Revision

1 **Aluminum ordering and clustering in Al-rich synthetic phlogopite: The**
2 **influence of fluorine investigated by {^{19}F/^{1}H} ^{29}Si CPMAS NMR**
3 **spectroscopy**

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6 **MICHAEL FECHTELKORD[*], RAMONA LANGNER[†]**
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9 Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum,
10 Universitätsstr. 150, 44780 Bochum, Germany
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[*]E-mail: Michael.Fechtelkord@ruhr-uni-bochum.de

[†]Present address: Fraunhofer-Institut für Naturwissenschaftlich-Technische Trendanaly-

sen (INT), Appelsgarten 2, 53879 Euskirchen, Germany

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16   **ABSTRACT**

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18   The influence of fluorine on cationic and anionic ordering in the mica mineral

19   phlogopite has been investigated using ^{29}Si, ^1H, and ^{19}F MAS as well as $\{^1H\}/\{^{19}F\} \rightarrow$

20   ^{29}Si CPMAS and CP-depolarization NMR spectroscopies. It can be shown that the mere

21   presence of fluorine achieves a tremendous loss of capability to incorporate aluminum

22   into the phlogopite structure. Fluorine is usually located in Mg-rich octahedral and Si-

23   rich tetrahedral clusters of the phlogopite structure while hydroxyl groups are located in

24   Al-rich octahedral and tetrahedral clusters as derived from $\{^1H\}/\{^{19}F\} \rightarrow \,^{29}Si$ CPMAS

25   NMR spectroscopies. The ordering effect in these two basic structural clusters can also

26   be proven by a smaller ^{29}Si linewidth in the $\{^{19}F\} \rightarrow \,^{29}Si$ CPMAS NMR experiments

27   compared to the usual ^{29}Si MAS NMR experiment showing a stronger ordering of Si –

28   environments near the two different anion types fluorine and hydroxyl. Intensities of the

29      $\{^1H\}/\{^{19}F\} \rightarrow \,^{29}Si$ CPMAS NMR signals as function of the contact-time show a

30   deviation from the classical I-S model and can be attributed to the I-I*-S model. Time

31   constants like the proton/fluorine spin diffusion time (T_{df}), the spin-spin relaxation time

32   (T_2), the lambda parameter (λ), and the proton/fluorine spin-lattice time in the rotating

33   frame ($T_{1\rho}$) were extracted to give information about the local structure.

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35   **KEYWORDS:** ^1H / ^{19}F / ^{29}Si / Solid State NMR / MAS / CPMAS /

36   DEPOLARIZATION / phlogopite / fluorine

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INTRODUCTION

39   F is often present in silicic magmas only in minor amounts, but it may be strongly

40   enriched in the melt during on-going crystallization because of its incompatible

41   character. As a result, F-rich minerals like phlogopite form in late-stage magmatic rocks

42   like pegmatites (e.g., Christiansen et al. 1983; London 1987). For certain A-type

43   granites, F-contents up to 1.8 wt% have been found (Whalen et al. 1987), and even

44   larger amounts of 3.2 wt% F have been reported for topaz rhyolites by Pichavant and

45   Manning (1984). These amounts may have a strong influence on the physical and

46   chemical properties of magma with effects similar to those of water dissolved in the

47   melt. F lowers the crystallization temperature of a melt (Manning 1981; Webster et al.

48   1987; Weidner and Martin, 1987), it decreases the melt density (Dingwell et al. 1993;

49   Knoche et al. 1995) and melt viscosity (Dingwell et al. 1985; Baker and Vaillancourt

50   1995; Giordano et al. 2004), and increases element diffusivity in the melt (Baker and

51   Bossànyi 1994). However, there is an important difference in the behavior of F and

52   H_2O: The water solubility decreases upon ascent of the magma, leading to a higher

53   viscosity and higher solidus temperatures, and thus a more explosive nature of

54   eruptions. In contrast, the fluorine solubility may still achieve several wt% of fluorine

55   even at low pressures, inhibiting degassing upon extrusion, corresponding to a

56   completely different behavior of the melt (Carroll and Webster 1994).

57   Therefore, it is essential to gain a deeper understanding of the stability of such F-rich

58   minerals and the processes controlling a partitioning of F between mineral and co-

59   existing melt. This includes studies of phase equilibria, partitioning coefficients and

60   thermal stability of micas. It is also necessary to obtain further information on the local

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61   F-environment in the melt as well as in the F-containing crystal structures. In contrast to

62   standard techniques like X-ray and neutron diffraction, spectroscopic methods are ideal

63   tools to obtain information on the local environment of single atoms in the structure.

64   The mica mineral phlogopite shows an extraordinary capability to incorporate larger

65   amounts of F than most other minerals. Within the class of mica minerals this is only

66   exceeded by the Li-mica lepidolite (Foster 1960). Phlogopite is the Mg-end-member of

67   the biotite solid-solution series with composition K Mg_3 ($AlSi_3O_{10}$) (OH, F)$_2$. The

68   mineral structure is made up of two-dimensional infinite octahedral sheets sandwiched

69   by two sheets of TO_4-tetrahedra. Three of the four tetrahedral sites per half unit-cell in

70   phlogopite are occupied by Si and the remaining site by Al. Potassium ions occupy the

71   interlayer sections for charge balancing. In nature, extensive replacement of Si and Mg

72   by Al according to Tschermak's substitution ($^{[6]}Mg + {}^{[4]}Si \rightarrow {}^{[6]}Al + {}^{[4]}Al$) takes place.

73   The composition then ranges towards the hypothetical end-member eastonite (K

74   (Mg_2Al) ($Al_2Si_2O_{10}$) (OH, F)$_2$).

75   In pure phlogopite the octahedral sites are occupied by Mg (three sites per half unit

76   cell). Two Mg sites are coordinated by four O atoms from the tetrahedral sheets and two

77   (OH)$^-$ and/or F$^-$ anions in cis-coordination. The third Mg site has a trans-coordination of

78   the hydroxyl and/or F$^-$ anions. The (OH)$^-$ and/or F$^-$ anions are always coordinated to

79   three Mg-sites. In the Al-rich phlogopites, some of the Mg sites are substituted by Al, so

80   that some of the (OH)$^-$ and/or F$^-$ anions are coordinated by two Mg cations and one Al

81   cation.

82   In their IR spectroscopic study, Papin et al. (1997) demonstrated that the OH/F

83   distribution in Al-rich phlogopite is not statistically random, but that the hydroxyl

84   groups prefer Mg_2Al coordination and the fluorine atoms prefer Mg_3 coordination. This

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85   is in agreement with a previous ^{19}F, ^{1}H, and ^{29}Si MAS NMR study (Fechtelkord et al.

86   2003a). The results of this study indicated a non-statistical distribution of cations and

87   anions in the octahedral sheets where F prefers sites coordinated by three Mg, whereas

88   OH prefers sites bonded to Al. In addition, it was shown that hydroxyl-rich

89   compositions indicate an increased Al-content in the tetrahedral sheets suggesting a

90   stabilizing effect on the formation of Al-rich phlogopite and for fluorine rich

91   compositions a stabilizing effect on the formation of Mg-rich phlogopite (Fechtelkord et

92   al. 2003a; Circone et al. 1991).

93   In another study, $\{^{1}H\} \rightarrow ^{27}Al$ 2D CPMAS (HETCOR) NMR experiments at short

94   contact times showed information about the local configuration of tetrahedral Al sites

95   and Mg_3OH as well as Mg_2AlOH sites whereas magnetization was only transferred to

96   the octahedral Al sites from hydroxyl groups in Mg_2AlOH sites (Fechtelkord et al.

97   2003b). The $\{^{19}F\} \rightarrow ^{27}Al$ 2D CPMAS (HETCOR) NMR spectrum in Fechtelkord et al.

98   (2003b) was dominated by ^{IV}Al sites coupled to the Mg_3F complex in phlogopite.

99   Resonances from Mg_2AlF complexes were not observed. Finally, the $\{^{1}H/^{19}F\}$ ^{27}Al

100   REDOR experiments in this study supported the results of the 2D CPMAS (HETCOR)

101   experiments. The slope of each REDOR curve gave a good hint about the strength of

102   heteronuclear dipolar coupling between Al and F or Al and H. The dipolar coupling

103   between the octahedral sites and OH/F should be stronger due to the smaller distance to

104   OH and fluorine groups compared to ^{IV}Al sites. The trend could be observed for all the

105   REDOR curves. The slope of the octahedral REDOR curves was always higher than for

106   the tetrahedral curve. In addition, $\{^{1}H\} \leftrightarrow ^{27}Al$ dipolar interaction is stronger than the

107     $\{^{19}F\} \leftrightarrow ^{27}Al$ dipolar interaction due to the higher gyromagnetic ratio of ^{1}H which could

108   be also observed in the graphs resulting in an increased slope for the $\{^{1}H\}$ ^{27}Al REDOR

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109   curves compared to the $\{^{19}F\}$ ^{27}Al REDOR curves (Fechtelkord et al. 2003b). It was not

110   possible to extract quantitative information from the REDOR curves due to the lack of

111   enough data points in the initial slope.

112   In a recent work (Langner et al. 2012) we showed that different ordering schemes can

113   be found in the tetrahedral and octahedral sheets of phlogopite: In the tetrahedral sheet

114   ordering patterns are dominated by short-range ordering in order to avoid the formation

115   of Al-O-Al linkages following Loewenstein's rule (Loewenstein 1954). Long-range

116   ordering is only present at Al-content close to $Si/^{[4]}Al = 1:1$ with Al and Si occupying

117   the tetrahedra alternately. For the octahedral sheet an Al-O-Al avoidance similar to that

118   of the tetrahedral sheets has been found, and Al is always surrounded by six Mg ions in

119   the neighboring octahedra. There is a relationship between the ordering in both types of

120   sheets in that Al-atoms in the octahedral and the tetrahedral sheets tend to be located

121   next to each other forming Al-rich clusters in the structure.

122   However, these observations have been made on pure OH-phlogopites, so the

123   question now arises whether the clustering of Al in the structure also influences the

124   distribution of F and OH in F-rich phlogopites as one would expect from the OH-Al

125   preference mentioned above.

126    $\{^{1}H\}/\{^{19}F\} \rightarrow ^{29}Si$ cross-polarization magic-angle spinning (CPMAS) experiments

127   combined with ^{1}H, ^{19}F, and ^{29}Si MAS NMR investigations are an ideal tool to correlate

128   octahedral H or F environments with Si-environments in the tetrahedral sheets. The

129   correlation of octahedral and tetrahedral Al with octahedral H or F environments was

130   already done in a former study described above (Fechtelkord et al. 2003b). It can be

131   shown that the ordering of cations and anions is coupled with F preferring sites in the

132   Si-rich clusters in the structure. Moreover, the analysis of $\{^{1}H\}/\{^{19}F\} \rightarrow ^{29}Si$ contact-

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133   time dependent CP and depolarization experiments (Pines et al. 1971, 1973;

134   Kolodziejski and Klinowski 2002; Wu et al. 1988) provide relaxation, spin-diffusion,

135   and cross-polarization parameters, which contain valuable information on dynamics and

136   the local neighborhood between protons/fluorine anions and silicon atoms.

137   A   number   of   phlogopite   samples   with   nominal   composition

138    $K\,(Mg_{3-x}Al_x)\,(Al_{1+x}Si_{3-x}O_{10})\,(OH)_y\,F_{2-y}$ have been prepared under synthesis conditions

139   of 873 K and 2 kbar to investigate the role of F on the ordering patterns in both sheets of

140   the phlogopite structure. In contrast to previous studies (e.g., Langner et al. 2012;

141   Circone et al. 1991), samples containing different amounts of fluorine ($y = 0.2 - 1.8$)

142   have been compared to samples of pure hydroxyl-phlogopite ($y = 2.0$).

143   In addition to the variation in the F-content, samples of different Al-contents $x = 0.0 -$

144   1.6 have been synthesized. Theoretically, the limit for incorporation of Al into the

145   phlogopite structure is $x = 1.0$ because then a ratio of $Si/^{[4]}Al$ of 1:1 is reached.

146   Incorporating further Al into the tetrahedral sheets would force Al-atoms to occupy

147   neighboring tetrahedra which is expected to be highly energetically unfavorable

148   (Loewenstein 1954). However, values of x_{nom} higher than 1.0 have been chosen for the

149   preparation of gels because not all of the Al present in the initial gel composition is

150   incorporated into the phlogopite structure.

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152   **EXPERIMENTAL METHODS**

153   Phlogopites of nominal composition $K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O_{10})(OH)_yF_{2-y}$ with $x_{nom} =$

154    $0.0 - 1.6$ and $y = 0.2 - 2.0$ were synthesized using sol-gel-synthesis and hydrothermal

155   techniques. Starting materials for the Al-rich F-containing phlogopites were prepared

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156   according to the gelling method of Hamilton and Henderson (1968). The F anions were

157   introduced by adding 1 M NH$_4$F solution to the starting gel solution in the appropriate

158   amounts. A typical experiment consisted of 150-300 mg of the dry gel together with 9-

159   12 wt% of deionized water in a sealed gold capsule (40 mm long and 3.5 mm inner

160   diameter). Experiments were carried out in Tuttle-type cold seal pressure vessels at

161   1073 K or 873 K and 2 kbar for a duration of 7 days using water as pressure medium

162   (for detailed description of the vessels see Berndt et al. 2001). The value of $f(O_2)$ was

163   close to that imposed by the Ni-NiO buffer.

164   The chemical composition of the dry oxide gels was checked for several samples by

165   wavelength dispersive X-ray fluorescence spectroscopy (XRF) on a Philips PW 2404

166   spectrometer equipped with an Rh X-ray tube. Oxides were mixed with LiBO$_2$/Li$_2$B$_4$O$_7$

167   (MERCK Spectromelt A12) in a ratio of 1:10 in a fused bead. Analysis results showed

168   no major deviations from the intended stoichiometry of the gels.

169   After synthesis the samples have been checked with powder X-ray diffraction on a

170   D8 Bruker diffractometer. Two phlogopite polytypes have been identified: At low Al-

171   contents polytypes 1M and 2M$_1$ co-exist, while at high Al-contents nearly pure

172   phlogopite-2M$_1$ has been found. In agreement with ^{27}Al MAS NMR experiments

173   corundum has been observed as an impurity phase as well as potassium aluminum

174   hexafluoride (K$_3$AlF$_6$·0.5H$_2$O) (mainly at high fluorine and aluminum contents). On the

175   other hand, the chemical composition of the phlogopite was difficult to estimate, e.g.,

176   by microprobe analysis. The average crystal size is about 1 - 2 μm and the crystals were

177   generally oriented with their thinnest side parallel to the plane of the thin section. In

178   addition, the thin section often contained large cavities between the phlogopite crystals

179   filled by epoxy resin so that analytical totals were too low to be used.

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180   The NMR spectra were recorded on a Bruker ASX 400 NMR spectrometer.

181   ^{29}Si MAS NMR measurements were carried out at 79.49 MHz using a standard Bruker

182   7 mm MAS NMR probe with sample spinning at 4.0 kHz, a single pulse duration of

183   2 μs (90° pulse length 5.8 μs) and 4,000 - 20,000 scans were accumulated with a 10 s

184   recycle delay. To ensure that the 10 s delay is sufficient with regard to spin-lattice

185   relaxation times (T_1), some experiments were repeated with a delay of 120 s, but no

186   change in absolute intensity could be observed. Tetramethylsilane was used as reference

187   standard. In addition, high-power-decoupled $\{^1\text{H}/^{19}\text{F}\}$ - ^{29}Si MAS NMR experiments

188   were carried out to check the dependence of ^{29}Si signal linewidths on $^1\text{H}/^{19}\text{F}$ – ^{29}Si

189   heteronuclear dipolar interaction.

190   ^{1}H MAS NMR experiments have been performed at 400.13 MHz with a standard

191   Bruker 4 mm MAS NMR probe at rotation frequencies of 12.5 kHz. Liquid

192   tetramethylsilane (TMS) was used as an external standard. A pulse length of 2 μs and a

193   recycle delay of 10 s were used, and 128 scans were accumulated. The spectral width

194   was 125 kHz. After the measurements, a spectrum of the rotor without sample has been

195   recorded and subtracted from the original spectrum to eliminate the broad signal

196   resulting from protons in the probehead and the rotor cap.

197   For ^{19}F MAS NMR experiments a Bruker 4 mm MAS NMR probe has been used.

198   300 scans were accumulated at a frequency of 376.46 MHz and rotation frequencies of

199   12.5 kHz. Single pulse duration was 2 μs, and a spectral width of 125 kHz and a recycle

200   delay of 10 s have been used. As external reference a liquid p-$C_6H_4F_2$ sample has been

201   measured, and the frequency with highest signal intensity has been set to -120 ppm with

202   respect to liquid $CFCl_3$.

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203   The $\{^1H\} \rightarrow ^{29}Si$ CPMAS NMR spectra were recorded at transmitter frequencies of

204   400.13 MHz and 79.49 MHz for ^1H and ^{29}Si, respectively. A standard 7mm Bruker

205   MAS NMR probe has been used at rotation frequencies of 4 kHz. The 90° pulse length

206   for ^1H was 7.6 µs ($\nu_{rf}(^1H) = \nu_{rf}(^{29}Si) = 33$ kHz), and the recycle delay was 5 s. A total of

207   360 – 400 scans were accumulated, and tetramethylsilane was used as a reference for

208   both ^1H and ^{29}Si. For the CPMAS contact time dependent experiments contact times of

209   0.1 to 120 ms have been chosen. The $\{^1H\} \rightarrow ^{29}Si$ cross-depolarization MAS NMR

210   experiments (Kolodziejski and Klinowski 2002; Wu et al. 1988) were carried out with a

211   contact-time of 10 ms, a dephase time of 5 ms for ^1H and 32 depolarization times

212   between 20 µs and 80 ms for ^{29}Si each totalling 1,200 scans.

213   The transmitter frequencies for the $\{^{19}F\} \rightarrow ^{29}Si$ CPMAS NMR experiments were

214   79.49 MHz and 376.45 MHz for ^{29}Si and ^{19}F, respectively. Sample spinning rate was

215   5.8 kHz in a standard 7 mm Bruker MAS probe. A total of 400 scans were accumulated.

216   Tetramethylsilane (TMS) and p-$C_6H_4F_2$ (δ = -120 ppm) have been used as reference for

217   ^{29}Si and ^{19}F, respectively. The 90° pulse length for ^{19}F was 5.6 µs ($\nu_{rf}(^{19}F)$ =

218    $\nu_{rf}(^{29}Si) = 45$ kHz), and a recycle delay of 5 s has been used. For the CPMAS contact-

219   time dependent experiments contact times of 0.1 to 120 ms have been chosen. The

220    $\{^{19}F\} \rightarrow ^{29}Si$ cross-depolarization MAS NMR experiments were carried with a contact-

221   time of 10 ms, a ^{19}F dephase time of 8 ms and 32 depolarization times between 20 µs

222   and 80 ms for ^{29}Si totalling 3,200 scans each.

223   All MAS and CPMAS NMR spectra were fitted with mixed Gaussian / Lorentzian

224   lineshapes using the DmFit 2010 program (Massiot et al. 2002). Tolerances were

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225   estimated by varying the line position and linewidth in the fit function observing χ^2

226   until a distinct change of χ^2 took place.

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228   **RESULTS AND DISCUSSION**

229   **^{29}Si MAS NMR spectroscopy**

230   In order to clarify the influence of F on ordering of Si/$^{[4]}$Al in the tetrahedral sheets of

231   phlogopite we compared ^{29}Si MAS NMR spectra of F-containing compositions to those

232   of pure hydroxyl-phlogopites (Fig. 1). Si has a tetrahedral coordination, being connected

233   through three bridging O atoms to three other tetrahedral sites which could be occupied

234   either by Al or Si. The fourth (non-bridging) O atom points to the octahedral sheet and

235   coordinates to Mg in phlogopite or Al in the Al-rich phlogopites. The four possible

236   signals at approximately -91, -87, -83 and -80 ppm can be assigned as Q^3(n Al) signals

237   with n = 0-3 (Fechtelkord et al. 2003a; Circone et al. 1991). An additional signal due to

238   an impurity phase has been found in the ^{29}Si MAS NMR spectra at about -94 to -95 ppm

239   for some of the samples. This has already been reported by Circone et al. (1991) who

240   suggested that it should result from some K-deficient clay-like layers in the phlogopites.

241   It could be also due to a talc component (Wunder and Melzer 2002) which cannot be

242   directly identified in the XRD patterns – it would only alter the cell dimensions of the

243   mica. The signal was only observed as a small shoulder but in some rare cases it showed

244   up to 10% relative signal intensity. The signal areas of the phlogopite signals correlate

245   with the relative amounts of those tetrahedral units in phlogopite, so that the Si/$^{[4]}$Al

246   ratio of the tetrahedral sheets can be easily determined by ^{29}Si MAS NMR from

247   equation 1 if Loewenstein's rule applies (Loewenstein 1954):

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$$\frac{Si}{^{IV}Al} = \frac{\sum\limits_{n=0}^{3} I\left(Q^3(nAl)\right)}{\sum\limits_{n=0}^{3} \frac{n}{3} I\left(Q^3(nAl)\right)}$$
(1)

249 Due to the fact that the real Si/Al ratio of the tetrahedral layers can now be determined,

250 it is possible to estimate the "real" x–value x_{est} in the stoichiometric phlogopite formula

251 $K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O_{10})(OH)_yF_{2-y}$ from equation 2.

252
$$x_{est} = \frac{3 - \dfrac{Si}{^{IV}Al}}{1 + \dfrac{Si}{^{IV}Al}}$$
(2)

253 The ^{29}Si MAS NMR data of Al-rich phlogopites with nominal composition

254 $K (Mg_{3-x}Al_x) (Al_{1+x}Si_{3-x}O_{10}) (OH)_y (F)_{2-y}$ is listed in Table 1. The table contains signal

255 positions (δ), linewidths (FWHM) and areas of the signals. The spectra were fitted with

256 mixed Gaussian / Lorentzian lineshapes using the DmFit 2010 program (Massiot et al.

257 2002). Uncertainties were estimated by varying the line position and linewidth in the fit

258 function observing χ^2 until a distinct change of χ^2 took place. Total signal areas with

259 less than 100% are due to non-phlogopite ^{29}Si NMR signals from K-deficient clay

260 signal areas not listed here and mentioned above. The linewidth of all ^{29}Si NMR signals

261 ranges mostly around 2.6 – 2.8 ppm. The isotropic chemical shift of the signals shows a

262 dependence on the Al-content of the tetrahedral layers. An increasing Al-content leads

263 to a small shift of the ^{29}Si NMR signal to higher ppm-values. This can be attributed to

264 the change of the tetrahedral angle due to substitution of silicon by the larger Al.

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265   Both the spectra and the calculation of the "real" Al-content x_{est} of the tetrahedral

266   sheets show a sharp decrease of the phlogopite's ability to incorporate Al as F enters the

267   structure. The effect can be very well observed in Figure 2 where the estimated

268   octahedral Al content x_{est} is plotted as a function of the nominal Al-content of the oxide

269   gel x_{nom}. The estimated Al-content of the hydroxyl-phlogopites ($y = 2.0$) is always much

270   higher than that of F-containing samples of the same nominal Al-content. In contrast,

271   there is hardly any difference in the estimated Al-contents of samples of different F-

272   contents ($y = 1.2 - 1.8$). At low Al-contents the curves for different F-contents y are

273   approximately in the same range. However, for high values of nominal x the amount of

274   Al actually incorporated into the tetrahedral sheets is much higher for $y = 2.0$ than for

275   other compositions. This means that the mere presence of F in the mixture reduces the

276   ability to incorporate Al into the phlogopite structure drastically and has a stronger

277   influence than the exact ratio of OH/F.

278   At very high initial Al-contents a saturation effect can be observed: For $x_{nom} = 1.0$

279   and 1.2 the amount of Al incorporated is nearly the same ($x_{est} = 0.83$ for $y = 2.0$), for

280    $x_{nom} = 1.6$ it even decreases slightly. This indicates that for our synthesis conditions ($P =$

281   2 kbar, $T = 873$ K) the maximum amount of Al in the phlogopite structure has been

282   reached.

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285   **^{1}H and ^{19}F MAS NMR spectroscopy**

286   In the octahedral sheets, each OH position is surrounded by three cation sites which can

287   be occupied either by Mg or by Al. We therefore could expect four different

288   configurations of ions leading to four different signals in ^{1}H MAS NMR spectra:

289   Mg_3OH, Mg_2AlOH, $MgAl_2OH$, and Al_3OH. However, in a previous publication

290   (Langner et al. 2012) we showed that only two of these four signals, those for Mg_3OH

291   and the Mg_2AlOH, can be observed. Mg/Al is ordering in such a way that never two Al-

292   atoms occupy adjacent octahedral sites (Loewenstein's rule applying on octahedral

293   sites). The same is true for the ^{1}H MAS NMR spectra of F-containing phlogopites

294   shown in Figure 3. The resonance at 4.7 ppm is thought to be due to molecular water

295   which could be surface or defect water. It varies in all samples and its intensity shows

296   no relationship to the Al- or F-contents of the initial composition (see Fechtelkord et al.

297   2003a). Thus, the water resonance in Figure 3 is truncated for better visibility of the two

298   main hydroxyl signals at approximately 1.8 ppm and 0.6 ppm. The intensities of these

299   signals correlate directly with the Al-content of the octahedral sheets: when $x_{nom} = 0.0$,

300   only the signal at 0.6 ppm is observed. With increasing x_{nom}, the second signal at

301   1.8 ppm appears and increases in relative intensity. The two signals can thus be

302   assigned to the Mg_3OH (OH_{Mg}) and Mg_2AlOH (OH_{Al}) environments in the octahedral

303   sheets, respectively (Fechtelkord et al. 2003a). The ^{1}H MAS NMR data of Al-rich

304   phlogopites with nominal composition $K (Mg_{3-x}Al_x) (Al_{1+x}Si_{3-x}O_{10}) (OH)_y (F)_{2-y}$ is listed

305   in Table 2. The table contains chemical shifts (δ), linewidths (*FWHM*) and areas of the

306   signals. The linewidth of both ^{1}H NMR signals is nearly constant around $1.0 - 1.4$ ppm.

307   The chemical shift of the two signals shows a similar dependence on the Al-content as

308   that of the ^{29}Si MAS NMR signals. An increasing Al-content leads to a slight shift of

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309   the ^1H NMR signal to higher ppm-values. The reason for that effect is very similar as

310   for the ^{29}Si NMR signal: the change of cation size from Mg to Al alters the bonding

311   angles of the OH-group to these cations.

312   Fechtelkord et al. (2003a) already demonstrated that OH-groups in the phlogopite

313   structure prefer coordination by two Mg and one Al (OH_{Al}) instead a coordination by

314   three Mg (OH_{Mg}). In contrast, F favors to be surrounded by Mg only. All experimental

315   values in Table 2 show higher $OH_{Al}/(OH_{Al}+OH_{Mg})$ ratios than predicted for a statistical

316   distribution. In the case of a statistical OH distribution inside the octahedral layers

317     $OH_{Al}/(OH_{Al}+OH_{Mg})$ should be equal to x_{est}. This implies a preferential occupation by

318   hydroxide ions of sites with Al as nearest neighbor which is in agreement with the

319   findings of Papin et al. (1997) from IR-spectroscopy.

320   The behaviors of ^1H MAS NMR signals of Al-rich phlogopites with different F-

321   contents support the findings made by ^{29}Si MAS NMR spectroscopy. As the hydroxyl

322   content increases, the $OH_{Al}/(OH_{Al}+OH_{Mg})$ ratio decreases because increasing the

323   number of OH groups per unit cell makes it progressively more difficult for them to

324   preferentially occupy only sites with Al coordinating them. However, similar to what

325   has been observed for the tetrahedral sheets in the ^{29}Si MAS NMR spectra, the Al-

326   content of samples with same x_{nom} increases with decreasing F-content.

327   The preference of OH for Al-containing sites and that of F for full Mg-containing

328   sites becomes visible when comparing the ^1H MAS NMR spectra to the ^{19}F MAS NMR

329   spectra of our phlogopite samples (Fig. 4). The ^{19}F MAS NMR spectra show two main

330   resonances at -150 ppm, and -173 ppm. Spinning sidebands of the main signals due to

331   the MAS technique are marked with asterisks. At low Al and F contents only the signal

332   at -173 ppm is observed (not shown in Fig. 4). With increasing Al-content the

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333   component at -150 ppm appears and increases in relative intensity. At high F contents

334   (y ≤ 1.0) and Al contents with x ≥ 0.1 a third signal at -157 ppm appears. The first two

335   signals can be assigned to fluorine in phlogopite and are in agreement with the results of

336   Huve et al. (1992) who described the resonance at -173 ppm as Mg_3F units (F_{Mg}) and

337   the resonance at -150 ppm as Mg_2AlF (F_{Al}) units. They found a linear correlation

338   between the Al content of the sample and the intensity of the -150 ppm signal. The

339   signal at -157 ppm can be assigned to AlF_6-units from the impurity phase potassium

340   aluminum hexafluoride ($K_3AlF_6 \cdot 0.5H_2O$). The signal position is characteristic for these

341   aluminum hexafluoride compounds (Harris and Jackson 1991). A fourth ^{19}F MAS NMR

342   signal from another minor F-containing impurity phase at approximately -176 ppm

343   (signal area is 3% and 9%) exists at compositions of x_{nom} = 1.0, 1.2 and y = 1.6. An

344   assignment of these broad and low intensity signals is difficult. The ^{19}F MAS NMR data

345   of   Al-rich   phlogopites   with   nominal   composition

346    $K (Mg_{3-x}Al_x) (Al_{1+x}Si_{3-x}O_{10}) (OH)_y (F)_{2-y}$ is listed in Table 3.

347   It can be observed that the intensity of the Mg_2AlF signal becomes stronger with

348   increasing Al-content of the octahedral layers which is very similar compared to the ^1H

349   MAS NMR signals. However, in the ^1H MAS NMR spectra the intensity of the

350   Mg_2AlOH signal is equal to or even higher than that of the Mg_3OH signal. In the ^{19}F

351   MAS NMR spectra the signal intensity corresponding to Mg_2AlF environments is

352   always much lower than the Mg_3F signal intensity which indicates that F prefers to be

353   co-ordinated by Mg only. As previously shown in Langner et al. (2012) Al is clustered

354   in both sheets. Therefore, it is possible that F and OH are also part of this clustering

355   with OH being located in the Al-rich parts of the structure and F favoring Mg- and Si-

356   rich environments.

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$\{^1H\}/\{^{19}F\} \rightarrow {}^{29}Si$ Cross polarization (CP) dynamics

359   In the cross polarization (CP) experiment the strong magnetic polarization of nuclei

360   with high natural abundance and high magnetogyric ratio such as ^1H or ^{19}F (the I

361   nucleus) is transferred to nuclei with low spectral sensitivity such as ^{29}Si via

362   heteronuclear dipolar interaction (the S nucleus). Contact time dependent $\{^1H\} \rightarrow {}^{29}Si$

363   CPMAS NMR experiments have been carried out to yield direct information about

364   atomic site configurations (Pines et al. 1971; Pines et al. 1973). One of the contact time

365   dependent $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR intensity data experiments is shown in Figure 5.

366   The exponential increase of magnetization depends on the number of I spins and the

367   distance of these spins to the S nuclei. On the other hand the intensity curve decays

368   exponentially during excitation of the radio frequency pulse to approach

369   thermodynamical equilibrium for the occupancy of the energy levels with the lower B_1

370   field. The described model is called the "classical I-S model" (Kolodziejski and

371   Klinowski 2002). The least-squares fit in Figure 5 using this model shows that it is too

372   simple to describe the experimental data.

373   In fact, a two stage rise as previously reported by Wu et al. (1988) can be observed.

374   In these cases the spin diffusion between I nuclei (the I^* nuclei) involved in the CP

375   transfer and other I nuclei not involved in the CP transfer is not sufficiently rapid and

376   produces an oscillatory CP transfer between I^* and S nuclei in stationary single crystals

377   (Müller et al. 1974). In polycrystalline material the oscillatory behavior sums up

378   because of angular distributions of the $I^* - S$ nuclei pairs. First, a very rapid increase in

379   the first tens of microseconds takes place related to heteronuclear spin-spin relaxation

380   (T_2) between I^* and S nuclei followed by a much slower increase due to spin diffusion

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381   (T_{df}) between I and I^* nuclei. The ratio (λ) of both processes depends on the number of

382   protons n near the observed nucleus ($\lambda = 1/(n + 1)$). However, in practice λ depends

383   also on group mobility. The whole cross-polarization can now be defined using the

384   following equation (Kolodziejski and Klinowski 2002)

$$I(t) = I_0 e^{\left(-\frac{t}{T_{1\rho}}\right)} \left[1 - \lambda e^{\left(-\frac{t}{T_{df}}\right)} - (1 - \lambda) e^{\left(-\frac{3t}{2T_{df}}\right)} e^{\left(\frac{t^2}{2T_2^2}\right)} \right] \qquad (3)$$

385

386   The model can be described as I-I*-S model. Two of the contact time dependent {^{1}H}

387    $\rightarrow$ ^{29}Si CP MAS NMR intensity data experiments are shown in Figure 6. The solid lines

388   represent the least-squares fits of the data to equation 3. The data plotted as black

389   diamonds represents the same {^{1}H} $\rightarrow$ ^{29}Si CP MAS NMR intensity data as in Figure 5.

390   In contrast, now the least-squares fit using equation 3 describes the experimental data

391   very well.

392   In addition, depolarization experiments can help to estimate the proton spin diffusion

393   time (T_{df}), the spin-spin relaxation time (T_2) and the lambda parameter (λ), because here

394   there is no influence of the proton spin-lattice time in the rotating frame ($T_{1\rho}$). A

395   depolarization experiment is set up like a normal cross-polarization experiment. First

396   magnetization is transferred from the I spin reservoir to the S nuclei. While the S nuclei

397   magnetization is still locked in the transverse plane of the rotating frame, the proton

398   pulse is switched off leading to a dephasing of the I spins. Thus, turning on the proton

399   pulse again causes an inversion of magnetization transfer from the S nuclei to the proton

400   reservoir (Wu et al. 1988). The functional dependence of the signal intensity can be

401   described as

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$$I(t) = I_0 \left[\lambda e^{\left(-\frac{t}{T_{df}} \right)} + (1 - \lambda) e^{\left(-\frac{3t}{2T_{df}} \right)} e^{\left(-\frac{t^2}{2T_2^2} \right)} \right]$$
(4)

403   where t is the depolarization time. It is obvious that the functional behavior is

404   opposite to the CP experiment described in equation 3. In the first ten to hundred

405   microseconds there is a fast decrease in signal intensity due to heteronuclear I^*-S spin-

406   spin relaxation related to T_2. Then there is a slower decrease due to I-I^* spin-spin

407   diffusion related to T_{df}.

408   Figure 7 shows the results of the $\{^1H\} \rightarrow {}^{29}Si$ CP-depolarization NMR experiments.

409   The signal intensity shows exactly the behavior described above. However, for longer

410   depolarization times the intensity decays with a time constant of $T^*_{1\rho} \sim T_{1\rho}(^1H)$. For this

411   case equation 4 can be multiplied by a term $A \exp(-t/ T^*_{1\rho})$, where A is the amplitude

412   (Kolodziejski and Klinowski 2002). The parameters derived from the depolarization

413   experiments can then be applied as fit parameters for the cross-polarization experiments

414   using equation 3. All experimental data extracted from the $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR

415   and CP-depolarization NMR are listed in Table 4. The intensity $I(t)$ of the ${}^{29}Si$ signal for

416   a subsequent contact-time has been determined by regarding the maximum intensity

417   (i.e., signal height) of the Si-Si$_2$Al or the Si-SiAl$_2$ signal (depending on sample

418   composition) or the overall signal area of all Si-nAl signals. This method could be used

419   because in nearly all experiments the separate $Q^3(n Al)$ signals showed all the same

420   time constants. This means that the relative ratio of $Q^3(n Al)$ signal areas does not

421   change with increasing contact- or depolarization time. As an example the time

422   constants for the different $Q^3(n Al)$ NMR signals of one $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR

423   experiment are the same within uncertainty (Table 5) compared to the data of the area /

424   maximum fit used in Table 4.

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425   The spin-spin relaxation times T_2 are longer than for hydrocarbons investigated with

426    $\{^1H\} \rightarrow {}^{13}C$ CP MAS NMR investigations by Kolodziejski and Klinowski (2002) and

427   in the range of 290 – 530 µs (for ^{13}C approx. 10 – 100 µs). This can be attributed to the

428   longer H-Si distance in the phlogopite structure (C-H bond usually 1.1 Å) and a weaker

429   heteronuclear dipolar interaction. Tateyama et al. (1974) reported H-Si distances of

430   3.18 Å, 3.20 Å, and 3.22 Å for a hydroxyl-phlogopite. With increasing hydroxyl content

431   of the phlogopite (y = 1.0 to y = 1.8) T_2 decreases from 530 µs to 300 µs. The increased

432   density of protons leads to stronger heteronuclear dipolar interaction. The spin-diffusion

433   time T_{df} shows no clear correlation with the phlogopite composition. Compared to

434   proton spin diffusion in $\{^1H\} \rightarrow {}^{13}C$ CP experiments (Kolodziejski and Klinowski

435   2002), the phlogopite proton spin diffusion is slow and in the range of tenths of

436   milliseconds (T_{df} in $\{^1H\} \rightarrow {}^{13}C$ CP experiments is around 0.2 – 6 ms). The lambda

437   parameter ranges around $\lambda = 0.66 – 0.75$. λ is dependent on the number of protons n

438   contributing to the polarization ($\lambda = 1/(n + 1)$). The lambda ratio clearly decreases with

439   increasing hydroxyl content of the phlogopite. The proton spin-lattice time in the

440   rotating frame ($T_{1\rho}$) is very large and it is impossible to estimate them from the data.

441   In the same way as described for the $\{^1H\} \rightarrow {}^{29}Si$ CPMAS and CP-depolarization

442   intensity data described above, $\{^{19}F\} \rightarrow {}^{29}Si$ CPMAS and CP-depolarization intensity

443   data have been acquired. Figure 8 shows one of the $\{^{19}F\} \rightarrow {}^{29}Si$ CP-depolarization

444   NMR experiments. The signal intensity shows the same behavior as for the $\{^1H\} \rightarrow {}^{29}Si$

445   CP-depolarization experiment. Similar, for longer depolarization times the intensity

446   decays with a time constant of $T^*_{1\rho} \sim T_{1\rho}(^{19}F)$ (Kolodziejski and Klinowski 2002).

447   Again, the parameters derived from the depolarization experiments can then be applied

448   as fit parameters for the cross-polarization experiments using equation 3. Results of two

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449   of the contact time dependent $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR experiments are shown in

450   Figure 9. The solid lines represent the least-squares fits to equation 3. All experimental

451   data extracted from the $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR and CP-depolarization NMR are

452   listed in Table 6. The intensity $I(t)$ of the ^{29}Si signal for a subsequent contact-time has

453   been determined by regarding the maximum intensity (i.e., signal height) of the Si-Si$_2$Al

454   or the Si-SiAl$_2$ signal (depending on sample composition) or the overall signal area of

455   all Si-nAl signals. This is possible because the relative ratio of Q^3(n Al) signal areas

456   does not change with increasing contact- or depolarization time (similar as for the

457    $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR experiments, see above).

458   Analyzing the data, the spin-spin relaxation times T_2 in the $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS

459   NMR are longer than for the $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR experiments and are in the

460   range of 1 – 17 ms (290 – 530 μs for $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR). This can be

461   attributed to two facts. Firstly, the gyromagnetic ratio of ^{19}F is lower than for ^1H leading

462   to a weaker dipolar interaction. Secondly, the F-Si distance in the phlogopite structure is

463   longer because F substitutes OH. In structures of fluoro-phlogopites reported by Takeda

464   and Morosin (1975) and McCauley et al. (1973) this distance is much longer with 3.53 –

465   3.54 Å compared to H-Si distances of 3.18 Å, 3.20 Å, and 3.22 Å for a hydroxyl-

466   phlogopite reported by Tateyama et al. (1974). T_2 and the spin-diffusion time T_{df} show

467   no clear correlation with the phlogopite composition. T_{df} is very large for phlogopites

468   with high fluorine content but at lower F-content they are comparable to proton spin

469   diffusion times in the $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR experiments and are around 10 – 14

470   ms. The comparison of T_{df} and T_2 for the first two samples ($x_{nom} = 0.0$, $y = 0.5$ and x_{nom}

471    $= 0.3$, $y = 0.5$) in Table 6 compared to the other samples suggest that the Al-content has

472   also a large effect. However, x_{nom} reflects only the Al-content of the sol-gel. Comparing

21

473 the estimated Al-content x_{est} reveals that due to the fluorine content of the gel much less

474 Al is incorporated into the structure (compare x_{est} values in Table 6). Thus, an influence

475 of the Al-content on the CP dynamic parameters cannot be inferred. The lambda

476 parameter ranges around $\lambda = 0.75$. In contrast to the $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR

477 experiments where the proton spin-lattice time in the rotating frame ($T_{1\rho}$) is very large

478 and not possible to estimate, the $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR data shows a clear

479 decrease of intensity with larger contact times (Fig. 9). It ranges around 50 ms for

480 phlogopites at high fluorine contents and increases with decreasing fluorine content of

481 the phlogopite.

482   Summarizing it can be seen that the proton concentration clearly influences T_2 in the

483 $\{^1H\} \rightarrow {}^{29}Si$ CPMAS NMR experiments while there is no similar trend regarding the

484 fluorine concentration in the $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR data. The lambda parameter

485 and the spin diffusion time T_{df} show no functional behavior in both cases. $T_{1\rho}$ is large in

486 the case for ^1H but shows for ^{19}F a clear dependence on the fluorine concentration

487 (lower values at higher fluorine concentration).

488

489 **$\{^1H\} \rightarrow {}^{29}Si$ CPMAS NMR spectra**

490 If we keep in mind that the signal intensities of HO-Mg$_3$ and HO-Mg$_2$Al environments

491 in the ^1H MAS NMR spectra are very often equal or the HO-Mg$_2$Al signal is sometimes

492 higher than the HO-Mg$_3$ signal, the separation into clusters of original phlogopite

493 composition (K(Mg$_3$)[AlSi$_3$O$_{10}$](OH)$_2$) and clusters of 'eastonite' composition

494 (K(Mg$_2$Al)[Al$_2$Si$_2$O$_{10}$](OH)$_2$) is not visible in one-dimensional $\{^1H\} \rightarrow {}^{29}Si$ CPMAS

495 NMR spectra. Magnetization is transferred from both environments (HO-Mg$_3$ and HO-

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496   Mg_2Al) to nearby silicons. Thus, the $\{^1H\} \rightarrow {}^{29}Si$ CPMAS NMR spectrum shows a

497   superposition of the ^{29}Si signals of both phlogopite regions. This can be nicely seen in

498   Figure 10. The top spectrum shows the normal ^{29}Si MAS NMR spectrum for a

499   composition of $x_{nom} = 0.8$ and $y = 1.0$ (sample synthesized at 1073 K). The $\{^1H\} \rightarrow {}^{29}Si$

500   CP MAS NMR spectra shown below the ^{29}Si MAS NMR spectrum have been recorded

501   using contact times of $t = 3$, 5 and 7 ms. Increasing contact time leads to farther

502   magnetization travel for the two spin-systems, and thus ^{29}Si nuclei at larger distances

503   from the hydrogen of the OH group can be reached. The CP MAS and the ^{29}Si MAS

504   NMR spectra look comparable: For the CPMAS NMR spectra, the estimated Al-content

505   x^*_{est} is between 0.38 and 0.41 while x_{est} obtained from the ^{29}Si MAS NMR spectrum is

506   0.37. x^*_{est} was calculated from the $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR signal intensities of the

507    $Q^3(nAl)$ signals similar as the ratio x_{est} from the ^{29}Si MAS NMR spectra using equations

508   1 and 2.

509   Differences are only visible in 2D $\{^1H\} \rightarrow {}^{29}Si$ heteronuclear correlation (HETCOR)

510   CP MAS NMR spectroscopy which is an ideal tool to investigate the relationship

511   between ordering in the tetrahedral and octahedral sheets because it combines

512   information on the local ^1H environment in the octahedral sheet with that on tetrahedral

513   ^{29}Si environments nearby. These experiments were already carried out with the pure

514   hydroxyl phlogopites samples ($y = 2.0$, synthesis temperature $T = 873$ K) from the

515   present investigation in a previous study (Langner et al. 2012). It could be shown that

516   Al-rich Si environments in the tetrahedral sheet are more likely to be found in direct

517   neighborhood of Al-rich proton environments in the octahedral sheets. In contrast, the

518   ^{29}Si with a lower number of Al-atoms as next-nearest-neighbors are more often located

519   next to Al-free OH environments. As a result the structure is separated into clusters of

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520 original phlogopite composition ($K(Mg_3)[AlSi_3O_{10}](OH)_2$) and clusters of 'eastonite'

521 composition ($K(Mg_2Al)[Al_2Si_2O_{10}](OH)_2$) that encompass a whole T-O-T layer

522 package, although Al is presumed to be distributed in the phlogopite structure

523 homogeneously on a macroscopic level (Langner et al. 2012). The cluster size of the

524 mica substructures 'phogopite' and 'eastonite' have been roughly estimated by

525 atomistic calculations given in Langner et al. (2012). The clusters are between 20 - 50 Å

526 in diameter. The size is too small to speak of two phases. However, they are large

527 enough for 2D $\{^1H\} \rightarrow {}^{29}Si$ heteronuclear correlation (HETCOR) CP MAS NMR

528 spectroscopy to show the effect of Al-rich ('eastonite') and Al-poor ('phlogopite')

529 containing regions. The results can also be transferred on the results of the $\{^{19}F\} \rightarrow {}^{29}Si$

530 CP MAS NMR spectra discussed below.

531 In addition, $\{^1H\} \rightarrow {}^{27}Al$ 2D CP MAS (HETCOR) spectroscopy has already been

532 carried out in Fechtelkord et al. (2003b) on samples synthesized at 1073 K with high Al

533 contents ($x_{nom} = 0.8$) and F contents ($y = 0.5, 1.0$). The spectra show site connectivities

534 between the tetrahedral ^{27}Al signal and the two ^1H NMR signals of HO-Mg_3 and HO-

535 Mg_2Al environments. The ^{27}Al octahedral signal is connected to the ^1H signal of HO-

536 Mg_2Al environments only.

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539 $\{^{19}F\} \rightarrow {}^{29}Si$ CPMAS NMR spectra

540   The $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR spectra shown have been recorded using contact times

541   of $t = 3$, 5 and 7 ms. Increasing contact time leads to farther magnetization travel for the

542   two spin-systems, and thus ${}^{29}Si$ nuclei at larger distances from F can be reached. An

543   example of the three 1D $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR spectra of a phlogopite sample of

544   composition $x_{nom} = 0.7$, $y = 1.0$, is displayed in Figure 11. For comparison, the ${}^{29}Si$ MAS

545   NMR spectrum of the same sample [nominal composition K $(Mg_{2.3}Al_{0.7})$ $(Al_{1.7}Si_{2.3}O_{10})$

546   (OH) F] is presented at the top. There is a large discrepancy between the CP MAS and

547   the ${}^{29}Si$ MAS NMR spectra: The Al-content of the octahedral sheet estimated from the

548   CPMAS NMR spectra, x^*_{est}, is always about 0.2 lower than that obtained from the ${}^{29}Si$

549   MAS NMR spectra. x^*_{est} was calculated from the $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR $Q^3(nAl)$

550   signal intensities in the same manner as the ratio x_{est} from the ${}^{29}Si$ MAS NMR spectra

551   using equations 1 and 2.

552   While the $\{^{1}H\} \rightarrow {}^{29}Si$ CP MAS NMR spectra and ${}^{29}Si$ MAS NMR spectra showed

553   very often similar lineshapes for one sample, this seems to be completely different for

554   the $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR spectra. The fact that the relative intensity of the F-

555   Mg_2Al signal is always very low can be used to directly show a relationship between

556   octahedral F environments and tetrahedral Si environments. In 1D $\{^{19}F\} \rightarrow {}^{29}Si$ CP

557   MAS NMR experiments, magnetization is transferred from the ${}^{19}F$ to the ${}^{29}Si$ nucleus,

558   and only those ${}^{29}Si$ nuclei that have ${}^{19}F$ nuclei nearby will contribute to the resulting CP

559   MAS NMR spectrum. If we assume that the amount of F being surrounded by Al can be

560   neglected, these 1D $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR spectra should reflect the local

561   composition and distribution of Si environments in the tetrahedral sheet next to F- and

562   Mg-rich clusters in the octahedral sheet.

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563　　It should be noted that the CPMAS NMR experiments are in principle

564　　non-quantitative. However, as contact time dependent experiments show very long $T_{1\rho}$

565　　times (as discussed below), the intensities depend greatly on the number and distance of

566　　the fluorines near the silicon nuclei. This means that ^{29}Si nuclei close to F- and Mg-rich

567　　octahedral environments have fewer tetrahedral Al atoms as next-nearest-neighbors than

568　　the average over the whole structure. This lower value does not change much for spectra

569　　recorded with different contact times which shows that this is not only true for Si-atoms

570　　directly adjacent to the F-ion but also to some further in the structure. In many cases the

571　　lower Al-content is also visible from a shift of the Si-nAl signal positions to more

572　　shielded values. All this indicates that F is ordered in the Al-poor clusters of the

573　　structure, consistent with the results for F-free compositions in a recent paper showing

574　　the separation into clusters of Al-rich ('eastonite') and Al-poor ('phlogopite') containing

575　　regions (Langner et al. 2012).

576　　In addition, nearly all samples also showed a decrease in FWHM of the $\{^{19}F\} \rightarrow {}^{29}Si$

577　　CP MAS NMR signals compared to ^{29}Si MAS NMR signals. A comparison is given in

578　　Table 7 containing the ^{29}Si MAS NMR data and Table 8 containing the $\{^{19}F\} \rightarrow {}^{29}Si$ CP

579　　MAS NMR data at a contact time of $t = 10$ ms. The ^{29}Si MAS NMR spectra contain

580　　information on all the Si environments throughout the structure. Si-O-Al bond length

581　　and bond angles slightly differ for Si-atoms in both types of clusters leading to broad

582　　^{29}Si MAS NMR signals. Signal widths in Table 7 are usually around 2.8 ppm. In

583　　contrast, in $\{^{19}F\} \rightarrow {}^{29}Si$ CPMAS NMR experiments only Si-atoms in one type of

584　　cluster are considered. These environments are more homogeneous resulting in a smaller

585　　signal width of approximately 2.1 ppm as shown in Table 8. High-power-decoupled

586　　$\{^1H/^{19}F\}$ ^{29}Si MAS NMR experiments were carried out to check the dependence of ^{29}Si

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587 signal linewidths on ^{1}H/^{19}F – ^{29}Si heteronuclear dipolar interaction. There was no

588 indication of broadening due to heteronuclear dipolar interaction (same lineshape with

589 and without decoupling).

590   Two-dimensional $\{^{19}F\} \rightarrow {}^{27}$Al 2D CPMAS (HETCOR) spectroscopy of fluorine-

591 and aluminum-rich phlogopites has been carried out in a previous study by Fechtelkord

592 et al. (2003b) on samples synthesized at 1073 K with high Al contents ($x_{nom} = 0.8$) and F

593 contents ($y = 0.5$, 1.0). It is not surprising that in comparison to the $\{^1H\} \rightarrow {}^{27}$Al 2D

594 CPMAS (HETCOR) spectrum there are no similar contributions from the Mg_3F and

595 Mg_2AlF sites to neighboring tetrahedral and octahedral Al sites in phlogopite. The

596 fluorine in the Mg_3F sites is only able to transfer magnetization to tetrahedral Al sites.

597 Magnetization transfer from fluorine to octahedral aluminum sites is not observed due

598 to the low abundance of Mg_2AlF sites.

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711 **FIGURE CAPTIONS**
712

713 **Figure 1** Comparison of ^{29}Si MAS NMR spectra of phlogopites with nominal

714 composition K $(Mg_{3-x}Al_x)$ $(Al_{1+x}Si_{3-x}O_{10})$ $(OH)_y$ F_{2-y} with different Al- and F-contents.

715 The Al-content of the tetrahedral sheets calculated from the relative signal intensities,

716 x_{est} (calculated from eq. 1 and 2), for each spectrum is given in the figure.

717 **Figure 2** Plot of the experimentally derived (additional) Al-content of tetrahedral sheets

718 x_{est} (calculated from eq. 1 and 2) of the phlogopites against the Al-content of the initial

719 gel mixture x_{nom}. The black line indicates a complete reaction of the starting material to

720 phlogopite ($x_{est} = x_{nom}$).

721 **Figure 3** Comparison of ^{1}H MAS NMR spectra of OH- and Al-rich phlogopites with

722 nominal composition K $(Mg_{3-x}Al_x)$ $(Al_{1+x}Si_{3-x}O_{10})$ $(OH)_y$ F_{2-y}. The ratio I[H-OMg$_2$Al]/

723 (I[H-OMg$_2$Al] + I[H-OMg$_3$]) for each spectrum is given in the figure, abbreviated as

724 'Al/(Mg+Al)'. The water resonance at 4.7 ppm is cut off for a better visibility of the two

725 main signals.

726 **Figure 4** Comparison of ^{19}F MAS NMR spectra of OH- and Al-rich phlogopites with

727 nominal composition K $(Mg_{3-x}Al_x)$ $(Al_{1+x}Si_{3-x}O_{10})$ $(OH)_y$ F_{2-y}. The ratio

728 I[F-Mg$_2$Al]/(I[F-Mg$_2$Al] + I[F-Mg$_3$]) is given below the spectra, abbreviated as

729 'Al/(Mg+Al)'. Spinning sidebands are marked by asterisks.

730 **Figure 5** Experimental CP magnetization data derived from contact-time dependent

731 $\{^1H\} \rightarrow ^{29}Si$ CP-MAS NMR experiments for phlogopites with nominal composition

732 K $(Mg_{3-x}Al_x)$ $(Al_{1+x}Si_{3-x}O_{10})$ $(OH)_y$ F_{2-y} with $x_{nom} = 0.5$, $y = 1.0$ (*black diamonds*). The

733 solid lines represent the least-squares fits using the 'classical I-S model' (Kolodziejski

734 and Klinowski 2002).

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735   **Figure 6** Experimental CP magnetization data derived from contact-time dependent

736    $\{^1H\} \rightarrow ^{29}Si$ CP-MAS NMR experiments for phlogopites with nominal composition

737    $K (Mg_{3-x}Al_x) (Al_{1+x}Si_{3-x}O_{10}) (OH)_y F_{2-y}$ with $x_{nom} = 0.8$, $y = 1.8$ (*open circles*) and $x_{nom} =$

738   0.5, $y = 1.0$ (*black diamonds*). The solid lines represent the least-squares fits of the data

739   to equation 3.

740   **Figure 7** Experimental depolarization data derived from $\{^1H\} \rightarrow ^{29}Si$ CP-depolarization

741   NMR experiments for phlogopites with nominal composition

742    $K (Mg_{3-x}Al_x) (Al_{1+x}Si_{3-x}O_{10}) (OH)_y F_{2-y}$ with $x_{nom} = 0.8$ and $y = 1.8$. The solid line

743   represents the least-squares fit of the data to equation 4.

744   **Figure 8** Experimental depolarization data derived from $\{^{19}F\} \rightarrow ^{29}Si$ CP-

745   depolarization NMR experiments for phlogopites with nominal composition

746    $K (Mg_{3-x}Al_x) (Al_{1+x}Si_{3-x}O_{10}) (OH)_y F_{2-y}$ with $x_{nom} = 0.3$ and $y = 0.5$. The solid line

747   represents the least-squares fit of the data to equation 4.

748   **Figure 9** Experimental CP magnetization data derived from contact-time dependent

749    $\{^{19}F\} \rightarrow ^{29}Si$ CP-MAS NMR experiments for phlogopites with nominal composition

750    $K (Mg_{3-x}Al_x) (Al_{1+x}Si_{3-x}O_{10}) (OH)_y F_{2-y}$ with $x_{nom} = 0.0$, $y = 0.5$ (*open circles*) and $x_{nom} =$

751   0.3, $y = 0.5$ (*black diamonds*). The solid lines represent the least-squares fits of the data

752   to equation 3.

753   **Figure 10** 1D $\{^1H\} \rightarrow ^{29}Si$ CPMAS NMR spectra of the sample with nominal

754   composition $x_{nom} = 0.8$, $y = 1.0$ (synthesized at 1073 K), recorded at contact times of $t =$

755   3, 5, and 7 ms, respectively. For comparison, the ^{29}Si MAS NMR spectrum of the same

756   sample is also shown (top). x^*_{est} was calculated from the $\{^1H\} \rightarrow ^{29}Si$ CP MAS NMR

757   signal intensities of the $Q^3(nAl)$ signals similar as the ratio x_{est} from the ^{29}Si MAS NMR

758   spectra using equations 1 and 2.

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759   **Figure 11** 1D $\{^{19}F\} \rightarrow {}^{29}Si$ CPMAS NMR spectra of the sample with nominal

760   composition $x_{nom} = 0.7$, $y = 1.0$ (synthesized at 873 K), recorded at contact times of $t =$

761   3, 5, and 7 ms, respectively. For comparison, the ^{29}Si MAS NMR spectrum of the same

762   sample is also shown (top). x^{*}_{est} was calculated from the $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR

763   signal intensities of the $Q^3(nAl)$ signals similar as the ratio x_{est} from the ^{29}Si MAS NMR

764   spectra using equations 1 and 2.

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Revision #3

766   Table 1. ^{29}Si MAS NMR data of Al-rich phlogopites with nominal composition
767   K (Mg$_{3-x}$Al$_x$) (Al$_{1+x}$Si$_{3-x}$O$_{10}$) (OH)$_y$ (F)$_{2-y}$. The table contains chemical shifts (δ), linewidths (FWHM) and areas
768   of the signals. x_{est} was calculated from equation 1 and 2. Total signal areas with less than 100% are due to
769   non-phlogopite ^{29}Si NMR signals from K-deficient clay signal areas not listed here.

x_{nom}	y	x_{est}	Q^3(3Al) δ [ppm]	FWHM [ppm]	Area [%]	Q^3(2Al) δ [ppm]	FWHM [ppm]	Area [%]	Q^3(1Al) δ [ppm]	FWHM [ppm]	Area [%]	Q^3(0Al) δ [ppm]	FWHM [ppm]	Area [%]
0.1	1.2	0.04				-84.1	2.8	25	-88.2	2.6	56	-92.3	2.8	19
0.2	1.2	0.11				-84.7	2.9	31	-88.5	2.4	53	-92.5	2.9	16
0.3	1.2	0.17	-80.4	2.8	5	-83.9	2.6	29	-87.7	2.7	44	-91.4	2.8	16
0.4	1.2	0.14	-80.0	2.7	3	-83.9	2.8	29	-87.8	2.7	45	-91.3	2.8	17
0.5	1.2	0.24	-79.9	2.8	9	-83.8	2.6	30	-87.7	2.7	42	-91.3	2.8	15
0.6	1.2	0.23	-79.9	2.8	8	-83.8	2.7	30	-87.7	2.7	40	-91.3	2.8	15
0.7	1.2	0.35	-80.1	2.6	10	-83.9	2.6	40	-87.6	2.6	43	-91.3	2.1	7
0.1	1.6	0.05	-79.6	2.8	3	-83.5	2.7	20	-87.4	2.6	46	-91.0	2.8	20
0.2	1.6	0.03				-83.6	2.6	24	-87.6	2.7	52	-91.2	2.8	20
0.3	1.6	0.08				-84.0	2.6	27	87.8	2.7	51	-91.4	2.8	17
0.4	1.6	0.10	-80.0	2.8	4	-83.7	2.7	25	-87.4	2.7	40	-90.2	2.8	21
0.5	1.6	0.35	-79.6	2.9	13	-83.3	2.6	38	-87.0	2.7	38	-90.7	2.8	11
0.6	1.6	0.28	-79.8	2.8	8	-83.5	2.3	35	-87.3	2.5	47	-91.2	2.8	10
0.8	1.6	0.36	-80.1	2.8	12	-83.7	2.7	40	-87.4	2.7	38	-91.3	2.8	10
1.0	1.6	0.63	-80.1	1.9	39	-83.7	2.4	34	-87.2	2.8	21	-91.1	2.9	6
1.2	1.6	0.66	-80.0	1.8	40	-83.6	2.6	38	-87.3	2.8	16	-90.7	2.9	6
0.2	1.8	0.14	-79.0	2.8	3	-82.8	2.6	27	-86.8	2.8	50	-90.3	2.8	14
0.3	1.8	0.17	-79.7	2.7	4	-83.2	2.4	33	-86.8	2.6	44	-90.3	2.8	17
0.5	1.8	0.26	-80.3	2.8	8	-83.5	2.6	35	-87.3	2.7	44	-90.5	2.8	13
0.6	1.8	0.46	-79.5	2.3	17	-83.0	2.4	43	-86.6	2.4	35	-90.2	2.1	5
1.2	1.8	0.71	-79.4	1.7	50	-83.0	2.4	30	-86.7	2.8	14	-90.2	2.9	6
1.6	1.8	0.67	-79.4	1.8	43	-82.8	2.5	36	-86.1	2.8	14	-89.6	2.9	7
0.4	2.0	0.25	-80.1	2.8	7	-83.7	2.6	34	-87.6	2.7	43	-90.8	2.8	13
0.5	2.0	0.29	-79.8	2.9	10	-83.1	2.7	34	-87.1	2.9	37	-90.9	2.9	14
0.8	2.0	0.67	-79.4	2.3	42	-82.8	2.5	36	-86.3	2.7	17	-89.8	2.4	5
1.0	2.0	0.83	-79.4	1.4	61	-82.6	2.5	31	-86.2	2.0	8			
1.2	2.0	0.87	-79.6	1.3	72	-82.8	2.6	20	-86.7	2.6	8			
1.6	2.0	0.65	-79.4	2.0	36	-82.9	2.6	42	-86.6	2.7	19	-90.0	2.9	3

Note: Error ranges are as follows: x_{est} ± 0.10, δ ± 0.3 ppm, FWHM ± 0.4 ppm, area ± 3%

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Revision #3

772 Table 2. ^1H MAS NMR data of Al-rich phlogopites with nominal composition
773 $K (Mg_{3-x}Al_x) (Al_{1+x}Si_{3-x}O_{10}) (OH)_y (F)_{2-y.}$ The table contains chemical shifts (δ), linewidths (FWHM) and areas
774 of the signals. x_{est} was calculated from equation 1 and 2.

x_{nom}	y	x_{est}	Mg₃OH (OH_Mg)			Mg₂AlOH (OH_Al)			$\dfrac{OH_{Al}}{\left(OH_{Al}+OH_{Mg}\right)}$
			δ [ppm]	FWHM [ppm]	Area [%]	δ [ppm]	FWHM [ppm]	Area [%]	
0.8	1.6	0.36	0.6	1.0	46	1.8	1.3	54	0.54
1.0	1.6	0.63	1.5	1.0	34	2.8	1.4	66	0.66
1.2	1.6	0.66	1.1	1.2	29	2.4	1.2	71	0.71
1.2	1.8	0.71	1.0	1.0	26	2.3	1.2	74	0.74
1.6	1.8	0.67	1.0	0.9	20	2.3	1.3	80	0.80
0.8	2.0	0.67	1.5	1.8	35	3.0	1.8	65	0.65
1.0	2.0	0.83	1.9	1.1	22	3.2	1.1	78	0.78
1.2	2.0	0.87	1.3	1.2	19	2.5	1.0	81	0.81
1.6	2.0	0.65	1.7	1.1	32	3.0	1.3	68	0.68

Note: Error ranges are as follows: x_{est} ± 0.10, δ ± 0.1 ppm, FWHM ± 0.2 ppm, area ± 3%

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Revision #3

777 Table 3. ^{19}F MAS NMR data of Al-rich phlogopites with nominal composition
778 $K(Mg_{3-x}Al_x)(Al_{1+x}Si_{3-x}O_{10})(OH)_y(F)_{2-y}$. The table contains chemical shifts (δ), linewidths (FWHM) and areas
779 of the signals. x_{est} was calculated related to equation 1 and 2.

x_{nom}	y	x_{est}	Mg₃F (F_Mg)			Mg₂AlF (F_Mg)			$\dfrac{F_{Al}}{(F_{Al}+F_{Mg})}$	K₃AlF₆*0.5 H₂O			Other phases[*]
			δ [ppm]	FWHM [ppm]	Area [%]	δ [ppm]	FWHM [ppm]	Area [%]		δ [ppm]	FWHM [ppm]	Area [%]	Area [%]
0.8	1.6	0.36	-173.3	3.5	88	-149.3	3.7	12	0.12				
1.0	1.6	0.63	-172.9	3.6	81	-149.1	3.5	16	0.16				3
1.2	1.6	0.66	-172.2	3.4	28	-147.8	1.7	5	0.16				9
			-175.5	3.0	50	-150.0	2.8	8					
1.2	1.8	0.71	-173.3	3.5	81	-149.3	4.0	10	0.11	-157.8	2.5	9	
1.6	1.8	0.67	-171.0	3.5	50	-147.4	3.2	19	0.28	-157.4	2.5	31	

Note: Error ranges are as follows: x_{est} ± 0.10. δ ± 0.5 ppm. FWHM ± 0.3 ppm. area ± 3%; [*]unidentified

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784   Table 4. $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR data of Al-rich phlogopites with nominal composition

785    $K\,(Mg_{3-x}Al_x)\,(Al_{1+x}Si_{3-x}O_{10})\,(OH)_y\,(F)_{2-y}$ and synthesis temperature T according to the I-I*-S Model. The spin-

786   spin relaxation time (T_2), the ^1H spin-diffusion time (T_{df}), the ^1H spin-relaxation time in the rotating frame

787   ($T_{1\rho}$) and the lambda factor (λ) were calculated from cross-polarization experiments according to equation 3

788   and depolarization experiments according to equation 4.

x_{nom}	y	x_{est}	T [K]	T_2 [µs]	T_{df} [ms]	$T_{1\rho}$ [s]	λ
0.4	1.0	0.25	1073	526 ± 30	10 ± 1	n.a.	0.78 ± 0.05
0.5	1.0	0.29	1073	517 ± 50	12 ± 1	n.a.	0.76 ± 0.02
0.6	1.0	0.29	1073	495 ± 50	15 ± 1	n.a.	0.71 ± 0.02
0.7	1.0	0.37	1073	382 ± 50	9 ± 2	n.a.	0.83 ± 0.02
0.8	1.0	0.37	1073	457 ± 60	14 ± 1	n.a.	0.79 ± 0.01
0.4	1.5	0.25	1073	372 ± 12	17 ± 1	n.a.	0.66 ± 0.01
0.6	1.5	0.35	1073	307 ± 8	12 ± 1	n.a.	0.68 ± 0.01
0.8	1.8	0.50	1073	292 ± 12	12 ± 1	n.a.	0.67 ± 0.01
0.5	1.6	0.35	873	378 ± 15	8 ± 2	n.a.	0.68 ± 0.01
0.7	1.8	0.46	873	350 ± 6	11 ± 1	n.a.	0.70 ± 0.01

Note: n.a.: Value cannot be estimated

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791   Table 5. $\{^1H\} \rightarrow {}^{29}Si$ CP MAS NMR data of Al-rich phlogopites with nominal composition
792     $K\,(Mg_{3-x}Al_x)\,(Al_{1+x}Si_{3-x}O_{10})\,(OH)_y\,(F)_{2-y}$ with x = 0.5 and y = 1.6 according to the I-I*-S Model for the different
793   ^{29}Si NMR signals. The spin-spin relaxation time (T_2), the ^1H spin-diffusion time (T_{df}), the ^1H spin-relaxation
794   time in the rotating frame ($T_{1\rho}$) and the lambda factor (λ) were calculated from cross-polarization
795   experiments according to equation 3 and depolarization experiments according to equation 4.

^{29}Si Signal	T_2 [µs]	T_{df} [ms]	$T_{1\rho}$ [s]	λ
$Q^3(3Al)$	323 ± 12	11 ± 1	n.a.	0.68 ± 0.02
$Q^3(2Al)$	312 ± 12	11 ± 1	n.a.	0.67 ± 0.02
$Q^3(1Al)$	352 ± 11	12 ± 1	n.a.	0.75 ± 0.05
$Q^3(0Al)$	301 ± 25	12 ± 4	n.a.	0.57 ± 0.08

Note: n.a.: Value cannot be estimated

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798   Table 6. $\{^{19}F\} \rightarrow {}^{29}Si$ CP MAS NMR data of Al-rich phlogopites with nominal composition

799   $K\,(Mg_{3-x}Al_x)\,(Al_{1+x}Si_{3-x}O_{10})\,(OH)_y\,(F)_{2-y.}$ according to the I-I*-S Model. The spin-spin relaxation time (T_2), the

800   ^1H spin-diffusion time (T_{df}), the ^1H spin-relaxation time in the rotating frame ($T_{1\rho}$) and the lambda factor (λ)

801   were calculated from cross-polarization experiments according to equation 3 and depolarization

802   experiments according to equation 4.

x_{nom}	y	x_{est}	T [K]	T_2 [ms]	T_{df} [ms]	$T_{1\rho}$ [ms]	λ
0.1	0.2	0.01	873	17 ± 1	222 ± 12	56 ± 1	0.76 ± 0.01
0.0	0.5	0.01	873	22 ± 2	162 ± 12	47 ± 2	0.76 ± 0.01
0.3	0.5	0.08	873	2.2 ± 0.2	9 ± 1	1780 ± 110	0.71 ± 0.03
0.6	0.5	0.33	873	12 ± 5	10 ± 1	385 ± 78	0.63 ± 0.01
0.8	0.8	0.41	873	1.4 ± 0.5	10 ± 2	n.a.	0.86 ± 0.01
0.7	1.0	0.51	873	1.2 ± 0.5	14 ± 1	n.a.	0.81 ± 0.02

Note: n.a.: Value cannot be estimated

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Revision #3

806 Table 7. ^{29}Si MAS NMR data of Al-rich phlogopites with nominal composition
807 K (Mg$_{3-x}$Al$_x$) (Al$_{1+x}$Si$_{3-x}$O$_{10}$) (OH)$_y$ (F)$_{2-y}$. The table contains chemical shifts (δ), linewidths (FWHM) and areas
808 of the signals. x_{est} was calculated related to equation 1 and 2. Total signal areas with less than 100% are
809 due to non-phlogopite ^{29}Si NMR signals from K-deficient clay signal areas not listed here.

x_{nom}	y	x_{est}	Q^3(3Al)			Q^3(2Al)			Q^3(1Al)			Q^3(0Al)		
			δ [ppm]	FWHM [ppm]	Area [%]	δ [ppm]	FWHM [ppm]	Area [%]	δ [ppm]	FWHM [ppm]	Area [%]	δ [ppm]	FWHM [ppm]	Area [%]
0.1	0.2	0.01				-85.1	2.5	22	-88.9	2.4	58	-93.1	2.8	20
0.0	0.5	0.01				-84.7	2.2	20	-88.4	1.9	61	-92.4	2.0	19
0.3	0.5	0.08				-84.2	2.7	27	-88.2	2.7	54	91.8	2.8	16
0.6	0.5	0.33	-80.7	2.8	10	-83.5	2.6	39	-86.9	2.7	41	-90.6	2.8	10
0.8	0.8	0.41	-80.2	2.8	13	-83.8	2.6	44	-87.4	2.5	36	-91.0	2.8	7
0.7	1.0	0.51	-79.9	2.6	23	-83.6	2.5	43	-87.2	2.5	27	90.7	2.8	7

Note: Error ranges are as follows: x_{est} ± 0.10, δ ± 0.3 ppm, FWHM ± 0.4 ppm, area ± 3%

810

811 Table 8. $\{^{19}$F$\} \rightarrow {}^{29}$Si CP MAS NMR data of Al-rich phlogopites with nominal composition
812 K (Mg$_{3-x}$Al$_x$) (Al$_{1+x}$Si$_{3-x}$O$_{10}$) (OH)$_y$ (F)$_{2-y}$ at a contact time of t = 10 ms. The table contains chemical shifts (δ),
813 linewidths (FWHM) and areas of the signals. x^*_{est} was calculated from the $\{^{19}$F$\} \rightarrow {}^{29}$Si CP MAS NMR signal
814 intensities of the Q^3(n Al) signals related to equation 1 and 2.

x_{nom}	y	x^*_{est}	Q^3(3Al)			Q^3(2Al)			Q^3(1Al)			Q^3(0Al)		
			δ [ppm]	FWHM [ppm]	Area [%]	δ [ppm]	FWHM [ppm]	Area [%]	δ [ppm]	FWHM [ppm]	Area [%]	δ [ppm]	FWHM [ppm]	Area [%]
0.1	0.2	-0.08				-84.6	1.9	17	-88.2	2.3	56	-92.2	3.0	27
0.0	0.5	-0.02				-85.4	2.2	19	-88.9	2.0	59	-92.7	2.2	22
0.3	0.5	0.06				-84.6	2.1	21	-88.3	2.4	66	-92.2	2.2	13
0.6	0.5	0.34	-80.7	1.5	2	-84.3	2.9	49	-87.9	2.5	47	-91.9	1.0	2
0.8	0.8	0.38	-80.7	2.0	5	-84.6	2.6	51	-88.0	2.3	41	-92.4	0.9	3
0.7	1.0	0.38	-80.8	2.0	7	-84.6	3.1	51	-88.1	2.4	35	-92.1	1.9	7

Note: Error ranges are as follows: x_{est} ± 0.10, δ ± 0.3 ppm, FWHM ± 0.4 ppm, area ± 3%

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Revision #3

819   Figure 1
820
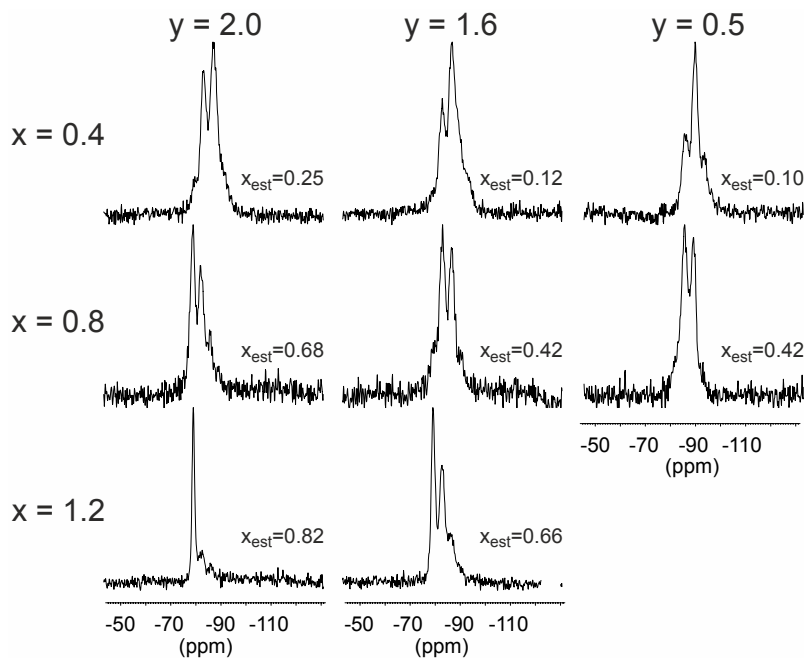
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Revision #3

825   Figure 2
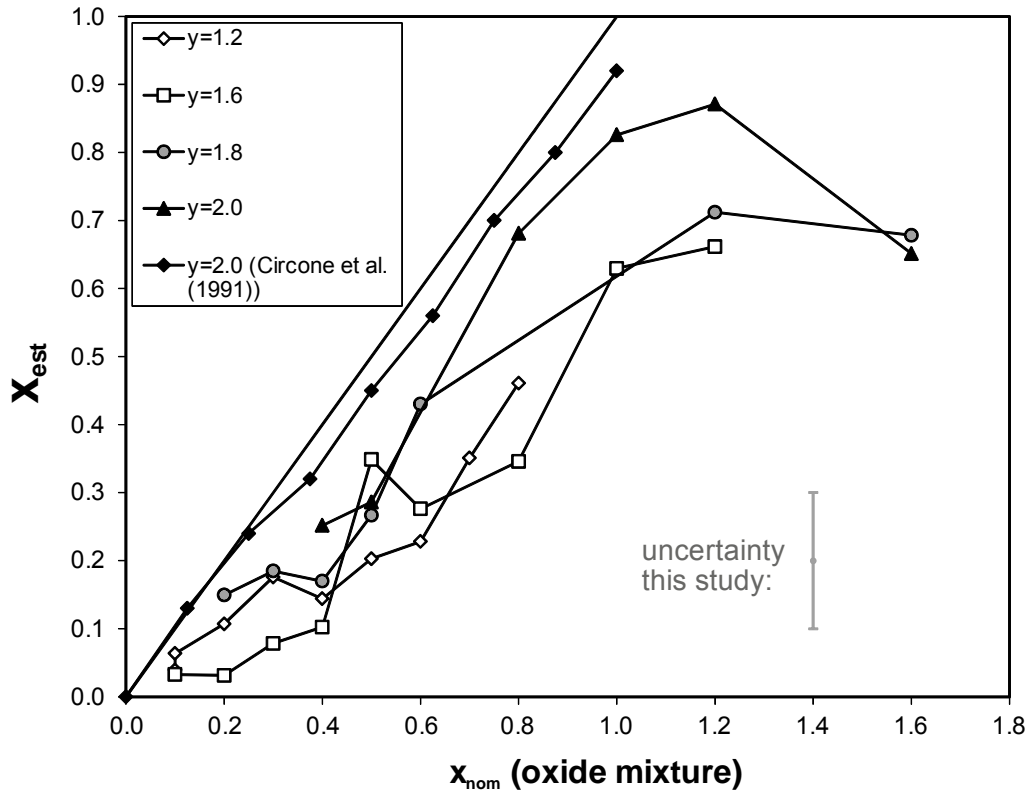
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Revision #3
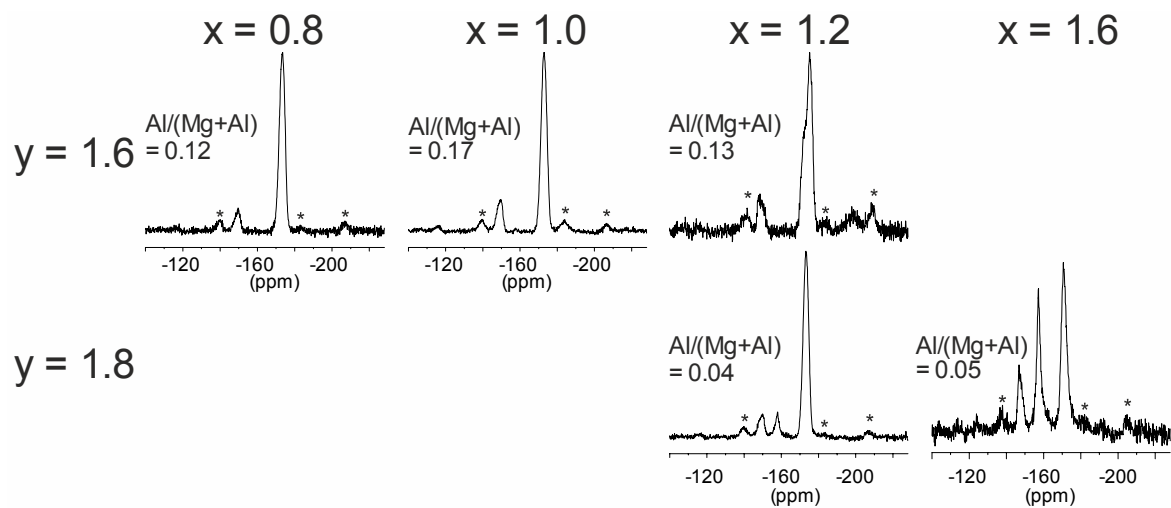
830   Figure 3

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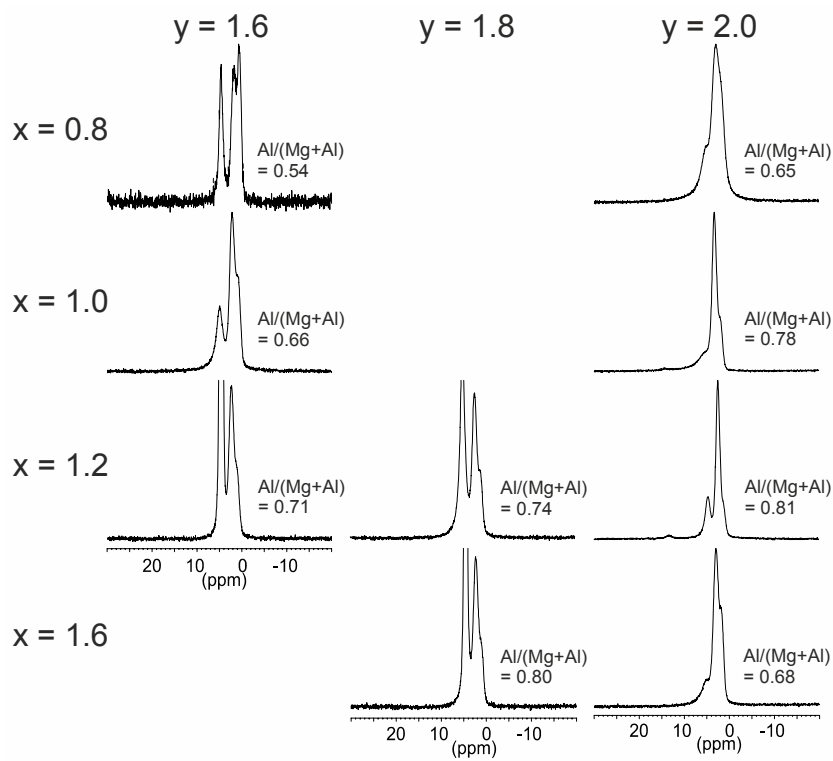
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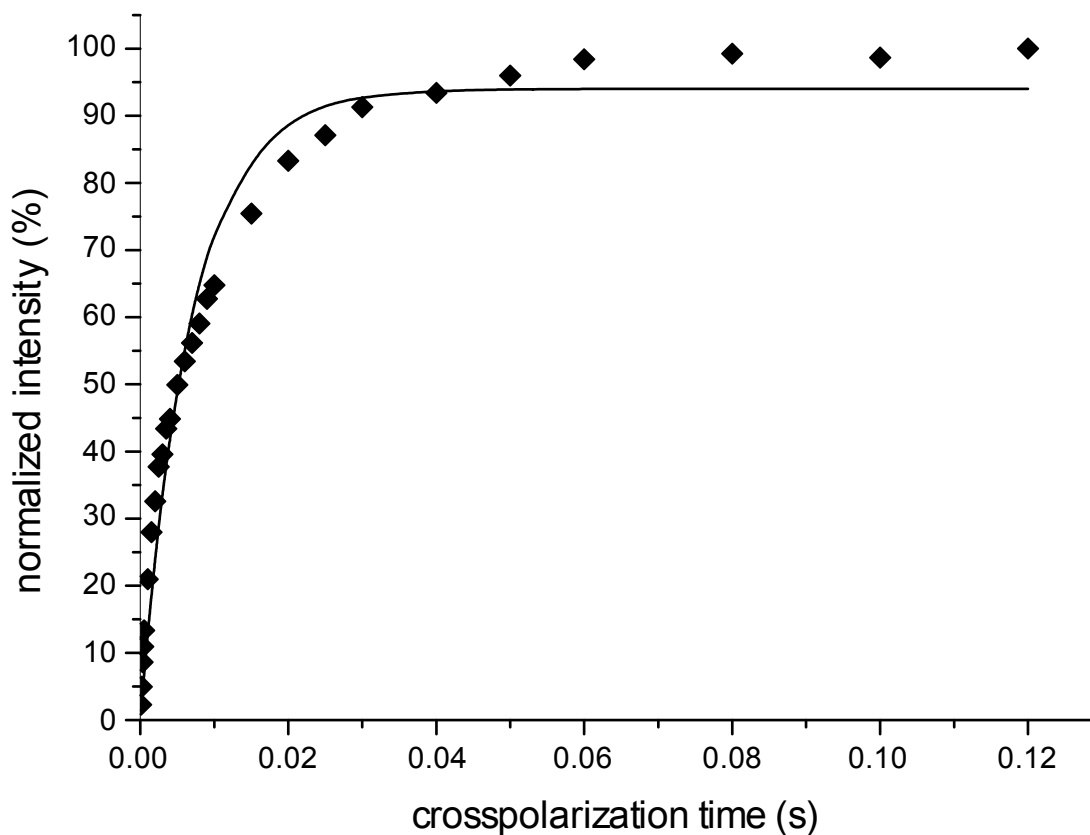
834   Figure 4
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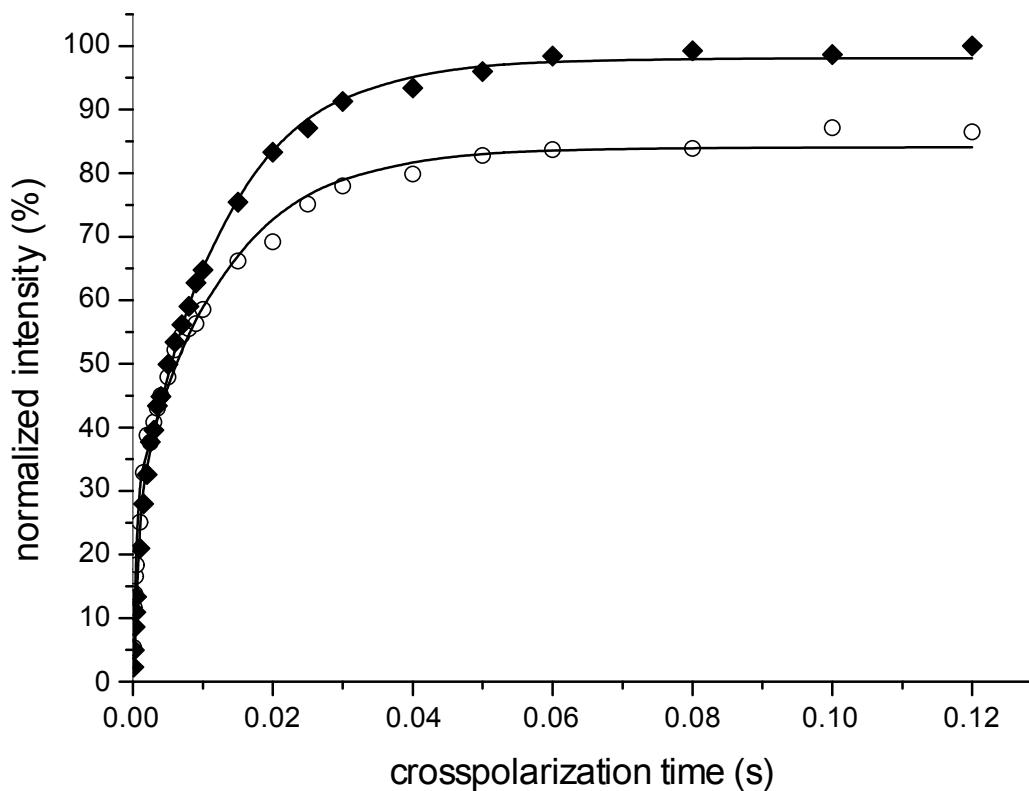
840   Figure 5
841

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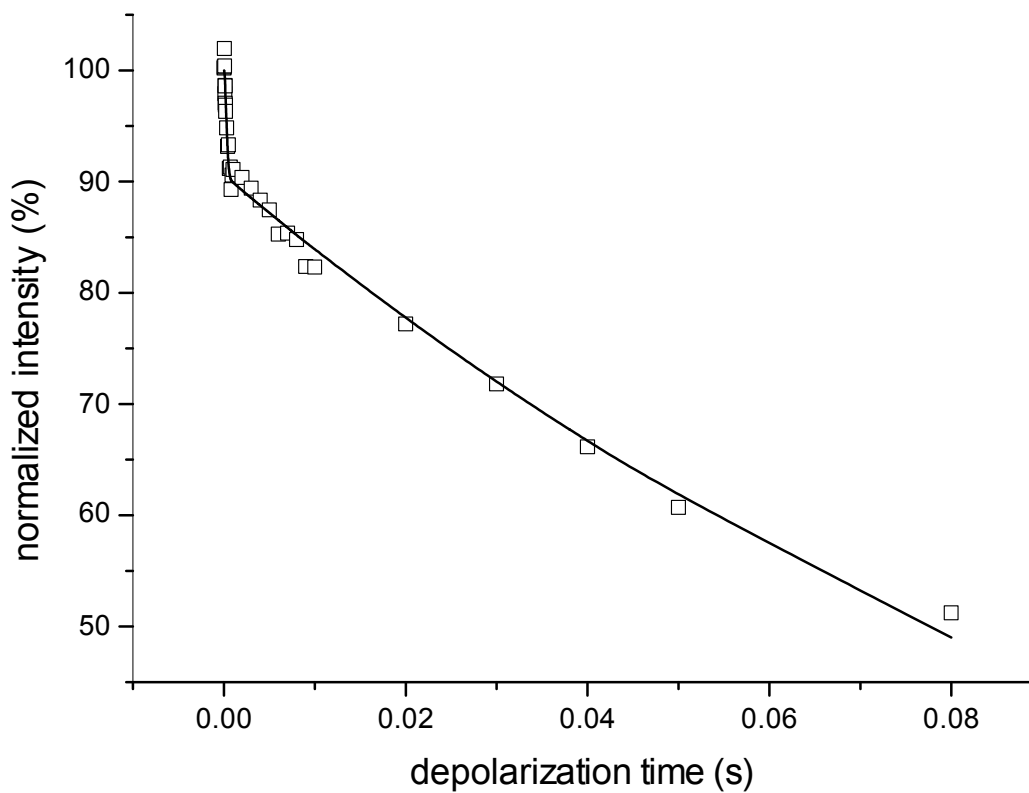843
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Revision #3

845   Figure 6
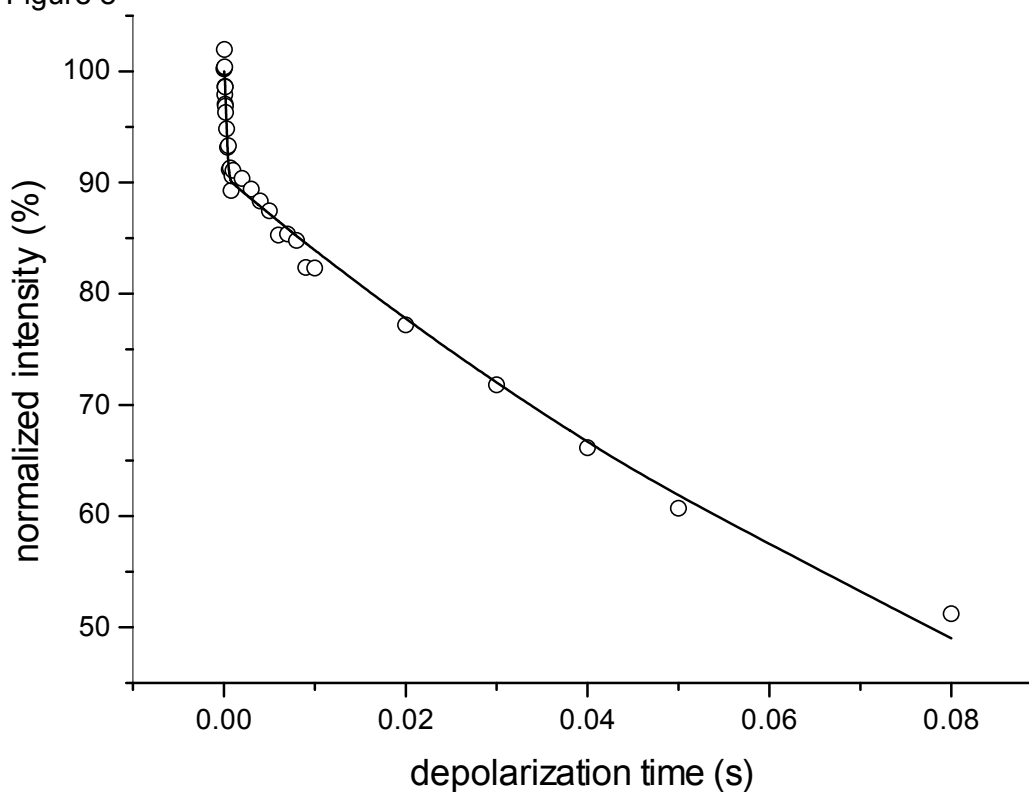846

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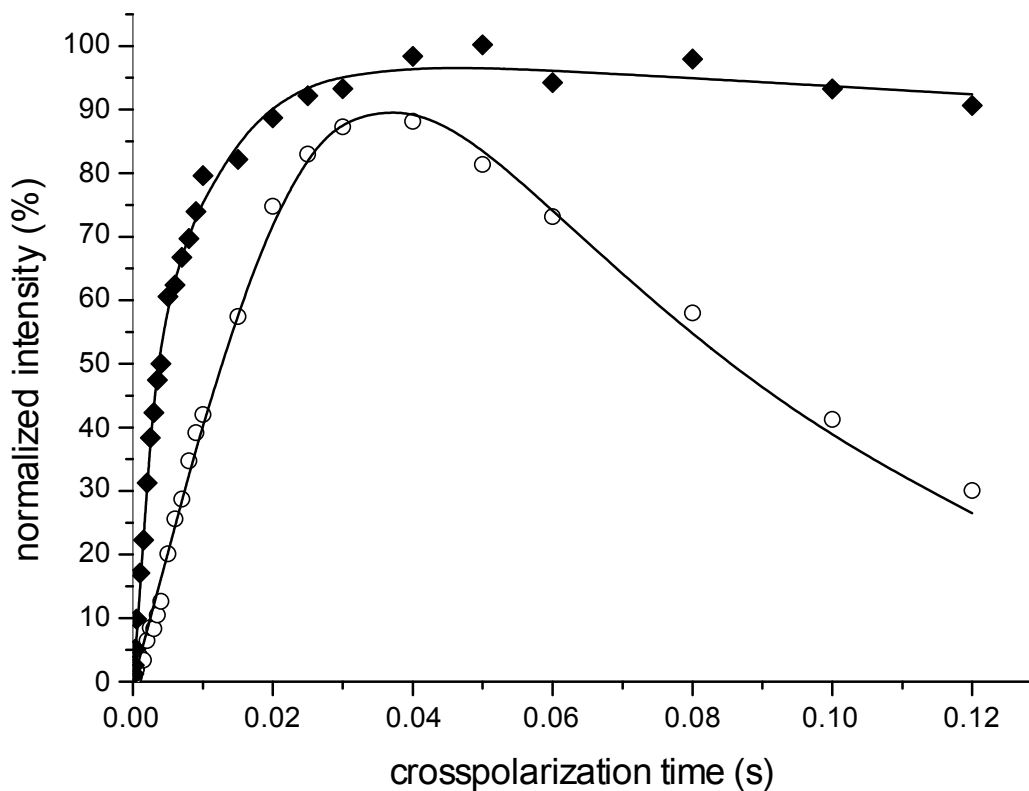Revision #3

849   Figure 7
850

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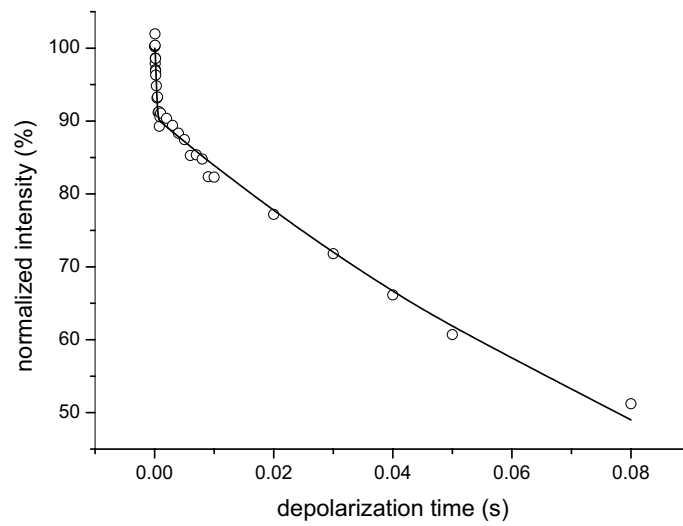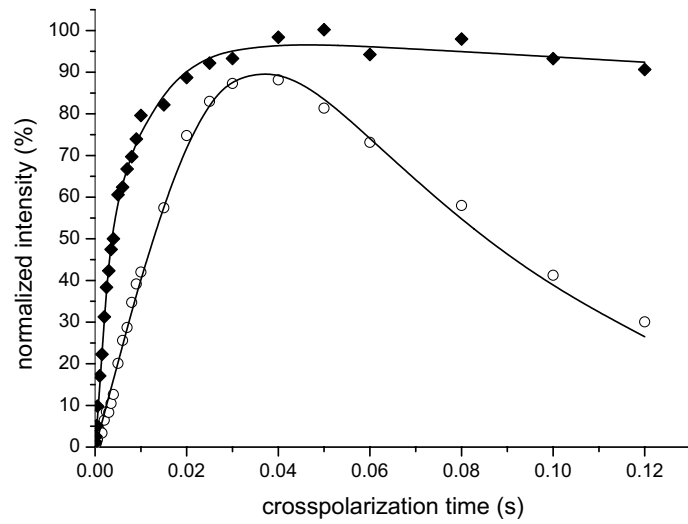
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Revision #3

853   Figure 8

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Revision #3

856   Figure 9
857

858
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Revision #3

860   Figure 10
861

^{29}Si MAS

x_{est}= 0.37

t = 3 ms
CPMAS

x^{*}_{est}= 0.41

t = 5 ms
CPMAS

x^{*}_{est}= 0.38

t = 7 ms
CPMAS x^{*}_{est}= 0.38

-70   -80   -90 -100

862   (ppm)
863
864

52
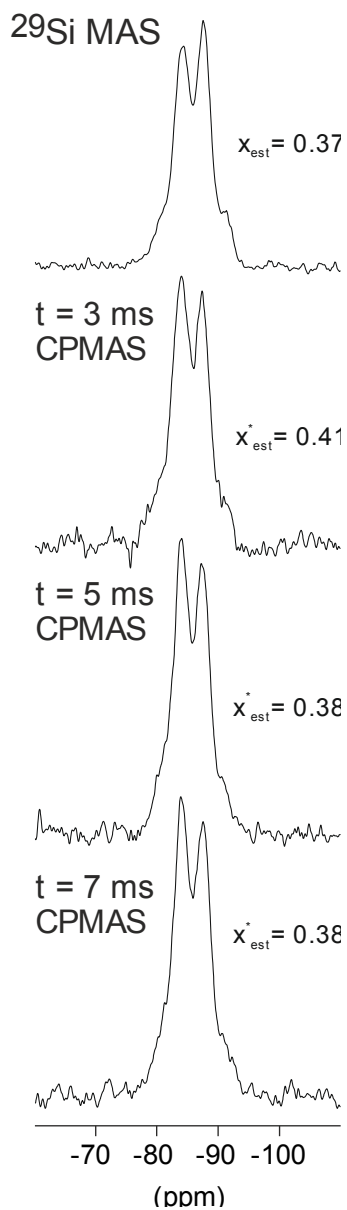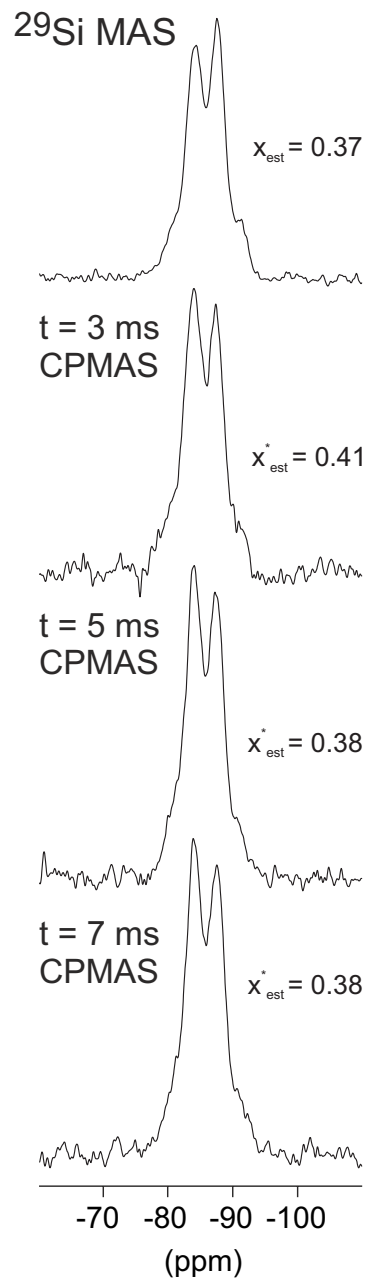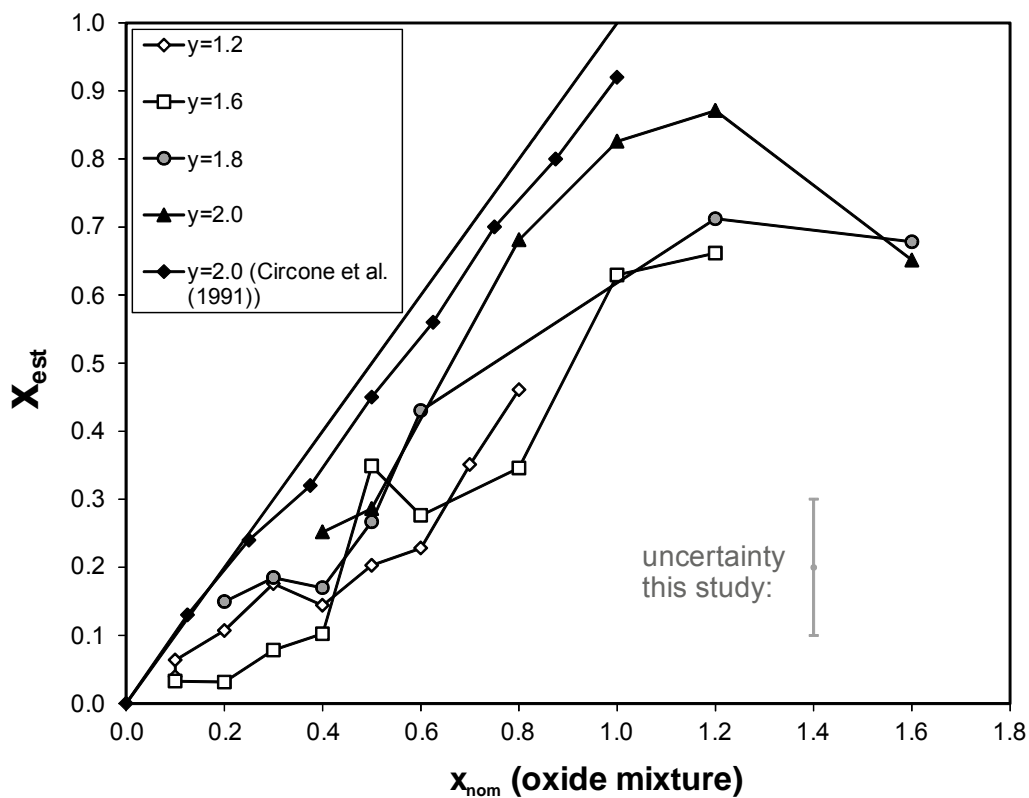
Revision #3

865   Figure 11
866
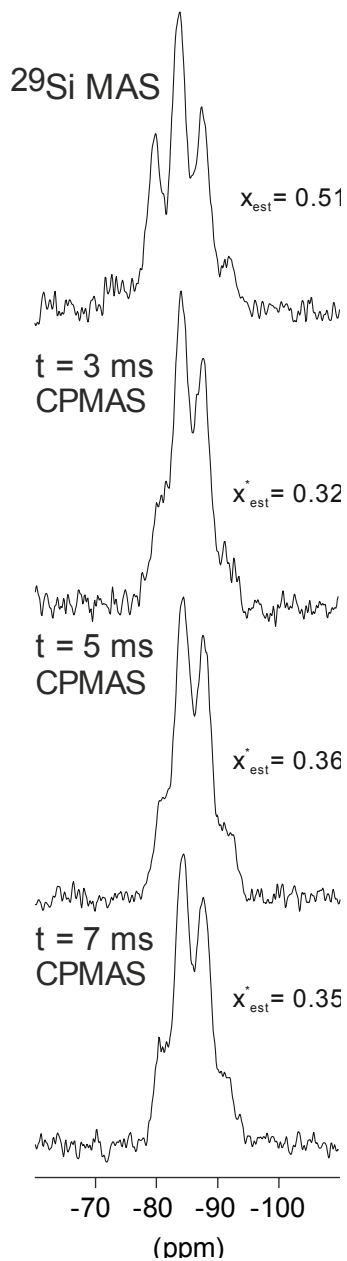
867   (ppm)
868
869
870

Revision #3

825   Figure 2

826
827
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