1   REVISE 2 – 15-06-2016

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3   Solid solution along the synthetic LiAlSi$_2$O$_6$ (spodumene) – LiFeSi$_2$O$_6$ (ferri-spodumene)

join: 4   a general picture of solid solutions, bond lengths, lattice strains, steric effects,

5   symmetries and chemical compositions of Li clinopyroxenes

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32   **Running title:** $LiAlSi_2O_6$ – $LiFeSi_2O_6$ clinopyroxenes

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34   **Keywords: lithium, clinopyroxenes, solid solutions, bond lengths, lattice strains, steric effects.**

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Abstract

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54   Seven clinopyroxene compositions along the join $^{M2}Li^{M1}Al^{T}Si_2O_6$ (spodumene) to

55   $^{M2}Li^{M1}Fe^{3+T}Si_2O_6$ (ferri-spodumene) were synthesized at 2 GPa, 800 °C under highly oxidizing

56   conditions (using H_2O_2 fluid) in an end-loaded piston cylinder. In addition, the $LiFe^{3+}Si_2O_6$

57   composition was also synthesized under the intrinsically reducing conditions in a piston cylinder, to

58   check the effect of fO_2 on iron speciation. The run-products were characterized by Field Emission

59   Scanning Electron Microscope (FE-SEM), Rietveld refinements on XRPD synchrotron data and

60   space group were assigned using SAED-TEM patterns. Run-products are composed mainly of

61   lithium clinopyroxene (Li-cpx), plus minor amounts of hematite (magnetite under reducing

62   condition) and corundum, as independently detected by image analysis (area %) and Rietveld

63   refinements (wt. %); moreover, Rietveld results were used to derive cell parameters, M1-site

64   occupancy (Al *vs* Fe^{3+}), atomic positions and average bond lengths of all these Li-cpx indexed in

65   the $C2/c$ space groups according to SAED-TEM.

66   Li-cpx with Al and Fe^{3+} amounts close to 50:50 are actually slightly richer in Al a.p.f.u. than

67   nominal; the $LiFe^{3+}Si_2O_6$ grown under very oxidized and reducing conditions have very similar cell

68   parameters, indicating that fO_2 is unable to induce a significant incorporation of Fe^{2+} in these Li-

69   cpx. The replacement of Al with Fe^{3+} induces a linear (%) increase of the cell edges following $b > a$

70   $> c$, whereas β is roughly constant and the cell volume increases linearly. Furthermore, the

71   substitution of Al with Fe^{3+} only weakly affects the T-O average length (< 1 %), whereas M2-O and

72   M1-O bonds increase linearly of 2.3 and 5.0 %, respectively.

73   These new experimental data have been compared with other available on Li-, Na and Ca-

74   cpx, i.e. $^{M2}(Li,Na,Ca,Mg,Fe^{2+})^{M1}(Mg,Fe^{2+}Al,Ni,Cr,Ga,V,Fe^{3+},Mn,Sc,In)^{T}Si_2O_6$, to model lattice

75   strain, bond lengths, steric effects and phase transitions behaviors. The replacement of Al with

76   progressively larger cations in $LiM^{3+}Si_2O_6$ cpx (M^{3+}: Ni, Cr, Ga, V, Fe^{3+}, Ti, Sc and In) results in a

77   linear increase following $V > b > a > c$, whereas β is roughly constant except for Ti-end-member

78   and $P2_1/c$ compositions. Lattice strains induced by *X, T* and *P* for Li-cpx in the $C2/c$ stability field

79   show that when M1-site is progressively filled with a large cation, ε_1 axis ($\varepsilon_1 > \varepsilon_2 > \varepsilon_3$) increases

80   along b, whereas ε_2 and ε_3 are nearly parallel to a and at about 30 ° from c. Conversely, T will

81   provoke a similar enlargement of ε_1 and ε_2 along b and a edges, respectively, whereas ε_3 is again

82   oriented at about 30 ° from c; the increasing of P will instead shorten all strain tensor components

83   (ε_1, ε_2 and ε_3) with a similar % amount; notably, high-P is the only stress that induces a strain

84   component to be almost parallel to c edge. Moreover, finite lattice strains and orientation in $C2/c$

85    $LiMe^{3+}Si_2O_6$ Li-cpx induced by Me^{3+}: Al-Fe^{3+}, Fe^{3+}-Sc, Sc-In are slightly different, with ε_1

86   invariably lying along b; conversely, Li-Na cation substitution is completely different with the

87   highest and lowest deformations on the ac plane and ε_2 along b; ε_3 vector is negative and oriented at

88   about 30 ° from T-chains.

89   The ideal replacement of Al with larger cations up to In in Li-cpx induces the M1-O, M2-O

90   and T-O average bond lengths to increase by 10.6, 4.3 and < 0.5 %. Steric effects in $Li^{M1}Me^{3+}Si_2O_6$

91   and $Na^{M1}Me^{3+}Si_2O_6$ cpx are significant and very similar, whereas several other Me^{1+} and Me^{2+}

92   substitutions in cpx at both the M1 and M2-site, keeping fixed the other site, display less or even

93   the absence of steric effects. Our new data also better elucidate relationships between Li-cpx

94   composition, symmetry at room and non-ambient conditions and T_c. The aggregate cation radii at

95   the M1-site does not exclusively control the stability of $C2/c$ and $P2_1/c$ polymorphs; instead valence

96   electrons can profoundly favor the stabilization of a polymorph.

97   Finally, Li can be easily and accurately detected (0.1/0.2 a.p.f.u.) in natural clinopyroxenes

98   by cell parameters, especially using the β angle.

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Introduction

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106   Clinopyroxenes are widespread minerals with the crystal-chemical formula M1M2T$_2$O$_6$

107   where most frequent cations at the M2-site are Na, Ca, Mg, Fe^{2+}, at M1-site are Mg, Fe^{2+}, Fe^{3+}, Al

108   and Ti, and where the T-site hosts prevalently Si and less commonly Al. In addition to these

109   abundant compositions, Li-cpx can also be found in the late stage crystallization products of Si-rich

110   magmas. The most common of these is the spodumene end-member ^{M2}Li^{M1}Al^{T}Si$_2$O$_6$ showing only

111   limited cation substitutions towards ^{M2}Na- and (more frequently) ^{M1}Fe^{3+}-rich poles (Deer et al.

112   1997). Despite their very limited chemical variability and rarity in nature, Li-cpx have been

113   extensively investigated in Earth and Material Sciences to derive the general crystal-chemical

114   behavior of clinopyroxene as a function of chemical substitution (Ohashi et al. 2003; Kopnin et al.

115   2003; Redhammer and Roth 2004a; Nestola et al. 2008 and references therein), low- and high-T

116   thermal expansion and phase transitions (Tribaudino et al. 2003; Càmara et al. 2003; Redhammer

117   and Roth 2004b; Tribaudino et al. 2009; Redhammer et al. 2010 and references therein), high-P

118   (Artl and Angel 2000; Gatta et al. 2005; Pommier et al. 2005; Nestola et al. 2008, 2009; Periotto et

119   al. 2013 and references therein), as well as magnetic properties (Redhammer et al. 2001, 2010;

120   Zhou et al. 2014).

121   All these studies have greatly improved our general understanding of physical and chemical

122   properties at ambient and non-ambient conditions and the phase transition behavior of single-chain

123   silicates (and analogue-germanates); the complex puzzle of crystal-chemistry and phase transitions

124   of Li-cpx provides a model for the generalized description of the response of structure to X, T and P

125   in chain silicates and in silicates in general. However, substitution of Al with Fe^{3+} at M1-site for Li-

126   cpx remains to be investigated. To fill this gap, we prepared seven compositions along this nominal

127   join, i.e. from spodumene (LiAlSi$_2$O$_6$) to ferri-spodumene (LiFe^{3+}Si$_2$O$_6$). Experiments were

128   performed at high-T, -P and extremely high fO$_2$ conditions; we also synthesized another nominal

129   ferri-spodumene composition but at moderate (intrinsic) fO$_2$ to induce a possible incorporation of

130   significant amount of Fe^{2+}. We characterized these eight run-products by both scanning (FE-SEM)

131 and transmission (TEM) electron microscopes, in addition to synchrotron X-ray powder diffraction

132 (XRPD) to quantitative constrain yield, composition and the symmetry of crystalline phases.

133 Our experimental results allow us to further depict: i) the general crystal-chemical behavior

134 of $LiMe^{3+}Si_2O_6$ clinopyroxenes (Me^{3+} = Al to In), ii) the comparison of lattice deformations

135 induced by chemical substitution at the M1-site *vs* those induced by *T* and *P* for Li-cpx, steric

136 effects induced by cations at M1- and M2-site in clinopyroxenes and iii) the parameters that impose

137 at ambient conditions the *C*2/*c* symmetry of these compounds. In fact it appears that the cation

138 radius of the cation substituting in the M1 site is not sufficient to account for the symmetry of the

139 studied phases. $Li(Al,Fe^{3+})Si_2O_6$ clinopyroxenes have an M1-site cation size higher than 0.535 and

140 lower than 0.645 Å, whereas in the same cation range $LiNiSi_2O_6$ and $LiCrSi_2O_6$ display $P2_1/c$

141 symmetry and cation radius 0.560 (in low spin state) and 0.615 Å, respectively. This contribution is

142 a further piece of knowledge in the complex puzzle of crystal-chemistry of Li-cpx; the general

143 outcomes and conclusions attained here can be extended to the entire clinopyroxene, and possibly to

144 all chain-silicates.

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146 **Experimental methods**

147 *Starting materials and sample charges*. The two end-member $LiAlSi_2O_6$ and $LiFe^{3+}Si_2O_6$

148 compositions were prepared by mixing for 2 hours in an automatic mortar Li_2SiO_3 + Al_2O_3 + SiO_2

149 and Li_2SiO_3 + Fe_2O_3 + SiO_2 high-purity reagents, in stochiometric amounts (1:1:3). The two fine-

150 grained powders were mixed to prepare the five intermediate compositions (Table 1).

151 Approximately 70 mg of each starting composition were loaded in AgPd capsules with a length of 5

152 mm; we also added 10 wt.% of H_2O_2 (with O_2 ~ 30 wt.%) to each starting composition to prevent

153 the reduction of Fe^{3+} to Fe^{2+} (Tab. 1), since the intrinsic redox state in piston cylinder experiments

154 is reducing due to pressure media and furnace materials (Iezzi et al. 2003a, 2003b, 2005; Della

155 Ventura et al. 2005). To check this experimental strategy, we prepared a capsule with $LiFe^{3+}Si_2O_6$

156 starting material plus 10 wt.% of H_2O, to compare $LiFe^{3+}Si_2O_6$ run-products synthesized in H_2O_2-

157   bearing with H_2O_2-free charges (Table 1). The capsules were carefully weighed before and after

158   welding in order to check loss of weight that would indicate the loss of O_2 and/or H_2O_2.

159   *High-T and -P experiments*. Two capsules per experiment were then inserted in dry alumina

160   cylinder sleeves; these capsule holders were then inserted in cylinders of graphite used as furnace to

161   generate high temperature. Finally, these assemblage of graphite were placed in dry salt-pyrex

162   (pressure medium) piston-cylinder assemblages. All experiments were carried out at 2 GPa and at

163   800 °C using the ''hot piston in'' method in an end-loaded piston cylinder apparatus installed at the

164   Bayereisches Geoinstitut using a 0.5 inch internal diameter bomb (Iezzi et al. 2005). The

165   temperature was monitored with an accuracy of ± 10°C using a $Pt–Pt_{90}Rh_{10}$ thermocouple placed

166   close to the sample charges and separated from it (about 2 mm) with an alumina disk. Pressure was

167   calibrated against the quartz–coesite and kyanite–sillimanite transitions, as well as the melting point

168   of diopside, and is estimated to be accurate to within ± 5% of the stated value (as described fully in

169   Bromiley et al. 2004). Each experiment lasted about 3 days; then, isobaric quenching was achieved

170   by switching off the power supply, with a decreasing in *T* from 800 °C down to 500 °C invariably

171   over less than 10 s.

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173   **Analytical methods**

174   *FE-SEM and image analysis.* Images and chemical data were collected at the micron scale

175   by FE-SEM Jeol-JSM6500F FESEM) installed at the INGV of Roma. The size, shape, distribution,

176   type and abundance of the synthesized phases, i.e. textures (Higgins 2006), were investigated using

177   electron microscopy back scattered images acquired on polished run-products mounted in epoxy

178   resin in a range of magnifications from 150X to 1500X to highlight general and detailed textural

179   features per sample, respectively. For each run-product we selected two FE-SEM fields of view to

180   quantify the phase abundance by image analysis. The image analysis protocol was the same

181   frequently used in petrological studies (Higgins 2006; Iezzi et al. 2008, 2011; Lanzafame et al. 2013

182   and references therein). For each phase a range of grey-levels was determined which scaled with

183   average chemical composition. Then, we automatically counted the area% of these phases with

184   Image-ProPlus 6.0 software, avoiding any mathematical correction of these data (Iezzi et al. 2008,

185   2011a; Lanzafame et al. 2013; Vetere et al. 2013, 2015). The presence of Li in the phase

186   assemblages as well as the relative slight zonation of Li-cpx containing both Al and Fe (possibly

187   Fe^{2+} and Fe^{3+}) limit the accuracy of micro-chemical data collected by Energy Dispersive

188   Spectroscopy during the FESEM observations. Hence, we checked the amount of Fe *vs* Al by

189   Rietveld refinement (see below) and using crystal-chemical constraints.

190   *SAED-TEM*: We collected a series of electron diffraction patterns from the eight run-

191   products. Initially, all samples were prepared by crushing the raw material with a mortar and pestle

192   to a fine powder and dispersing each sample on a 200 mesh Copper TEM grid with a continuous

193   film of amorphous carbon. The diffraction patterns were collected at an accelerating voltage of 200

194   keV using a JEOL 2100 transmission electron microscope with a LaB_6 filament, available at the

195   department of Biology, at University of Patras, Greece. The data were collected in selected area

196   diffraction (SAD) mode, using a parallel beam and a 70 μm C2 aperture and were recorded from a

197   Gatan ES500W, a 12-bit charge-coupled device (CCD). Selected area diffraction patterns were

198   obtained by selected sub-region of the crystal using a 50 μm diameter SAD aperture. Crystals of

199   approximately 400 nm were located in imaging mode; the diffraction data were then collected

200   following the manual diffraction tomography (MDT) method (Gorelik et al. 2011), by rotating the

201   crystal around an arbitrary axis and diffraction patterns were collected every 1° of tilt. A standard

202   single tilt JEOL holder permitted us a tilting of ± 30°. At each step, a static diffraction pattern and

203   then a precessed diffraction pattern was collected using the spinning star precession unit

204   (Nanomegas SPRL: http://www.nanomegas.com, Belgium).

205   Tilting a crystal around an arbitrary crystallographic axis reduces the dynamical diffraction

206   effects, inevitable in electron diffraction and the data are treated as being kinematical. The reduction

207   in dynamical scattering occurs because fewer reflections are excited simultaneously, thus less

208   dynamical scattering is detected and the intensities recorded are more reliable. The use of

209   precession in this experimental setup is to integrate the reciprocal volume. A precession semi-angle

210   of 1° was used to integrate the data, meaning a 2° volume was integrated, and there is overlap

211   between each diffraction pattern. The purpose of this is to allow us only to consider fully integrated

212   reflections during the data processing steps. Partially integrated reflections are disregarded,

213   significantly reducing the complexities of the data analysis.

214   Cross-validation of the data was performed by collecting additional data on one sample of

215   this series (Fe#0) at the Institute of Physical Chemistry, in Mainz, using an FEI TECNAI F30

216   transmission electron microscope, operating at 300 keV. Diffraction patterns, in this case, were

217   collected using a defocused stem probe, which is a quasi-parallel beam made by using a 10 μm C2

218   aperture and a large defocus. The patterns were recorded from a 14 bit Gatan 794MSC slow scan

219   CCD detector. Data obtained from both instruments were of comparable quality, enabling us to

220   define assuredly the space group symmetry. Experimental diffraction patterns, from each sample,

221   were processed using the ADT3D software (NanoMEGAS SPRL, Belgium).

222   *Synchrotron XRPD.* A monochromatic X-ray beam ($\lambda = 0.3263$ Å) at the ID11 beamline of

223   the ESRF in Grenoble (France) was used for collecting data on a 2D area detector (Frelon 2K CCD)

224   (Labiche et al. 2007) with a 2048 x 2048 pixel resolution and pixel size ~ 47 x 47 μm. The beam

225   centre was offset on the 2D detector to give improved angular resolution. The sample to detector

226   distance was calibrated using CeO_2 powder at 186.6 mm. Samples were mounted for diffraction

227   measurements by picking up a small fragment from the powder sample using a cryoloop and

228   paratone oil. Data collection was performed by rotating the samples over a range of 360° in steps of

229   20° giving 18 images in total per sample. This rotation scan was repeated with two different X-ray

230   beam sizes; 0.05 x 0.05 and 0.3 x 0.3 mm. With the small beam size the powder data have sharper

231   peaks but the powder averaging is not as good compared to the data set from the large beam size

232   and lower angular resolution. Images from the rotation scan were averaged and integrated using the

233   fit2d software package (Hammersley et al. 1996).

234   Based on SEM data, we assigned peaks in diffraction patters to the crystalline phases grown

235   in each run-product. Then, all the diffraction patterns were first refined with the software EXPGUI-

236   GSAS (Larson and Von Dreele 1997; Toby 2001) using the Le Bail method (Le Bail 2005),

237   following the procedure adopted by Iezzi et al. (2010) and (2011b) to accurately model background

238   (Chebyshev function with 10-12 adjustable parameters), cell parameters (of all crystalline material)

239   and pseudo-Voigt peak shape function (Finger et al. 1994). After that the Le Bail models fully

240   reproduced each recorded XRPD patterns, we fixed these parameters (background, cell and profile

241   of Bragg peaks) and determined with Rietveld refinement the phase abundance (wt. %), atomic

242   positions using isotropic displacement parameters per crystallographic site and cation occupancy at

243   the M1-site. For all the run-products with Al and Fe (Tables 1 and 2) we fixed the amount of Li and

244   Si both at 1 and 2 a.p.f.u. at M2- and T-sites, respectively, whereas the amount of Al *vs* Fe^{3+} were

245   refined using the constraint that their sum is 1 a.p.f.u. In contrast, the Fe#2+ run-product was not

246   refined with Rietveld approach, since it was not possible to attain a satisfactory determination of Li

247   *vs* Fe^{2+} at the M2-site and especially Fe^{2+} *vs* Fe^{3+} at the M1-site.

248   For each run-product, at the beginning of Le Bail and Rietveld refinements we used the

249   crystal structural models of spodumene and ferri-spodumene reported in Redhammer and Roth

250   (2004a) for the most Fe-poor ($LiAlSi_2O_6$) and Fe-rich ($LiFe^{3+}Si_2O_6$) run-products, respectively, plus

251   the starting models of corundum and hematite from the ICSD (Inorganic Crystal Structural

252   Database). According to TEM data (see below), we refined all clinopyroxene in the *C*2/*c* space

253   group; at the end of each Rietveld refinement a good reproduction of experimental XRPD patterns

254   were attained, agreement indexes were of high quality and un-indexed Bragg reflections were not

255   recognized (Table 2). We further validated our Rietveld refinement by comparing cell parameters

256   and bond lengths measured here for the two end-members with those obtained by single crystal X-

257   ray diffraction (SC-XRD) for $LiAlSi_2O_6$ and $LiFe^{3+}Si_2O_6$, as reported by Redhammer and Roth

258   (2004a).

259

260   **Results**

261   *Textures of Li-cpx.* The textural features of the run products are displayed in Fig. 1. The

262   area% of phases quantified by image analysis is reported in Table 3. Clinopyroxene is by far the

263   most abundant phase in any sample. Minor amounts of corundum plus tiny and rare crystals of an

264   Al_2SiO_5 phase, probably kyanite, occur in the Fe#0 and Fe#20 run-products (Figs. 1 and 2).

265   Hematite is present in the other Fe-bearing run-products synthesized with H_2O_2 (Fe#20, Fe#40,

266   Fe#50, Fe#60 Fe#80 and Fe#100 run-products); the Fe#2+ run-product is composed of Li-cpx and

267   few tiny crystals of magnetite (Figs. 1 and 2).

268   Non-crystalline materials have been not detected by FE-SEM, probably due to their low

269   amount in area% (and/or wt.%). Small amounts of corundum and of an Al_2SiO_5 phase, hematite and

270   magnetite in the Fe#0, Fe#100 and Fe#2+ experimental charges, respectively (Table 3), indicates

271   the presence of a very low amount of a phase (or phases) composed of Li, Si and O, possibly the

272   non-crystalline Li_2SiO_3 phase solidified during quenching. Li-cpx with intermediate amount of Al

273   and Fe of this study show slight chemical zoning, especially the Fe#40 and Fe#50 samples (Fig. 1).

274   Quantitatively, the amount of un-desired phases of corundum, hematite plus magnetite is lower than

275   ~ 10 area% in any experimental charge, and lower in the end members; in turn, the yield of Li-cpx

276   is always higher than 90 area% (Figs. 1 and 2 and Table 3). The stochiometry of these Li-cpx was

277   not analyzed directly by micro-chemical data, although the low amount of the other un-desired

278   phases with simple chemistries (corundum, hematite and magnetite), suggest that the departure of

279   all synthesized Li-cpx from the nominal composition is limited. Under an extremely oxidizing

280   environment, i.e. Fe^{2+}-free, and with Li-cpx amount higher than 90 area% (and wt.% except for the

281   Fe#40 and Fe#50) (Table 3), the chemical variations of these Li-cpx is restricted to the M1 site; in

282   turn, their chemical compositions can be straightforwardly calculated by XRPD data by refining

283    $Al_xFe^{3+}_{1-x}$, where $0 \leq x \leq 1$ (see below).

284   The shape of Li-cpx is invariably nearly equant with crystal lengths equal or double their

285   widths, i.e. aspect ratio range from 1 to 2. By contrast, the absolute size strongly increases with Fe

286   content (Fig. 1). The three Al richer run-products have maximum crystal size dimension invariably

287   lower than 10 μm, up to 15-20 μm for the Fe#50 and Fe#60 samples, around 20-25 μm for the

288   Fe#80 crystals, whereas Fe#100 and Fe#2+ show crystal maximum edges up to about 100 and 200

289   μm, respectively (Fig. 1).

290   *Space group of Li-cpx*. Data analysis of diffraction tomography patterns, using a precessed

291   beam, allowed for space group determination due to the reduced dynamical scattering and multiple

292   diffraction. All single crystals employed exhibit similar monoclinic symmetry. Accurate unit cell

293   parameters however were extracted without precessing the beam, because later adds a significant

294   error to the positions of the reflections. For this reason we used the diffraction patterns from a

295   stationary beam to determine a more accurate unit cell size (Table 4)

296   The reciprocal volumes were reconstructed from the measured intensities, and the volume

297   was checked for systematic absences. From the observed extinction conditions, the space groups

298   *C2/c* and *Cc* were selected, both were tested, and C2/c was derived as the most feasible solution

299   (Table 3). The 3D reconstruction of the reciprocal space from the extracted intensities, for one

300   representative run product, Fe#50, presented in Fig. 3 shows the violation of extinction conditions

301   for all other possible monoclinic space groups. The output from ADT3D software is a list of

302   reflections with their Miller indices and intensities. Additionally, processing the extracted

303   reflections, using the direct methods software SIR2014 (Burla et al. 2015), also confirmed *C2/c* and

304   *Cc* as the most likely space groups, with the highest figures of merit.

305   *Cell parameters, site occupancy and bond lengths of Li-cpx from XRPD*. The agreement

306   indexes of Rietveld refinements for all run-product crystallized with H_2O_2 fluid are lower than 5 %

307   (except R_p for Fe#100) (Table 2). As Fe content increases the diffraction peaks of Li-cpx become

308   broader (Fig. 1) and their diffraction patterns show also an increase of "spottiness" (Fig. 4) (Debye

309   rings are lesser and lesser continuous) roughly from Fe#0 to Fe#100 due to sample preparation. In

310   turn, a progressive reduction in accuracy of crystallographic results are observed for the Fe#100 Li-

311   cpx due to a slight increasing of crystallographic preferred orientation of Li-cpx crystallites (Fig. 4

312   and Tab 2). Even with these minor limitations, the calculated Rietveld patterns accurately

313   reproduced the experimental XRPD pattern (Fig. 4S).

314   The amount of crystalline phases in wt.% and the site occupancies at the M1-site, i.e. the

315   actual crystal-chemical formula of Fe#20 to Fe#80 Li-cpx, are reported in Table 3. The actual and

316   nominal comparison of our Li-cpx are displayed again in Fig. 2, as well as the amount of crystalline

317   phases determined by Rietveld (wt. %) *vs* image analysis (area %). The majority of our Li-cpx show

318   a very slight deviation from the nominal composition, except for the run-products Fe#40 and Fe#50

319   that are richer in Al and poorer in Fe^{3+} compared to their nominal compositions, in agreement with

320   the presence of hematite (Fig. 2 and Table 3). The discrepancy between area% and wt.% phase

321   proportions per each run-product is very small, with maximum differences for the Fe#40 and Fe#60

322   samples (Fig. 2). Taking into account that the actual composition of Fe#60 Li-cpx is close to the

323   nominal one, it could be inferred that Fe#60 Li-cpx has an actual composition richer in Al a.p.f.u.

324   than measured by Rietveld refinement (Tables 3 and 5, Fig. 2). For the Fe#2+ run-product a direct

325   determination of site occupancies was not attainable, due to the possible presence of Fe^{2+} at both

326   M1- and M2 site for local charge balance requirements (Càmara et al. 2003, 2006); however, its

327   composition can be constrained by cell parameter data (see below).

328   The evolution of *a*, *b*, *c*, *β* cell and volume parameters are reported in Table 4 and displayed

329   in Fig. 5. The cell data refined here on polycrystalline Li-cpx with $LiAlSi_2O_6$ (Fe#0) and

330   $LiFe^{3+}Si_2O_6$ (Fe#100) compositions are practically identical to those obtained by single crystal data

331   (Redhammer and Roth 2004a, 2004b). All our cell parameters determined here can be thus

332   considered highly accurate, as well as the crystal-chemistry of our Li-cpx end-members, i.e.

333   absence of any Fe^{2+} at both M1- and M2-sites. Therefore, all Li-cpx grown with H_2O_2 have only Li

334   and Si at M2- and T-site, respectively, whereas M2 site is occupied only by Al and Fe^{3+}; the

335   absence of Fe^{2+} agrees with the crystallization of hematite (Table 3).

336   The replacement of Al with Fe^{3+} induces a linear (%) increase of the cell edges following *b*

337   > *a* > *c*, whereas *β* is roughly constant (Fig. 5); the cell volume increases linearly by about 6 %

338 from spodumene to ferri-spodumene. The Fe#2+ Li-cpx grown at reducing intrinsic fO_2 shows a

339 very limited deviation of its cell data in comparison to Li-cpx in Fe#100 and to that determined in

340 Redhammer and Roth (2004a). This suggests that although the redox state is markedly different

341 between the Fe#2+ and Fe#100 syntheses, i.e. reducing intrinsic vs H_2O_2 experimental conditions

342 and reflected by the crystallization of hematite and magnetite, respectively, Li-cpx is unable to

343 incorporate a significant amount of Fe^{2+} at both M1- and M2-sites, as it would be required by

344 charge balancing (Càmara et al. 2003, 2006). Moreover, the Fe#100 and Fe#2+ run-products have

345 dark red and green colors, respectively. This suggests that Li-cpx in Fe#2+ contains some Fe^{2+}

346 amounts; however, due to the high similarities in cell parameters (Fig. 5), it can be expected that the

347 amount of Fe^{2+} which can be incorporated is limited. As an evidence, the β angle of Li-cpx is

348 extremely sensitive to cation occupancy at M2-site; Fe#2+ and Fe#100 have practically the same β

349 of 110.2° (Table 4), whereas the $(Li_{0.85}Mg_{0.09}Fe^{2+}_{0.06})(Fe^{3+}_{0.85}Mg_{0.15})Si_2O_6$ cpx has 109.83° (Càmara

350 et al. 2003). To summarize, Li-cpx in Fe#2+ has a crystal-chemical formula lying along $(Li_{1-}$

351 $_xFe^{2+}_x)(Fe^{2+}_xFe^{3+}_{1-x})Si_2O_6$ with x ($0 \leq x \leq 1$) close to 0 a.p.f.u.. The amount of Fe^{3+} is instead well

352 constrained by Rietveld refinement for all other Fe-bearing Li-cpx, due to the significant difference

353 in scattering of X-ray by Al vs Fe. The slight horizontal offsets of Fe#60 and Fe#80 Li-cpxs in Fig.

354 5 from the linear regressions can be due to a slight underestimation of Al; nonetheless, this

355 discrepancy is invariably below 0.05 a.p.f.u (Fig. 5).

356   The atomic positions and derived average bond lengths are reported in Tables 5 and 6 and

357 plotted in Fig. 6. Again, these data are compared with single crystal X-ray structural refinement for

358 $LiAlSi_2O_6$ and $LiFe^{3+}Si_2O_6$ (Redhammer and Roth 2004a, 2004b). These average bond lengths are

359 almost identical to those refined here by XRPD for Fe#0 and Fe#100, respectively (Fig. 6).

360 Substitution of Al with Fe^{3+} only weakly affects the T-O average length (< 1 %). Instead M2-O and

361 M1-O bonds both increase by 2.3 and 5.0 % (Fig. 6). Similarly to cell parameters, also M2- and

362 M1-O average bond lengths evolve in a linear manner.

363

364 **Discussion**

365   *Li-cpx cell parameters*. The investigated spodumene - ferri-spodumene join is the first

366 substitution vector involving a metal and a non-metal cations at M1-site of Li-cpx. Here, the XRPD

367 and TEM data point out that Al can be completely replaced by Fe^{3+} (at 800 °C and 2 GPa), the solid

368 solution is nearly ideal due to an almost linear evolution of cell volume and space group is

369 invariably $C2/c$ at room conditions (Figs. 3, 5 and 6, Tables 2, 3, 4, 5 and 6). As mentioned

370 previously, these new data allow further clarification of several general crystal-chemical features of

371 Li-cpx, that are one of the most detailed investigated silicate sub-groups (room-T and -P, low- and

372 high-T, high-P). Therefore, it is possible to model relations between structural and compositional

373 parameters using previous data on Li-cpx with those provided here. The general constraints of Li-

374 cpx can be then extrapolated to the entire clinopyroxene family or even for the chain silicates super-

375 group.

376   The first important outcome concerns the evolution of cell parameters of $LiMe^{3+}Si_2O_6$, with

377 $^{VI}Me^{3+}$ ranging from Al to In, corresponding to an increase in cation radii from 0.535 to 0.800 Å,

378 respectively. This substitution is only theoretical, since a direct exchange of the smallest with the

379 largest $^{VI}Me^{3+}$ cation is not yet proved and probably is limited due to the significant difference in

380 atom size dimension of about 33 % [$\Delta\% = (r^{In} - r^{Al}) / r^{In}$]. The evolution of cell volume at ambient

381 conditions for Li-cpx as a function of the M1-site occupancy, with M2- and T-site occupied only by

382 Li (except the sample of Càmara et al. 2003) and Si, respectively, is displayed in Fig. 7. This

383 increasing trend as a function of Me^{3+} cation size is almost linear, with only a slight tendency to

384 level off from Sc to In. The Li-cpx for whom temperatures of displacive phase transitions (Tc) are

385 determined are also reported (Fig. 7). $P2_1/c$ Li-cpx structural polymorphs have two not-

386 symmetrically equivalent tetrahedral chains, one kinked and one relatively extended as classically

387 measured by the O3-O3-O3 angle, whereas $C2/c$ polymorphs have equivalent and extended

388 tetrahedral chains. Large M1 cation and high-T tend to stabilize the $C2/c$ structural topology (Arlt

389 and Angel 2000; Tribaudino et al. 2009). A third polymorph has again the $C2/c$ space group but

390   with strongly kinked equivalent T-chains and is stabilized at high-P (Arlt et al. 1998; Arlt and

391   Angel 2000). Compared to $C2/c$, $P2_1/c$ Li-cpx at room show only a very minor cell volume

392   deviation with respect to the linear regression (Fig. 7); $LiNiSi_2O_6$, invariably $P2_1/c$ at least up to 773

393   K (Tribaudino et al. 2009), most offsets down the linear regression (Fig. 7). On the other hand, $C2/c$

394     $LiTiSi_2O_6$ most offsets upwards the linear regression (Fig. 7).

395   The same cell edge trends as a function of the M1 cation radii are reported in Fig. 7S; as are

396   the a, b and c edges which also increase as the M1-site size augments, similar to cell volume

397   evolution. However, the a cell edge increases only from Al to Sc; further cation substitution,

398   between Sc and In, does not promote an increase in the a cell parameter. $P2_1/c$ Li-cpx at room

399   temperature/pressure are almost indistinguishable by their b and c cell edges, whereas the a

400   parameter is slightly downshifted respect to the general trend (Fig. 7S). A larger downshift is found

401   for the $LiNiSi_2O_6$ clinopyroxene. With the exception of the $LiTiSi_2O_6$ compound, the three Li-cpx

402   with a $P2_1/c$ space group at ambient conditions are clearly off trend for the monoclinic β angle (Fig.

403   7S). Resuming, Li-cpx with variable cation at the M1-site and thus size at room-T and -P have b

404   and c cell edges that increase linearly and Li-cpx with $P2_1/c$ and $C2/c$ space groups are

405   indistinguishable. By contrast, a cell first increases in a linear way and then saturates from Sc to In;

406   a and especially the monoclinic β angle promptly discriminates P- to C-lattice, except for the

407     $LiTiSi_2O_6$ pole (Figs 7S). Finally, the $a\sin\beta$ dimension, corresponding to the distance between

408   parallel T-chains, follow the same trend of the a cell alone (Figs. 7S).

409   *Li-cpx cell strains*. We calculate the strain tensor induced by cell parameter variations, using

410   the program "win_strain" compiled by R.J. Angel (http://www.rossangel.com/text_strain.htm).

411   Thus, we calculate lattice strains using selected couples of cell parameters plotted in Fig. 7S of

412     $LiMe^{3+}Si_2O_6$, where $Me^{3+} >$ Al up to In, always with respect to that of $LiAlSi_2O_6$. Hence, from the

413   smallest cation Al at M1-site towards In, we outlined lattice strain paths by calculating the

414   orthogonal finite strain tensor (%) ε_1, ε_2 and ε_3 components ($\varepsilon_1 > \varepsilon_2 > \varepsilon_3$) and their orientations with

415   respect to Li-cpx cell. Monoclinic symmetry imposes a strain vector that is fixed along b, whereas

416 the other two components are on the 010 plane and form an angle with a and c edges (Gatta et al.

417 2005; Iezzi et al. 2005, 2010, 2011b and reference therein). The lattice deformation of Li-cpx

418 induced by chemical substitution (X) at M1-site is displayed in Fig. 10 and compared with those

419 induced by T and P for $LiAlSi_2O_6$ and $LiFe^{3+}Si_2O_6$ end-members in the $C2/c$ stability fields. We

420 also reported a structural model of Li-cpx plotted down b edge, to facilitate the visualization of the

421 deformations as a function of the structure of Li-cpx.

422 The substitution of Al with larger cations at M1 induces that the highest deformation, i.e. ε_1,

423 is along b, whereas ε_2 and ε_3 are disposed at about 15/20 and 105/110 ° from c on the 010 surface up

424 to Sc then they suddenly re-orient to 35 and 125 ° from c when Li-cpx approach the In pole (Fig. 8).

425 The deformations induced by the substitutions of Al with Ni and Cr from a C- to P-lattices (to be

426 directly investigated) occur under a slightly different orientation for Ni and very similar to other C-

427 lattice for Cr. The still undetermined phase transition occurring between Al and Ni again has ε_1

428 fixed along b, but ε_2 and ε_3 are disposed along and normal to c, respectively, very differently from

429 all other lattice strains induced by chemical substitution; moreover, the ε_3 component is negative,

430 hence the replacement of Al by Ni should be accompanied by an expansion of Li-cpx along b and c

431 and a contraction along a (Fig. 8). The % variation of finite strain components induced by the

432 increasing size of M1 cation radii is similar for ε_2 and ε_3, whereas ε_1 has a significantly higher

433 increasing rate towards the In end-member (Fig. 8). Specifically, ε_2 first increases and then levels

434 off, whereas ε_3 has invariably the same trend with a very low rate of increase (Fig. 8). On the whole,

435 the increasing size of cation radii at M1-site imposes the highest deformation (ε_1) along b, and a

436 moderate to low strain on the other two mutual orthogonal components (ε_2 and ε_3) on the ac plane

437 (Fig. 8). The virtual substitutions of Al with Ga, V, Fe^{3+}, Ti, Sc and In result in normalized strain

438 components ($\varepsilon_1/\varepsilon_1$:$\varepsilon_2/\varepsilon_1$:$\varepsilon_3/\varepsilon_1$) of 1:0.60:0.52, 1:0.75:0.47, 1:0.67:0.43, 1:0.64:0.44, 1:0.55:0.38 and

439 1:0.48:0.37, respectively; indeed, the ε_1 component increases more than ε_2 and ε_3 moving from Al to

440 In (Fig. 8).

441   To compare lattice deformations induced by chemical substitution with those induced by

442 temperature and pressure it has been considered only the two $LiAlSi_2O_6$ and $LiFe^{3+}Si_2O_6$ poles with

443 the $C2/c$ space group (with tetrahedral chains extended). From room temperature to around 700 °C,

444 lattice deformations of both $LiAlSi_2O_6$ and $LiFeSi_2O_6$ poles are similar in orientation and

445 magnitude. The ε_1 and ε_2 are very close between them although their deformation accounts less than

446 1%. The highest strain ε_1 component is along b and at about 120 ° from c for $LiAlSi_2O_6$ and

447 $LiFe^{3+}Si_2O_6$, respectively; the ε_3 component is instead very small and oriented around 30 ° from c

448 edge of Li-cpx (Fig. 8). The normalized strain components for $LiAlSi_2O_6$ and $LiFe^{3+}Si_2O_6$ are close

449 to 1:0.78:0.14 and 1:0.95:0.23, respectively (Fig. 8).

450   The same comparison has been done with respect to pressure only for $LiAlSi_2O_6$ that retains

451 its $C2/c$ space group with extended chains from ambient to pressure < 3.3 GPa (Arlt and Angel

452 2000), whereas $LiFe^{3+}Si_2O_6$ transforms from $C2/c$ to $P2_1/c$ at a relative low pressure < 1 GPa

453 (Pommier et al. 2005). Similar to temperature, the effect of pressure induces an absolute

454 deformation from room- to high-P (3.2 GPa) of < 1 % per strain vectors. This deformation induces

455 a contraction of strain tensor. The absolute magnitude of ε_1 and ε_2 are very similar, but ε_3 is close in

456 % to these other two components, with normalized strain components close to 1:0.97:0.73 (Fig. 8).

457 The strain tensor induced by pressure is completely different from that related to X and T; the ε_2

458 axes lies on b cell edge, whereas ε_1 and ε_3 are close to be normal and parallel to c side (Fig. 8). A

459 general reappraisal of main features of lattice strains induced by X, T and P for Li-cpx in the $C2/c$

460 stability field with extended tetrahedral chains is reported on top of Fig. 8. Li-cpx with M1-site

461 progressively larger determine a significant increase in the ε_1 axis along b, whereas intermediate

462 and low strain axes (ε_2 and ε_3) are nearly parallel to a and at about 30 ° from c (Fig. 8). The lattice

463 strain induced by T will provoke a similar enlargement (ε_1 and ε_2) along b and a edges, whereas a

464 minor elongation (ε_3) will be observed at about 30 ° from c (Fig. 8). The cell deformation induced

465 by P will instead shorten all strain tensor components (ε_1, ε_2 and ε_3) with a similar % amount;

466   notably, high-P is the only stress (also Al - Ni substitution will shorten along c, see before) that

467   induces a strain component to be almost parallel to c edge (Fig. 8).

468   To gain further insight in the mechanism of deformation induced by chemical substitution

469   (Fig. 8), we calculated the strain between Al-Fe^{3+}, Fe^{3+}-Sc and Sc-In and in addition that induced by

470   the replacement of Li by Na in $(Li,Na)Fe^{3+}Si_2O_6$ compounds (Fig. 9). For the substitution at the

471   M1-site (Al-Fe^{3+}, Fe^{3+}-Sc and Sc-In), it is invariably shown that ε_1 is coaxial with the b cell edge;

472   conversely, either the strain tensor ratios and the orientation of ε_2 and ε_3 with respect to Li-cpx cell

473   are different among them (Fig. 9). The replacement of Al by Fe^{3+} imposes that intermediate and

474   smallest ε_2 and ε_3 tensors are close to two thirds and half of the highest one (ε_1) respectively,

475   oriented at about 100-105 ° and 10-15 ° from c edge, respectively. The substitution of Fe^{3+} by Sc

476   imposes that intermediate and lowest axes of strain tensors are 45 and 32 % of the maximum strain

477   axis (ε_1) with an orientation at about 135 and 45 ° from the c direction (Fig. 9). The Sc-In cation

478   substitutions are peculiar (Figs. 8 and 9) with the smallest strain component very close to 0 and

479   almost co-axial with c, i.e. coaxial to the elongation of the tetrahedral chains, whereas the

480   intermediate strain vector is aligned perpendicular to the T-chains and is about 40 % of the

481   maximum strain axis (ε_1) lying along b (Fig. 9). The very limited deformation induced by Sc - In

482   substitution along c, as already shown by cell edges saturation effects (Figs. 7 and 7s), evidence that

483   fully stretched tetrahedral chains cannot be further extended. Sc and In are at the limit of a sixfold

484   coordination in the M1 and the tetrahedral units are rather undeformable. In turn, the deformation of

485   the cell induced by the replacement of Sc by In reaches a limiting value along the c axis and further

486   expansion in cell volume must occur on other directions (Fig. 9). The substitution of Li by Na at the

487   M2 site (considering ^{VIII}Li), with M1-site occupied only by Fe^{3+}, unravels a very different behavior

488   compared to any previous lattice deformation mechanisms (Figs. 8 and 9). The highest and lowest

489   deformations occur on the ac plane, whereas the intermediate strain tensor is coaxial with the b cell

490   edge; significantly, the ε_2 and ε_3 vectors are very similar in absolute modules, but the former is

491 positive and the latter is negative. In other words on the *ac* plane at about 30 ° from the direction of

492 the tetrahedral chains the replacement of Li by Na induces a significant contraction (Fig. 9).

493 *Li-cpx average bond lengths*. The replacement of the smallest cation, Al with larger ones

494 towards the largest, In, in Li-cpx also induces modifications of average bond lengths. Our XRPD

495 data are unable to accurately determine single atomic bonds and bond angles, hence we compared

496 only the average atomic bond lengths per site obtained here with those reported in previous studies

497 performed with single-crystal X-ray diffraction method (Càmara et al. 2003; Kopnin et al. 2003;

498 Redhammer and Roth 2004a, 2004b; Nestola et al. 2008). These average bond lengths are plotted in

499 Fig. 10; the progressive substitution of Al towards In induces that M1-O average bond length

500 increases of 10.6 % [$\Delta\% = (^{In}M1-O_{(max)} - {}^{Al}M1-O_{(min)}) / {}^{In}M1-O_{(max)}$], M2-O of 4.3 %, whereas T-O

501 are virtually unmodified, i.e. < 0.5 %.

502 Conversely, the strong T-O bonds are very slightly affected by the substitution of adjacent

503 M1-site; as already pointed out, tetrahedrons accommodate this substitution by rotating themselves

504 as rigid units (Redhammer and Roth 2004a). It is also worth noting that both M1- and M2-O

505 average bonds increase linearly from Al to In, differently to cell parameters (Figs. 7, 7S and 10).

506 The slight scatter from the general two linear regressions of our two Fe-richest Li-cpx (Fe#80 and

507 Fe#100) can be attributed to a reduced accuracy of atomic positions determined by Rietveld (Table

508 5), whereas the highest shifting from both linear M1- and M2-O regressions is observed for the

509 LiVSi$_2$O$_6$ compound (Redhammer and Roth 2004a). This feature couples with the singular low *T*c

510 of LiVSi$_2$O$_6$ compound (Redhammer and Roth 2004b) when compared with all other Li-cpx (see

511 below).

512 *Steric effects in* $^{M2}Me^{1+M1}Me^{3+}Si_2O_6$ *and* $^{M2}Me^{2+M1}Me^{2+}Si_2O_6$ *cpx*. The substitution of

513 cations at only M1- or M2-sites affects also the adjacent site occupied by the same cation (Figs. 6

514 and 10). This "steric effect" was first reported in clinopyroxenes by Ghose et al. (1987) and recently

515 expanded by Gori et al. (2015); in clinopyroxene, as well as for other silicate structures, the

516 absolute shapes and sizes of all polyhedra can be also dependent to some extent on the interaction

517   with the adjacent polyhedra. Following Ghose et al (1987) and Gori et al (2015), and using a large

518   and updating dataset of M1-O and M2-O average bond lengths, it is possible here to further

519   highlight steric effects for the most important and key cpx crystal-chemical compositions and joins.

520   For $^{M2}Me^{1+M1}Me^{3+}Si_2O_6$ cpx, the increase of M1-O and M2-O average bond lengths induced by the

521   same trivalent cation substitution ($^{M1}Me^{3+}$: Al from In, 0.535 to 0.800 Å, Δ = 33 %) for Li- and Na-

522   cpx are very similar; in Li- and Na-cpx, M1-O increase of 10.6 and 10.1%, whereas M2-O of 4.3

523   and 4.1 %, respectively (Fig. 11). Conversely, when the M1 site is kept occupied only by Fe^{3+} and

524   the M2 site changes from Li to Na ($^{M2}Me^{1+}$: ^{VIII}Li from Na, 0.92 to 1.18 Å, Δ = 26 %), the M1-O

525   average lengths change lesser than 0.6 % and the M2-O of 3.4 % (Redhammer and Roth 2002), i.e.

526   the steric effect of M2 site on M1 is very limited. Therefore, the structure of $^{M2}Me^{1+M1}Me^{3+}Si_2O_6$

527   cpx are much more affected by changes of $^{M1}Me^{3+}$ than by $^{M2}Me^{1+}$, as clearly observable in Fig. 11.

528   This analysis can be extended to $^{M2}Me^{2+M1}Me^{2+}Si_2O_6$ to have a more general reappraisal of

529   the steric effect in clinopyroxene. When the M2-site is occupied only by Ca and the M1-site

530   changes from Ni up to Mn^{2+} (Me^{2+}: Ni to Mn, 0.56 to 0.81 Å, Δ = 31 %) the M1-O average bond

531   length increases of 4.7 % and induces a slight increase of 1.3 % in the M2-O mean length (Fig. 11).

532   Hence, under a similar range of size differences of trivalent (Me^{3+} with Δ = 33 %) and divalent

533   (Me^{2+} with Δ = 31 %) cations hosted at the M1-site, the M1-O and M2-O average bond lengths

534   extend more than two times and the steric effect is by far more marked in $^{M2}Me^{1+M1}Me^{3+}Si_2O_6$ than

535    $^{M2}Me^{2+M1}Me^{2+}Si_2O_6$ cpx (Fig. 11). In contrast, when the substitution occur at M2-site for a fixed

536   M1-site cation occupancy for $^{M2}Me^{2+M1}Me^{2+}Si_2O_6$, the situation is more complicated; when the M2-

537   site is occupied by variable amounts of Ca-Mg, Ca-Fe^{2+}, Ca-Co and Ca-Zn (considering average

538   bond lengths for eight-fold coordination of the M2-site (in both $C2/c$ and $P2_1/c$ space groups) and

539   the M1-site is occupied only by Mg, Fe^{2+}, Co and Zn, respectively, two general different situations

540   are depicted (Alvaro et al., 2010, 2011; Gori et al. 2015). The substitution of Ca with Mg (^{VIII}Ca

541   and ^{VIII}Mg: 1.12 to 0.89 Å, from Ca_1 to $Ca_{0.2}Mg_{0.8}$, Δ = 16%) determines an increase of the M2-O

542   mean lengths of only 1.5 %, whereas M1-O is little modified (0.5 %), i.e. the steric effect is very

543   low (Fig. 11); the substitution of Ca with Fe^{2+} (^{VIII}Ca and $^{VIII}Fe^{2+}$: 1.12 to 0.92 Å, from Ca_1 to $Ca_{0.15}$

544    $Fe^{2+}_{0.85}$, $\Delta = 20$ %) behaves similarly to that of Ca to Mg (Fig. 11) and the substitution of Ca with

545   Co (^{VIII}Ca and ^{VIII}Co: 1.12 to 0.9 Å, from Ca_1 to $Ca_{0.4}Co_{0.6}$, $\Delta = 12$ %) determines an increase of the

546   M2-O mean lengths of only 1.6 %, whereas M1-O is again weakly modified being 0.6 % (Fig. 11).

547   The situation is instead significantly different for substitution of Ca with Zn (^{VIII}Ca and ^{VIII}Zn: 1.12

548   and 0.9 Å, from Ca_1 to $Zn_{1.0}$, $\Delta = 20$ %); this determines an increase in both M1-O and M2-O mean

549   lengths of 2.2 and 2.0 %, i.e. both average lengths are faintly modified but with an almost identical

550   rate (Fig. 11).

551   *Phase transitions in $^{M2}Li^{M1}Me^{3+}Si_2O_6$ cpx.* Crystal-chemistry of Li-cpx is probably one or

552   even the best investigated sub-group of minerals at room-, low-, high-T and high-P (see before).

553   Several general reappraisals have been thus inferred also the relation between symmetry and

554   chemical compositions, i.e. the influence of crystal-chemical formulas of Li-cpx and the $P2_1/c$

555   polymorph with kinked and relatively extended not-symmetrically equivalent tetrahedral chains

556   and/or the two $C2/c$ polymorphs with respectively extended and kinked symmetrically equivalent T-

557   sites (Artl and Angel 2000; Càmara et al. 2003; Tribaudino et al. 2003, 2009; Redhammer and Roth

558   2004b; Gatta et al. 2005; Pommier et al. 2005; Nestola et al. 2008; Periotto et al. 2013 and

559   references therein).

560   However, the Li-cpx characterized in this study allow us to put further constraints on this

561   topic. In Fig. 12 it is reported the space group of Li-cpx at ambient conditions plus the available

562   stability fields at low- and high-T XRD of $P2_1/c$ and $C2/c$ (with extended T-chains) polymorphs; a

563   similar plot as a function of P is not considered due to the limited amount of similar XRD data. In

564   general, at room-T only M1-site hosting cations with a relative low size can crystallize with the

565    $P2_1/c$ space group; however, there is not a systematic behavior relating M1-site size and space

566   group; in fact, $LiNiSi_2O_6$ and $Li(Al_{0.77}Fe^{3+}_{0.23})Si_2O_6$ have practically the same dimensions, but the

567   former is $P2_1/c$ and the latter $C2/c$ (Fig. 12). Similarly, $P2_1/c$ $LiCrSi_2O_6$ has a M1-site size

568   intermediate between $C2/c$ $Li(Al_{0.43}Fe^{3+}_{0.57})Si_2O_6$ and $Li(Al_{0.15}Fe^{3+}_{0.85})Si_2O_6$ (Fig. 12). Therefore, it

569   is definitively demonstrates that M1-site size only partially contributes to induce changes in crystal

570   topology. Further and stringent evidences of this behavior are provided by the comparison between

571    $LiTiSi_2O_6$ with $Li(Fe^{3+}_{0.74}Sc_{0.26})Si_2O_6$ and $(Li_{0.85}Mg_{0.06}Fe^{2+}_{0.09})$ $(Mg_{0.15}Fe^{3+}_{0.85})Si_2O_6$, as well as by

572   the long known absence of a $P2_1/c$ polymorph of Li-cpx with the smallest M1-size, i.e. $LiAlSi_2O_6$

573   (Fig. 12). The fact that clinopyroxene polymorphs do not exclusively switch their space group and

574   arrangement of tetrahedral chains as a function of M2- and M1-site has been already proposed by

575   Tribaudino et al. (2009) for Li-cpx and by Angel et al. (1998) for Mg-, Mn-, Cr- and Fe^{2+}-cpx. In

576   turn, we can further stress that besides the M1-site effective ionic radii, also the electron

577   configuration of trivalent cations in Li-cpx can play an important role on the existence (or not) of

578   different polymorphs and of the occurrence of Tc; this aspect could be also relevant for the M2-site.

579   Here, it can be concluded that Me^{3+} cations with variable outer electron configurations impose

580   different site size, distortions and eventual crystal field stability energies (CFSE); all these

581   contributions are relevant of the stability of clinopyroxene polymorphs as a function of T and P.

582   Further studies are required to model the relations among site size, valence electron arrangements

583   and stability filed of Li-cpx, as well for other mineral groups.

584

585   **Implications: detection of Li in natural pyroxenes**

586   Li cannot be detected by EPMA-WDS and/or SEM-EDS analyses standardly used in

587   petrological studies; in parallel, Li being a light element, even if present with a relative significant

588   a.p.f.u. in a clinopyroxene. For instance $Na_{0.9}Li_{0.1}Fe^{3+}Si_2O_6$ is composed of 0.65, 12.16, 34.81 and

589   52.38 wt.% of Li_2O, Na_2O, Fe_2O_3 and SiO_2, respectively, and $Na_{0.8}Li_{0.2}Fe^{3+}_{01}Si_2O_6$ is composed of

590   1.28, 13.24, 34.12 and 51.35 wt.% of Li_2O, Na_2O, Fe_2O_3 and SiO_2, respectively. Hence, its

591   detection could be difficult even indirectly by difference to 100 wt.%, especially when both Fe^{2+}

592   and Fe^{3+} are present. By contrast, the accurate determination of cell parameters of an alkaline

593   clinopyroxene mineral hosted in a rock can be performed quickly and used to constrain the presence

594   of this light and elusive element, as already pointed out for Li-bearing amphiboles, where the M4-

595   site occupancy the corresponding M2-site in clinopyroxene) is well correlated with the β angle

596   (Hawthorne et al. 1993; Iezzi et al. 2003b, 2006, 2010; Della Ventura et al. 2005). This is important

597   for the semi-quantitative determination of chemical compositions of spodumene, especially the

598   possible presence of Fe^{2+} *vs* Fe^{3+} and/or Na, that is used for extraction of Li (London 1984; Deer et

599   al. 1997; Dill 2010). Jadeite and aegirine with ideal formula $NaAlSi_2O_6$ and $NaFe^{3+}Si_2O_6$,

600   respectively, could incorporate some amount of Li at their M2 site, as shown by the near ideal solid

601   solution investigated by Redhammer and Roth (2002) (Fig. 5); it is, therefore, important to

602   constrain the actual amount of Li at M2-site for rocks containing alkali clinopyroxenes, especially

603   for jadeite that is one of the most used mineral for geobarometric models (Deer et al. 1997).

604   The *a*, *b*, *c* and volume cell parameters *vs* their β angles for several clinopyroxene solid

605   solutions with compositions accurately constrained are reported in Fig. 13. Similar to alkali

606   amphiboles, also for clinopyroxenes the angular value of the β angle straightforward scales with

607   cation type and abundance (and average cation size), whereas the M1-site occupancy very poorly or

608   slightly influences this angular value for $^{M2}Me^{1+M1}Me^{3+}Si_2O_6$ and $^{M2}Me^{2+M1}Me^{2+}Si_2O_6$ (variable Mg

609   and Fe^{2+} amounts at M1-site in diopside produces a shift in β), respectively. Hence, these four plots

610   show that Li-cpx have the highest β angle, Na-cpx the intermediate and Ca-cpx the lowest ones. The

611   increasing of cation size at M1-site for $^{M2}(Na,Li)^{M1}Me^{3+}Si_2O_6$ cpx tends to shift the *a*, *b*, *c* and

612   volume lattice parameters towards high value, leaving practically unchanged their β value, except

613   for Li-cpx with a $P2_1/c$ symmetry ($LiNiSi_2O_6$ and $LiCrSi_2O_6$) and $LiTiSi_2O_6$; similarly, even a slight

614   presence of Fe^{2+} and/or Mg at the M2-site in $^{M2}(Li,Fe^{2+},Mg)^{M1}(Fe^{3+},Fe^{2+},Mg)Si_2O_6$ cpx shifts

615   leftwards the β value (Fig. 13). Being that either *b* and volume parameters changes together with β

616   value for $^{M2}(Na,Li)^{M1}Me^{3+}Si_2O_6$ cpx, it can be valuable using these two plots to accurately

617   determine the possible amounts of Li in jadeite-aegirine cpx, as well as to exploit the regression

618   provided in Fig. 5 (Li a.p.f.u. *vs* β value) using the data of Redhammer and Roth (2002). To

619   summarize, simple crystallographic data of cell parameters can accurately constrain (0.1/0.2

620   a.p.f.u.) the presence of Li in natural clinopyroxenes.

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Acknowledgments

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836   **Figure captions**

837   Figure 1. Textural features of the eight run-products analysed by back-scattered scanning

838   electron microscopy (BS-SEM); labels of run-products, experimental conditions, their paragenesis

839   and clinopyroxene nominal and measured compositions are reported in Tables 1 and 3; in the Fe#0

840   run-product the light grey phase is corundum (plus a very low amount of Al_2SiO_5), in the Fe#2+

841   run-product the white phases is magnetite, whereas in the other run-products the white phase is

842   hematite (Table 3); Fe- and Al-bearing clinopyroxenes show intermediate grey tones indicative of

843   slight inter- and intra-crystalline variable compositions.

844

845   Figure 2. (top) Differences in Al occupancy at M1-site between nominal and measured by

846   Rietveld refinement on synchrotron XRPD patterns. (bottom) Phase amounts in weight % (left) and

847   area % (right) determined by Rietveld refinement on synchrotron XRPD patterns and image

848   analysis on back-scattered SEM data, respectively (see Table 3). The amount of Al (a.p.f.u.) is

849   obtained by Rietveld refinement at the M1-site (Al = 1 - Fe), while M2- and T-site are occupied

850   only by Li and Si, respectively.

851

852   Figure 3. Projections of the extracted intensities obtained from SAED patterns of the Fe#50

853   run-product. Figures illustrate projections of b* direction. The size of spots is proportional to the

854   intensity. White spots correspond to the extracted intensity from the experimental data, whereas red

855   spots illustrate the reflections representing (a) a centering, (b) b centering, (c) c centering, (d) c

856   glide plane perpendicular to the b axis direction, (e) 2_1 screw axis along the b axis direction, for the

857   reported cell. Panels a & b show that the experimental data violate the extinction conditions for

858   these types of centering, thus c centering describes better the reciprocal space. Moreover panel d is

859   indicative that C2/c space group is the right one. All figures were generated using the ADT3D

860   software (NanoMEGAS SPRL, Belgium).

861

862   Figure 4. The synchrotron XRPD patterns (except Fe#50) collected on image plates. The

863   Debye rings are more uniform and well defined moving from Fe#100 to Fe#0.

864

865   Figure 4S (supplementary material). The Fe#0 (up) and Fe#50 (down) synchrotron XRPD

866   patterns refined by the Rietveld method. Black crosses and red lines are the observed and calculated

867   XRPD patterns, respectively; the green and blue lines are background and residual between

868   observed and calculated XRPD patterns, respectively.

869

870   Figure 5. (left column) Evolution of cell parameters as a function of the ^{M1}Al measured by

871   Rietveld refinements between $LiAlSi_2O_6$ and $LiFe^{3+}Si_2O_6$ (plus linear regressions and equations);

872   the red circles are the data of the FE#2+ run-product and the blue crosses are SC-XRD data from

873   Redhammer and Roth (2004); (right column) The SC-XRD data of Redhammer and Roth (2002)

874   between $LiFe^{3+}Si_2O_6$ and $NaFe^{3+}Si_2O_6$ are also reported (green triangles) as a comparison (plus

875   linear regressions and equations). The evolution of both cell volume parameters are almost linear,

876   suggesting ideal solid solutions between ^{M1}Al and $^{M1}Fe^{3+}$ and ^{M2}Li and ^{M2}Na of Li-cpx. The relative

877   variations (%) are calculated as: (max-min)/max. The substitution of Al with Fe^{3+} and Li with Na

878   induce an increasing (from low to high %) of *c*, *a*, *b*, *V* with *β* unmodified and of *b*, *β*, V with *c* plus

879   *a* almost un-affected, respectively.

880

881   Figure 6. Evolution of average bond lengths (top: M2-site, middle: M1-site, bottom: T-site)

882   as a function of the ^{M1}Al (a.p.f.u.) measured by Rietveld refinements (black circles); the linear

883   regressions are performed only on the samples of this study, whereas the blue crosses are reported

884   with comparison with our data (single-crystal X-ray diffraction data from Redhammer and Roth,

885   2004). The substitution of Al by Fe^{3+} at the M1-site mainly affect the M1-O and to a lesser extent

886   the M2-O average bond lengths, respectively, whereas the T-site is only slightly modified. The

887   relative variations (%) are calculated as: (max-min)/max.

888   Figure 7. Evolution of cell volume at 298 K as a function of the average cation size at the

889   M1-site of $LiMe^{3+}Si_2O_6$ clinopyroxenes; filled symbols are *C*2/*c* clinopyroxenes, whereas open

890   ones are $P2_1/c$ crystals with available temperature of $P2_1/c$ - *C*2/*c* phase transitions. The other cell

891   parameters are reported in the supplementary materials (Fig. 7S). The relative variations (%) are

892   calculated as: (max-min)/max.

893

894   Figure 7S (to be deposited as supplementary material). From top to bottom: evolution of cell

895   edges, *β* angle and *a*sin(*β*) at 298 K as a function of the average cation size at the M1-site of

896    $LiMe^{3+}Si_2O_6$ clinopyroxenes and $(Li_{0.85}Mg_{0.09}Fe^{2+}_{0.06})(Fe^{3+}_{0.85}Mg_{0.15})Si_2O_6$; filled and open symbols

897   indicate *C*2/*c* and $P2_1/c$ clinopyroxenes, respectively. Symbols are those of Fig. 7. The relative

898   variations (%) are calculated as: (max-min)/max.

899

900   Figure 8. Finite lattice strain (rectangular plots) and orientation (semi-circular plots) of

901   principal strain axes of $C2/c$ Li^{M1}Me^{3+}Si$_2$O$_6$ pyroxenes, plus two $P2_1/c$ ^{M1}Ni and ^{M1}Cr reported as

902   empty symbols, induced by chemical substitution (left column of graphs), temperature and pressure

903   (middle and right columns of graphs). The lattice strain induced by the ideal substitution was

904   calculated from ^{M2}Li^{M1}AlSi$_2$O$_6$ to Li^{M1}Me^{3+}Si$_2$O$_6$, where Me is a progressive large cation, i.e. ^{M1}Al

905   vs ^{M1}In; cell parameters of Li(Al,Fe^{3+})Si$_2$O$_6$ are from this study, LiNiSi$_2$O$_6$ from Tribaudino et al.

906   (2009), LiTiSi$_2$O$_6$ from Kopnin et al. (2009), Li(Cr,Ga,V,Sc,In)Si$_2$O$_6$ from Redhammer and Roth

907   (2004a). Cell parameters of LiAlSi$_2$O$_6$ and LiFe^{3+}Si$_2$O$_6$ at high-T are from Cameron et al. (1973)

908   and Redhammer et al. (2001), respectively. Cell parameters of LiAlSi$_2$O$_6$ at high-P are from Arlt

909   and Angel (2000).

910

911   Figure 9. Finite lattice strain (rectangular plots) and orientation (semi-circular plots) of

912   principal strain axes of three sub-sets of $C2/c$ Li^{M1}Me^{3+}Si$_2$O$_6$ (reported in Fig. 8) and one $C2/c$

913   ^{M1}(Li,Na)Fe^{3+}Si$_2$O$_6$ pyroxenes. From left to right, the lattice strain for each sub-set was calculated

914   for four compositions between Al-Fe^{3+} (data from this study), Li-Na (data from Redhammer and

915   Roth, 2002), Fe^{3+}-Sc and Sc-In (data from Redhammer and Roth, 2004a). The schematic ε_1, ε_2 and

916   ε_3 (top) lattice strains induced by these four cation substitutions are reported their schematic

917   orientation and the crystal structure of spodumene on the a-c and a-b planes. The relative Δ

918   variations (%) are calculated as: (max-min)/max.

919

920   Figure 10. Evolution of M2- (up), M1- (middle) and T- (bottom) O average bond lengths at

921   298 K as a function of the average cation size at the M1-site of LiMe^{3+}Si$_2$O$_6$ clinopyroxenes. The

922   relative variations (%) are calculated as: (max-min)/max.

923

924   Figure 11. Trends of average M2-O (considering $^{VIII}Me^{1+}$ and $^{VIII}Me^{2+}$ at M2-site) *versus*

925   M1-O (considering $^{VI}Me^{2+}$ and $^{VI}Me^{3+}$ at M1-site) bond lengths of different clinopyroxenes, as a

926   function of cation substitution occurring a) only at M1-site by trivalent cations with M2-site

927   occupied only by Li (black circles) or Na (red squares), b) only at M1-site by divalent cations with

928   M2-site occupied only by Ca (violet crosses) and c) only at M2-site by Ca and another divalent

929   cations (Mg, Co and Zn) with M1-site occupied only by the same divalent cation hosted in M2-site

930   together with Ca (Mg: orange diamonds, Co: blu upward triabgles, Zn: green downward triangles).

931

932   Figure 12. Relations among average cation size at the M1-site of $LiMe^{3+}Si_2O_6$

933   clinopyroxenes, space group and Tc (T of phase transitions from $C2/c$ and $P2_1/c$). Full and open

934   symbols are $C2/c$ and $P2_1/c$ at room-T, respectively. Thin-yellow and thick-grey vertical bars refer

935   to $C2/c$ and $P2_1/c$ space groups at non-ambient T as investigated by XRD data, respectively.

936    $Li(Al,Fe^{3+})Si_2O_6$ at room-T are from this study, $LiTiSi_2O_6$ at room-T from Kopnin et al. (2009),

937    $LiNiSi_2O_6$ at high-T from Tribaudino et al. (2009), $Li(Al,Cr,Ga,V, Fe^{3+},Sc,In)Si_2O_6$ at high- and

938   low-T from Redhammer and Roth (2004b), $(Li_{0.85}Mg_{0.09}Fe^{2+}_{0.06})(Mg_{0.15},Fe^{3+}_{0.85})Si_2O_6$ at high-T

939   Càmara et al. (2003). This plot straightforwardly shows that M1-site dimension only partially rules

940   out the symmetry of Li-cpx; valence electrons and site distortions of trivalent cation at the M1-site

941   also strongly affects the space group and potential Tc.

942

943   Figure 13. β *vs* a, b, c and volume cell parameters for clinopyroxenes of joins:

944    $Li(Al,In)Si_2O_6$ from this study, Redhammer and Roth (2004a) and Tribaudino et al. (2009) (black

945   dots); $LiTiSi_2O_6$ from Kopnin et al. (2003) (black-pink circle); $(Li_{1-x}M^{2+}_x)(M^{2+}_xFe^{3+}_{1-x})Si_2O_6$ ($M^{2+} =$

946   Mg or Fe, $x \leq 0.15$) from this study and Càmara et al. (2003) (red stars); $(Li_{1-x}Na_x)Fe^{3+}Si_2O_6$ ($0 \leq x$

947   ≤ 1) from Redhammer and Roth (2002) (green triangles); $(Ca_{1-x}Na_x)(Fe^{2+}_{1-x} Fe^{3+}_x)Si_2O_6$ ($0 \leq x \leq 1$)

948   from Redhammer et al. (2006) (orange squares); $Ca(Fe^{2+}_{1-x}Mg_x)Si_2O_6$ ($0.5 \leq x \leq 1$) from

949   Redhammer et al. (2006) and Raudsepp et al. (1990) (blue diamonds); $Na(Fe^{3+}_{1-x}Al_x)Si_2O_6$ ($0 \leq x \leq$

950   1) from Nestola et al. (2006) (brown crosses). Open symbols are $P2_1/c$ clinopyroxenes ($LiNiSi_2O_6$

951   and $LiCrSi_2O_6$) at room conditions. The bottom-right diagrams highlights the most common

952   chemical substitutions occurring in natural Li-cpx. Similar to the original plot of Brown (1971),

953   these diagrams readily and accurately discriminate Li amount in clinopyroxene, as well as cation

954   occupancy at the M1 and M2 sites.

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Table 1. Sample labels, nominal formulas and experimental conditions.					
sample label	nominal formula (a.p.f.u.)	solid/H_2O_2 (wt.%)	T (°C)	P (GPa)	duration (day)
Fe#0	$LiAlSi_2O_6$	9:1	800	2	3
Fe#20	$Li(Al_{0.8}Fe^{3+}_{0.2})Si_2O_6$	9:1	800	2	3
Fe#40	$Li(Al_{0.6}Fe^{3+}_{0.4})Si_2O_6$	9:1	800	2	3
Fe#50	$Li(Al_{0.5}Fe^{3+}_{0.5})Si_2O_6$	9:1	800	2	3
Fe#60	$Li(Al_{0.4}Fe^{3+}_{0.6})Si_2O_6$	9:1	800	2	3
Fe#80	$Li(Al_{0.2}Fe^{3+}_{0.8})Si_2O_6$	9:1	800	2	3
Fe#100	$LiFe^{3+}Si_2O_6$	9:1	800	2	3
Fe#2+	$LiFe^{3+}Si_2O_6$	intrinsic fO_2	800	2	3

1

sample label	λ (Å)	2θ (°) range	2θ (°) step	d (Å) range	no. of points	no. of refined parameters	R_p	R_{wp}
Fe#0	0.325802	3.5 – 31.7	0.004	0.597 – 5.236	7050	72	0.028	0.024
Fe#20	0.325802	3.5 – 31.7	0.004	0.597 – 5.236	7050	76	0.055	0.045
Fe#40	0.325802	3.5 – 31.7	0.004	0.597 – 5.236	7050	74	0.040	0.034
Fe#50	0.325802	3.5 – 31.7	0.004	0.597 – 5.236	7050	71	0.030	0.029
Fe#60	0.325802	3.5 – 31.7	0.004	0.597 – 5.236	7050	69	0.032	0.029
Fe#80	0.325802	3.5 – 31.7	0.004	0.597 – 5.236	7050	69	0.041	0.033
Fe#100	0.325802	3.5 – 31.7	0.004	0.597 – 5.236	7050	72	0.072	0.046
Fe#2+	0.325802	3.5 – 31.7	0.004	0.597 – 5.236	7050	-	-	-

Table 2. Synchrotron powder diffraction data collection and refinement parameters.

Footnotes: R_p = Σ|y$_{obs}$ - y$_{calc}$| / Σy$_{obs}$ and R_{wp} = [Σw(y$_{obs}$ - y$_{calc}$)^2 / Σwy$_{obs}^2$]$^{1/2}$ refer to Rietveld refinements. The run-product Fe#2+ was refined only by the Le Bail method.

2

sample label	[f]actual formula (a.p.f.u.)	[*]space group	% of phases	pyroxene	corundum	hematite
Fe#0	$LiAlSi_2O_6$	$C2/c$	[#]by weight	92	8	-
			[$]by area	95	5	-
Fe#20	$Li(Al_{0.86}Fe^{3+}_{0.14})Si_2O_6$	$C2/c$	[#]by weight	92	5	3
			[$]by area	94	1	5
Fe#40	$Li(Al_{0.77}Fe^{3+}_{0.23})Si_2O_6$	$C2/c$	[#]by weight	87	1	12
			[$]by area	93	-	7
Fe#50	$Li(Al_{0.65}Fe^{3+}_{0.35})Si_2O_6$	$C2/c$	[#]by weight	89	-	11
			[$]by area	91	-	9
Fe#60	$Li(Al_{0.43}Fe^{3+}_{0.57})Si_2O_6$	$C2/c$	[#]by weight	87	-	13
			[$]by area	95	-	5
Fe#80	$Li(Al_{0.15}Fe^{3+}_{0.85})Si_2O_6$	$C2/c$	[#]by weight	92	-	8
			[$]by area	93	-	7
Fe#100	$Li\,Fe^{3+}Si_2O_6$	$C2/c$	[#]by weight	99	-	1
			[$]by area	97	-	3
Fe#2+	-	$C2/c$	[$]by area	98	-	2[*]

Table 3. Synchrotron XRPD data and image analysis data

Footnotes: [f]actual formulas were determined by Rietveld refinement imposing that M2 and T sites are occupied only by Li and Si, respectively, whereas the M1 site was constrained to be $Al_xFe^{3+}_{1-x}$ with $0 \leq x \leq 1$; [#]weight and [$]area % of phases were determined by Rietveld refinement and by image analyses on back-scattered SEM pictures (see Figure 1), respectively; *in this run-product the iron-rich phases is magnetite; *the $C2/c$ space group of pyroxene was determined by SAED-TEM data.

3

Table 4.Cell parameters obtained by powder X-ray and electron diffraction data											
sample label	#actual formula (a.p.f.u.)	a (Å)	*a (Å)	b (Å)	*b (Å)	c (Å)	*c (Å)	β (°)	*β (°)	V (Å^3)	*V (Å^3)
Fe#0	$LiAlSi_2O_6$	9.4657(1)	9.47(1)	8.3942(1)	8.39(1)	5.2204(1)	5.22(1)	110.15(1)	110.15(1)	389.41(1)	389.37(1)
Fe#20	$Li(Al_{0.86}Fe^{3+}_{0.14})Si_2O_6$	9.4898(1)	9.49(1)	8.4257(1)	8.43(1)	5.2317(1)	5.23(1)	110.14(1)	110.14(1)	392.74(1)	392.82(1)
Fe#40	$Li(Al_{0.77}Fe^{3+}_{0.23})Si_2O_6$	9.4992(1)	9.50(1)	8.4396(1)	8.44(1)	5.2362(1)	5.24(1)	110.128(1)	110.13(1)	394.15(1)	394.48(1)
Fe#50	$Li(Al_{0.65}Fe^{3+}_{0.35})Si_2O_6$	9.5306(1)	9.53(1)	8.4785(1)	8.48(1)	5.2488(1)	5.25(1)	110.136(1)	110.14(1)	398.20(1)	398.34(1)
Fe#60	$Li(Al_{0.43}Fe^{3+}_{0.57})Si_2O_6$	9.5598(1)	9.56(1)	8.5103(1)	8.51(1)	5.2588(1)	5.26(1)	110.177(1)	110.18(1)	401.59(1)	401.67(1)
Fe#80	$Li(Al_{0.15}Fe^{3+}_{0.85})Si_2O_6$	9.6127(2)	9.61(2)	8.5849(2)	8.58(2)	5.2778(1)	5.28(1)	110.178(1)	110.18(1)	408.81(2)	408.64(2)
Fe#100	$LiFe^{3+}Si_2O_6$	9.6702(1)	9.67(1)	8.6626(1)	8.66(1)	5.2966(1)	5.30(1)	110.20(1)	110.20(1)	416.41(3)	416.54(1)
Fe#2+	-	9.6745(1)	9.67(1)	8.6757(1)	8.68(1)	5.2968(1)	5.30(1)	110.18(1)	110.18(1)	417.29(2)	417.56(1)

Footnotes: #the $C2/c$ space group was used for the XRPD Rietveld refinements derived from SAED-TEM data; the Fe#2+ run-product was refined

only by the Le Bail method; *electron diffraction data.

4

Table 5. Atomic coordinates and equivalent isotropic displacement parameters.						
sample label or study	actual formula (a.p.f.u.)	site	x	y	z	U_{ISO}
Fe#0	$LiAlSi_2O_6$	M2	0	0.276(1)	0.25	0.007(1)
		M1	0	0.907(1)	0.25	0.003(1)
		T	0.294(1)	0.093(1)	0.256(1)	0.004(1)
		O1	0.109(1)	0.083(1)	0.140(1)	0.003(1)
		O2	0.364(1)	0.267(1)	0.301(1)	0.006(1)
		O3	0.357(1)	0.987(1)	0.059(1)	0.005(1)
Fe#20	$Li(Al_{0.86}Fe^{3+}_{0.14})Si_2O_6$	M2	0	0.273(1)	0.25	0.002(1)
		M1	0	0.905(1)	0.25	0.002(1)
		T	0.294(1)	0.093(1)	0.258(1)	0.006(1)
		O1	0.110(1)	0.084(1)	0.141(1)	0.004(1)
		O2	0.364(1)	0.265(1)	0.304(1)	0.005(1)
		O3	0.355(1)	0.988(1)	0.058(1)	0.006(1)
Fe#40	$Li(Al_{0.77}Fe^{3+}_{0.23})Si_2O_6$	M2	0	0.271(1)	0.25	0.004(1)
		M1	0	0.905(1)	0.25	0.002(1)
		T	0.295(1)	0.092(1)	0.257(1)	0.004(1)
		O1	0.110(1)	0.084(1)	0.141(1)	0.003(1)
		O2	0.363(1)	0.265(1)	0.305(1)	0.004(1)
		O3	0.355(1)	0.989(1)	0.055(1)	0.006(1)
Fe#50	$Li(Al_{0.65}Fe^{3+}_{0.35})Si_2O_6$	M2	0	0.272(1)	0.25	0.001(1)
		M1	0	0.904(1)	0.25	0.001(1)
		T	0.295(1)	0.092(1)	0.258(1)	0.006(1)
		O1	0.111(1)	0.084(1)	0.144(1)	0.004(1)
		O2	0.364(1)	0.264(1)	0.309(1)	0.006(1)
		O3	0.356(1)	0.990(1)	0.056(1)	0.007(1)
Fe#60	$Li(Al_{0.43}Fe^{3+}_{0.57})Si_2O_6$	M2	0	0.266(1)	0.25	*0.004(1)
		M1	0	0.908(1)	0.25	
		T	0.295(1)	0.092(1)	0.259(1)	
		O1	0.112(1)	0.084(1)	0.144(1)	
		O2	0.364(1)	0.263(1)	0.311(1)	
		O3	0.355(1)	0.991(1)	0.054(1)	
Fe#80	$Li(Al_{0.15}Fe^{3+}_{0.85})Si_2O_6$	M2	0	0.268(1)	0.25	*0.004(1)
		M1	0	0.901(1)	0.25	
		T	0.295(1)	0.092(1)	0.262(1)	
		O1	0.113(1)	0.084(1)	0.147(1)	
		O2	0.367(1)	0.262(1)	0.319(1)	
		O3	0.354(1)	0.997(1)	0.054(1)	
Fe#100	$LiFe^{3+}Si_2O_6$	M2	0	0.268(1)	0.25	*0.004(1)
		M1	0	0.899(1)	0.25	
		T	0.296(1)	0.089(1)	0.264(1)	
		O1	0.117(1)	0.083(1)	0.150(1)	
		O2	0.367(1)	0.264(1)	0.322(1)	
		O3	0.357(1)	0.999(1)	0.056(1)	

Footnote: *refined with a unique global U_{ISO}. The average relative differences of atomic coordinates and U_{ISO} between single-crystal (Redhammer and Roth, 2004) and powder diffraction data (this study) for the $LiAlSi_2O_6$ end-member are ~ 0.1 (max < 0.2) and ~ 0.3 (max < 0.9) %, respectively; the average relative differences of atomic coordinates and U_{ISO} between single-crystal (Redhammer and Roth, 2004) and powder diffraction data (this study) for the $LiFe^{3+}Si_2O_6$ end-member are ~ 0.2 (max < 0.6) and ~ 0.4 (max < 1.1) %, respectively.

5

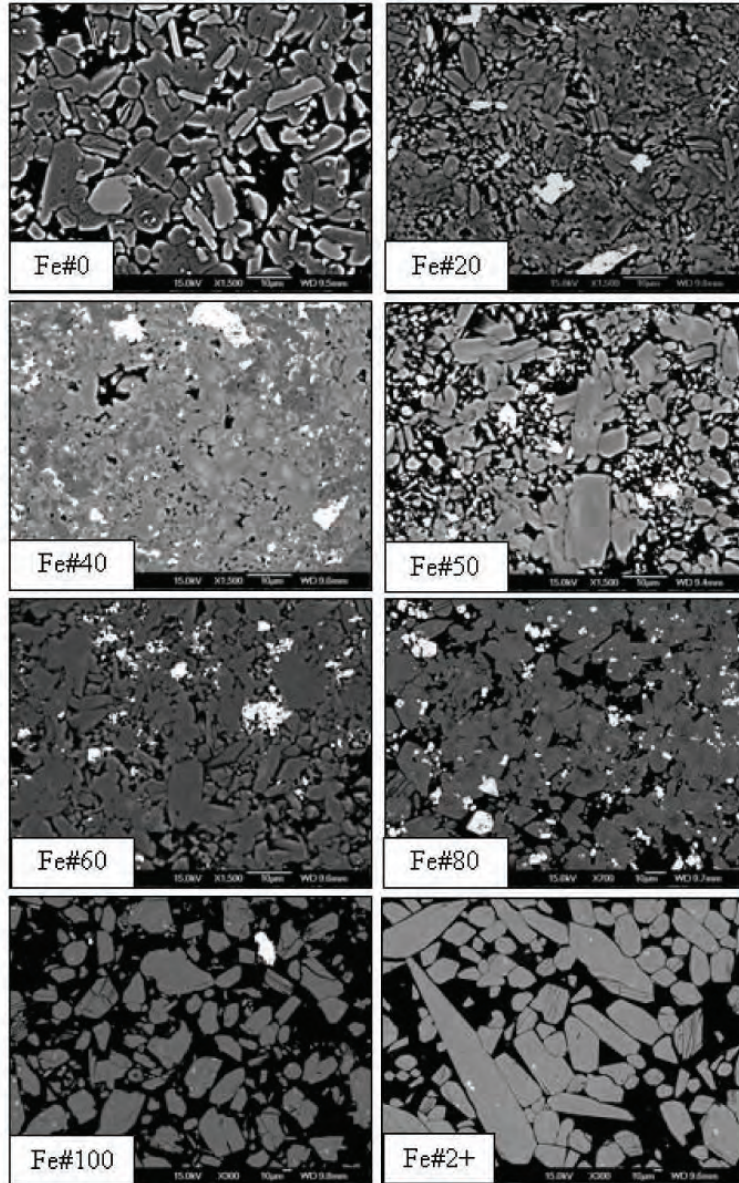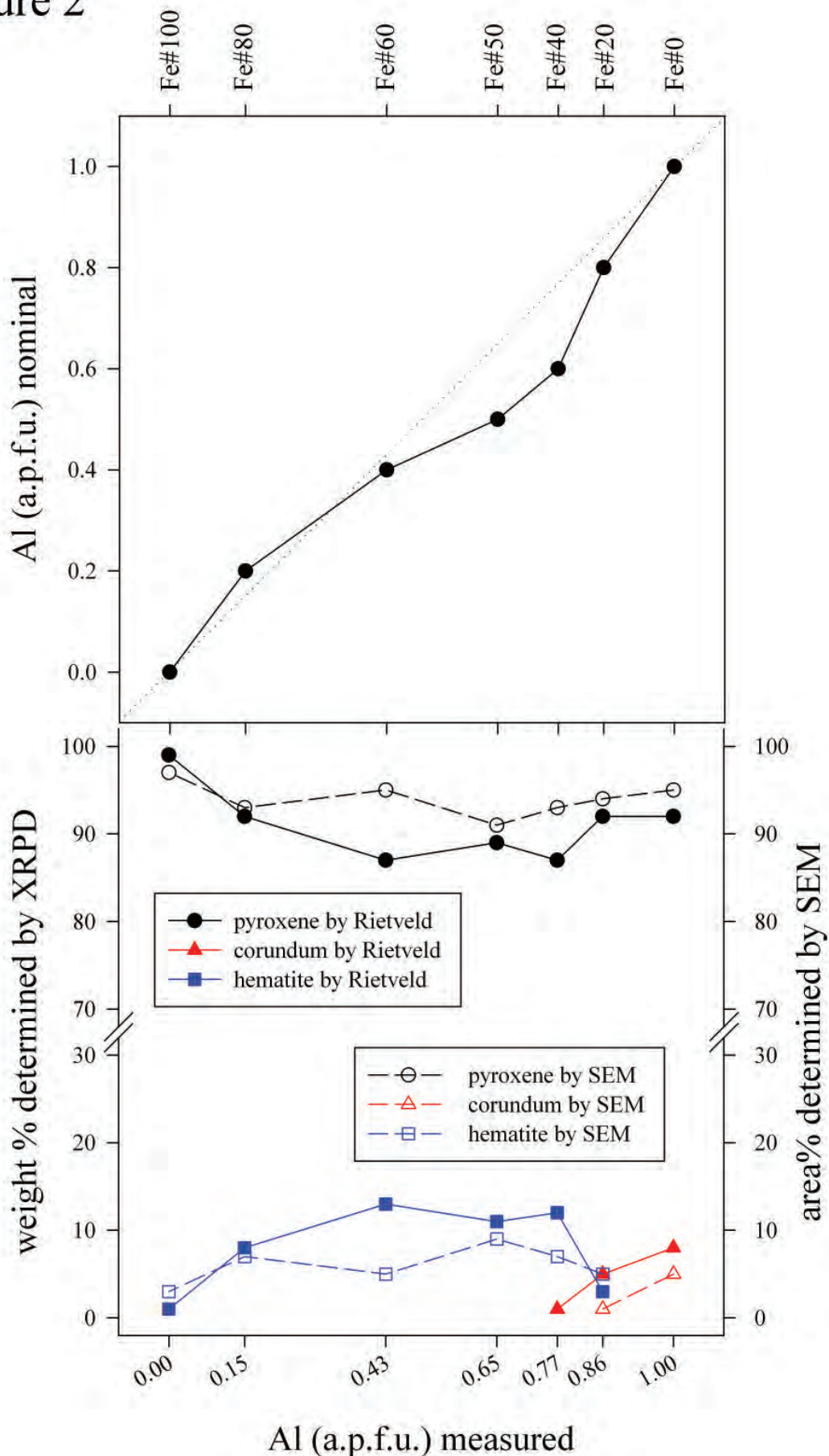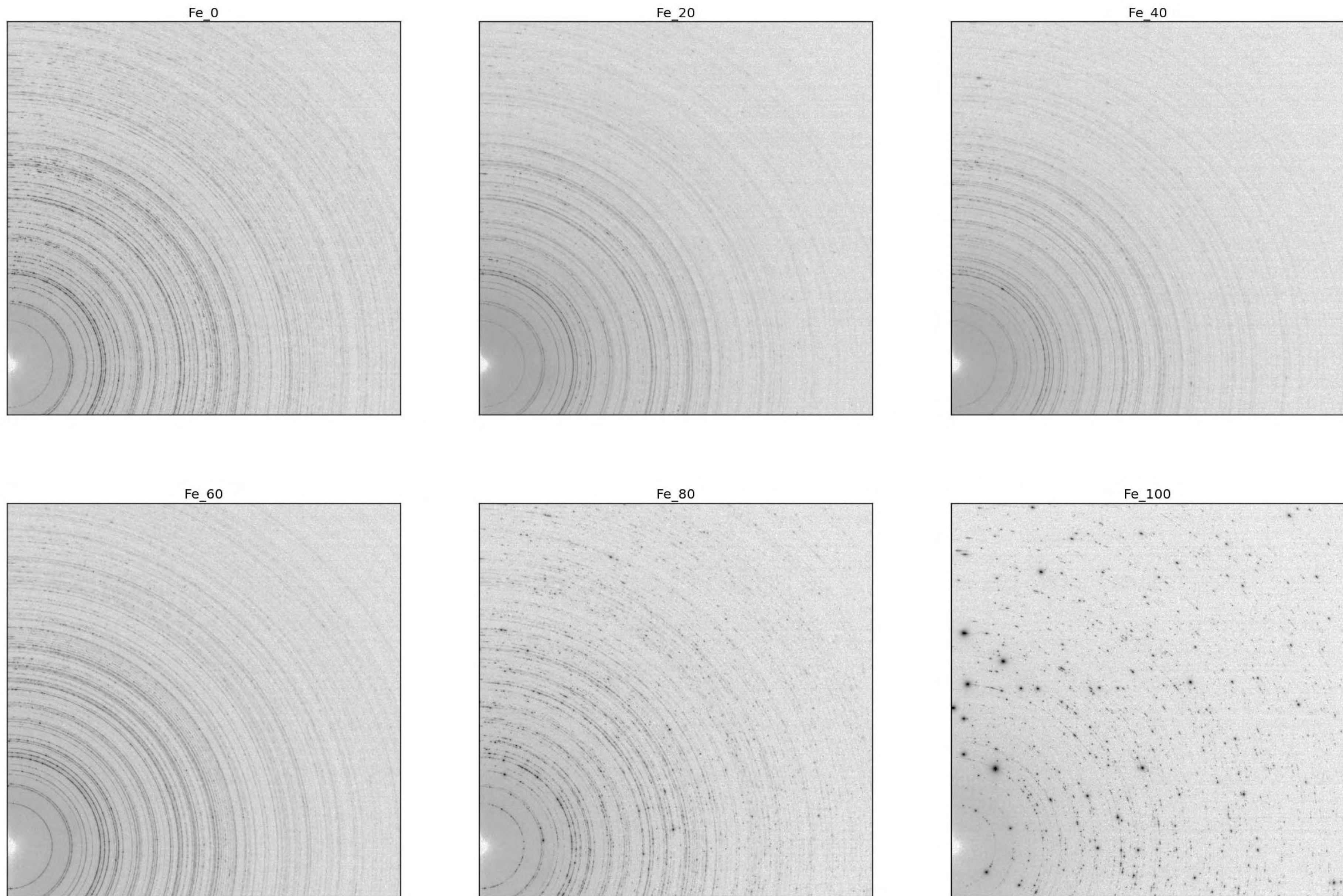| sample label	actual formula (a.p.f.u.)	M2-O1	M2-O2	M2-O3	M2-O (average)	M1-O1	M1-O1	M1-O2	M1-O (average)	T-O1	T-O2	T-O3	T-O3	T-O (average)
Fe#0	$LiAlSi_2O_6$	2.108	2.280	2.241	2.210	1.943	1.995	1.831	1.923	1.648	1.580	1.622	1.630	1.620
Fe#20	$Li(Al_{0.86}Fe^{3+}_{0.14})Si_2O_6$	2.088	2.267	2.283	2.213	1.950	2.019	1.845	1.938	1.649	1.578	1.622	1.622	1.618
Fe#40	$Li(Al_{0.77}Fe^{3+}_{0.23})Si_2O_6$	2.075	2.266	2.315	2.218	1.956	2.022	1.854	1.944	1.651	1.579	1.619	1.621	1.617
Fe#50	$Li(Al_{0.65}Fe^{3+}_{0.35})Si_2O_6$	2.090	2.252	2.322	2.221	1.973	2.043	1.860	1.959	1.647	1.586	1.622	1.624	1.620
Fe#60	$Li(Al_{0.43}Fe^{3+}_{0.57})Si_2O_6$	2.067	2.237	2.376	2.226	1.979	2.031	1.892	1.967	1.645	1.587	1.616	1.632	1.620
Fe#80	$Li(Al_{0.15}Fe^{3+}_{0.85})Si_2O_6$	2.093	2.204	2.425	2.241	2.002	2.087	1.878	1.989	1.646	1.599	1.617	1.635	1.624
Fe#100	$LiFe^{3+}Si_2O_6$	2.130	2.203	2.449	2.261	2.036	2.126	1.873	2.012	1.627	1.644	1.618	1.642	1.633

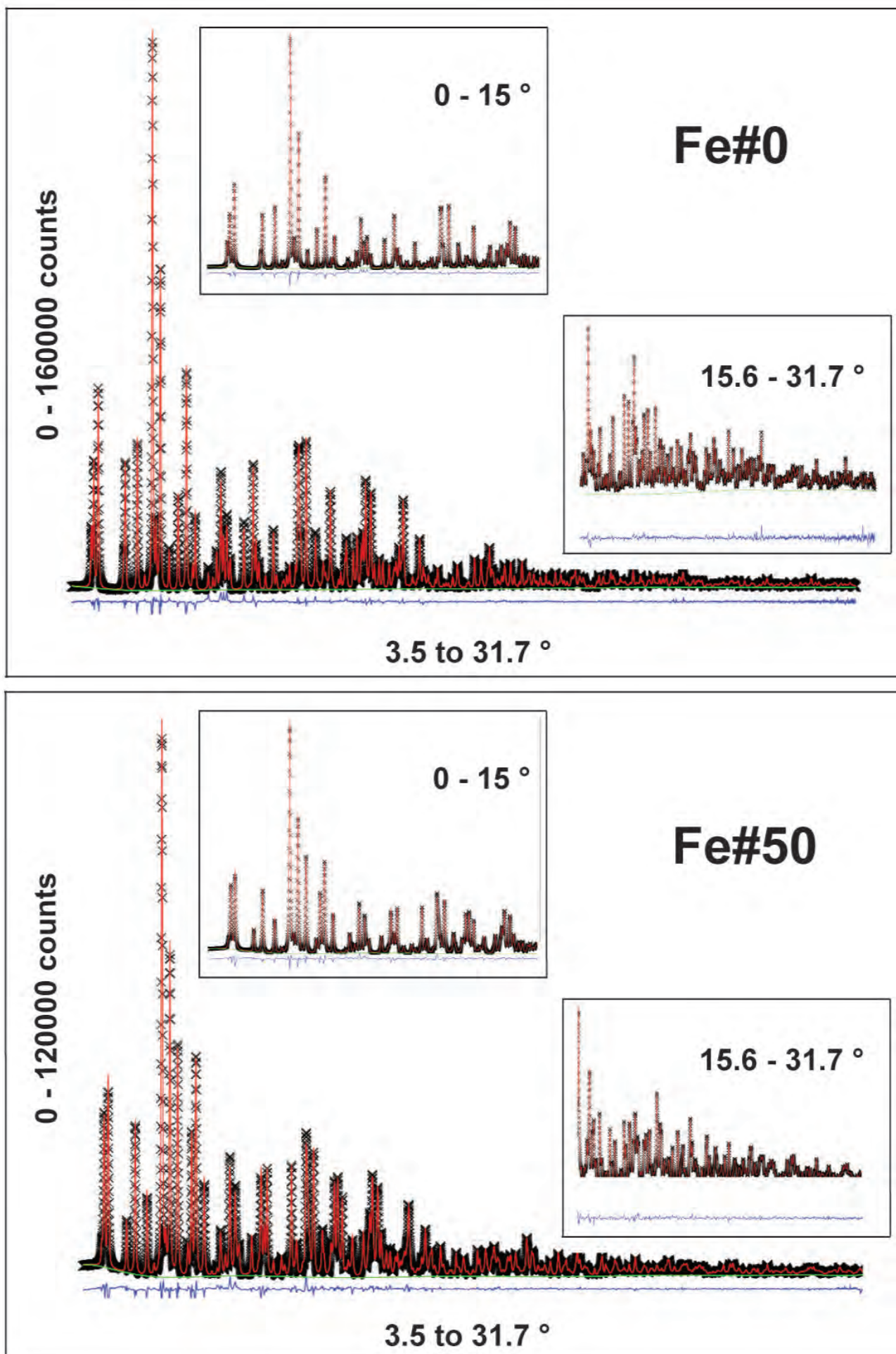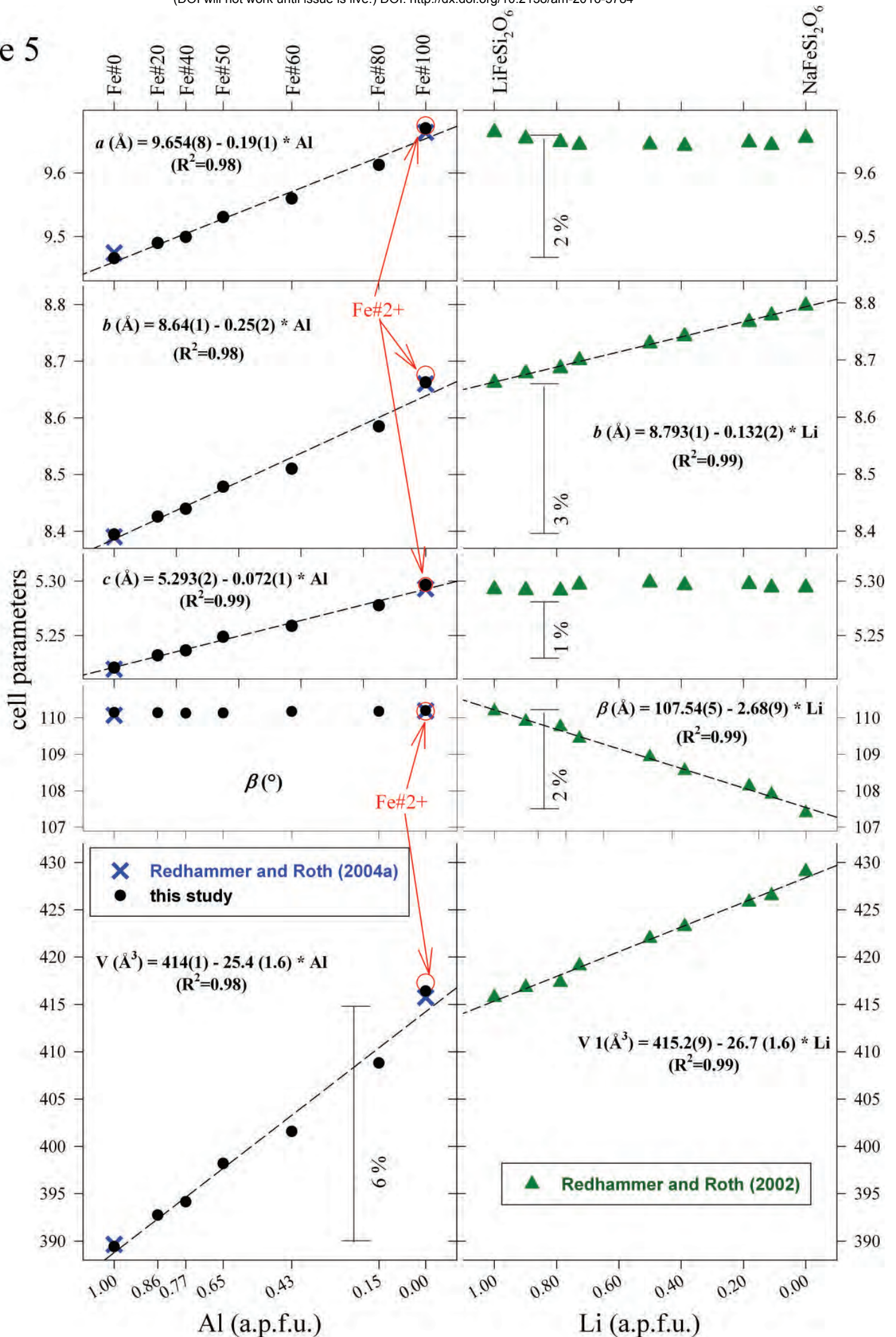Table 6. Cation-oxygen bond lengths.
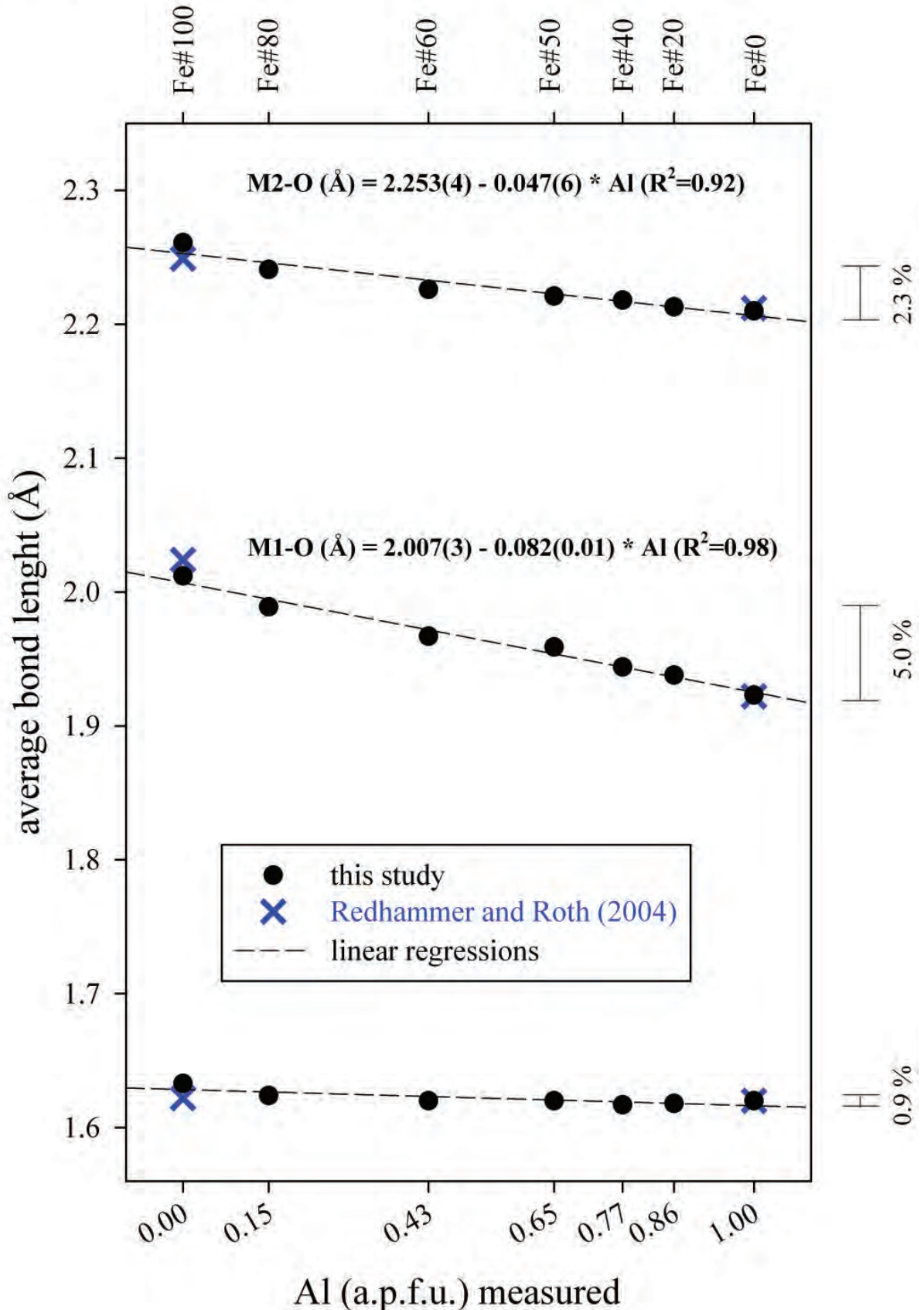
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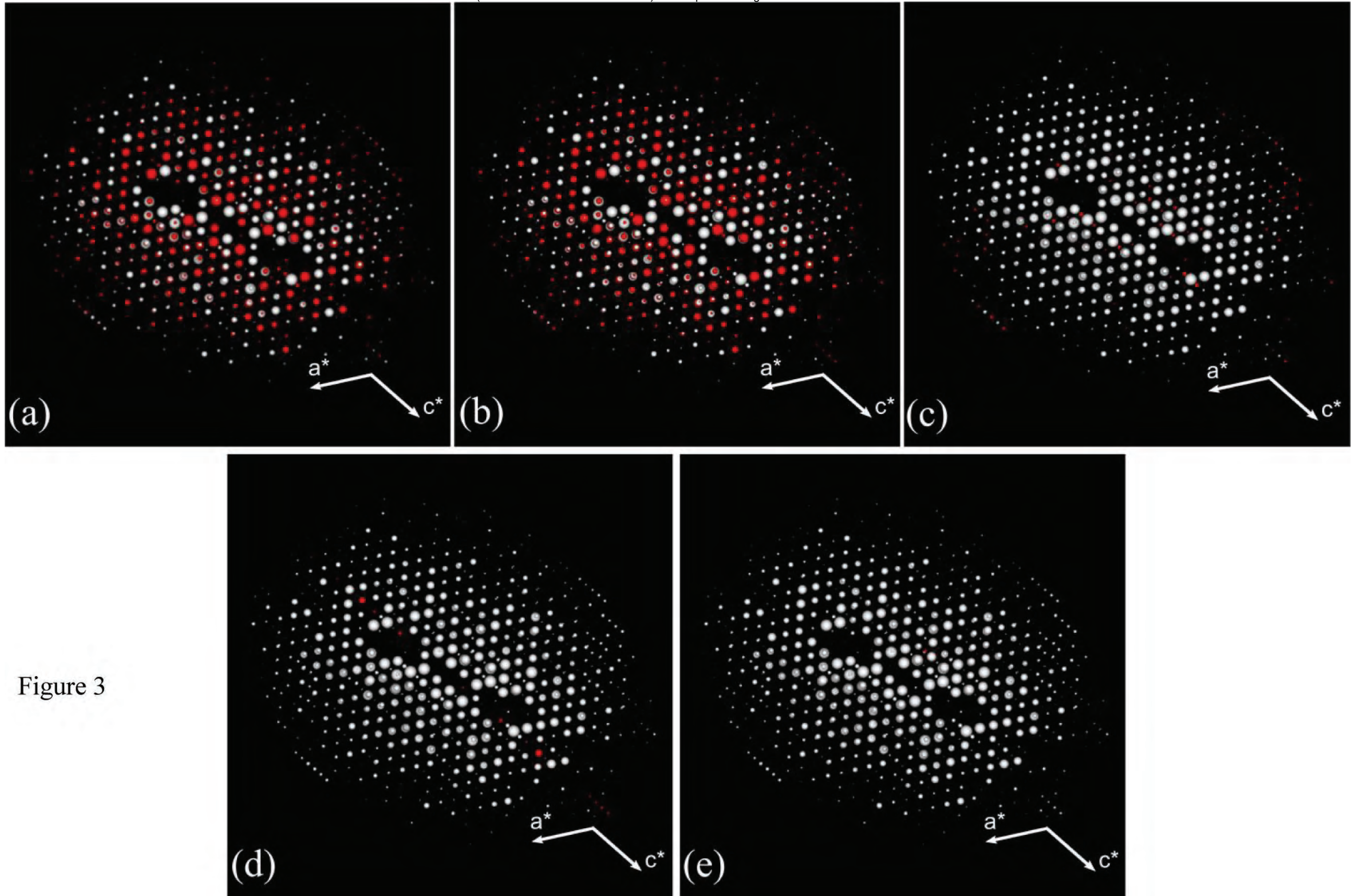
Figure 1

Figure 2

Figure 3

Figure 4

Figure 4S

Figure 5

Figure 6

Figure 7

Figure 7S

Legend:
- ● Li(Al,Fe^{3+})Si$_2$O$_6$ - this study
- ✕ Li(Al,Ga,V,Fe^{3+},Sc,In)Si$_2$O$_6$ - (Redhammer and Roth, 2004a)
- ◆ LiTiSi$_2$O$_6$ - Kopnin et al. (2003)
- ☆ LiNiSi$_2$O$_6$ - Tribaudino et al. (2009)
- △ LiCrSi$_2$O$_6$ - Redhammer and Roth (2004b)
- ▽ (Li$_{0.85}$Mg$_{0.09}$Fe$^{2+}_{0.06}$)(Fe$^{3+}_{0.85}$Mg$_{0.15}$)Si$_2$O$_6$ - Càmara et al. (2003)
- ■ Li(Al$_{0.53}$Ga$_{0.47}$)Si$_2$O$_6$ - Nestola et al. (2008)

a (Å) = 8.66(4) + 1.49(7) * <^{M1}r>
(R^2=0.94)

b (Å) = 6.96(2) + 2.63(4) * <^{M1}r>
(R^2=0.99)

c (Å) = 4.88(1) + 0.3(2) * <^{M1}r>
(R^2=0.99)

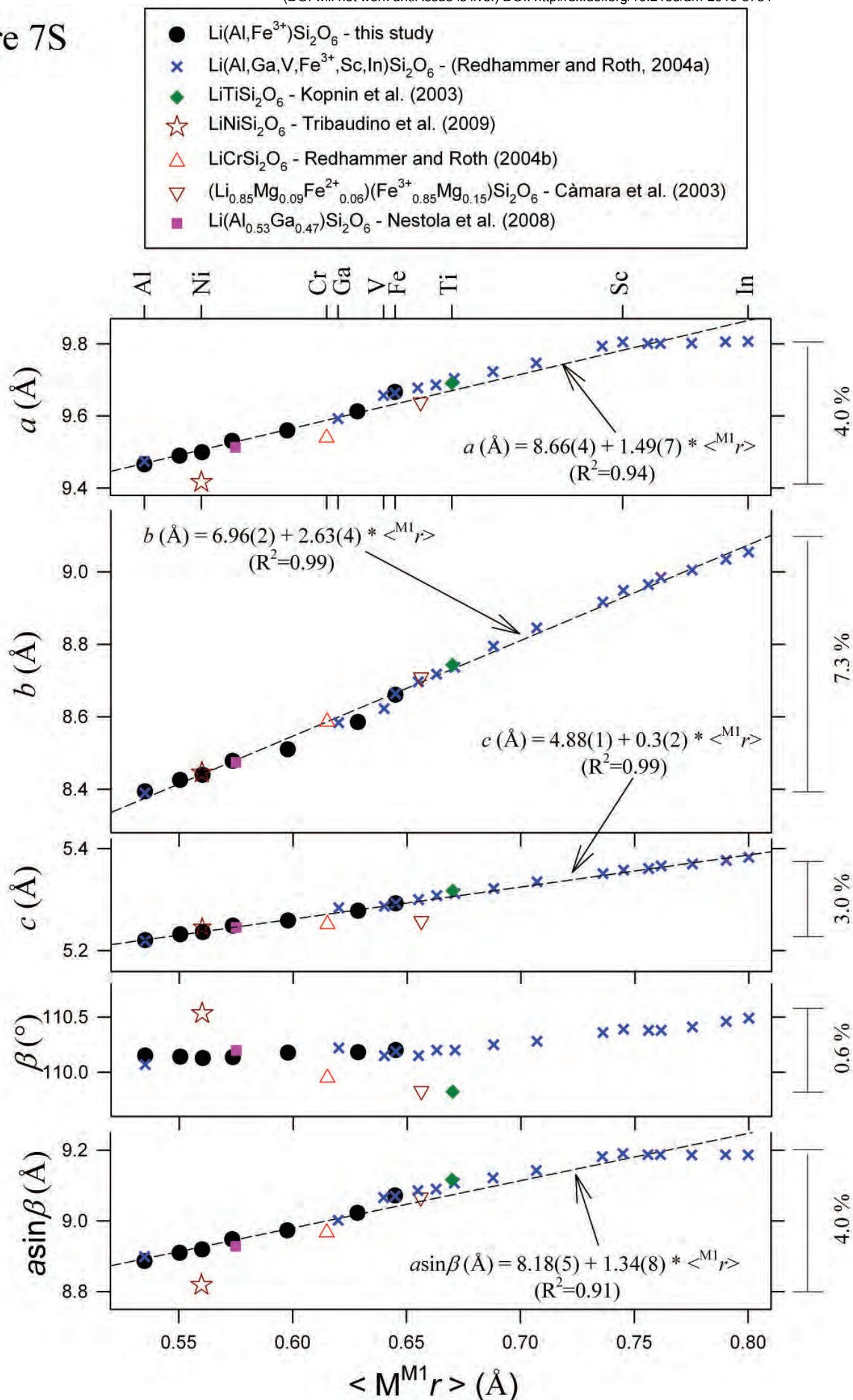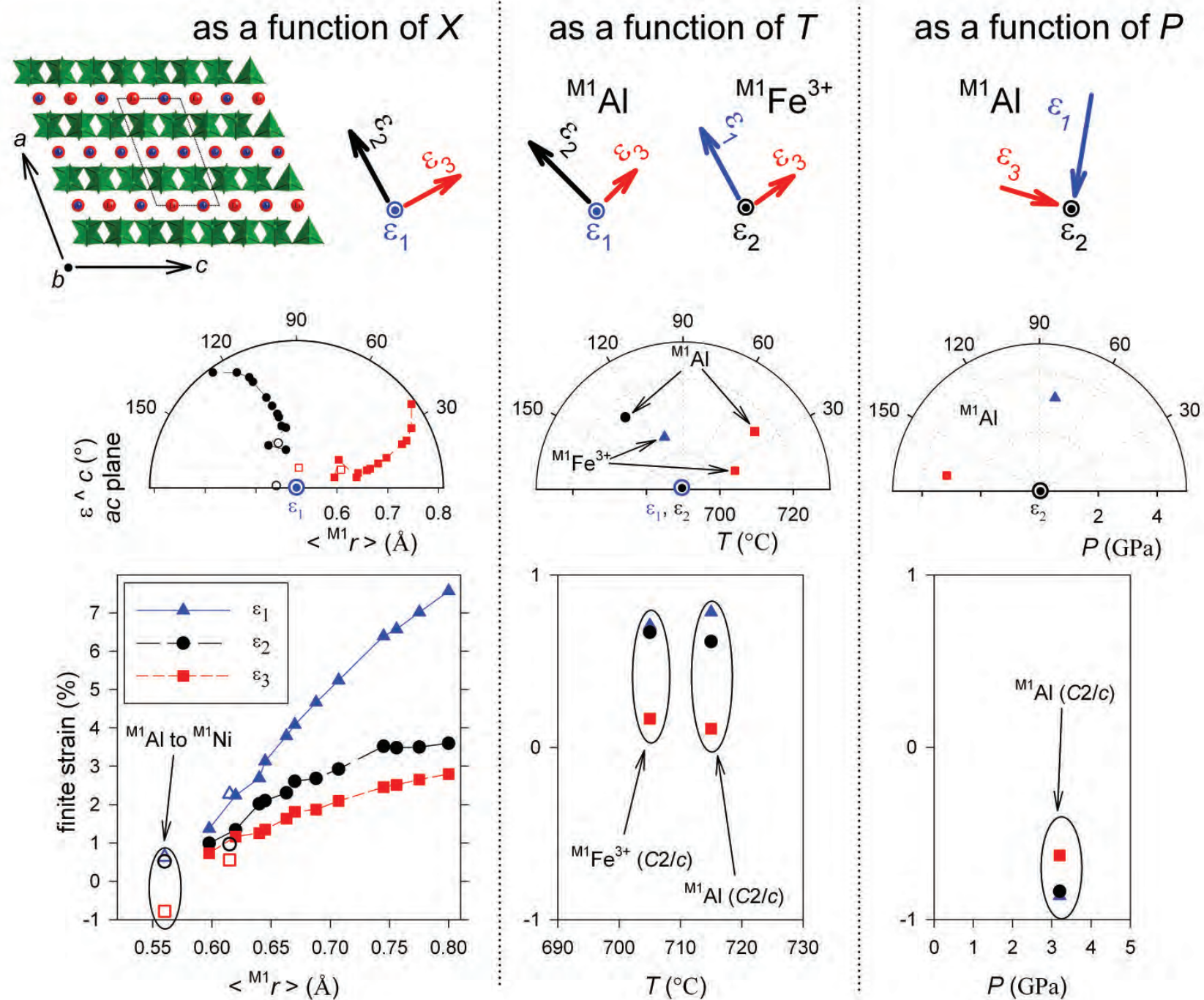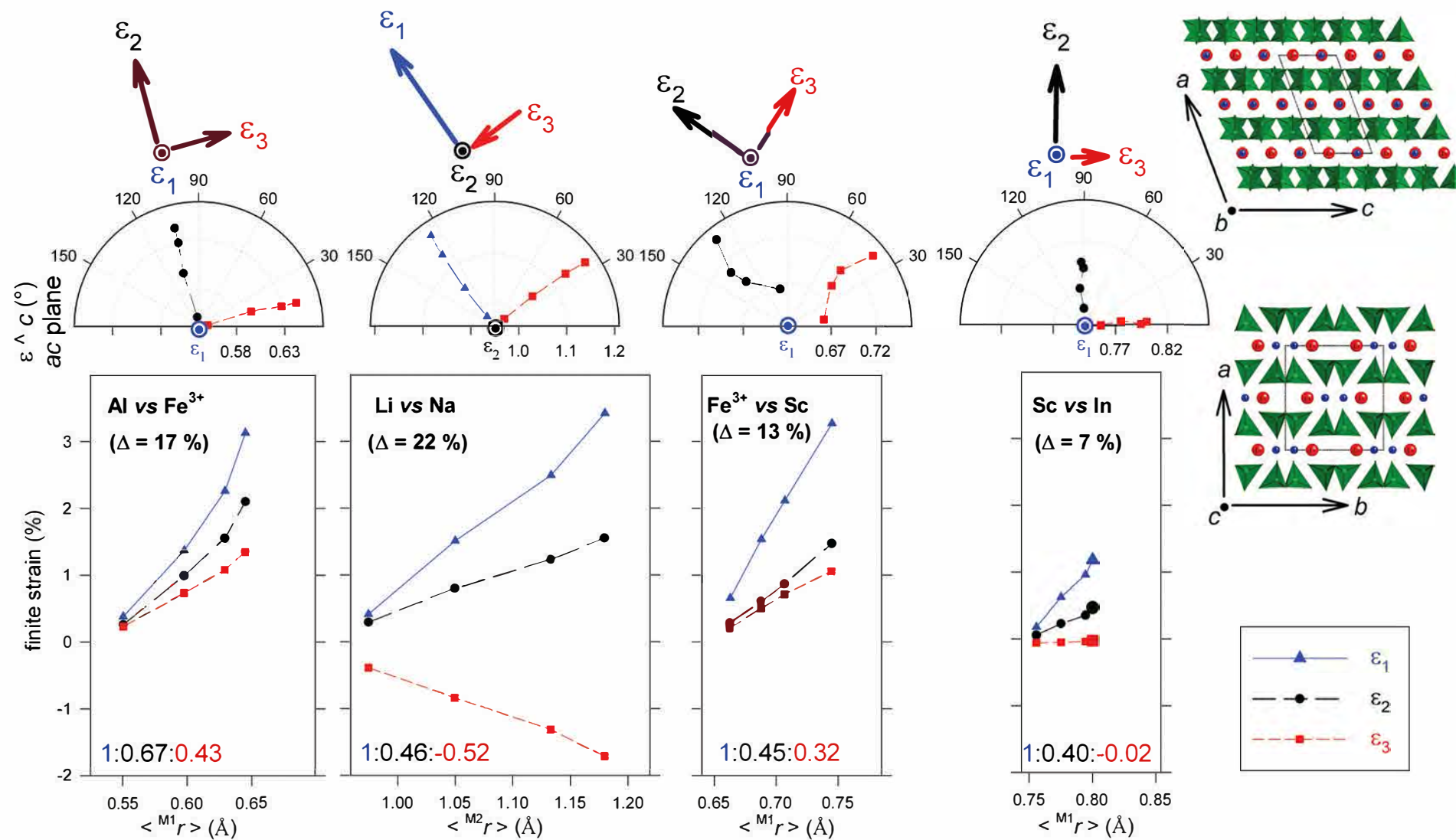$a\sin\beta$ (Å) = 8.18(5) + 1.34(8) * <^{M1}r>
(R^2=0.91)

< M^{M1}r > (Å)
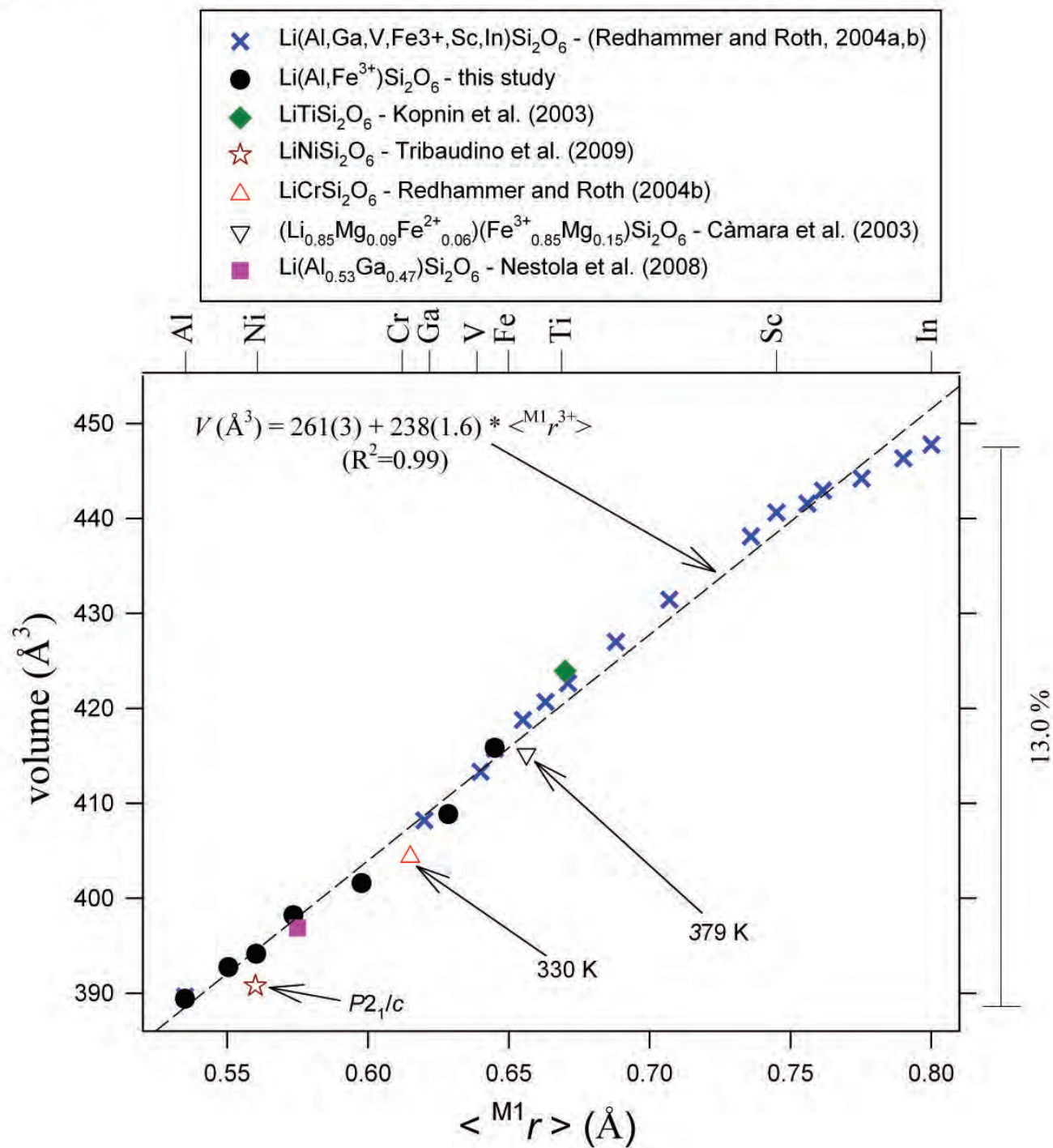
Figure 8

Figure 9

Figure 10

Figure 11

Legend:

- ☆ $^{M2}(Ca_{1/0.15}, Fe^{2+}_{0/0.85})^{M1}Fe^{2+}Si_2O_6$ (Ohashi et al., 1975; Ghose et al., 1987)
- ● $^{M2}Li^{M1}(Al,Cr,Ga,V,Ti,Fe^{3+},Sc,In)Si_2O_6$ (this study, Redhammer and Roth, 2004a; Kopnin et al., 2009)
- ■ $^{M2}Na^{M1}(Al,Ti,Fe^{3+},Sc,In)Si_2O_6$ (Nestola et al. 2007; Ulrich et al., 2010; Periotto et al., 2012)
- ▲ $^{M2}(Ca_{1/0.4}, Co_{0/0.6})^{M1}CoSi_2O_6$ (Mantovani et al., 2013)
- ▼ $^{M2}(Ca_{1/0}, Zn_{0/1})^{M1}ZnSi_2O_6$ (Gori et al., 2015)
- ◆ $^{M2}(Ca_{1/0.2}, Mg_{0/0.8})^{M1}MgSi_2O_6$ (Bruno et al., 1982; Tribaudino et al., 1989 and 2005)
- ✚ $^{M2}Ca^{M1}(Ni_{1/0}, Mg_{1/0}, Fe^{2+}_{1/0}, Mn^{2+}_{1/0})Si_2O_6$ (Ghose et al., 1987)
- ▲ $^{M2}(Na_{1/0}, Li_{0/1})Fe^{3+}Si_2O_6$ (Redhammer and Roth, 2002)

Figure 12

Figure 13