1   **Revision 1**

2   **Cathodoluminescence properties of radiation-induced alkali feldspars**

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4   **Masahiro Kayama[1]*, Hirotsugu Nishido[2], Shin Toyoda[3], Kosei Komuro[4], Adrian A.**

5   **Finch[5], Martin R. Lee[6], and Kiyotaka Ninagawa[3]**

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7   [1]Department of Earth and Planetary Systems Science, Graduate School of Science,

8   Hiroshima University, Kagami-yama 1-3-1, Higashi-Hiroshima, 739-8526, Japan

9   [2]Research Institute of Natural Sciences, Okayama University of Science, 1-1 Ridaicho,

10   Kita-ku, Okayama 700-0005, Japan

11   [3]Department of Applied Physics, Okayama University of Science, 1-1 Ridaicho, Kita-ku,

12   Okayama 700-0005, Japan

13   [4]Earth Evolution Sciences, University of Tsukuba, 1-1-1 Ten-nodai, Tsukuba, 305-8571,

14   Japan

15   [5]Department of Earth Sciences, University of St Andrews, Irvine Building, North Street,

16   St Andrews, Fife, KY16 9AL, U.K.

17   [6]School of Geographical and Earth Sciences, University of Glasgow, Lilybank Gardens,

18   Glasgow G12 8QQ, U.K.

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19   *Email: kayama27@hiroshima-u.ac.jp

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21   **ABSTRACT**

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23   Cathodoluminescence (CL) spectroscopy provides useful information about the

24   existence of radiation-induced defect centers with a few micrometer resolutions and

25   therefore has great potential to estimate the accumulated dose of natural radiation in

26   micron-ordered mineral grain from radioactive decay. Although great scientific interest

27   exists concerning the CL of various types of minerals, very few investigation have been

28   conducted on the luminescence properties of radiation-induced alkali feldspars. This

29   study, therefore, has sought a clarification of radiation effects on emission centers

30   detected by CL analysis of alkali feldspar implanted with He$^+$ ions at 4.0 MeV, which

31   corresponds to the energy of an α particle derived from radioactive decay of ^{238}U and

32   ^{232}Th.

33   Panchromatic CL images of cross-sections of sanidine, orthoclase and microcline show

34   a dark line with ~1 μm width on the bright luminescent background at 12–15 μm

35   beneath the implanted surface, of which behavior may be corresponding to the

36   electronic energy loss process of 4.0 MeV He$^+$ ion. CL and Raman spectroscopy

37   revealed that He^+ ion implantation may leads to a partial destruction of the feldspar

38   framework and Na^+ migration, resulting in a quenching of CL emission from alkali

39   feldspar, in proportion to the radiation dose. CL spectra of unimplanted and

40   He^+-ion-implanted sanidine, orthoclase and microcline have emission bands at

41   ~400–410 nm and at ~730 nm. Deconvolution of the CL spectra can successfully

42   separate these emission bands into emission components at 3.05, 2.81, 2.09, 1.73 and

43   1.68 eV. These components are assigned to the Ti^{4+} impurity, $Al-O^--Al/Ti$ defect, a

44   radiation-induced defect center, and Fe^{3+} impurities on the T1 and T2 sites, respectively.

45   The intensity at 3.05 eV negatively correlates with radiation dose owing to decreases in

46   the luminescence efficiency. A slight Na^+ diffusion and breaking of the linkage between

47   Ti^{4+} and oxygen as a ligand might reduce the activation energy, which decreases

48   availability of radiative energy in luminescence process of Ti^{4+} impurity center.

49   Furthermore, He^+ ion implantation causes electron holes to be trapped at and released

50   from Löwenstein bridges as a consequence of Na^+ migration and leads to a partial

51   destruction of Al-O bond, which might be responsible for an increase and decrease in

52   the intensity of emission component at 2.81 eV. With an enhanced radiation dose, there

53   is a decrease in intensity at 1.73 eV and an increase in intensity at 1.68 eV.

54   Deconvoluted CL spectra of the alkali feldspars reveal a positive correlation between

55   intensity at 2.09 eV and the radiation dose, which may be due to the formation of a

56   radiation-induced defect center. These correlations can be fitted by an exponential curve,

57   where the gradients differ between the alkali feldspars studied, and are largest for the

58   microcline, followed by the orthoclase and then the sanidine. The intensity at 2.09 eV

59   has the potential to be used in geodosimetry and geochronometry.

60   **Keywords:** cathodoluminescence, alkali feldspar, quenching, radiation-induced defect

61   center, He$^+$ ion implantation

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63   **INTRODUCTION**

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65   Luminescence of minerals has been extensively applied in geosciences for

66   geodosimetry and geochronometry (e.g. Smith and Stenstrom 1965; Marshall 1988;

67   Gaft et al. 2005). The accumulated doses of natural radiation that have been

68   accumulated by rock-forming minerals such as quartz and feldspar can be quantitatively

69   estimated using thermoluminescence (TL) and optical stimulated luminescence (OSL)

70   spectroscopy. If the annual dose rate is known, these techniques can then be used to

71   determine the luminescence dating of the minerals in sedimentary rocks and volcanic

72   ejecta. Electron spin resonance (ESR) analysis also enables the detection of lattice

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73   defects in minerals, where intensity of ESR from the radiation-induced defect center has

74   been used as an indicator for geodosimetry and geochronometry. It is, however,

75   necessary for estimating the accumulated dose or dating the geological age by TL, OSL

76   and ESR methods to extract a large amount of mineral from the target sediment, so that

77   these techniques are difficult to apply to micrometer sized grains. Cathodoluminescence

78   (CL) spectroscopy also provides useful information about the existence and distribution

79   of radiation-induced defect centers in quartz and feldspar, and with a spatial resolution

80   of a few micrometers (Owen 1988; Komuro et al., 2002; Okumura et al., 2008; Kayama

81   et al. 2011a; Kayama et al. 2011b), suggesting a potential for geodosimetry and

82   geochronometry with respect to a micron-ordered heterogeneous minerals or single

83   grain analysis.

84   The effect of ion implantation on CL emissions from quartz has been investigated to

85   explore the processes whereby radiation-induced defect centers are formed and to

86   estimate the accumulated dose of natural radiation from radioactive decay (e.g. Owen

87   1988; Komuro et al., 2002; Okumura et al., 2008; Krickl et al., 2008; King et al., 2011).

88   According to Komuro et al. (2002) and Okumura et al. (2008), He^+-ion-implanted

89   quartz at 4.0 MeV shows a bright luminescent band of ~ 14 μm width from the

90   implanted surface as a CL halo, within which the intensity positively correlates with

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91   radiation dose. A similar CL halo with ~45 μm width from the implanted surface has

92   been also recognized in He^{2+}-ion-implanted quartz and SiO_2 glass at 8.8 MeV, where the

93   intensities increase with radiation dose (Krickl et al., 2008). Although these previous CL

94   studies of ion-implanted quartz have demonstrated a good correspondence between CL

95   intensity and radiation dose, the dose response to ion implantation differs between

96   quartz samples of various origins, suggesting that the use of CL of quartz in

97   geodosimetry is not straightforward. Okumura et al. (2008) concluded that the CL

98   intensity of quartz depends on not only the radiation dose, but also other factors such as

99   density of defect centers (e.g., $[AlO_4/M^+]^0$ defect, self-trapped exciton, non-bridging

100   oxygen hole centers) and on the concentration of impurity centers (e.g., Ge^{4+} and Fe^{3+}

101   impurities). Accordingly, further work is required to elucidate how CL of

102   radiation-induced quartz can be used in geodosimetry.

103   CL has also been used to detect radiation-induced defect centers in He^+-ion-implanted

104   albite (Kayama et al. 2011a; Kayama et al., 2011b). In this case, radiation resulted in a

105   characteristic red emission, whose intensity increased with radiation dose.

106   Deconvolution of CL spectra by Gaussian fitting revealed an emission component at

107   1.861 eV that was assigned to a radiation-induced defect center produced by He^+ ion

108   implantation. No investigations of ion implantation on the CL properties of alkali

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109   feldspars (e.g. sanidine, orthoclase and microcline) have been performed. Most alkali

110   feldspars show a blue CL emission assigned to Al-O$^-$-Al defect center, and the intensity

111   depends on the natural radiation dose (Finch and Klein, 1999). Ion implantation

112   corresponding to α particle radiation, therefore, potentially affects the CL emissions

113   assigned to Al-O$^-$-Al defect centers as well as other emission centers such as Ti^{4+} and

114   Fe^{3+} impurities, which should be interpreted in detail for the application of CL to

115   geodosimetry and geochronometry.

116   In this study, CL of He^+-ion-implanted alkali feldspars at 4.0 MeV, corresponding to

117   energy of α particle from radioactive decay of ^{238}U and ^{232}Th, was measured to clarify

118   the effect of ion implantation on luminescent emissions derived from defect and

119   impurity centers. Raman spectroscopy was also conducted for the implanted alkali

120   feldspar to investigate a formation process of radiation-induced defect centers produced

121   by He^+ ion implantation.

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123   **SAMPLES AND METHODS**

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125   CL and Raman analyses were carried out for unimplanted and He^+-ion-implanted

126   samples of single crystals of sanidine (Sa) ($Or_{87}Ab_{13}$) phenocrysts from syenite and

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127   phonolite xenoliths in Quaternary diatreme from Eifel, Germany, microperthitic

128   orthoclase (Or) (Or$_{93}$Ab$_7$) from Late Variscan granite in the Karlovy Vary Massif from

129   Karlovy Vary, Czech Republic and microperthitic microcline (Mi) (Or$_{89}$Ab$_{11}$) as

130   pegmatite minerals from Naegi granite in Late Cretaceous Sanyo-type granitic zone

131   from Nakatsugawa, Gifu, Japan. These alkali feldspars were identified by X-ray

132   diffraction analysis. Microstructures and microtextures associated with exsolution,

133   micropores and twining were located by optical microscopy and backscattered electron

134   SEM imaging of the plagioclase grains and avoid in subsequent CL work owing to their

135   potential impact on the results. The sliced samples ($10 \times 10 \times 1$ mm) were cut

136   perpendicular to c-axis for CL and Raman measurements in order to avoid a polarization

137   effects as suggested by Finch et al. (2003). The sliced samples were polished and

138   finished with a 1 μm diamond abrasive. CL microscopy and spectroscopy were

139   preliminarily conducted on the surface of the sliced samples to select the areas with

140   comparable CL intensity and homogeneous distribution of the intensity before the He+

141   ion implantation experiments.

142   He$^+$ ion implantation was conducted perpendicular to their surface using a 3M-tandem

143   ion accelerator located at Takasaki Research Center of the Japan Atomic Energy

144   Research Institute. The ion-beam condition had a 4.0 MeV implantation energy,

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145   corresponding to the energy of alpha particles from ^{238}U and ^{232}Th disintegrations,

146   where a specific dose density was set in the range from 2.18×10^{-6} to 6.33×10^{-4} C/cm^2

147   for the sanidine and 4.83×10^{-6} to 4.64×10^{-4} C/cm^2 for the orthoclase and microcline

148   (Table 1). The implanted samples for sanidine, orthoclase and microcline were

149   numbered in order of dose density, e.g., Sa00 for unimplanted sanidine and Sa10 for the

150   highest dose. CL spectra were acquired from the implanted surface of the samples,

151   which is indicated by the postscript "S", e.g., Or01S for orthoclase implanted at the

152   lowest dose and Or08S for oligoclase implanted at the highest dose. The implanted

153   samples were also cut perpendicular to their exposed surface to enable CL line analysis

154   and high-resolution CL imaging of the surface in cross-section. The sectional samples

155   are denoted by the postscript "C", e.g., Mi00C for unimplanted microcline and Mi10C

156   for microcline implanted at the highest radiation dose. Further details of the He$^+$ ion

157   implantation experiment and sample preparation can be found in Okumura et al. (2008)

158   and Kayama et al. (2011a).

159   A scanning electron microscopy-cathodoluminescence (SEM-CL) instrument was

160   carried out using a JEOL: JSM-5410 SEM combined with a grating monochromator

161   (Oxford: Mono CL2) to measure CL spectra. All CL spectra obtained in the range from

162   300 to 800 nm in 1 mm steps were corrected for the total instrumental response, which

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163   was determined using a calibrated standard lamp. CL line analysis was measured across

164   a profile from He$^+$ ion implanted surface (0 μm) to a depth of 20 μm with 0.25 μm steps,

165   where the bulk intensity of the panchromatic CL (300 to 800 nm) was obtained. The

166   operating conditions were set as follows: an accelerating voltage of 15 kV and a beam

167   current of 2.0 nA in scanning mode with a 220 × 185 μm scanning area, which was

168   established based on the preliminary CL spectroscopy for prevention of electron

169   irradiation damage and enhancement of the signal/noise (S/N) ratio. According to

170   Kayama et al. (2010), the corrected CL spectra in energy units were deconvoluted into

171   the Gaussian components corresponding to each emission center using the peak-fitting

172   software (Peak Analyzer) implemented in OriginPro 8J SR2. Peak position and integral

173   intensity of the Gaussian component were acquired from each five deconvoluted CL

174   spectra of unimplanted and He$^+$ ion-implanted sanidine, orthoclase and microcline at

175   different radiation dose. High-resolution CL images were obtained using the Gatan:

176   MiniCL imaging system under the same condition as CL spectral analysis by SEM-CL.

177   More details of the equipment construction and analytical procedures are in Ikenaga et

178   al. (2000) and Kayama et al. (2010).

179   A laser Raman microscope (Thermo Electron; Nicolet: Almega XR) was used for

180   Raman spectral measurements, where the Nd:YAG laser (532 nm excitation line) was

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181   selected and controlled at 20 mW with a ~1 μm spot size. The operating conditions were

182   set as five accumulations of 10 s each in the range 120 to 900 cm^{-1} in steps of 1 cm^{-1}.

183   Raman bands were calibrated by monitoring the position of the O-Si-O stretching

184   vibration (464 cm^{-1}) in reference to a standard high optical grade quartz before and after

185   the measurements. Details of instrument construction and analytical procedures can

186   found in Kayama et al. (2009).

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188   **RESULTS**

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190   **CL microscopy**

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192   Panchromatic CL images of cross-sections of sanidine implanted at 3.03×10^{-4} C/cm^2

193   (Sa09C) and of orthoclase (Or08C) and microcline (Mi08C) both implanted at $4.64 \times$

194   10^{-4} C/cm^2 show a dark line with ~1 μm width on the bright luminescent background at

195   12–15 μm beneath the implanted surface (Fig. 1). Similar dark lines occur in CL images

196   of all other implanted samples, but they are absent from unimplanted alkali feldspars.

197   The reduction in CL intensity that produces the dark line is more obvious for high dose

198   than low dose implanted samples. Optical microscopy, and secondary electron (SE), and

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199   backscattered electron (BSE) imaging reveal no microstructures or textures

200   corresponding to the dark line observed in the CL image (Fig. 1).

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202   **CL line analysis**

203

204   CL line analyses were carried out on cross-sections of Sa09C, Or08C and Mi08C (Fig.

205   2). The analysis line is shown in Fig. 1, and extends from the implanted surface to a

206   depth of 20 μm, which includes the dark line at 12–15 μm. CL intensities of Sa09C

207   appear to slightly decrease with the implantation depth, show a drastic drop at 12–15

208   μm, then increase to 16 μm (Fig. 2). Similar changes in intensity were found in CL line

209   analyses of other sanidine cross-section samples. All implanted orthoclase and

210   microcline samples also show similar depth-dependent change in CL intensities (Fig. 2).

211

212   **CL spectroscopy**

213

214   CL spectra of unimplanted sanidine (Sa00S) and microcline (Mi00S) have emission

215   bands in the blue (~410 nm) and red-IR regions (~730 nm) (Figs. 3a and c). A UV

216   emission at ~320 nm also occurs in the spectrum of Mi00S, and the intensity of this

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217   peak is appreciably lower than of the emission bands in the blue and red-IR regions (Fig.

218   3c). Unimplanted orthoclase (Or00S) has similar UV, blue and red-IR emission with

219   higher intensities than Sa00S and Mi00S. CL spectroscopy of Sa09S reveals emission

220   bands at ~410 and ~730 nm, similar to those of Sa00S, whereas CL intensity of the blue

221   emission in Sa09S is lower than in Sa00S (Fig. 3a). Also, CL of Sa09S exhibits a

222   yellow-orange emission from 550 to 600 nm overlapped and concealed by the blue and

223   red-IR emissions. The intensity of the yellow-orange emission increases with the

224   radiation dose. CL spectra of Or08 and Mi08 consist of emission bands at ~320 nm in

225   the UV, ~410 nm in the blue and ~730 nm in the red-IR regions, and these spectral

226   patterns are similar to unimplanted orthoclase and microcline (Figs. 3b and c). The

227   implanted orthoclase and microcline show a decrease in the blue emission intensities

228   and an increase in the yellow-orange ones with an increase in radiation dose.

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230   **Raman spectroscopy**

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232   Raman spectra of unimplanted sanidine, orthoclase and microcline have pronounced

233   peaks at ~160, ~285, ~455, ~480 and ~515 cm^{-1}, and weak ones at ~360, ~405, ~750

234   and ~810 cm^{-1}. Similar peaks are also observed in Raman spectra of dark line areas at

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235   12–15 μm depth in Sa09C, Or08C and Mi08C, which have lower intensities, larger

236   bandwidths and high background compared to those of unimplanted samples. Raman

237   line analyses of Sa09C, Or08C and Mi08C that were obtained from the implanted

238   surface to the inside with 20μm depth reveal that the integral-peak intensities at 515

239   cm^{-1} slightly decrease at 12–15 μm depth, then increase with greater depth (Fig. 4).

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241   **DISCUSSION**

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243   **Characteristics of CL on implanted surface**

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245   Panchromatic CL images of the cross-sections show a dark line at 12–15 μm beneath

246   the implanted surface (Fig. 1), and this distance is close to the maximum of electronic

247   energy loss (~12.5 μm) of 4.0 MeV He^{+} ion in alkali feldspars (Bragg and Kleeman

248   1905; Nogami and Hurley 1948; Faul 1954; Owen 1988; Komuro et al., 2002; Okumura

249   et al., 2008). By monochromatic CL imaging, Kayama et al. (2011a) found a similar

250   dark line beneath the implanted surface of albite, again, corresponding to the range of

251   He^{+} ion implantation at 4.0 MeV. CL line analyses acquired through the cross-sections

252   of all implanted alkali feldspars also reveal decreases in emission intensities at 12–15

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253 μm (Fig. 2). However, the distance at 12–15 μm is not completely concordant with the

254 maximum of electric energy loss process, which may be due to He^+ ion implantation

255 condition or spatial resolution of CL microscopy proposed by Okumura et al. (2008).

256 Nevertheless, it is noteworthy that He^+ ion implantation definitely make a quench of CL

257 emission from alkali feldspar around the end of the ion track, in proportion to the

258 radiation dose.

259 Raman spectra acquired from the dark line in CL imaging of Sa09, Or08 and Mi08

260 are of a lower peak intensity, broader bandwidth and high background than those seen in

261 unimplanted samples. Raman line analyses of Sa09C, Or08C and Mi08C show a slight

262 decrease in the integral-peak intensity at 515 cm^{-1} in the dark line at 12–15 μm,

263 assigned to T-O stretch and O-T-O deformation modes in TO_4 group (Fig. 4) (von

264 Stengel 1977; Freedman et al. 2003). A similar phenomenon has been recognized in the

265 Raman spectra of He^+-ion-implanted albite (Kayama et al., 2011a; Kayama et al.,

266 2011b). These facts imply that He^+ ion implantation may destroy the linkage between

267 TO_4 tetrahedra or induce a strain, and consequently quenches CL in alkali feldspar. This

268 has been also observed in zircon, where the luminescence and Raman intensity is

269 reduced in proportion to metamictization (Nasdala et al. 2002; Kempe et al. 2010).

270 According to the previous studies, ion implantation also results in the migration of

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271   monovalent cations in alkali feldspar. Monovalent cations such as Na^+ migrate in the

272   lattice of feldspar during Pb ion implantation (Petit et al., 1987). The extent of lattice

273   damage caused by ion implantation and its consequent diffusion are determined by the

274   implantation dose (Watson and Dohmen 2010). According to Jambon and Carron (1976),

275   diffusion coefficient of alkali element in feldspar may depend on the defect density.

276   Lineweaver (1963) demonstrated that electron irradiation transfers alkali elements into

277   unirradiated areas due to formation of the electric fields produced by defection of

278   oxygen. Although the cation migration potentially occurs in associated with ion

279   implantation, it may be slight effective because there is almost no difference of Na^+

280   content, obtained from chemical analysis by wavelength dispersive X-ray spectroscopy

281   (WDS), between unimplanted and the implanted alkali feldspars. Taken together these

282   findings indicate that the partial destruction, introduction of strain and the slight Na^+

283   migration due to He^+ ion implantation may be the cause of quenching of CL in alkali

284   feldspar rather than the Na^+ migration. This CL quenching may be responsible for a

285   conversion of emission center related to the present alkali feldspar into non-luminescent

286   center due to an alteration of the energy state or a change of luminescence efficiency

287   due to a variation of the activation energy, as will be described in the section of

288   "Radiation effects on each emission center".

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289   With an increase in the radiation dose on alkali feldspars, emission intensities of blue

290   CL decrease sharply, whereas yellow-orange emissions intensities increase and red-IR

291   intensities slightly decrease or increase depending on the samples (Fig. 3). This pattern

292   indicates that He^+ ion implantation effect on CL vary depending on type of emission

293   center. Although CL line analysis reveals a decrease in the intensity at 12–15 μm caused

294   by an elimination of the emission center due to the partial destruction, introduction of

295   strain or the Na^+ migration, there should also be an accumulation of radiation-induced

296   defect centers related to the brightening CL emission around the end of the ion track.

297   Therefore, CL halo in feldspars may be produced and characterized by both elimination

298   and creation of the emission centers due to radiation, where the former should be the

299   dominant process for the present alkali feldspar with the dark line and the later should

300   be for albite with bright luminescent band reported by Kayama et al. (2011a).

301

302   **Assignment of emission centers**

303

304   The blue emission at 400–410 nm, shown in Fig. 3, is assigned to the following

305   centers; (1) an oxygen defect associated with the electron hole trapped Löwenstein

306   bridge (Al-O⁻-Al defect center) formed with two Al atoms, one of which is structural Al

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307   and the others is impurity Al (Marfunin 1979; Finch and Klein 1999; Götze et al. 2000;

308   Słaby et al. 2008; Kayama et al. 2010) and (2) Ti^{4+} incorporated with Al sites, which act

309   as impurity center and/or oxygen defect associated with Al-O-Ti bridges (Marfunin and

310   Bershov 1970; Mariano et al. 1973; Mariano and Ring 1975; Speit and Lehmann 1976;

311   Kirsh et al. 1987; Smith and Brown 1988; Ginibre et al. 2004; Lee et al. 2007; Parsons

312   et al. 2008; Kayama et al. 2010). According to Kayama et al. (2010), the blue emission

313   band consists of an overlap of two components, namely the oxygen defect centers

314   associated with Al-O-Al and Al-O-Ti bridges (Al-O$^-$-Al/Ti defect center) and the Ti^{4+}

315   impurity center. The alkali feldspars also have the red-IR CL emission attributed to a

316   Fe^{3+} impurity that substitutes for Al^{3+} ions in tetrahedral sites for the luminescence

317   caused by the radiative transition of the electrons from $^4T_1$ to $^6A_1$ (Telfer and Walker

318   1978; Finch and Klein 1999; Götze et al. 2000). Kayama et al. (2010) clarified the

319   suggestion of Finch and Klein (1999) that the red-IR CL emission is composed of two

320   components assigned to Fe^{3+} impurity centers on T1 and T2.

321   CL spectra of the implanted alkali feldspars have yellow-orange emission from 550 to

322   600 nm (Fig. 3), of which intensities increase with radiation dose. Ionoluminescence

323   (IL) spectrum of alkali feldspar shows a similar increase in the intensity depending on

324   the radiation dose (Brooks et al. 2002). A comparable increase in the CL intensity with

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325   radiation dose has been also observed in red emissions from He^+-ion-implanted albite,

326   which is characteristic of the radiation-induced defect center (Kayama et al. 2011a;

327   Kayama et al. 2011b). Krickl et al. (2008) also demonstrated a similar yellow emission

328   assigned to the radiation-induced defect center in He^{2+} irradiated natural and synthetic

329   SiO_2 phase as well as natural α-quartz with radiohaloes. This suggests the formation of

330   radiation-induced defect center in alkali feldspar by He^+ ion implantation and/or change

331   in quantum efficiency of the recombination site.

332   According to deconvolution method suggested by Stevens-Kalceff (2009) and Kayama

333   et al. (2010), the emission bands in CL spectra from the sanidine, orthoclase and

334   microcline can be separated into five Gaussian components, at 3.05, 2.81, 2.09, 1.73 and

335   1.68 eV, where their peak position and integral intensity are obtained from each five

336   deconvoluted CL spectral of unimplanted and the implanted alkali feldspar at different

337   radiation dose. The emission components at 3.05 and 2.81 eV are constituents of the

338   emission bands in the blue spectral region, where the former is assigned to Ti^{4+} impurity

339   center and the latter to $Al-O^--Al/Ti$ defect center (Kayama et al. 2010). The red-IR

340   emission comprises the components at 1.73 and 1.68 eV that Kayama et al. (2010)

341   attributes to the Fe^{3+} impurity centers on the T1 and T2 sites, respectively. Intensity of

342   the component at 2.09 eV increases with radiation dose, implying a characteristic CL

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343   signal of the radiation-induced defect center (Fig. 5). The emission component assigned

344   to the radiation-induced defect center is also detectable in the deconvoluted CL spectra

345   of He^+-ion-implanted albite, but the peak wavelength (1.861 eV) is distinct from that

346   obtained from the alkali feldspar in the present study (2.09 eV). According to Blasse

347   and Grabmaier (1994), Götze et al. (2000) and Stevens-Kalceff et al. (2000), the peak

348   position of an emission band varies with chemical composition, crystal structure in host

349   lattice, and type of emission center. Therefore, further studies such as annealing

350   experiment and ESR analysis will be necessary for an identification of type of

351   radiation-induced defect center.

352

353   **Radiation effects on each emission center**

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355   Figures 6, 7, 8 and 9 plot intensities of Gaussian components at 3.05 eV, 2.81 eV, 2.09

356   eV, 1.73 eV and 1.68 eV against dose density of He^+ ion implantation on the sanidine,

357   orthoclase and microcline, where the averaged intensities and the standard deviations

358   are obtained from five deconvoluted CL spectra of each of these feldspar implanted at

359   respective radiation dose. They elucidate radiation effects on CL of alkali feldspar

360   activated by each emission center, as follows.

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Ti^{4+} impurity center

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364   Intensities of the emission component at 3.05 eV decrease sharply with increasing

365   radiation doses up to 1.07×10^{-4} C/cm^2 for sanidine and 9.42×10^{-5} C/cm^2 for

366   orthoclase and microcline, then decrease more gradually above that threshold. As

367   described above, He$^+$ ion implantation potentially leads to the partial destruction,

368   introduction of strain and the slight Na$^+$ migration in the alkali feldspars judging from

369   the present results obtained by Raman spectroscopy and EPMA analysis and the

370   previous studies, which may be responsible for quenching of the CL activated by Ti^{4+}

371   impurity center. According to Brooks et al. (2001), ion implantation reduces activation

372   energy associated with hopping between adjacent channels, which is a function of the

373   luminescence efficiency (Curie 1963). Kayama et al. (2009) demonstrated that the

374   activation energy depends on the structural state in SiO$_2$ polymorphs, which may be due

375   to a change of the energy state in host. Therefore, luminescence efficiency as well as the

376   activation energy varies depending on the structural state in the host, as suggested by

377   Blasse and Grabmaier (1994). A change of the structural state by partial destruction,

378   introduction of strain or the Na$^+$ migration during He$^+$ ion implantation may decreases a

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379   luminescence efficiency of Ti^{4+} impurity center in the alkali feldspars due to a change in

380   the activation energy. Alternatively, it may lead to an alteration of the energy state in

381   Ti^{4+} impurity center, resulting in a conversion of the emission center into

382   non-luminescent center. Nevertheless, these outcomes of these processes may quench

383   the blue CL in alkali feldspars. The energy used as CL activated by the Ti^{4+} impurity

384   center might be transferred into lattice vibration as phonon, or applied for radiative

385   transition of the electron at other emission centers. However, further works will be

386   necessary to validate an adequacy of this model.

387

388   **Al-O⁻-Al/Ti defect center**

389

390   The emission components at 2.81 eV increase in intensity with an increase in low

391   radiation level of He^+ ion for sanidine and microcline (Figs. 6b and 8b). IL spectroscopy

392   of alkali feldspar also revealed an increase in the blue emission intensity with the

393   radiation dose, which may be due to a formation of defect or vacancy in the structure

394   (Brooks et al. 2002). Finch and Klein (1999) modeled the CL intensity of the blue

395   emission in feldspar scales with the percentage of Löwenstein bridges with electron

396   holes (Al-O⁻-Al defect center) in the structure, which is closely related to natural

22

397   radiation dose received by the feldspar during its geological history. ESR analysis

398   demonstrated that electron holes at oxygen positions (e.g., Al-O⁻-Al) in feldspars are

399   produced by natural gamma ray and X-ray radiation (Petrov et al., 1989). Furthermore,

400   the diffusion of monovalent cations in quartz in response to ion implantation converts

401   the $[AlO_4/M^+]^0$ defect (M: H^+, Li^+, Na^+ and K^+) into the $[AlO_4]^0$ defect (equivalent to

402   the Al-O⁻-Al defect in feldspar), resulting in an increase in the blue emission intensity

403   with elevated radiation doses (King et al., 2011). Electron holes may be derived from

404   the slight Na^+ migration in sanidine and microcline with He^+ ion implantation and

405   subsequently trapped in Löwenstein bridges in various extents depending on the

406   radiation dose, which might be responsible for an increase in the blue CL intensity at

407   relatively low radiation level.

408   The intensities at 2.81 eV, however, decrease with as a function of radiation dose up to

409   2.41×10^{-5} C/cm^2 for orthoclase (Fig. 7b). The emission intensity is substantially higher

410   in unimplanted orthoclase than unimplanted sanidine and microcline (Fig. 6, 7 and 8),

411   which, taking the Finch and Klein (1999) model at face value, implies that the

412   orthoclase may have quite high percentage of Löwenstein bridges with electron holes.

413   The sanidine at 1.07×10^{-4} C/cm^2 and the microcline at 9.42×10^{-5} C/cm^2 have a

414   maximum intensity at 2.81 eV in Figure 6b and 8b, implying their sufficient high

23

415   percentage of Löwenstein bridges. Electron holes, therefore, may have been already

416   trapped in almost all Löwenstein bridges in the orthoclase before He^+ ion implantation

417   and in the sanidine and microcline after the implantation at relatively high radiation

418   dose, which may contributes to no increase in the intensity at 2.81 eV for the orthoclase

419   as well as the implanted sanidine and microcline at high level of radiation dose.

420   According to King et al. (2011), a mobility of an electron in quartz by ion implantation

421   also changes $[AlO_4]^0$ defect into $[AlO_4]^-$ defect, where the former acts as emission

422   center, but latter as non-luminescent center. $Al\text{-}O^-\text{-}Al/Ti$ defect centers in the orthoclase,

423   and the implanted sanidine and microcline at relatively high radiation dose might be

424   eliminated and converted into non-luminescent centers due to the Na^+ migration by He^+

425   ion implantation, which quenches their blue CL. Furthermore, Raman spectroscopy

426   shows a slight decrease in the integral-peak intensity at 515 cm^{-1} in the dark lines.

427   Radiation dose leads to a breaking of many Al-O bond in framework structure of the

428   alkali feldspar and then eliminating a large amount of $Al\text{-}O^-\text{-}Al/Ti$ defect centers. An

429   introduction of strain of AlO^4 tetrahedra due to He^+ ion implantation may be also due to

430   a change of the energy state in $Al\text{-}O^-\text{-}Al/Ti$ defect centers. These processes might be

431   also responsible for the quenching effect on the blue CL.

432

24

433 **Fe^{3+} impurity center**

434

435 The radiation doses on sanidine up to 1.07×10^{-4} C/cm^2 decrease the intensity of

436 emission components at 1.73 eV assigned to the Fe^{3+} impurity center on T1 sites. This

437 effect is also seen to doses of up to 9.42×10^{-5} C/cm^2 for the microcline. The

438 component at 1.68 eV, which is the Fe^{3+} impurity center on T2 sites, increases in

439 intensity with the radiation dose up to 1.07×10^{-4} C/cm^2 in sanidine, 4.83×10^{-5} C/cm^2

440 in orthoclase and 2.50×10^{-4} C/cm^2 in microcline (Figs. 6, 7 and 8). This may

441 contributes to an energy transition between Fe^{3+} impurity centers on T1 and T2 sites.

442 The minimal partial destruction, introduction of strain or slight Na^+ migration may

443 causes a decrease in the luminescence efficiency of Fe^{3+} impurity center on T1 site as a

444 consequence of a change of activation energy or a conversion of the emission center

445 into non-luminescent center by an alteration of the energy state, the same as in the case

446 of Ti^{4+} impurity center. Consequently, the red-IR CL in alkali feldspar may be quenched

447 by these processes derived from He^+ ion implantation. These results are concordant with

448 IL spectral data of Fe^{3+}-activated emission obtained from alkali feldspar (Brooks et al.

449 2002). A part of energy for luminescence emission from the Fe^{3+} impurity center on the

450 T1 site should be consumed by radiative transition of Fe^{3+} impurity center on T2 site as

25

451   the energy transition process, resulting in an enhancement of the red-IR CL intensity.

452   The rate of increase of emission intensity at 1.68 eV is lower for orthoclase than for

453   sanidine and microcline (Figs. 6c, 7c and 8c). This may be due to the low concentration

454   of Fe^{3+} impurity centers on the T1 site judging from undetectable emission component

455   at 1.73 eV in orthoclase, although further works will be necessary for an establishment

456   of this model.

457   The emission component at 1.68 eV in sanidine shows a decrease in the intensity with

458   an increase in the radiation dose above 1.07×10^{-4} C/cm^2 (Fig. 6c). According to

459   Kayama et al. (2009), a change in framework configuration by partial destruction of its

460   structure alters the emission centers into non-luminescent centers with consequent

461   quenching of CL due to an increase in the population of non-radiative transition. This is

462   observed in other mineral systems, for example, Nasdala et al., (2002) demonstrated

463   that natural radiation destroys the structure of zircon, leading to a decrease in emission

464   intensity depending on the radiation dose. These facts indicate that the linkages between

465   the Fe^{3+} ions on T2 site and oxygen as their ligands might be appreciably broken or

466   strained by He^{+} ion implantation at relatively high radiation dose, and consequently the

467   emission center is converted into non-luminescent center. Similarly, such change of the

468   energy state of the emission center should be caused by the slight Na^{+} migration, which

26

469   also results in a quenching of CL activated by Fe^{3+} impurity centers on the T2 site. On

470   the other hand, the intensities at 1.68 eV for orthoclase and microcline increase with

471   radiation dose up to 4.64×10^{-4} C/cm^2 and reach a the saturation level above $4.83 \times$

472   10^{-5} C/cm^2 for orthoclase and 2.50×10^{-4} C/cm^2 for microcline. Since Raman

473   spectroscopy indicates that the framework of the disordered feldspar appears to be more

474   prone to damage than ordered feldspar (Fig. 4), He$^+$ ion implantation effects of the

475   structure-breaking may be potentially exerted to the sanidine rather than the orthoclase

476   and microcline. Most Fe^{3+} impurity centers on the T2 site act as an emission center in

477   orthoclase and microcline, but not in the sanidine at relatively high radiation dose,

478   which might explain the lack of a decrease in intensity at 1.68 eV in the orthoclase and

479   microcline with the enhanced radiation dose.

480

481   **Radiation-induced defect center**

482

483   The emission components at 2.09 eV exponentially increase in intensity with radiation

484   dose in the low radiation level, although the gradients differ between the alkali feldspars,

485   and are largest for the microcline, followed by the orthoclase and then the sanidine (Fig.

486   9). Saturation of the intensity is reached at 4.02×10^{-6} C/cm^2 for sanidine, above $2.41 \times$

487   10^{-5} C/cm^2 for orthoclase and above 4.83×10^{-5} C/cm^2 for microcline; the saturated

488   intensity of the ordered alkali feldspar tends to be higher than that of the disordered one.

489   This pattern implies that an increase in the CL intensity of the yellow-orange emission

490   assigned to the radiation-induced defect center might be closely related to the degree of

491   Si-Al order. ESR studies on feldspar have also demonstrated that signals attributed to

492   oxygen vacancies linked between Si and Al tetrahedra vary depending on natural

493   gamma and X-ray radiation doses and the degree of Si-Al ordering (Matyash et al.,

494   1982; Petrov et al., 1989). The emission component at 2.09 eV in the alkali feldspar,

495   therefore, might be assigned to one or more of the oxygen vacancy centers. Further

496   investigations such as annealing experiment and ESR analysis of radiation-induced

497   alkali feldspars will allow us to specify type of the oxygen vacancy centers.

498   Figure 9 reveals that there is no decrease in the intensity at 2.09 eV with the enhanced

499   radiation dose up to 6.33×10^{-4} C/cm^2 for sanidine and up to 4.64×10^{-4} C/cm^2 for the

500   orthoclase and microcline. The components at 2.81 eV, however, decrease sharply in

501   intensity in the range of relatively high radiation doses, which might be due to breaking

502   of Al-O bonds related to the Al-O$^-$-Al/Ti defect center by He$^+$ ion implantation. These

503   results indicate that formation of the radiation-induced defect center assigned to

504   component at 2.09 eV in the alkali feldspar should be a dominant process rather than an

28

505   elimination of the center due to the partial breaking of the structure in the present range

506   of the radiation dose.

507   The dose response of intensity at 2.09 eV appears to be mainly controlled only by the

508   degree of Si-Al ordering, even though other properties including chemical composition,

509   crystal structure, concentration and distribution of other emission centers and the

510   presence of microstructures or microtextures also differ between the alkali feldspars.

511   Kayama et al. (2011b) demonstrated that several albite from different localities show

512   almost same dose response of the intensity at 1.86 eV, not depending on other properties

513   of these albite crystals. In the case of alkali feldspar, therefore, a quantitative estimation

514   of α radiation dose from natural radionuclides using the intensity at 2.09 eV requires a

515   correction for the CL spectral data on the basis of the degree of Si-Al ordering, but

516   probably not to other mineralogical features. Eventually, the intensity at 2.09 eV may be

517   used as an indicator for geodosimetry, and then geochronometry based on the additive

518   dose method, which provide progressive application in geoscience and planetary science,

519   e.g. clarification of space weathering on lunar regolith and micron-order grain recovered

520   from Itokawa asteroid, sedimentary dating in wide applicable range, estimation of

521   leakage of nuclear waste from geologic disposal facilities and atomic power plant.

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REFERENCES

537

538   Blasse, G. and Grabmaier, B.C. (1994) Radiative return to the ground state: Emission. In

539   Luminescent Materials, 52, chapter 3, p. 33–70. Springer Verlag, Berlin.

540   Bragg, W. H., and Kleeman, R. (1905) Alpha particles or radium, and their loss of range

541   passing through various atoms and molecules. Philosophical Magazine, 10, 318–334.

542   Brooks, R. J., Ramachandran, V., Hole, D. E., Townsend, P. D. (2001) Dose rate effects

543   in ion beam luminescence. Radiation Effects and Defects in Solids: Incorporating

544   Plasma Science and Plasma Technology, 155, 177–181.

545   Brooks, R. J., Finch, A. A., Hole, D. E., Townsend, P. D., and Wu, Z. (2002) The red to

546   near-infrared luminescence in alkali feldspar. Contributions to Mineralogy and

547   Petrology, 143, 484–494.

548   Curie, D. (1963) Thermal and optical activation of trapped electrons: Quenching effects.

549   In Luminescence in Crystals, chapter 7, p. 202–208. Methuen and Co. Ltd., London.

550   Faul, H. (1954) Nuclear geology, John Wiley (New York), 414.

551   Freeman, J. J., Wang, A., Kuebler, K. E., and Haskin, L. A. (2003) Raman spectroscopic

552   characterization of the feldspars-Implications for in situ surface mineral characterization

553   in planetary exploration. Lunar and Planetary Science XXXIV, 1676.

554   Finch, A. A., and Klein, J. (1999) The causes and petrological significance of

555   cathodoluminescence emission from alkali feldspars. Contributions to Mineralogy and

556   Petrology, 135, 234–243.

557   Finch, A. A., Hole, D. E., and Townsend, P. D. (2003) Orientation dependence of

558   luminescence in plagioclase. Physics and Chemistry of Minerals, 30, 373–381.

559   Gaft, M., Reisfeld, R., and Panczer, G. (2005) Luminescence Spectroscopy of Minerals

560   and Materials, Springer-Verlag (Berlin), 52.

561   Götze, J., Krbetschek, M.R., Habermann, D., and Wold, D. (2000) High-resolution

562   cathodoluminescence of feldspar minerals. In M. Pagel, V. Barbin, P. Blanc, and D.

563   Ohnenstetter, Eds., Cathodoluminescence, p. 245–270. Geosciences, Springer Verlag,

564   Berlin.

565   Ginibre, C., Wörner, G., and Kronz, A. (2004) Structure and dynamics of the Laacher

566   see magma chamber (Eifel, Germany) from major and trace element zoning in sanidine:

567   A cathodoluminescence and electron microprobe study. Journal of Petrology, 45,

568   2197–2223.

569   Ikenaga, M., Nishido, H., and Ninagawa, K. (2000) Performance and analytical

570   conditions of cathodoluminescence scanning electron microscope (CL-SEM). The

571   Bulletin of Research Institute of Natural Sciences Okayama University of Science, 26,

572   61–75.

573   Jambon, A., and Carron, J. P. (1976) Diffusion of Na, K, Rb and Cs in glasses of albite

574   and orthoclase composition. Geochimica et Cosmochimica Acta, 40, 897–903.

575   Kayama, M., Nishido, H., and Ninagawa, K. (2009) Cathodoluminescence

576   characterization of tridymite and cristobalite: Effects of electron irradiation and sample

577   temperature. American Mineralogist, 94, 1018–1028.

578   Kayama, M., Nakano, S., and Nishido, H. (2010) Characteristics of emission centers in

579   alkali feldspar: A new approach by using cathodoluminescence spectral deconvolution.

580   American Mineralogist, 95, 1783–1795.

581   Kayama, M., Nishido, H., Toyoda, S., Komuro, K., and Ninagawa, K. (2011a) Radiation

582   effects on cathodoluminescence of albite, American Mineralogist, 96, 1238–1247.

583   Kayama, M. Nishido, H., Toyoda, S., Komuro, K., and Ninagawa, K. (2011b)

584   Combined Cathodoluminescence and Micro-Raman Study of Helium-Ion-Implanted

585   Albite. Spectroscopy Letters, 44, 526–529.

586   Kempe, U., Thomas, S-M., Geipel, G., Thomas, R., Plötze, M., Böttcher, R. Grambole,

587   G., Hoentsch, J., and Trinkler, M. (2010) Optical absorption, luminescence, and electron

588   paramagnetic resonance (EPR) spectroscopy of crystalline to metamict zircon: Evidence

589   for formation of uranyl, manganese, and other optically active centers. American

590   Mineralogist, 95, 335–347.

591   King, G. E., Finch, A. A., Robinson, R. A. J., and Hole, D. E. (2011) The problem of

592   dating quartz 1: Spectroscopic ionoluminescence of dose dependence.   Radiation

593   Measurements, 46, 1–9.

594   Kirsh, Y., Shoval, S., and Townsend, P.D. (1987) Kinetics and emission spectra of

33

595   thermoluminescence in the feldspar albite and microcline. Physica status solidi (a), 101,

596   253–262.

597   Komuro, K., Horikawa, Y., and Toyoda, S. (2002) Development of radiation-damage

598   halos in low-quartz: cathodoluminescence measurement after He^+ ion implantation.

599   Mineralogy and Petrology, 76, 261–266.

600   Krickl, R., Nasdala, L., Götze, J., Grambole, D., and Wirth, R. (2008) Alpha-irradiation

601   effects in SiO2. European Journal of Mineralogy, 20, 517–522.

602   Lee, M. R., Parsons, I., Edwards, P. R., and Martin, R. W. (2007) Identification of

603   cathodoluminescence activators in zoned alkali feldspars by hyperspectral imaging and

604   electron-probe microanalysis. American Mineralogist, 92, 243–253.

605   Marfunin, A. S. (1979) Spectroscopy, luminescence and radiation centers in minerals.

606   Springer-Verlag (Berlin), 352.

607   Marfunin, A.S. and Bershov, L.V. (1970) Electron-hole centers in feldspars and their

608   possible crystalchemical and petrological significance. Doklady Akademii Nauk, 193,

609   412–414.

610   Mariano, A.N. and Ring, P.J. (1975) Europium-activated cathodoluminescence in

611   minerals. Geochimica et Cosmochimica Acta, 56, 175–185.

612   Mariano, A. N., Ito, J., and Ring, P. J. (1973) Cathodoluminescence of plagioclase

34

613   feldspars. Geological Society of America, Abstract Program, 5, 726.

614   Marshall, D. J. (1988) Cathodoluminescence of Geological Materials. Hyman (Boston),

615   146.

616   Matyash, V. I., Bagmut, N. N., Litovchenko, C. A., and Proshko, Ya. V. (1982) Electron

617   paramagnetic resonance study of new paramagnetic centers in microcline-perthites from

618   pegmatites. Physics and Chemistry of Minerals, 8, 149–152.

619   McKeown, D. A. (2005) Raman spectroscopy and vibrational analyses of albite: From

620   25 °C through the melting temperature. American Mineralogist, 90, 1506–1517.

621   Nasdala, L., Lengauer, C. L., Hanchar, J. M., Kronz, A., Wirth, R., Blanc, P., Kennedy,

622   A. K., and Seydoux-Guikkaume, A. M. (2002) Annealing radiation damage and the

623   recovery of cathodoluminescence, Chemical Geology, 191, 121–140.

624   Nogami, H., and Hurley, P. M. (1948) The absorption factor in counting alpha rays from

625   thick mineral sources. American Geophysical Union Transactions, 29, 335–340.

626   Okumura, T., Nishido, H., Toyoda, S., Kaneko, T., Kosugi, S., and Sawada, Y. (2008)

627   Evaluation of radiation-damage halos in quartz by cathodoluminescence as a

628   geochronological tool. Quaternary Geochronology, 3, 342–345.

629   Owen, M. R. (1988) Radiation-damage halos in quartz. Geology, 16, 529–532.

630   Parsons, I., Steele, D. A., Lee, M. R., and Magee, C. W. (2008) Titanium as a

35

631   cathodoluminescence activator in alkali feldspar. American Mineralogist, 93, 875–879.

632   Perny, B., Eberhardt, P., Ramseyer, K., Mullis, J., and Pankrath, R. (1992)

633   Microdistribution of Al, Li, and Na in α-quartz: Possible causes and correlation with

634   short-lived cathodoluminescence. American Mineralogist, 77, 534–544.

635   Petit, J. C., Dran, J. C., and Della Mea, G. (1987) Effects of ion implantation on the

636   dissolution of minerals. In Part II. Selective dissolution. Bulletin de Minéralogie, 110,

637   25–42.

638   Petrov, I., Agel, A., and Hafner, S. S. (1989) Distinct defect centers at oxygen positions

639   in albite. American Mineralogist, 74, 1130–1141.

640   Słaby, E., Götze, J., Simon, K., and Wörner, G. (2008) K-feldspar phenocrysts in

641   microgranular magmatic enclaves: Cathodoluminescence and geochemical studies on

642   crystal growth as a marker of magma mingling dynamics. Lithos, 105, 85–97.

643   Smith, J.V. and Brown, W.L. (1988) Feldspar Minerals. 1. Crystal structures, physical,

644   chemical, and microtextural properties, 828 p. Springer-Verlag, Berlin.

645   Smith, J. V., and Stenstrom, R. C. (1965) Electron-excited luminescence as a petrologic

646   tool. Journal of Geology, 73, 627–635.

647   Speit, B. and Lehmann, G. (1976) Hole centers in the feldspar sanidine. Physica status

648   solidi (a), 36, 471–481.

36

649   Stengel, M. O. von (1977) Normalschwingungen von Alkalifeldspäten. Zeitschrift für

650   Kristallographie, 146, 1–18.

651   Stevens-Kalceff, M. A. (2009) Cathodoluminescence microcharacterization of point

652   defect in α-quartz. Mineralogical Magazine, 73, 585–605.

653   Stevens-Kalceff, M. A., Matthew, R. P., Anthony, R. M., and Kalceff, W. (2000)

654   Cathodoluminescence microcharacterisation of silicon dioxide polymorphs. In M. Pagel,

655   V. Barbin, P. Blanc, and D. Ohnenstetter, Eds., Cathodoluminescence in Geosciences,

656   chapter 8, p. 193–223. Springer, Berlin.

657   Telfer, D.J., and Walker, G. (1978) Ligand field bands of Mn^{2+} and Fe^{3+} luminescence

658   centers and their site occupancy in plagioclase feldspar. Modern Geology, 6, 199–210.

659   Watson, E. B., and Dohmen, R. (2010) Non-traditional Emerging Methods for

660   Characterizing Diffusion in Minerals and Mineral Aggregates. In Y. Zhang, and D. J.

661   Cherniak, Eds., Reviews in Mineralogy & Geochemistry. Mineralogical Society of

662   America Geochemical Society, p. 61–105.

663

664   **FIGURE AND TABLE CAPTION**

665

666   **Figure 1.** (a) Panchromatic CL image of a cross-section of He^+-ion-implanted (a)

37

667   sanidine (Sa09C), (b) orthoclase (Or08C) and (c) microcline (Mc08C). White lines

668   indicate trace of CL and Raman line analyses for the alkali feldspars, shown in Figures

669   2a and 4d . Scale bars are 20 μm.

670

671   **Figure 2.** Plot of the relationship of CL emission intensity over the 300–800 nm range

672   obtained by CL line analysis from the He$^+$-ion-implanted surface to 20 μm. The samples

673   analyzed are Sa09C, Or08 and Mi08. The path of the line analysis is indicated by the

674   white lines in Figure 1.

675

676   **Figure 3.** CL spectra of (a) unimplanted (Sa00S) and He$^+$-ion-implanted sanidine

677   (Sa09S), (b) unimplanted (Or00S) and He$^+$-ion-implanted orthoclase (Or08S), and (c)

678   unimplanted microcline (Mi00S) and He$^+$-ion-implanted microcline (Mi08S).

679

680   **Figure 4.** Plot showing the change in intensity of the Raman peak at 515 cm^{-1} from the

681   implanted surfaces of cross-section samples of Sa09C, Or08C and Mi08C to 20 μm

682   depth. A slight decrease in the intensity at 515 cm^{-1} is observed at ~10 μm, which is

683   responsible for the cracks. Measured areas of the Raman line analysis are indicated in

684   Fig. 1 as white lines.

38

685

686 **Figure 5.** Deconvolution of CL spectra in energy units obtained from

687 He^+-ion-implanted (a) sanidine (Sa09S), (b) orthoclase (Or08S) and microcline (Mi08S).

688 Data are fitted by several Gaussian curves.

689

690 **Figure 6.** A plot of the intensity of the Gaussian component at 2.09 eV obtained using

691 CL spectral deconvolution against dose density of He^+ ion implantation for the sanidine

692 (Sa00S to Sa10S), orthoclase (Or00S to Or08S) and microcline (Mi00S to Mi08S).

693

694 **Figure 7.** Plots of intensities of Gaussian components at (a) 3.05 eV, (b) 2.81 eV, (c)

695 1.68 eV and (d) 1.73 eV obtained using CL spectral deconvolution for the sanidine

696 (Sa00S to Sa10S) against dose density of He^+ ion implantation.

697

698 **Figure 8.** Plots of intensities of Gaussian components at (a) 3.05 eV, (b) 2.81 eV and (c)

699 1.68 eV obtained using CL spectral deconvolution for the orthoclase (Or00S to Or08S)

700 against dose density of He^+ ion implantation.

701

702 **Figure 9.** Plots of intensities of Gaussian components at (a) 3.05 eV, (b) 2.81 eV, (c)

39

703   1.68 eV and (d) 1.73 eV obtained using CL spectral deconvolution for the microcline

704   (Mi00S to Mi08S) against dose density of He$^+$ ion implantation..

705

706   **Table 1.** Samples of alkali feldspars for CL and Raman measurements.

707

No.	Dose density (C/cm^2)	No.		Dose density (C/cm^2)
Sa00	Unimplanted	Or00	Mi00	Unimplanted
Sa01	2.18×10^{-6}	Or01	Mi01	4.83×10^{-6}
Sa02	4.02×10^{-6}	Or02	Mi02	9.65×10^{-6}
Sa03	2.54×10^{-5}	Or03	Mi03	2.41×10^{-5}
Sa04	6.97×10^{-5}	Or04	Mi04	4.83×10^{-5}
Sa05	1.07×10^{-4}	Or05	Mi05	9.42×10^{-5}
Sa06	1.19×10^{-4}	Or06	Mi06	1.77×10^{-4}
Sa07	1.40×10^{-4}	Or07	Mi07	2.32×10^{-4}
Sa08	1.49×10^{-4}	Or08	Mi08	4.64×10^{-4}
Sa09	3.03×10^{-4}			
Sa10	6.33×10^{-4}			

Sa, Or and Mi indicate sanidine, orthoclase and microcline, respectively.

40

a Radiation-induced area

He⁺

b Radiation-induced area
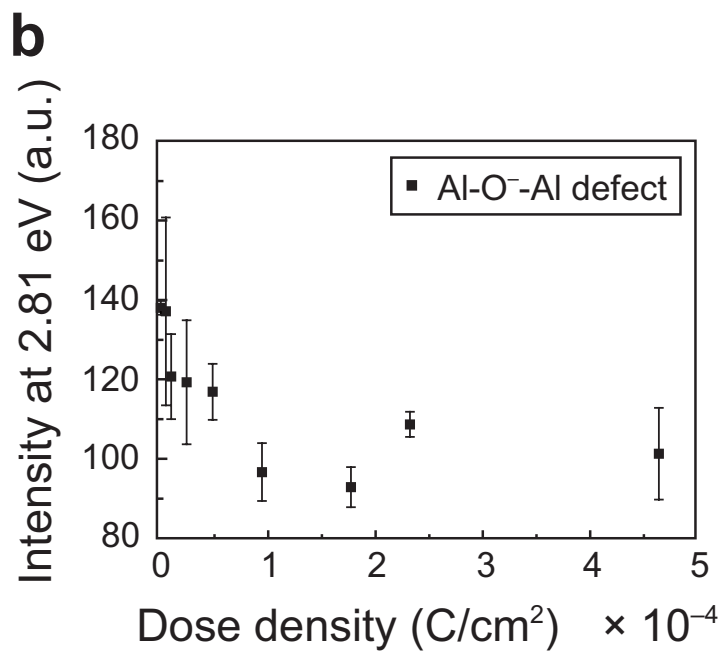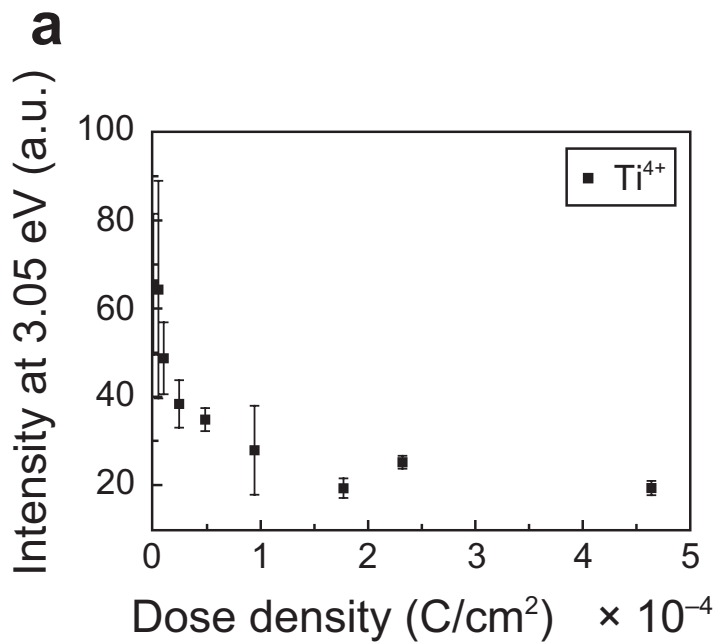
He⁺

c Radiation-induced area

He⁺
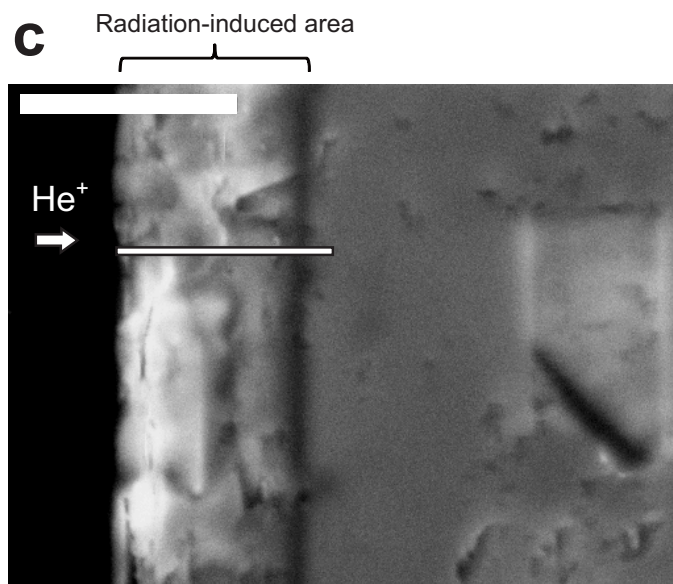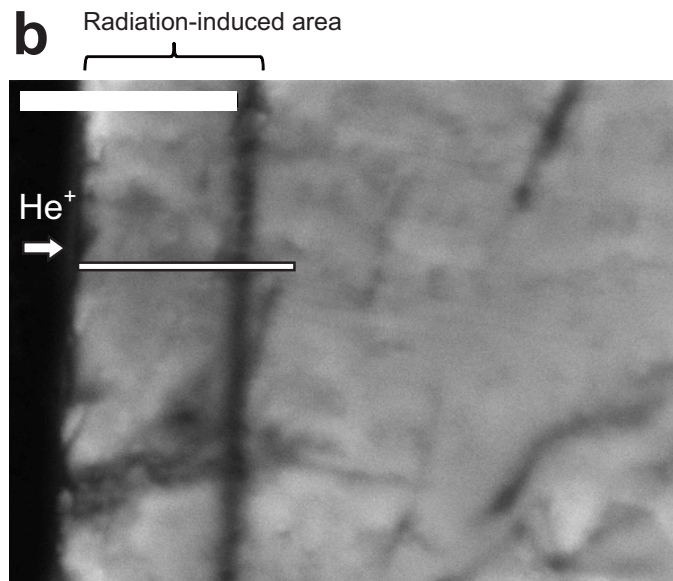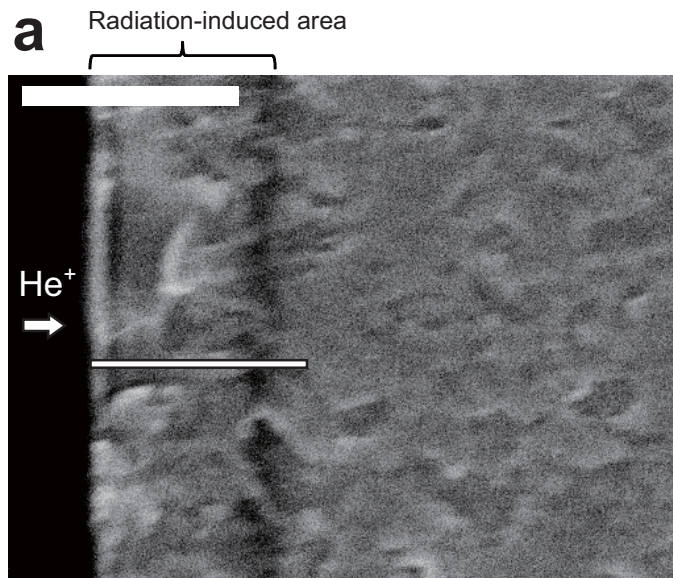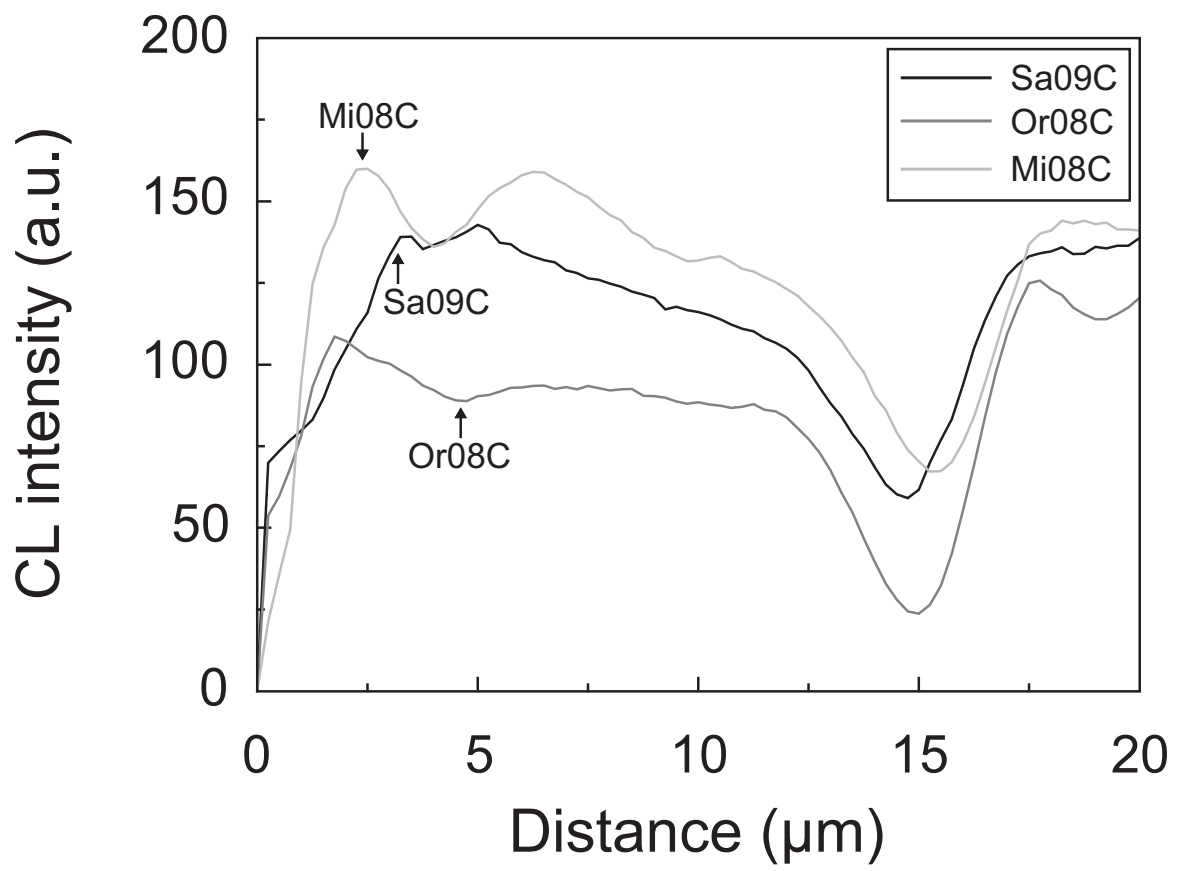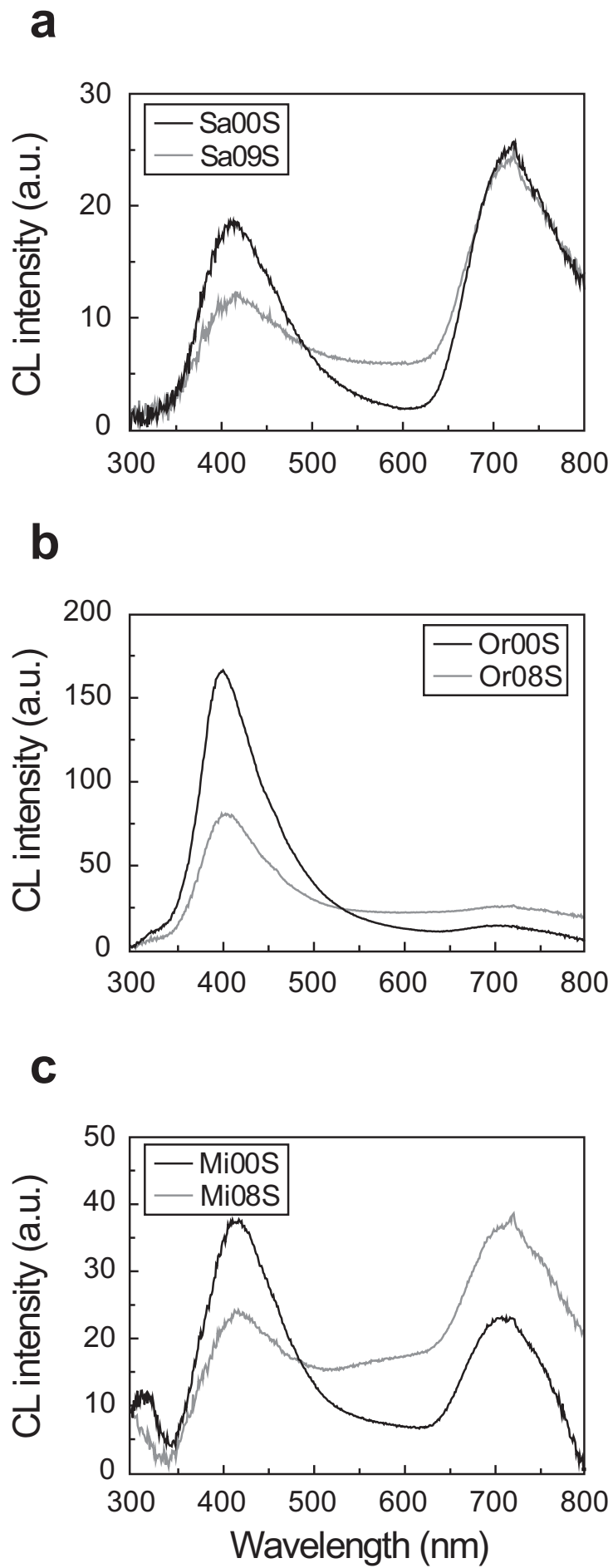
Figure 1

Figure 2

Figure 3
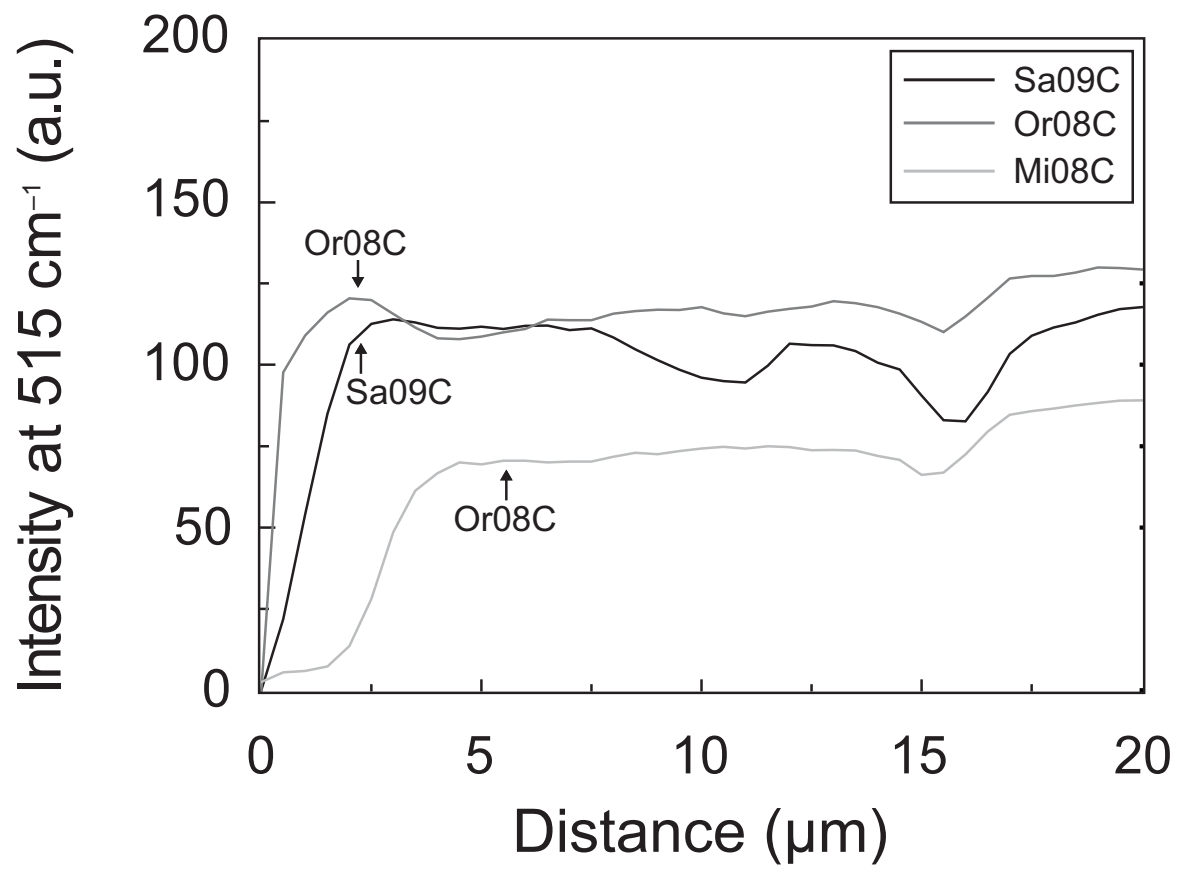
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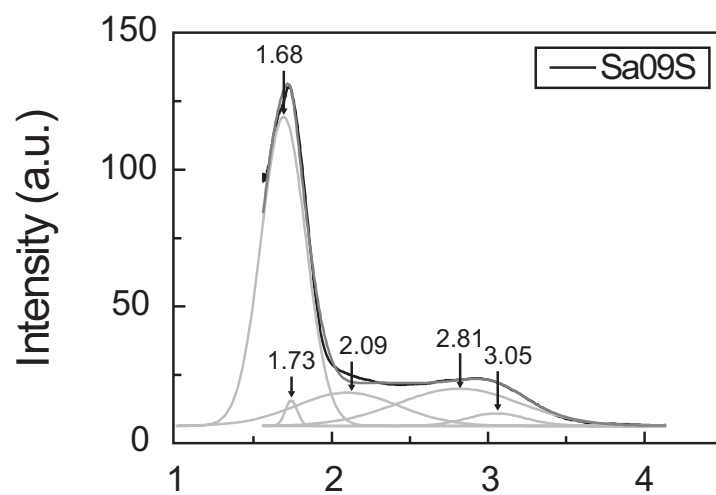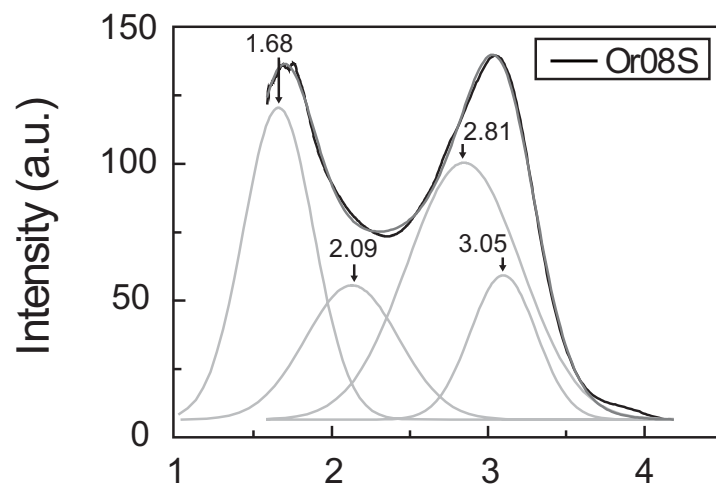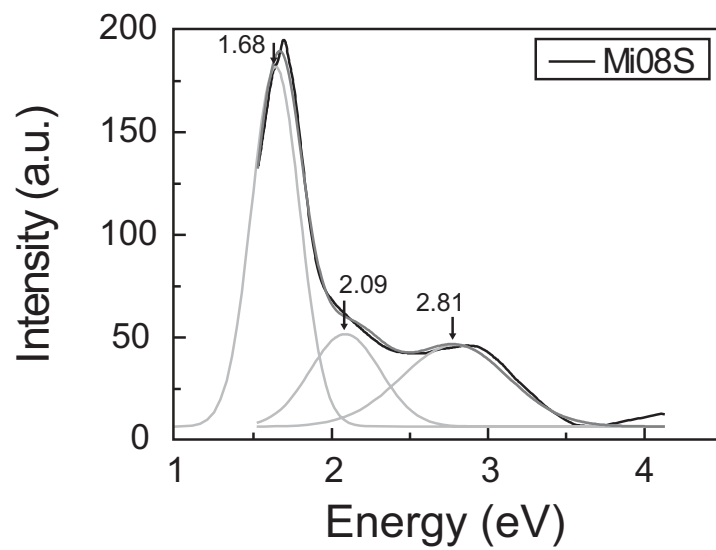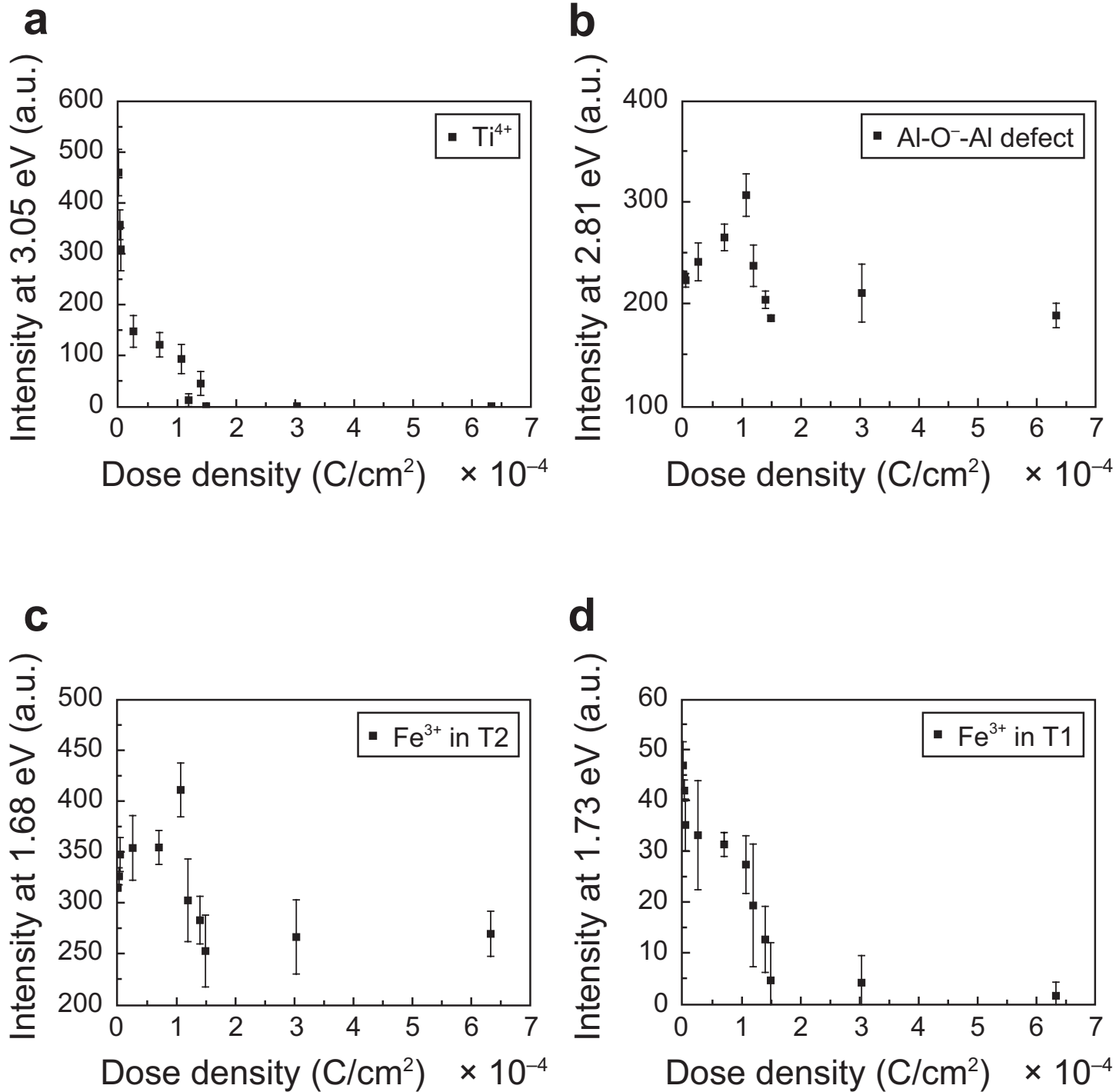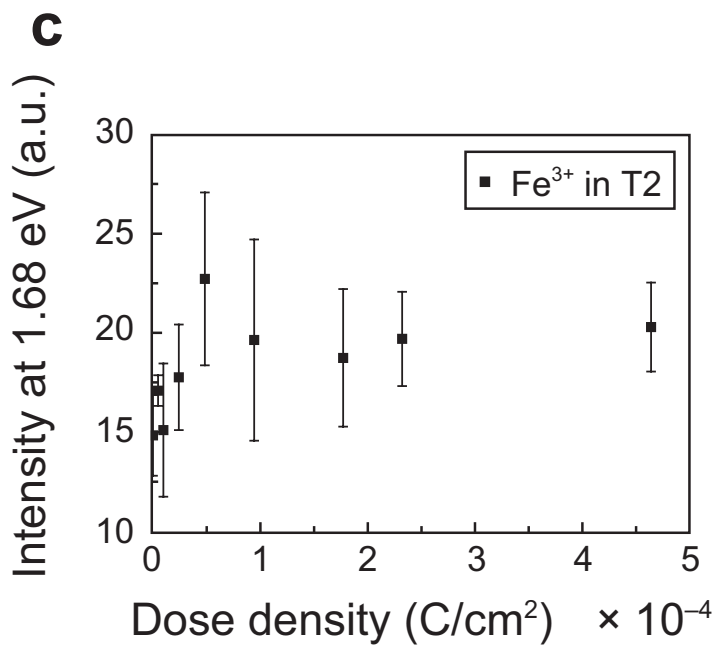
Figure 5

Figure 6

Figure 7

Figure 8

Figure 9