Gjerdingenite-Fe FROM NORWAY, A NEW MINERAL SPECIES IN THE LABUNTSOVITE GROUP: DESCRIPTION, CRYSTAL STRUCTURE AND TWINNING

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ABSTRACT

Gjerdingenite-Fe occurs as yellow prisms or laths up to 1 mm long in miarolitic cavities of a sodic granite ("ekerite") at Gjerdingelsva, Lunner, Oppland, Oslo Region, Norway. The simplified formula is K$_2$[(H$_2$O)$_2$(Fe,Mn)](Nb,Ti)$_4$(Si$_{15.90}$Al$_{0.10}$)$_8$(OH)$_2$O$_{48}$[(OH)$_4$.16O$_{3.84}$]•4H$_2$O, i.e., the mineral is an analogue of those with root name kuzmenkoite, which have Ti > Nb. The mineral is monoclinic, $C2/m$, with $a = 14.529(2)$, $b = 13.943(2)$, $c = 7.837(2)$ \AA, $\beta = 117.61(1)^\circ$, $V = 1406.8(9)$ \AA$^3$. $Z = 2$. The crystal structure was refined to $R = 0.054$ on the basis of 1677 observed reflections; twinning on {001} simulates an orthorhombic $F$-centered lattice. The partitioning of cations and H$_2$O molecules in the sites B, B', C (occupying channels of the zeolite-like structure) is discussed; for the refined crystal, the following crystal-chemical formula is established by comparison of chemical and structure-refinement data: {[K$_{1.20}$Na$_{0.72}$H$_2$O$_{2.08}$]}$_4$[(Fe$_{0.95}$Mn$_{0.75}$Zr$_{0.05}$)$_8$(Si$_{15.90}$Al$_{0.10}$)$_8$(OH)$_2$O$_{48}$[(OH)$_4$.16O$_{3.84}$]•4H$_2$O (Z = 1). The strongest six reflections of the powder pattern $[d_{obs}$, in \(\AA)hkl$] are: 6.92(80)(020,001), 6.42(50)(200,\bar{2}01), 4.94(70)(021), 3.225(100)(\bar{4}21,400,\bar{4}02), 3.114(80)(041,022), and 2.512(50)(\bar{4}41,401,\bar{4}03). The mineral is optically biaxial (+) with $\alpha = 1.7001(4)$, $\beta = 1.794(1)$, $\gamma = 1.794(1)$. $2V_{meas} = 58.5(2)$°, $2V_{calc} = 63.71(1)$°. The Mohs hardness is about 5; $D_{calc} = 2.830$ g/cm$^3$. The pseudo-orthorhombic crystals are flattened on {001} and elongate along [010]. Five crystal forms were observed: {100}, {010} (subordinate), {001}, {201}, and {021}. Keywords: gjerdingenite-Fe, new mineral species, labuntsovite group, zeolite-like structure, twinning, miarolitic cavities, ekerite, Oslo Region, Norway.

SOMMAIRE

La gjerdingenite-Fe se présente en prismes jaunes ou en lamelles atteignant 1 mm de long dans des cavités miarolitiques d’un granite sodique ("ékerite") à Gjerdingelsva, Lunner, Oppland, dans la région d’Oslo, en Norvège. La formule simplifiée de cette nouvelle espèce serait: K$_2$[(H$_2$O)$_2$(Fe,Mn)](Nb,Ti)$_4$(Si$_{15.90}$Al$_{0.10}$)$_8$(OH)$_2$O$_{48}$[(OH)$_4$.16O$_{3.84}$]•4H$_2$O, i.e., elle est un analogue des minéraux ayant la racine kuzmenkoite dans leur nom, et donc Ti > Nb. La gjerdingenite-Fe est monoclinique, $C2/m$, avec $a = 14.529(2)$, $b = 13.943(2)$, $c = 7.837(2)$ \AA, $\beta = 117.61(1)^\circ$, $V = 1406.8(9)$ \AA$^3$. $Z = 2$. La structure cristalline en a été affinée jusqu’à un résidu $R = 0.054$ en utilisant 1677 réflexions observées; un maclage sur {001} simule une maille orthorhombique à faces centrées. Nous évaluons la répartition des cations et des molécules de H$_2$O sur les sites B, B', C (occupant des canaux de la structure de zéolite) dans cette structure, semblable à celle d’une zéolite; dans le cas du cristal qui a servi à l’affinement de la structure, voici la formule cristallochimique, établie en évaluant les données sur la composition et les résultats de l’affinement: {[K$_{1.20}$Na$_{0.72}$H$_2$O$_{2.08}$]}$_4$[(Fe$_{0.95}$Mn$_{0.75}$Zr$_{0.05}$)$_8$(Si$_{15.90}$Al$_{0.10}$)$_8$(OH)$_2$O$_{48}$[(OH)$_4$.16O$_{3.84}$]•4H$_2$O (Z = 1). Les six raies les plus intenses du spectre de diffraction (méthode des poudres) $[d_{obs}$, en \(\AA)hkl$] sont: 6.92(80)(020,001), 6.42(50)(200,\bar{2}01), 4.94(70)(021), 3.225(100)(\bar{4}21,400,\bar{4}02), 3.114(80)(041,022), et 2.512(50)(441,401,403). Le minéral est biaxial (+) avec $\alpha = 1.6676(2)$, $\beta = 1.7001(4)$, $\gamma = 1.794(1)$. $2V_{meas} = 58.5(2)$°, $2V_{calc} = 63.71(1)$°. La dureté de Mohs est d’environ 5; $D_{calc} = 2.830$ g/cm$^3$. Les cristaux pseudo-orthorhombiques sont aplatis sur {001} et allongés selon {010}. Nous notons la présence des cinq formes suivantes: {100}, {010} (subordonné), {001}, {201}, et {021}.

(Traduit par la Rédaction)

Mots-clés: gjerdingenite-Fe, nouvelle espèce minérale, groupe de la labuntsovite, structure zéolitique, maclage, cavités mioralitiques, ékerite, région d’Oslo, Norvège.

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INTRODUCTION

The history of investigation of the new mineral species gjerdigenite-Fe spans quite a few years. X-ray powder-diffraction diagrams made in 1973 gave a pattern resembling that of nenadkevichite (Kuz’menko & Kazakova 1955), albeit with an apparently larger cell. The interpretation of Weissenberg and precession patterns made in 1975 proved to be difficult, and twinning was suspected. Tentative and approximate unit-cell dimensions of 13.8, 27.6 and 14.45 Å were determined. Potassium was found to be a major element and, unfortunately, collectors distributed the mineral very early, labeled as a K-dominant analogue of nenadkevichite. New investigations with a four-circle single-crystal diffractometer in 1987 gave an orthorhombic cell with a 7.287(2), b 13.904(4), c 6.987(2) Å, space group Phan. However, the twinning problem could not be handled at that time. Only recently, new single-crystal diffraction data and the use of modern software designed to handle twinning brought a solution to the problem and showed that the mineral is monoclinic with twinning on {001}, simulating an orthorhombic F-centered lattice (see below). The numerous publications by Russian scientists on minerals related to nenadkevichite and labuntsovite and their crystal structures, culminating in the recently approved nomenclature of the labuntsovite group (Chukanov et al. 2002), have been a useful prerequisite for our own investigations.

The mineral and name were approved by the Commission on New Minerals and Mineral Names, IMA (2001–009). The name is derived from the type locality, Lake Gjerdingen, with the suffix –Fe to indicate the dominant cation in the D site (see below). The type material is deposited at the Geological Museum, University of Oslo (catalogue nos. 33712, 33713, and 33715).

OCCURRENCE

Ekerite is a local name of a sodic granite from the Permian Oslo Region, a paleoarift area in southern Norway. Its petrography was described by Barth (1945), Sæther (1962) and Dietrich et al. (1965). A mineralogically unique pluton of ekerite, measuring about 2 × 4 km², is situated east–southeast of Lake Gjerdingen in the forest area of Nordmarka, some 30 km north of Oslo. The locality is commonly known as Gjerdingen, but is actually close to Gjerdingselva, a river that flows from the forest area of Nordmarka, some 30 km north of Oslo.

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The new mineral species gjerdigenite-Fe has a hydrothermal origin, as it lines miarolitic cavities, and is most closely associated with quartz, orthoclase, albite, aegirine, kupletskite, elpidite, lorenzenite, pyrochlore, monazite-(Ce), gagarinite-(Y), ralstonite, gaurksute, and molybdenite. It may form an epitaxic overgrowth on elpidite (which has a 7.120, b 14.665, c 14.740 Å) and may have a coating of microcrystalline ralstonite. Epitaxic growth of labuntsovite on elpidite and elpidite on labuntsovite is known from Mont Saint-Hilaire, Quebec, Canada (Henderson 1979, 1994). Petersen et al. (1996) have described crystals of “K-dominant nenadkevichite” (probably vuoriyarvite-K, cf. Chukanov et al. 2002) epitaxically overgrown on elpidite from Narssârssuk, Greenland. Gjerdingenite-Fe is quite widespread in the miarolitic cavities but invariably in small amounts. It is one of the few K-rich minerals (besides orthoclase and kupletskite) in a paragenesis dominated by Na-rich silicates and fluorides.

MORPHOLOGY AND PHYSICAL PROPERTIES

A color photograph and an SEM photomicrograph of the mineral now known as gjerdigenite-Fe were published by Raade & Haug (1982). A different SEM photomicrograph is reproduced here (Fig. 1). The mineral occurs as prismatic to lath-shaped crystals up to 1 mm in length. They may form subparallel or irregular aggregates to 3 mm. Five crystal forms were identified by goniometric measurements: pinacoids {100}, {010}, {001}, {201); prism {021} (Fig. 2). The crystals are flattened on {001} and elongate along {010}. The form {010} is invariably subordinate or may be lacking. The crystals have a distinct pseudo-orthorhombic habit. Twinning on {001} is shown to be present on a structural basis (see below). The color varies from pale yellow to orange yellow or brownish yellow, and the streak is white to faintly yellow. The crystals are translucent or rarely transparent, with a vitreous to waxy luster. They show no fluorescence in long- or short-wave ultraviolet light. No cleavage or parting was observed. The fracture is uneven, and the mineral is very brittle. By suspension in bromoform, a density of 2.82(2) g/cm³ was determined.

Spindle-stage measurements (λ = 589 Å), using the microrefractometer equipment designed by Medenbach (1985), showed the mineral to be biaxial (+), with α 1.6676(2), β 1.7001(4), γ 1.794(1); 2V 58.5 ± 2.3°, 2V calc 63.71(1)°; orientation: y = b. No axial dispersion was observed, and the mineral is non-pleochroic. Gjerdingenite-Fe has the largest β index among the Nb-dominant labuntsovite-group minerals (e.g., for organovaitke-subgroup minerals, which are analogues of gjerdigenite with a doubled c parameter, 1.685 < β < 1.700).
GJERDINGENITE-Fe, A NEW MINERAL SPECIES IN THE LABUNTSOVITE GROUP

1.692). This feature could possibly be used as a diagnostic characteristic of gjerdingenite.

CHEMICAL DATA AND INFRARED SPECTRUM

Chemical analyses

Three crystals of gjerdingenite-Fe, including the one used for the present single-crystal study, were analyzed by two different wavelength-dispersion electron microprobes. The Cameca Camebax electron microprobe housed at the Geological Museum in Oslo was operated at an accelerating voltage of 15 kV and a sample current of 10 nA (and a fourth crystal was also analyzed there), using the following standards: albite (Na), orthoclase (K), wollastonite (Ca, Si), MnTiO$_3$ (Mn, Ti), Fe$_2$O$_3$ (Fe), Al$_2$O$_3$ (Al), Zr metal (Zr), and Nb metal (Nb). Areas of 50 × 50 μm$^2$ were scanned to minimize any loss of Na and H$_2$O. The ARL-SEMQ electron microprobe of the University of Modena and Reggio Emilia was operated at 15 kV and a sample current of 20 nA, using the following standards: albite (Na), microcline (K), clinopyroxene (Ca, Si), ilmenite (Fe, Ti), spessartine (Al, Mn), Zr metal (Zr), and Nb metal (Nb). A dearth of material prevented a direct determination of H$_2$O; its presence is shown by the infrared spectrum and structural results (see below). Bands of carbonate groups were not observed in the infrared spectrum. All Fe is assumed to be divalent.

Fig. 1. SEM photomicrograph of gjerdingenite-Fe. Length of the aggregate is ~0.5 mm.

The mineral is dusted with tiny crystals of two phases. At high magnification, one of them is seen to form cubes and is probably ralstonite.
All the analyses show low totals and low silica contents relative to the structural results (Table 1). The following considerations could justify the low values: (i) poor contact of the crystals with the surrounding epoxy (it is known that the preparation technique used for isolated small single crystals often leads to poor conductivity of the sample); (ii) too thin a carbon coating; (iii) voids in the crystals. Actually, the three Oslo mounts, which were re-polished and analyzed in Modena, gave anhydrous results with higher totals around 88 wt.% but with poorer values of the (Nb,Ti):(Si,Al) ratio. Bearing these difficulties with the analytical results in mind, we have refrained from calculating empirical formulae from any one of the analytical datasets.

On the basis of (Si + Al) = 16 and the refinement of the structure (see below for a discussion), the following crystal-chemical formula is obtained: \([\{\text{K}_1.20\text{Na}_0.72(\text{H}_2\text{O})_{2.08}\}/\text{H}_9\text{O}18 \times \{\text{K}_2.08(\text{H}_2\text{O})_{1.92}\}/\text{H}_9\text{O}18 \times \{\text{H}_2\text{O}\}_3.40\text{K}_0.56\text{Ca}_0.04\}_8(\text{Fe}_{0.95}\text{Mn}_{0.75}\text{Zr}_{0.05})_8(\text{Si}_{15.90}\text{Al}_{10.10})_8(\text{OH})_{1.16}\text{O}_4\text{Si}_{1.84}\times 4\text{H}_2\text{O}\). The chemical composition corresponding to this formula is given in Table 1 (column C). Iron substituting for (Nb,Ti) is here treated as divalent, although considering charge and ionic size, \(\text{Fe}^{3+}\) would be closer to \(\text{Nb}\) and \(\text{Ti}\) than \(\text{Fe}^{2+}\). The amount of \(\text{Fe}\) in the \(M\) site being low, its valence has only a minor influence on the \(\text{OH}/\text{O}\) ratio.

The calculated density, based on the crystal-chemical formula (unit-formula weight 2397.72) and the cell volume from the single-crystal study, is 2.830 g/cm\(^3\), in good agreement with the measured density of 2.82(2) g/cm\(^3\). The Gladstone–Dale relationship gives a compatibility index \(1 - (\text{K}\ P/\text{K}\ C)\) of 0.0012 using \(\text{D}_{\text{calc}}\) and –0.0024 using \(\text{D}_{\text{meas}}\); both are superior (Mandarino 1981).

It should be noted that some parts of crystal no. 1 have Mn > Fe (Table 1). Of the seven individual analyses made in Oslo on this crystal, all show Mn > Fe (mean wt.%: MnO 3.15, FeO 2.46), whereas three of the six individual analyses made in Modena on the same crystal have Mn > Fe. Strictly speaking, this is a different mineral species, the Mn-dominant analogue of gjerdigenite-Fe. We have based the definition of our new species on crystals where Fe > Mn; the chemical data of crystal no. 1 are reported for completeness.

### Infrared-absorption data

The infrared-absorption spectrum of gjerdigenite-Fe was recorded with a Perkin–Elmer spectrophotometer using a Nujol mull with ca. 0.03 wt.% of the mineral. Owing to this low concentration, some of the...
absorption bands are not well resolved. The wave-
numbers of the absorption bands are (in cm^{-1}): ~3560
(broad), 1640, 1595 (shoulder), 1110 (strong), ~1070,
~1020, 950 (strong), 775, and 690 (strong).

The band at 3560 cm^{-1} is due to O–H stretching, and
the ones at 1640 and 1595 cm^{-1}, to H–O–H bending.
The splitting of the ~1600 cm^{-1} band indicates that H2O
is present in at least two different sites (the structure
refinement shows that H2O is located in four positions:
B, B', C and W, see below). The prominent 690 cm^{-1}
band, representing a (Nb,Ti)–O stretching vibration, has
a similar wavenumber to that in the structurally related
minerals kuzmenkoite-Mn (Chukanov et al. 1999),
organovaite-Mn (Chukanov et al. 2001a), and parakuz-
menkoite-Fe (Chukanov et al. 2001b). The other mem-
bers of the labuntsovite group have wavenumbers below
690 cm^{-1} for this mode. The three absorption bands in
the region 1000–1200 cm^{-1} are Si–O–Si stretching
modes.

X-RAY POWDER-DIFFRACTION DATA

The X-ray powder-diffraction pattern of gjerdin-
genite-Fe, obtained with a Guinier – de Wolff quadruple
focusing camera, is given in Table 2. Correct indexing
of the 19 observed reflections was achieved by com-
parison with the powder-diffraction pattern calculated
from the structure data. The pseudo-orthorhombic sym-
metry is reflected in the multiple indexing of most of
the reflections. The agreement between observed and
calculated intensities is reasonably good, considering
the visual estimates of observed intensities and the high
number of overlapping reflections. Refined unit-cell
parameters from powder data are: a = 14.54(1), b
= 13.941(7), c = 7.844(4) Å, β = 117.59(3), V = 1409(1) Å^3.
The refinement included all multiple indices listed in
Table 2, except three, as noted.

**Single-Crystal Diffractometry and Twinning**

A suitable single crystal was selected from several
crystals tested. We used a single-crystal X-ray
diffractometer (Table 3) to collect 3809 reflections on
the basis of an F-centered orthorhombic lattice with cell
parameters a = 14.529(3), b = 13.943(2), c = 7.877(6) Å,
A, obtained by least-squares refinement of 24 reflections
with 21.2° < 2θ < 28.8°. The occurrence of non-space-
group systematic absences, besides the systematic abs-
ences required by the space group Fmmm, suggested
the presence of twinning in our crystal, as already
observed in other labuntsovite-group minerals by
Rastsvetaeva et al. (1994).

The type of twinning occurring in gjerdingenite-Fe
deserves a detailed analysis as an illustrative and com-
plex example where the crystal structure can be solved
by the aid of available software like the SHELX–97
package (Sheldrick 1997), which includes the treatment
of twinning according to Herbst-Irmer & Sheldrick

Twinning in real space

Figure 3 shows that the monoclinic C-centered
lattice of gjerdingenite-Fe can be split into two identical
orthorhombic F-centered sublattices with a relative shift
of (± 0.0 0.3). The monoclinic C-centered cell is obtained
from the orthorhombic F-centered supercell by the
transformation | 100 010 – ¼ 0 ¼ |
and has parameters
a_{mon} = a_{or} = 14.529(2), b_{mon} = b_{or} = 13.943(2), c_{mon} = 7.837(6) Å ≈ c_{or}/3.5 and β_{mon} = 117.61(1)°. With refer-

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**Table 2. X-Ray Powder-Diffraction Data for Gjerdingenite-Fe**

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<th>2θ (°)</th>
<th>(h,k,l)</th>
<th>I / 100</th>
<th>d(h,k,l) (Å)</th>
<th>d_{calc} (Å)</th>
<th>δ (%)</th>
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</tr>
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</table>

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**Table 2. Experimental Conditions and Crystal Data for Gjerdingenite-Fe**

- Chemical formula: X_{(0.5)O}Y_{(0.5)O}·Z_{(0.0)O}·[Y_{(0.0)O}·Z_{(0.0)O}·Z_{(0.0)O}]_{3+4} \cdot \text{H}_{2}O
- Radiation and wavelength: MoKα, λ = 0.71069 Å
- Unit cell: monoclinic Si, axes a = 14.529(3), b = 13.943(2), c = 7.844(4) Å, α = 90°, β = 117.59(3), γ = 90°
- Volume: 1409(1) Å^3
- Space group: C2/m, Z = 2
- Unit-cell dimensions: a = 14.529(3), b = 13.943(2), c = 7.844(4) Å, β = 117.59(3)
- Unit-cell volume: 1409(1) Å^3
- Crystal size: 0.20 x 0.10 x 0.07 mm
- Index Miller: +1 x ≤ 2 ≤ 1, 0 ≤ z ≤ 1, 0 ≤ y ≤ 7
- Four standard reflections: every 200 reflections
- Standard reflections: 3809
- Collected reflections: 3809
- Refinement method: full-matrix least-squares on F^2
- Crystallographic parameters:
  - Wavelength: MoKα, λ = 0.71069 Å
  - Unit cell: monoclinic Si, axes a = 14.529(3), b = 13.943(2), c = 7.844(4) Å, α = 90°, β = 117.59(3), γ = 90°
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Twinning in reciprocal space

Figure 3 shows the (h0l) and (h11) planes of the reciprocal lattice, twinned according to the (001) plane. Indices refer to both the two monoclinic components of the twin and to the resulting orthorhombic twin-lattice; the k index is the same for all types of indexing. For k = 2n, each node of one component (orange axes in Fig. 3) exactly overlaps a non-equivalent node of the second component (blue axes); for k = 2n + 1, the nodes of the two components intercalate such as to halve the periodicity along c*.

According to the indexing in the orthorhombic reference-system (green color), besides the space-group systematic absences of an F-centered lattice (h,k,l) and (h,k,l + 1), the nodes of the two components intercalate such as to halve the periodicity along c*.

Mathematically, the non-space-group systematic absences can be proved by splitting the formula of the structure factor into two parts: one part contributed only by the subset of atoms j in the positions (xj, yj, zj), and a second one contributed only by the subset of j’ atoms in the positions (xj’ + ¼, yj’; zj’ + ¼). Each of the two subsets of atoms corresponds to one of the two orthorhombic sublattices, with the relative shift being (¾ 0 ¼) as mentioned above.

Refinement of the structure

The anisotropic refinement (isotropic for the sites B and W; Table 4) of gjerdingenite-Fe in the space group C2/m converged to R(F) = 0.054 for 1677 independent reflections with I > 2σ(I) obtained by merging the equivalent reflections of the measured set (Rint = 0.05). The two components of the twin have the same volume, as refined by SHELEX–97 (Sheldrick 1997). Taking into account the main ion occupying each crystallographic site, the following scattering curves have been used for the refinement: B = C = K, B’ = K’ + O (the ratio K/O was refined), D = Fe, M = Ti + Nb (the ratio Ti/Nb was refined), and W = O. Except for the Si and O sites, the total content of electrons was refined as shown in Table 4. The site B can have a maximum occupancy of 50% only because it is close [0.90(1) Å] to the corresponding position generated by the mirror plane. Attempts to solve and refine the structure in the lower-symmetry space groups C2 and Cm were inconsistent. Information on data collection and refinement, atom coordinates and equivalent thermal-displacement parameters, and selected interatomic distances are reported in Tables 3, 4, and 5, respectively. Tables with F0 and Fc and the values of the anisotropic displacement parameters are deposited at the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

STRUCTURE AND CRYSTAL-CHEMICAL FORMULA

The nomenclature of the labustovite group has recently been approved by the IMA–CNMMN (Chukanov et al. 2002). The group includes alkali silicates of Ti and Nb represented by the general formula: \( A_B^4\left\{ C_{4-x}(H_2O,OH)_2\right\} D_{(M_4Si_4O_{12})_4}(OH,O)_6'hH_2O \). Here, A and B are mainly alkalies; in the present case, A is vacant. The C and D sites can contain several types of cations but exclude each other, their distance being only ~2 Å \([C–D = 2.226(7)\ Å \text{ in the present case}]\). If the site D is occupied by cations, to a maximum of \( x = 2 \), 2x oxygen atoms (usually H2O molecules or OH groups) occur in C to complete the octahedral coordination of the D cations. M contains mainly Ti or Nb and corresponds to two independent sites in the present case; besides the site W (Table 4), some of the nH2O molecules partially occupy also the sites B and B’ in the present case.

The structure

On the whole, the crystal structure of gjerdingenite-Fe (Fig. 4) shows the typical framework of minerals of the labustovite group. It is built up by chains of (Nb,Ti) octahedra linked by four-membered rings of \( Si_4O_{12}^- \) tetrahedra to form a complex anion \([M_4(Si_4O_{12})_{14}(OH,O)_6]\)~. The D site can be considered as part of the framework (Chukanov et al. 2002). The extra-framework cation sites B, B’, and C occupy zeolite-like channels and cavities.

A bond-valence calculation (Brown & Shannon 1973; not reported), even though approximate because of the complex composition, shows that the oxygen atoms of the sites B, B’, C and W must be assigned to H2O molecules; in fact, they are involved only in weak bonds (Table 5) that cannot neutralize the OH groups. The most underbonded oxygen atom is O1, which is the only framework oxygen atom not bonded to Si; therefore, it represents OH groups. The oxygen atom of the H2O molecule in the site W is at 2.67(2) Å from B’ and 3.03(1) Å from C (Table 5). These distances allow either coordination with cations or a hydrogen bond with H2O occupying the sites B’ and C instead of cations. Also the distances B–oxygen, with a minimum value of 2.7 Å, allow the presence in this site of H2O where a
cation vacancy occurs. The distances $D$–oxygen are instead too short for an $O$...$O$ distance; consequently, a cation vacancy in this site cannot be filled by a molecule of $H_2O$; this latter feature is common to all known labuntsovite-group minerals.

Except those of the site $C$, the $H_2O$ molecules are only weakly bonded to alkali cations and do not form strong hydrogen bonds. As shown by the range of chemical compositions, leaching of alkalies, favored by the presence of zeolite-like channels, is presumably easy and, as a consequence of the weak bonds mentioned, $H_2O$ molecules also are lost together with cations. The amount of $H_2O$ and alkalies that can be retained by the structure presumably depends on the overall chemical composition, as shown by the different situations encountered in kuzmenkoite-Mn. The samples of this mineral, refined by Golovina et al. (1998) in space group $C2/m$ and by Rastsvetaeva et al. (2000) in space group $Cm$, show a different distribution and higher content of $H_2O$ relative to gjerdingenite-Fe. The latter authors also claim the presence of $(H_2O)^+$. 

### Crystal-chemical formula

According to the refined occupancy (number of electrons $e_{ref}$; see Table 6), the site $B'$ shows $e_{ref} = 13.7(4)$; therefore, it contains not only $H_2O$ but also an element heavier than oxygen. The content of $B'$ is within the coordination sphere of the site $B$ (which is occupied by both $H_2O$ and alkalies) at a distance $B'$–$B = 2.667(9)$ Å. If a cation is in $B'$, locally the site $B$ must bear either an oxygen atom or a vacancy. Refinement of the scattering factor of $O$ against that of $K$ for the site $B'$ converges to an occupancy of $0.48O + 0.52K$. A very small occurrence of $K$ in this site has already been reported in the structure of kuzmenkoite-Mn by Rastsvetaeva et al. (2000). 

On the basis of the values of $e_{ref}$, a reasonable content of the sites can be established, taking into account the results of the chemical analyses (Table 1) and that (1) the site $A$ is empty, (2) the site $B'$ contains $0.48O + 0.52K$, (3) the site $B$ cannot be vacant where $B'$ carries $K$, otherwise its $e_{ref}$ cannot be reasonably accounted for by the available ions (its number of electrons can be matched by putting in it an amount of oxygen equal to the amount of $K$ in $B'$), and (4) the content $x$ of the site $D$ is limited by the related content $2x$ of $H_2O$ in the site $C$.

### Table 6. Atom Coordinates, Refined Number of Electrons per Site ($e_{ref}$) and Equivalent Displacement Factor $U_{eq}$

<table>
<thead>
<tr>
<th>Site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$e_{ref}$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Si_1$</td>
<td>0.207(2)</td>
<td>0.162(1)</td>
<td>0.799(3)</td>
<td>-</td>
<td>0.014(7)</td>
</tr>
<tr>
<td>$Si_2$</td>
<td>0.605(7)</td>
<td>0.809(7)</td>
<td>0.754(2)</td>
<td>-</td>
<td>0.017(7)</td>
</tr>
<tr>
<td>$M_1$</td>
<td>0</td>
<td>0.789(6)</td>
<td>0.509(4)</td>
<td>14.9(2)</td>
<td>0.051(9)</td>
</tr>
<tr>
<td>$M_2$</td>
<td>0.5</td>
<td>0.5</td>
<td>16.4(3)</td>
<td>0.020(19)</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>0.430(7)</td>
<td>0.025(5)</td>
<td>0.73(1)</td>
<td>5.5(2)</td>
<td>0.078(7)</td>
</tr>
<tr>
<td>$B'$</td>
<td>0.431(3)</td>
<td>0.025(3)</td>
<td>0.73(1)</td>
<td>5.5(2)</td>
<td>0.078(7)</td>
</tr>
<tr>
<td>$C$</td>
<td>0.369(6)</td>
<td>0.265(1)</td>
<td>0.358(1)</td>
<td>10.0(3)</td>
<td>0.075(7)</td>
</tr>
<tr>
<td>$D'$</td>
<td>0.65(1)</td>
<td>0.365(1)</td>
<td>0.53(1)</td>
<td>10.0(3)</td>
<td>0.075(7)</td>
</tr>
<tr>
<td>$O_1$</td>
<td>0.003(5)</td>
<td>0.729(5)</td>
<td>0.611(8)</td>
<td>-</td>
<td>0.017(1)</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.06(1)</td>
<td>0.802(5)</td>
<td>0.373(4)</td>
<td>-</td>
<td>0.016(1)</td>
</tr>
<tr>
<td>$O_3$</td>
<td>0.259(5)</td>
<td>0.870(5)</td>
<td>0.278(7)</td>
<td>-</td>
<td>0.018(1)</td>
</tr>
<tr>
<td>$O_4$</td>
<td>0.272(9)</td>
<td>0.810(5)</td>
<td>0.753(7)</td>
<td>-</td>
<td>0.018(1)</td>
</tr>
<tr>
<td>$O_5$</td>
<td>0.455(4)</td>
<td>0.829(5)</td>
<td>0.103(4)</td>
<td>-</td>
<td>0.023(1)</td>
</tr>
<tr>
<td>$O_6$</td>
<td>0.325(5)</td>
<td>0.720(9)</td>
<td>0.426(7)</td>
<td>-</td>
<td>0.017(1)</td>
</tr>
<tr>
<td>$O_7$</td>
<td>0.231(5)</td>
<td>0.872(9)</td>
<td>0.326(7)</td>
<td>-</td>
<td>0.012(1)</td>
</tr>
<tr>
<td>$O_8$</td>
<td>0.242(5)</td>
<td>0.784(9)</td>
<td>0.806(7)</td>
<td>-</td>
<td>0.022(1)</td>
</tr>
<tr>
<td>$O_9$</td>
<td>0.146(1)</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>0.103(2)</td>
</tr>
</tbody>
</table>

* Isotopic $[A(x)]$ for $H$ and $H'$. 

### Table 7. Selected Bond Lengths (Å) for Gjerdingenite-Fe

| $Si$ - $O$ | 1.612(3) | $Si$ - $Si$ | 1.539(3) |
| $O_4$ | 1.505(5) | $O_3$ | 1.502(5) |
| $O_6$ | 1.623(5) | $O_6$ | 1.527(5) |
| $O_7$ | 1.654(5) | $O_7$ | 1.536(5) |
| Average | 1.524 | Average | 1.512 |

| $O_5$ - $O_2$ | 1.982(5) | $O_6$ - $O_2$ | 1.567(5) |
| $O_6$ - $O_2$ | 1.596(6) | $O_6$ - $O_6$ | 1.565(6) |
| $O_2$ - $O_2$ | 2.073(5) | $O_2$ - $O_2$ | 1.596(6) |
| Average | 1.982 | Average | 1.576 |

| $O_2$ - $C_2$ | 2.106(5) | $C_2$ - $C_2$ | 2.106(5) |
| Average | 2.147 | Average | 2.041 |

| $C$ - $O_3$ | 2.561(7) | $O_3$ | 2.106(7) |
| $O_2$ - $O_2$ | 2.505(8) | $O_2$ - $O_2$ | 2.505(8) |
| $O_2$ - $O_2$ | 2.505(8) | $O_2$ - $O_2$ | 2.505(8) |
| Average | 2.130(8) | Average | 0.003(1) |
| $O_5$ - $O_5$ | 1.170(9) | $O_5$ - $O_5$ | 1.170(9) |
| $O_5$ - $O_5$ | 2.525(7) | $O_5$ - $O_5$ | 2.525(7) |
| Average | 1.178 | Average | 2.963 |

* The multiplicity of the site is given in parentheses. 
* Estimated standard deviation in parentheses. 
* Assigning to the content of the site $x$. 
* Maximum occupancy 50% because of disorder.
Fig. 3. Projection (top) along [010] of the lattice of gjerdingenite-Fe. The green circles represent nodes centering the (001) faces of the C-centered monoclinic cell, which is shown in black. The full-line and dotted red cells belong to the two F-centered orthorhombic sublattices into which the monoclinic lattice can be split. A pseudohexagonal multiple cell is also shown in blue. The lower parts of the figure show the position of the h0l (middle part) and h1l nodes (bottom part) of the diffraction pattern of a (001) twin of gjerdingenite-Fe. Reciprocal axes and nodes of the two monoclinic components of the twin are shown in blue and orange, respectively; the overlapped nodes are shown in green. The same colors are used for the indices. The directions only and not the lengths of the reciprocal axes are shown; the red axes pertain to the orthorhombic cell.
GJERDINGENITE-Fe, A NEW MINERAL SPECIES IN THE LABUNTSOVITE GROUP

The crystal formula already mentioned above ($B$ and $B'$ are in braces): 

\[
\left\{\left[\left[\text{K}_{1.20}\text{Na}_{0.72}\left(\text{H}_2\text{O}\right)_{2.08}\right]\left[\text{K}_{2.08}\left(\text{H}_2\text{O}\right)_{1.92}\right]\right]_{\text{H}_9\text{O}_{18}}^+\left[\left[\text{K}_{2.08}\left(\text{H}_2\text{O}\right)_{1.92}\right]\left[\text{K}_{1.20}\text{Na}_{0.72}\left(\text{H}_2\text{O}\right)_{2.08}\right]\right]_{\text{H}_9\text{O}_{18}}^+\left[\left(\text{H}_2\text{O}\right)_{3.40}\text{K}_{0.56}\text{Ca}_{0.04}\right]\left[\left(\text{Fe}_{0.95}\text{Mn}_{0.75}\text{Zr}_{0.30}\right)\left(\text{Nb}_{4.30}\text{Ti}_{3.45}\text{Fe}_{0.20}\text{Zr}_{0.05}\right)\right]\left(\text{Si}_{15.90}\text{Al}_{0.10}\right)\right]_{\text{H}_9\text{O}_{18}}^+\left[\left(\text{OH}\right)_{4.16}\left(\text{O}_{3.84}\right)\right]\left[\text{H}_2\text{O}\right]_{\text{H}_9\text{O}_{18}}^+\cdot4\text{H}_2\text{O}.
\]


The number of H atoms in addition to H$_2$O is established by balancing the formula. The minor amount of Fe assigned to the $M$ sites could be trivalent rather than divalent. This would require a bit less H in the formula. The total H$_2$O content is close to the difference in some of the chemical datasets from 100%; on the whole, the wt.% calculated from the crystal-chemical formula compares well with the analytical data (Table 1). Grouping together the contents of the sites $C$ and $D$ and the H$_2$O molecules coordinated by alkali atoms, the following simplified formula is obtained for gjerdingenite-Fe, referred to two unit formulae per unit cell: 

\[
\text{K}_2\left(\text{H}_2\text{O}\right)_{3}\left(\text{Fe},\text{Mn}\right)\left(\text{Nb},\text{Ti}\right)_2\left(\text{Si}_4\text{O}_{12}\right)_2\left(\text{OH},\text{O}\right)_4\cdot4\text{H}_2\text{O}.
\]

GJERDINGENITE-Fe AND THE LABUNTSOVITE GROUP

Several monoclinic and two orthorhombic members of the labuntsovite group are known (Table 7). In the latter case (nenadkevitchite and korobitsynite with $a \approx 7.4$, $b \approx 14.2$, $c \approx 7.1$ Å), the chains of octahedra are straight, and there are only two extra-framework sites, with Na in 8- and 9-fold coordination. The monoclinic members show a doubled $a$ and, in some cases, also doubled $c$ (subgroups of paralabuntsovite, parakuzmenkoite, and organovaite). In general, they contain...
an A site (Na,□), which corresponds to the 9-fold site in the orthorhombic structure, and three sites B, C, and D, which correspond to the 8-fold orthorhombic site. The D site becomes larger in the monoclinic structures because of the deformation of the framework and, in particular, the zig-zag disposition of chains of (Ti,Nb) octahedra. The B site is larger than A and is normally filled with K; C may have K, Ba, Sr, □, but only oxygen atoms where D is occupied by cations; D = Fe, Mg, Mn, Zn, □.

The naming of the monoclinic minerals of the labuntsovite group is based on combinations of root names and suffix modifiers by analogy with the nomenclature of REE minerals, zeolites, etc. (Chukanov et al. 2002). Mineral species have different root names (Table 7) if at least one of the following conditions is satisfied: (1) the structure is of different type; (2) the dominant cations occupying the sites A (not Na), B (not K), and M (Ti,Nb) are different; (3) the total content of cations in these sites is 50 to 100% of the full occupancy of these sites. If the D site is more than 50% occupied (i.e., cations > □), the cation that predominates in this sum is considered to be a species-forming cation, and a suffix modifier defining that mineral species is added.

Gjerdingenite (as a root name) has Nb > Ti in M and is an analogue of kuzmenkoite (root name), which has Ti > Nb (Table 7). The species name is determined by the prevailing D cation, i.e., gjerdingenite-Fe. Organovaite-Mn is claimed to be the Nb-dominant analogue of kuzmenkoite-Mn by Chukanov et al. (2001a); however, with a doubling of the c parameter for organovaite-Mn, this conclusion cannot be correct. According to the recently approved nomenclature of the labuntsovite group (Chukanov et al. 2002), the prefix para- is used to indicate a cell doubling, thus the root name organovaite is not in accordance with this rule (cf. Table 7).

Table 7: Root Names of the Minerals of the Labuntsovite Group

<table>
<thead>
<tr>
<th>Species group</th>
<th>M site: Nb &gt; Ti</th>
<th>M site: Ti &gt; Nb</th>
<th>Correction for species name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phan</td>
<td>Nenadikovite</td>
<td>Konotnovite</td>
<td>Nomenclature</td>
</tr>
<tr>
<td>C2m</td>
<td>Cation-</td>
<td>Cation-</td>
<td></td>
</tr>
<tr>
<td>C2m</td>
<td>Gjerdingenite</td>
<td>Kuzmenkoite</td>
<td>D cation</td>
</tr>
<tr>
<td>C2m</td>
<td>Organovite</td>
<td>Patassiumtubinite</td>
<td>D cation</td>
</tr>
<tr>
<td>Cm</td>
<td>Voskodatovite</td>
<td>Tempestite</td>
<td>A cation</td>
</tr>
<tr>
<td>Cm</td>
<td>Voskodatovite</td>
<td>Cation-</td>
<td></td>
</tr>
</tbody>
</table>

* The prefix para- is used to indicate a doubling of the unit cell. (Chukanov et al. 2001)

** REFERENCES **


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