

1 **High temperature behavior of fedorite from Murun Alkaline Complex (Russia)**

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28 **Abstract**

29 The thermal behavior of fedorite from the Murun massif (Russia) has been investigated by
30 means of differential thermal analysis (DTA), thermogravimetry (TG), *in situ* High Temperature
31 Single Crystal X-ray Diffraction (HT SCXRD) and *ex situ* High Temperature Fourier Transform
32 Infrared Spectroscopy (HT FTIR). Petrographic and Electron Probe Microanalyses (EPMA)
33 were also carried out. In thin section, fedorite (92 vol.%) is associated to quartz (5 vol.%) and
34 other minor phases (each < 1 vol.%). The morphogenetic features of minerals and their
35 paragenetic associations in the thin section allowed us to determine the sequence of mineral
36 crystallization from early to late ones: aegirine, apatite, amphibole, fedorite, microcline, rutile,
37 quartz, pectolite, and calcite. The crystal chemical formula of fedorite is:
38 $(\text{Na}_{1.56}\text{K}_{0.72}\text{Sr}_{0.12})_{\Sigma=2.40}(\text{Ca}_{4.42}\text{Na}_{2.54}\text{Mn}_{0.02}\text{Fe}_{0.01}\text{Mg}_{0.01})_{\Sigma=7.00}(\text{Si}_{15.98}\text{Al}_{0.02})_{\Sigma=16.00}(\text{F}_{1.92}\text{Cl}_{0.09})_{\Sigma=2.01}(\text{O}_{3}$
39 $7.93\text{OH}_{0.07})_{\Sigma=38.00}\cdot 3.2\text{H}_2\text{O}$. The TG curve provides a total mass decrease of ~5.5%, associated to
40 the release of H₂O, H and F from 25 to 1050 °C. Fedorite crystallizes in the $P\bar{1}$ space group and
41 has: $a = 9.6458(2)$, $b = 9.6521(2)$, $c = 12.6202(4)$ Å, $\alpha = 102.458(2)$, $\beta = 96.225(1)$, $\gamma =$
42 $119.902(1)^\circ$ and cell volume, $V = 961.69(5)$ Å³. The HT-SCXRD was carried out in air in the
43 25-600 °C T range. Overall, a continuous expansion of the unit cell volume was observed
44 although the c cell dimension slightly decreases from 25 to 600 °C. Structure refinements
45 indicated that the mineral undergoes a dehydration process with the loss of most of the interlayer
46 H₂O molecules from 25 to 300 °C. The HT-FTIR spectra confirmed that fedorite progressively
47 dehydrates until 700 °C.

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52 **Keywords:** fedorite, petrographic analysis, not-ambient, *in situ* HT-SCXRD, *ex situ* HT-FTIR.

53

54 **Introduction**

55 Fedorite, $A_{2-3}M_7T_{16}O_{38}X_2 \cdot nH_2O$, where $A = Na, K, Ba, Ca$; $M = Ca, Na, Mn^{2+}, Fe^{2+}$; $T = Si, Al,$
56 Ti ; $X = F, Cl, OH$, is a rare mineral occurring in alkaline rocks of Turiy and Murun complexes,
57 Russia (Kukharensko *et al.*, 1965; Konev *et al.*, 1993, 1996). This mineral was included in the
58 group of silicates with stacked modules of sheets of tetrahedra and octahedra (Ferraris, 1997).

59 Hawthorne *et al.* (2019) described fedorite as a sheet silicate with a structural unit consisting of
60 two directions of infinite polymerization of tetrahedra, and an interstitial complex consisting of
61 four Ca^{2+} and Na^+ -octahedral sites with coordinations O_6^{2-} , $O_5^{2-}F^- (\times 2)$ and $O_4^{2-}F_2^-$, as well as
62 sites occupied by Na^+ and K^+ cations with positional disorder and coordinated by O^{2-} and partly
63 disordered H_2O molecules.

64 Difficulties in modelling interlayer cations and H_2O molecules were experienced in the structural
65 studies of fedorite (Sokolova *et al.*, 1983; Joswig *et al.*, 1988; Mitchell and Burns, 2001; Kaneva
66 *et al.*, 2020b). Elongated displacement ellipsoids were, initially, reported for one of the two
67 interlayer cation sites (Joswig *et al.*, 1988). The same sites, affected by strong anisotropy, were
68 split into $A1$ and $A1a$, $A2$ and $A2a$ in structure refinement of the Turiy and Murun fedorite
69 (Mitchell and Burns, 2001). The refinement also showed: correlations between site occupancy
70 factor and displacement parameters for one of the three H_2O sites, labelled $W3$; short distance
71 between $W3$ and $A1a$ sites; short distance between $A1a$ and $A2$ sites. Different hypotheses were
72 reported: $W3$ locally vacant when $A1a$ is occupied; $A2$ locally vacant when $A1a$ is occupied; $A2$
73 containing H_2O if locally occupied (Mitchell and Burns, 2001). Elongated displacement
74 parameters for interlayer cations and oxygen of the H_2O molecules were associated to mixed
75 cationic-anionic site occupancy in fedorite from three districts of the Murun complex (Kaneva *et*
76 *al.*, 2020b). In particular, four K-occupied interlayer sites ($K1$ to $K4$) were identified: one ($K2$) or
77 more of them ($K2$ to $K4$) were split in two or three new positions. From one ($O20w$) to four
78 ($O20w$ to $O24w$) H_2O molecules were also identified in the different analysed samples.

79 The hydration degree of the alkaline cations in the interlayer of sheet silicate phases may
80 strongly affect the chemical and physical properties of these materials, especially in relation to
81 temperature changes. The dehydration process of fedorite was never explored so far.
82 In the present study, data from *in situ* High Temperature Single Crystal X-Ray Diffraction (HT-
83 SCXRD) as well as *ex situ* High Temperature Fourier Transform Infrared Spectroscopy (HT-
84 FTIR) experiments of fedorite are provided. Results from optical microscopy observations,
85 Electron Probe Microanalysis (EPMA), Differential Thermal Analysis (DTA),
86 Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) are also reported.
87 This work is part of an ongoing research activity pointing to enhance the knowledge on the
88 stability of rare Russian alkaline minerals under non ambient conditions (Schingaro *et al.*, 2018;
89 Comboni *et al.*, 2019; Lacalamita *et al.*, 2019).

90

91 **Experimental**

92 *Sample description and petrographic analysis*

93 Fedorite-bearing sample Gav-33 was taken from brookite-quartz-feldspar rocks of the
94 Gavrilovskaya zone (same locality as sample Gav-43 from Kaneva *et al.*, 2020b). The zone is
95 situated at the watershed of the Davan and Atbastakh Rivers, Irkutsk region, Bodaibo district
96 (58°19'51"N 119°5'45"E). The sample is an almost monomineral rock composed of scaly pale
97 pink fedorite (Fig. 1).

98 A thin section ~30 µm thick was studied by the optical petrographic method in transmitted light
99 using Olympus BX-51 polarized microscope. The morphogenetic features of fedorite and its
100 paragenetic associations were investigated, and the sequence of the crystallization was
101 determined from the relationships of minerals (Table 1).

102

103 *Chemical analysis*

104 A fedorite single crystal was embedded in epoxy resin, polished and carbon coated before
105 carrying out electron probe microanalysis. A JEOL JXA-8200 electron microprobe in full
106 wavelength dispersive spectrometry (WDS) mode was used. Operating conditions were: 15 kV
107 accelerating voltage, 5 nA sample current, ~ 1 μm spot size and 40 s counting time. The used
108 standards were: grossular (Si, Al, Ca), omphacite (Na), olivine (Mg), K-feldspar (K), rhodonite
109 (Mn), fayalite (Fe), celestine (Sr), sanbornite (Ba), scapolite (Cl), horneblende (F).
110 A Phi-Rho-Z routine was employed for the conversion from X-ray counts to oxide weight
111 percentages (wt. %).

112

113 *Thermal analysis*

114 Simultaneous differential thermal, thermogravimetric and derivative thermogravimetric analysis
115 (DTA/TG/DTG) were obtained by means of a Seiko SSC 5200 thermal analyzer equipped with
116 an ESS GeneSys Quadstar 422 quadrupole mass spectrometer which allowed the analysis of
117 gases evolved during thermal processes. The measurements were performed both in air at a
118 heating rate of 10 $^{\circ}\text{C}/\text{min}$ in the temperature range 25-1075 $^{\circ}\text{C}$ and in ultrapure helium at 20
119 $^{\circ}\text{C}/\text{min}$ in the heating range 25-1100 $^{\circ}\text{C}$. Mass analyses were done in multiple ion
120 detection mode measuring the m/z ratios (ratio between the mass number and the charge of an
121 ion) 17 to 20 for H_2O and 19 for F.

122

123 *X-ray diffraction analysis*

124 Single crystals of fedorite were selected under an optical microscope and glued on the tip of a
125 glass fiber. The crystal (0.60x0.59x0.05 mm^3) with the best diffraction behavior was used for the
126 *in situ* high temperature X-ray diffraction experiment by means of a Bruker AXS APEX II
127 diffractometer equipped with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a CCD area detector. The
128 measurements were carried out in air from 25 to 600 $^{\circ}\text{C}$ by means of a Bruker AXS FR 559
129 home modified device (Zema *et al.*, 2022). A total of seven data collections were performed;

130 each data collection lasted ca. 11 hours. Before starting a new data collection, the crystal was
131 equilibrated for ca. 30 min. Data reduction was done using the software SAINT (Bruker, 2007);
132 empirical absorption corrections were applied by means of SADABS (Bruker, 2009); structure
133 refinements were performed by means of the program CRYSTALS (Betteridge *et al.*, 2003)
134 using reflections with $I > 3\sigma(I)$ and starting from the atomic coordinates in Kaneva *et al.*
135 (2020b). The structures were all solved in the triclinic space group $P\bar{1}$ (confirming the same
136 space group as found in Kaneva *et al.*, 2020b). Overall scale factor, atomic positions, and atomic
137 displacement parameters were refined, starting from the coordinates of fedorite (Gav-43 sample)
138 in Kaneva *et al.* (2020b). At room temperature all cation and H₂O molecules occupancies were
139 refined, whereas starting from 100 °C only the occupancies of the H₂O molecules were refined.
140 The occupancy of the tetrahedral site was constrained to 1; a restraint (1.00 ± 0.01) on the
141 occupancy of the Na plus Ca occupancies in the octahedral site was used to allow the occupancy
142 of this site to assume values higher or lower than 1. The attempts to anisotropically refine the
143 thermal ellipsoids of the interlayer Na cations and of the oxygen of the H₂O molecules result to
144 instable refinements. As a consequence, they were isotropically modeled. The analysis of the
145 difference-Fourier maps evidenced the presence of a residual electron density peak of about 1
146 $e^{-}/\text{\AA}^3$ which may be considered as a consequence of the positional disorder of Na atoms. The
147 disorder modeling does not lead to a significant improvement of the refinement. Therefore, it
148 was not included in the final structure model. The effective coordination numbers (ECoN) of the
149 cations were calculated using the ECoN21 Software (Gheorghe, 2022) using a maximum
150 coordination radius of 4 Å.

151 Cif files of the refined crystal structures are submitted as supplementary material together with
152 details on structure analysis (Tables S1, S2).

153

154 *Fourier Transform Infrared Spectroscopy*

155 The infrared absorption spectra of fedorite were measured using an FT-801 spectrometer (Simex,
156 Novosibirsk, Russia). Powdered samples were mixed with anhydrous KBr, pelletized, and
157 analyzed at a resolution of 1 cm^{-1} . A total of 32 scans were collected in the wavenumber range
158 500 to 4000 cm^{-1} . The IR spectrum of an analogous pellet of pure KBr was used as a reference.
159 IR variable temperature measurement, aimed at the study of fedorite dehydration were carried
160 out *ex-situ*, in the temperature range 25-700 °C, in steps of 50 °C following the procedure
161 described in Kaneva *et al.* (2020a) and Sapozhnikov *et al.* (2021) and here briefly summarized.
162 Fedorite and KBr were ground in a crucible, held at a given temperature for 5 min in a muffle
163 furnace, and then quenched to room temperature. Afterwards, two pressed pellets were prepared:
164 one consisting of a mixture of fedorite and KBr and another one of the pure KBr. Next, powders
165 of both samples were heated to the next temperature in the interval from 25–700 °C, and the
166 procedure was repeated. All pressed pellets were prepared and measured under the same
167 conditions of low relative humidity (<20%). In this way, water adsorption in heated samples can
168 be neglected.

169

170 **Results and Discussion**

171 *Petrography*

172 The host rock has a is holocrystalline coarse- and medium-grained structure and uniform texture
173 (massive). In the thin section, the sample mainly consists of fedorite (92 vol.%), with minor
174 components such as quartz (5 vol.%), microcline (less than 1 vol.%), aegirine (less than 1
175 vol.%), amphibole (less than 1 vol.%), calcite (less than 1 vol.%), pectolite (less than 1 vol.%);
176 accessory minerals are apatite and rutile (Fig. 2).

177 Fedorite is represented by elongated scaly subhedral grains up to $5.5 \times 1.2 \times 1.0\text{ mm}$ in size,
178 showing perfect cleavage along {001}. Small euhedral crystals of aegirine (0.07×0.01 – $0.07 \times$
179 0.05 mm), amphibole (0.04×0.02 – $0.10 \times 0.04\text{ mm}$), and apatite (0.02×0.05 – $0.04 \times 0.09\text{ mm}$)
180 were found as inclusions in fedorite (Fig. 2c, d, k, l) which indicates its earlier crystallization

181 (Table 1). Fedorite grains are slightly cataclastic and can be replaced by secondary minerals
182 (probably, pectolite) along the cleavage and the cracks of the cataclase. Needle-like aegirine
183 grains are often located along the cleavage of the mineral (Fig. 2c). Larger subhedral aegirine
184 grains (0.4×0.1 mm) are located at the boundary between fedorite and quartz grains (Fig. 2). In
185 thin section, aegirine grains exhibit pleochroism (from yellowish-green to blue-green).
186 Larger subhedral grains of amphibole (0.2×0.15 – 0.07×0.05 mm) and apatite (0.4×0.3 – $0.1 \times$
187 0.15 mm) also occur in xenomorphic relation to fedorite (Fig. 2g, j, l). In the thin section,
188 amphibole grains are pleochroic from light green to gray, and the interference colors have an
189 unusual ink color. Microcline grains up to 0.4×0.3 mm in size and anhedral quartz grains are
190 also xenomorphic in relation to fedorite (Fig. 2a, b, d-g, i).
191 In turn, quartz is xenomorphic with respect to the microcline. The grain sizes of quartz vary from
192 0.1×0.15 to 0.5×0.2 mm. Quartz contains inclusions of apatite and fedorite crystals up to $0.1 \times$
193 0.25 mm and 0.15×0.1 mm in size, respectively. At the grain boundary of quartz, single
194 elongated small grains of rutile up to 0.02×0.05 mm in size were found.
195 Calcite is rare. Its grains are quite small and do not exceed 0.05×0.05 mm. They are
196 xenomorphic in relation to fedorite.
197 Fibrous grains of pectolite form fan-shaped aggregates and, possibly, were formed as a result of
198 hypergene processes.

199

200 *Chemical composition*

201 The average chemical composition of fedorite (wt%), determined over ten spots, is: SiO₂ (65.74),
202 Al₂O₃ (0.07), CaO (16.74), SrO (0.83), MnO (0.11), MgO (0.02), FeO (0.03), BaO (0.01), Na₂O
203 (8.58), K₂O (2.28), F (2.46), Cl (0.21). The crystal chemical formula, calculated on the basis of
204 $16(\text{Si}+\text{Al})$ and assuming the H₂O content derived by the structure refinement (see below), is:

205 $(\text{Na}_{1.56}\text{K}_{0.72}\text{Sr}_{0.12})_{\Sigma=2.40}(\text{Ca}_{4.42}\text{Na}_{2.54}\text{Mn}_{0.02}\text{Fe}_{0.01}\text{Mg}_{0.01})_{\Sigma=7.00}(\text{Si}_{15.98}\text{Al}_{0.02})_{\Sigma=16.00}$

206 $(F_{1.92}Cl_{0.09})_{\Sigma=2.01}(O_{37.93}OH_{0.07})_{\Sigma=38.00} \cdot 3.2H_2O$. In the literature it is found that the number of H₂O
207 molecules may vary from 0.6 gpfu (sample Irk-53 in Kaneva *et al.*, 2020b) to 3.69 gpfu (Turiy
208 fedotite in Mitchell and Burns, 2001). In addition, the Na/K ratio of our sample is close to that of
209 fedorite from Murun in Mitchell and Burns (2001) whereas fedorite in Kaneva *et al.* (2020b)
210 shows an enrichment in K atoms.

211

212 *TG/DTA/DTG data*

213 The TG-DTA-DTG experiments in air and He provided similar results (compare Fig. 3 and Fig.
214 S1). The DTA curve showed an exothermic peak at about 950 °C which may be associated to the
215 breakdown of fedorite. The thermogravimetric analysis, instead, exhibits a weight mass decrease
216 of about 4% (650-700 °C T range) and 1.5% (1000-1050 °C). The former mass decrease is
217 compatible with the theoretical one associated to the loss of 3.4 H₂O gpfu. This value of the H₂O
218 content is close to that (3.2 H₂O gpfu) derived from the X-ray data (see below). The weight loss
219 above 900 °C, instead, may be ascribed to the loss of fluorine as indicated by the measurement in
220 the He atmosphere (Fig. S1).

221

222 *Crystal structure at room temperature*

223 Room temperature refinement of Gav-33 sample of fedorite was carried out in $P\bar{1}$ space group
224 and converged to $R_1 = 3.29\%$, $wR_2 = 4.01\%$ (Table 2). Unit cell parameters and cell volume (a
225 $= 9.6458(2)$, $b = 9.6521(2)$, $c = 12.6206(4)$ Å, $\alpha = 102.458(2)$, $\beta = 96.2250(10)$, $\gamma = 119.902(1)^\circ$,
226 $V = 961.69(5)$ Å³, Table 2) are almost identical to those reported in literature (Mitchell and
227 Burns, 2001; Kaneva *et al.* 2020b). Atomic coordinates, site occupancy, and mean bond
228 distances at 25 °C are reported in Tables 3 and 4, respectively, in comparison with those
229 collected at 400 °C. A sketch of the mineral structure is, instead, reported in Fig. 4a, b. It is
230 characterized by eight symmetry independent tetrahedra ($T1$ to $T8$) which form regular
231 hexagonal rings of downward-pointing tetrahedra and distorted hexagonal rings of four

232 downward-pointing tetrahedra and two upward-pointing tetrahedra ($T1$ and $T6$) extending in the
233 ab plane (Fig. 4b). The $T1$ and $T6$ tetrahedra which share the apical oxygen atom, O19, show
234 slightly short mean tetrahedral distances due to the low values of the Si-O19 individual distances
235 (Fig. 4a; Table 4). The structure of fedorite also consists of four symmetry independent
236 octahedra ($M1$ to $M4$) with mixed Na, Ca occupancy. Specifically, X-ray site-scattering
237 refinement indicated a preferential partitioning of Na for the octahedral $M1$ site, an almost equal
238 distribution of Na and Ca in $M2$, and the prevalence of Ca in $M3$ and $M4$ sites (Table 3). Similar
239 octahedral site occupancies were reported for other fedorite from Murun by Kaneva *et al.*
240 (2020b). The $M1$ octahedron which has $O_4^{2-}F_2^-$ coordination, exhibits the longest mean
241 octahedral bond distance and the highest bond length distortion (BLD_{M2} parameter) whereas the
242 $M3$ polyhedron, which is not coordinated by F atoms, is more regular (Table 4).

243 The interlayer site of the studied fedorite is occupied by four cation sites ($Na5$ to $Na8$) with the
244 $Na5$ showing a mixed Na/K occupancy whereas the $Na6$ to $Na8$ sites only contain Na atoms.
245 These cations coordinate five H₂O molecules, labelled from O20w to O24w, Table 3 and Fig. 4b.
246 The refinement also showed short K1-O20w, Na6-O21w, Na7-O24w, Na8-O22w, Na8-O23w
247 distances (2.041(4), 1.42(3), 1.50(2), 0.445(8), 2.01(3) Å, respectively) indicating a mixed
248 cation/anion occupancy. Short distances between H₂O molecules (1.41-1.87 Å) point out to a
249 statistical distribution of the molecules.

250 Similar octahedral site occupancies but different interlayer composition were reported for other
251 fedorite from Murun by Kaneva *et al.* (2020b). In the literature samples, indeed, the interlayer
252 site is K-occupied and the K atoms, which are also affected by positional disorder, coordinate
253 from one to five H₂O molecules.

254

255 *Crystal structure modifications and vibrational features upon heating*

256 The thermal expansion of the fedorite structure proceeds from room temperature to 600 °C
257 without change in symmetry ($P\bar{1}$) and with a variation of the cell volume which encompasses

258 the expansion along the *a* and *b*-axis but also the decrease of the *c* cell dimension (Fig. 5; Table
259 2). With increasing temperature, the mineral progressively dehydrated up to 300 °C when
260 fedorite lost most of the H₂O molecules as testified by the trend of the occupancies of O20w to
261 O24w sites (Tables 3, S1). In particular, the occupancy of O22w which is very close to the *Na*8
262 interlayer cation at RT (Fig. 6a), indicates that the relevant H₂O molecule is lost at 100 °C. The
263 O21w, O23w and O24w molecules, which are located in the *ab* plane around the O20w, tend to
264 shift toward the latter site (Fig. 6a-e; Table 5) which indeed is the only one occupied at $T \geq 400$
265 °C (Table 3, S1). Fig. 7 shows that the total mean atomic numbers of the H₂O sites progressively
266 decrease with the temperature whereas the electron density of the O20w increases at $T > 300$ °C
267 as a consequence of the H₂O migration from the O21w, O23w and O24w sites towards the
268 O20w. At 400 °C a reduction of the effective coordination number (ECoN parameter, from 11 to
269 8) of the Na cations coordinating the H₂O molecules was also observed (Table 4).

270 The dehydration process proceeds from RT up to 400 °C causing a distortion of the hexagonal
271 rings of downward-pointing tetrahedra as testified by the shortening of the O8-O17 and O7-O15
272 internal diagonal distances (Fig. 6a, e; Table 5). The cations in the *Na*5/*K*1 site shift along the *c*
273 axis direction by moving away from the O20w and toward the F atoms, with a consequent
274 remarkable lengthening of the *Na*/*K*-O20w distance which is balanced by the shortening of the
275 *Na*/*K*-F distance (Fig. S2; Tables 4, S2). On the contrary, the cations in the *Na*6, *Na*7 and *Na*8
276 interlayer sites seem to move substantially in the *ab* plane, being their *z* coordinates almost
277 unchanged during heating (Table 3, S1). In particular, they progressively increase their distance
278 from the O20w (Fig. S2). In addition, the cation in *Na*6 moves away from the O10 atom and
279 approximates the O14; the cation in *Na*7 moves away from the O16 and O17 and shifts toward
280 the O11 and O13; the cation in *Na*8 moves from the O7 and O15 atom toward the O16, O18 and
281 O19 oxygens (Fig. S2, 6f). This also results in the shortening of the distances between equivalent
282 Na cations (Fig. 6f).

283 Finally, structure refinements of the partially dehydrated fedorite (from 400 to 600 °C) evidence
284 that no significant geometric modifications of the tetrahedral and octahedral sheets were induced
285 by the heating process, since quite similar values were obtained for tetrahedral and octahedral
286 mean distances and geometrical parameters (Tables 4, S2).

287 The infrared spectra of the fedorite sample annealed at different temperatures (from 25 to 700
288 °C) are given in Fig. 8. The group of peaks observed at 1119, 1030, 790, 618 cm^{-1} may be
289 assigned to the asymmetric and symmetric Si–O stretching modes of the SiO_4 tetrahedra.

290 The peak at 618 cm^{-1} in the studied sample is slightly shifted in comparison with the same peak
291 in Gav-43 and Irk-53 samples (615 cm^{-1} ; Kaneva *et al.* 2020b). The energy of bending vibration
292 of SiO_4 at 615 cm^{-1} is slightly increased in the studied sample which contains higher H_2O
293 concentration. The same behavior of SiO_4 bending vibrations has been observed in elpidite
294 samples in Bogdanov *et al.* (2021).

295 Intensities of H–O–H asymmetric and symmetric stretching vibrations in the region 3000–3700
296 cm^{-1} (in the inset of Fig. 8) and bending ones at 1627 cm^{-1} decreased during annealing. This
297 indicates that the fedorite sample was losing H_2O molecules. Also the peak at 790 cm^{-1} in initial
298 sample shifts to 796 cm^{-1} in annealed at 700 °C sample when the fedorite has lost almost all the
299 H_2O molecules. It could be due to slightly change in Si–O–Si angles during annealing (Shendrik
300 *et al.*, 2021).

301 The region 3000-3700 cm^{-1} of absorption spectrum related to stretching vibrations of H_2O
302 molecules has a complicated shape (Fig. 8). Six peaks at 3177, 3429, 3549, 3588, 3635, and
303 3656 cm^{-1} can be clearly seen in the sample at room temperature. Such peaks are similar to those
304 found in the Irk-53 sample (Kaneva *et al.* 2020b). Three groups of peaks can be distinguished on
305 the basis of the behavior during heating (Figs 8, 9). Group 1 includes the 3588 and 3656 cm^{-1}
306 peaks. The intensity of these peaks decreases as the temperature increases, becomes negligible at
307 temperatures above 327 °C (Fig. 9). Group 2 includes the 3177, 3429, 3549, and 3635 cm^{-1} .

308 Their intensity gradually decreases upon annealing and becomes negligible above 627 °C (Fig.

309 9). Group 3 includes 3576 and 3650 cm^{-1} peaks. The latter start to be observed at above 150 °C
310 and show the maximum intensity at 350 °C (Fig. 9). Further annealing at higher temperatures
311 leads to a decrease in their intensity. Peaks belonging to Group 1 and 3 are sharp and may be
312 attributed to OH-anions in different positions or to O–H stretching vibrations (hydrogen bonds of
313 medium strengths). Group 2 bands may be attributed to H₂O molecules with a strong hydrogen
314 bond. The trends of the band intensities (Fig. 9) in the FTIR spectra may be explained by taking
315 into account the results of the HT-SXRD structure refinements. Specifically, the quick
316 decrement of the intensity observed for the Group 1 agrees with the reduction of the total water
317 means atomic numbers until ~ 300 °C (Fig. 7). The intensity variation of the Group 3 seems to
318 describe the migration of the H₂O molecules at $T \geq 100$ °C (Fig. 6). Finally, the gradual
319 decreasing of the band intensity of Group 2 well represents the evolution of the dehydration
320 process affecting the fedorite up to $T \sim 600$ °C as described above (see the *Crystal structure*
321 *modifications upon heating* section).

322

323 **Conclusions**

324 The combination of thermal, *in situ* HT-SCXRD and *ex situ* HT-FTIR analyses allowed to detail
325 the thermal behavior, and specifically, the dehydration process of fedorite from Murun massif.
326 The mineral contains about 3 H₂O gpfu which occupy five different crystallographic sites (O20w
327 to O24w) in the structure refined at room temperature, while at 600 °C only the O20w resulted
328 occupied. Fedorite underwent thermal expansion in the whole temperature range (25-600 °C)
329 explored by XRD with a preferential dilatation along the *a* and *b* axes while a decrement of the *c*
330 cell parameter was a consequence of the dehydration process. All the used analytical techniques
331 testified for a continuous dehydration reaction up to $T \sim 600$ °C whereas the complete loss of
332 H₂O molecules at 650-700 °C was highlighted by the TG curve. The combination of the XRD
333 and FTIR results allowed to detail the features of the partial dehydrated structures. In particular,
334 one H₂O molecule (O22w) early left the interlayer site whereas the reduction in concentration of

335 the remaining molecules rapidly proceeded up to $T \sim 300$ °C. This process was accompanied by
336 the migration of the molecules in O21w to O24w toward the inversion center (O20w) of the
337 crystal structure. The dehydration also caused the decrease in the coordination of the interlayer
338 Na cations which yielded their shift toward their symmetry equivalents. The release of the F
339 atoms occurred above 700 °C (TG curve) whereas the breakdown of the structure at about 1000
340 °C was pointed out by the DTA curve.

341

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351

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353 please visit

354

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356

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407

408 **FIGURE CAPTIONS**

409 **Fig. 1.** Sample of fedorite from the Gavrilovskaya zone (sample Gav-33): (a) unpolished sample;
410 (b) polished sample.

411 **Fig. 2.** Thin section image of sample Gav-33 in transmitted light. (a, d, e, g, i, l) polarizers are
412 parallel; (b, c, f, h, j, k) polarizers are crossed. The interference color corresponds to a thickness
413 of thin section ($\sim 30 \mu\text{m}$).

414 **Fig. 3.** Differential thermal analysis (DTA, black line), thermogravimetric analysis (TG, blue
415 line), and the TG first derivative (DTG, red line) of Gav-33 sample measured in air.

416 **Fig. 4.** (a) Crystal structure of the fedorite sample, Gav-33; (b) a detail, as seen along [001], of
417 the tetrahedral (orange), octahedral (blue) and of the interlayer site which is occupied by Na^+
418 (dark yellow) and K^+ (light yellow) cations. Oxygen and fluorine atoms are represented in red
419 and green, respectively.

420 **Fig. 5.** Normalized unit cell parameters and volume of the studied fedorite *versus* temperature.
421 a_0 , b_0 , c_0 and V_0 are cell parameters and volume at room temperature, respectively. The size of
422 the symbols is larger than the associated esd's.

423 **Fig. 6.** (a-e) Interlayer cavity of fedorite from refined structure in the RT-600 °C T range; (f)
424 extended interlayer cavity view at 400 °C. Colors as reported in Fig. 4; gray arrows indicate the
425 shift of Na cations with the temperature.

426 **Fig. 7.** Mean atomic numbers (m.a.n.'s, e^-) of the H_2O molecules *versus* temperature.

427 **Fig. 8.** IR absorption spectra of fedorite annealed at different temperatures. In the inset, the
428 region of O-H stretching vibrations is given.

429 **Fig. 9.** Temperature dependence as a function of the relative intensity of IR absorption of
430 different OH stretching vibrations of annealed fedorite sample.