The Canadian Mineralogist
Vol. 36, pp. 673-680 (1998)

SCANDIUM SUBSTITUTION IN COLUMBITE-GROUP MINERALS AND IXIOLITE

MICHAEL A. WISE[1]

Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

PETR ČERNÝ

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

ALEXANDER U. FALSTER

Department of Geology and Geophysics, University of New Orleans, New Orleans, Louisiana 70148, U.S.A.

ABSTRACT

Columbite-group minerals and ixiolite with extremely variable concentrations of scandium are widespread in moderately to highly fractionated rare-element granitic pegmatites. Columbite-group minerals with 1–3 wt.% Sc_2O_3 are referred to as scandian columbite – tantalite and show degrees of structural order similar to columbite – tantalite lacking Sc. Disordered structures remain orthorhombic and become ordered upon heating. Pseudo-orthorhombic stannian (Sn-rich), titanian (Ti) and wolframian (W) variants of ixiolite may contain as much as 3.7 wt.% Sc_2O_3 and revert to monoclinic phases upon heating. Similarly, scandian ixiolite that contains Sc in excess of 3.0 and up to 18.8 wt.% Sc_2O_3 converts from orthorhombic to monoclinic symmetry upon heating and has a stoichiometry that approaches $Sc(Nb,Ta)O_4$. Scandium-bearing columbite – tantalite and ixiolite show similar ranges in Mn/(Mn + Fe) and Ta/(Ta + Nb) values, but noticeably different Sn, Ti and Sc contents. Scandium is incorporated into the columbite and ixiolite structures *via* the coupled substitution $Sc^{3+} + (Ti,Sn)^{4+} = (Fe,Mn)^{2+} + (Nb,Ta)^{5+}$; it is strongly partitioned into the (Fe,Mn) site, whereas the Ti and Sn prefer the (Nb,Ta) site. Within the (Fe,Mn) site, the substitution of Sc for Fe is more prevalent. In most pegmatites, Sc fractionation in columbite – tantalite, stannian ixiolite, titanian ixiolite and wolframian ixiolite is erratic, unlike scandian ixiolite, which shows strong enrichment in Sc with increasing Mn, Ta and Sn.

Keywords: scandium, columbite, tantalite, ixiolite, granitic pegmatite.

SOMMAIRE

Les minéraux du groupe de la columbite et l'ixiolite des pegmatites granitiques à éléments rares dont le degré d'évolution est moyen à avancé font preuve de concentrations extrêmement variables de scandium. Les minéraux du groupe de la columbite ayant de 1 à 3% (poids) de Sc_2O_3 ont un degré d'ordre semblable à celui de la columbite – tantalite sans Sc. Les structures désordonnées demeurent orthorhombiques et deviennent ordonnées suite au chauffage. Les variantes pseudo-orthorhombiques de l'ixiolite riches en étain, en titane et en tungstène peuvent contenir jusqu'à 3.7% de Sc_2O_3 (poids), et deviennent monocliniques après chauffage. De même, l'ixiolite, dont la teneur en Sc dépasse 3.0% et peut atteindre 18.8% de Sc_2O_3, passe de la modification orthorhombique à monoclinique suite au chauffage, et possède une stoechiométrie se rapprochant de $Sc(Nb,Ta)O_4$. La columbite – tantalite et l'ixiolite contenant le Sc montrent des intervalles de valeurs de Mn/(Mn + Fe) et de Ta/(Ta + Nb) semblables, mais leurs teneurs en Sn, Ti et Sc diffèrent beaucoup. Le scandium serait accommodé dans la structure de la columbite et celle de l'ixiolite selon la substitution couplée $Sc^{3+} + (Ti,Sn)^{4+} = (Fe,Mn)^{2+} + (Nb,Ta)^{5+}$; le Sc favorise le site (Fe,Mn), tandis que le Ti et le Sn préfèrent le site (Nb,Ta). Dans le site (Fe,Mn), le remplacement du Fe par le Sc est plus important. Dans la plupart des pegmatites, le degré d'enrichissement du Sc dans la columbite – tantalite et dans l'ixiolite stannifère, titanifère ou tungstènifère est aléatoire, en comparaison de l'ixiolite, qui fait preuve d'un fort enrichissement en Sc à mesure qu'augmente la teneur en Mn, Ta et Sn.

(Traduit par la Rédaction)

Mots-clés: scandium, columbite, tantalite, ixiolite, pegmatite granitique.

---

[1] *E-mail address*: wise.michael@nmnh.si.edu

INTRODUCTION

Scandium is one of several lithophile elements that may be a minor constituent in Nb,Ta oxide minerals from rare-element granitic pegmatites. The presence of trace amounts of Sc in columbite-group minerals and ixiolite from a number of localities has been well documented (*cf.* Borisenko 1963, Hodkinson & Clark 1977, von Knorring & Fadipe 1981, Černý & Němec 1995). However, it is only in Sc-rich provinces, such as those found near Tørdal (Norway), Antsirabe (Madagascar), Muiane (Mozambique) and the Ilmen Mountains, in the central Urals (Russia), that significant Sc enrichment, up to several percent, may occur in Nb,Ta oxide minerals. In such instances, these minerals may also be accompanied by other Sc-rich minerals such as thortveitite and bazzite. The Sc content of most columbite – tantalite and ixiolite is typically very low, in most cases ranging from near the detection limits to just less than 1 wt.% Sc_2O_3 (*cf.* Neumann 1961, Borisenko 1963, Haapala *et al.* 1967). However, ixiolite with a Sc content in excess of 5.0 wt.% Sc_2O_3 has been reported from Mozambique, Madagascar and Norway (Borisenko *et al.* 1969, von Knorring *et al.* 1969, Bergstøl & Juve 1988).

Detailed studies describing the occurrence of Sc in Nb,Ta oxide minerals are few, and the available data are too limited to draw reliable conclusions regarding the behavior of Sc in columbite – tantalite and ixiolite. Our understanding of the mechanism of incorporation and fractionation of Sc in columbite – tantalite and ixiolite has been greatly hindered, largely by the generally low concentrations of Sc occurring in these minerals. Perhaps equally significant is the failure to acquire data on Sc during routine analysis of Nb–Ta oxide minerals. As a result of our ongoing crystal-chemical and geochemical studies on Nb,Ta oxide minerals from granitic pegmatites, a brief discussion of the behavior of Sc in columbite – tantalite and ixiolite is presented in this paper.

EXPERIMENTAL METHODS

Samples of columbite-group minerals and ixiolite used in this study were selected to cover a broad compositional range. Given the extremely rare occurrence of Sc-enriched phases and the ubiquitous association of Sc and Ti, it was not possible to select only those samples with high levels of Sc and low levels of Ti and Sn. The bulk of the data is extracted from the unpublished dataset of M. Wise and is augmented by selected data from the literature. The sources of data from the literature and a list of samples used in this study are provided in Table 1.

Columbite – tantalite and ixiolite were analyzed by means of an ARL–SEMQ electron microprobe under conditions as described in Wise & Černý (1996). Atomic contents were calculated on the basis of 24 atoms of oxygen per formula unit for direct comparison of the columbite and ixiolite unit-cells. Results that showed cation sums in excess of the structurally available sites were adjusted by converting Fe^{2+} to Fe^{3+} as required to eliminate the cation surplus (*cf.* Ercit *et al.* 1992).

TABLE 1. LOCALITIES OF Sc-BEARING COLUMBITE AND IXIOLITE

Sample	Location	Source/Reference	Mineral
Phillips	Phillips, Maine	research coll. MW	Ct
AT	Phillips, Maine	research coll. MW	Ct
BMT	Black Mountain, Maine	research coll. MW	Ct
Pingree	Pingree, Maine	research coll. MW	Ct
Lord Hill	Lord Hill, Maine	research coll. MW	Ct
Emmons	Emmons, Maine	research coll. MW	Ct
BB#7	BB#7, Maine	research coll. MW	Ct
Hayes	Hayes, Maine	research coll. MW	Ct
Waisanen	Waisanen, Maine	research coll. MW	Ct
Songo Pond	Songo Pond, Maine	research coll. MW	Ct
DN6 #32	Kosov, Czech Republic	research coll. PČ	Ct
TA-SL-62	Slocum quarry, Connecticut	research coll. PČ	Ct
Animikie	Animikie Red Ace, Wisconsin	research coll. AF	Ct
Luster	Luster, Colorado	research coll. AF	Ct
Ercit-1	Blue Star, Ontario	Ercit (1994)	Ct
Ercit-3	Davis Mica, Ontario	Ercit (1994)	Ct
Ercit-4	Hybla, Ontairo	Ercit (1994)	Ct
Ercit-5	Quadeville Beryl, Ontario	Ercit (1994)	Ct
Ercit-6	Quadeville Rose Qtz, Ontario	Ercit (1994)	Ct
Ercit-7	Ryan–Sheehan, Ontario	Ercit (1994)	Ct
Ercit-8	Woodcox, Ontario	Ercit (1994)	Ct
TA-SL-63, -65, -66	Slocum quarry, Connecticut	research coll. PČ	TIX
TA-SL-68d	Simpson quarry, Connecticut	research coll. PČ	TIX
MM5-2 to -5	Maršikov, Czech Republic	research coll. PČ	TIX
DN4 #21, -23	Bradlo, Czech Republic	research coll. PČ	TIX
MSX-65	Muskox Lake, NWT	research coll. PČ	TIX
KVV-78, -79	Věžná II, Czech Republic	research coll. PČ	TIX
TRT-5 to -7	Tanco, Manitoba	research coll. PČ	TIX
NN-50	Locality unknown	USNM 174077	TIX
NOR-57	Norway	USNM 107397	TIX
AMB-59	Ambatofotsikely, Madagascar	USNM 88876	TIX
JOH-3, -4	Cinovec, Czech Republic	Johan & Johan (1994)	TIX
GL-74 to -77	Greer Lake, Manitoba	Černý *et al.* (1986)	TIX
JIH-86, -87	Bradlo, Czech Republic	Černý & Němec (1995)	TIX
LOT-93	Lower Tanco, Manitoba	Ferreira (1984)	TIX
PR-95 to -98	Prašivá–Dribrana, Czech Rep.	Uher *et al.* (1998)	TIX
Knorring-2	Antsirabe, Madagascar	von Knorring *et al.* (1969)	TIX
More	Amelia, Virginia	research coll. MW	SNIX
Dolní Bory	Dolní Bory, Czech Republic	research coll. PČ	WIX
Cyrilov	Cyrilov, Czech Republic	research coll. PČ	WIX
Carrock	Carrock Fell, England	Beddoe-Stephens & Fortey (1981)	WIX
Cornwall	Cornwall, England	Hodkinson & Clark (1977)	WIX
Cinovec	Cinovec, Czech Republic	Johan & Johan (1994)	WIX
Heftetjern6	Heftetjern, Norway	research coll. MW	SCIX
Beta button	Betanimena, Madagascar	research coll. MW	SCIX
Beta beryl	Betanimena, Madagascar	research coll. MW	SCIX
C1634	Muiana, Mozambique	research coll. MW	SCIX
C1762	Naquissupa, Mozambique	research coll. MW	SCIX
Muiane Rosette	Muiane, Mozambique	research coll. MW	SCIX
Fisher-1	Fisher, Maine	research coll. MW	SCIX
DN6 #30	Kosov, Czech Republic	research coll. PČ	SCIX
Knorring-1	Naquissupa, Mozambique	von Knorring *et al.* (1969)	SCIX
Knorring-3	Betanimena, Madagascar	von Knorring *et al.* (1969)	SCIX

Symbols: Ct: columbite, TIX: titanian ixiolite, SNIX: stannian ixiolite, WIX: wolframian ixiolite, SCIX: scandian ixiolite.

CHEMICAL COMPOSITION

Back-scattered electron images of Sc-bearing columbite – tantalite and ixiolite show various degrees of patchy to oscillatory zoning. Crystals of columbite – tantalite and ixiolite that are zoned with respect to variations in Mn/(Mn + Fe) and Ta/(Ta + Nb) do not show zoning in terms of Sc. In all specimens examined, the distribution of Sc appears to be homogeneous throughout the crystal.

The composition of all the analyzed samples and selected data from the literature are plotted in the columbite quadrilateral and the (Sc) – (Fe, Mn)$^{2+}$ – (Nb, Ta)$^{5+}$ diagram (Fig. 1). Representative compositions of Sc-bearing columbite – tantalite and ixiolite are given in Tables 2 and 3, respectively. On the whole, columbite-group minerals contain significantly lower levels of Sc than scandian ixiolite.

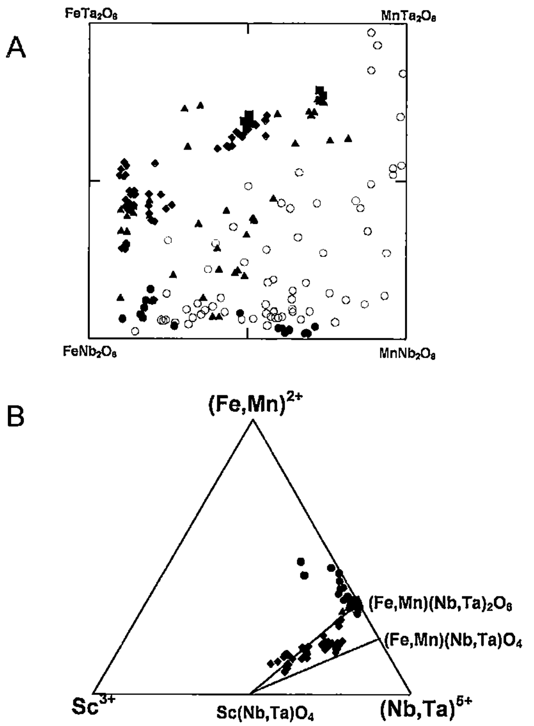

FIG. 1. Plot of Sc-bearing columbite and ixiolite in (A) columbite quadrilateral and (B) the Sc – (Fe,Mn) – (Nb,Ta) diagram. Open circles: scandian columbite, diamonds: scandian ixiolite, squares: stannian ixiolite, triangles: titanian ixiolite, dots: wolframian ixiolite. Black field in B represents data for columbite and stannian and titanian ixiolites.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF Sc-BEARING COLUMBITE – TANTALITE AND IXIOLITE

	BMT Ct	Lord Hill Ct	Luster Ct	AMB-59 TIX	TRT-5 TIX	More-L1 SNIX	JOH-1$^+$ WIX
FeO wt.%	3.49	9.25	13.59	11.54	3.40	6.64	15.74
CaO	0.00	0.00	0.00	0.00	0.20	0.00	0.08
MnO	15.57	8.54	3.24	7.16	7.90	6.52	3.40
Nb_2O_5	64.58	66.84	55.45	69.64	13.50	15.01	47.86
Ta_2O_5	14.05	6.89	20.09	5.13	55.10	54.29	10.78
TiO_2	0.04	2.01	4.49	5.57	15.80	3.84	1.81
SnO_2	0.06	0.37	0.00	0.00	3.60	11.68	0.23
Sc_2O_3	0.41	0.78	2.27	1.52	1.00	0.17	0.66
Fe_2O_3	1.10	3.34	0.00	0.00	0.00	0.00	2.91
MgO	0.00	0.07	0.00	0.00	0.00	0.00	0.00
WO_3	0.73	2.15	0.00	0.00	0.00	1.57	16.82
ZrO_2	0.00	0.00	0.00	0.00	0.00	0.51	0.00
Total	100.03	100.33	99.13	100.56	100.50	100.25	100.47*
Fe^{2+}	0.692	1.774	2.724	2.139	0.755	1.625	3.228
Ca^{2+}	0.000	0.012	0.000	0.000	0.000	0.000	0.020
Mn^{2+}	3.131	1.651	0.665	1.344	1.776	1.617	0.708
Nb^{5+}	6.931	6.896	6.007	6.979	1.620	1.986	5.308
Ta^{5+}	0.907	0.428	1.309	0.309	3.978	4.321	0.720
Ti^{4+}	0.007	0.345	0.809	0.928	3.154	0.846	0.332
Sn^{4+}	0.006	0.034	0.000	0.000	0.381	1.363	0.024
Sc^{3+}	0.085	0.155	0.473	0.294	0.231	0.043	0.140
Fe^{3+}	0.197	0.574	0.000	0.000	0.000	0.000	0.536
Mg^{2+}	0.000	0.022	0.000	0.000	0.000	0.000	0.000
W^{6+}	0.045	0.127	0.000	0.000	0.000	0.119	1.068
Zr^{4+}	0.000	0.000	0.000	0.000	0.000	0.073	0.000
Total	12.000	12.018	11.980	11.993	11.952	11.996	12.084

Symbols: Ct: columbite, TIX: titanian ixiolite, SNIX: stannian ixiolite, WIX: wolframian ixiolite. $^+$ Johan & Johan (1994). * total includes 0.03% ThO_2, 0.15% Y_2O_3.

Columbite-group minerals

Columbite – tantalite with low levels of Sc show bulk compositions that cover the full range of Mn/(Mn + Fe) and Ta/(Ta + Nb) values (Fig. 1). Scandium contents fall within the range of 0 to ~3.0 wt.% Sc_2O_3, but less than 1.0 wt.% in most cases. Subordinate Fe^{3+}, Sn, Ti, and W also vary greatly, with maximum concentrations of 4.4 wt.% Fe_2O_3, 2.0 wt.% SnO_2, 3.6 wt.% TiO_2 and 3.2 wt.% WO_3 occurring in addition to Sc. In the (Sc) – (Fe,Mn)$^{2+}$ – (Nb,Ta)$^{5+}$ diagram, most of the columbite data plot near the composition represented by $(Fe,Mn)(Nb,Ta)_2O_6$ stoichiometry (Fig. 1).

Titanian, stannian and wolframian ixiolite

Ixiolite with up to 3% Sc_2O_3 typically shows variable Mn/(Mn + Fe) and Ta/(Ta + Nb) values. The range of Mn/(Mn + Fe) and Ta/(Ta + Nb) values is slightly less than in the case of Sc-bearing columbite. Titanian ixiolite with Ti > Sn generally contains low to moderate concentrations of Sc (0 – 2.8 wt.% Sc_2O_3). Mn/(Mn + Fe) and Ta/(Ta + Nb) values are highly variable, ranging from 0.10 to 0.82 and from 0.05 to 0.76, respectively. Representative stannian ixiolite (Sn > Ti), by comparison, typically shows high, yet more

TABLE 3. REPRESENTATIVE COMPOSITIONS OF SCANDIAN IXIOLITE

	BBe	FIS	BBu	C1634	C1762	ROS	HEF	HEF
WO_3	0.99	0.00	1.51	2.17	2.12	4.20	0.12	0.20
Nb_2O_5	39.67	58.82	23.78	24.55	28.45	26.69	16.78	17.58
Ta_2O_5	26.18	13.26	41.81	35.90	37.18	37.52	52.80	51.57
ZrO_2	1.16	0.00	2.37	2.09	2.13	0.69	2.25	1.71
TiO_2	5.99	6.79	6.38	7.56	4.72	3.32	0.34	0.41
SnO_2	2.76	0.02	2.30	5.57	5.94	5.24	7.27	7.66
Sc_2O_3	4.81	5.36	5.75	6.81	7.83	11.09	13.56	15.17
Fe_2O_3	9.72	0.00	7.87	7.50	5.39	2.90	0.00	1.65
FeO	6.65	11.71	5.61	4.57	6.42	5.63	3.22	1.65
MnO	1.74	2.92	1.53	1.63	1.45	1.88	2.74	2.87
CaO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.13	0.17	0.10	0.14	0.08	0.00	0.00	0.00
Total	99.79	99.08	99.01	98.49	101.71	99.16	99.08	100.47
W^{6+}	0.061	0.000	0.101	0.143	0.137	0.281	0.009	0.014
Nb^{5+}	4.295	6.065	2.782	2.820	3.214	3.119	2.112	2.144
Ta^{5+}	1.705	0.822	2.942	2.480	2.527	2.637	3.998	3.782
Zr^{4+}	0.135	0.000	0.299	0.259	0.260	0.087	0.305	0.225
Ti^{4+}	1.079	1.164	1.241	1.444	0.887	0.645	0.071	0.083
Sn^{4+}	0.264	0.002	0.237	0.564	0.592	0.540	0.807	0.824
Sc^{3+}	1.004	1.065	1.296	1.508	1.705	2.498	3.290	3.565
Fe^{3+}	1.751	0.000	1.533	1.434	1.014	0.565	0.000	0.335
Fe^{2+}	1.331	2.232	1.213	0.971	0.307	1.217	0.750	0.371
Mn^{2+}	0.353	0.564	0.335	0.351	1.341	0.412	0.646	0.656
Ca^{2+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg^{2+}	0.046	0.058	0.039	0.053	0.030	0.000	0.000	0.000
Total	12.023	11.972	12.019	12.026	12.014	12.000	11.988	11.999

Compositions quoted in wt.% oxides. Localities: BBe: Beta Beryl, FIS: Fisher, BBu:Beta Button, ROS: Rosette, HEF: Heftetjern.

restricted ranges of Mn/(Mn + Fe) [0.49–0.74] and Ta/(Ta + Nb) [0.67–0.78]. Scandium concentrations are generally less than 1.0 wt.% Sc_2O_3, but can attain 4.0 wt.% Sc_2O_3 in rare instances. Rare W-rich "wolframo-ixiolite", usually with subordinate Ti, may contain up to 3.65 % Sc_2O_3 (Novák & Šrein 1989). The Mn/(Mn + Fe) values are highly variable [$0.11 < Mn/(Mn + Fe) < 0.72$] whereas Ta/(Ta + Nb) values are extremely limited [$0.02 < Ta/(Ta + Nb) < 0.15$].

Scandian ixiolite

The Sc values of scandian ixiolite are typically in excess of 4.0 wt.%, with the highest values reaching ~19 wt.% Sc_2O_3. Scandian ixiolite typically contains significantly higher Sn (up to 9 wt.% SnO_2) and Ti contents (up to 10 wt.% TiO_2) than Sc-bearing columbite-group minerals. With few exceptions, Ti and Sn concentrations of scandian ixiolite are generally lower than those of stannian or titanian ixiolite. The Mn/(Mn + Fe) of scandian ixiolite is highly variable, but the Ta/(Ta + Nb) ratios are more limited, ranging primarily from ~0.35 to ~0.70. In terms of the (Sc) – $(Fe,Mn)^{2+}$ – $(Nb,Ta)^{5+}$ diagram, scandian ixiolite generally plots between the $(Fe,Mn)(Nb,Ta)_2O_6$ – $Sc(Nb,Ta)O_4$ and $(Fe,Mn)(Nb,Ta)O_4$ – $Sc(Nb,Ta)O_4$ joins (Fig. 1) suggesting that Fe^{3+} is an important component of the scandian ixiolite composition.

STRUCTURAL STATE

Columbite-group minerals and ixiolite commonly show large variations in structural states (*i.e.*, degree of order), which can be evaluated qualitatively from a plot of *c versus a* cell edges (Černý & Turnock, 1971, Wise *et al.* 1985). Enrichment of Ti and Sn in the Nb- and Ta-bearing oxide minerals may affect the structural state (*cf.* Černý *et al.* 1986), but the role of Sc on the structural state of columbite-group minerals and ixiolite has yet to be determined. Assessing the effect of Sc on the structural state is complicated by the fact that most samples of Sc-bearing columbite and ixiolite also contain appreciable Ti and Sn.

The structural state of natural Sc-bearing columbite – tantalite is similar to that of Sc-free columbite – tantalite. Partially to fully ordered orthorhombic structures were noted, with no correlation existing between Sc content and degree of order. Titanian and stannian ixiolite also is orthorhombic, but these variants are highly disordered in their natural state. After heating, their structures revert to an ordered (monoclinic) wodginite cell (Wise & Černý 1986). "Wolframo-ixiolite" is monoclinic in its natural state with a unit cell that is similar to that of wolframite, but forms a mixture of ordered columbite – tantalite and UTa_2O_8-type phase upon heating (Ginsburg *et al.* 1969). The structure of natural, unheated scandian ixiolite has been described as orthorhombic (von Knorring *et al.* 1969, Bergstøl & Juve 1988). However, a recent refinement of the structure of scandian ixiolite from the Heftetjern locality indicates that the structure is highly disordered and pseudo-orthorhombic, with a slight departure toward monoclinic symmetry (unpubl. data of MW). The monoclinic symmetry of the structure, which is apparently related to that of wolframite, becomes more obvious after heating.

CRYSTAL CHEMISTRY

The pattern of substitution of the major components (Fe^{2+}, Mn, Nb, Ta) and the incorporation of minor elements (Fe^{3+}, Ti and Sn) in the cation sites of the columbite structure have been well established. However, the amount of Sc normally found in columbite – tantalite is usually so small that its structural role cannot be easily identified; thus the mechanism of incorporation by which Sc enters the columbite structure has been less clearly defined.

The ionic radius (0.75 Å) and charge (3+) of 6-coordinated Sc are intermediate to that of Fe, Mn, Nb and Ta, and so it is expected that Sc will reside in both the *A* and *B* sites of the columbite structure. However, the charge and ionic radius of Sc are closer to Fe (and, to a lesser degree, Mn) than to Nb or Ta. The mean *Sc*–O distance for 6-coordinated Sc in Sc_2O_3 is ~2.10 Å (*cf.* Geller *et al.* 1967), which is very similar to the mean *A*–O distance of 2.14 Å found in the columbite structure. The *B* site (mean *B*–O distance ~2.02 Å), on the other hand, is significantly smaller than the *A* site and therefore probably less favorable for the entry of Sc into the ordered structure of columbite. Highly disordered structural states (*i.e.*, ixiolite structure), by comparison, tend to favor the introduction of high Sc contents.

TABLE 4. SCHEMES OF SUBSTITUTION FOR THE ENTRY OF Sc IN COLUMBITE AND IXIOLITE

1. Sc^{3+}_{+2} $(Fe,Mn)^{2+}_{-1}$ $(Ti,Sn)^{4+}_{-1}$
2. Sc^{3+}_{+3} $(Fe,Mn)^{2+}_{-2}$ $(Nb,Ta)^{5+}_{-1}$
3. Sc^{3+}_{+4} $(Fe,Mn)^{2+}_{-3}$ W^{6+}_{-1}
4. Sc^{3+}_{+1} $(Ti,Sn)^{4+}_{+1}$ $(Fe,Mn)^{2+}_{-1}$$(Nb,Ta)^{5+}_{-1}$
5. Sc^{3+}_{+1} W^{6+}_{+1} $(Ti,Sn)^{4+}_{-1}$ $(Nb,Ta)^{5+}_{-1}$

The substitution of trivalent Sc into the columbite structure requires a charge-distribution mechanism in order to maintain electrostatic balance. Table 4 lists a variety of possible coupled substitutions that may be responsible for the entry of Sc into the columbite structure. In all of the samples considered, W was found invariably to be extremely low, and thus was probably not a significant factor in the incorporation of Sc into the columbite structure. Therefore, substitution schemes (3) and (5) are probably of minor importance, if any. Substitution scheme (2) is similar to that proposed for Fe^{3+}, and involves no other cations except the major components (Fe, Mn) and (Nb, Ta). However, in columbite – tantalite with appreciable Sc, the number of atoms per formula unit of Ti or Sn (or both) is always greater than that of Sc, thus suggesting that R^{4+} cations may play a significant role in the entry of Sc into the columbite structure. Plots of Sc *versus* $R^{2+} + R^{4+}$ as well as Sc *versus* $R^{2+} + R^{5+}$ failed to show any strong correlation, thereby eliminating substitution schemes (1) an (2) as likely possibilities. The remaining scheme of substitution (4) invokes a coupled entrance of Sc and R^{4+} cations with R^{2+} and R^{5+} cations. This *euxenite-type* substitution has been suggested by Beddoe-Stephens & Fortey (1981) and Novák & Čech (1996) as the primary mechanism by which Sc may enter the columbite structure. In most of the samples examined, the calculated level of Fe^{3+} was proved to be of significant importance and therefore cannot be ignored when considering the overall mechanism of substitution. Figure 2 shows a strong negative correlation between $\Sigma R^{3+}R^{4+}$ and $\Sigma R^{2+}R^{5+}$, in support of the *euxenite-type* scheme of substitution.

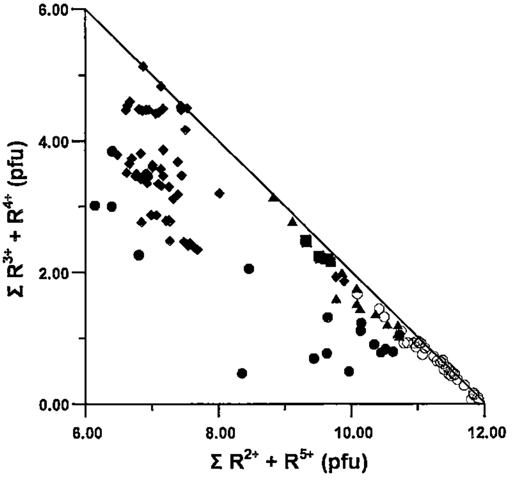

FIG. 2. Relationship between $\Sigma R^{3+}R^{4+}$ and $\Sigma R^{2+}R^{5+}$ cations (atoms *pfu*). Symbols as in Figure 1.

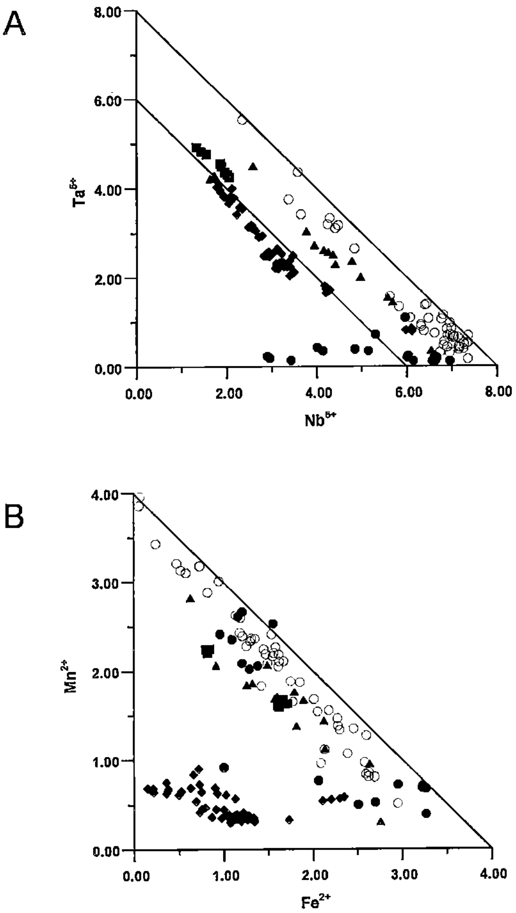

FIG. 3. Variation diagrams. (A) Nb *versus* Ta; (B) Fe *versus* Mn (atoms *pfu*). Symbols as in Figure 1. Upper and lower boundaries represent trends of ideal AB_2O_6 and ABO_4 stoichiometries, respectively.

Figure 3 shows cation–cation plots summarizing the homovalent mechanisms of substitution mechanisms observed in Sc-bearing columbite and ixiolite. Figure

3a shows the nature of Ta-for-Nb substitution in Sc-bearing columbite-group minerals and ixiolite. The majority of the data fall between two parallel boundaries drawn to represent the ideal AB_2O_6 and ABO_4 stoichiometries. The data for columbite plot on or close to the upper boundary, whereas the data points for ixiolite with Sc contents less than 4.0 wt.% plot between the two boundaries, and those for scandian ixiolite lie along the lower boundary representing ABO_4 stoichiometry. For Sc-bearing columbite, the correlation between Nb and Ta is reasonably strong. However, many of the data points fall off the main trend, indicating that constituents other than Nb or Ta substitute at the *B* site. Similar behavior is observed for stannian and titanian variants of ixiolite. The few data points representing wolframian ixiolite do not follow any particular trend and require further study. Scandian ixiolite, by comparison, shows a very strong linear correlation with a slope of −1, indicating that Ta-for-Nb substitution is dominant; unlike the columbite-group minerals, no other substitution involving other elements is involved at the *B* site. In addition, the trend of the scandian ixiolite data along the ABO_4 boundary strongly implies a structure type other than columbite for scandian ixiolite.

Mn-for-Fe substitution results in similar trends for columbite and low-Sc ixiolite (Fig. 3b) Significant replacement of the principal constituents by Sc^{3+}, Fe^{3+}, Ti^{4+} and Sn^{4+} is responsible for the deviation from AB_2O_6 stoichiometry observed in columbite – tantalite. Although the correlation between Mn and Fe^{2+} is reasonably strong but based on limited data for scandian ixiolite, the majority of the data points plot well below the AB_2O_6 boundary, again implying a difference in structure type between columbite and scandian ixiolite.

The composition of stannian and titanian ixiolite generally approaches the stoichiometry of wodginite and ideal titanowodginite, ABC_2O_8. Many of the analyzed samples can be expressed with Sc occupying the *B* site along with Ta and tetravalent Sn and Ti. As is the nature of ixiolite, Sc may be disordered over all three sites; however, this is merely speculation at this time, and the matter requires a more in-depth study.

At Sc concentrations in excess of 8 wt.% Sc_2O_3, Sc greatly exceeds (Fe,Mn), and it becomes the dominant cation occupying the *A* site. The result is a change in stoichiometry from AB_2O_6 to ABO_4, with a subsequent structural change from orthorhombic to monoclinic symmetry. Few natural occurrences of ABO_4-type niobates or tantalates are known, none of which crystallize with the orthorhombic structure of columbite (Table 5). Synthetic $ScNbO_4$ and $ScTaO_4$ have been reported to have a monoclinic wolframite-type structure, and scandian ixiolite containing in excess of 8 wt.% Sc_2O_3 has a stoichiometry approaching $Sc(Nb,Ta)O_4$, with a structure related to wolframite (MW, in prep.).

TABLE 5. STRUCTURAL COMPARISON OF NATURALLY OCCURRING ABO_4-TYPE NIOBATES AND TANTALATES

Mineral	Formula	Radius*	Crystal system	Structure type
Alumotantite	$AlTaO_4$	0.54	Orthorhombic	Alumotantite
Stibiocolumbite	$SbNbO_4$	0.76	Orthorhombic	Stibiocolumbite
Stibiotantalite	$SbTaO_4$	0.76	Orthorhombic	Stibiocolumbite
Fergusonite	$YNbO_4$	0.90	Tetragonal	Fergusonite
Formanite	$YTaO_4$	0.90	Tetragonal	Fergusonite
Bismutocolumbite	$BiNbO_4$	1.03	Orthorhombic	Stibiocolumbite
Bismutotantalite	$BiTaO_4$	1.03	Orthorhombic	Stibiocolumbite

* Radius of *A*-site cation, in Å.

Sc Fractionation

The nature of Sc fractionation during the evolution of pegmatite-forming melts is not easily resolved. During crystallization of a granitic pegmatite, Sc is generally dispersed in garnet, micas, various oxides and rare-earth-element (*REE*) minerals. The principal carriers of Sc in granitic pegmatites are thortveitite, euxenite, samarskite, fergusonite, xenotime, gadolinite, zircon, columbite and cassiterite. Such Sc-enriched minerals usually do not occur in the earliest stages of pegmatite crystallization. Thortveitite, for example, occurs in the intermediate zone, whereas Sc-bearing *REE* minerals are generally formed during late-stage albitization (Borisenko 1963).

The elevated Sc content of pegmatite-forming melts has been attributed to two possible mechanisms: 1) accumulation of Sc resulting from the contamination by mafic country-rocks by the pegmatite-forming melt, and 2) destabilization of Sc complexes that are thermally stable in the parental granitic melt, with Sc incorporated in precipitating phases in lower-temperature pegmatite-forming melts. Neumann (1961), Ercit (1986) and Bergstøl & Juve (1988) cited examples where the reaction of a pegmatite-forming melt with mafic country-rocks is considered to be responsible for the presence of thortveitite, Sc-bearing columbite or scandian ixiolite in pegmatites. However, the enrichment of Sc in pegmatites hosted by granite (*e.g.*, Kobe, Japan: Sakurai *et al.* 1962) or tonalitic to granitic gneisses (*e.g.*, Greer Lake, Manitoba: Černý *et al.* 1986) suggests that the accumulation of Sc in the residual melt without assimilation of mafic country-rocks is equally viable.

Within the columbite-group minerals, the behavior of Sc during the fractionation of pegmatites is highly erratic. Ercit (1994) observed that Sc contents generally increase with increasing Ta/(Ta + Nb), but show a negative correlation with Mn/(Mn + Fe) for some poorly fractionated pegmatites within the southwestern Grenville province of the Canadian Shield. However, some of the columbite samples also show increasing Sc with Mn enrichment, but no enrichment in Ta. In the Tanco (Manitoba) pegmatite, the concentration of Sc decreases nonlinearly in columbite, from the outer

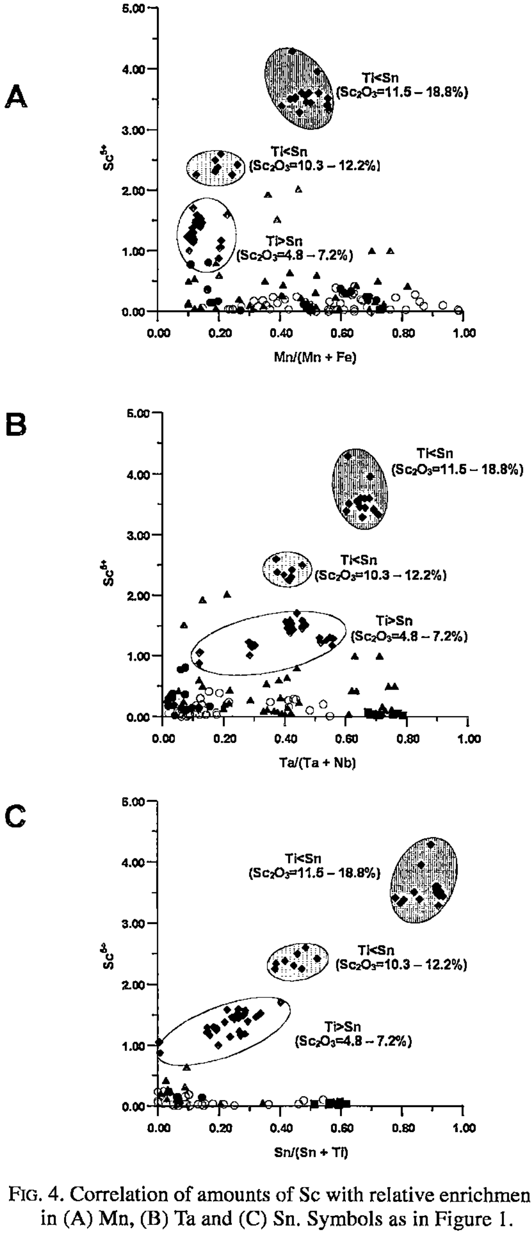

FIG. 4. Correlation of amounts of Sc with relative enrichment in (A) Mn, (B) Ta and (C) Sn. Symbols as in Figure 1.

zones toward the central units (Ercit 1986). Columbite from the spodumene-bearing Black Mountain (Maine) pegmatite shows similar fractionation of Sc (unpubl. data of C. Brown); a decrease in Sc correlates with increasing Mn and Ta enrichment. On the other hand, columbite from the Animikie Red Ace pegmatite, in Wisconsin, which is unusual in that the highest Mn/Fe and Ta/Nb values occur in the wall zone and decrease toward the interior zones, show decreasing levels of Sc from the margins to the core.

Regional fractionation trends of Sc are similarly enigmatic. A decrease in Sc with increasing fractionation has been observed in the Sebago group of granitic pegmatites in southwestern Maine (unpubl. data of M. Wise). The average Sc contents range from 0.22 wt.% Sc_2O_3 in columbite from the most moderately fractionated beryl – columbite subtype pegmatites to 0.04 in complex spodumene- and petalite-bearing pegmatites. However, the Greer Lake leucogranite and related pegmatites, in southeastern Manitoba, exhibit an increase in Sc in columbite – tantalite (and associated ixiolite) with progressive fractionation (Černý *et al.* 1986). Our data for columbite – tantalite and ixiolite show no general relationship between Sc and degree of fractionation in the pegmatite (Fig. 4).

On the basis of the samples of scandian ixiolite examined thus far, Sc behaves in a fairly regular manner during pegmatite fractionation. Figure 4 shows that, on the whole, the Sc content of scandian ixiolite increases with increasing Mn, Ta and Sn enrichment. Scandian ixiolite with Ti > Sn from Maine, Madagascar and Mozambique is characterized by low to moderate Mn and Ta enrichment [$0.10 < Mn/(Mn + Fe) < 0.26$; $0.12 < Ta/(Ta + Nb) < 0.56$]. By comparison, scandian ixiolite with Sn > Ti, as represented by the Heftetjern locality, in Norway, shows a more advanced level of fractionation [$0.40 < Mn/(Mn + Fe) < 0.58$], $0.60 < Ta/(Ta + Nb) < 0.75$].

CONCLUSIONS

Scandian columbite is an orthorhombic phase with stoichiometry AB_2O_6, containing up to 3 wt.% Sc_2O_3. Scandian ixiolite, by comparison, contains between 4 and 19 wt.% Sc_2O_3, and its formula approaches ideal $Sc(Nb,Ta)O_4$. The structure of scandian ixiolite is probably a modification of the monoclinic wolframite-type structure.

Scandium enters the columbite structure *via* a coupled substitution. For Sc-bearing columbite and ixiolite, a euxenite-like substitution ($Sc^{3+} R^{4+} R^{2+}_{-1} R^{5+}_{-1}$) seems to be responsible for the incorporation of Sc. Scandium is disordered over the *A* and *B* sites of the columbite structure. Fe^{3+} plays a significant role in the entry of Sc into the columbite and ixiolite structures, particularly in the case of scandian ixiolite, which almost always contains abundant Fe^{3+}.

The fractionation trend of Sc is not clearly defined for single crystals of columbite or ixiolite, within individual pegmatites or within granite – pegmatite systems. The behavior of Sc in columbite and stannian, titanian and wolframian ixiolite is erratic and warrants further study. In scandian ixiolite, the concentration of Sc increases with increasing enrichment of Mn,Ta and Sn, whereas for columbite – tantalite and other varieties of ixiolite, the concentration of Sc is relatively constant regardless of the extent of pegmatite fractionation.

ACKNOWLEDGEMENTS

This research was supported in part by NSERC operating grants to P. Černý and Sprague funding through the Smithsonian Institution to M. Wise. The paper has benefitted greatly from the critical reviews of S.L. Hanson and W.B. Simmons, Jr.

REFERENCES

BEDDOE-STEPHENS, B. & FORTEY, N.J. (1981): Columbite from the Carrock Fell tungsten deposit. *Mineral. Mag.* **44**, 217-223.

BERGSTØL, S. & JUVE, G. (1988) Scandian ixiolite, pyrochlore and bazzite in granite pegmatite in Tørdal, Telemark, Norway. A contribution to the mineralogy and geochemistry of scandium and tin. *Mineral. Petrol.* **38**, 229-243.

BORISENKO, L.F. (1963): *Scandium, its Geochemistry and Mineralogy.* Russian Consultants Bureau, New York, N.Y.

________, MAKSIMOVA, N.V. & KAZAKOVA, M.YE. (1969): Scandium ixiolite, a new tantalo-niobate species with formula $(A,B)_nO_{2n}$. *Dokl. Akad. Nauk SSSR* **189**, 148-151 (in Russ.).

ČERNÝ, P., GOAD, B.E., HAWTHORNE, F.C. & CHAPMAN, R. (1986): Fractionation trends of the Nb-and Ta-bearing oxide minerals in the Greer Lake pegmatitic granite and its pegmatite aureole, southeastern Manitoba. *Am. Mineral.* **71**, 501-517.

________ & NĚMEC, D. (1995): Pristine vs. contaminated trends in Nb, Ta-oxide minerals of the Jihlava pegmatite district, Czech Republic. *Mineral. Petrol.* **55**, 117-129.

________ & TURNOCK, A. (1971): Niobium – tantalum minerals from granitic pegmatites at Greer Lake, southeastern Manitoba. *Can. Mineral.* **10**, 755-772.

ERCIT, T.S. (1986): *The Simpsonite Paragenesis: The Crystal Chemistry and Geochemistry of Extreme Ta Fractionation.* Ph.D. thesis, Univ. Manitoba, Winnipeg, Manitoba.

________ (1994): The geochemistry and crystal chemistry of columbite-group minerals from granitic pegmatites, southwestern Grenville province, Canadian Shield. *Can. Mineral.* **32**, 421-438.

________, ČERNÝ, P., HAWTHORNE, F.C. & MCCAMMON, C.A. (1992): The wodginite group. II. Crystal chemistry. *Can. Mineral.* **30**, 613-631.

FERREIRA, K.J. (1984): *The Mineralogy and Geochemistry of the Lower Tanco Pegmatite, Bernic Lake, Manitoba, Canada.* M.Sc. thesis, Univ. of Manitoba, Winnipeg, Manitoba.

GELLER, S., ROMO, P. & REMEIKA, J.P. (1967): Refinement of the structure of scandium sesquioxide. *Z. Kristallogr.* **124**, 136-142.

GINSBURG, A.I., GORZHEVSKAYA, S.A., SIDORENKO, G.A. & UKHINA, T.A. (1969): Wolframoixiolite – a variety of ixiolite. *Zap. Vses. Mineral. Obshchest.* **98**(1) 63-73 (in Russ.).

HAAPALA, I., SIIVOLA, J. & LÖFGREN, A. (1967): On the Haapaluoma Sc-bearing columbite and its inclusions. *C.R. Soc. géol. Finlande* **39**, 95-100.

HODKINSON, I.P. & CLARK, A.M. (1977): Columbite from St. Austell, Cornwall. *Mineral. Mag.* **41**, 131-132.

JOHAN, V. & JOHAN, Z. (1994): Accessory minerals of the Cínovec (Zinnwald) granite cupola, Czech Republic. 1. Nb-, Ta- and Ti-bearing oxides. *Mineral. Petrol.* **51**, 323-343.

VON KNORRING, O.V. & FADIPE, A. (1981): On the mineralogy and geochemistry of niobium and tantalum in some granite pegmatites and alkali granites of Africa. *Bull. Minéral.* **104**, 496-507.

________, SAHAMA, T.G. & LEHTINEN, M. (1969): Scandian ixiolite from Mozambique and Madagascar. *Bull. Geol. Soc. Finland* **41**, 75-77.

NEUMANN, H. (1961): The scandium content of some Norwegian minerals and the formation of thortveitite, a reconnaissance survey. *Norsk Geol. Tidsskr.* **41**, 197-210.

NOVÁK, M. & ČECH, F. (1996): Scandian columbite and niobian rutile from pegmatites penetrating the Trebíc durbachite massif, western Moravia, Czech Republic. *Acta Mus. Moraviae, Sci. nat.* **80**, 3-8.

________ & ŠREIN, V. (1989): Chemical composition and paragenesis of wolframite from the Dolní Bory pegmatites, western Moravia, Czechoslovakia. *Acta Univ. Carolinae* **4**, 495-500.

SAKURAI, K., NAGASHIMA, K. & KATO, A. (1962): Thortveitite from Kobe, Omiya, Kyoto, Japan. *Chem. Soc. Japan Bull.* **35**, 1776-1779.

UHER, P., ČERNÝ, P., CHAPMAN, R., HATÁR, J. & MIKO, O. (1998): Evolution of Nb,Ta-oxide minerals in the Prasivá granitic pegmatites, Slovakia. I. Primary Fe,Ti-rich assemblage. *Can. Mineral.* **36**, 525-534.

WISE, M.A. & ČERNÝ, P. (1986): The status of ixiolite. *Int. Mineral. Assoc., 14th Gen. Meeting*, 265 (abstr.).

________ & ________ (1996): The crystal chemistry of the tapiolite series. *Can. Mineral.* **34**, 631-647.

________, TURNOCK, A.C. & ČERNÝ, P. (1985) Improved unit cell dimensions for ordered columbite – tantalite end-members. *Neues Jahrb. Mineral., Monatsh.*, 372-378.

Received August 15, 1997, revised manuscript accepted May 15, 1998.