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A REFINEMENT OF THE STRUCTURE OF FERRITUNGSTITE FROM KALZAS MOUNTAIN, YUKON, AND OBSERVATIONS ON THE TUNGSTEN PYROCHLORES

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ABSTRACT

Ferritungstite occurs at the Flo property on Kalzas Mountain, near Mayo, Yukon. It is hosted by ferberite-bearing quartz veins, which form a stockwork in tourmalinized metasediments of the Grit Unit of the Windermere Supergroup. The ferritungstite replaces ferberite, and lines solution cavities, cleavages and crystal margins of the ferberite. Crystals are yellow to orange to brown octahedra up to 0.1 mm across. There are two generations of ferritungstite: an early Cs-bearing generation, and a later Cs-free one. The crystal structure of Cs-free ferritungstite, *Fd*3*m*, with an *a* cell edge of 10.352(1) Å, has been refined to R = 1.95%, wR = 2.30% for 84 observed reflections (Mo*K*α radiation). Ferritungstite is isostructural with pyrochlore, with structural properties closest to those of the variety having the defect pyrochlore structure. The sample studied is similar to kalipyrochlore: it has H_2O dominant at the pyrochlore *A* and ϕ sites, tungsten dominant at the *B* site, and O and OH at the O site. On the basis of electron-microprobe and X-ray-diffraction data, the formula is $([H_2O]_{0.59}Ca_{0.06}Na_{0.02})_{\Sigma 0.67}(W_{1.46}Fe^{3+}_{0.54})_{\Sigma 2}(O_{4.70}OH_{1.30})_{\Sigma 6}([H_2O]_{0.80}K_{0.20})_{\Sigma 1}$. Ferritungstite is part of a potential subgroup of tungsten pyrochlores; nomenclature problems prevent formal inclusion of the tungsten pyrochlores into the pyrochlore group at present.

Keywords: ferritungstite, tungsten, crystal structure, pyrochlore structure, cesstibtantite, kalipyrochlore, Kalzas Mountain, Yukon.

SOMMAIRE

La ferritungstite est présente à l'indice de Flo, sur le mont Kalzas, près de Mayo, au Yukon. On la trouve dans des veines de quartz à ferberite, qui forment un stockwerk dans les roches métasédimentaires tourmalinisées de l'unité dite Grit, du Supergroupe de Windermere. La ferritungstite remplace la ferberite, et tapisse les cavités dues à la dissolution, les clivages et les bordures des cristaux de ferberite. Les cristaux sont des octaèdres jaunes, oranges ou bruns jusqu'à 0.1 mm de diamètre. Deux générations sont évidentes, une première, précoce, riche en Cs, et une tardive, sans Cs. La structure cristalline de la ferritungstite tardive, groupe spatial *Fd*3*m*, *a* égal à 10.352(1) Å, a été affinée jusqu'à un résidu R de 1.95% (R pondéré de 2.30%) en utilisant 84 réflexions observées (rayonnement Mo*K*α). La ferritungstite est isostructurale avec le pyrochlore, et ses propriétés se rapprochent sensiblement du pyrochlore à lacunes. L'échantillon étudié ressemble à la kalipyrochlore. Il possède H_2O comme espèce prédominante aux sites *A* et ϕ, et le W occupe surtout le site *B*, avec O et OH dans le site O. A la lumière des données obtenues à la microsonde électronique et par diffraction X, la formule chimique en serait $([H_2O]_{0.59}Ca_{0.06}Na_{0.02})_{\Sigma 0.67}(W_{1.46}Fe^{3+}_{0.54})_{\Sigma 2}(O_{4.70}OH_{1.30})_{\Sigma 6}([H_2O]_{0.80}K_{0.20})_{\Sigma 1}$. La ferritungstite fait partie d'un sous-groupe potentiel de pyrochlores à tungstène. Les problèmes de nomenclature empêchent pour l'instant l'inclusion formelle des pyrochlores à tungstène dans le groupe du pyrochlore.

(Traduit par la Rédaction)

Mots-clés: ferritungstite, tungstène, structure cristalline, structure du pyrochlore, cesstibtantite, kalipyrochlore, mont Kalzas, Yukon.

INTRODUCTION

The status and nature of ferritungstite have been the subject of several investigations since Schaller (1911) first described it as a new mineral from the Germania tungsten mine, Washington. Kerr (1946) carried out the first X-ray investigation of ferritungstite, and found type samples to have variable properties, but generally similar to those of jarosite. Richter *et al.* (1957) showed that Kerr's samples consist of a mixture of jarosite and ferritungstite, and in a study of samples from the Nevada scheelite mine, interpreted ferritungstite as tetragonal with $a \cong 10.3$, $c \cong 7.3$ Å, with a formula $Ca_2Fe^{2+}_2Fe^{3+}_2(WO_4)_7{\cdot}9H_2O$. In a study of samples from central Africa, Van Tassel (1961) showed that ferritungstite is cubic, not tetragonal, and is isostructural with pyrochlore; he suggested that cation ordering results in iron and aluminum occupying one site of the pyrochlore structure, and tungsten the other. Burnol *et al.* (1964) found the Al:Fe^{3+} ratio of ferritungstite from La Bertrande, France to be variable. Machin & Süsse (1975) published part of a structure analysis of ferritungstite from the Bjordal mine, Uganda ($R = 10.5\%$), which indicated the ideal formula of ferritungstite to be $(W,Fe^{3+})_2O_4(OH)_2{\cdot}½H_2O$; thus, ferritungstite is a tungsten oxide, not a tungstate. Jedwab & Preat (1980) described a Pb-bearing variety of ferritungstite from Gifurwe, Rwanda, and samples with high Al/Fe^{3+} ("alumotungstite"). Sahama (1981) presented a review of the status of ferritungstite and "alumotungstite".

New occurrence

In 1986 we encountered the first Canadian occurrence of ferritungstite, from the Flo property, Kalzas Mountain, Yukon Territory. The property is located approximately 5 km north of Big Kalzas Lake, which is 67 km southeast of the town of Mayo. The Flo property contains a hydrothermal tungsten deposit, which consists of a stockwork of mineralized quartz veins of probable Cretaceous age in tourmalinized clastic metasediments of the Upper Proterozoic "Grit Unit" of the Windermere Supergroup. The quartz veins are typically a few cm to over 30 cm in thickness and host large (to 15 cm) crystals of ferberite. A number of secondary tungsten minerals are associated with the ferberite blades; these include scheelite, ferritungstite, russellite, anthoinite and mpororoite. The secondary W-oxide minerals occur in small cavities, as encrustations on ferberite and quartz; crystal size is typically less than 30 μm. The crystals of ferritungstite from Kalzas Mountain are well developed for the species; crystals range from yellow to orange to brown octahedra up to 100 μm in diameter. As these crystals provide an excellent opportunity to study the crystallography of ferritungstite, and as published structural data on ferritungstite are incomplete, we report here a structure refinement of ferritungstite from Kalzas Mountain.

Synthetic tungsten pyrochlores

Ferritungstite has the pyrochlore structure. Hogarth (1977) defined the general formula for the pyrochlore group as $A_{2-m}B_2O_6\phi_{1-n}{\cdot}pH_2O$, where A is a large monovalent to tetravalent cation, typically Na and Ca, B is a high-field-strength cation, typically Nb, Ta or Ti, and ϕ is O, OH or F. Several structural varieties exist (normal, defect and inverse pyrochlores); the structures of these varieties are reviewed in Ercit *et al.* (1993, 1994). The tungsten pyrochlores are largely unrecognized mineralogically; hence they are not formally included in the pyrochlore group, nor do they have a subgroup name such as exists for the pyrochlore (Nb end-members), microlite (Ta end-members) or betafite (Ti end-members) subgroups.

Tungsten pyrochlores are a chemically important class of synthetic pyrochlore. They show the highest degree of defect-pyrochlore character, and some exhibit enhanced cation conduction (Catti *et al.* 1992). They show extensive heterovalent W – (Ta,Nb) isomorphism at the B site, aided by complex substitutions at the A site, by protonation of O at the O site and, in some extreme cases, by the inclusion of vacancies at the O site (Darriet *et al.* 1971, Michel *et al.* 1975, Groult *et al.* 1982). Several refinements of the crystal structures of synthetic tungsten pyrochlores have been carried out (*e.g.*, Groult *et al.* 1982); many of these involve hydrated tungsten pyrochlore (*e.g.*, Günter *et al.* 1989). All studies of end-member tungsten pyrochlores indicate H_2O to occur at or in the vicinity of the ϕ site; the results have been inconclusive for mixed (W,Ta)-bearing pyrochlores; H_2O might be present at either the ϕ site or disordered with vacancies at the A site (Darriet *et al.* 1971, Tréhoux *et al.* 1983). To date, no refinements exist for synthetic Al- or Fe^{3+}-bearing tungsten pyrochlores.

EXPERIMENTAL

Electron-microprobe analysis

Electron-microprobe analysis (wavelength dispersion) involved a JEOL 733 electron microprobe using Tracor–Northern 5500 and 5600 automation. Operating conditions for these analyses were 15 kV, a beam current of 20 nA, and a beam diameter of 5 μm. All samples were examined for chemical heterogeneities by back-scattered electron (BSE) imaging. BSE images show two generations of ferritungstite: an early Cs-bearing generation, and a later Cs-free one. Data for standards were collected for 50 s or 0.25% precision (1σ level), whichever was attained first; data for samples were collected for 25 s or 0.5% precision. Data reduction was done with a conventional ZAF

TABLE 1. MISCELLANEOUS INFORMATION CONCERNING FERRITUNGSTITE

Na_2O, wt.%	0.16	*a* (Å):	10.352(1)
K_2O	2.16	Space group:	*Fd*3*m*
CaO	0.73	μ (cm^{-1}, Mo*K*α):	306
Fe_2O_3	9.99	Crystal radius (mm):	0.03
WO_3	77.71	Total no. of $\|F_o\|$:	102
H_2O (calc.)	8.45	No. $\|F_o\| > 3\sigma(I)$:	84
	99.20	Final *R* (obs)%:	1.95
		Final *wR* (obs)%:	2.30

$AB_2O_6\phi$, where A = 0.59(7) H_2O, 0.06 Ca, 0.02 Na
B = 1.46 W, 0.54 Fe^{3+}
(*Z*=8) O = 4.70 O, 1.30 OH
ϕ = 0.80 H_2O, 0.20 K

$R = \sum(|F_o|-|F_c|)/\sum|F_o|$ $wR = [\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1$

TABLE 2. SELECTED CHEMICAL COMPOSITIONS OF W MINERALS, KALZAS MOUNTAIN

	1	2	3	4	5	6	7
K_2O, *wt.%*	0.20	0.15	0.04	0.00	0.00	0.00	0.00
Cs_2O	0.00	0.16	0.00	0.00	0.00	0.00	0.00
CaO	0.71	0.18	0.55	0.00	0.00	0.00	19.00
MnO	0.00	0.00	0.00	0.00	0.00	10.77	0.00
FeO	0.00	0.00	0.00	0.00	0.00	12.38	0.00
PbO	0.00	9.44	0.00	1.89	0.00	0.00	0.00
Bi_2O_3	0.00	8.56	0.00	59.04	0.00	0.00	0.00
Al_2O_3	2.62	0.92	2.01	0.00	14.53	0.00	0.00
Fe_2O_3	4.03	6.98	7.85	1.92	1.80	0.00	0.00
WO_3	87.40	66.19	82.55	31.30	66.92	75.97	80.30
	94.96	92.58	93.00	94.15	83.25	99.12	99.30
				Formula Contents			
K	0.018	0.016	0.003	0.000	0.000	0.000	0.000
Cs	0.000	0.006	0.000	0.000	0.000	0.000	0.000
Ca	0.053	0.016	0.040	0.000	0.000	0.000	1.967
Mn	0.000	0.000	0.000	0.000	0.000	0.929	0.000
Fe^{2+}	0.000	0.000	0.000	0.000	0.000	1.055	0.000
Pb	0.000	0.216	0.000	0.053	0.000	0.000	0.000
Bi	0.000	0.188	0.000	1.593	0.000	0.000	0.000
Al	0.215	0.092	0.160	0.000	0.478	0.000	0.000
Fe^{3+}	0.211	0.447	0.398	0.151	0.038	0.000	0.000
W	1.575	1.460	1.442	0.849	0.484	2.005	2.011
	2.072	2.441	2.043	2.646	1.000	3.989	3.978
O	4.847	5.433	4.409	4.431	4.452	8.000	8.000
OH	1.153	0.567	1.591	1.569	1.548		

1-3: Ferritungstite; formulae on a basis of 2(W,Fe^{3+},Al).
4: Russellite; formula on a basis of 1(W,Fe^{3+}).
5: Anthoinite-mpororoite (average of 3); formula basis of 1(W,Al, Fe^{3+}).
6: Ferberite (average of 2); formula on a basis of 8 oxygens.
7: Scheelite (average of 3); formula on a basis of 8 oxygens.

routine in the Tracor–Northern TASK series of programs. The following standards were used: synthetic huebnerite (W*M*α), synthetic ferberite (Fe*K*α), YAG (Al*K*α), microlite (Na*K*α), synthetic fersmite (Ca*K*α), sanidine (K*K*α), pollucite (Cs*L*α), crocoite (Pb*M*α) and bismutotantalite (Bi*M*α); in addition, Si, Sb, Mn, Ti, Ta, Nb and Sn were sought, but not detected.

Selected results of the electron-microprobe study are given in Tables 1 and 2 for both ferritungstite and associated tungsten minerals.

Collection of the X-ray intensity data

An octahedron of ferritungstite, 0.06 mm in diameter, was used for the study. Crystal quality and cubic symmetry were confirmed by precession photographs prior to collection of intensity data, which were obtained with a Nicolet *R*3*m* four-circle diffractometer at the University of Manitoba, using the experimental method of Ercit *et al.* (1986). Twenty-five intense reflections (to a 2θ of 25°) were used to center the crystal; least-squares refinement of the setting angles gave the orientation matrix used for data collection and the unit-cell edge given in Table 1. One octant of reciprocal space (six asymmetric units) was collected to a $2\theta_{max}$ of 60°. The data were empirically corrected for absorption using a ψ-scan calibration data-set (*R*[merge] = 1.9% after correction). Data reduction (correction for Lorentz, polarization and background effects) was done with the SHELXTL PC system of programs; the reflections were merged to give the numbers shown in Table 1.

Structure refinement

Structure refinement was done with SHELXTL PC. Scattering curves for neutral atoms were taken from Cromer & Mann (1968), and anomalous scattering factors were from Cromer & Liberman (1970). Starting positions for the *A*, *B*, O and ϕ sites were taken from a refinement of the microlite structure (Ercit 1986). The initial model had all Ca, Na and Fe at *A*, all W at *B*, O at O, and O and K at ϕ. All cation site-occupancies were constrained at microprobe-determined values (normalized on a basis of 2 *B* cations per formula unit, *pfu*), the O site was set at full occupancy, and the O occupancy of the ϕ site was set at (1–K). The refinement converged to *R* = 4.4, *wR* = 4.2%; however, the displacement parameter for the *A* site converged at an unrealistically high value (U_{eq} = 1.79 Å^2), indicating that the total occupancy of the *A* site was grossly overestimated. For the next stage of the refinement, all Fe was assigned to the *B* site; this resulted in improved discrepancy-factors of *R* = 2.6, *wR* = 2.9%. However, the displacement parameter for the *A* site was negative, indicating that the model underestimated the total *A*-site occupancy. On the basis of the structure refinement for kalipyrochlore (Ercit *et al.* 1994), we considered the possibility of H_2O at the *A* site. When the occupancy of O (≡ H_2O) at *A* was refined, the model converged to *R* = 2.1, *wR* = 2.4%. The displacement parameter for *A* was now found to be positive; however, its absolute value was too small to be considered realistic (U_{eq} = 0.0007 Å^2). The constraints on the occupancies of other sites were relaxed to see whether the displacement parameter for *A* would adopt a more realistic value; none of these approaches resulted in a significant improvement, and many led to a worse result (*e.g.*, when the occupancy of the O site was refined, the occupancy factor converged to a value greater than 1, and *U*[*A*] was negative again). We assumed that the assignment of K to the ϕ site was wrong; consequently, K was assigned to the *A* site. Although refinement of this model gave reasonable *R* factors and displacement

TABLE 3. POSITIONAL AND DISPLACEMENT PARAMETERS FOR FERRITUNGSTITE

	Position	*x*	*y*	*z*	U_{eq}
A	16*d*	1/2	1/2	1/2	200
B	16*c*	0	0	0	258(3)
O	48*f*	0.3101(7)	1/8	1/8	197(14)
ϕ	8*b*	3/8	3/8	3/8	1264(137)

Anisotropic Displacement Parameters

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B	258(4)	258(4)	258(4)	-67(2)	-67(2)	-67(2)

All *U* values are Å^2 x 10^4

TABLE 4. SELECTED INTERATOMIC DISTANCES AND ANGLES IN FERRITUNGSTITE

		B Octahedron			
B-O x 6	1.933(3)	O-*B*-O	x 6	2.710(11)	89.0(3)
			x 6	2.757(4)	91.0(3)
		<O-O>		2.733 Å	
		<O-*B*-O>			90.0 °

parameters [$R = 2.3\%$, $wR = 2.7\%$, $U(A) = 0.0193$ Å^2], the amount of H_2O that it represented was not satisfactory. The deficit in the analytical total indicated 9.25 wt.% H_2O, but the structure refinement gave only 6.07 wt.% H_2O; given the standards used, the 3.2% discrepancy is too large to be attributed to analytical error [this is confirmed by the quality of the analyses of scheelite and ferberite in Table 2 and by comparison with analyses of ferritungstite from other localitites for water: 7.80% H_2O (Van Tassel 1961), 8.3% H_2O (Burnol *et al.* 1964)]. Consequently, K was re-assigned to the ϕ site, and H_2O was disordered over the *A* and ϕ sites. The H_2O content of the ϕ site was fixed at 1–K; the H_2O content of the *A* site was refined unconstrained, so that $U(A)$ was fixed at 0.02 Å^2. An isotropic extinction-parameter was added to this final model; refinement gave $R = 1.95$, $wR = 2.30\%$ ($R = 3.08$, $wR = 3.41\%$ for all 102 data). All maxima in the final difference-Fourier map were less than 1 *e*/Å^3.

The observed and calculated structure-factors for the final model are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Final positional parameters are given in Table 3; selected interatomic distances and angles are given in Table 4.

DISCUSSION

The crystal structure of ferritungstite

Ferritungstite is isostructural with pyrochlore. The ferritungstite structure most closely approximates a hydrated equivalent of the defect pyrochlore structure; it consists of a framework of corner-linked BO_6 octahedra with mainly H_2O at the *A* and ϕ sites. H_2O groups are weakly bonded to the framework *via* hydrogen bonding, and the structure is slightly reinforced by bonds involving the few cations that occur at the *A* (4%) and ϕ (20%) sites.

As with kalipyrochlore (Ercit *et al.* 1994), the BO_6 octahedron has a nearly ideal geometry: *x*(O) is within four standard deviations of the ideal value for an undistorted octahedron [0.3101(7) *cf.* 0.3125, ideal]. As (1) the octahedra in the ferritungstite structure are in an all-corner-sharing arrangement, (2) *B*–O bonds are constrained by symmetry to be equal in length, and (3) *B*–O bonds are much stronger than all other bonds, ideal symmetry for the BO_6 octahedron is to be expected.

The refinement confirms the result of Machin & Süsse (1975) for the behavior of Fe^{3+}, *i.e.*, it occupies the *B* site. This assignment is also confirmed by a bond-valence analysis. If all Fe^{3+} occurs at *B*, the predicted bond-valence sum for the *B* site is 5.18 *v.u.*, in agreement with a value of 5.12 *v.u.* calculated from the observed *B*–O bond length with the curves of Brown (1981).

Like kalipyrochlore and cesstibtantite, ferritungstite has OH at the O site. For charge-balance, 21.7% OH is required at the site. The bond-valence sum for the O site is at least 1.70 *v.u.* (1.70 *v.u.* with no *A*-site contribution, larger value with an *A*-site contribution); this compares well with the predicted value of 1.78 *v.u.* for a model with minimal hydrogen bonding. The results of Machin & Süsse (1975) imply local order of O and OH in their sample of ferritungstite, with 4(O):2(OH). As they did not provide evidence for this model, we assume that their 4:2 ratio is an artifact of the *A*-cation-absent composition of their sample. Ferritungstite should have variable amounts of O and OH at the O site, as necessitated by the variable numbers of cations at the *A* site, and the variable W:Fe^{3+} ratios for the *B* site.

The high displacement-parameter for the oxygen of the ϕ site (Table 3) confirms its identity as part of a H_2O group. Comparable behavior is observed for synthetic hydrated tungsten pyrochlores (Günter *et al.* 1989). Difference-Fourier maps indicate that the electron density around the ϕ site is isotropic; consequently, H_2O is randomly disordered about the site. This is unlike the behavior of H_2O in kalipyrochlore (Ercit *et al.* 1994), where H_2O is locally ordered about the ϕ site. This difference in the style of long-range disorder of H_2O may in part be related to the H_2O occupancy of the *A* site. The amount of H_2O at the *A* site of ferritungstite is only two-thirds that of kalipyrochlore; presumably the higher H_2O content of kalipyrochlore necessitates local ordering of H_2O groups (Ercit *et al.* 1994).

The structure analysis reported by Machin & Süsse (1975) for ferritungstite from the Bjordal mine, Uganda indicated only 0.5 H_2O at the ϕ site; ferritungstite from Kalzas Mountain has 0.8 H_2O at ϕ, *and* 0.6 H_2O at *A*. As with formal members of the pyrochlore group, the H_2O content of ferritungstite is variable. Ercit *et al.* (1994) showed that the stereochemical limits to the degree of hydration of the pyrochlore structure are 1.75 H_2O *pfu* for the defect pyrochlore structure (no cations at the *A* site), and 1 H_2O *pfu* for the ideal pyrochlore structure (*A* site fully occupied by cations). All synthetic tungsten pyrochlores, the ferritungstite of Machin & Süsse (1975) and the ferritungstite of the present study fall within these limits.

The structural formula of ferritungstite

The formula of the sample of ferritungstite studied here is $([H_2O]_{0.59}Ca_{0.06}Na_{0.02})_{\Sigma 0.67}(W_{1.46}Fe^{3+}{}_{0.54})_{\Sigma 2}(O_{4.70}OH_{1.30})_{\Sigma 6}([H_2O]_{0.80}K_{0.20})_{\Sigma 1}$. A general structural formula for the tungsten pyrochlores, of which ferritungstite is an example, is $(H_2O,A)_x(W,M^{3+})_2(O,OH)_6(H_2O,A')_y$ where A = Ca, Na, Pb, Bi, A' = K, Cs, M^{3+} = Fe, Al, $x << 2$, and $y \leq 1$. If the *A* and *A′* cations are considered as unessential, then ferritungstite is ideally a defect pyrochlore; its ideal empirical formula becomes $(W,Fe^{3+})_2(O,OH)_6{\cdot}pH_2O$, where *p* is less than or equal to 1.75.

The crystal chemistry of ferritungstite

In addition to the results of the structure analysis, compositional data for ferritungstite also give information on its crystal chemistry. Figure 1 is a plot of the ratio of trivalent to hexavalent cations in the ferritungstite structure. The plot shows that there is no fixed ratio of M^{3+} to M^{6+} cations in this species. This variability is most likely a response to similarly variable amounts of *A* cations in the structure. Charge imbalance introduced by *A* cations can be potentially offset by two mechanisms: decreased substitution of OH for O at the O site, and increased substitution of trivalent cations for W at the *B* site. Figure 1 confirms the validity of the latter mechanism.

Figure 2 is a plot of concentrations of Fe *versus* Al. The data for Kalzas Mountain show a strong negative correlation between concentrations of Fe and Al. As there are no crystallographic constraints that fix the W:(Fe+Al) ratio, the global data-set shows a higher degree of scatter than the Kalzas data-set; nonetheless, the negative correlation is confirmed. Aluminum is incorporated into the ferritungstite structure by substitution for Fe^{3+} and W. It has already been established that ferritungstite and "alumotungstite" are isostructural (Davis & Smith 1971); given that iron and aluminum occur in subordinate amounts to tungsten in all samples of ferritungstite and "alumotungstite", and that all three cations occur in the *B* site, ferritungstite and "alumotungstite" are apparently compositional varieties of the same species. This is difficult to assess further, as no detailed description of "alumotungstite" has been published (Sahama 1981).

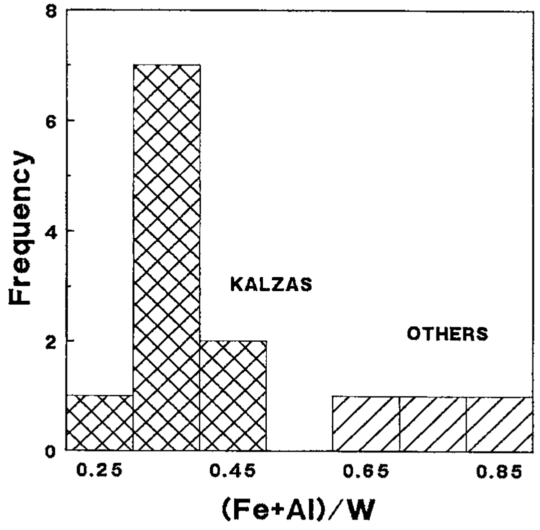

FIG. 1. Histogram of the ratio of trivalent to hexavalent cations in the ferritungstite structure. The spread of values shows that M^{3+}:M^{6+} is variable in ferritungstite.

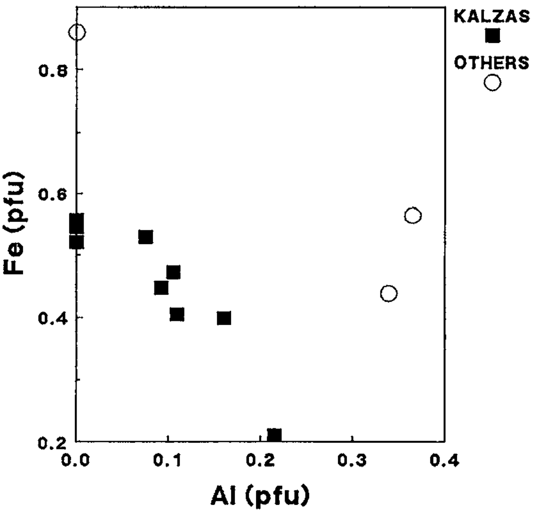

FIG. 2. Concentration of Fe^{3+} *versus* that of Al in ferritungstite. Filled squares are samples from Kalzas Mountain; open circles are samples from other localities.

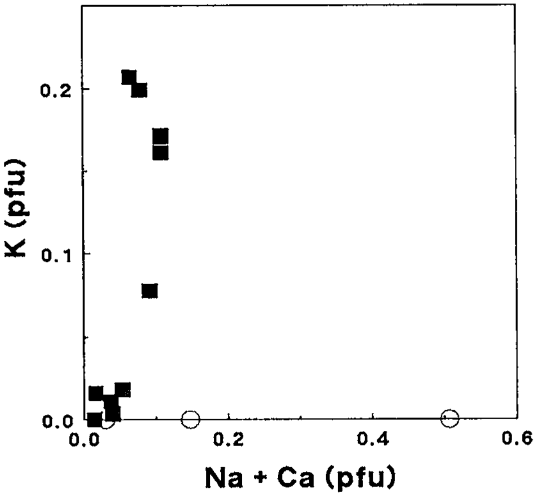

FIG. 3. Behavior of K, Na and Ca in ferritungstite. K variation is largely independent of (Na + Ca) variation. Symbols are as in Fig. 2.

Figure 3 reinforces the inferences about ordering of K, Ca and Na in ferritungstite. The plot shows that K variation is independent of Na and Ca variation; K shows no evidence of substituting for Na and Ca (negative correlation), nor of behaving indiscriminately like an *A* cation (*i.e.*, a positive correlation might indicate an indiscriminate increase in all *A* cations as the proportion of vacancies or H_2O at the *A* site decreases).

Nomenclature problems with tungsten pyrochlores

To date, there are three known tungsten oxide minerals with the pyrochlore structure: ferritungstite, "alumotungstite" (Al^{3+} analogue of ferritungstite) and "jixianite" (Pb^{2+}-stuffed analogue of ferritungstite). Of these, only ferritungstite is an IMA-accepted species (Nickel & Nichols 1991). To date, no guidelines exist for the nomenclature of tungsten-dominant pyrochlores, which is not surprising, given that they have not generally been recognized as members of the pyrochlore group. As there are only sparse data available for known occurrences of ferritungstite and its relatives, it is premature to develop guidelines for the nomenclature of tungsten pyrochlores. Nonetheless, now that the ferritungstite structure is confirmed, it is important to anticipate potential problems in the nomenclature of the tungsten pyrochlores.

(1) *B-site cations.* Formal members of the pyrochlore group are divided into subgroups on the basis of *B*-site chemistry (Hogarth 1977). This is reflected in the generic root-name for each subgroup; hence species of the pyrochlore group all have "pyrochlore", "microlite", and "betafite" as their root name, plus an adjectival chemical modifier reflecting *A*-site chemistry. The problem with formally including the tungsten pyrochlores in the pyrochlore group exists with the separate generic names presently accorded to ferritungstite, "alumotungstite" and "jixianite", all of which have W as the dominant *B*-site cation. Clearly, the status of "alumotungstite" and "jixianite" needs to be resolved.

(2) *A-site cations.* Nomenclature problems arise as a consequence of the variable chemistry of the *A* site. By analogy with the current members of the pyrochlore group, (Ca,Na)-, Pb-, and Bi-rich ferritungstites could potentially receive names as separate species. However, as ferritungstite is a defect pyrochlore, the amounts of these cations would be expected to be extremely small. It would not seem prudent to indiscriminately propose names of new species based on the dominant occupant of the *A* site: (1) the total cation occupancy of the *A* site does not tend to exceed 25% (the sole exception is "jixianite" at 55%); (2) if the 20% rule currently in use for the pyrochlore group (Hogarth 1977) were applied to the tungsten pyrochlores, then for an average tungsten pyrochlore with less than 25% cation occupancy of the *A* site, *less than 5%* occupancy by a dominant "atypical" cation (*e.g.*, Pb or Bi) is needed for status as a new species.

(3) *Cs and K.* Special problems in nomenclature are associated with the occurrence of K and Cs in ferritungstite, and in pyrochlore-group minerals in general (Ercit *et al.* 1994). For stereochemical reasons, Cs occupies the ϕ site of the pyrochlore structure (Fourquet *et al.* 1973, Ercit *et al.* 1993). As Cs is not an *A* cation, Cs-bearing pyrochlores apparently violate the nomenclature for the pyrochlore group, hence *cesstibtantite* (≡ Cs-bearing stibiomicrolite). Cesium comprises up to one-third of the ϕ site in cesstibtantite; however, it tends to occur in much lower concentrations in other pyrochlore-group minerals: the Cs-bearing ferritungstite of Table 2 has less than 1% Cs at ϕ, and the Cs-bearing microlite samples of Eid & von Knorring (1976) similarly have less than 1% Cs at ϕ. Although cesstibtantite with 33% Cs at the ϕ site could follow different rules of nomenclature than other pyrochlore-group minerals, this would not be appropriate for compositions with less than 1% Cs at ϕ. Nomenclature problems for K are similar to those for Cs, but are further complicated by composition-dependent disorder of K over the A and ϕ sites (Grins & Nygren 1980, Ercit *et al.* 1994). Thus, in some cases K is a formal *A* cation; however, it is not usually so.

(4) *H_2O.* Molecular H_2O can occur at either the ϕ or *A* site. The occurrence of H_2O at the ϕ site poses no problems in nomenclature; however, its occurrence at the *A* site is problematic if H_2O is the dominant occupant of the site. The problem arises because species designation is traditionally made on the basis of the

dominant *cation* at the *A* site, which thus ignores H_2O even where it is grossly dominant at *A*. This problem has been encountered both with formal members of the pyrochlore group (*e.g.*, kalipyrochlore) and the tungsten pyrochlores.

In short, recent structural investigations have resolved many scientific problems with synthetic and natural pyrochlores, at the expense of complicating the existing mineralogical nomenclature. More structural work is called for before any adjustments to the existing nomenclature should be considered.

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