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THE STRUCTURAL CHEMISTRY OF KALIPYROCHLORE, A "HYDROPYROCHLORE"

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ABSTRACT

The crystal structure of kalipyrochlore from the Lueshe carbonatite, Zaire, *Fd3m*, *a* 10.604(1) Å, has been refined to an *R* of 1.62% (*wR* = 1.65%) for 100 observed reflections (Mo*K*α radiation). On the basis of electron-microprobe and X-ray-diffraction data, the formula is $([H_2O]_{0.99}Sr_{0.05}Ca_{0.01})_{\Sigma 1.05}(Nb_{1.80}Ti_{0.20})_{\Sigma 2}(O_{4.06}OH_{1.94})_{\Sigma 6}([H_2O]_{0.86}K_{0.14})$, which results in an ideal empirical formula of $Nb_2(O,OH)_6{\cdot}pH_2O$, where $p \leq 1.75$. Kalipyrochlore has several unusual features not shown by other pyrochlore-group minerals. It is extremely deficient in *A* cations, so much so that by far the dominant occupant of the *A* site is H_2O; it has some OH at the site normally occupied only by O, and has more than 1 H_2O group *pfu*. The maximum amount of H_2O in the pyrochlore structure is controlled by the cation occupancy of the *A* site; the maximum H_2O content ranges from 1.00 H_2O *pfu* for ideal pyrochlores (two *A* cations *pfu*) to 1.75 H_2O *pfu* for defect pyrochlores (no *A* cations).

Keywords: kalipyrochlore, Nb-oxide mineral, crystal structure, pyrochlore structure, Lueshe carbonatite, Zaire.

SOMMAIRE

La structure cristalline du kalipyrochlore provenant de la carbonatite de Lueshe, au Zaïre, *Fd3m*, *a* 10.604(1) Å, a été affinée jusqu'à un résidu *R* de 1.62% (*wR* = 1.65%) en utilisant 100 réflections observées (rayonnement Mo*K*α). A la lumière de données obtenues avec une microsonde électronique et par diffraction X, la formule en serait $([H_2O]_{0.99}Sr_{0.05}Ca_{0.01})_{\Sigma 1.05}(Nb_{1.80}Ti_{0.20})_{\Sigma 2}(O_{4.06}OH_{1.94})_{\Sigma 6}([H_2O]_{0.86}K_{0.14})$, ce qui mène à la formule empirique $Nb_2(O,OH)_6{\cdot}pH_2O$, avec $p \leq 1.75$. Le kalipyrochlore possède plusieurs aspects inusités non partagés par les autres membres du groupe du pyrochlore. Il est très fortement appauvri en cations du site *A*, à un point tel que H_2O constitue l'espèce dominante du site; de plus, une faible proportion de OH remplace les atomes d'oxygène, et la structure contient plus d'un groupe de H_2O par unité formulaire. La teneur maximale de H_2O dans la structure du pyrochlore dépend de la proportion de cations dans le site *A*; elle va de 1.00 groupe de H_2O par unité formulaire dans le cas des pyrochlores idéaux (deux cations *A* par unité formulaire) à 1.75 groupes de H_2O pour tout pyrochlore non stoechiométrique (sans cations *A*).

(Traduit par la Rédaction)

Mot-clés: kalipyrochlore, oxyde de Nb, structure cristalline, structure du pyrochlore, carbonatite de Lueshe, Zaïre.

INTRODUCTION

The pyrochlore group is chemically diverse. Hogarth (1977) defined the general formula as $A_{2-m}B_2O_6\phi_{1-n}{\cdot}pH_2O$, where *A* represents a large monovalent to tetravalent cation (typically Na and Ca), *B*, a high-field-strength cation (Nb, Ta or Ti), "O", oxygen, and ϕ, O, OH or F. Known members of the pyrochlore group are structurally *normal*, *i.e.*, with normal distributions of cations at the *A* site and anions at the ϕ site: the cation at the *A* site occupies an [8]-coordinated 16*d* position, and the anion at the ϕ site occupies an 8*b* position. A normal pyrochlore has a structure intermediate between the *ideal* and *defect* structures of pyrochlore, which are respectively defined as *A*-cation-stuffed ($m = 0$) and *A*-cation-absent ($m = 2$) varieties. Some structural relatives of the normal pyrochlores show an inverted distribution of *A* cations and ϕ-site vacancies; *i.e.*, the *A* cations ($m \leq 1$) occupy the 8*b* position, and the vacancies occupy the 16*d* position. These are known as *inverse* pyrochlores. Cesstibtantite, a relative of the pyrochlore group and ideally $(Sb,Na)_{2-m}Ta_2O_6(OH,Cs)_{1-n}$, shows mixed inverse–normal character (Ercit *et al.* 1993).

Members of the pyrochlore group are subdivided on the basis of their *B*-site chemistry. The pyrochlore and microlite subgroups have $M^{5+} > 2Ti$; members of the pyrochlore subgroup have Nb as the dominant pentavalent cation, whereas members of the microlite subgroup have Ta dominant. The betafite subgroup has $2Ti \geq M^{5+}$. Chemists do not use the mineralogical nomenclature; consequently, synthetic compounds with the pyrochlore structure are referred to by chemists, and here, as "pyrochlores", regardless of their composition.

There have been numerous structural investigations of synthetic anhydrous pyrochlores with large monovalent cations (K, Rb, Cs, Tl) (*e.g.*, Fourquet *et al.* 1973). Phases that host Rb and Cs show true inverse-pyrochlore character, with Rb or Cs at or about the 8*b* position. Cations with [8]-coordinate ionic radii in the range $1.50 \leq r \leq 1.60$ Å (*i.e.*, K, Tl) can occur at either or both of the ϕ and *A* sites, depending upon the ratio of the number of *A* cations to *B* cations (English *et al.* 1980, Grins *et al.* 1980). For these compositions, the normal structure is stable at high values of the *A*:*B* ratio, and the inverse structure is stable at low values; thus at high values of *A*:*B*, the *A* cations are forced into the 16*d* position. From impedance measurements on ionically conductive (Ta,W)-pyrochlores with a range of K occupancies, Grins *et al.* (1980) predicted that end-member K-pyrochlores with $m \leq 1.5$ should have a normal distribution of K atoms (*i.e.*, largely at 16*d*), and those compositions with $m > 1.5$ should have a distribution of K atoms over 16*d* and 8*b*, with greater preference for 8*b* as *m* approaches 2 (*i.e.*, as K approaches 0). This has been confirmed to an extent by crystal-structure investigations: the series of compositions $K_{2-m}(Ta,W)_{\Sigma 2}O_6{\cdot}H_2O$ with $0 \leq m \leq 1$ has all K at 16*d* (Michel *et al.* 1975), as do $K(Ta,W)_{\Sigma 2}O_6{\cdot}H_2O$ ($m = 1$; Darriet *et al.* 1971) and $(K_{1.12}Bi^{3+}_{0.35})_{\Sigma 1.47}(Bi^{5+}_{1.85}Bi^{3+}_{0.15})_{\Sigma 2}O_6{\cdot}1.07H_2O$ ($m = 0.53$; Tréhoux *et al.* 1983). However, $K_{0.51}Sb^{3+}_{0.67}Sb^{5+}_2O_{6.26}$ ($m = 0.82$; Piffard *et al.* 1978) has *all* K localized about the 8*b* position, not at 16*d*; presumably, the presence of Sb^{3+} in the vicinity of the 16*d* position (at 1/3 occupancy) results in the localization of all K in the vicinity of the 8*b* position.

The role of H_2O in the pyrochlore structure has only been conclusively established in recent years. In the past, there have even been speculations regarding the species present (*i.e.*, H_2O or H_3O^+); however, Groult *et al.* (1982) showed that for the defect pyrochlore $HTaWO_6{\cdot}H_2O$, (1) H_2O is the species present, and (2) it resides in the vicinity of the 8*b* position. Groult *et al.* (1982) and Catti *et al.* (1992) showed that $HTaWO_6{\cdot}H_2O$ is truly a defect pyrochlore; the proton is localized along edges of the BO_6 octahedron, not in the vicinity of the *A* site. For synthetic pyrochlores with intermediate ideal–defect character (*i.e.*, most like natural pyrochlore-group minerals), the picture is not clear. For $K(TaW)_{\Sigma 2}O_6{\cdot}H_2O$ (Darriet *et al.* 1971) and $K_{0.14}Bi^{3+}_{0.43}(Bi^{5+}_{1.74}Bi^{3+}_{0.26})_{\Sigma 2}O_6{\cdot}H_2O$ (Tréhoux *et al.* 1983), refinements with H_2O localized at or about 8*b* were found to be statistically no better than those with all H_2O at 16*d*. Thus, studies of synthetic pyrochlores have not resolved the role of H_2O in products with compositions similar to those found in nature, and have failed to explain the behavior of H_2O in products with H_2O-excessive compositions (*i.e.*, with $p > 1$).

The present paper describes an investigation of the crystal structure of kalipyrochlore. Kalipyrochlore is known only from the Lueshe carbonatite, Zaire, where it occurs as a pseudomorphous product of weathering of pyrochlore (Van Wambeke 1978), due to exchange of Na and Ca in the original pyrochlore for K and H_2O. Van Wambeke (1978) originally described kalipyrochlore as $(K_{0.18}Sr_{0.07}Na_{0.04}Ca_{0.01})(Nb_{1.82}Ti_{0.16}Zr_{0.02})O_{5.13}([H_2O]_{1.43}F_{0.04})$. The important implications of this formula are (1) the apparent presence of vacancies at the O site, (2) a high degree of defect-pyrochlore character, and (3) the existence of an excess in H_2O content.

Experimental

All data were collected on an equant (Table 1), hand-rounded crystal fragment of kalipyrochlore (personal collection of FCH). Crystal quality was confirmed by precession photography prior to collection of intensity data. Following collection of the data, the crystal was mounted in epoxy and analyzed by electron-microprobe techniques.

Electron-microprobe analyses

Energy-dispersion (ED) microprobe analyses were done at the University of Manitoba. The X-ray spectra were collected with a MAC 5 electron microprobe using a Kevex Micro-X 7000 spectrometer. Spectra were collected for 200 live seconds with an operating voltage of 15 kV and a sample current of 5 nA (measured on synthetic fayalite), and were corrected for both current and voltage drift. Data were reduced

TABLE 1. MISCELLANEOUS INFORMATION FOR KALIPYROCHLORE

K_2O, wt.%	2.12	*a* (Å):	10.604(1)
SrO	1.75	Space group:	*Fd3m*
CaO	0.12	μ (cm^{-1}, Mo$K\alpha$):	41
TiO_2	5.01	Crystal size (mm):	0.14 x 0.21 x 0.28
Nb_2O_5	75.69	Total no. of $\|F_o\|$:	108
H_2O †	16.05	No. $\|F_o\| > 3\sigma(1)$:	100
	100.74	Final *R* (obs)%:	1.62
		Final *wR* (obs)%:	1.65

$(A,A')B_2O_6(\phi',\phi'')$, where A = 0.05 Sr 0.01 Ca
A' = 0.99 H_2O
B = 1.80 Nb, 0.20 Ti
O = 4.06 O, 1.94 OH
ϕ',ϕ'' = 0.86 H_2O, 0.14 K

$R = \sum(|F_o|-|F_c|)/\sum|F_o|$ $\quad wR = [\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1$
† H_2O calculated from structure refinement

with Kevex software using the MAGIC V program (Colby 1980). The following standards were used: microlite (Ca$K\alpha$), $CoNb_2O_6$ (Nb$L\alpha$), $SrTiO_3$ (Sr$L\alpha$, Ti$K\alpha$) and orthoclase (K$K\alpha$). No other element with Z greater than 10 was detected in the 200-s spectrum. The analytical data are given in Table 1.

X-ray intensity data

Intensity data were collected with a Nicolet *R3m* four-circle diffractometer using the experimental method of Ercit *et al.* (1986). Twenty-five intense reflections (to a 2θ of 35°) 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 φ-scan calibration data-set (R[merge] = 1.5% after correction). Data reduction (correction for Lorentz, polarization and background effects) was done with the SHELXTL PC package of programs; the reflections were merged to give the numbers shown in Table 1.

TABLE 2. POSITIONAL AND DISPLACEMENT PARAMETERS FOR KALIPYROCHLORE

	Position	x	y	z	U_{eq}
A	16*d*	1/2	1/2	1/2	42(19)
A′	32*e*	0.5100(8)	0.5100(8)	0.5100(8)	42(19)
B	16*c*	0	0	0	259(2)
O	48*f*	0.3120(3)	1/8	1/8	159(6)
φ′	96*g*	0.398(5)	0.398(5)	0.331(7)	500(112)
φ″	32*e*	0.407(7)	0.407(7)	0.407(7)	500(112)

Anisotropic Displacement Parameters

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B	259(3)	259(3)	259(3)	-65(2)	-65(2)	-65(2)

All U values are Å² x 10⁴; $U(A)$ was constrained to equal $U(A')$; $U(\phi')$ was constrained to equal $U(\phi'')$.
* Refined occupancy of A' = 0.50(2), of $\phi' : \phi''$ = 0.68(14).

TABLE 3. SELECTED INTERATOMIC DISTANCES AND ANGLES IN KALIPYROCHLORE

B Octahedron			H_2O-H_2O Separations		
B-O x 6	1.986(1)		φ′-*A′* x 1/8	2.54(7)	
			x 1/8	2.66(7)	
O-*B*-O x 6	2.804(4)	89.8(1)	x 1/8	3.03(6)	
x 6	2.814(1)	90.2(1)			
<O-O>	2.809 Å		φ″-*A′* x 3/8	2.73(7)	
<O-*B*-O>		90.0 °			
			<O-O>	2.74 Å	

Structure refinement

Structure refinement was done with the SHELXTL PC system of programs. Scattering curves for neutral atoms were taken from Cromer & Mann (1968), with anomalous scattering factors 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 Sr and Ca at *A*, all Nb and Ti at *B*, O at *O*, and O and K at φ. All cation site-occupancies were constrained at electron-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 occupancy of the φ site was refined. The refinement converged to R = 5.4, wR = 5.9%; however, the displacement parameters for the *A* site were strongly nonpositive definite, and the difference-Fourier map showed large positive maxima in the vicinity of the *A* and φ sites. The anomalous density in the vicinity of the *A* site was investigated first. As microprobe constraints were used for the refinement, no other cation could be responsible for the anomalously high electron-density; consequently, H_2O must be present at *A*. The anomalous density in the vicinity of the φ site is interpreted to be due to positional disorder; specifically, the constituents of the φ site are observed to fractionally occupy one 96*g* position (henceforth φ′) and one 32*e* position (φ″) near the ideal 8*b* position. The model was modified as follows: the cationic contents of the *A* site were set at electron-microprobe-imposed constraints, the occupancy of H_2O at *A* was refined, and the anions at φ were modeled as positionally disordered. This model converged to R = 2.7, wR = 2.5%. The difference map calculated at this stage showed evidence of some positional disorder of *A*-site constituents; *i.e.*, some constituents were displaced from the ideal 16*d* position to a 32*e* position. As published refinements of the pyrochlore structure show positional disorder for Ca and Sr at the *A* site, it was assumed that the H_2O was positionally disordered; the model was adjusted to reflect this assumption. To summarize, the final model has positionally ordered *A* cations, *B* cations and O, positionally disordered H_2O in the vicinity of the *A* site, and positionally disordered O and K in the vicinity of the φ site; refinement of this final model converged to R = 1.62, wR = 1.65%.

Because Van Wambeke (1978) reported kalipyrochlore to be O deficient, we investigated the O-site occupancy at the last stage of refinement. The refinement converged to a value slightly greater than 1; hence the O site is fully occupied.

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 2; selected interatomic distances and angles are given in Table 3.

Discussion

General framework of pyrochlore

The kalipyrochlore structure consists of a framework of corner-linked BO_6 octahedra with weakly bonded constituents in the vicinity of the *A* and φ sites

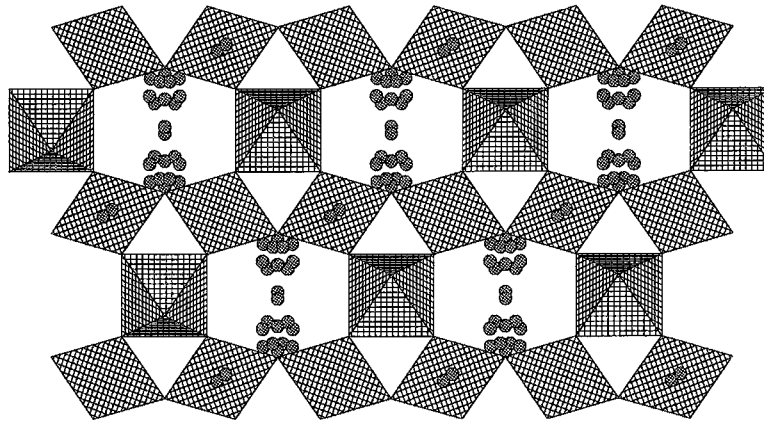

FIG. 1. Projection down [110] of the kalipyrochlore structure. Shaded polyhedra are NbO_6 octahedra; spheres are the oxygen atoms of positionally disordered H_2O groups.

occupying distorted cubic and tetrahedral interstices, respectively (Fig. 1). However, in kalipyrochlore, the BO_6 octahedron is nearly ideal in geometry: for ideal geometry, $x(O) = 0.3125$; in kalipyrochlore, $x(O) = 0.3120(3)$. This is also reflected in the bond lengths: all *B*–O bonds are constrained by symmetry to be equal, and the bond-valence sum for the *B* cation is nearly ideal: 4.88 *v.u.* (obs.) *versus* 4.90 *v.u.* [predicted for Nb:Ti = 9:1; bond-valence curves of Brown (1981) and Ercit (1986)]. For kalipyrochlore, it would seem that nearest-neighbor effects on the BO_6 octahedron are negligible.

The role of H_2O

The occupancy refinements for the *A* site show that H_2O is the dominant *A*-site constituent. Furthermore, (1) the low ratio of *A* cations to ϕ-site constituents, (2) the high displacement parameters for the ϕ-site constituents, and (3) the positional disorder of the ϕ-site constituents all indicate that the "O" of the ϕ′ and ϕ″ sites is actually H_2O.

For a normal pyrochlore $AB_2O_6\phi$ in which *A* and *B* are cations, and O and ϕ are anions, there are no stereochemical constraints on the maximum occupancies of the *A* and ϕ sites. However, for kalipyrochlore, with H_2O in the vicinity of both the *A* and ϕ sites, the maximum occupancies of both sites are limited owing to the short separation of the ideal *A* and ϕ sites, in the neighborhood of 2.3 Å. Partial occupancy of the *A* site and positional disorder of H_2O at *A* and ϕ permit stable O–O separations for neighboring H_2O groups in kalipyrochlore. Specifically, positional disorder results in eight fractionally occupied *A* sites around each ϕ′ and ϕ″ site. Five of the eight are too close to the ϕ′ or ϕ″ site to represent stable O–O separations for H_2O groups; however, three of the eight are sufficiently distant to represent stable separations (averaging 2.74 Å; Table 3). For synthetic *A*-cation-free "hydropyrochlore", the maximum H_2O content *pfu* may be limited by this stereochemistry; if there is one H_2O group *pfu* in the vicinity of the 8*b* position, then there can be only 3/8 H_2O groups in the vicinity of the 16*d* position. This translates to a maximum of 1.75 H_2O *pfu* for *A*-cation-free "hydropyrochlore", which compares well with the observed value of 1.85(18) H_2O in kalipyrochlore.

Previous refinements of the structures of H_2O-bearing pyrochlores have shown H_2O only in the vicinity of the 8*b* position (*e.g.*, Groult *et al.* 1982). As no synthetic or natural pyrochlores have been found with all H_2O ordered at 16*d* or its environs, we presume that 8*b* and its environs are the preferred loci for H_2O, and that H_2O only enters the 16*d* region if the 8*b* region cannot accommodate more H_2O. The maximum amount of H_2O *pfu* in the pyrochlore structure is thus given as 1 + 3/8 (*m*). For ideal pyrochlores with full *A*-site occupancies ($m = 0$), there can be no more than 1 H_2O *pfu*; as described above, the limit for defect pyrochlores ($m = 2$) is 1.75 H_2O *pfu*.

The oxygen position: occupancy by O and OH

One potential problem with kalipyrochlore involves the *O* site (48*f*). For charge balance, and on the basis of chemical data, Van Wambeke (1978) calculated that oxygen occupies only 85.5% of this site. However, the present structure-refinement indicates full occupancy; clearly, OH must be present in order to maintain charge balance and to fill the site. This is confirmed by comparing ideal and predicted bond-valences: given full occupancy of the *O* site, the amount of OH needed for charge balance is 1.94 atoms *pfu*, which, if hydrogen bonding is not appre-

ciable, results in a predicted bond-valence sum to O of 1.68 *v.u.*, in excellent agreement with the observed value of 1.63 *v.u.* The implications of this observation are important for pyrochlores with a high degree of defect-pyrochlore character.

For the defect-pyrochlore structure, only *B*–O bonds contribute to the bond-valence sum for O. For *Fd3m* symmetry, the bond valence for *B*–O bonds is 5/6 *v.u.* and 4/6 *v.u.* for $B = M^{5+}$ and $B = M^{4+}$, respectively. This results in bond-valence sums to O of 1.67 *v.u.* and 1.33 *v.u.* for M^{5+} and M^{4+} pyrochlores, respectively. Within *Fd3m* symmetry, there are only two ways that this bond-valence sum can approach the ideal value of 2 *v.u.* for pyrochlore-group minerals with a high degree of defect-pyrochlore character. The first is by shortening of existing *A*–O bonds, thus increasing the bond-valence contribution to O; the second is by protonation of the O. As the *A* cation is very weakly bonded to the O anion in the pyrochlore structure, and as there are stereochemical restrictions on excessive shortening of the *A*–O bond, then without a reduction in symmetry, shortening of *A*–O bonds cannot be invoked to satisfy the bond-valence requirements of O. Consequently, it is expected that pyrochlore-group minerals with a high proportion of *A*-site vacancies also have a significant amount of OH (or possibly F) at the O site. Furthermore, as defect betafites have lower bond-valence sums to O than defect pyrochlores and microlites, the defect betafites should tend to have either (1) more highly charged cations at *A*, or (2) more OH at the O site than pyrochlores and microlites. The first condition is observed for betafites in general; more work needs to be done before the second condition can be evaluated.

The correctness of the H_2O and OH assignments is further supported by inspection of the electron-microprobe data. The structure refinement gives a total amount of H_2O of 16.1 wt.% (σ = 1.6%), a good match to the analytical deficit of 15.3 wt.% (Table 1).

The structural formula of kalipyrochlore

We conclude that the structural formula of kalipyrochlore is $([H_2O]_{0.99}Sr_{0.05}Ca_{0.01})_{\Sigma 1.05}(Nb_{1.80}Ti_{0.20})_{\Sigma 2}(O_{4.06}OH_{1.94})_{\Sigma 6}([H_2O]_{0.86}K_{0.14})$, which points to an ideal empirical formula of $Nb_2(O,OH)_6{\cdot}pH_2O$, where $p \leq 1.75$. Both formulae deviate from the IMA recommendation for the general formula of the pyrochlore group, and the name *kalipyrochlore* hardly seems warranted for such a composition. However, we are reluctant at the present to suggest a renaming or redefinition of the species or a modification of the rules of nomenclature for the pyrochlore group until the structural properties of other natural H_2O-bearing pyrochlores are investigated and the nomenclature and status of the inverse pyrochlores are fully examined. We are, at present, pursuing these objectives.

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