Cafetite, Ca[Ti$_2$O$_5$](H$_2$O): Crystal structure and revision of chemical formula

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Abstract

The crystal structure of cafetite, ideally Ca[Ti$_2$O$_5$](H$_2$O), (monoclinic, $P2_1/n$, $a = 4.9436(15)$, $b = 12.109(4)$, $c = 15.911(5)$ Å, $\beta = 98.937(5)°$, $V = 940.9(5)$ Å^3, $Z = 8$) has been solved by direct methods and refined to $R_1 = 0.057$ using X-ray diffraction data collected from a crystal pseudo-merohedrally twinned on (001). There are four symmetrically independent Ti cations; each is octahedrally coordinated by six O atoms. The coordination polyhedra around the Ti cations are strongly distorted with individual Ti-O bond lengths ranging from 1.743 to 2.223 Å (the average <Ti-O> bond length is 1.98 Å). Two symmetrically independent Ca cations are coordinated by six and eight anions for Ca1 and Ca2, respectively. The structure is based on [Ti$_2$O$_5$] sheets of TiO$_6$ octahedra parallel to (001). The Ca atoms and H$_2$O groups are located between the sheets and link them into a three-dimensional structure. The structural formula of cafetite confirmed by electron microprobe analysis is Ca[Ti$_2$O$_5$](H$_2$O), in contrast to the formula (Ca,Mg)(Fe,Al)$_2$Ti$_4$O$_{12}$·4H$_2$O suggested by Kukharenko et al. (1959). The wrong chemical formula suggested for cafetite by Kukharenko et al. (1959) is probably due to admixtures of magnetite or titanomagnetite in their samples. Cafetite is chemically related to kassite, CaTi$_2$O$_4$(OH)$_2$, but differs from it in structure and structural formula.

Introduction

Cafetite was first described by Kukharenko et al. (1959) from alkaline rocks in the Afrikanda massif, Kola peninsula, Russia. The mineral was found in close association with titanomagnetite, phlogopite, ilmenite, baddeleite, chlorite, titanite, and an "undefined" mineral later described by Kukharenko et al. (1965) as kassite. As pointed out by Kukharenko et al. (1959), chemical analyses performed by V.M. Kovyazina gave the empirical formula (Ca$_{0.67}$Na$_{0.06}$K$_{0.05}$ Mn$_{0.02}$Mg$_{0.01}$)$_{0.81}$(Fe$^{3+}_{1.68}$Al$_{0.24}$Ti$^{3+}_{0.03}$Ti$^{4+}_{0.05}$)$_{2.00}$(Ti$_{3.92}$Si$_{0.09}$)$_{4.01}$O$_{12}$·4H$_2$O, ideally (Ca,Mg)(Fe,Al)$_2$Ti$_4$O$_{12}$·4H$_2$O. The mineral was reported as orthorhombic, $a = 31.34(5)$, $b = 12.12(3)$, $c = 4.96(1)$ Å, $V = 1884.01$ Å^3. However, optical studies indicated that the γ axis of the optical indicatrix and the c axis are inclined to each other by ~2–4°, which suggested that cafetite is monoclinic.

Later, Kukharenko et al. (1965) provided a full description of the "undefined" mineral which they named kassite. Its ideal chemical composition was determined as CaTi$_2$O$_4$(OH)$_2$ and its cell was reported as orthorhombic, $a = 8.99(3)$, $b = 9.55(3)$, $c = 5.26(1)$ Å, $V = 451.59$ Å^3. According to the chemical formulae, crystallographic parameters, and powder diffraction patterns, cafetite and kassite were clearly designated as two distinct mineral species. It is noteworthy that their chemical formulae have different Ca:Ti ratios, 1:4 and 1:2 for cafetite and kassite, respectively.

In 1986, Evans et al. reported a find of a mineral from the Magnet Cove alkaline complex in Arkansas that had unit-cell parameters close to those of cafetite, whereas its chemical composition was CaTi$_2$O$_4$(OH)$_2$, i.e., identical to that of kassite as described by Kukharenko et al. (1965). As a consequence, Evans et al. (1986) suggested that samples of cafetite and kassite were somehow intermixed by Kukharenko et al. (1959, 1965) during their X-ray study. As a consequence of Evans et al. (1986), the cafetite and kassite entries were interchanged in Set 39 of the powder diffraction file (PDF-2) (see also Self and Buseck 1991). For the mineral they designated as kassite, Evans et al. (1986) reported an orthorhombic cell, $a = 12.10(2)$, $b = 31.65(3)$, $c = 4.95(1)$ Å, $V = 1899$ Å^3, with possible space groups $Ammm$, $A2mm$, $A222$, or $A2_122$.

Self and Buseck (1991) described kassite from Josephine Creek, Oregon, and studied the structure using electron-diffraction techniques. They found a B-centered orthorhombic unit cell with dimensions $a = 9.08$, $b = 4.78$, $c = 5.23$ Å, which is similar to that determined by Kukharenko et al. (1965) for kassite, except that the b dimension is halved. Chemical analyses showed that the chemical formula of the mineral under study was essentially CaTi$_2$O$_4$(OH)$_2$, i.e., identical to that of kassite. On the basis of their studies, Self and Buseck (1991) suggested a structure model for kassite that is similar to that of lucasite-Ce, CeTi$_2$(O,OH)$_6$ (Nickel et al. 1987). Comparing their results with those of Evans et al. (1986), Self and Buseck (1991) pointed out that "…kassite and cafetite should not be distinguished by Fe content but rather by crystallographic properties" and that "…the status of kassite and the related mineral cafetite are destined to remain controversial until more specimens have been characterized."

Recently, Yakovenchuk et al. (1999) found cafetite in two

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natrolite veins in alkaline rocks of the Kukisvumchorr and Rasvumchorr mountains, Khibiny, Kola peninsula. The mineral occurs as orange and yellowish spherolites composed from thin plates up to 1 mm in diameter (Fig. 1). X-ray powder and single-crystal diffraction studies showed that the mineral has crystallographic parameters identical to those reported by Kukharenko et al. (1959) for cafetite. However, its chemical composition is close to $CaTi_2O_4(OH)_2$, i.e., very different from that of cafetite and identical to kassite. To resolve the problem, we obtained a holotype specimen of cafetite that was given by A.A. Kukharenko to the Mineralogical Museum of the Department of Mineralogy, St. Petersburg State University. The crystals of cafetite in that specimen were large enough to perform a single-crystal structural study the results of which, together with chemical analyses, are presented here.

EXPERIMENTAL METHOD

Data collection

The crystals of cafetite used in this study were from specimen no. 13420 from the collection of the Mineralogical Museum, Department of Mineralogy, St. Petersburg State University. A suitable single crystal was mounted on a Bruker three-circle X-ray diffractometer operated at 50 kV and 40 mA and equipped with a CCD APEX area detector with a crystal-to-detector distance of 5 cm. More than a hemisphere of three-dimensional data was collected to $2\theta_{max} = 34.50°$ using monochromatic $MoK\alpha$ X-radiation, with frame widths of 0.3° in ω, and with 20 seconds spent counting for each frame. The orthorhombic unit-cell parameters were refined from 1980 reflections using least-squares techniques that gave a C-centered cell with dimensions $a = 4.9436(4)$, $b = 31.435(2)$, $c = 12.1086(9)$ Å. The intensity data were integrated and corrected for Lorentz, polarization, and background effects using the Bruker program SAINT. A semi-empirical absorption-correction was done based upon 944 intense reflections. The crystal was modeled as an ellipsoid, which reduced R_{int} from 0.117 to 0.096.

Structure solution and refinement

The Bruker SHELXTL Version 5 system of programs was used for determination and refinement of the crystal structure. The attempts to solve the structure in the C-centered orthorhombic cell were unsuccessful. The cell was then transformed to a monoclinic primitive cell using the transformation matrix

(1 0 0 | 0 0 1 | –1/2 1/2 0). Systematic absences of reflections indicated space groups $P2_1$ or $P2_1/n$. The structure was solved by direct methods in space group $P2_1/n$ and a reasonable structure model was obtained, but the $R1$ factor was unacceptably high (0.189). Examination of the calculated and observed structure factors revealed that the largest discrepancies corresponded to F_{obs} that were much greater than F_{calc}, a situation that is common when dealing with a merohedrally or pseudo-merohedrally twinned crystal. We corrected for twinning using the operator $[100\,010\,\overline{1}0\overline{1}]$ with the methods of Jameson (1982) and Herbst-Irmer and Sheldrick (1998), which reduced R_1 to 0.065. The refinement indicated two twin components with 29 and 71% of the volume of the crystal, respectively. Inspection of the difference Fourier map revealed the positions of the H atoms. The H_2O-H distances were constrained to 0.96 Å, and isotropic displacement parameters for the H atoms were constrained to be equal. Refinement of the site occupancy factors for the Ca positions resulted in values of 0.96 and 1.03 for Ca1 and Ca2, respectively, which is in agreement with the almost complete absence of Na in these positions, as suggested by chemical analyses of crystals from the same sample (see below). The final model included atomic positional and anisotropic-displacement parameters for all non-hydrogen atoms. The model was refined on the basis of F^2 for all 3836 unique reflections. The final refinement converged to an R_1 value of 0.056, calculated for the 3019 unique observed ($|F_o| \geq 4\sigma_F$) reflections (Table1). The final atomic coordinates and displacement parameters are in Table 2, selected interatomic distances are in Table 3, and a bond-valence analysis is provided in Table 4. A table of calculated and observed structure factors is available from the authors upon request.

Chemical analysis

Electron-microprobe analyses were done with a Cameca MS-46 instrument operating at 20 kV (30 kV for Sr) and 20–40 nA. The following standards were used: lorenzenite (Na), wadeite (K), pyrope (Al), diopside (Ca and Si), rutile (Ti), synthetic $MnCO_3$ (Mn), hematite (Fe), celestite (Sr), and metallic Nb (Nb). The analyses were done for both Khibiny samples and the holotype specimen of cafetite used in the structural study. The latter specimen has very minor amount of Na (0.64 wt%) which is in agreement with the results of the single-crystal X-ray analysis that shows that both Ca positions are fully occupied. A water content of ~11 wt% was determined for the Khibiny samples using thermal gravimetry. The results of analy-
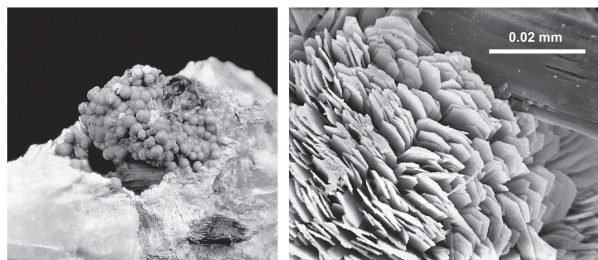

FIGURE 1. Spherolites of cafetite (~8 × 8 × 8 mm³) (**a**) and the SEM image of cafetite crystals (**b**).

TABLE 1. Crystallographic data for cafetite

a (Å)	4.9436(15)	Crystal size (mm)	0.26 × 0.04 × 0.02
b (Å)	12.109(4)	Radiation	$MoK\alpha$
c (Å)	15.911(5)	Total Ref.	10045
β (°)	98.937(5)	Unique Ref.	3836
V (Å³)	940.9(5)	Unique $|F_o| \geq 4\sigma_F$	3019
Space group	$P2_1/n$	R_1	0.056
μ (cm⁻¹)	44.27	wR_2	0.131
D_{calc} (g/cm³)	3.30	S	0.887
Unit-cell contents 8{Ca[Ti₂O₅](H₂O)}			

Note: $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; $S = \{\Sigma[w(|F_o| - |F_c|)^2] / (m - n)\}$, for m observations and n parameters; $w = 1 / [\sigma^2(F_o^2) + (0.0583P)^2]$ where $P = (F_o^2 + 2F_c^2) / 3$.

TABLE 2. Atomic coordinates and displacement parameters ($10^4 \times Å^2$) for cafetite

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti1	0.8280(2)	0.69732(8)	0.45767(5)	81(2)	90(4)	66(3)	76(4)	0(3)	−21(3)	−3(3)
Ti2	0.2259(2)	0.51318(8)	0.43865(6)	94(2)	102(4)	88(4)	83(4)	5(3)	−16(3)	−1(3)
Ti3	0.9742(2)	0.91031(7)	0.57249(6)	78(2)	91(4)	74(4)	60(4)	7(3)	−18(3)	2(3)
Ti4	0.5820(2)	0.11252(7)	0.54933(6)	77(2)	91(4)	69(4)	60(4)	−4(3)	−18(3)	1(3)
Ca1	0.5198(3)	0.95070(10)	0.74000(7)	149(2)	171(6)	154(5)	107(5)	−11(4)	−26(4)	−22(4)
Ca2	0.5906(2)	0.30997(8)	0.37755(6)	98(2)	103(5)	85(4)	97(4)	−11(3)	−16(3)	2(4)
O1	0.9544(8)	0.4030(3)	0.4588(2)	87(7)	79(17)	103(16)	72(15)	−10(13)	−11(13)	10(13)
O2	0.6707(8)	0.8122(3)	0.5478(2)	90(6)	71(16)	91(15)	100(15)	−19(12)	−15(13)	−13(13)
O3	0.8802(9)	0.1926(3)	0.5150(2)	117(7)	139(19)	92(15)	126(16)	−13(13)	33(14)	−16(14)
O4	0.2691(8)	0.0043(3)	0.5342(2)	87(7)	107(17)	88(15)	63(15)	10(12)	6(13)	1(13)
O5	0.5430(8)	0.6009(3)	0.4870(2)	107(7)	102(18)	117(17)	89(16)	-6(13)	−25(13)	−7(14)
O6	0.4351(8)	0.2114(3)	0.6174(2)	100(7)	116(18)	102(16)	68(15)	−10(13)	−34(13)	10(14)
O7	0.7844(8)	0.0199(3)	0.6331(2)	101(7)	99(18)	120(17)	71(15)	−7(12)	−33(13)	7(14)
O8	0.1721(8)	0.8480(3)	0.6616(2)	114(7)	156(19)	104(16)	70(16)	−1(12)	−18(14)	11(15)
H₂O9	0.2450(9)	0.2208(4)	0.2645(2)	154(8)	150(20)	220(20)	73(16)	14(14)	−29(15)	19(16)
H₂O10	0.2148(9)	0.1098(3)	0.7410(3)	153(8)	160(20)	179(19)	112(17)	−1(14)	−14(15)	−30(16)
O11	0.3218(9)	0.4661(3)	0.3440(2)	144(8)	190(20)	129(17)	105(17)	−4(13)	8(16)	76(16)
O12	0.9673(9)	0.6219(3)	0.3763(2)	126(8)	140(20)	139(18)	96(16)	11(13)	−8(14)	48(15)
H1	0.069(9)	0.211(7)	0.282(6)	430(140)						
H2	0.079(14)	0.083(6)	0.696(4)	430(140)						
H3	0.167(19)	0.246(7)	0.209(2)	430(140)						
H4	0.302(17)	0.162(5)	0.709(5)	430(140)						

ses are presented in Table 5. The ideal chemical formula for cafetite according to the analyses is $CaTi_2O_5 \cdot H_2O$, close to the formula $CaTi_2O_4(OH)_2$ proposed by Kukharenko et al. (1965) and Self and Buseck (1991) for kassite and by Evans et al. (1986) for the mineral from the Magnet Cove, Arkansas. In all specimens, including that studied by Kukharenko et al. (1959), the Ca:Ti ratio is about 1:2 and the Fe content is low (<1.02 wt%). This is in contradiction with the chemical formula $(Ca,Mg)(Fe,Al)_2Ti_4O_{12} \cdot 4H_2O$ suggested for cafetite by Kukharenko et al. (1959). We suggest that the sample used for chemical analysis in their study contained a significant amount of magnetite or titanomagnetite crystals, probably in thin intergrowths with cafetite needles. This explains the problem of kassite and cafetite as it was formulated by Evans et al. (1986) and Self and Buseck (1991).

RESULTS

Cation polyhedra

There are four symmetrically independent Ti cations in the structure of cafetite. Each is octahedrally coordinated by six O atoms. The coordination polyhedra around the Ti cations are strongly distorted with individual Ti-O bond lengths ranging from 1.743 to 2.223 Å. The average <Ti-O> bond length for the TiO_6 octahedra is 1.98 Å.

There are two symmetrically independent Ca cations coordinated by six and eight anions for Ca1 and Ca2, respectively. The Ca1 cation is in octahedral coordination to four O atoms and two H_2O groups with an average Ca1-φ bond length (φ = O, H_2O) of 2.38 Å, whereas individual Ca2-φ bond lengths are in the range 2.283–2.450 Å. The Ca2 cation is coordinated by six O atoms and two H_2O groups with an average Ca2-φ bond length of 2.49 Å. There are seven Ca2-φ bonds in ranging from 2.324 to 2.586 Å and one long Ca2-O bond distance of 2.807 Å.

Bond-valence analysis and hydrogen bonding

The bond valence analysis presented in Table 4 was calculated using the parameters for Ca^{2+}-O and Ti^{4+}-O bonds from

TABLE 3. Selected interatomic distances (Å) in the structure of cafetite

Ti1-O12	1.806(4)	Ti4-O6	1.838(4)
Ti1-O5	1.942(4)	Ti4-O7	1.903(4)
Ti1-O3b	1.963(4)	Ti4-O3	1.914(4)
Ti1-O6a	1.964(4)	Ti4-O4	2.013(4)
Ti1-O1b	1.989(4)	Ti4-O2a	2.044(4)
Ti1-O2	2.223(4)	Ti4-O4g	2.148(4)
<Ti1-O>	1.98	<Ti4-O>	1.98
Ti2-O11	1.743(4)	Ca1-O11h	2.283(4)
Ti2-O5	1.950(4)	Ca1-O8	2.322(4)
Ti2-O1c	1.954(4)	Ca1-H₂O9a	2.387(4)
Ti2-O12c	1.989(4)	Ca1-O12i	2.390(4)
Ti2-O5a	2.047(4)	Ca1-H₂O10e	2.448(4)
Ti2-O1a	2.222(4)	Ca1-O7e	2.450(4)
<Ti2-O>	1.98	<Ca1-φ>	2.38
Ti3-O8d	1.763(4)	Ca2-O11	2.324(4)
Ti3-O2	1.906(4)	Ca2-O1	2.335(4)
Ti3-O7e	1.963(4)	Ca2-O8a	2.377(4)
Ti3-O4f	2.017(4)	Ca2-O2a	2.397(4)
Ti3-O3b	2.078(4)	Ca2-H₂O9	2.523(4)
Ti3-O4a	2.182(4)	Ca2-H₂O10j	2.541(4)
<Ti3-O>	1.98	Ca2-O5a	2.586(4)
		Ca2-O3	2.807(4)
		<Ca2-φ>	2.49

Hydrogen bonding system

D-H	d(D-H)	d(H⋯A)	D-H⋯A	A	d(D⋯A)
H₂O9-H1	0.961	1.751	156.8	O8	2.661
H₂O9-H3	0.958	1.784	163.7	O6	2.717
H₂O10-H2	0.954	1.806	166.3	O7	2.743
H₂O10-H4	0.957	1.789	155.8	O6	2.690

Notes: a = −x + 1, −y + 1, −z + 1; b = −x + 2, −y + 1, −z + 1; c = x − 1, y, z, d = x + 1, y, z, e = x, y + 1, z, f = x + 1, y + 1, z, g = −x + 1, −y, −z + 1; h = x + 1/2, −y + 3/2, z + 1/2; i = x − 1/2, −y + 3/2, z + 1/2; j = x + 1/2, −y+1/2, z − 1/2.
* φ = O, H_2O.

Brese and O'Keeffe (1991). The bond-valence sums for all the cations are typical values for cations in similar structures. The bond-valence sums at the H_2O9 and H_2O10 sites are 0.54 and 0.49 valence units (v.u.), in agreement with their identification as water molecules. The bond-valence sums at the O1, O2, O3, O4, O5, O11, and O12 sites are in the range of 1.95–2.12 v.u., which is typical for O atoms, whereas the bond-valence sums for O6, O7, and O8 sites are 1.61, 1.73, and 1.86 v.u.. The geometry of the hydrogen bonding scheme in cafetite is given in Table 3; it is also depicted in Figure 2. The distances and
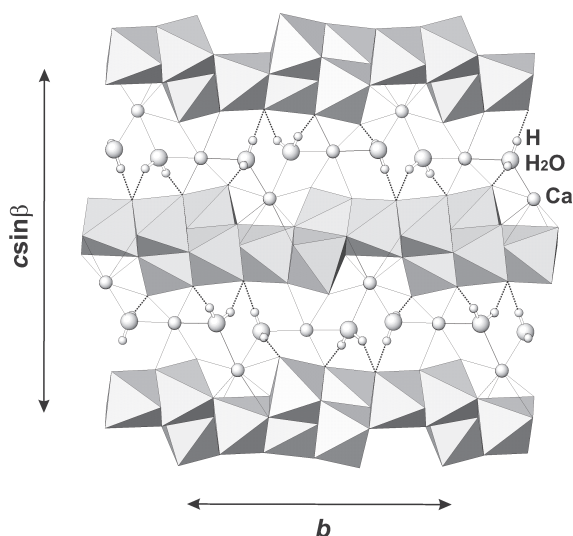
FIGURE 2. Projection of the crystal structure of cafetite along the *a* axis.

TABLE 4. Bond-valence analysis (v.u.) for cafetite

	Ti1	Ti2	Ti3	Ti4	Ca1	Ca2	Σ
O1	0.62	0.69, 0.33				0.37	2.01
O2	0.33		0.78	0.54		0.31	1.96
O3	0.67		0.49	0.77		0.10	2.03
O4			0.58, 0.37	0.59, 0.41			1.95
O5	0.71	0.69, 0.53				0.19	2.12
O6	0.67			0.94			1.61
O7			0.67	0.79	0.27		1.73
O8			1.15		0.38	0.33	1.86
H_2O9					0.32	0.22	0.54
H_2O10					0.27	0.21	0.49
O11		1.21			0.43	0.38	2.02
O12	1.02	0.62			0.32		1.96
Σ	4.02	4.04	4.04	4.04	1.98	2.11	

Note: Bond-valence parameters from Brese and O'Keeffe (1991). Contributions of hydrogen bonds are not included.

angles are in good agreement with the values usually observed for the $H_2O \cdots H$ bonds in inorganic oxysalt hydrates (Chiari and Ferraris 1982; Jeffrey 1997). Each H_2O group donates two moderate $H_2O \cdots O$ hydrogen bonds. The H_2O9 group donates hydrogen bonds to the O6 and O8 atoms from two adjacent octahedral sheets, whereas the H_2O10 group is hydrogen bonded to the O6 and O7 atoms from the same octahedral sheet. Participation of the O6, O7, and O8 atoms in the hydrogen bonding scheme is in good agreement with their relatively low bond-valence sums (Table 4).

Structure description

Figure 2 shows a projection of the structure of cafetite along the **a** axis. The TiO_6 octahedra form $[Ti_2O_5]$ sheets parallel to (001). The Ca atoms and H_2O groups are located between the sheets to form a three-dimensional structure. The hydrogen bonds are shown in Figure 2 as dashed lines. The octahedral $[Ti_2O_5]$ sheet in the structure of cafetite is shown in Figure 3a. It consists of edge-sharing TiO_6 octahedra. The structure of the sheet can be described in a graphical fashion using an approach recently elaborated by Hawthorne et al. (2000) for octahedral-tetrahedral structures in sulfate minerals. Octahedra are represented by the white vertices. Linking of polyhedra is denoted by one, two, or three edges between two vertices for corner-, edge-, and face-sharing between polyhedra, respectively. The octahedral sheet in cafetite is graphically represented in Figure 3c. Since moving from polyhedral to graphical representation is accompanied by lack of geometrical information, it makes sense to describe linkage of each polyhedron by its connectivity diagram. The connectivity diagrams were proposed by Krivovichev (1997) and Krivovichev et al. (1997) for describing tetrahedral units with edge-sharing between tetrahedra, and recently has been adopted by Krivovichev and Burns (2000) and Krivovichev et al. (2002) for the description of heteropolyhedral structures. As a basis for connectivity diagram, one has to use a Schlegel diagram or projection of the respective polyhedron (the latter is more convenient for octahedra). It is worthy to note that Schlegel diagrams were introduced into crystal chemistry by Moore

TABLE 5. Chemical composition of cafetite

	Samples			
	Khibiny massif			
	Mt. Kukisvumchorr	Mt. Rassvumchorr	Afrikanda massif*	Theoretical composition†
Na_2O	1.63 (1.40–1.90)‡	0.80 (0.42–2.38)	0.64	–
K_2O	0.18 (0.11–0.24)	0.17 (0.06–0.24)	–	–
Al_2O_3	0.05 (0.00–0.13)	0.41 (0.13–0.75)	–	–
SiO_2	0.13 (0.08–0.20)	0.41 (0.00–1.20)	–	–
CaO	19.17 (18.52–20.13)	20.21 (16.81–22.46)	20.80	23.98
TiO_2	64.83 (64.23–65.46)	66.23 (63.53–67.86)	67.78	68.32
MnO	0.06 (0.04–0.08)	0.06 (0.00–0.15)	–	–
FeO	0.97 (0.93–1.02)	0.66 (0.49–0.78)	0.27	–
Nb_2O_5	2.14 (1.98–2.31)	2.35 (1.46–3.31)	0.15	–
SrO	–	0.12 (0.00–0.26)	–	–
Subtotal	89.18	91.42	89.64	92.30
H_2O	~11.0	~11.0	~11.0	7.70
Total	100.18	102.53	100.64	100.00

* Sample no. 13420, Mineralogical Museum, Dept. Mineralogy, St. Petersburg State University (holotype specimen of cafetite studied by Kukharenko et al. 1959)
† Calculated from the structural formula $Ca[Ti_2O_5](H_2O)$.
‡ Average values; ranges of compositional variations are given in brackets.
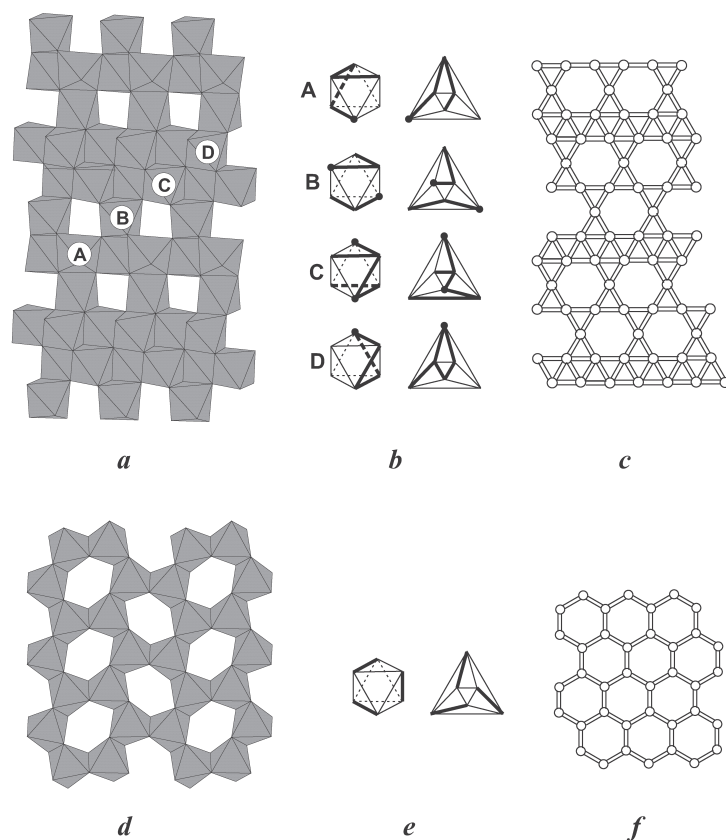
FIGURE 3. The $[Ti_2O_5]$ sheet of TiO_6 octahedra in the structure of cafetite. (**a**) Polyhedral representation. (**b**) Projections and connectivity diagrams for the TiO_6 octahedra. (**c**) Graphical representation. The $[Ti_2(O,OH)_6]$ sheet in the structure of lucasite-(Ce), $CeTi_2(O,OH)_6$, that is probably present in the structure of kassite, $CaTi_2O_4(OH)_2$. (**d**) Polyhedral representation. (**e**) Projections and connectivity diagrams for the Ti_{j6} octahedra (j = O, OH). (**f**) Graphical representation. See text for details.

(1970) for describing the geometrical parameters of octahedra in structures of basic iron phosphate compounds. The heavy lines represent edges shared between polyhedra. The circles indicate shared vertices. Figure 2b shows projections and connectivity diagrams for the octahedra that form the $[Ti_2O_5]$ sheet in the structure of rimkorolgite. There are four types of connectivity diagrams of TiO_6 octahedra in the structure of cafetite. The $Ti1O_6$ octahedron belongs to the B type (6 adjacent octahedra; 4 shared edges and 2 shared vertices), the $Ti2O_6$ octahedron belongs to the A type (5 adjacent octahedra; 4 shared edges and 1 shared vertex), the $Ti3O_6$ octahedron is of the D type (6 adjacent octahedra; 5 shared edges and 1 shared vertex), and $Ti4O_6$ octahedron belongs to the C type (7 adjacent octahedra; 5 shared edges and 2 shared vertices). The essential distortion of the TiO_6 octahedra can be explained by topological properties of the O atoms at their vertices. The O4 atom is shared between four octahedra; the Ti-O4 bond lengths are range from 2.013 to 2.182 Å. The O1, O2, O3, and O5 atoms are shared between three octahedra; the Ti-O bond lengths are in the ranges 1.954–2.222, 1.906–2.223, 1.914–2.078 and 1.942–2.047 Å, respectively. The O6 and O7 atoms are shared between two octahedra and the corresponding bond lengths are within 1.838–1.964 and 1.903–1.963 Å, respectively. The O8, O11, and O12 atoms belong to only one octahedron; the Ti-O bond lengths are 1.763, 1.743, and 1.806 Å, respectively. In general, the smaller the number of octahedra sharing a vertex, the shorter the corresponding Ti-O bond lengths.

DISCUSSION

Chemical formula of cafetite

On the basis of the crystal-structure analysis, the structural formula for cafetite is $Ca[Ti_2O_5](H_2O)$. The theoretical composition is (in wt%) CaO 23.98, TiO_2 68.32, H_2O 7.70, total 100.00, which is in good agreement with the results of the chemical analyses presented in Table 5. As can be seen from the data in Table 5, the cafetite crystals from Mt. Kukisvumchorr contain 1.63 wt% Na_2O. It is very likely that, in these samples, Na is incorporated into one of the two Ca positions. In this case, the most likely charge-balance mechanism would be OH^--O^{2-} at one of the O positions. Unfortunately, the Mt. Kukisvumchorr sample contains no crystals suitable for single-crystal structural studies.

The problem of kassite and cafetite

Self and Buseck (1991) suggested a structural model for kassite, $CaTi_2O_4(OH)_2$, that is similar to the structure of lucasite-(Ce), $CeTi_2(O,OH)_6$ (Nickel et al. 1987). Preliminary studies of kassite using single crystals (Ian Grey, personal communication) showed that this model is generally correct. The structure of lucasite consists of $[Ti_2(O,OH)_6]$ sheets of $Ti\phi_6$ octahedra (ϕ = O, OH) as shown in Figure 3d. Connectivity diagrams of octahedra and graphical representation of the octahedral sheet are shown in Figures 3e and 3f, respectively. As the structure of kassite consists of sheets of this type, it is different from the structure of cafetite. The structural formula for kassite should

be written as $Ca[Ti_2O_4(OH)_2]$, whereas that for cafetite is $Ca[Ti_2O_5](H_2O)$. Thus, kassite and cafetite have identical general compositions, which prompted Evans et al. (1986) to suggest that Kukharenko et al. (1959, 1965) intermixed their samples during their X-ray study. It is now clear that they did not but, rather, they did chemical analyses on a specimen that was not free from admixtures of Fe-containing minerals, probably magnetite or titanomagnetite. It is noteworthy that the suggestions of Self and Buseck (1991) regarding the status of kassite and cafetite were absolutely correct, taking into account that they had no access to the samples studied by Kukharenko et al. (1959, 1965).

We hope that this study proves that cafetite is a distinct mineral species. A final solution of the problem will be possible after refinement of the structure of kassite.

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REFERENCES CITED

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Chiari, G. and Ferraris, G. (1982) The water molecule in crystalline hydrates studied by neutron diffraction. Acta Crystallographica, B38, 2331–2341.

Evans, H.T.E. Jr., Dwornik, E.J., and Milton, C. (1986) Kassite from the Diamond Jo quarry, Magnet Cove, Hot Spring County, Arkansas: the problem of cafetite and kassite. American Mineralogist, 71, 1045–1048.

Hawthorne, F.C., Krivovichev, S.V., and Burns, P.C. (2000) The crystal chemistry of sulfate minerals. In C.N. Alpers, J.L. Jambor, and D.K. Nordstrom, Eds., Sulfate Minerals—Crystallography, Geochemistry, and Environmental Significance, 40, 1–112. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Washington, D.C.

Herbst-Irmer, R. and Sheldrick, G.M. (1998) Refinement of twinned structures with SHELXL97. Acta Crystallographica, B54, 443–449.

Jameson, G.B. (1982) On structure refinement using data from a twinned crystal. Acta Crystallographica, A38, 817–820.

Jeffrey, G.A. (1997) An Introduction to Hydrogen Bonding, 303 p. Oxford University Press, New York.

Krivovichev, S.V. (1997) On the using of Schlegel diagrams for description and classification of minerals' crystal structures. Zapiski Vserossiyskogo Mineralogicheskogo Obshchestva (Proceedings of Russian Mineralogical Society), 126(2), 37–46 (in Russian).

Krivovichev, S.V. and Burns, P.C. (2000) Crystal chemistry of uranyl molybdates. I. The structure and formula of umohoite. Canadian Mineralogist, 38, 717–726.

Krivovichev, S.V., Filatov, S.K., and Semenova, T.F. (1997) On the systematics of polyions of linked polyhedra. Zeitschrift für Kristallographie, 212, 411–417.

Krivovichev, S.V., Britvin, S.N., Burns, P.C., and Yakovenchuk, V.N. (2002) Crystal structure of rimkorolgite, $Ba[Mg_5(H_2O)_7(PO_4)_4](H_2O)$, and its comparison with bakhchisaraitsevite. European Journal of Mineralogy, 14, 397–402.

Kukharenko, A.A., Kondratyeva, V.V., and Kovyazina, V.M. (1959) Cafetite, a new hydrous titanate of calcium and iron. Zapiski Vserossiyskogo Mineralogicheskogo Obshchestva (Proceedings of Russian Mineralogical Society), 88, 444–453 (in Russian).

Kukharenko, A.A., Orlova, M.P., Bulakh, A.G., Bagdasarov, E.A., Rimskaya-Korsakova, O.M., Nefedov, Ye.I., Ilinskiy, G.A., Sergeyev, A.S., and Abakumova, N.B. (1965) The Caledonian complex of ultrabasic alkalic rocks and carbonatites of the Kola peninsula and northern Karelia. Nedra, Moscow, p. 368–375 (in Russian).

Moore, P.B. (1970) Crystal chemistry of the basic iron phosphates. American Mineralogist, 55, 135–169.

Nickel, E.H., Grey, I.E., and Madsen, I.C. (1987) Lucasite-(Ce), $CeTi_2(O,OH)_6$, a new mineral from the Western Australia: its description and structure. American Mineralogist, 72, 1006–1010.

Self, P.G. and Buseck, P.R. (1991) Structure model for kassite, $Ca_2Ti_2O_4(OH)_2$. American Mineralogist, 76, 283–287.

Yakovenchuk, V.N., Ivanyuk, G.Yu., Pakhomovsky, Ya.A., and Menshikov, Yu.P. (1999) Minerals of the Khibiny massif. Zemlya, Moscow, 326 p.