

## Crystal chemistry and nomenclature of the lovozerite group

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**Abstract:** The paper summarizes crystal–chemical data and describes the IMA-accepted nomenclature of lovozerite-group minerals (LGM). The lovozerite group includes nine zeolite-like cyclosilicates with the general formula  $A_3B_3C_2MSi_6O_{12}O_{6-x}(OH)_x \cdot nH_2O$ , with species-defining  $M = \text{Zr, Ti, Fe}^{3+}, \text{Ca}$ ;  $C = \text{Ca, Mn}^{2+}, \text{Na, } \square$ ;  $A = \text{Na, Ca}$ ;  $B = \text{Na, } \square$ ;  $0 \leq x \leq 6$ ;  $n = 0-1$ . Their structures are based upon a heteropolyhedral framework consisting of rings of Si-centred tetrahedra and  $M$ -centred octahedra forming a 3D system of channels that host  $A$ ,  $B$ , and  $C$  cations. The structures can be also considered as based upon pseudocubic modules centred at the midpoint of the Si tetrahedral ring. The  $M$ ,  $A$ , and  $B$  cations are located at the borders of the module, whereas  $C$  cations are inside the module. The modules are stacked in three different arrangements in LGM allowing distinction of three subgroups: (1) zirsinalite–lovozerite subgroup (includes cation-saturated combeite, kapustinite, kazakovite and zirsinalite, and cation-deficient litvinskite, lovozerite and tisinalite), (2) koashvite subgroup (incl. koashvite) and (3) imandrite subgroup (incl. imandrite). The nature of cation-deficient LGM is discussed. The calculation scheme for empirical formulae of LGM and the criteria of definition of a mineral species (end-members) in the group are given.

**Key-words:** lovozerite group, cyclosilicate, combeite, imandrite, kapustinite, kazakovite, koashvite, litvinskite, lovozerite, tisinalite, zirsinalite, crystal structure, nomenclature of minerals.

### 1. Introduction

The lovozerite group includes nine valid mineral species – cyclosilicates with closely related crystal structures: combeite, imandrite, kapustinite, kazakovite, koashvite, litvinskite, lovozerite, tisinalite and zirsinalite. Structurally, the lovozerite group can be subdivided into three subgroups different in cation arrangement and, as a consequence, in symmetry and unit-cell parameters (Table 1).

All lovozerite-group minerals (LGM) contain Na as an essential mineral-forming constituent. They occur in only alkaline rocks. With the exception of combeite, all these minerals were first discovered in the Khibiny–Lovozero alkaline complex, Kola Peninsula, Russia (Gerasimovsky, 1940; Kapustin *et al.*, 1973, 1974a and b, 1980; Khomyakov *et al.*, 1974; Pekov *et al.*, 2000, 2003). Zirconium-dominant members of the group occur as accessory or even rock-forming minerals in some peralkaline magmatic rocks and pegmatites of the Lovozero intrusion. Lovozerite-group minerals, except combeite, have been studied using samples from the Khibiny–Lovozero complex, and the majority of the original publications on these

minerals are in Russian. Zirconium representatives of the group have also been found in other alkaline complexes (Ilímaussaq in Greenland; Mont Saint-Hilaire in Québec, Canada; Wind Mountain in New Mexico, U.S.A.; Norra Kärr in Sweden; Konder in Siberia, Russia; Aris in Namibia), but the minerals from these localities are only poorly studied lacking any compositional data. Combeite was found in alkaline volcanic rocks of Shaheru (DR Congo) (Sahama & Hytönen, 1957), Oldoinyo Lengai (Tanzania) and Ettringer Bellerberg (Eifel, Germany) (Fischer & Tillmanns, 1987).

Lovozerite-type structures possess certain zeolite-like features that cause wide variations in the extra-framework content charge-balanced by the chemical variability of the framework forming polyhedra. The empirical data on chemical composition, X-ray crystallography and crystal chemistry of minerals with lovozerite-type structures show wide ranges of cation substitutions; in particular, those involving vacancies in some sites, as well as symmetry variations in chemically related minerals, even those belonging to the same subgroup (Table 1). As a result of this variability, there is an actual problem with the

Table 1. Mineral species of the lovozerite group.

Mineral	IMA status <sup>a</sup>	Crystal data		References
		Crystal system, space group	Unit cell parameters ( <i>a</i> , <i>b</i> , <i>c</i> , Å; β, °)	
Idealized end-member formula				
Generalized formula				
First mineralogical description (reference)				
<b>Zirsinalite-Lovozerite subgroup</b>				
<i>cation-saturated members (with occupied B site)</i>				
<b>Zirsinalite</b>	A	Trigonal, <i>R-3c</i>	<i>a</i> 10.29, <i>c</i> 26.31	Pudovkina <i>et al.</i> (1980)
Na <sub>6</sub> CaZrSi <sub>6</sub> O <sub>18</sub>				
Na <sub>5-6</sub> (Ca,Mn) <sub>0.5-1</sub> (Zr,Ti,Fe <sup>3+</sup> ) Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ; 0 ≤ <i>x</i> ≤ 2		Trigonal, <i>R-3m</i>	<i>a</i> 10.32, <i>c</i> 13.16	Zolotarev <i>et al.</i> (2008)
Kapustin <i>et al.</i> (1974a)				
<b>Kapustinite</b>	A	Monoclinic, <i>C2/m</i>	<i>a</i> 10.69, <i>b</i> 10.31, <i>c</i> 7.41, β 92.4	Yamnova <i>et al.</i> (2004)
Na <sub>6</sub> ZrSi <sub>6</sub> O <sub>16</sub> (OH) <sub>2</sub>				
Na <sub>5-6</sub> (Mn,Ca) <sub>0-0.5</sub> (Zr,Ti,Nb,Fe <sup>3+</sup> ) Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ; 1 ≤ <i>x</i> ≤ 3		Trigonal, <i>R-3m</i>	<i>a</i> 10.31, <i>c</i> 13.13	Zolotarev <i>et al.</i> (2008)
Pekov <i>et al.</i> (2003)				
<b>Kazakovite</b>	A	Trigonal, <i>R-3m</i>	<i>a</i> 10.17, <i>c</i> 13.05	Voronkov <i>et al.</i> (1979)
Na <sub>6</sub> Mn <sup>2+</sup> TiSi <sub>6</sub> O <sub>18</sub>				
Na <sub>5-6</sub> (Mn,Ca) <sub>0.5-1</sub> (Ti,Zr,Nb,Fe <sup>3+</sup> ) Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ; 0 ≤ <i>x</i> ≤ 2		Trigonal, <i>R-3m</i>	<i>a</i> 10.16, <i>c</i> 13.04	Zolotarev <i>et al.</i> (2008)
Khomyakov <i>et al.</i> (1974)				
<b>Combeite</b>	G	Trigonal, <i>R-3m</i>	<i>a</i> 10.43, <i>c</i> 13.15	Fischer & Tillmanns (1987)
Na <sub>4.5</sub> Ca <sub>3.5</sub> Si <sub>6</sub> O <sub>17.5</sub> (OH) <sub>0.5</sub> <sup>b</sup>				
Na <sub>4-5</sub> Ca <sub>3-4</sub> Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ; 0 ≤ <i>x</i> ≤ 1		Trigonal, <i>P3<sub>1</sub>21</i>	<i>a</i> 10.46, <i>c</i> 13.18	the same
Sahama & Hytönen (1957)				
<i>Cation-deficient members (with vacant B site)</i>				
<b>Lovozerite</b>	G	Monoclinic, <i>C2</i>	<i>a</i> 10.48, <i>b</i> 10.20, <i>c</i> 7.33, β 92.5	Ilyukhin & Belov (1960)
Na <sub>3</sub> CaZrSi <sub>6</sub> O <sub>15</sub> (OH) <sub>3</sub>				
Na <sub>3-y</sub> (Ca,Mn) <sub>0.5-</sub> 1(Zr,Ti,Fe <sup>3+</sup> )Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ●0–1H <sub>2</sub> O; 3 ≤ <i>x</i> ≤ 5.5; <i>y</i> ≤ 1.5		Trig., <i>R-3m</i> , <i>R3m</i> or <i>R32</i>	<i>a</i> 10.18, <i>c</i> 13.10	Kapustin (1973)
Gerasimovsky (1940)		Trigonal, <i>R3</i>	<i>a</i> 10.18, <i>c</i> 13.13	Yamnova <i>et al.</i> (2001a)
		Trigonal, <i>R-3m</i>	<i>a</i> 10.10–10.18, <i>c</i> 13.04–13.17	Zolotarev <i>et al.</i> (2008)
<b>Litvinskite</b>	A	Trigonal, <i>R-3m</i>	<i>a</i> 10.34, <i>c</i> 13.15	Malinovskii <i>et al.</i> (1993) <sup>c</sup>
Na <sub>3</sub> ZrSi <sub>6</sub> O <sub>13</sub> (OH) <sub>5</sub>				
Na <sub>3-y</sub> (Mn,Ca) <sub>0-0.5</sub> (Zr,Ti,Nb,Fe <sup>3+</sup> ) Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ●0–0.5H <sub>2</sub> O; 4 ≤ <i>x</i> ≤ 6; <i>y</i> ≤ 1		Monoclinic, <i>Cm</i>	<i>a</i> 10.59, <i>b</i> 10.22, <i>c</i> 7.36, β 92.9	Yamnova <i>et al.</i> (2001b)
Pekov <i>et al.</i> (2000)		Trigonal, <i>R-3m</i>	<i>a</i> 10.21, <i>c</i> 13.18	Zolotarev <i>et al.</i> (2008)
<b>Tisinalite</b>	A	Trigonal, <i>P-3</i>	<i>a</i> 10.04, <i>c</i> 12.88	Yamnova <i>et al.</i> (2003)
Na <sub>3</sub> Mn <sup>2+</sup> TiSi <sub>6</sub> O <sub>15</sub> (OH) <sub>3</sub>				
Na <sub>3-y</sub> (Mn,Ca) <sub>0.5-1</sub> (Ti,Zr,Nb,Fe <sup>3+</sup> ) Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ; 3 ≤ <i>x</i> ≤ 5; <i>y</i> ≤ 1		Trigonal, <i>R-3m</i>	<i>a</i> 10.02–10.06, <i>c</i> 12.89–13.09	Zolotarev <i>et al.</i> (2008)
Kapustin <i>et al.</i> (1980)				
<b>Koashvite subgroup</b>				
<b>Koashvite</b>	A	Orthorhombic, <i>Pmnb</i>	<i>a</i> 10.18, <i>b</i> 20.89, <i>c</i> 7.34	Chernitsova <i>et al.</i> (1980b)
Na <sub>6</sub> CaTiSi <sub>6</sub> O <sub>18</sub>				
Na <sub>5-6</sub> (Ca,Mn,Fe) <sub>0.5-1.2</sub> (Ti,Fe <sup>3+</sup> )Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ●0–0.5H <sub>2</sub> O; 0 ≤ <i>x</i> ≤ 2 <sup>d</sup>		Orthorhombic, <i>Pmnb</i>	<i>a</i> 10.23, <i>b</i> 21.01, <i>c</i> 7.36	Zolotarev <i>et al.</i> (2008)
Kapustin <i>et al.</i> (1974b)				
<b>Imandrite subgroup</b>				
<b>Imandrite</b>	A	Orthorhombic, <i>Pnmm</i>	<i>a</i> 10.55, <i>b</i> 7.43, <i>c</i> 10.33	Chernitsova <i>et al.</i> (1980a)
Na <sub>6</sub> Ca <sub>1.5</sub> Fe <sup>3+</sup> Si <sub>6</sub> O <sub>18</sub>		Orthorhombic, <i>Pnmm</i>	<i>a</i> 10.51, <i>b</i> 7.42, <i>c</i> 10.30	Zolotarev <i>et al.</i> (2008)
Na <sub>5-6</sub> (Ca,Mn) <sub>1-1.5</sub> (Fe <sup>3+</sup> ,Ti)Si <sub>6</sub> O <sub>18-x</sub> (OH) <sub>x</sub> ; 0 ≤ <i>x</i> ≤ 2				
Khomyakov <i>et al.</i> (1979)				

Note: generalized formulae are given taking into account the totality of credible empirical data.

<sup>a</sup>IMA status: A – approved by the IMA–CNMNC; G (grandfathered) – original description preceded the establishment of the IMA–CNMNC in 1959, and generally regarded as a valid species.

<sup>b</sup>The idealized formula of combeite is the average of two modifications with studied crystal structures (Fischer & Tillmanns, 1987) which are chemically slightly different (see Table 3).

<sup>c</sup>In the paper by Malinovskii *et al.* (1993) the mineral was named lovozerite but the sum Ca+Mn in the *C* site is 0.45 *apfu*, therefore it corresponds to litvinskite.

<sup>d</sup>Surplus of the *C* cations over 1 *apfu* results from significant substitution of Ti by Fe<sup>3+</sup> in the *M* site.

assignment of some samples to definite mineral species within the lovozerite group. This prompted the elaboration of a nomenclature for the lovozerite group with clear definitions of the mineral species and criteria for their identification.

The present nomenclature scheme was accepted by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) on 19 January 2009. It is based upon available empirical data and theoretical considerations in chemistry, crystallography and crystal chemistry of the LGM. Data on related synthetic compounds and specific chemical properties have also been taken into account.

## 2. Crystal chemistry

### 2.1. General description

Taking into account coordination polyhedra occupied by high-valence cations, the structures of the lovozerite-group minerals can be considered as based upon a heteropolyhedral framework consisting of six-membered  $[\text{Si}_6\text{O}_{18}]$  rings of  $\text{SiO}_4$  tetrahedra (Fig. 1) and  $\text{MO}_6$  octahedra, where  $M = \text{Zr}^{4+}, \text{Ti}^{4+}, \text{Fe}^{3+}$  and  $\text{Ca}^{2+}$  (Fig. 2) (Ilyukhin & Belov, 1960; Chernitsova *et al.*, 1975; Fischer & Tillmanns, 1983; Tamazyán & Malinovskii, 1990). Within the silicate ring, each  $\text{SiO}_4$  tetrahedron possesses three types of anions: two  $\text{O}^{2-}$  anions bridging adjacent Si atoms, one bridging Si and  $M$ , and one that does not form bonds to framework-forming

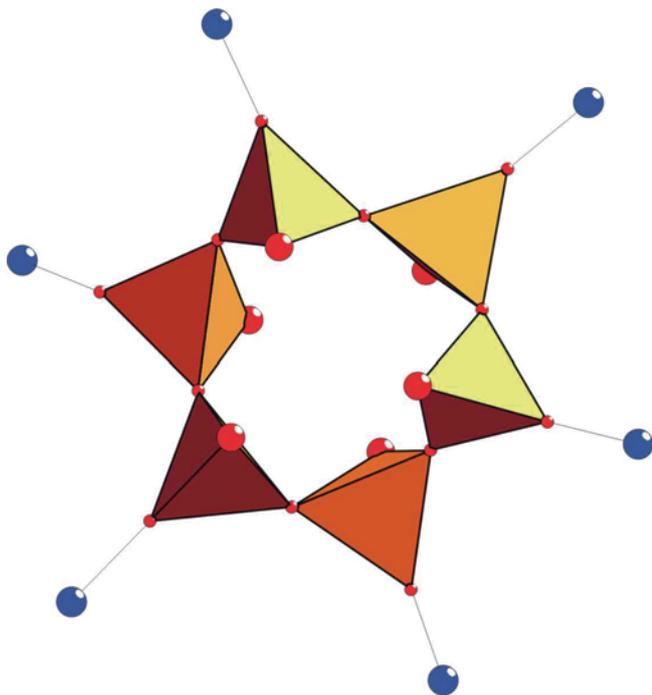


Fig. 1. Lovozerite-type ring  $[\text{Si}_6\text{O}_{12}(\text{O},\text{OH})_6]$ ; small circles are O atoms forming the bridges Si–O–Si and Si–O– $M$ , large circles in “pendent” vertices of Si tetrahedra represent (O,OH), large circles connected with small circles are  $M$  cations.

cations. The latter anion, occupying the so-called “pendent” vertex of a tetrahedron, can be protonated resulting in a Si–OH (silanol) group. The polyhedral framework forms a 3D system of channels hosting  $A$ ,  $B$ , and  $C$  cation sites (Fig. 2 and 3). The  $A$  cations ( $A = \text{Na}, \text{Ca}$ ) are in eightfold coordination close to a hexagonal bipyramid, whereas the  $B$  cations ( $B = \text{Na}$ ) have eightfold coordination with anions arranged at the vertices of a distorted cube. The  $C$  cations ( $\text{Ca}, \text{Na}, \text{Mg}$  or  $\square$ ) centre octahedra that share faces with the  $M$ -centred octahedra.

### 2.2. Modular description

The first review of the structures of the lovozerite group was presented by Chernitsova *et al.* (1975) who proposed an elegant approach to visualize the structural flexibility. According to Chernitsova *et al.* (1975), the structures of the lovozerite-type compounds can be described as derived from double 4-membered ring (4-MR) of  $\text{SiO}_4$  tetrahedra. The ideal double 4-MR has a cubic symmetry  $m3m$  with an

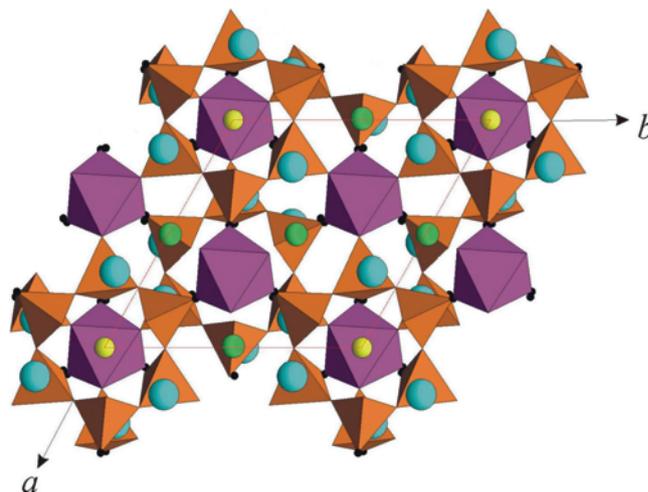


Fig. 2. Structure of lovozerite (after Yamnova *et al.*, 2001a): Si tetrahedra,  $M$  octahedra,  $C$  (small circles),  $A$  (medium circles) and  $B$  (large circles) sites are shown.

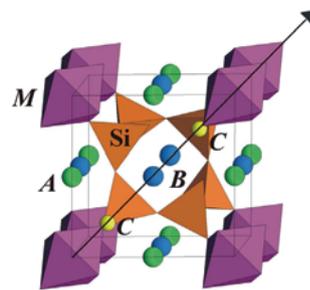


Fig. 3. Pseudocubic ( $a' \approx 7.5 \text{ \AA}$ ) module in the lovozerite structure-type. The arrow along the space diagonal in the cube represents a three-fold axis.  $A$  sites are on the cube edges,  $B$  sites centre the cube faces and  $C$  sites are on the three-fold axes.

inversion centre at the centre of the ring. Elimination of two tetrahedra related by the inversion centre results in a single 6-MR in chair conformation (Fig. 1). This ring possesses a three-fold rotation axis running through its centre. All structures of the lovozerite-group minerals can be considered as based upon these pseudocubic modules centred at the midpoint of the 6-MR. The *M*, *A*, and *B* cations are located at the borders of the module, whereas *C* cations are inside the module and approximately replace the “missing” Si tetrahedra.

The pseudocubic module has an average edge length of 7.5 Å and possesses rhombohedral symmetry  $3m$ . In the structures of the LGM, the pseudocubic modules are stacked in four different arrangements shown in Fig. 4. In the simplest structure (Fig. 4a), all modules share whole faces and are in parallel orientation. This arrangement is the most common and is observed in trigonal members of the group and related synthetic compounds (Zolotarev *et al.*, 2008). The rhombohedral unit cell of lovozerite exactly corresponds to the outlines of the lovozerite module (with a slight trigonal distortion).

In the imandrite-type structures, modules share two opposite faces to form columns of face-sharing cubes. The remaining four faces participate in a half-face linkage shown in Fig. 4b. In koashvite (Fig. 4c) and the synthetic phase  $\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2(\text{Si}_6\text{O}_{18})$ ,  $x = 0-0.5$  (Tamazyán & Malinovskii, 1989) (Fig. 4d), cubic modules share opposite faces forming face-sharing columns. In addition, out of four remaining equatorial faces, two are shared in the whole-face fashion but mutual arrangement of these faces is different. In  $\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2(\text{Si}_6\text{O}_{18})$ , the faces are opposite to each other, *i.e.* in *trans*-conformation, whereas, in koashvite, they share one edge, *i.e.* in *cis*-conformation.

The four basic types of arrangements of cubic modules are completely defined by the local interactions of cubic modules with each other, *i.e.* the resulting 3D structure can be derived from the exact definition of how a central cube is surrounded by its neighbours. Note that, in the structures shown in Fig. 4b–d, modules share their half-faces. As a consequence, the arrangement of the *A*, *B*, and *M* cations in the resulting structure should be modified. Figure 5 demonstrates this re-arrangement using the *M* cations as an example. In “classic” lovozerite module (see, *e.g.*,

Fig. 2), *M* cations occupy the vertices of the module (Fig. 5a). Linkage of modules via half-faces may lead either to the appearance of the *M* cations both at the vertices and at the midpoints of the edges (as shown in Fig. 5b and c), or in “transition” of some *M* cations from the vertices to the midpoints of edges (as shown in Fig. 5d and e). Note that, in the former case, the *M*:Si ratio changes from 1:6 to 2:6 as found in synthetic  $\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2(\text{Si}_6\text{O}_{18})$ . In all lovozerite-group minerals known to date, only the schemes with the *M*:Si ratio = 1:6, shown on Fig. 4a–c, are realized. Accordingly, the location of the *M*, *B*, and *A* positions differs from those in the “classic” lovozerite module (*M* at the vertices, *A* at the midpoints of edges, *B* at centres of faces: Fig. 6 a). Figures 6b and c show arrangements of the *A*, *B*, and *M* cations relative to the outlines of the modules in koashvite and imandrite, respectively. It can be seen that the relationship of the sites to the borders of the cubic module are no longer geometrically defined.

### 2.3. Subgroup subdivision

Only three out of four arrangements have so far been found in the structures of naturally occurring minerals (Fig. 4a–c), thus, we distinguish three different subgroups in the lovozerite group:

- 1) the *zirsinalite-lovozerite subgroup*, which includes combeite, kapustinite, kazakovite, litvinskite, lovozerite, tinsinalite and zirsinalite;
- 2) the *koashvite subgroup*, which has only koashvite as natural representative;
- 3) the *imandrite subgroup*, which has only imandrite as natural representative.

In order to avoid confusion with the name of the group, structures with face-sharing arrangements of the modules are assigned to the zirsinalite–lovozerite subgroup. This combined name also reflects existence of two kinds of members of this subgroup with different degrees of Na occupancy in the structure channels:

- a) cation-saturated (kapustinite, kazakovite, and zirsinalite with ideally 6 Na *apfu* based on  $\text{Si}_6$  and combeite with 5 cations *pfu* + one vacancy =  $\text{Na}_{3.5}\text{Ca}_{1.5}\square$ );

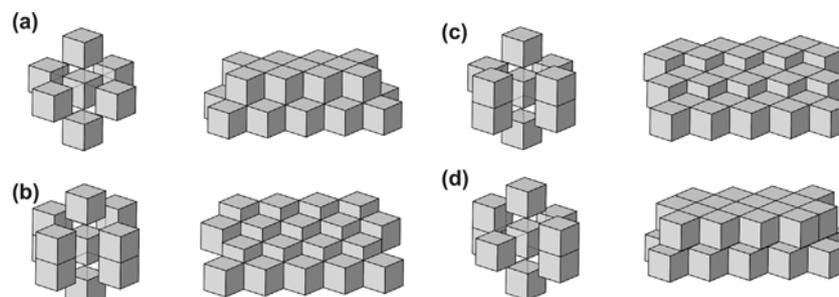


Fig. 4. Four types of arrangements of cubic modules in the lovozerite structure-types: (a) in trigonal members; (b) in imandrite; (c) in koashvite; (d) in synthetic  $\text{Na}_5(\text{Na}_{0.5+x}\text{Ca}_{0.5-x})_2(\text{Nd}_x\text{Ca}_{1-x})_2(\text{Si}_6\text{O}_{18})$ .

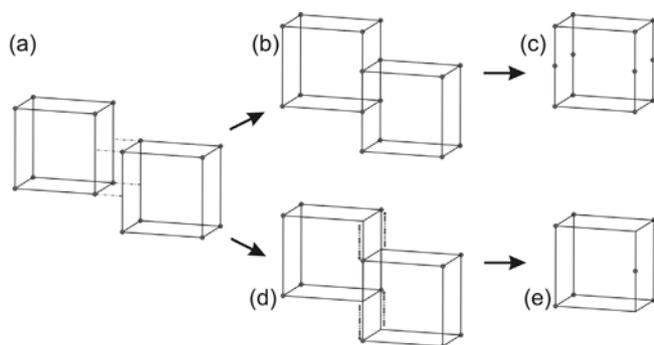


Fig. 5. Linkage of the lovozerite modules via half-faces (a) may lead either to the formation of the module with  $M$  cations at the vertices and at the midpoints of four vertical edges (b, c) or in “transition” (shown by arrows) of the  $M$  cations from the two vertices to the midpoint of edge between them (d, e). See text for details.

b) cation-deficient (litvinskite, lovozerite, and tisinalite with ideally 3 *apfu* Na) – Table 1.

Representatives of these three subgroups can easily be distinguished on the basis of their powder X-ray diffraction patterns and optical properties (Khomyakov, 1995). These characteristics are important diagnostic tools when chemical compositions seem to be insufficient for assignment of a mineral to one of these three subgroups (*e.g.*, for the intermediate members of the kazakovite–koashvite solid-solution series).

Note that petarasite,  $\text{Na}_5\text{Zr}_2\text{Si}_6\text{O}_{18}(\text{Cl},\text{OH})\cdot 2\text{H}_2\text{O}$ , included by Mandarino (1999) in the lovozerite group, has a structure that is significantly different from the lovozerite-like structures (Ghose *et al.*, 1980). The 6-membered silicate ring in petarasite is almost planar resulting in a very differently shaped stacking module. In addition, petarasite is characterized by presence of the additional anion (Cl,OH) absent in LGM.

## 2.4. General formula

The general formula of the lovozerite-group minerals is  $A_3B_3C_2MSi_6O_{12}O_{6-x}(\text{OH})_x\cdot n\text{H}_2\text{O}$ , with  $0 \leq x \leq 6$  and  $n = 0-1$ .

Species-defining constituents in lovozerite-group minerals are:

$M$ : tetra-, tri- or divalent cations:  $\text{Zr}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$  (Zr-, Ti- and Fe-dominant minerals can form continuous solid-solution series: Pekov, 2005);

$C$ : in minerals with  $M^{4+}$  and  $M^{3+}$ : divalent cations Ca or  $\text{Mn}^{2+}$  plus vacancy ( $\square$ ); in combeite with  $M^{2+}$ :  $\text{Ca} \approx \text{Na}$ ;

$A$ : Na (in combeite:  $\text{Na} \approx \text{Ca}$ );

$B$ : Na and  $\square$ .

The following admixtures (non-species-defining constituents) may be significant for lovozerite-group minerals:  $\text{Nb}^{5+}$  – up to 17 atomic % of the  $M$  cations in titanium-dominant members (Yamnova *et al.*, 2003), and K substituting for Na probably in the  $A$  site. Negligible admixtures of Al (probably substitutes Si), Hf (in zirconium-dominant minerals, in the  $M$  site), Mg and Zn (probably in the  $C$  site), Sr, Y and lanthanides (probably in the  $A$  site: Yamnova *et al.*, 2001b; Zolotarev *et al.*, 2008) were detected in some cases. Fe may not only occupy the  $M$  site, but probably as  $\text{Fe}^{2+}$ , in subordinate amounts, also the  $C$  site. Semenov (1972) and Khomyakov (1995) have assumed that  $\text{Mn}^{4+}$  together with  $\text{Mn}^{2+}$  occurs in dark to black, altered zirconium-dominant members from Lovozero. The presence of  $\text{H}_2\text{O}$  molecules in some lovozerite-group minerals has been confirmed by IR spectroscopy and structural data (Yamnova *et al.*, 2001a and b; Pekov *et al.*, 2003; Pekov, 2005) – they partially occupy the  $A$  and  $B$  sites.

## 2.5. Cation-saturated members of the group

For “non-defect” lovozerite-type phases, *i.e.* those with all cation sites fully occupied, with a tetravalent cation in the  $M$  octahedron, only monovalent cations can be present in the  $A$ ,  $B$  and  $C$  sites due to charge constraints:  $A^+_3B^+_3C^+_2M^{4+}Si_6O_{18}$ . An example of such a compound is synthetic  $\text{Na}_8\text{Sn}^{4+}\text{Si}_6\text{O}_{18}$  (Safronov *et al.*, 1980; Zayakina *et al.*, 1980). If tri- or divalent cations occupy the  $M$  octahedron, then divalent cations may be

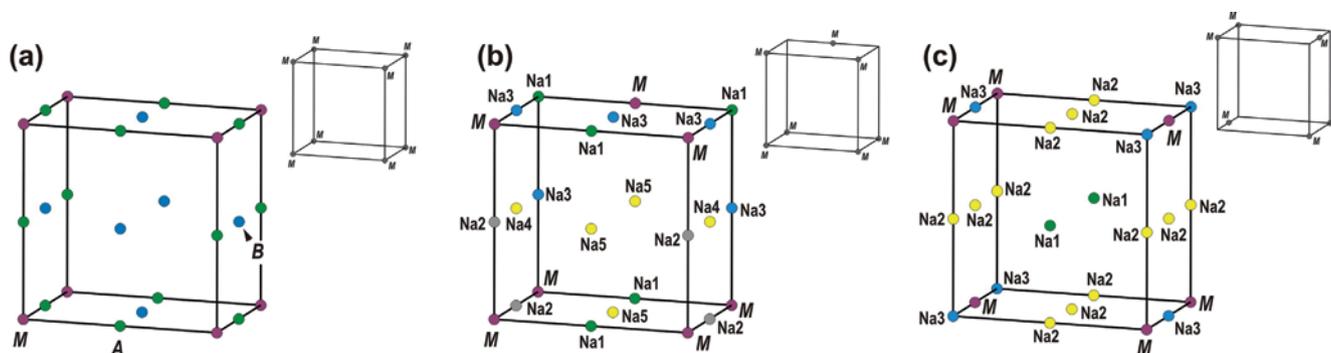


Fig. 6. Location of the  $A$ ,  $B$ , and  $M$  cations relative to the outline of the cubic module in minerals of the lovozerite group: (a) the lovozerite-zirsinalite subgroup, (b) the koashvite subgroup and (c) the imandrite subgroup. The insets show the location of the  $M$ -type cations.

present in the *C* sites, even if all sites are completely occupied. Such “non-defect” synthetic lovozerite-type compounds do also exist:  $\text{Na}_6\text{Cd}_3\text{Si}_6\text{O}_{18}$  (Simonov *et al.*, 1967),  $\text{Na}_5(\text{Mn},\text{Na})_3\text{MnSi}_6\text{O}_{18}$  (Otroshchenko *et al.*, 1973),  $\text{Na}_6\text{Mn}_3\text{Si}_6\text{O}_{18}$  (Pushcharovsky *et al.*, 1976),  $\text{Na}_6\text{Ca}_3\text{Si}_6\text{O}_{18}$  (Ohsato *et al.*, 1985), and  $\text{Na}_5(\text{Na},\text{Ca})_2(\text{Nd},\text{Ca})_2\text{Si}_6\text{O}_{18}$  (Tamazyán & Malinovskii, 1989).

All lovozerite-group minerals are characterized by structures with vacancies in the *B* and/or *C* sites (both sites may be up to 100 % vacant), and sometimes also in the *A* site (partial occupancy), *i.e.*  $(A + B + C + M) < 9$  *apfu* in all studied natural samples.

If the *M* site is occupied by a tetravalent cation (Zr or Ti) and the *A* and *B* sites are fully occupied by Na (6 *apfu*), then no more than 50 % occupancy of the *C* site by divalent cations (Ca or  $\text{Mn}^{2+}$ ) is possible as a result of: (1) general charge constraints and (2) local steric constraints due to the cation-cation repulsion in the cluster of face-connected *M* and *C* octahedra where the *M* and *C* cations are located within a short distance of  $\sim 3.2$  Å (Pyatenko *et al.*, 1999). If the central *M* octahedron is occupied by a tetravalent cation in this  $MC_2$  cluster (Fig. 7), then only one of two *C* octahedra can be occupied by a divalent cation (typically two *C* sites are statistically occupied, 50 % or less). All structural data on lovozerite-group minerals with  $M^{4+}$  (Voronkov *et al.*, 1979; Pudovkina *et al.*, 1980; Malinovskii *et al.*, 1993; Yamnova *et al.*, 2001a and b, 2003, 2004; Zolotarev *et al.*, 2008) are in agreement with this conclusion. A surplus of divalent cations (over 1 *apfu*) in the *C* site can only exist in case of a corresponding substitution in the *M* site of a tetravalent cation by a trivalent cation (*e.g.*, koashvite – Chernitsova *et al.*, 1980b) or if Na occupies the *C* octahedron (*e.g.*, for anhydrous minerals, the hypothetical end-member  $\text{Na}_6\text{Na}_2M^{4+}\text{Si}_6\text{O}_{18}$  could be supposed). Unlike the *C* site, the *A* and *B* sites in such cation-saturated lovozerite-group minerals are fully or almost fully (90–100 %) occupied by Na (Voronkov *et al.*, 1979; Chernitsova *et al.*, 1980a and b; Pudovkina *et al.*, 1980; Yamnova *et al.*, 2004; Zolotarev *et al.*, 2008).

The end-member formulae of cation-saturated minerals with species-defining  $M^{4+}$  and  $C^{2+}$  cations are thus as follows: kazakovite –  $\text{Na}_6\text{MnTiSi}_6\text{O}_{18}$ , koashvite –  $\text{Na}_6\text{CaTiSi}_6\text{O}_{18}$ , and zirsinalite –  $\text{Na}_6\text{CaZrSi}_6\text{O}_{18}$ . For kapustinite, the Zr-dominant member with a vacant *C* site, the end-member formula is  $\text{Na}_6\text{ZrSi}_6\text{O}_{16}(\text{OH})_2$ .

If the *M* site is occupied by a trivalent cation (*e.g.*,  $\text{Fe}^{3+}$ ) and the *A* and *B* sites are fully occupied by Na (6 *apfu*), then maximally 1.5 divalent cations occupy the *C* site. This cation arrangement is realized in imandrite with the end-member formula of  $\text{Na}_6\text{Ca}_{1.5}\text{Fe}^{3+}\text{Si}_6\text{O}_{18}$ .

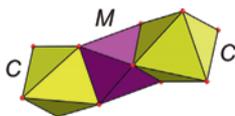


Fig. 7. Octahedral cluster  $MC_2$  in the lovozerite-type structure.

In combeite, the *M* site is occupied by Ca. The *C* and *A* sites are occupied by both Ca and Na, and the Na occupancy on the *B* site is approximately 2/3. The studied samples of two structural modifications of combeite are slightly different in their Na:Ca ratio in the *A* site:  $\text{Ca} > \text{Na}$  in the modification with space group  $R\bar{3}m$ , whereas  $\text{Na} > \text{Ca}$  in the modification with  $P3_121$  (Fischer & Tillmanns, 1983, 1987).

## 2.6. Cation-deficient members of the group (zirsinalite–lovozerite subgroup) and their nature

Beside the minerals discussed above, having their *A* and *B* sites fully or almost fully occupied by cations, the zirsinalite–lovozerite subgroup includes members with halved Na contents, namely lovozerite, litvinskite and tisinallite (Table 1). In these minerals, charge balance is controlled by the  $\text{O}^{2-} \leftrightarrow (\text{OH})^-$  substitution.

In all known synthetic lovozerite-type compounds, the sum of the *A* and *B* cations is 6 *apfu* (*i.e.*, all *A* and *B* sites are fully occupied), except in  $\text{Na}_4\text{Ca}_4\text{Si}_6\text{O}_{18}$  (Ohsato *et al.*, 1986) which contains 5 (Na + Ca) *apfu*, due to the vacancies in the *B* site (3 Ca *apfu* occupy the *C* and *M* sites). There are no synthetic lovozerite-type phases with lower occupancies of the *A* and *B* sites.

Lovozerite, the “forefather” of the group, was discovered in surface-exposed peralkaline rocks of the Lovozero intrusion (Gerasimovsky, 1940). This mineral and its *C*-vacant analogue litvinskite were later found at numerous places in the Khibiny–Lovozero complex, in outcrops of peralkaline magmatic rocks and pegmatites (Semenov & Razina, 1962; Semenov, 1972; Kapustin *et al.*, 1973; Khomyakov, 1995; Pekov, 2005; *etc.*). Unlike these cation-deficient minerals, the cation-saturated members of the group (zirsinalite, kapustinite, kazakovite, koashvite, and imandrite) are only known from deeper levels in the Khibiny–Lovozero complex, they are found in “fresh” samples from mine workings and drill cores.

Immediately after the discoveries of zirsinalite (Kapustin *et al.*, 1974a) and kazakovite (Khomyakov *et al.*, 1974), their instability in air was noticed: after several days in room conditions, these minerals become covered by efflorescence of natron and thermonatrite. Special experimental studies of this process were performed, and it was found that zirsinalite and kazakovite alter in air to lovozerite and “H-kazakovite” (= tisinallite), respectively. This process is complete after exposure for several weeks to moist air (Khomyakov, 1977; Khomyakov *et al.*, 1978). Kapustinite is more stable: its partial alteration to litvinskite takes about one year. Experiments show that the transformation of kapustinite to litvinskite in hot water (80–100 °C) occurs already after several hours (Pekov *et al.*, 2003).

Chernitsova *et al.* (1975) and Pyatenko *et al.* (1999) have demonstrated a strong violation of local charge balance on “pendent” vertices of Si tetrahedra if they are occupied by  $\text{O}^{2-}$  in lovozerite-type structures – they are characterized by a significant surplus of negative charge

that can be balanced through the  $O^{2-} \leftrightarrow (OH)^-$  substitution. According to Chernitsova *et al.* (1975), the minimum number of two (OH) groups per Si ring is needed for structure stabilization. An example is kapustinite which is significantly more stable in air than (OH)-free zirsinalite.

The absence or insufficiency of (OH) groups is thus the main cause for the instability of cation-saturated members of the group under atmospheric conditions (*i.e.*, in the presence of water). The process of their fast alteration is due to hydration accompanied by loss of some Na, according to the following scheme:  $Na^+ + O^{2-} \rightarrow (\square, H_2O)^0 + (OH)^-$ .

The zeolite-like character of the structure and protonation of “pendent” vertices of Si tetrahedra causes an easy transformation of cation-saturated lovozerite-group (first, zirsinalite-lovozerite subgroup) members to cation-deficient species. The initial symmetry of the framework part of the structure usually remains the same, whereas the symmetry of the full structure may change. In the latter case, reduction of symmetry usually results in a non-equal distribution of residual Na, vacancies and  $H_2O$  molecules among the structural sites.

All data on the occurrence and the chemical properties of lovozerite-group minerals, including their behaviour in hydrolysis experiments (Semenov, 1972; Kapustin *et al.*, 1973, 1974a and b, 1980; Khomyakov *et al.*, 1974, 1978; Khomyakov, 1977, 1980, 1995; Pekov *et al.*, 2000, 2003; Pekov, 2005), and the information on their synthetic analogues (Ilyushin *et al.*, 1983) and related lovozerite-type compounds (Simonov *et al.*, 1967; Otroshchenko *et al.*, 1973; Pushcharovsky *et al.*, 1976; Zayakina *et al.*, 1980; Safronov *et al.*, 1980; Ohsato *et al.*, 1985, 1986; Tamazyan & Malinovskii, 1989) clearly demonstrate that: (1) only cation-saturated lovozerite-type compounds may nucleate from liquid (melt, solution) or fluid phases and (2) for this heterogeneous nucleation, high-temperature conditions and Na-saturated medium are necessary. Generally, a lovozerite-type framework, by analogy to other frameworks of zeolite-like structures, can probably only be formed if the zeolitic cavities are fully or almost fully saturated by large cations (for details see Belov, 1976; Barrer, 1982) or  $H_2O$  molecules.

There are no indications that cation-deficient members of the lovozerite group could be formed as primary phases, skipping the initial stage of their cation-saturated forms, in support of the conclusion by Khomyakov (1980, 1995) that all cation-deficient lovozerite-group minerals are only secondary phases. They form as the result of partial loss of Na from primary cation-saturated minerals coupled with the  $O^{2-} \leftrightarrow (OH)^-$  substitution. Their crystals are in all cases homo-axial pseudomorphs after crystals of the primary phases. In Nature, this transformation occurs in low-temperature hydrothermal or supergene systems.

The results of structural studies of lovozerite, litvinskite and tisinialite (Ilyukhin & Belov, 1960; Malinovskii *et al.*, 1993; Yamnova *et al.*, 2001a and b, 2003; Zolotarev *et al.*, 2008) indicate that the *B* sites in these minerals are vacant (or contain few  $H_2O$  molecules), whereas the *A* sites are fully or significantly (> 50 %) occupied by Na. Indeed, the

*B* sites located in the channels (Fig. 3) are most favourable for cation leaching. The mechanism of Na loss is shown in Table 2 on three examples.

The compositions of the cationic part of the framework, *i.e.* the contents of Si and the *M* and *C* cations, remain invariable or change very slightly: cation-deficient minerals inherit these from their cation-saturated precursors.

The transformation of cation-saturated LGM to cation-deficient ones is thus a regular, structurally controlled process. All data obtained show its distinct character that underlines the individuality of cation-deficient representatives of the group as mineral species: lovozerite, litvinskite, and tisinialite have been defined as the *B*-vacant analogues of zirsinalite, kapustinite, and kazakovite, respectively (Table 2).

### 3. Calculation scheme for empirical formulae

Taking into account the crystal-chemical features of the LGM discussed above, the optimal and complete calculation scheme for their empirical formulae from chemical data only (including electron-microprobe data, without determination of Fe valence and  $H_2O$  content) is as follows:

- 1) the calculation is based upon  $Si + Al = 6 \text{ apfu}$ ;
- 2) Zr, Ti, Nb, and Hf are placed into the *M* site; if their sum is < 1.00 *apfu*, then  $Fe^{3+}$  should be added; if the sum of all these constituents is still < 1.00 *apfu*, then place consecutively  $Mg^{2+}$ ,  $Mn^{2+}$  and eventually Ca in the *M* site;
- 3) the rest of Ca, Mn, Mg and Fe should be placed into the *C* site (if the Fe valency is unknown, then consider Fe in the *C* site as  $Fe^{2+}$ );
- 4) Na and K, Sr, Y and lanthanides should be assigned to the *A* site; the maximum number of cations in the *A* site is 3.00 *apfu*;

Table 2. Schemes of sodium leaching and hydration transforming cation-saturated lovozerite-group minerals into their cation-deficient analogues.

Site	<i>A</i>	<i>B</i>
Zirsinalite	Na <sub>3</sub>	Na <sub>3</sub>
↓	↓	↓
Lovozerite	(Na <sub>0.8</sub> □ <sub>0.2</sub> ) <sub>3</sub>	(□ <sub>0.7</sub> [H <sub>2</sub> O] <sub>0.3</sub> ) <sub>3</sub>
Kapustinite	Na <sub>3</sub>	(Na <sub>0.8</sub> □ <sub>0.2</sub> ) <sub>3</sub>
↓	↓	↓
Litvinskite	(Na <sub>0.8</sub> [H <sub>2</sub> O] <sub>0.1</sub> □ <sub>0.1</sub> ) <sub>3</sub>	□ <sub>3</sub>
Kazakovite	Na <sub>3</sub>	Na <sub>3</sub>
↓	↓	↓
Tisinialite	(Na <sub>0.7</sub> □ <sub>0.3</sub> ) <sub>3</sub>	□ <sub>3</sub>

Note: data on the site occupancies were taken from the following publications: zirsinalite, Pudovkina *et al.* (1980); lovozerite, Yamnova *et al.* (2001a); kapustinite, Yamnova *et al.* (2004); litvinskite, Yamnova *et al.* (2001b); kazakovite, Voronkov *et al.* (1979); tisinialite, Yamnova *et al.* (2003).

- 5) the rest of Na should be assigned to the *B* site;
- 6) calculate the total positive charge and adjust the O/OH ratio (to obtain charge balance);
- 7) if the H<sub>2</sub>O content was determined, then add its rest (after deduction of the amount used for calculating the number of OH groups) to the formula as H<sub>2</sub>O molecules.

## 4. Nomenclature

### 4.1. General rules

The definition of a mineral species of the lovozerite group is based upon five criteria. Boundaries between species within each subgroup are established according to the well-known “dominant-constituent rule” called the “50 % rule” in binary systems (Nickel, 1992), recently extended by Hatert & Burke (2008).

The five criteria are as follows (all values are given for a formula based on Si<sub>6</sub> and calculated as shown above).

- 1) *The structure type is determined by the cation arrangement of pseudocubic modules*: zirsinalite–lovozerite, koashvite, imandrite or, hypothetically, any other possible lovozerite-like compound [in the case of discovery of a mineral chemically identical to an earlier-known species but belonging to a different structure type, it must be considered as an individual species; in particular, the poorly-studied phase M42 briefly reported by Khomyakov (1995), the chemical analogue of koashvite belonging to the zirsinalite–lovozerite subgroup, can be considered as a potential new species dimorphic with koashvite];
- 2) *the predominant cation in the M site*;
- 3) *the predominant cation in the A site*: in all currently known lovozerite-group minerals, it is Na, except combeite with Na ≈ Ca;
- 4) *the predominance of a cation (Na) or vacancy (□) in the B site*: if the *B* site is occupied by Na < 50 %, then the mineral is considered as a representative of the cation-deficient subgroup; the boundaries in the zirsinalite–lovozerite, kapustinite–litvinskite

- and kazakovite–tisinalite series are established as Na<sub>1.5</sub>□<sub>1.5</sub> in the *B* site or, equivalently, as the gross amount of (Na + K ...) <sup>A+B</sup> = 4.5 apfu;
- 5) *the predominant component in the C site*: in the case of a prevailing tetravalent cation (Zr or Ti) in the *M* site and divalent cation in the *C* site, the latter site is considered as cation-dominant (cation-occupied) if the sum of the *C* cations is > 0.5 apfu and, correspondingly, the prevailing *C* cation (Ca or Mn as currently known in minerals) is considered as species-defining; if the sum of the *C* cations is < 0.5 apfu, then the mineral is considered as vacancy-dominant [boundaries in the presently known zirsinalite–kapustinite and lovozerite–litvinskite series are thus established as (Ca + Mn ...) <sup>C</sup> = 0.5 apfu].

The idealized end-member formulae of the lovozerite-group minerals are given in Table 1, along with the generalized formulae and with the compositional limits, taking into account all reliable empirical data. Table 3 shows the distribution of species-defining components over the structural sites in the end-members of the lovozerite-group minerals.

In the two combeite modifications known, Na and Ca contents are close to one another in both the *C* and *A* sites (Fischer & Tillmanns, 1987) and, in accordance with IMA-accepted rules for the nomenclature of solid solutions (Nickel, 1992; Hatert & Burke, 2008), the contents of the *C* and *A* sites are given as (CaNa) and (Na<sub>1.5</sub>Ca<sub>1.5</sub>), respectively, in the end-member formula of this mineral. End-members with “combined” contents on structural sites (similar to the heterovalent pairs NaCa, Ca□ and Mn□ in the *C* site, and NaCa in the *A* site of lovozerite-group minerals – Table 3) were recently also used in the IMA-approved nomenclature of the hellandite group (the heterovalent pairs CaREE<sup>3+</sup> in both the *X* and *Y* sites, and REE<sup>3+</sup>Th in the *Y* site); these are also characterized by complicated heterovalent isomorphism with coupled O/OH substitutions (Oberti *et al.*, 2002). This approach has been also used in the nomenclature of amphiboles (the pair NaCa in the *B* site: Hawthorne & Oberti, 2006) and some other mineral groups containing end-members with valency-imposed double site occupancy produced by heterovalent substitutions (Hatert & Burke, 2008).

Table 3. End-member structural formulae of lovozerite-group minerals.

Mineral	Structural sites						
	<i>A</i>	<i>B</i>	<i>C</i>	<i>M</i>	Si	O	(O,OH)
Zirsinalite	Na <sub>3</sub>	Na <sub>3</sub>	Ca□	Zr	Si <sub>6</sub>	O <sub>12</sub>	O <sub>6</sub>
Kapustinite	Na <sub>3</sub>	Na <sub>3</sub>	□ <sub>2</sub>	Zr	Si <sub>6</sub>	O <sub>12</sub>	O <sub>4</sub> (OH) <sub>2</sub>
Kazakovite	Na <sub>3</sub>	Na <sub>3</sub>	Mn <sup>2+</sup> □	Ti	Si <sub>6</sub>	O <sub>12</sub>	O <sub>6</sub>
Combeite	Na <sub>1.5</sub> Ca <sub>1.5</sub>	Na <sub>2</sub> □	CaNa	Ca	Si <sub>6</sub>	O <sub>12</sub>	O <sub>5.5</sub> (OH) <sub>0.5</sub>
Lovozerite	Na <sub>3</sub>	□ <sub>3</sub>	Ca□	Zr	Si <sub>6</sub>	O <sub>12</sub>	O <sub>3</sub> (OH) <sub>3</sub>
Litvinskite	Na <sub>3</sub>	□ <sub>3</sub>	□ <sub>2</sub>	Zr	Si <sub>6</sub>	O <sub>12</sub>	(OH) <sub>5</sub> O
Tisinalite	Na <sub>3</sub>	□ <sub>3</sub>	Mn <sup>2+</sup> □	Ti	Si <sub>6</sub>	O <sub>12</sub>	O <sub>3</sub> (OH) <sub>3</sub>
Koashvite	Na <sub>3</sub>	Na <sub>3</sub>	Ca□	Ti	Si <sub>6</sub>	O <sub>12</sub>	O <sub>6</sub>
Imandrite	Na <sub>3</sub>	Na <sub>3</sub>	Ca <sub>1.5</sub> □ <sub>0.5</sub>	Fe <sup>3+</sup>	Si <sub>6</sub>	O <sub>12</sub>	O <sub>6</sub>

The H<sub>2</sub>O amount is not considered as a species-defining criterion, similar to the nomenclature of zeolite minerals (Coombs *et al.*, 1998). Symmetry differences (*e.g.*, due to cation order) within the same structure type (zirsinalite-lovozerite, koashvite, imandrite or hypothetically, for each possible lovozerite-like compound) for minerals with identical end-member formulae are not considered as sufficient argument for the corresponding samples to be treated as different mineral species. This is also consistent with the nomenclature of zeolite minerals (Coombs *et al.*, 1998). Petarasite is considered as related to the lovozerite group, but not a member of it.

#### 4.2. Species names

The present nomenclature of the lovozerite group preserves all its valid mineral species having the IMA-status G (grandfathered) and A (approved) without modification of their names. New names are not proposed. The nomenclature scheme defines end-members and determines species names (Tables 1 and 3).

For potentially new species of the lovozerite group, taking into account both general principles of mineralogical nomenclature and the individual crystal-chemical features of this group, the following rules of naming are recommended:

- a unique name should be used for any new mineral different from the earlier-known species in its structure type understood in terms of arrangement of pseudocubic modules;
- a unique name should be used for any new mineral different from the earlier-known species with respect to the cation predominant in the *M* site;
- a unique name should be used for any new mineral different from the earlier-known species with respect to the cation predominant in the *A* and/or *B* sites;
- a unique name should be used for any new mineral which is an analogue of the earlier-known species with vacancy prevailing in the cation sites *A*, *B* and/or *C*;
- for a new mineral with occupied (not vacancy-dominant) *C* site different from the earlier-known species in the prevailing *C* cation, the use of the Levinson-type suffix could be proposed indicating this cation: *e.g.* if an analogue of lovozerite with Mn > Ca in the *C* site is discovered, then it should be named *lovozerite-Mn* with renaming of “old” lovozerite to *lovozerite-Ca* (by analogy with the nomenclature of zeolites – Coombs *et al.*, 1998).

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## Appendix

### A1. List of synonyms and unnecessary names of lovozerite-group minerals

H-combeite (Khomyakov, 1980) = combeite;  
H-kazakovite (Khomyakov, 1980) = tisinialite;  
lovozerite M (Khomyakov, 1980) = lovozerite;  
lovozerite T (Khomyakov, 1980) = lovozerite;  
M40 (Khomyakov, 1995) = kapustinite;

mineral No. 7 (Chirvinsky: in Bonshtedt *et al.*, 1937) = lovozerite;  
monoclinic lovozerite (Kapustin *et al.*, 1973) = lovozerite;  
oxy-lovozerite (Semenov, 1972) = lovozerite;  
trigonal lovozerite (Kapustin *et al.*, 1973) = lovozerite.

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