

1 **Revision 1**

2 **Oxy-schorl, $\text{Na}(\text{Fe}^{2+}_2\text{Al})\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$, a new mineral from Zlatá Idka, Slovak**
3 **Republic and Příbyslavice, Czech Republic**

4
5 Peter Bačík^{1*}, Jan Cempírek^{2,3}, Pavel Uher¹, Milan Novák⁴, Daniel Ozdín¹, Jan Filip⁵, Radek
6 Škoda⁴, Karel Breiter⁶, Mariana Klementová⁷ and Rudolf Ďud'a⁸

7
8 ¹Department of Mineralogy and Petrology, Comenius University, Mlynská dolina, 842 15
9 Bratislava, Slovakia

10 ²Department of Mineralogy and Petrography, Moravian Museum, Zelný trh 6, 659 37 Brno,
11 Czech Republic

12 ³Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia,
13 6339 Stores Road, Vancouver, BC, V6T 164 Canada

14 ⁴Department of Geological Sciences, Masaryk University, Kotlářská 2, 611 37 Brno, Czech
15 Republic

16 ⁵Regional Centre of Advanced Technologies and Materials, Palacký University in Olomouc,
17 17. listopadu 12, 771 46 Olomouc, Czech Republic

18 ⁶Geological Institute of the Academy of Science of Czech Republic, v.v.i., Rozvojová 269,
19 165 00 Praha 6, Czech Republic

20 ⁷Institute of Physics of the AS CR, v.v.i., Na Slovance 2, 182 21 Praha 8, Czech Republic

21 ⁸Bystrická 87, 040 11 Košice, Slovakia

22 *E-mail: bacikp@fns.uniba.sk

23
24 **ABSTRACT**

25 Oxy-schorl (IMA 2011-011), ideally $\text{Na}(\text{Fe}^{2+}_2\text{Al})\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$, a new
26 mineral species of the tourmaline supergroup, is described. In Zlatá Idka, Slovak Republic
27 (type locality), fan-shaped aggregates of greenish black acicular crystals ranging up to 2 cm in
28 size, forming aggregates up to 3.5 cm thick were found in extensively metasomatically altered
29 metarhyolite pyroclastics with Qtz+Ab+Ms. In Příbyslavice, Czech Republic (co-type
30 locality), abundant brownish black subhedral, columnar crystals of oxy-schorl, up to 1 cm in
31 size, arranged in thin layers, or irregular clusters up to 5 cm in diameter, occur in a foliated
32 muscovite-tourmaline orthogneiss associated with Kfs+Ab+Qtz+Ms+Bt+Grt. Oxy-schorl
33 from both localities has a Mohs hardness of 7 with no observable cleavage and parting. The
34 measured and calculated densities are 3.17(2) and 3.208 g cm⁻³ (Zlatá Idka) and 3.19(1) and

35 3.198 g cm⁻³ (Přibyslavice), respectively. In plane polarized light, oxy-schorl is pleochroic –
36 *O* = green to bluish-green, *E* = pale yellowish to nearly colorless (Zlatá Idka) and *O* = dark
37 greyish-green, *E* = pale brown (Přibyslavice), uniaxial negative, $\omega = 1.663(2)$, $\epsilon = 1.641(2)$
38 (Zlatá Idka) and $\omega = 1.662(2)$; $\epsilon = 1.637(2)$ (Přibyslavice). Oxy-schorl is trigonal, space group
39 *R3m*, *Z*=3, *a* = 15.916(3) Å, *c* = 7.107(1) Å, *V* = 1559.1(4) Å³ (Zlatá Idka) and *a* = 15.985(1)
40 Å, *c* = 7.154(1) Å, *V* = 1583.1(2) Å³ (Přibyslavice). The composition (average of 5 electron
41 microprobe analyses from Zlatá Idka and 5 from Přibyslavice) is (in wt.%): SiO₂ 33.85
42 (34.57), TiO₂ <0.05 (0.72), Al₂O₃ 39.08 (33.55), Fe₂O₃ not determined (0.61), FeO 11.59
43 (13.07), MnO <0.06 (0.10), MgO 0.04 (0.74), CaO 0.30 (0.09), Na₂O 1.67 (1.76), K₂O <0.02
44 (0.03), F 0.26 (0.56), Cl 0.01 (<0.01), B₂O₃ (calc.) 10.39 (10.11), H₂O (from the crystal-
45 structure refinement) 2.92 (2.72), sum 99.29 (98.41) for Zlatá Idka and Přibyslavice (in
46 parenthesis). A combination of EMPA, Mössbauer spectroscopy and crystal-structure
47 refinement yields empirical formulae
48 (Na_{0.591}Ca_{0.103}□_{0.306})_{Σ1.000}(Al_{1.885}Fe²⁺_{1.108}Mn_{0.005}Ti_{0.002})_{Σ3.000}(Al_{5.428}Mg_{0.572})_{Σ6.000}(Si_{5.506}Al_{0.494})_{Σ6}
49 _{.000}O₁₈(BO₃)₃(OH)₃(O_{0.625}OH_{0.236}F_{0.136}Cl_{0.003})_{Σ1.000} for Zlatá Idka, and
50 (Na_{0.586}Ca_{0.017}K_{0.006}□_{0.391})_{Σ1.000}(Fe²⁺_{1.879}Mn_{0.015}Al_{1.013}Ti_{0.093})_{Σ3.000}(Al_{5.732}Mg_{0.190}Fe³⁺_{0.078})_{Σ6.000}(Si
51 _{5.944}Al_{0.056})_{Σ6.000}O₁₈(BO₃)₃(OH)₃(O_{0.579}F_{0.307}OH_{0.115})_{Σ1.000} for Přibyslavice. Oxy-schorl is
52 derived from schorl end-member by the AlOFe₋₁(OH)₋₁ substitution. The studied crystals of
53 oxy-schorl represent two distinct ordering mechanisms: disorder of R²⁺ and R³⁺ cations in
54 octahedral sites and all O ordered in the *W* site (Zlatá Idka), and R²⁺ and R³⁺ cations ordered
55 in the *Y* and *Z* sites and O disordered in the *V* and *W* sites (Přibyslavice).

56

57 **Keywords:** oxy-schorl, tourmaline-supergruop minerals, new mineral, electron
58 microanalysis, crystal-structure refinement, Přibyslavice, Zlatá Idka

59

60

INTRODUCTION

61

62 Minerals of tourmaline-supergruop are common in many geological environments.
63 Complexity of their structure, variability of structural sites and chemical composition are
64 manifested in a relatively large number of mineral species (Henry et al. 2011). Oxy-schorl,
65 ideally Na(Fe²⁺₂Al)Al₆Si₆O₁₈(BO₃)₃(OH)₃O, is a new member of the alkali group and oxy-
66 series of the tourmaline supergruop (sensu nomenclature of Henry et al. 2011). The coupled
67 general substitution ${}^Y R^{2+} + {}^W(OH) \leftrightarrow {}^Y Al + {}^W O$ derived from ideal schorl
68 NaFe²⁺₃Al₆Si₆O₁₈(BO₃)₃(OH)₃OH and leading to the ideal oxy-schorl was discussed already

69 by Foit and Rosenberg (1977); Povondra (1981), Povondra et al. (1985, 1987) and Foit (1989)
70 published several chemical analyses of tourmalines corresponding to oxy-schorl including
71 samples from the co-type locality Příbyslavice (Povondra et al. 1987). However, the term
72 oxy-schorl was first introduced by Hawthorne and Henry (1999). Subsequently, oxy-schorl
73 was described from several localities worldwide (e.g., Henry and Dutrow 2001, Novák et al.
74 2004, Baksheev et al. 2011). Finally, oxy-schorl was defined as a potential new species of the
75 tourmaline supergroup in the recent tourmaline nomenclature (Henry et al. 2011). Oxy-schorl
76 is likely quite a common mineral species; however, many tourmaline compositions are close
77 to the simplified formula $(\text{Na}_{0.5}\square_{0.5})\text{Fe}^{2+}_2\text{AlAl}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{OH}_{0.5}\text{O}_{0.5})$ (see e.g.,
78 Povondra 1981, Foit 1989, Novák et al. 2004) and owing to problems with the determination
79 of H (and other light elements), exact classification of such schorlitic tourmalines is
80 complicated.

81 Oxy-schorl was approved by the Commission on New Minerals, Nomenclature and
82 Classification of the International Mineralogical Association under the number IMA 2011–
83 011. The holotype material from the type locality (Zlatá Idka, Slovak Republic) is preserved
84 in the collection of the East-Slovak Museum, Košice, Slovakia (specimen number G-12760),
85 and in the collection of Department of Mineralogy and Petrology, Comenius University,
86 Bratislava, Slovakia (specimen number 7279). Oxy-schorl from co-type locality (Příbyslavice,
87 Czech Republic) is deposited in the collections of the Department of Mineralogy and
88 Petrography, Moravian Museum, Brno, Czech Republic, specimen number B10521. We
89 provide here a description of physical, chemical and structural characteristics of oxy-schorl as
90 a new mineral species.

91

92 OCCURRENCE AND PHYSICAL PROPERTIES

93

94 Oxy-schorl was found in fracture fillings cutting altered metarhyolite pyroclastics, in the
95 abandoned Marianna adit, ca 2.5 km WNW from Zlatá Idka village (48°46'7"N, 20°57'50"E),
96 Slovak Ore Mountains (Slovenské Rudohorie), near Košice, eastern Slovakia. The acid
97 metapyroclastic rocks of Middle Ordovician age belong to the Bystrý Potok Formation of the
98 Gelnica Group, Gemeric Superunit, Central Western Carpathians (Vozárová et al. 2010).
99 Associated minerals of the host-rock include quartz, albite and muscovite. Oxy-schorl is
100 probably a product of interaction between the metarhyolite pyroclastics and boron-enriched,
101 hydrothermal fluids generated from adjacent Permian tourmaline-bearing leucogranites. Oxy-
102 schorl from Zlatá Idka occurs in fan-shaped aggregates of greenish black acicular crystals

103 ranging up to 2 cm in size, with aggregates up to 3.5 cm across. Tourmaline aggregates
104 display chemical zoning in back-scattered electron (BSE) images (Fig. 1), locally with more
105 Mg-rich (dravite to oxy-dravite) and also *X*-site vacant composition (“□-Fe-O root name”
106 according to Henry et al., 2011) but oxy-schorl composition prevails.

107 The second occurrence of oxy-schorl is in a foliated muscovite-tourmaline orthogneiss
108 at Příbyslavice (Tisá skála outcrop, ~1 km ENE from Příbyslavice, 49°50'48"N, 15°25'1"E)
109 near Kutná Hora, Central Bohemia Region, Czech Republic. The host Lower Palaeozoic
110 muscovite-tourmaline alkali-feldspar granite was metamorphosed during the Variscan
111 orogeny in the amphibolite facies (Breiter *et al.*, 2010). The orthogneiss is composed of K-
112 feldspar (orthoclase perthite), albite, quartz, muscovite, biotite, garnet and apatite with
113 accessory zircon, magnetite, pyrite and ilmenite. Oxy-schorl from Příbyslavice formed as a
114 primary magmatic mineral of the granite, but its composition was influenced by the later
115 metamorphic processes (e.g., Povondra et al. 1987, 1998). It forms abundant subhedral,
116 columnar homogeneous crystals, up to 1 cm in size, arranged in thin layers, or irregular
117 clusters up to 5 cm in diameter.

118 Oxy-schorl from both localities has vitreous luster and is translucent in thin edges, non-
119 fluorescent and paramagnetic. Its Mohs hardness is 7, it is brittle and has conchoidal fracture;
120 cleavage and parting were not observed. The streak is pale grey. The density was measured
121 using a pycnometric method as 3.17(2) and 3.19(1) g cm⁻³; calculated density using empirical
122 formula and unit-cell data yields 3.208 and 3.198 g cm⁻³ for oxy-schorl from Zlatá Idka and
123 Příbyslavice, respectively. Oxy-schorl is negative uniaxial with the following optical
124 properties: $\omega = 1.663(2)$, $\epsilon = 1.641(2)$, birefringence: 0.022 (589.9 nm) in Zlatá Idka and $\omega =$
125 $1.662(2)$; $\epsilon = 1.637(2)$; birefringence: 0.025 (589.9 nm) in Příbyslavice: At both localities,
126 oxy-schorl has distinct pleochroism; *O* = green to bluish-green, *E* = pale yellowish to nearly
127 colorless (Zlatá Idka) and *O* = dark greyish-green, *E* = pale brown (Příbyslavice).

128

129

ANALYTICAL METHODS

130

Chemical composition

132 Representative chemical analyses (5 from Zlatá Idka, 5 from Příbyslavice) were carried
133 out on crystals used for structure refinement using a CAMECA SX100 electron microprobe
134 (WDS mode, 15 kV, 10 and 20 nA, 5 μ m beam diameter) and the following standards:
135 almandine (SiK α , FeK α), titanite (TiK α), sanidine (AlK α , KK α), chromite (CrK α), vanadinite
136 (VK α), spessartine (MnK α), MgO (MgK α), grossular (CaK α), albite (NaK α), topaz (FK α) and

137 NaCl ($ClK\alpha$). Detection limits of the measured elements vary between 0.01 and 0.05 wt.%.
138 Formulae of tourmalines were calculated on a basis of 15 $Y+Z+T$ cations. H_2O was calculated
139 on the basis of electroneutral formula and structure refinement results. The presence of H_2O
140 was confirmed by IR spectroscopy. B_2O_3 was calculated from ideal formulae since the
141 structure refinement data indicate full occupancy of the B -site and absence of ^{14}B in the T site.
142 Ti and Cl were below detection limits (0.05 and 0.01 wt.%, respectively). Analytical data are
143 given in Table 1. The content of Li in oxy-schorl from Zlatá Idka was determined by LA-ICP-
144 MS analysis with a laser ablation system UP 213 (New Wave, USA) and quadrupole ICP-MS
145 spectrometer Agilent 7500 CE (Agilent, Japan), at the Central European Institute of
146 Technology, Masaryk University, Brno. It was always lower than a detection limit which
147 corresponded to 0.04 wt. % Li_2O . Oxy-schorl from Příbyslavice yielded $Li_2O \leq 0.06$ wt. %
148 determined by wet chemical analysis (Povondra et al. 1987).

149

150 **Mössbauer spectroscopy**

151 The ^{57}Fe Mössbauer spectrum of powdered tourmaline (ground under acetone using an
152 agate mortar) was acquired at constant acceleration mode using a ^{57}Co in Rh source at room
153 temperature (293 K), at the Department of Nuclear Physics, Slovak Technical University,
154 Bratislava, Slovakia (Zlatá Idka) and Centre for Nanomaterial Research, Faculty of Science,
155 Palacký University in Olomouc (Příbyslavice). The isomer shift was calibrated against an α -
156 Fe foil at room temperature. Spectra were fitted by Lorentz functions using the NORMOS
157 program (Brand 1997) on the Zlatá Idka sample and CONFIT2000 program (Žák and
158 Jirásková 2006) on the Příbyslavice sample. The fitting results are listed in Table 2.

159

160 **Infrared spectroscopy**

161 The FTIR spectrum of tourmaline from Příbyslavice was recorded using a Nicolet
162 Nexus 670 spectrometer equipped with DTGS detector and XT-KBr beamsplitter. The sample
163 was prepared by mixing 1 mg of powdered sample with 300 mg of KBr (dried beforehand at
164 150 °C) and pressing in an evacuated die at 10 tons. A total of 32 scans in air were carried out
165 for the sample in the wavenumber range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} . The
166 spectrum is shown in Figure 2, and a basic interpretation of the peaks (after Reddy et al. 2007)
167 is listed in Table 3.

168

169 **Thermogravimetric analysis**

170 Thermal decomposition of oxy-schorl from Zlatá Idka and Příbyslavice was studied in
171 an inert atmosphere (Ar) using a simultaneous thermal analyzer (STA 449 C Jupiter, Netzsch)
172 including both thermogravimetric analysis (TGA) and differential scanning calorimetry
173 (DSC) in the range of 30 - 1100 °C on the Department of Inorganic Chemistry, Comenius
174 University in Bratislava (Zlatá Idka) and Department of Physics, Palacký University in
175 Olomouc (Příbyslavice). The sample from Zlatá Idka was placed into Pt crucible with lid and
176 dynamically heated with a heating rate of 20 Kmin⁻¹. TG correction: 020/5000 mg, DSC
177 correction: 020/50 mV. The Příbyslavice sample was dynamically heated in open alumina
178 crucible with a heating rate of 5 K/min.

179

180

181 **Powder X-ray diffraction**

182 Powder XRD measurements of oxy-schorl from Zlatá Idka were made on the BRUKER
183 D8 Advance diffractometer (Department of Mineralogy and Petrology, Faculty of Natural
184 Sciences, Comenius University in Bratislava, Slovakia) under the following conditions:
185 Bragg-Brentano geometry, Cu anticathode, NiK β filters, accelerating voltage: 40 kV, beam
186 current: 40 mA. Data was obtained by the BRUKER LynxEye detector. The step size was
187 0.01° 2 θ , the step time was 5 s per one step, and the range of measurement was 4 – 65° 2 θ .
188 Measured data was fitted and lattice parameters were refined with DIFFRAC^{plus} TOPAS
189 software (Bruker 2010) using pseudo-Voight function. Indexed diffraction data are listed in
190 Table 4.

191 Powder XRD data for oxy-schorl from Příbyslavice were recorded with a PANalytical
192 X'Pert PRO MPD diffractometer (CoK α radiation) in Bragg-Brentano geometry, equipped
193 with an X'Celerator detector and programmable divergence and diffracted beam anti-scatter
194 slits. Diffraction pattern of the sample on a zero-background Si slide was scanned with a step
195 size of 0.017° in 2 θ range 5-90°. Data were indexed and refined with Stoe WinXPow package
196 (version 1.06), using built-in Treor (Werner et al. 1985) and least-square refinement routines
197 (Stoe and Cie 1999). Indexed diffraction data are listed in Table 5.

198

199 **Crystal structure refinement**

200 Single-crystal X-ray studies were carried out using a 4-circle Oxford Diffraction KM-
201 4/Xcalibur diffractometer with a Sapphire2 (large Be window) CCD detector. The CrysAlis
202 (Oxford Diffraction Ltd) and SHELXTL (PC Version) (Sheldrick 2000) program packages

203 were used for data reduction and structure refinement, respectively, using neutral scattering
204 factors and anomalous dispersion corrections. The structure of oxy-schorl was refined in $R3m$
205 and converged to a final R index of 3.32% for Zlatá Idka and 1.91% for Příbyslavice data.
206 Crystal and refinement details of tourmaline from Zlatá Idka are listed in Table 6, structural
207 data are summarized in Tables 7 to 9 and bond-valence table is presented in Table 10. Crystal
208 and refinement details of tourmaline from Příbyslavice are listed in Table 11 and structural
209 data are summarized in Tables 12 to 14; its bond-valence table is presented in Table 15.

210

211

212

213

RESULTS

214

215 The samples of oxy-schorls from Zlatá Idka and Příbyslavice display some differences in
216 chemical composition and site allocation. A combination of EMPA, Mössbauer spectroscopy
217 and crystal-structure refinement yields following empirical formulae:

218 $(\text{Na}_{0.591}\text{Ca}_{0.103\ 0.306})_{\Sigma 1.000}(\text{Al}_{1.885}\text{Fe}^{2+}_{1.108}\text{Mn}_{0.005}\text{Ti}_{0.002})_{\Sigma 3.000}(\text{Al}_{5.428}\text{Mg}_{0.572})_{\Sigma 6.000}(\text{Si}_{5.506}\text{Al}_{0.494})_{\Sigma 6.000}\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{O}_{0.625}\text{OH}_{0.236}\text{F}_{0.136}\text{Cl}_{0.003})_{\Sigma 1.000}$ and

219
220 $(\text{Na}_{0.586}\text{Ca}_{0.017}\text{K}_{0.006}\square_{0.391})_{\Sigma 1.000}(\text{Fe}^{2+}_{1.879}\text{Mn}_{0.015}\text{Al}_{1.013}\text{Ti}_{0.093})_{\Sigma 3.000}(\text{Al}_{5.732}\text{Mg}_{0.190}\text{Fe}^{3+}_{0.078})_{\Sigma 6.000}(\text{Si}_{5.944}\text{Al}_{0.056})_{\Sigma 6.000}\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3(\text{O}_{0.579}\text{F}_{0.307}\text{OH}_{0.115})_{\Sigma 1.000}$ for oxy-schorl from Zlatá Idka and

221 Příbyslavice, respectively. They are in good agreement with the end-member formula
222 $\text{Na}(\text{Fe}^{2+}_2\text{Al})\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH})_3\text{O}$ requiring SiO_2 35.22, Al_2O_3 34.87, FeO 14.04, Na_2O
223 3.03, B_2O_3 10.20, H_2O 2.64, total 100.00 wt.%. As suggested by the empirical formulae, oxy-
224 schorl from Zlatá Idka is moderately disordered in the octahedral sites, while disorder in oxy-
225 schorl from Příbyslavice is only negligible.

227 The content of OH^- was calculated from electroneutral formula based on the crystal-
228 structure refinement and Mössbauer spectroscopy data. Ferric iron takes only 4 % of all Fe in
229 oxy-schorl from Příbyslavice and it was not detected in the sample from Zlatá Idka. The
230 content of H_2O was also measured using TGA; the TGA curve shows a mass change -2.96 %
231 (Zlatá Idka) and -2.69 % (Příbyslavice) at ca. 950-1020 °C which corresponds to breakdown
232 of the structure and release of water (bound in form of OH^-). Reduced content of ^wOH is also
233 supported by the low intensity of the O–H stretching peak at 3628 cm^{-1} in the infrared
234 absorption spectrum (Fig. 2). With regard to the possible chemical inhomogeneity of the
235 samples (Fig. 1), the calculated H_2O contents were preferred to the TGA results.

236 Both tourmalines slightly differ structurally as represented by lattice parameters: $a =$
237 $15.9074(9) \text{ \AA}$, $c = 7.1039(2) \text{ \AA}$, $V = 1557.4(2) \text{ \AA}^3$ (powder XRD) and $a = 15.916(3) \text{ \AA}$, $c =$
238 $7.107(1) \text{ \AA}$, $V = 1559.1(4) \text{ \AA}^3$ (crystal-structure refinement) for Zlatá Idka and $a =$
239 $15.9865(8)$, $c = 7.1608(3) \text{ \AA}$, $V = 1584.9(2) \text{ \AA}^3$ (powder XRD) and $a = 15.985(1) \text{ \AA}$, $c =$
240 $7.154(1) \text{ \AA}$, $V = 1583.1(2) \text{ \AA}^3$ (crystal-structure refinement) for Příbyslavice. Differences in
241 lattice parameters result from different Fe^{2+} , Fe^{3+} and Al^{3+} occupancies in Y , Z and T sites in
242 both tourmalines.

243 Despite all differences between studied samples, they both belong to alkali group (Fig.
244 3a), they represent oxy species (Fig. 3b) and their contents of Fe and Mg correspond to the
245 composition of oxy-schorl (Fig. 3c).

246

247

DISCUSSION AND CONCLUSIONS

248

249 Oxy-schorl is chemically and structurally related to schorl. The name oxy-schorl has
250 been abundantly used for tourmalines with the composition similar to schorl but containing
251 more than 6.5 *apfu* Al, and O in the W site if known (e.g. Hawthorne and Henry 1999; Henry
252 and Dutrow 2001; Buriánek and Novák 2004, 2007; Novák et al. 2004; Ertl et al. 2010a,
253 2010b; Baksheev et al. 2011; Bosi 2011). Since the current classification of the tourmaline
254 supergroup (Henry et al. 2011) uses ordered formulae for tourmaline classification, it is
255 generally possible to recognize oxy-schorl from electron microprobe data using the
256 approximate limits: $\text{Na} > 0.5 \text{ apfu}$, $\text{Al} > 6.5 \text{ apfu}$, $\text{Fe} > \text{Mg}$ and $\text{F} < 0.5 \text{ apfu}$. However,
257 ordering of ions in the structure of different samples can be variable. In the tourmaline
258 structure the W site is located on the 3-fold axis passing through the unit cell, and surrounded
259 by three Y sites (Hawthorne 1996, 2002). From the crystallographic point of view there are
260 two different possible arrangements: 1) $W = \text{OH}$ or F with valence bond ca. 0.33 vu ; 2) $W = \text{O}$
261 - valence bond is ca. 0.67 vu ($\text{vu} = \text{valence units}$, Hawthorne 1996, 2002). The substitution of
262 O for OH results in the increase of charge requirements in the neighboring Y sites and the
263 substitution of Al for divalent cations, or disorder of divalent and trivalent cations among the
264 octahedral Y and Z sites. If the W site is fully occupied by O, the structural arrangements with
265 3^YR^{2+} or $2^Y\text{R}^{2+} + ^Y\text{R}^{3+}$ cations are less favorable than the arrangements with 3^YR^{3+} or
266 $2^Y\text{R}^{3+} + ^Y\text{R}^{2+}$ (Hawthorne 2002). Therefore, in natural samples with the mixed occupancy of the
267 W site, combination of $2^Y\text{R}^{2+} + ^Y\text{R}^{3+}$ and $2^Y\text{R}^{3+} + ^Y\text{R}^{2+}$ arrangements is the most probable.

268 The crystal-structure refinement of oxy-schorl from Zlatá Idka showed that significant
269 amount of divalent cations is allocated in the Z site, resulting in the content of $^Y\text{Al}^{3+}$ of 1.885

270 *apfu*, the possible *Y* site short-range arrangements favor dominant O^{2-} in *W* site. The observed
271 Al-Mg disorder in tourmalines was already studied (e.g., Grice and Ercit 1993; Hawthorne et
272 al. 1993; Bloodaxe et al. 1999; Bosi and Lucchesi 2004). Although the Fe^{2+} - Al^{3+} disorder
273 could be allowed by local short- and long-range arrangements (Bosi 2011), Mg is more likely
274 substituting for Al in the *Z* site due to its smaller ionic radii similar to Al^{3+} , as was observed in
275 the oxy-schorl from Zlatá Idka. In contrast, the oxy-schorl from Příbyslavice shows only
276 negligible disorder of Al and (Mg,Fe) in octahedral sites; the vast majority of R^{2+} ($Fe^{2+} \gg$
277 Mg) is allocated to the *Y* site. However, the calculated bond valence values for the *O1* and *O3*
278 sites suggest a disorder of O and OH among the anion sites *V* and *W* (Table 15).

279 The formula of end-member oxy-schorl may be expressed either as
280 $Na(Fe^{2+}Al_2)(Fe^{2+}Al_3)Si_6O_{18}(BO_3)_3(OH)_3O$ with cations disordered in two structural sites, or
281 with cations disordered only in one structural site such as
282 $NaAl_3(Al_4Fe^{2+}_2)Si_6O_{18}(BO_3)_3(OH)_3O$ and $Na(Fe^{2+}_2Al)Al_6Si_6O_{18}(BO_3)_3(OH)_3O$ – the formula
283 used in the valid nomenclature (Henry et al. 2011). It recommends allocation of trivalent
284 cations to the *Z* site initially, followed by assignment of the remainder of R^{3+} to *Y* site.
285 Nevertheless, this end-member formula could not be stable owing to the local charge
286 requirements, and the first formula with cations disordered in two sites is closely approaching
287 the composition of natural samples (Hawthorne 2002).

288 These two studied oxy-schorl samples confirm the two distinct ordering mechanisms in
289 natural oxy-tourmalines: (1) disorder of divalent and trivalent cations in octahedral sites and
290 all O ordered in the *W* site (favored by the Mg-bearing oxy-schorl from Zlatá Idka); (2)
291 cations ordered in the *Y* and *Z* sites and O disordered in the *V* and *W* sites (in Fe-dominant
292 oxy-schorl from Příbyslavice). The elevated content of Mg in oxy-schorl from Zlatá Idka (Fig.
293 3c, Table 1) very likely facilitates higher degree of disorder in *Y* and *Z* sites and higher
294 ordering in *W* site relative to Mg-poor oxy-schorl from Příbyslavice. Since formula with
295 ordered *V* and *W* sites is recommended for the classification purposes (Henry et al. 2011),
296 both compositions result in the same ordered formula that meets nomenclatural requirements
297 for oxy-schorl.

298 The presence of oxy-schorl does not necessary imply oxidizing geological environment.
299 Mineral association in the Příbyslavice orthogneiss suggests more reductive conditions
300 documented by magnetite and pyrite (e.g., Povondra et al. 1987, 1998). Thus the reasons of
301 the formation of oxy-schorl in spite of schorl are different than high oxygen fugacity. It could
302 take a part in oxy-tourmalines with an increased proportion of Fe^{3+} as buergerite (e.g. Donnay
303 et al. 1966; Grice and Ercit 1993) or povondraite component (e.g. Grice et al. 1993; Bačík et

304 al. 2008; Baksheev et al. 2011; Novák et al. 2011), respectively, in which the deprotonization
305 is driven by ${}^Y\text{Fe}^{2+} + {}^{W+V}\text{OH}^- \leftrightarrow {}^Y\text{Fe}^{3+} + {}^{W+V}\text{O}^{2-}$ reaction (Pieczka and Kraczka 2004; Bačík et
306 al. 2011). In contrast, the deprotonization was driven by ${}^Y\text{R}^{2+} + {}^{W+V}\text{OH}^- \leftrightarrow {}^Y\text{Al} + {}^{W+V}\text{O}^{2-}$
307 reaction in studied samples of oxy-schorl from both localities. Consequently, the
308 deprotonization in studied oxy-schorls was likely the result of local charge-balance
309 requirements owing to the excess of Al and the formation of Al-enriched oxy-schorl is the
310 result of the specific geochemistry of the host rock.

311

312 **Acknowledgement:**

313 Authors would like to thank Tomáš Vaculovič for LA-ICP-MS analysis. This work was
314 supported by projects APVV-VVCE-0033-07 to PB, PU and DO and GAP210/10/0743 to JC,
315 JF, MN and RŠ and by the Operational Program Research and Development for Innovations -
316 European Regional Development Fund (Project No. CZ.1.05/2.1.00/03.0058 of the Ministry
317 of Education, Youth and Sports of the Czech Republic) to JF. We thank Martin Kunz and
318 Fernando Colombo for editorial handling and for detailed reviews and fruitful discussion.

319

320

321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352

REFERENCES:

- Bačík, P., Uher, P., Sýkora, M., and Lipka, J. (2008) Low-Al tourmalines of the schorl-dravite-povondraite series in redeposited tourmalinites from the Western Carpathians, Slovakia. *Canadian Mineralogist*, 46, 1117–1129.
- Bačík, P., Ozdín, D., Miglierini, M., Kardošová, P., Pentrák, M., and Haloda, J. (2011) Crystallochemical effects of heat treatment on Fe-dominant tourmalines from Dolní Bory (Czech Republic) and Vlachovo (Slovakia). *Physics and Chemistry of Minerals*, 38, 599–611.
- Baksheev, I.A., Prokof'ev, V.Y., Yapaskurt, V.O., Vigasina, M.F., Zorina, L.D., and Solov'ev, V.N. (2011) Ferric-iron-rich tourmaline from the Darasun gold deposit, Transbaikalia, Russia. *Canadian Mineralogist*, 49, 263–276.
- Bloodaxe, E.S., Hughes, J.M., Dyar, M.D., Grew, E.S., and Guidotti, C.V., (1999) Linking structure and chemistry in the schorl-dravite series. *American Mineralogist*, 84, 922–928.
- Bosi, F. (2011) Stereochemical constraints in tourmaline: From a short-range to a long-range structure. *Canadian Mineralogist*, 49, 17–27.
- Bosi, F. and Lucchesi S. (2004) Crystal chemistry of the schorl-dravite series. *European Journal of Mineralogy*, 16, 335–344
- Brand, R.A. (1997) NORMOS: Mössbauer fitting program, version 1997, unpublished.
- Breiter, K., Škoda, R. and Novák, M. (2010) Field stop 5: Příbyslavice near Čáslav – complex of peraluminous phosphorus-rich tourmaline-bearing orthogneiss, and associated granite and pegmatite with garnet, tourmaline, and primary Fe-Mn phosphates. In: Novák, M. and Cempírek, J. (eds) *Granitic pegmatites and mineralogical museums in the Czech Republic. Acta Mineralogica-Petrographica, Field Guide Series*, 6, 29-36.
- Bruker (2010) DIFFRAC^{plus} TOPAS. <http://www.bruker-axs.de/topas.html>
- Buriánek, D. and Novák, M. (2004) Morphological and compositional evolution of tourmaline from nodular granite at Lavičky near Velké Meziříčí, Moldanubicum, Czech Republic. *Journal of Czech Geological Society*, 49, 81–90.
- Buriánek, D. and Novák, M. (2007) Compositional evolution and substitutions in disseminated and nodular tourmaline from leucocratic granites: Examples from the Bohemian Massif, Czech Republic. *Lithos*, 95, 148–164.

- 353 Donnay, G., Ingamells, C. O., and Mason B. (1966) Buergerite, a new species of tourmaline.
354 American Mineralogist, 51, 198–199.
- 355 Ertl, A., Marschall, H.R., Giester, G., Henry, D.J., Schertl, H.P., Ntaflos, T., Luvizotto, G.L.,
356 Nasdala, L., and Tillmanns, E. (2010a): Metamorphic ultrahigh-pressure tourmaline:
357 Structure, chemistry, and correlations to P-T conditions. American Mineralogist, 95, 1–
358 10.
- 359 Ertl, A., Rossman, G.R., Hughes, J.M., London, D., Wang, Y., O'Leary, J.A., Dyar, M.D.,
360 Prowatke, S., Ludwig, T., and Tillmanns, E. (2010b) Tourmaline of the elbaite-schorl
361 series from the Himalaya Mine, Mesa Grande, California: A detailed investigation.
362 American Mineralogist, 95, 24–40.
- 363 Foit, F.F. (1989) Crystal chemistry of alkali-deficient schorl and tourmaline structural
364 relationships. American Mineralogist, 74, 422–431.
- 365 Foit, F.F. Jr. and Rosenberg, P.E. (1977) Coupled substitutions in the tourmaline group.
366 Contributions to Mineralogy and Petrology, 62, 109–127.
- 367 Grice, J.D. and Ercit, T.S. (1993) Ordering of Fe and Mg in tourmaline: The correct formula.
368 Neues Jahrbuch für Mineralogie Abhandlungen, 165, 245–266.
- 369 Grice, J. D., Ercit, T. S., and Hawthorne, F. C. (1993) Povondraite, a redefinition of the
370 tourmaline ferridravite. American Mineralogist, 78, 433–436.
- 371 Hawthorne, F.C. (1996) Structural mechanisms for light elements in tourmaline. Canadian
372 Mineralogist, 34, 123–132.
- 373 Hawthorne, F.C. (2002) Bond-valence constraints on the chemical composition of tourmaline.
374 Canadian Mineralogist, 40, 789–797.
- 375 Hawthorne, F.C. and Henry, D.J. (1999) Classification of the minerals of the tourmaline
376 group. European Journal of Mineralogy, 11, 201–215.
- 377 Hawthorne, F.C., MacDonald, D.J., and Burns, P.C. (1993) Reassignment of cation site
378 occupancies in tourmaline: Al-Mg disorder in the crystal structure of dravite. American
379 Mineralogist, 78, 265–270.
- 380 Henry, D.J. and Dutrow, B. (2001) Compositional zoning and element partitioning of
381 nickeloan tourmaline in a metamorphosed karstbauxite from Samos, Greece. American
382 Mineralogist, 86, 1130–1142.
- 383 Henry, D., Novák, M., Hawthorne, F.C., Ertl, A., Dutrow, B., Uher, P., and Pezzotta, F.
384 (2011) Nomenclature of the tourmaline supergroup-minerals. American Mineralogist,
385 96, 895–913.

- 386 Novák, M., Povondra, P., and Selway, J.B. (2004) Schorl-oxy-schorl to dravite-oxy-dravite
387 tourmaline from granitic pegmatites; examples from the Moldanubicum, Czech
388 Republic. *European Journal of Mineralogy*, 16, 323–333.
- 389 Novák, M., Škoda, R., Filip, J., Macek, I., and Vaculovič, T. (2011) Compositional trends in
390 tourmaline from intragranitic NYF pegmatites of the Třebíč Pluton, Czech Republic:
391 electron microprobe, Mössbauer and LA-ICP-MS study. *Canadian Mineralogist*, 49,
392 359–380.
- 393 Pieczka, A. and Kraczká, J. (2004): Oxidized tourmalines – a combined chemical, XRD and
394 Mössbauer study. *European Journal of Mineralogy*, 16, 309–321.
- 395 Povondra, P. (1981) The crystal chemistry of tourmalines of the schorl-dravite series. *Acta*
396 *Universitatis Carolinae, Geologica*, 223–264.
- 397 Povondra, P., Čech, F., and Staněk, J. (1985) Crystal chemistry of elbaïtes from some
398 pegmatites of the Czech Massif. *Acta Universitatis Carolinae, Geologica*, 1–24.
- 399 Povondra, P., Lang, M., Pivec, E., and Ulrych, J. (1998) Tourmaline from the Příbyslavice
400 peraluminous alkali-feldspar granite, Czech Republic. *Journal of Czech Geological*
401 *Society*, 43, 3–8.
- 402 Povondra, P., Pivec, E., Čech, F., Lang, M., Novák, F., Prachař, I., and Ulrych, J. (1987)
403 Příbyslavice peraluminous granite. *Acta Universitatis Carolinae, Geologica*, 183–283.
- 404 Reddy, B.J., Frost, R.L., Martens, W.N., Wain, D.L. and Kloprogge, J.T. (2007)
405 Spectroscopic characterization of Mn-rich tourmalines. *Vibrational Spectroscopy*, 44,
406 42–49.
- 407 Sheldrick, G. M. (2000) SHELXTL. Version 6.10. Bruker AXS Inc., Madison, Wisconsin,
408 USA
- 409 Stoe & Cie (1999) WinXPow. Stoe & Cie, Darmstadt, Germany.
- 410 Vozárová, A., Šarinová, K., Larionov, A., Presnyakov, S., and Sergeev, S. (2010) Late
411 Cambrian/Ordovician magmatic arc type volcanism in the Southern Gemicum
412 basement, Western Carpathians, Slovakia: U-Pb (SHRIMP) data from zircons.
413 *International Journal of Earth Sciences*, 99 (Suppl. 1), 17–37.
- 414 Werner, P.-E., Eriksson, L., and Westdahl, M. (1985) TREOR, a semi-exhaustive trial-and-
415 error powder indexing program for all symmetries. *Journal of Applied Crystallography*,
416 18, 367-370.
- 417 Žák, T. and Jirásková, Y. (2006) CONFIT: Mössbauer spectra fitting program. *Surface and*
418 *Interface Analysis*, 38, 710–714.
- 419

420

421 Figure 1. BSE image of oxy-schorl from Zlatá Idka. The zoning is given by the variation in
422 Fe, Mg and Al content; dark grey zone corresponds to transitional oxy-schorl to “□-Fe-O root
423 name” tourmaline composition.

424

425 Figure 2. FTIR spectrum of oxy-schorl from Příbyslavice.

426

427 Figure 3. Ternary diagrams for minerals of tourmaline group used for determination of
428 dominant occupancy at the X (a), W (b) and Y site (c).

429

430 **TABLE 1. CHEMICAL COMPOSITION AND FORMULA OF OXY-SCHORL FROM ZLATÁ IDKA AND**
 431 **PŘIBYSLAVICE**
 432

Zlatá Idka				Přibyslavice			
SiO ₂ wt%	33.10	Si <i>apfu</i>	5.506	SiO ₂ wt%	34.57	Si <i>apfu</i>	5.944
TiO ₂	0.02	^Z Al	0.494	TiO ₂	0.72	^Z Al	0.056
B ₂ O ₃ *	10.45	Sum <i>T</i>	6.000	B ₂ O ₃ *	10.11	Sum <i>T</i>	6.000
Al ₂ O ₃	39.81			Al ₂ O ₃	33.55		
FeO	7.97	B	3.000	Fe ₂ O ₃	0.61	B	3.000
MgO	2.31			FeO	13.07		
MnO	0.03	^Z Al	5.428	MnO	0.10	^Z Al	5.732
CaO	0.58	^Z Mg	0.572	MgO	0.74	^Z Mg	0.190
Na ₂ O	1.83	Sum <i>Z</i>	6.000	CaO	0.09	Fe ³⁺	0.078
F	0.26			K ₂ O	0.03	Sum <i>Z</i>	6.000
Cl	0.01	Ti	0.002	Na ₂ O	1.76		
H ₂ O**	2.92	^Y Al	1.885	Cl	0.00	^Y Al	1.013
O=F	0.11	Fe ²⁺	1.108	F	0.56	Ti ⁴⁺	0.093
Total	99.18	Mn	0.005	H ₂ O**	2.72	Fe ²⁺	1.879
		Sum <i>Y</i>	3.000	-O = F,Cl	-0.24	Mn ²⁺	0.015
				Total	98.39	Sum <i>Y</i>	3.000
		Ca	0.103				
		Na	0.591			Ca	0.017
		□	0.306			Na	0.586
		Sum <i>X</i>	1.000			K	0.006
						□	0.391
		^V OH	3.000			Sum <i>X</i>	1.000
		^W OH	0.236			^V OH	3.000
		F	0.136				
		Cl	0.003			^W OH	0.115
		O	0.625			O	0.579
		Sum <i>W</i>	1.000			F	0.307

433 * calculated by structural refinement; ** calculated on the basis of electroneutral formula and
 434 structure refinement results

435

436
437
438

TABLE 2. HYPERFINE PARAMETERS (MÖSSBAUER SPECTROSCOPY) OF OXY-SCHORL

	Isomer shift (mm s ⁻¹)	Quadrupole splitting (mm s ⁻¹)	Assignment	Relative abundance (%)
Zlatá Idka	0.98	2.45	Y ¹ Fe ²⁺	43
	0.98	2.13	Y ² Fe ²⁺	13
	0.98	1.64	Y ³ Fe ²⁺	44
Přibyslavice	1.09	2.47	Y ¹ Fe ²⁺	37
	1.08	2.15	Y ² Fe ²⁺	35
	1.04	1.58	Y ³ Fe ²⁺	25
	0.37	0.32	YFe ³⁺	4

439
440
441
442

TABLE 3. IR SPECTROSCOPIC DATA FOR OXY-SCHORL FROM PŘIBYSLAVICE

Peak [cm ⁻¹]	Assignment
400 – 840	lattice vibrations
840 – 1200	Si ₆ O ₁₈ stretching vibrations (Fe,Mg)-OH bending vibrations
1200 – 2000	BO ₃ stretching vibrations
~ 3000 – 3600	O–H stretching (at O3; overlapping peaks from variable configurations of Y- and Z- site cations around O3)
3600 – 3700	O–H stretching (at O1; overlap of peaks from variable configurations of Y-site cations)

443
444

445
446
447

TABLE 4. POWDER X-RAY DIFFRACTION DATA FOR OXY-SCHORL FROM ZLATÁ IDKA.
THE 5 STRONGEST LINES ARE HIGHLIGHTED

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.} [Å]	<i>I</i> [%]	<i>d</i> _{calc.} [Å]	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.} [Å]	<i>I</i> [%]	<i>d</i> _{calc.} [Å]
1	0	1	6.314(1)	10	6.3130	1	0	4	1.7614(7)	6	1.7620
0	2	1	4.945(2)	8	4.9471	6	3	0	1.7356(8)	7	1.7364
0	3	0	4.592(2)	7	4.5940	0	7	2	1.7215(8)	4	1.7222
2	1	1	4.200(2)	25	4.2013	5	3	2	1.7215(8)	4	1.7222
2	2	0	3.977(2)	53	3.9785	0	2	4	1.7197(7)	5	1.7204
0	1	2	3.439(1)	53	3.4407	5	4	1	1.7119(8)	7	1.7126
1	3	1	3.365(1)	11	3.3664	2	6	2	1.6825(8)	9	1.6832
2	0	2	3.157(1)	3	3.1581	2	1	4	1.6809(7)	13	1.6815
4	0	1	3.099(1)	4	3.1003	0	8	1	1.6736(8)	6	1.6743
4	1	0	3.006(1)	13	3.0075	0	6	3	1.6484(7)	26	1.6490
1	2	2	2.934(1)	59	2.9354	6	0	3	1.6484(7)	26	1.6490
3	2	1	2.888(1)	6	2.8888	2	7	1	1.6377(8)	38	1.6384
3	1	2	2.602(1)	3	2.6025	2	5	3	1.6141(7)	3	1.6147
0	5	1	2.569(1)	100	2.5699	5	2	3	1.6141(7)	3	1.6147
0	0	3	2.3680(9)	14	2.3688	1	3	4	1.6105(7)	7	1.6111
2	3	2	2.361(1)	10	2.3621	5	5	0	1.5907(8)	48	1.5914
5	1	1	2.336(1)	13	2.3376	4	5	2	1.5798(7)	15	1.5805
5	0	2	2.177(1)	6	2.1779	4	0	4	1.5785(7)	6	1.5791
4	3	1	2.158(1)	8	2.1587	8	1	1	1.5724(7)	11	1.5731
3	0	3	2.1046(9)	4	2.1054	8	0	2	1.5495(7)	7	1.5502
0	3	3	2.1046(9)	4	2.1054	3	2	4	1.5483(6)	2	1.5489
4	2	2	2.0998(9)	2	2.1007	4	6	1	1.5425(7)	13	1.5432
2	2	3	2.0346(9)	37	2.0354	0	9	0	1.5307(7)	11	1.5313
1	5	2	2.0303(9)	41	2.0311	4	4	3	1.5228(7)	8	1.5234
1	6	1	2.0146(9)	10	2.0155	7	2	2	1.5209(7)	4	1.5216
4	4	0	1.9884(9)	3	1.9893	7	3	1	1.5143(7)	3	1.5150
3	4	2	1.9096(9)	54	1.9104	1	7	3	1.4454(6)	8	1.4459
4	1	3	1.8602(8)	3	1.8609	7	1	3	1.4454(6)	8	1.4459
1	4	3	1.8602(8)	3	1.8609	6	4	2	1.4438(7)	4	1.4444
6	2	1	1.8449(9)	9	1.8456	5	1	4	1.4428(6)	15	1.4433
3	3	3	1.7661(8)	8	1.7668						

448

449
450
451

TABLE 5. POWDER X-RAY DIFFRACTION DATA FOR OXY-SCHORL FROM PŘIBYSLAVICE.
THE 5 STRONGEST LINES ARE HIGHLIGHTED

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.} [Å]	<i>I</i> [%]	<i>d</i> _{calc.} [Å]	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.} [Å]	<i>I</i> [%]	<i>d</i> _{calc.} [Å]
1	0	1	6.364(4)	75	6.3604	0	2	4	1.7333(2)	2	1.7332
0	2	1	4.9775(7)	28	4.977	5	3	2	1.7312(1)	1.5	1.7312
3	0	0	4.616(1)	12	4.6149	2	6	2	1.6920(1)	1.9	1.692
2	1	1	4.2254(6)	48	4.225	6	0	3	1.6589(2)	14.1	1.659
2	2	0	3.9969(5)	52	3.9966	2	7	1	1.6461(1)	6.7	1.6461
0	1	2	3.4664(1)	100	3.4664	1	3	4	1.6227(3)	0.6	1.6225
1	3	1	3.3839(3)	6	3.384	5	5	0	1.5986(2)	7.3	1.5987
2	0	2	3.1803(2)	1	3.1802	4	0	4	1.5896(6)	2.4	1.5901
4	0	1	3.1164(3)	2	3.1163	8	1	1	1.5804(1)	0.7	1.5804
4	1	0	3.0211(3)	8	3.0212	3	2	4	1.5591(5)	1	1.5595
1	2	2	2.9549(1)	79	2.9549	4	6	1	1.5504(1)	1.9	1.5504
3	2	1	2.9035(2)	5	2.9034	9	0	0	1.5383(1)	1.8	1.5383
3	1	2	2.6188(3)	3	2.6186	7	2	2	1.5293(1)	1.6	1.5293
0	5	1	2.5826(1)	65	2.5826	7	3	1	1.5221(1)	0.8	1.5221
0	4	2	2.4883(3)	3	2.4885	8	2	0	1.5105(2)	2.6	1.5106
2	4	1	2.4576(2)	3	2.4575	0	5	4	1.5033(2)	9.3	1.5034
0	0	3	2.3868(2)	12	2.3869	2	4	4	1.4772(4)	2.3	1.4775
2	3	2	2.3761(2)	16	2.376	5	1	4	1.4528(2)	10.2	1.4529
5	1	1	2.3490(1)	9	2.349	7	4	0	1.4355(2)	1.6	1.4356
6	0	0	2.3072(4)	1	2.3075	0	1	5	1.4247(2)	3.1	1.4246
1	1	3	2.2869(3)	1	2.2871	6	5	1	1.4224(1)	3.5	1.4224
5	2	0	2.2171(3)	1	2.2169	4	3	4	1.4072(2)	6.6	1.4071
5	0	2	2.1903(2)	9	2.1904	3	8	1	1.3793(2)	0.6	1.3794
4	3	1	2.1692(2)	7	2.1691	10	0	1	1.3593(1)	3.8	1.3593
3	0	3	2.1200(2)	11	2.1201	9	1	2	1.3450(1)	2	1.345
4	2	2	2.1125(1)	4	2.1125	6	6	0	1.3321(2)	1.2	1.3322
2	2	3	2.0494(2)	12	2.0493	7	0	4	1.3277(5)	2.8	1.3273
1	5	2	2.0423(2)	31	2.0424	0	4	5	1.3234(0)	1.7	1.3234
1	6	1	2.0252(2)	5	2.0251	10	1	0	1.3140(2)	3.5	1.3141
4	4	0	1.9983(1)	2	1.9983	8	3	2	1.3087(2)	1	1.3085
3	4	2	1.9207(2)	17	1.9208	2	3	5	1.3055(2)	1.2	1.3056
7	0	1	1.9065(2)	2	1.9064	9	0	3	1.2931(2)	0.5	1.293
4	1	3	1.8729(1)	8	1.8729	0	10	2	1.2913(1)	0.7	1.2913
6	2	1	1.8545(2)	4	1.8544	8	4	1	1.2869(1)	0.8	1.2869
7	1	0	1.8340(3)	1	1.8338	9	3	0	1.2799(1)	1.3	1.2799
6	1	2	1.8186(2)	2	1.8187	8	2	3	1.2765(2)	1	1.2764
3	3	3	1.7779(1)	3	1.7779	5	0	5	1.2720(2)	4.1	1.2721
1	0	4	1.7754(1)	3	1.7754						

452

453
454

TABLE 6. CRYSTAL AND REFINEMENT DATA FOR OXY-SCHORL FROM ZLATÁ IDKA

$a = 15.916(3) \text{ \AA}$	Space group: $R3m$
$c = 7.1071(12) \text{ \AA}$	MoK α radiation, $\lambda = 0.71073 \text{ \AA}$
$V = 1559.1(4) \text{ \AA}^3$	Cell parameters from 1225 reflections
$Z = 3$	
Elongated grain, brown	$0.20 \times 0.10 \times 0.10 \text{ mm}$
$\theta = 3.2\text{--}36.1^\circ$	$(-26 \leq h \leq 17, -17 \leq k \leq 26, -11 \leq l \leq 11)$
$\mu = 1.68 \text{ mm}^{-1}$	$F(000) = 1468$
$T = 293 \text{ K}$	
Reflections measured:	3174
Independent reflections:	1474
Reflections $> 2\sigma$:	1111
$R [F^2 > 2\sigma(F^2)] = 0.034$	$(\Delta/\sigma)_{\text{max}} = <0.001$
$wR(F^2) = 0.066$	extinction coef. : none
$S = 0.84$	92 parameters refined
$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$

455
456
457
458
459

TABLE 7. FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (\AA^2) OF OXY-SCHORL FROM ZLATÁ IDKA

	x	y	z	Uiso*/Ueq	Occ. (<1)
Na	0.0000	0.0000	0.0825 (5)	0.0229 (12)	0.859 (14)
Y(Al)	0.12237 (7)	0.06118 (4)	0.50346 (13)	0.0119 (3)	0.799 (7)
Y(Fe)	0.12237 (7)	0.06118 (4)	0.50346 (13)	0.0119 (3)	0.201 (7)
Z(Al)	0.29700 (6)	0.36937 (6)	1.14311 (12)	0.0104 (2)	0.959 (5)
Si	0.19214 (5)	0.19002 (5)	0.86941 (10)	0.0080 (2)	0.899 (5)
O1	0.0000	0.0000	0.6394 (8)	0.0269 (12)	
O2	0.06060 (11)	0.1212 (2)	0.3556 (4)	0.0210 (7)	
O3	0.2620 (2)	0.13101 (12)	0.3745 (4)	0.0189 (7)	
O4	0.1869 (2)	0.09346 (11)	0.9640 (4)	0.0198 (6)	
O5	-0.1883 (2)	-0.09417 (11)	-0.0580 (4)	0.0192 (6)	
O6	0.19549 (14)	0.18438 (14)	0.6403 (3)	0.0150 (4)	
O7	0.28759 (14)	0.28731 (13)	0.9447 (3)	0.0142 (4)	
O8	0.20909 (14)	0.26975 (14)	1.3046 (3)	0.0145 (4)	
B	0.10971 (18)	0.2194 (4)	0.3182 (6)	0.0142 (8)	

460
461
462
463

464 **TABLE 8. ATOMIC DISPLACEMENT PARAMETERS (\AA^2) OF OXY-SCHORL FROM ZLATÁ IDKA**

465

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na	0.0223 (15)	0.0223 (15)	0.024 (2)	0.0111 (8)	0.000	0.000
Y(Al)	0.0113 (5)	0.0098 (4)	0.0151 (5)	0.0057 (2)	-0.0019 (3)	-0.00095 (17)
Y(Fe)	0.0113 (5)	0.0098 (4)	0.0151 (5)	0.0057 (2)	-0.0019 (3)	-0.00095 (17)
Z(Al)	0.0113 (4)	0.0109 (4)	0.0098 (4)	0.0060 (3)	0.0001 (3)	-0.0004 (3)
Si	0.0081 (4)	0.0082 (4)	0.0076 (3)	0.0041 (3)	-0.0002 (3)	-0.0008 (3)
O1	0.0314 (19)	0.0314 (19)	0.018 (3)	0.0157 (9)	0.000	0.000
O2	0.0251 (13)	0.0147 (14)	0.0197 (14)	0.0073 (7)	0.0001 (6)	0.0002 (12)
O3	0.0291 (17)	0.0171 (11)	0.0144 (13)	0.0146 (8)	0.0005 (12)	0.0003 (6)
O4	0.0243 (16)	0.0168 (10)	0.0208 (14)	0.0121 (8)	-0.0001 (12)	0.0000 (6)
O5	0.0250 (16)	0.0188 (11)	0.0160 (13)	0.0125 (8)	0.0018 (11)	0.0009 (6)
O6	0.0165 (10)	0.0169 (10)	0.0111 (8)	0.0080 (8)	0.0012 (7)	0.0008 (7)
O7	0.0135 (9)	0.0138 (9)	0.0133 (8)	0.0053 (8)	0.0002 (7)	-0.0003 (7)
O8	0.0136 (9)	0.0152 (10)	0.0153 (9)	0.0075 (8)	-0.0001 (7)	0.0018 (7)
B	0.0172 (16)	0.015 (2)	0.0094 (16)	0.0077 (10)	-0.0002 (7)	-0.0004 (14)

466

467

468 **TABLE 9. SELECTED BOND LENGTHS FOR OXY-SCHORL FROM ZLATÁ IDKA**

469

Site	Anion	Distance	s.d.	Site	Anion	Distance	s.d.	
X	O2 ⁱ	2.561	(4)	Z	O6 ^{vii}	1.869	(2)	
	O2 ⁱⁱ	2.561	(4)		O7	1.876	(2)	
	O2	2.561	(4)		O8	1.889	(2)	
	O4 ⁱⁱⁱ	2.710	(3)		O8 ^{viii}	1.918	(2)	
	O4 ^{iv}	2.710	(3)		O7 ^{ix}	1.925	(2)	
	O4 ^v	2.710	(3)		O3 ^{vii}	1.9890	(15)	
	O5 ⁱ	2.781	(3)		avg.	1.911		
	O5 ⁱⁱ	2.781	(3)		T	O7	1.625	(2)
	O5	2.781	(3)			O5 ^x	1.6298	(12)
avg.	2.684		O6	1.633		(2)		
			O4	1.6412		(15)		
Y	O1	1.944	(3)	1.632				
	O6 ^{vi}	1.965	(2)	B	O2	1.380	(6)	
	O6	1.965	(2)		O8 ⁱⁱⁱ	1.373	(3)	
	O2	1.981	(2)		O8 ^{xi}	1.373	(3)	
	O2 ⁱ	1.981	(2)		avg.	1.375		
	O3	2.132	(3)					
	avg.	1.995						

Symmetry codes: (i) $-x+y, -x, z$; (ii) $-y, x-y, z$; (iii) $x, y, z-1$; (iv) $-y, x-y, z-1$; (v) $-x+y, -x, z-1$; (vi) $x, x-y, z$; (vii) $-x+y+1/3, -x+2/3, z+2/3$; (viii) $-x+y+1/3, -x+2/3, z-1/3$; (ix) $-y+2/3, x-y+1/3, z+1/3$; (x) $-x+y, -x, z+1$; (xi) $-x+y, y, z-1$.

470

471
472

TABLE 10. BOND VALENCE TABLE FOR OXY-SCHORL FROM ZLATÁ IDKA

	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>B</i>	<i>T</i>	Σ
	Na _{0.591} Ca _{0.10} 3 K _{0.004} □ _{0.302}	Al _{1.808} Fe ²⁺ _{1.105} Ti _{0.002} Mn _{0.005} Mg _{0.079}	Al _{5.5} Mg _{0.5}	B	Si _{5.509} Al _{0.491}	
O1*†		0.478				1.435
O2	0.098 0.098 0.098	0.450 0.450		0.946		1.973
O3*		0.299	0.405			1.109
O4	0.065 0.065 0.065				0.960	1.986
O5	0.054 0.054 0.054				0.991	2.035
O6		0.469 0.469	0.560		0.982	2.012
O7			0.550 0.482		1.003	2.035
O8			0.531 0.491	0.995 0.995		2.016
Σ	0.649	2.616	3.019	2.965	3.937	
IC(avg)	0.801	2.603	2.917	3.000	3.918	
Δ	0.152	-0.013	-0.102	0.035	-0.019	
IC(avg) = average ionic charge of atoms occupying the site. *Hydrogen bond donor. † content of the O1 site is: O _{0.536} OH _{0.328} F _{0.136} .						

473
474
475
476
477
478

479
480
481

TABLE 11. CRYSTAL AND REFINEMENT DATA FOR OXY-SCHORL FROM PŘIBYSLAVICE

$a = 15.9853(12) \text{ \AA}$	Space group: $R3m$
$c = 7.1538(6) \text{ \AA}$	MoK α radiation, $\lambda = 0.71073 \text{ \AA}$
$V = 1583.1(2) \text{ \AA}^3$	Cell parameters from 2936 reflections
$Z = 3$	
Elongated grain, brown	$0.30 \times 0.10 \times 0.10 \text{ mm}$
$\theta = 2.9\text{--}36.1^\circ$	$(-26 \leq h \leq 18, -25 \leq k \leq 23, -8 \leq l \leq 11)$
$\mu = 2.20 \text{ mm}^{-1}$	$F(000) = 1501$
$T = 293 \text{ K}$	
Reflections measured:	4166
Independent reflections:	1380
Reflections $> 2\sigma$:	1285
$R [F^2 > 2\sigma(F^2)] = 0.0191$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$wR(F^2) = 0.0400$	extinction coef. = $0.00058(10)$
$S = 0.98$	96 parameters refined
$\Delta\rho_{\text{max}} = 0.65 \text{ e \AA}^{-3}$	$\Delta\rho_{\text{min}} = -0.49 \text{ e \AA}^{-3}$

482
483
484
485
486

TABLE 12. FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (\AA^2) FOR OXY-SCHORL FROM PŘIBYSLAVICE

Site		x/a	y/b	z/c	$U_{\text{iso}}^*/U_{\text{eq}}$	Occup.
X	Na	0	0	0.9019 (5)	0.0266 (11)	0.676(10)
Y	Fe	0.87496 (3)	0.937481 (16)	0.50264 (6)	0.00869 (12)	0.621(4)
	Al	0.87496 (3)	0.937481 (16)	0.50264 (6)	0.00869 (12)	0.379(4)
Z	Al	0.70355 (3)	0.63191 (3)	-0.14783 (6)	0.00590 (13)	0.974(3)
	Fe	0.70355 (3)	0.63191 (3)	-0.14783 (6)	0.00590 (13)	0.026(3)
T	Si	0.80806 (3)	0.81008 (3)	0.12963 (6)	0.00569 (10)	
O1	O1	0	0	0.3485 (5)	0.0363 (9)	0.69**
	F	0	0	0.3485 (5)	0.0363 (9)	0.31**
O2	O2	0.93822 (6)	0.87643 (12)	0.6435 (3)	0.0151 (4)	
O3	O3	0.73144 (14)	0.86572 (7)	0.6201 (2)	0.0123 (3)	
O4	O4	0.81267 (12)	0.90634 (6)	0.0387 (2)	0.0103 (3)	
O5	O5	0.18631 (12)	0.09316 (6)	0.0618 (2)	0.0104 (3)	
O6	O6	0.80182 (8)	0.81238 (8)	0.35415 (17)	0.0089 (2)	
O7	O7	0.71481 (8)	0.71419 (8)	0.05039 (16)	0.0086 (2)	
O8	O8	0.79017 (8)	0.72936 (8)	-0.31139 (16)	0.0097 (2)	
B	B	0.88991 (10)	0.77981 (19)	0.6753 (4)	0.0076 (4)	
H3	H3	0.735 (2)	0.8677 (12)	0.732 (5)	0.21 (2)*	

* Isotropic displacement parameter (\AA^2). **Fixed according to EMPA analyses.

487
488

489
490
491

TABLE 13. ANISOTROPIC DISPLACEMENT PARAMETERS (\AA^2) FOR OXY-SCHORL FROM PŘIBYSLAVICE

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
<i>X</i>	0.0267 (13)	0.0267 (13)	0.0263 (18)	0.0134 (7)	0	0
<i>Y</i>	0.0087 (2)	0.00611 (15)	0.0121 (2)	0.00433 (10)	-0.00216 (15)	-0.00108 (7)
<i>Z</i>	0.0062 (2)	0.0058 (2)	0.0058 (2)	0.00309 (18)	0.00034 (15)	-0.00008 (16)
<i>T</i>	0.0054 (2)	0.00520 (19)	0.0064 (2)	0.00266 (15)	-0.00021 (15)	-0.00044 (14)
O1	0.0494 (15)	0.0494 (15)	0.0102 (15)	0.0247 (8)	0	0
O2	0.0207 (7)	0.0069 (7)	0.0132 (8)	0.0035 (4)	0.0004 (3)	0.0008 (6)
O3	0.0213 (9)	0.0123 (6)	0.0063 (7)	0.0107 (4)	0.0007 (6)	0.0004 (3)
O4	0.0145 (8)	0.0074 (5)	0.0114 (8)	0.0072 (4)	0.0011 (6)	0.0006 (3)
O5	0.0149 (8)	0.0082 (5)	0.0105 (7)	0.0075 (4)	0.0012 (6)	0.0006 (3)
O6	0.0090 (5)	0.0103 (5)	0.0070 (5)	0.0047 (4)	-0.0003 (4)	-0.0009 (4)
O7	0.0088 (5)	0.0068 (5)	0.0082 (5)	0.0024 (4)	-0.0009 (4)	-0.0008 (4)
O8	0.0075 (5)	0.0115 (5)	0.0111 (5)	0.0054 (5)	0.0010 (4)	0.0021 (4)
<i>B</i>	0.0077 (7)	0.0074 (10)	0.0074 (10)	0.0037 (5)	0.0000 (4)	0.0000 (8)

492
493
494

TABLE 14. SELECTED BOND LENGTHS FOR OXY-SCHORL FROM PŘIBYSLAVICE

Site	Anion	Distance	s.d.	Site	Anion	Distance	s.d.	
<i>X</i>	O2 ⁱ	2.519	(3)	<i>Z</i>	O6 ^{xiii}	1.8615	(13)	
	O2 ⁱⁱ	2.519	(3)		O7	1.8804	(12)	
	O2 ⁱⁱⁱ	2.519	(3)		O8	1.8857	(12)	
	O4 ^{iv}	2.772	(2)		O8 ^{xiv}	1.9264	(12)	
	O4 ^v	2.772	(2)		O7 ^{xv}	1.9589	(12)	
	O4 ^{vi}	2.772	(2)		O3 ^{xiii}	1.9814	(9)	
	O5 ^{vii}	2.821	(2)		avg.	1.916		
	O5 ^{viii}	2.821	(2)		<i>T</i>	O6	1.6108	(13)
	O5 ^{ix}	2.821	(2)			O7	1.6149	(11)
avg.	2.704		O5 ^{xvi}	1.6253		(7)		
<i>Y</i>	O2	1.9941	(12)	O4	1.638	(8)		
	O2 ^x	1.9942	(12)	1.622				
	O6 ^{xi}	2.0387	(13)	<i>B</i>	O2	1.357	(3)	
	O6	2.0387	(13)		O8 ^{viii}	1.3841	(18)	
	O1 ^{xii}	2.052	(2)		O8 ^{xvii}	1.3841	(18)	
	O3	2.1572	(19)		avg.	1.375		
avg.	2.046							

Symmetry codes: (i) $x-1, y-1, z$; (ii) $-x+y, -x+1, z$; (iii) $-y+1, x-y, z$; (iv) $-x+y, -x+1, z+1$; (v) $x-1, y-1, z+1$; (vi) $-y+1, x-y, z+1$; (vii) $-y, x-y, z+1$; (viii) $x, y, z+1$; (ix) $-x+y, -x, z+1$; (x) $-x+y+1, -x+2, z$; (xi) $x, x-y+1, z$; (xii) $x+1, y+1, z$; (xiii) $-x+y+2/3, -x+4/3, z-2/3$; (xiv) $-x+y+2/3, -x+4/3, z+1/3$; (xv) $-y+4/3, x-y+2/3, z-1/3$; (xvi) $-x+y+1, -x+1, z$; (xvii) $-x+y+1, y, z+1$.

495
496

TABLE 15. BOND VALENCE TABLE FOR OXY-SCHORL FROM PŘIBYSLAVICE

	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>B</i>	<i>T</i>	Σ
O1*		0.363				1.088
O2	0.091 0.091 0.091	0.466 0.466		1.039		2.063
O3*		0.298	0.411			1.119
O4	0.046 0.046 0.046				0.965	1.975
O5	0.040 0.040 0.040				0.997	2.033
O6		0.415 0.415	0.571		1.033	2.020
O7			0.545 0.439		1.021	2.005
O8			0.535 0.480	0.964 0.964		1.978
Σ	0.531	2.423	2.980	2.966	4.015	
IC(avg)	0.632	2.400	2.968	3.000	3.991	
Δ	0.101	-0.024	-0.012	0.034	-0.025	
IC(avg) = average ionic charge of atoms occupying the site. *Hydrogen bond donor.						

497
498

Figure 1

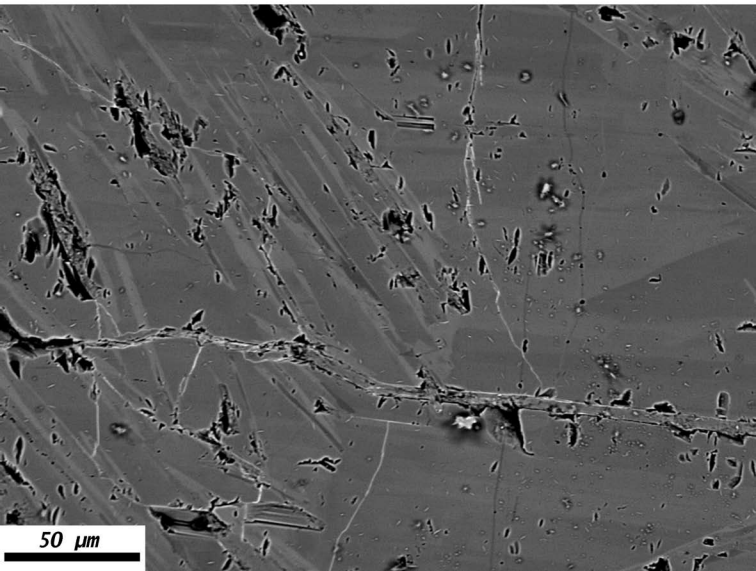


Figure 2

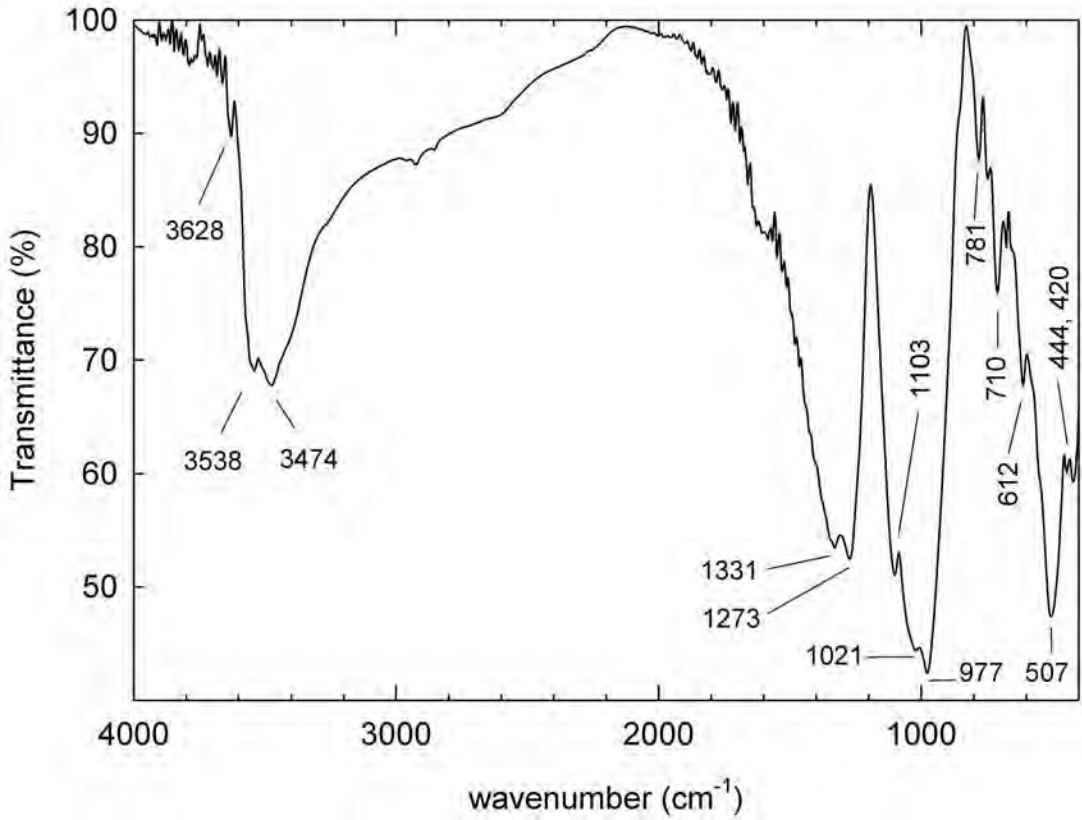


Figure 3