08^{+} (0.001) Sm_2O_3, 0.003^{+} (0.000) Eu_2O_3, 0.14^{+} (0.003) Gd_2O_3, 0.03 (0.001) Tb_2O_3, 0.26^{+} (0.003) Dy_2O_3, 0.07^{+} (0.001) Ho_2O_3, 0.22^{+} (0.004) Er_2O_3, 0.045^{+} (0.001) Tm_2O_3, 0.41^{+} (0.006) Yb_2O_3, 0.08^{+} (0.001) Lu_2O_3, 2.28^{++} (0.053) Y_2O_3, 0.13^{+} (0.002) ThO_2, 0.03^{+} (0.000) UO_2, 0.02^{++} (0.000) HfO_2, 0.20^{+} (0.005). Values given in wt. %. Values in parentheses are stoichiometric proportions.

[2] Total also includes 0.27^{+} Nb_2O_5, 0.037^{+} SnO_2, 0.037^{+} La_2O_3, 0.13^{+} Ce_2O_3, 0.023^{+} Pr_2O_3, 0.14^{+} Nd_2O_3, 0.033^{+} Sm_2O_3, 0.005^{+} Eu_2O_3, 0.037^{+} Gd_2O_3, 0.007^{+} Tb_2O_3, 0.046^{+} Dy_2O_3, 0.010^{+} Ho_2O_3, 0.024^{+} Er_2O_3, 0.004^{+} Tm_2O_3, 0.022^{+} Yb_2O_3, 0.004^{+} Lu_2O_3, 0.40^{+} Y_2O_3, 0.013^{+} ThO_2, 0.008^{+} UO_2, 0.002^{+} HfO_2, 0.052^{+} ZrO_2. Values given in wt. %.

EMPIRICAL FORMULAS

Thortveitite:	$M_{2.00}(Si,Al)_{2.01}O_7$ [M = $\sum$stoich - (Si,Al)] on 7.0 oxygen atoms
Sc-rich diopside: Mill conc.	$(Ca_{0.80}Na_{0.18})_{\Sigma 0.98}(Mg_{0.51}Fe^{2+}{}_{0.29}Sc^{3+}{}_{0.16}Al^{3+}{}_{0.04}Mn^{2+}{}_{0.01})_{\Sigma 1.01}(Si_{1.99}Al_{0.01})_{\Sigma 2.00}O_6$ on 6.0 oxygen atoms
Sc-poor diopside: Mill conc.	$(Ca_{0.93}Na_{0.07})_{\Sigma 1.00}(Mg_{0.59}Fe^{2+}{}_{0.37}Al^{3+}{}_{0.04}Mn^{2+}{}_{0.01}Sc^{3+}{}_{0.01})_{\Sigma 1.02}(Si_{1.99}Al_{0.01})_{\Sigma 2.00}O_6$ on 6.0 oxygen atoms
Sc-bearing diopside: CM-18-2	$(Ca_{0.87}Na_{0.11})_{\Sigma 0.98}(Mg_{0.57}Fe^{2+}{}_{0.36}Al_{0.06}Sc^{3+}{}_{0.03}Mn^{2+}{}_{0.01})_{\Sigma 1.03}Si_{2.00}O_6$ on 6.0 oxygen atoms
Edenite: CM-18-2	$(Na_{0.57}K_{0.34}Ca_{0.09})_{\Sigma 1.00}(Ca_{1.81}Fe^{2+}{}_{0.14}Mn^{2+}{}_{0.05})_{\Sigma 2.00}(Mg_{2.65}Fe^{2+}{}_{1.94}Al_{0.40}Sc_{0.23})_{\Sigma 5.22}(Si_{6.69}Al_{1.31})_{\Sigma 8.00}O_{22}(O_1F_{0.83})_{\Sigma 1.83}$ on 23 oxygen atoms
Edenite: CM-18-1	$(Na_{0.54}K_{0.32}Ca_{0.14})_{\Sigma 1.00}(Ca_{1.75}Fe^{2+}{}_{0.20}Mn^{2+}{}_{0.05})_{\Sigma 2.00}(Mg_{2.97}Fe^{2+}{}_{1.64}Al_{0.41}Sc_{0.22})_{\Sigma 5.24}(Si_{6.86}Al_{1.14})_{\Sigma 8.00}O_{22}(O_1F_{1.08})_{\Sigma 2.08}$ on 23 oxygen atoms
Edenite: Mill conc.	$(Na_{0.58}K_{0.28}Ca_{0.14})_{\Sigma 1.00}(Ca_{1.77}Fe^{2+}{}_{0.28}Mn^{2+}{}_{0.05})_{\Sigma 2.00}(Mg_{2.71}Fe^{2+}{}_{1.79}Al_{0.63}Sc_{0.22}Ti_{0.02})_{\Sigma 5.27}(Si_{7.03}Al_{0.97})_{\Sigma 8.00})O_{24}$ on 24 oxygen atoms
Actinolite: Mill conc.	$(Ca_{1.78}Na_{0.19}K_{0.05})_{\Sigma 2.02}(Mg_{3.62}Fe^{2+}{}_{1.15}Sc_{0.25}Al_{0.12}Mn_{0.02})_{\Sigma 5.16}(Si_{7.82}Al_{0.18})_{\Sigma 8.00}O_{22}(O_1F_{0.32})_{\Sigma 1.32}$ on 23 oxygen atoms
Titanite: Mill conc.	$(Ca_{0.95}REE_{0.02})_{\Sigma 0.97}(Ti_{0.68}Al_{0.23}Fe^{3+}{}_{0.08}Se_{0.01}Mg_{0.01})_{\Sigma 1.01}Si_{1.01}(O_{4.71}F_{0.29})_{\Sigma 5.00}$ on 5.0 oxygen and fluorine atoms

TABLE 2. CRYSTALLOGRAPHIC DATA

Crystal system	monoclinic
Space Group	C2/m
a (Å)	6.5304 (4)
b (Å)	8.5208 (4)
c (Å)	4.6806 (5)
β (°)	102.630 (7)
V (Å^3)	254.1 (1)
Z	2
D$_m$	3.50
D$_x$	3.50 g cm^{-3}
Min. transmission factor	0.87
Scan mode	ω - 2θ
omega scan width (°)	0.8 + 0.35tan θ
theta-range (°)	1 - 40
reciprocal space explored	h,±k,±l
measured reflections	1706
unique observed reflections with I>3σ(I)	797
Final R and Rw indices $^{\$}$	0.015, 0.029
No. of variables	33
GOF $^{\&}$	1.238

$^{\$}$ $R=[\Sigma(F_o-k|F_c|)/\Sigma F_o]$ $R_w=[\Sigma w(F_o-k|F_c|)^2/\Sigma wF_o^2]^{1/2}$

$^{\&}$ $GOF=[[\Sigma w(F_o-k|F_c|)^2/(N_{observations}-N_{variables})]^{1/2}$
$w=1/(\sigma(F_o))^2$, $\sigma(F_o)=[\sigma^2(I)+(0.04I)^2]^{1/2}/2F_oL_p$

TABLE 3. INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Si-O(1)	1.606(1)	O(1)-Si-O(2)	103.83(3)
Si-O(2)	1.626(1)	O(1)-Si-O(3)x2	107.81(2)
Si-O(3)x2	1.631(1)	O(2)-Si-O(3)x2	113.28(2)
		O(3)-Si-O(3)^a	110.34(4)
O(1)···O(2)	2.543(1)		
O(1)···O(3)x2	2.615(1)		
O(2)···O(3)x2	2.720(1)		
O(3)···O(3)^a	2.678(1)		
Sc-O(2)^{b}x2	2.113(1)	O(2)^b-Sc-O(2)^e	78.80(3)
Sc-O(3)^{c}x2	2.088(1)	O(2)^a-Sc-O(3)^{c}x2	93.94(2)
Sc-O(3)^{d}x2	2.199(1)	O(2)^b-Sc-O(3)^{d}x2	89.42(2)
		O(2)^b-Sc-O(3)^{f}x2	78.69(2)
		O(3)^c-Sc-O(3)^g	103.76(3)
		O(3)^c-Sc-O(3)^{f}x2	115.60(2)
		O(3)^c-Sc-O(3)^{d}x2	74.50(2)
O(2)^b···O(2)^e	2.682(1)		
O(2)^b···O(3)^c	3.071(1)		
O(2)^b···O(3)^d	3.034(1)		
O(2)^b···O(3)^f	2.735(1)		
O(3)^c···O(3)^g	3.285(1)		
O(3)^c···O(3)^f	3.628(1)		
O(3)^c···O(3)^d	2.597(1)		

Symmetry transformations as follows: a) x,-y,z; b) -1/2+x,1/2+y,z; c) -x,y-z; d) -1/2+x,1/2-y,1+z; e) 1/2-x,1/2-y,1-z; f) 1/2-x,1/2-y,-z; g) x,y,1+z.

TABLE 4. ATOMIC POSITIONS AND EQUIVALENT U'S

Atom	x	y	z	100 U (Å^2) eq
Sc	0.000	0.30841(2)	0.500	0.486(2)
Si	0.22329(4)	0.000	-0.09078(6)	0.396(3)
O(1)	0.000	0.000	0.000	1.51(2)
O(2)	0.3921(1)	0.000	0.2211(2)	0.547(9)
O(3)	0.23549(8)	0.15714(6)	-0.2854(1)	0.672(7)

For the atoms here mentioned, anisotropic displacement parameters U$_{ij}$'s have been used: these are reported in Table 5. In the last column, an isotropic equivalent displacement parameter defined as: $U_{eq}(\text{Å}^2) = 1/3\ \Sigma_{ij}U_{ij}a_ia_ja_i{}^*a_j{}^*$ is reported.

TABLE 5. ANISOTROPIC DISPLACEMENT PARAMETERS

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Sc	0.00577(5)	0.00634(5)	0.00618(5)	0	0.00091(4)	0
Si	0.00490(8)	0.00570(8)	0.00424(7)	0	0.00057(6)	0
O(1)	0.0070(3)	0.0319(6)	0.0204(5)	0	0.0069(3)	0
O(2)	0.0076(2)	0.0071(2)	0.0050(2)	0	-0.0010(2)	0
O(3)	0.0111(2)	0.0069(2)	0.0077(2)	0.0019(2)	0.0026(1)	0.0022(1)

The temperature factor is in the form:
$\exp[-2\pi^2\{h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + 1c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)\}]$ where a*, b*, and c* are reciprocal lattice constants.

not accurately represent the proportion of either valence state at the time of crystallization (Fryklund & Fleischer 1963, Norman & Haskin 1968). This being so, Sc normally behaves as a compatible element and is readily accommodated in mineral groups such as amphibole, pyroxene, and biotite; however, in systems rich in Sc, it may be concentrated in the late stages of pegmatite formation in thortveitite, bazzite (the Sc-analog of beryl, $Be_3Sc_2Si_6O_{18}$), and other Sc-bearing minerals that rarely occur in granitic pegmatites (Schetelig 1922, Lacroix 1923, Neumann 1961, Fryklund & Fleischer 1963, Krol *et al.* 1969, Juve & Bergstøl 1990, Voloshin *et al.* 1991). Similarly, in carbonatites, Sc is fractionated by mafic minerals but may be enriched in the final differentiates (Mitchell & Brunfelt 1974, Åmli 1977). For pegmatites with notable concentrations of Sc, assimilation of amphibolites or other rocks enriched in Sc by the intruding magma, or Sc extraction from wallrocks by pegmatitic fluids, commonly is cited as a mechanism for enrichment (Phan *et al.* 1967, Schaller *et al.* 1962, Goldschmidt 1934). For the thortveitite-bearing pegmatites in the Iveland–Evje district, Norway, Goldschmidt (1934) proposed that Sc had been extracted by the granitic magma from adjacent amphibolite. Phan *et al.* (1967) found that some Malagasy Republic (Madagascar) pegmatites enriched in Sc are very closely associated with amphibole-rich rocks, which acted to collect Sc. Sc enrichment occurs in beryl replacing schist (200 ppm) compared to beryl replacing granite (50 ppm) at Lake George, Colorado (W.R. Griffitts, unpubl. data, 1962). Similar enrichment in Sc also was found for beryl in feldspathic veins compared to that in pegmatites at several localities in Colorado and New Mexico (Staatz *et al.* 1965). More recently, the occurrence of bazzite, scandian ixiolite, and scandian pyrochlore in "cleavelandite" – "amazonite" pegmatites at Heftetjern, Tørdal, Telemark, Norway, was attributed to Sc enrichment during the passage of pegmatites through a mafic volcanosedimentary sequence (Bergstøl & Juve 1988, Juve & Bergstøl 1990). At the surface at Crystal Mountain, the bodies of thortveitite-bearing pegmatite are isolated from large masses of mafic rocks, except for occasional xenoliths (<100 m across) of biotite – quartz – plagioclase gneiss and hornblende–plagioclase gneiss, by a large expanse of felsic biotite granodiorite (<20 ppm Sc). The xenoliths have <40 ppm Sc and are genetically distinct from thortveitite-bearing melagabbro. The field relationships at Crystal Mountain are unlike those of Iveland–Evje and Heftetjern, Norway, with respect to possible source-rocks for the Sc, and thus it seems doubtful that the pegmatites share the assimilation–extraction mechanism for Sc enrichment proposed by Goldschmidt (1934), Bergstøl & Juve (1988) and Juve & Bergstøl (1990). Electron-probe microanalyses of edenite and actinolite within thortveitite-bearing rocks from Crystal Mountain showed between 1.6 and 2.0 wt.% Sc_2O_3 (Table 1). The Sc probably was derived from the magma responsible for the melagabbro, and the unusual texture of the thortveitite in these rocks may be the result of exsolution from amphibole upon cooling. Although most thortveitite in this association has irregular outlines, some blebs seem to follow crystallographic directions within the amphibole. There is an excess of cations, just about equal to the amount of Sc, for the three samples of edenite and one of actinolite (Table 1). Because thortveitite has just about the same amount of SiO_2 (44.6 wt.%) as the edenite, it is not simple to detect the presence of thortveitite in edenite. The polished thin sections containing edenite were examined carefully in a scanning electron microscope; no evidence for a second Sc-bearing mineral within the edenite was found. The distribution of Sc in the amphibole seems to be uniform. TEM studies will be necessary to possibly resolve the answer as to why there is a stoichiometric excess of cations that happens to equal the amount of Sc present. We contend that the source of Sc is magmatic and that thortveitite formed because the limit of Sc solid solution in amphibole and other minerals was exceeded.

In synthetic scandium-enriched pargasite, fluor-pargasite, fluor-eckermannite, and fluor-nyöbite, Sc has been shown to be strongly ordered in the M(2) site in substitution for octahedral Al (Raudsepp *et al.* 1987a, b, 1989). A composition of 0.8 a.f.p.u. has been found for scandian fluor-pargasite and 0.6 a.f.p.u. for scandian pargasite (Raudsepp *et al.* 1989). No natural analogs of these compounds have been reported, but Sc contents of about 100–400 ppm (0.015–0.062 wt.% Sc_2O_3) have been noted for amphibole from several localities (Borisenko & Rodionov 1961, Borisenko & Delitsin 1965, Sen *et al.* 1959, Nekrasov & Lebedeva 1970, Krylova *et al.* 1970). Thus it seems that the edenite – edenitic hornblende and actinolite associated with thortveitite at Crystal Mountain are anomalously rich in Sc. Krylova *et al.* (1970) reported a weak correlation between concentrations of Sc and ^{IV}Al in amphibole, but suggested that Sc also may occupy the ^{VI}Al sites. However, the possibility of tetrahedrally coordinated Sc in minerals is not supported by crystallographic evidence. On the basis of ionic radius, ^{VI}Sc (0.83 Å) would be more likely to substitute for ^{VI}Al (0.61 Å) than ^{IV}Al (0.47 Å), but the complexity of amphibole compositions makes assignment to a particular site arbitrary (radii from Whittaker & Muntus 1970).

A chondrite-normalized ratio (CNR) plot of the *REE* (Fig. 4) shows the strong fractionation of the *HREE* by thortveitite, and the strong negative Eu spike. The pattern is attributable to the similarity in ionic radii, ionic charges, and other properties of Sc^{3+} and the *HREE* capable of being admitted into the thortveitite structure. Although thortveitite is enriched in *HREE* and Y, a strong geochemical correlation of these elements with Sc has not been established for igneous or sedimentary rocks in general (Norman & Haskin 1968). A CNR pattern for associated titanite also is shown in Figure 4.

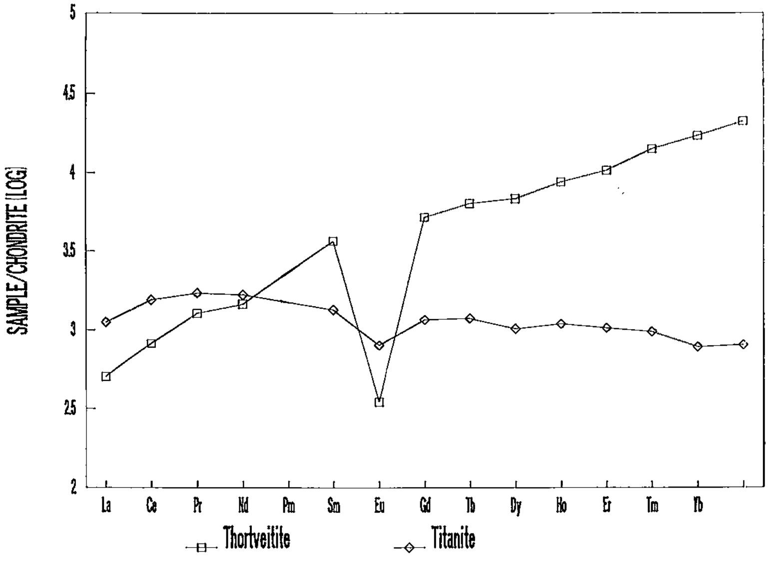

FIG. 4. Plot of chondrite-normalized concentrations of the rare-earth elements in coexisting thortveitite and titanite.

CNR patterns for associated purple fluorite (ΣREE + Y = 473 ppm) and ferroan diopside are essentially flat, with strong Eu-depletion spikes.

Schneider *et al.* (1975, 1977), Möller *et al.* (1976), and Ekambaram *et al.* (1986) have used log Tb/Ca *versus* log Tb/La to define three genetic types of fluorite. A high ratio of Tb/Ca is believed to reflect a differentiated source-region such as that for granite pegmatites, whereas low values suggest a depleted, sedimentary-type source. Intermediate values are interpreted to be of hydrothermal origin. The precise ranges are given in Möller *et al.* (1976). Using this method, Ekambaram *et al.* (1986) have recently shown that the fluorite – carbonate – quartz deposits of Mineral, Missoula, and Ravalli counties in western Montana are hydrothermal in origin. Fluorite from Crystal Mountain is of apparent hydrothermal origin on the basis of log Tb/Ca *versus* log Tb/La using our analytical data. However, the Tb/La ratio for Crystal Mountain fluorite is lower than for any of the other examples of fluorite in southwestern Montana.

EDS and ICP-MS analyses of ferroan diopside associated with thortveitite in a heavy-mineral concentrate from the fluorite-processing mill show a range in Sc content from 0 to 4.8 wt.% Sc_2O_3. BSE images show no other minerals to be present within the diopside, and X-ray-diffraction studies of purified separates also show no other mineral phases. An average result of three analyses for one grain containing close to the maximum amount of Sc_2O_3 also is given in Table 1. As the Sc_2O_3 and Na_2O contents increase, the FeO and CaO contents decrease, respectively, reflecting the coupled substitution: $Sc^{3+} + Na^+ = Fe^{2+} + Ca^{2+}$ to maintain charge balance. The ionic radius of Sc^{3+} (0.83Å) is close to that of Fe^{2+} (0.76 Å). Na_2O contents range from 0.92 to 2.53 wt.%, CaO contents range from 19.7 to 22.6 wt.%, and FeO contents range from 9.3 to 11.6 wt.%. The mineral jervisite (Mellini *et al.* 1982) is a scandium-rich pyroxene from the Baveno Granite, Italy. Synthetic Sc-analogs of aegirine and spodumene were characterized by Ito & Frondel (1968). In such a Sc-rich environment, it is not surprising that the ferroan diopside contains appreciable amounts of Sc, and likewise associated amphiboles, allanite and titanite. Scandium-bearing allanite (0.80 wt.% Sc_2O_3) from Finland was described by Meyer (1911). Likewise, Sc-bearing (0.22 wt.% Sc) titanite was reported from a pegmatite in Kazakhstan (Semenov *et al.* 1966).

The thortveitite from Crystal Mountain is not particularly enriched in Sn, as is the thortveitite reported from the Norwegian localities (Oftedal 1969). Likewise, there appears to be no correlation between Sc and Sn, Li, or Be in rocks from Crystal Mountain, in contrast to that reported for the Tørdal area of Norway (Bergstøl & Juve 1988). Sc at Crystal Mountain best correlates, in decreasing order, with F, Fe^{2+}, Th, Y, and Yb. Yb and Y are known only in the thortveitite; Th correlates with Sc because of the common inclusion of thorium minerals within the thortveitite, and in associated allanite-(Ce) and fergusonite.

The unit-cell dimensions of thortveitite from Montana are smaller than those of most thortveitite, but are close to those of thortveitite from the Malagasy Republic (Bianchi *et al.* 1988). The composition is similar, with a marked prevalence of Sc and low content of Y and the rare-earth elements.

A contraction of the cell volume of thortveitite with increasing scandium content is evident in the study by Bianchi *et al.* (1988), and can be explained on the grounds of the smaller ionic radius of Sc^{3+} with respect to Y^{3+}. Similarly, the metal–oxygen distances (2.088 to 2.199 Å) are smaller than for most natural specimens of thortveitite, but do not significantly differ from the corresponding values for thortveitite from Malagasy Republic.

The Sc site contents (a.p.f.u.) of thortveitite from Crystal Mountain (CM) and Malagasy Republic (MR) are nearly identical (see Table 1 and Bianchi *et al.* 1988): Sc 1.831 (CM), 1.836 (MR); Y 0.054 (CM), 0.054 (MR); Fe^{3+} 0.049 (CM), 0.046 (MR); and *R* (all others by difference) 0.066 (CM), 0.064 (MR).

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