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The crystal structure of orlovite, $KLi_2Ti(Si_4O_{10})(OF)$: the first example of the short-range order of Ti in true trioctahedral micas

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Abstract: The crystal structure of orlovite, ideally $KLi_2Ti(Si_4O_{10})(OF)$, from the Darai-Pioz alkaline massif, Tien-Shan, Garmskii district, northern Tajikistan, was solved and refined in the space $C2/m$ to $R_1 = 3.56\%$ based on 729 independent reflections with $F_o > 4\sigma F$, $a = 5.198(4)$, $b = 9.046(7)$, $c = 10.093(8)$ Å, $\beta = 99.53(2)°$, $V = 468.1(1.1)$ Å^3. In the O sheet of orlovite, there are two crystallographically independent M sites: $M1$ and $M2$. In many true trioctahedral micas with space group $C2/m$, the $M1$ site corresponds to the Wyckoff position c, with multiplicity of 2 and site symmetry of $2/m$. In orlovite, M1 (= Ti) atoms are displaced from the inversion centre and hence the $M1$ site corresponds to the Wyckoff position i, with multiplicity of 4 and site symmetry of m. The $M1$ site is 50% occupied primarily by Ti, ideally $Ti_{1.00}$ per formula unit (pfu), with $\langle M1–\phi \rangle = 1.977$ Å. The two points of the $M1$ site occur 0.432 Å apart. Each M1 atom is coordinated by four O2 atoms, with M1–O2 = 2.009 Å and two A anions of the composition (OF); M1–A = 1.699 Å, where A = O and M1–A = 2.130 Å, where A = F. This is the first occurrence of short-range order of Ti in a true trioctahedral mica. The $M2$ site is occupied solely by Li, giving Li_2 pfu, with $\langle M2–\phi \rangle = 2.106$ Å. In the T sheet, there is one tetrahedrally coordinated T site occupied solely by Si, $\langle T–O \rangle = 1.624$ Å. The interstitial $^{[12]}I$ site is occupied primarily by K, ideally $K_{1.00}$ pfu, with $\langle I–O \rangle = 3.075$ Å. The empirical formula of orlovite was calculated on the basis of 12 (O + F), with the constraint F + OH = 1 pfu: $(K_{0.98}Rb_{0.03}Cs_{0.01})_{1.02}Li_{2.01}(Ti_{0.94}Nb_{0.02}Fe_{0.02}Al_{0.02})_{1.00}Si_4O_{10}[O_{1.00}F_{0.95}(OH)_{0.05}]_{2.00}$, $Z = 2$; $D_{calc.} = 2.814$ g/cm^3.

Key-words: orlovite; true trioctahedral mica; crystal structure; titanium; lithium; short-range order (SRO).

1. Introduction

Orlovite, $KLi_2Ti(Si_4O_{10})(OF)$, was described from the the Darai-Pioz alkaline massif, Tien-Shan, Garmskii district, northern Tajikistan, by Agakhanov *et al.* (2011). They reported a chemical analysis by electron microprobe, ICP MS (Li_2O, Rb_2O) and SIMS (H_2O) which gave SiO_2 58.31, TiO_2 18.05, Nb_2O_5 0.50, Al_2O_3 0.22, FeO 0.40, MnO 0.03, K_2O 11.13, Cs_2O 0.24, Li_2O 7.25, Rb_2O 0.69, H_2O 0.21, F 4.35, $-O{=}F_2-$ 1.83, sum 99.55 wt% and the empirical formula calculated on the basis of 12 (O + F): $(K_{0.97}Rb_{0.03}Cs_{0.01})_{1.01}Li_{2.00}$ $(Ti_{0.93}Nb_{0.02}Fe_{0.02}Al_{0.02})_{0.99}$ $Si_4O_{11.04}$ $(F_{0.94}OH_{0.10})_{1.04}$, $Z = 2$; $D_{meas.} = 2.91(2)$ and $D_{calc.} = 2.914$ g/cm^3. Agakhanov *et al.* (2011) wrote the simplified formula of orlovite in the form $IM_3T_4O_{10}A_2$ (Rieder *et al.*, 1998) as follows: $KLi_2Ti(Si_4O_{10})(OF)$, Z = 2. Because all crystals of orlovite were deformed/bent plates it was not possible to find a crystal suitable for single-crystal X-ray diffraction. The unit-cell parameters of orlovite were measured by electron diffraction: $a = 5.21(1)$, $b = 9.026(3)$, $c = 10.05(1)$ Å, $\beta = 99.6(1)°$, $V = 466(2)$ Å^3. Agakhanov *et al.* (2011) defined orlovite as a mineral of the mica group, a subgroup of true trioctahedral micas in accord with Rieder *et al.* (1998) and as a $1M$ polytype. Agakhanov *et al.* (2011) emphasized the similarity of orlovite and polylithionite, $KLi_2AlSi_4O_{10}F_2$ (Rieder *et al.*, 1998). Polylithionite has the space group $C2/m$ and in its structure, the A site is occupied by F, giving $A_2 = F_2$ per formula unit (pfu). In the formula of orlovite, A_2 = (OF) (Agakhanov *et al.*, 2011) compared to $A_2 = F_2$ in polylithionite. Agakhanov *et al.* (2011) considered possible order of O and F at two independent sites in the structure of orlovite and suggested the space group $C2$ for orlovite.

Although lower symmetry seems a reasonable option where ordering of anions occurs, it does not work in case of the $C2/m \rightarrow C2$ transition: the A site in space group $C2/m$ (Wyckoff position i) and the A site in space group $C2$ (Wyckoff position c) have the same multiplicity of 4. Hence lowering of symmetry does not result in splitting of the A site into two sites that could be occupied by O and F, respectively. We could not understand how Ti responds to the occurrence of O and F in the ratio 1:1 in the structure of orlovite. Dr. Agakhanov finally found a suitable crystal for single-crystal X-ray diffraction and here we report the crystal structure of orlovite, the first example of the short-range order of Ti in a true trioctahedral mica.

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2. X-ray data collection and structure refinement

We collected single-crystal X-ray data for a single crystal of orlovite which was a central (reasonably flat) part of a larger crystal that was bent at the edges. X-ray data for orlovite were collected with a Bruker APEX II ULTRA three-circle diffractometer equipped with a rotating-anode generator (Mo$K\alpha$), multilayer optics and an APEX II 4K CCD detector. Details of data collection and structure refinement are given in Table 1. The intensities of reflections with $-7 \leq h \leq 7$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$ were collected with a frame width of 0.5° and a frame time of 30 s, and an empirical absorption correction (SADABS, Sheldrick, 2008) was applied. The crystal structure of orlovite was solved and refined in space group *C*2/*m* to $R_1 = 3.56\%$ with the Bruker SHELXTL Version 5.1 (Sheldrick, 2008). The occupancies of three cation sites were refined with the following scattering curves: *M*1, Ti; *M*2, Li, and *I*, K. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Wilson, 1992). In orlovite, the Ti-dominant *M*1 site corresponds to the Wyckoff position *i*, with multiplicity of 4 (*cf.* the *M*1 site in other trioctahedral micas, where it corresponds to the Wyckoff position *c*, with multiplicity of 2, *e.g.* in oxykinoshitalite (Kogarko *et al.*, 2005), see text below). We observed a short distance of 0.432 Å between two points of the *M*1 site and assumed that the *M*1 site must be occupied at ≤ 50%. The occupancy of the *M*2 site refined close to an integer value and was fixed in accord with the chemical analysis (Agakhanov *et al.*, 2011). The scattering curve of 8.5 *e* was used for the refinement of anisotropic displacement parameters for the *A* site (see discussion below).

We refined the crystal structure of orlovite in space groups *C*2 and *Cm* to $R_1 = 5.72$ and 3.55%, respectively. In the *C*2-structure, (1) the *M*1 and *A* sites show stereochemistry analogous to that of the *C*2/*m*-structure; (2) there are short Li–O distances, *e.g.*, 1.584 Å; (3) the U_{ij} of several atoms have become non-positive definite (NPD) and (4) the Flack parameter of ~0.5 indicates that the absolute structure cannot be determined reliably. In the *Cm*-structure, (1) the *M*1 site splits into two sites, *M*(11) and *M*(12), each 50% occupied by Ti, therefore there is no order of Ti and vacancy over these two sites; (2) the *A* site splits into two sites, *A*(1) and *A*(2), and we found no evidence of order of O and F over these two *A* sites; (3) the stereochemistry of the *Cm*-structure is analogous to that of the *C*2/*m*-structure; (4) the U_{ij} of several atoms have become NPD and (5) the Flack parameter is ~0.5 indicating that the absolute structure cannot be determined reliably. We conclude that there is no possibility of a lower symmetry for orlovite.

Final atom coordinates and anisotropic displacement parameters are given in Table 2, selected interatomic distances and angles in Table 3, refined site-scattering values and assigned site-populations in Table 4, and bond-valence values in Table 5. A list of observed and calculated structure factors and a Crystallography Information File are freely available online as Supplementary Material linked to this article on the GSW website of the journal, https://pubs.geoscienceworld.org/eurjmin/.

Table 1. Miscellaneous information on data collection and structure refinement for orlovite.

a (Å)	5.198(4)
b	9.046(7)
c	10.093(8)
β (°)	99.53(2)
V (Å^3)	468.1(1.1)
Space group	*C*2/*m*
Z	2
Absorption coefficient (mm^{-1})	2.14
F(000)	387.8
D_{calc}(g/cm^3)	2.814
Crystal size (mm)	0.12 × 0.10 × 0.02
Radiation/monochromator	Mo$K\alpha$/ graphite
$2\theta_{max}$(°)	60.34
R(int) (%)	1.80
Reflections collected	2747
Independent reflections	737
Reflections with $F_o > 4\sigma F$	729
Refinement method	Full-matrix least squares on F^2, fixed weights proportional to $/\sigma F_o{}^2$
Final $R_{(obs)}$ (%)	
R_1 [$F_o > 4\sigma F$]	3.56
R_1 (all data)	3.68
wR_2	12.13
Goodness of fit on F^2	1.302
Largest diffr. peak and hole (e Å^{-3})	1.35, −0.74

3. Structure description

Orlovite is a true trioctahedral mica in which two T sheets of T tetrahedra and a central trioctahedral O sheet constitute the main structural unit, the TOT layer, and interstitial I cations occur in the space between TOT layers (Rieder *et al.*, 1998). In the O sheet of orlovite, there are two crystallographically independent *M* sites: *M*1 and *M*2. In many true trioctahedral micas with space group *C*2/*m*, the *M*1 site corresponds to the Wyckoff position *c*, with multiplicity of 2 and site symmetry of 2/*m*. In orlovite, M1 (= Ti) atoms are displaced from the inversion centre and hence the *M*1 site corresponds to the Wyckoff position *i*, with multiplicity of 4 and site symmetry of *m*. The two points of the *M*1 site occur 0.432 Å apart (Fig. 1a, Table 3) and cannot be locally fully occupied. In accord with the chemical analysis (Agakhanov *et al.*, 2011), the *M*1 site is 50% occupied, primarily by Ti, giving ideally $Ti_{1.00}$ pfu (Table 4). Each M1 atom is coordinated by four O2 atoms, with M1–O2 = 2.009 Å and two A anions of composition (OF), with ⟨M1–ϕ⟩ = 1.977 Å (ϕ = unspecified anion) (Table 3). There are two distances M1–A: 1.699 and 2.130 Å. An anion at the *A* site receives a larger bond-valence contribution from Ti where the distance is shorter, M1–A = 1.699 Å, and a smaller bond-valence contribution

Table 2. Atom coordinates and anisotropic displacement parameters (Å^2) for orlovite.

Atom	x	y	z	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}	U_{eq}
M1	0.0375(4)	0	0.5130(3)	0.0055(15)	0.0041(5)	0.0084(13)	0	0.0008(9)	0	0.0060(6)
M2	0	0.3389(9)	½	0.016(3)	0.017(3)	0.019(3)	0	−0.000(2)	0	0.0178(14)
T	0.07324(13)	0.16481(7)	0.22849(7)	0.0080(4)	0.0054(4)	0.0114(4)	0.0001(2)	0.0022(2)	0.0002(2)	0.0082(2)
I	0	½	0	0.0229(7)	0.0223(7)	0.0291(7)	0	0.0053(5)	0	0.0246(4)
O1	0.3036(4)	0.2492(2)	0.16600(18)	0.0108(8)	0.0129(9)	0.0137(8)	0.0001(6)	0.0028(6)	−0.0038(6)	0.0124(4)
O2	0.125(4)	0.15812(19)	0.38800(18)	0.0101(8)	0.0055(8)	0.0127(8)	0.0006(6)	0.0030(6)	−0.0002(6)	0.0093(4)
O3	0.0509(6)	0	0.1602(3)	0.0158(12)	0.0066(11)	0.0131(11)	0	0.0021(9)	0	0.0119(5)
A	0.6615(5)	0	0.3911(3)	0.0126(11)	0.0118(11)	0.0207(12)	0	0.0003(8)	0	0.0153(5)

Table 3. Selected interatomic distances (Å) and angles (°) for orlovite.

T–O2		1.589(2)	M1–Ab		1.699(3)
T–O1		1.632(2)	M1–O2	×2	2.009(3)
T–O1a		1.636(2)	M1–Ac		2.130(3)
T–O3		1.639(1)	⟨M1–ϕ⟩		1.978
⟨T–O⟩		1.624			
O1–O1a		2.599(2)	O2–Ab	×2	2.726(3)
O1–O3		2.604(3)	O2–O2i	×2	2.788(4)
O1–O2		2.693(3)	O2–Ac	×2	2.807(3)
O2–O3		2.681(3)	O2–O2j	×2	2.861(4)
O2–O1a		2.697(3)	⟨O–ϕ⟩		2.786
O3–O1a		2.614(3)			
⟨O–O⟩		2.648			
M2–Ad	×2	2.084(6)	I–O3f	×2	3.047(4)
M2–O2e	×2	2.086(2)	I–O3d	×2	3.051(3)
M2–O2	×2	2.149(6)	I–O1d	×2	3.081(3)
⟨M2–ϕ⟩		2.106	I–O1	×2	3.094(3)
			⟨I–O⟩		3.075
O2–Ab	×2	2.726(3)			
O2–O2i		2.788(4)			
O2–O2e	×2	2.931(4)			
O2–O2h	×2	3.085(3)			
A–O2h	×2	3.098(3)			
A–O2	×2	3.130(4)			
A–Ab		2.978(6)			
⟨ϕ–ϕ⟩		2.975			
M1–M1g		0.432(7)	⟨T–O1–Th⟩		135.2(1)

ϕ = O, (OF); a: x−½, −y + ½, z; b: −x + 1, −y, −z +1 c: x−1, y, z; d: x−½, y + ½, z; e: −x + ½, −y + ½, −z+1; f: x + ½, y + ½, z; g: −x, −y, −z+1; h: x + ½, −y + ½, z; i: −x, y, −z + 1; j: x, −y, z.

Table 4. Refined site-scattering values (epfu) and assigned site-populations (apfu) for orlovite

Site	Refined site-scattering	Site population	Calculated site-scattering	(Ct−ϕ)$_{obs}$* (Å)
$^{[6]}M1$	21.0(2)	$Ti_{0.94}Nb_{0.02}Fe^{2+}_{0.02}Al_{0.02}\square_{1.00}$	22.28	1.978
$^{[6]}M2$	6.00	$Li_{2.00}$	6.00	2.106
$^{[12]}I$	20.45(2)	$K_{0.98}Rb_{0.02}$	19.36	3.075
$^{[3]}A$	17.00	$O_{1.00}F_{0.95}(OH)_{0.05}$	16.95	

* *Ct = cation, ϕ = O, F, OH.

Table 5. Bond-valence values* for orlovite.

Atom	T	M1	M2	I	Σ
O1	0.97 0.96			$0.06^{\downarrow 8 \rightarrow 2}$	2.05
O2	1.09	$0.57^{\downarrow 4}$	$0.19^{\downarrow 2}$ $0.16^{\downarrow 2}$		2.01
O3	$0.96^{\rightarrow 2}$			$0.07^{\downarrow 4 \rightarrow 2}$	2.06
A = O		1.37	$0.19^{\rightarrow 2}$		1.75
A = F		0.30	$0.15^{\rightarrow 2}$		0.60
Total	3.98	3.95	0.85	0.76	

* Bond-valence parameters (vu) are from Brown (1981); bonds to oxygen were used for Si [T] and K [I]; bonds to oxygen and fluorine were used for Ti [M1] and Li [M2] when calculating bond-valence values for O2 plus A = O and A = F, respectively; 50% occupancy by Ti at the M1 site was taken into account for calculation of total bond-valence contribution to O2.

where the distance is longer, M1–A = 2.130 Å. We suggest that M1–A distances of 1.699 Å and 2.130 Å correspond to the occurrence of O and F atoms at the A site. Consider short-range order (SRO) of Ti in the structure of orlovite. There are two positions of Ti atoms within the M1 octahedron: (1) (x = −0.037, y = 0, z = 0.487) and (2) (x = 0.037, y = 0, z = 0.513) (Fig. 1a). SRO-1 occurs where the position (1) of Ti in Fig. 1a is fully occupied by Ti (Fig. 1b) and SRO-2 occurs where the position (2) of Ti in Fig. 1a is fully occupied by Ti (Fig. 1c). Correspondence of shorter (1.699 Å) and longer (2.130 Å) M1–A distances to the occurrence of O and F atoms at the A site is supported by bond-valence sums of 1.75 and 0.60 vu (valence units) (Table 5). This is the first occurrence of short-range order of Ti in a true trioctahedral mica where Ti-anion bond-lengths vary from 1.699 to 2.130 Å. This amazing ability of Ti to form a wide range of Ti–anion bonds allows the $C2/m$ structure of mica to retain the close-packed trioctahedral sheet. Sokolova (2006) considered in detail similar behaviour of Ti in the TS-block (Titanium-Silicate) minerals where the stability of the TS block is due to an extremely wide range in mainly Ti(+ Nb)–O bond-lengths, 1.66–2.38 Å, which allows the chemistry of the TS block to vary drastically while retaining close-packing of the cations in forty-five minerals of the seidozerite supergroup (Sokolova & Cámara, 2017).

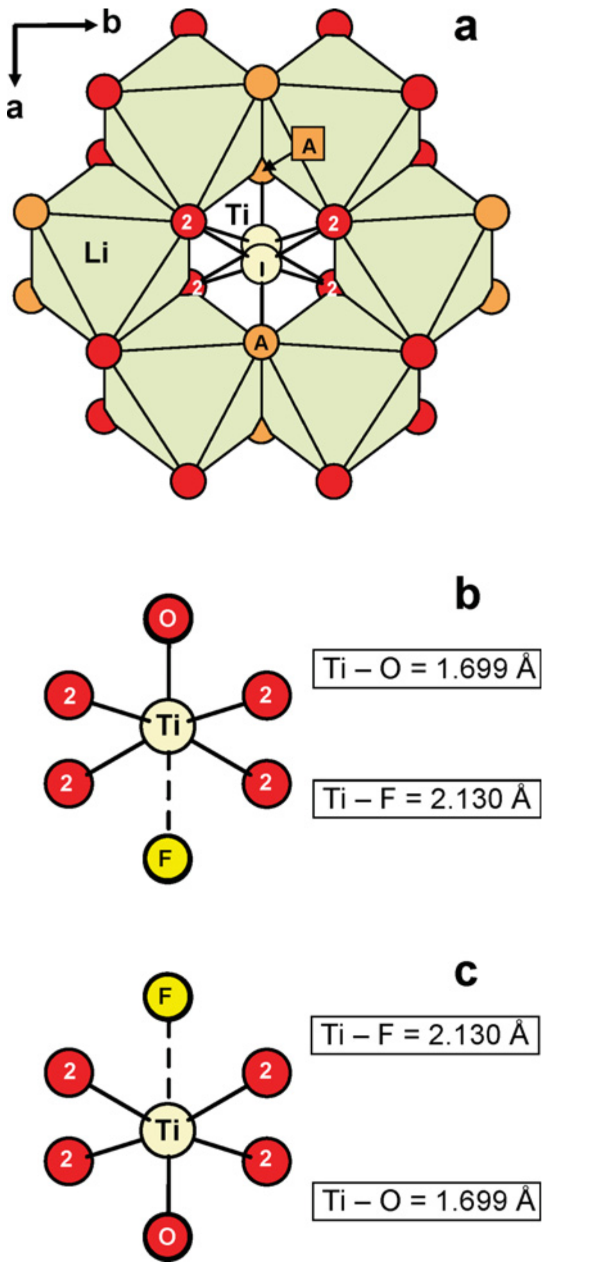

Fig. 1. Short-range order (SRO) of Ti in the trioctahedral sheet of orlovite: (a) a fragment of the O sheet showing two positions of Ti within the M1 octahedron [(1) $x = -0.037$, $y = 0$, $z = 0.487$ and (2) $x = 0.037$, $y = 0$, $z = 0.513$] which occur 0.432 Å apart; (b) SRO-1: position (1) is fully occupied by Ti, position (2) is vacant and not shown; (c) SRO-2: position (2) is fully occupied by Ti, position (1) is vacant and not shown. The Li octahedra are green; Ti atoms are shown as pale yellow spheres; anions O, F and A = OF are shown as red, yellow and orange spheres; Ti–O and Ti–A (= OF, O) bonds are shown as solid black lines, Ti–A (= F) as dashed black lines.

The *M*2 site is occupied solely by Li, giving Li_2 pfu, with $\langle M2–\phi\rangle = 2.106$ Å (Table 3). In the T sheet, there is one tetrahedrally coordinated *T* site occupied solely by Si, $\langle T–O\rangle = 1.624$ Å. The interstitial $^{[12]}I$ site is occupied primarily by K, ideally $K_{1.00}$ pfu, with $\langle I–O\rangle = 3.075$ Å (Tables 2,3).

The 50% occupancy of the *M*1 site requires occupancy of the *A* site by monovalent and divalent anions in the ratio 1:1 (Table 4). As the empirical formula of Agakhanov *et al.* (2011) gives $F_{0.95}$ pfu we need to add $(OH)_{0.05}$ pfu so that (F + OH) = 1 pfu and (F + OH): O = 1:1 at the *A* site. We recalculated the empirical formula of orlovite on the basis of 12 (O + F), with the constraint F + OH = 1 pfu: $(K_{0.98}Rb_{0.03}Cs_{0.01})_{1.02}Li_{2.01}(Ti_{0.94}Nb_{0.02}Fe_{0.02}Al_{0.02})_{1.00}$ $Si_4O_{10}[O_{1.00}F_{0.95}(OH)_{0.05}]_{2.00}$, $Z = 2$; $D_{calc.} = 2.814$ g/cm^3.

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