Revision 1

Probing transformation path from aluminum (oxy)hydroxides (boehmite, bayerite, and gibbsite) to metastable alumina: A view from high-resolution ^{27}Al MAS NMR

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28 **Abstract**

29 Detailed knowledge of the structural evolution of diverse aluminum

30 (oxy)hydroxides with varying temperatures up to ~300 °C provides insights into the

31 dehydration processes involving transitions among *metastable* phases in Earth's surface and

32 crust. Here, we report the high-resolution solid-state ^{27}Al NMR spectra for three different

33 types of aluminum (oxy)hydroxides (i.e., boehmite, bayerite, and gibbsite) with varying

34 annealing temperatures up to 300 °C, revealing the effect of distinct precursor minerals on

35 the stability of metastable alumina. ^{27}Al MAS NMR results allow us to obtain the

36 quantitative fractions and NMR parameters for each phase during transformation. The

37 results demonstrate that each aluminum (oxy)hydroxide phase follows the unique

38 transformation path to metastable alumina. The ^{27}Al MAS and 3QMAS NMR spectra of

39 boehmite show that a minor but observable [4]Al signal (~2%) is detected at ~50 °C, and the

40 [4]Al fraction gradually increases up to 300 °C (~16%), indicating that the phase

41 transformation from boehmite to γ-/η-Al$_2$O$_3$ occurs at a temperature as low as ~50 °C,

42 significantly lower than earlier estimations based on XRD. Together with the [4]Al fraction,

43 the [5]Al fraction increases from < 1% at 50 °C to ~2.3% at 300 °C, whereas the NMR results

44 of bayerite and gibbsite do not show the presence of [5]Al. In addition, the ^{27}Al 3QMAS

45 NMR spectra resolved the [6]Al site in boehmite and that in γ-/η-Al$_2$O$_3$, which could not be

46 uniquely determined from 1D NMR spectra. The population of bayerite abruptly decreases

47 from 100% (at 150 °C), through ~47% (at 200 °C), to 0% (at 250 °C), indicating that the phase

48 transition from bayerite to boehmite + γ-/η-Al$_2$O$_3$ occurs within a narrow temperature

49 range. As for gibbsite, while [4]Al is not observed in the spectra up to 200 °C, the [4]Al

50 fraction of ~2% is observed in the spectra for gibbsite annealed at 250 °C, and the [4]Al

51 fraction increases rapidly to ~15% as the annealing temperature increases to 300 °C,

52 suggesting that the phase transformation into γ-/η-Al$_2$O$_3$ occurs at ~250 °C. The results

53 confirm that the phase transformation paths (gradual *vs.* dramatic) depend on the type of

54 precursor minerals. Particularly, the threshold temperature at which the onset of the phase

55 transformation from boehmite to metastable alumina (~50 °C) is lower than those from

56 other precursor minerals (>150 °C). Furthermore, the phase transformation from boehmite

57 to γ-/η-Al$_2$O$_3$ occurs gradually within broad temperature ranges from ~50 °C. This is due to

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58 their configurational disorder as evidenced by the presence of [5]Al. The observed structural

59 evolution in aluminum (oxy)hydroxides in the low-temperature range facilitates the

60 understanding of the nature of phase transformation and dehydration of oxides and

61 hydroxides on the Earth's surface environments.

62

63 **Keywords:** Metastable (transition) alumina, aluminum (oxy)hydroxide, solid-state NMR, γ-

64 /η-Al$_2$O$_3$, phase transformation, extent of disorder

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Introduction

68   The aluminum (oxy)hydroxides and aluminum oxides (i.e., alumina) exist in various

69 stable and metastable polymorphs in the Earth's surface environments. Particularly,

70 bauxite, which is the primary ore source of aluminum, consists of diverse types of

71 aluminum (oxy)hydroxides, such as boehmite and gibbsite (e.g., Kloprogge et al., 2006;

72 Radusinović et al., 2017 and references therein). In addition, the various forms of metastable

73 aluminum (oxy)hydroxides [e.g., pseudoboehmite and amorphous Al(OH)$_3$] are found in

74 the precipitates in acid mine drainage (e.g., Jones et al., 2011; Kim, 2015). The dehydration

75 (and dehydroxylation) of aluminum (oxy)hydroxides (i.e., gibbsite and boehmite) in natural

76 bauxite occurs at 200-300 °C (e.g., Kloprogge et al., 2002), which corresponds to the

77 temperature range of diagenesis. Although it is difficult to identify the metastable Al$_2$O$_3$ in

78 natural bauxite due to their poor crystallinity, earlier studies have reported the presence of

79 η-Al$_2$O$_3$ and hydrated-Al$_2$O$_3$ [i.e., akdalaite (5Al$_2$O$_3$·H$_2$O)] in natural bauxite (e.g., Tilley and

80 Eggleton, 1996; Hwang et al., 2006).

81   Aluminum oxides also exist in diverse metastable polymorphs, called transition

82 alumina (such as γ-, δ-, θ-, κ-, χ-, and η-Al$_2$O$_3$), and stable α-Al$_2$O$_3$. Metastable aluminas

83 have diverse industrial applications such as catalyst supports, absorbents, and protective

84 barriers to prevent corrosion on alumina-forming alloys, because of their high surface area

85 and the high catalytic activity at their surfaces (e.g., Che and Bennett, 1989; Cai et al., 2003

86 and references therein). Extensive experimental and theoretical studies have revealed the

87 structures and catalytic properties of metastable aluminas (e.g., John et al., 1983; Krokidis et

88   al., 2001; Sohlberg et al., 2001; Cai et al., 2002; Paglia et al., 2003; Alphonse and Courty, 2005;

89   Paglia et al., 2006; Kwak et al., 2008; Boumaza et al., 2009; Kim and Lee, 2013b). Metastable

90   aluminas can be obtained by the heat treatments of various aluminum (oxy)hydroxides

91   precursors, such as boehmite (γ-AlOOH), bayerite [α-Al(OH)$_3$], and gibbsite [γ-Al(OH)$_3$].

92   Figure 1 shows the crystal structures for three different types of aluminum (oxy)hydroxides

93   and γ-Al$_2$O$_3$. The crystallographic information of aluminum (oxy)hydroxide precursors (i.e.,

94   boehmite, bayerite, and gibbsite) and metastable alumina (i.e., γ- and η-Al$_2$O$_3$) are shown in

95   Table 1 (Hill, 1981; Balan et al., 2006; Balan et al., 2008).

96   The phase transformation paths from aluminum (oxy)hydroxides to stable α-Al$_2$O$_3$

97   via metastable aluminas have been extensively explored (e.g., Levin and Brandon, 1998;

98   Digne et al., 2002; Chandran et al., 2019 and references therein). The transformation

99   temperatures are also affected by various factors such as particle size (IngramJones et al.,

100 1996; Tsukada et al., 1999; Bokhimi et al., 2007; Kim and Lee, 2013b), morphology (Lee et al.,

101 2015; Karouia et al., 2016), and synthesis conditions (Kim et al., 2005; Chen et al., 2018).

102 Briefly, the annealing of boehmite (γ-AlOOH) produces the series of metastable alumina of

103 γ- (~300-500 °C), δ- (~700-800 °C), and θ-Al$_2$O$_3$ (900-1000 °C), and then stable α-Al$_2$O$_3$ (1000-

104 1100 °C) (e.g., Levin and Brandon, 1998; Chagas et al., 2014). Bayerite [α-Al(OH)$_3$]

105 transforms into α-Al$_2$O$_3$ via η- (200-300 °C) and θ-Al$_2$O$_3$ (600-800 °C), or via boehmite

106 (~150 °C), γ- (300-450 °C), δ- (~700-800 °C), and θ-Al$_2$O$_3$ (900-1000 °C) (e.g., Pecharroman et

107 al., 1999; Digne et al., 2002). The transformation to boehmite from bayerite is reported to

108 occur above 150 °C with a fast heating rate (above 2 °C/min) (e.g., Maruthiprasad et al.,

109 1988; Kim et al., 2005). As for gibbsite [γ-Al(OH)$_3$], the transformation sequence follows two

110 paths depending on the particle size and water contents (e.g., Rouquerol et al., 1975;

111 Mercury et al., 2006). Coarse gibbsite (i.e., > ~10 um) with excess water content generally

112 transforms to boehmite at ~200 ºC (IngramJones et al., 1996; Hill et al., 2007; Chen et al.,

113 2018). The annealing of fine gibbsite (~0.5 um) under a dry condition follows the sequence

114 of χ- (150-300 °C), κ- (650-750 °C), and α-Al$_2$O$_3$ (~1000 °C) (Brindley and Choe, 1961;

115 IngramJones et al., 1996). The phase transformation occurs over a broad temperature range

116 rather than at a well-defined single temperature due to the pronounced metastability (see

117 Levin and Brandon, 1998; Kim and Lee, 2013b; Chandran et al., 2019 and references therein).

118 Furthermore, the metastability results in the coexistence of two or more phases at the same

119 temperature.

120 Diverse experimental techniques such as differential thermal analysis (DTA),

121 infrared (IR) spectroscopy, X-ray diffraction (XRD), and solid-state nuclear magnetic

122 resonance (NMR) have observed phase transformation from aluminum (oxy)hydroxides

123 into metastable aluminas (e.g., Bastow et al., 1994; Tsukada et al., 1999; Alphonse and

124 Courty, 2005; Karouia et al., 2016; Chen et al., 2018; Chandran et al., 2019). In particular, [27]Al

125 NMR has revealed the Al coordination environments in diverse disordered crystalline (i.e.,

126 metastable)/amorphous Al_2O_3 and Al-(oxy)hydroxides (e.g., Lippmaa et al., 1986; Lee et al.,

127 2003; Boissiere et al., 2006; Shen et al., 2007; Lee et al., 2009b; Lee et al., 2010; Sabarinathan et

128 al., 2010; Kim and Lee, 2013b; Cui et al., 2018; Lee and Ryu, 2018; He et al., 2019 and

129 references therein). The Al coordination environments and the NMR parameters, including

130 quadrupolar coupling constant (C_q), isotropic chemical shifts (δ_{iso}), and asymmetry

131 parameter (η) for aluminum (oxy)hydroxides and metastable aluminas from these earlier

132 studies are summarized in Table 2. Whereas a presence of a small amount of metastable

133 alumina is often difficult to identify via XRD, earlier ^{27}Al NMR results enable quantification

134 of the fractions of coexisting phases in the transition aluminas and aluminum

135 (oxy)hydroxides from the simulation of NMR spectra, even though the fraction of the minor

136 phase is very small percentage. (Pecharroman et al., 1999; O'Dell et al., 2007; Kwak et al.,

137 2008; Kim and Lee, 2013b; Chagas et al., 2014; Chandran et al., 2019). We also showed that

138 the particle size and structural disorder in metastable alumina nanoparticles significantly

139 affects their thermal stability above 600 °C (Kim and Lee, 2013b).

140 Despite the geochemical implications and industrial applications, the precise

141 determination of the short-range structure and stability (e.g., temperature conditions) of

142 metastable aluminas in the low-temperature range (< 300 °C) remains challenging.

143 Particularly, the transformation temperatures at which the formation of metastable alumina

144 from diverse aluminum (oxy)hydroxides occurs remain to be determined. A systematic

145 study of the changes in the Al coordination number with varying temperatures below

146 300 °C would therefore provide mechanistic details of the low-temperature surface

147 processes. In this study, we investigated the dehydration paths to metastable alumina from

148 various aluminum (oxy)hydroxide precursors (i.e., boehmite, bayerite, and gibbsite) in the

149 low-temperature range up to 300 ºC using high-resolution ^{27}Al MAS and 3QMAS NMR. We

150 explored the effect of aluminum (oxy)hydroxide precursors (i.e., boehmite, bayerite, and

151 gibbsite) on the stability of metastable alumina below 300 ºC. Based on our spectroscopic

152 results in the low-temperature range, we discuss the importance of the structural findings

153 in understanding the geological (dehydration) processes involving metastable phase

154 transformation on the Earth's surface environments.

155

Materials and methods

157 **Sample preparation.** Boehmite (γ-AlOOH) and bayerite [α-Al(OH)$_3$] were synthesized by

158 hydrolysis of aluminum tri-*sec*-butoxide (ASB, Sigma Aldrich, product no. 2269-22-9). The

159 type of precursor synthesized depends on the amount of water used for hydrolysis of

160 ASB (e.g., Serna et al., 1977; Vaudry et al., 1996). Particularly, boehmite is formed by the

161 hydrolysis of ASB with H$_2$O/Al of ~3, while the hydrolysis with the higher amount of

162 excess water (i.e., H$_2$O/Al > 20) results in the formation of bayerite. Boehmite was

163 prepared by adding 4.52 g of aluminum tri-sec-butoxide to 1.04 mL of distilled water. The

164 mixture was dried for a week at 25 ºC in air. Bayerite was synthesized from a mixture of

165 5.23 g of aluminum tri-*sec*-butoxide with 200 mL of distilled water, which was dried at

166 room temperature. Gibbsite [99.7% of γ-Al(OH)$_3$] was obtained from KC Corporation in

167 Korea and was used as received. The medium value of the particle size distribution (D$_{50}$)

168 for as-received gibbsite is ~50 µm. The samples were annealed at varying temperatures in

169 a vertical tube furnace from 110 ºC to 300 ºC and in a heating mantle up to 50 ºC (2 hours).

170 The annealing temperature of the samples was increased with the rate of 275 ºC/h to the

171 target temperatures (e.g., 110~300 ºC), and further isothermal annealing was performed

172 for 2 hours. Note that the total heating time (i.e., time to elevate temperature + isothermal

173 annealing time) slightly varies with the target temperature from 2.5 h for 110 ºC to 3 h for

174 300 ºC.

175 **X-ray diffraction.** X-ray diffraction patterns for starting materials (i.e., boehmite, bayerite,

176 and gibbsite) and heat-treated samples were collected on Rigaku Miniflex 600

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177   diffractometer using CuKα X-ray (a voltage of 40 kV and a current of 15 mA) with 2θ

178   range of 10-80°, step size of 0.02-0.04°, and a scan rate of 1-3 s per point.

179   **NMR spectroscopy.** ^{27}Al MAS NMR spectra were obtained using a Bruker Avance II 500

180   MHz NMR system (11.7 T, at Seoul National University) with 4 mm triple-resonance

181   MAS probe at Larmor frequency of 130.28 MHz. For a series of boehmite, ^{27}Al NMR

182   spectra were also obtained with a Varian 600 spectrometer (14.1 T, at Korea Basic Science

183   Institute) with 2.5 mm double-resonance probe at Larmor frequency of 156.34 MHz.

184   Sample spinning speeds of 15 kHz (11.7 T) and 20 kHz (14.1 T) were used. A single-pulse

185   sequence with ~ 0.2 μs (~15° tip angle for central transition in solids) and delay time of 1 s

186   were used. The baseline of the collected 1D NMR spectra was fitted by a fourth-order

187   polynomial function using Topspin 3.5 software, and then, was subtracted from the

188   obtained spectra for flattening the baseline around central transition peaks (~200 ppm to

189   ~-200 ppm). The phase of each spectrum was carefully adjusted to optimize the baseline

190   of the spectra. The simulation of ^{27}Al MAS NMR spectra was performed with the Dmfit

191   program (Massiot et al., 2002). ^{27}Al 3QMAS NMR spectra were collected on the Varian

192   400 MHz (9.4 T) spectrometer with Doty Scientific double-resonance MAS probe and 4

193   mm thick-wall zirconia rotor. The fast amplitude modulation-based on shifted-echo pulse

194   sequences comprising two hard pulses (with 3 μs and 0.7 μs) and, a soft pulse (with 15 μs)

195   were used. An echo-delay of approximately 0.5 ms (half-integer multiple of the rotor

196   period) were used with a phase table of 96 cycles, designed to select full echo. The pulse

197   lengths used in the current sequence are carefully optimized to ensure maximum

198   intensity. The radio-frequency (*rf*) field strengths for hard pulses for ^{27}Al 3QMAS NMR

199   are ~125 kHz. Approximately 120-200 FIDs (with the 192 number of scans) were collected

200   to construct the 2D spectra. To achieve the current signal-to-noise ratio, ~16 hours of

201   collection time were required for each spectra. 3QMAS NMR spectra were processed with

202   a shear transformation, with the isotropic dimension frequencies scaled as described

203   previously (e.g., Baltisberger et al., 1996; Lee, 2011; Kim and Lee, 2014 and references

204   therein). The recycle delay of 1 s and spinning speed of 15 kHz were used. All spectra

205   were referenced to AlCl$_3$ (1M) solution.

206

Results and discussion

Transformation from boehmite to γ-/η-Al_2O_3

209 **XRD results.** Figure 2A shows the XRD patterns of boehmite with varying temperatures

210 up to 300 °C. The XRD pattern at 25 °C shows the broad diffraction peaks of boehmite,

211 consistent with previous XRD studies (e.g., MacKenzie et al., 2000; Krokidis et al., 2001;

212 Boumaza et al., 2009 and references therein). The diffraction patterns do not change much

213 with annealing temperature up to 250 °C, suggesting that the transformation from

214 boehmite to metastable Al_2O_3 at the range of 25-250 °C is not prevalent. In contrast, the

215 pattern of boehmite annealed at 300 °C revealed the (400) and (440) peaks of metastable

216 Al_2O_3 increased, indicating the presence of metastable Al_2O_3 (i.e., γ- and/or η-Al_2O_3).

217 Note that the XRD patterns of γ-Al_2O_3 and η-Al_2O_3 are *almost* identical (Lippens

218 and De Boer, 1964; Zhou and Snyder, 1991). As shown in Table 1, both γ- and η-Al_2O_3

219 structures are described as defect spinel structures with space group of $Fd\bar{3}m$ (e.g., Levin

220 and Brandon, 1998). The only difference stems from the variations in the distribution of

221 vacancy in the cation sites: the vacancy in ideal γ-Al_2O_3 is located in the tetrahedral sites,

222 while that in η-Al_2O_3 appears to favor octahedral sites (e.g., Lippens and De Boer, 1964).

223 As γ- and η-Al_2O_3 are not well-distinguished (e.g., Zhou and Snyder, 1991), we refer to

224 the metastable alumina as γ-/η-Al_2O_3. The width of the diffraction patterns of boehmite

225 at 25 °C is broader than those of bayerite and gibbsite, indicating the low crystallinity

226 and/or a more pronounced structural disorder in boehmite (see below).

227 **^{27}Al NMR results.** Figures 2B and 2C show the ^{27}Al MAS NMR spectra (11.7 T and 14.1 T)

228 for synthesized boehmite with varying annealing temperatures up to 300 °C. At 25 °C (as-

229 synthesized boehmite), the spectrum predominantly shows [6]Al at ~10 ppm, consistent

230 with previous NMR studies (Bastow et al., 1994; Isobe et al., 2003). Though minor, ~1% of

231 [4]Al peak at ~68 ppm is observed at 25 °C. As the [4]Al peak is not due to the rotor

232 background (e.g., Lee et al., 2010; Lee et al., 2016). This may be partly due to the presence of

233 aluminum (oxy)hydroxide complex with [4]Al, such as Al_{13} [i.e., $AlO_4Al_{12}(OH)_{24}(H_2O)^{7+}_{12}$]

234 (e.g., Phillips et al., 2000a; Kim, 2015). In addition, while the boehmite in the current study

235 was not ground, the earlier studies have reported that the grinding of boehmite can result

236 in the presence of [4,5]Al in boehmite (e.g., Chen et al., 1992; MacKenzie et al., 2000).

237 Furthermore, the possible presence of a minor amount of γ-/η-Al_2O_3 at ambient

238 temperature may not be fully discarded.

239 As the annealing temperature increases, the [4]Al peak intensity (at ~70 ppm)

240 gradually increases. The [4]Al peak width also increases with increasing annealing

241 temperature. Particularly, the peak width of [4]Al increases from ~16 ppm (for boehmite

242 annealed at 50 °C) to ~22 ppm (for boehmite annealed at 300 °C) at 11.7 T, and that

243 increases from ~14 ppm (at 50 °C) to ~20 ppm (at 300 °C) at 14.1 T (see Figure 3). The

244 narrower peak widths of Al sites at 14.1 T (than those at 11.7 T) is because the magnitude of

245 quadrupolar interaction decreases with increasing magnetic fields (e.g., Kohn et al., 1998;

246 Stebbins et al., 2000 and references therein). The spectra at both fields reveal a small but

247 noticeable presence of [5]Al (at ~35 ppm), and the fraction of [5]Al apparently increases with

248 increasing annealing temperature. These results indicate that the phase transformation from

249 boehmite to γ-/η-Al_2O_3 occurs at a temperature as low as ~50 °C. The presence of small

250 amounts of γ-/η-Al_2O_3 below 300 °C, which was observed in high-resolution NMR spectra,

251 is not revealed in the XRD patterns. Note that, while ideal γ- and η-Al_2O_3 structures have

252 different [4]Al:[6]Al ratios, it is difficult to distinguish γ- and η-Al_2O_3 in the NMR spectra and

253 these phases often coexist (Lippens and De Boer, 1964; Damodaran et al., 2002; Digne et al.,

254 2002; Chandran et al., 2019).

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256 **Transformation from bayerite to boehmite + γ-/η-Al_2O_3**

257 **XRD results.** Figure 4A shows the XRD patterns for bayerite with varying annealing

258 temperatures up to 300 °C. The width of the main diffraction peaks [i.e., (002) peak] for

259 bayerite at 25 °C (~0.2°) is significantly narrower than that for boehmite at 25 °C (~5°),

260 indicating that the crystallinity of bayerite is higher than that of boehmite. As shown in

261 Figure 4A, there are no significant changes in the XRD patterns with increasing

262 temperature for bayerite up to 200 °C. However, for the bayerite annealed at 250 °C, the

263 diffraction patterns of bayerite abruptly disappear. Instead, patterns of both boehmite

264 and metastable alumina are observed. The XRD results confirm that the bayerite

265 transformed into boehmite and metastable Al_2O_3 (i.e., γ-/η-Al_2O_3) above ~250 °C,

266 consistent with previous studies (Zhou and Snyder, 1991; Digne et al., 2002).

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267 **27Al NMR results.** Figures 4B-D present the ^{27}Al MAS NMR spectra at 11.7 T of bayerite

268 with varying annealing temperatures up to 300 °C, showing the evolution of Al sites due

269 to the phase transformation of bayerite to boehmite + metastable γ-/η-Al_2O_3. For the

270 spectra of bayerite at 25 °C, the asymmetric shape of [6]Al peak (with peak maximum at

271 ~11.4 ppm) is observed. The [6]Al peak shape with a shoulder at ~8 ppm may be due to

272 two crystallographic inequivalent [6]Al sites, consistent with the previous NMR study

273 (Bastow et al., 1994). The previously reported NMR parameters for bayerite are shown in

274 Table 2 (Damodaran et al., 2002). As shown in Figure 4B, only [6]Al peak is observed in

275 the spectra for annealed bayerite up to 150 °C. A noticeable fraction of [4]Al sites is

276 observed in the spectra for bayerite annealed at 200 °C, and the fraction of [4]Al increases

277 with increasing temperature from 200 °C to 300 °C. Though the difference is minor, the

278 [6]Al peak width increases with increasing temperature from ~7 ppm (at 150 °C) to ~8

279 ppm (at 200 °C), suggesting the increase in the fraction of disordered phase (i.e,

280 metastable alumina) with increasing temperature. In addition, the peak shape evolves

281 with the long tails extending lower frequency due to larger extent of distribution of C_q

282 above 200 °C. These results indicate that the phase transformation from bayerite to γ-/η-

283 Al_2O_3 occurs at ~200 °C. We also note that the presence of γ-/η-Al_2O_3 is not observed in

284 the XRD pattern at 200 °C (Figure 4A). The [5]Al sites are not observed in the spectra of

285 the bayerite series, even at 300 °C (Figure 4C), in contrast to the results of the boehmite

286 series. Furthermore, the peak widths of [4]Al and [6]Al of the spectra of the phases formed

287 from bayerite at 300 °C appears to be wider than those formed from the boehmite

288 precursor at 300 °C (Figure 2B), suggesting a larger fraction of metastable alumina in the

289 former (see below for the quantification of phases).

290

291 **Transformation from gibbsite to boehmite + γ-/η-Al_2O_3**

292 **XRD results.** In the XRD patterns of the gibbsite series (Figure 5A), it is observed that the

293 phase transformation from gibbsite to boehmite with increasing temperature occurs from

294 ~200 °C. The intensity of the XRD pattern for boehmite gradually increases with

295 increasing temperature from 200 °C to 300 °C. The XRD pattern for the gibbsite annealed

296 at 300 °C shows that gibbsite is completely transformed into boehmite. Note that the peak

10

297   width of gibbsite-derived boehmite (at 200 °C) is narrower than that of annealed

298   boehmite formed from sol-gel synthesis at 200 °C, suggesting the higher crystallinity in

299   the former. Though minor, the broad diffraction peaks of metastable-Al_2O_3 (at the 2θ of

300   ~37°, ~43°, and 66°) are observed in the pattern of heat-treated gibbsite at 300 °C.

301   However, for gibbsite annealed at 250 °C, the presence of γ-/η-Al_2O_3 is not confirmed in

302   the current XRD pattern.

303   **^{27}Al NMR results.** Figures 5B-D show the ^{27}Al MAS NMR spectra at 11.7 T for gibbsite

304   with varying annealing temperatures. The spectra at 25 °C show two crystallographically

305   distinct [6]Al sites (Bastow et al., 1994; Hill et al., 2007). See Table 2 for detailed

306   information on the previously reported NMR parameters for two different [6]Al sites.

307   Above 200 °C, the spectra show subtle and gradual changes in the peak shape of [6]Al,

308   suggesting the phase transformation to boehmite. At 250 °C, the [4]Al peak is observed,

309   and the peak intensity of [4]Al increases with increasing temperature (Figure 5D).

310   Although the presence of γ-/η-Al_2O_3 at 250 °C is not observed in the XRD patterns, the

311   presence of [4]Al peak in the NMR spectra at 250 °C confirms the formation of γ-/η-Al_2O_3.

312   This indicates that XRD alone may not reveal the presence of minor amount of structural

313   disordered (or poorly crystalline) metastable Al_2O_3 phases. The [5]Al peak in the heat-

314   treated gibbsite is not evident in the NMR spectra, while the presence of [5]Al is observed

315   in the heat-treated boehmite (see discussion below).

316

317   **^{27}Al 3QMAS NMR results for boehmite with varying temperature**

318   In addition to structural insights from 1D MAS NMR spectra (Figures 2-5), 2D

319   3QMAS NMR spectra for the samples allow us to trace the detailed changes in the

320   populations of phases involving transformation. Figure 6 shows the ^{27}Al 3QMAS NMR

321   spectra for boehmite before and after annealing at 110, 200, and 300 °C for 2 h, providing

322   enhanced resolution among Al sites. By achieving the current signal-to-noise ratio, a minor

323   fraction of [4,5]Al sites can be resolved in the current 2D NMR spectra. Note that the noise

324   overlapping the signal of [n]Al was not observed on the 1% contour lines [see Supplemental

325   Materials 1 (SI-1)]. In addition, the overlap between the signals and spinning sideband was

326   not observed in the current spectra. The [6]Al peak at ~-10 ppm in the isotropic dimension is

327   observed at 25 °C. As the temperature increases from 110 °C to 300 °C, the [5]Al peak at ~-28

328   ppm and [4]Al peak at ~-45 ppm in the isotropic dimension apparently increase (e.g.,

329   Baltisberger et al., 1996; Stebbins et al., 2000; Lee et al., 2009b). The increase in the intensities

330   of [4,5]Al sites indicates that phase transformation of boehmite → γ-/η-Al$_2$O$_3$ occurs

331   gradually within a broad temperature ranges. These results are consistent with those of the

332   ^{27}Al MAS NMR spectra (Figure 3).

333   Figure 7 shows the changes in [6]Al increasing annealing temperature resulting from

334   the variations in the relative fractions between boehmite and γ-/η-Al$_2$O$_3$. The 2D NMR

335   spectra resolved the [6]Al site in boehmite and that in γ-/η-Al$_2$O$_3$, which could not be

336   uniquely determined from 1D NMR spectra. The expected position of [6]Al peak in boehmite

337   and γ-/η-Al$_2$O$_3$ can be estimated from the NMR parameters shown in Table 2 (Kraus et al.,

338   1996; Pecharroman et al., 1999; Perander et al., 2007; Kim and Lee, 2013b) and currently

339   estimated parameters from simulation of ^{27}Al MAS NMR spectra (Table 3). These are

340   marked in the ^{27}Al 3QMAS NMR spectra (Figure 7) where the evolution of the shape of [6]Al

341   peaks with varying annealing temperature are highlighted. These changes confirm that the

342   onset of the phase transformation boehmite → γ-/η-Al$_2$O$_3$ is evident at the temperature

343   lower than the expected (< 300 °C).

344

345   **Quantification of coexisting phases in the heat-treated aluminum (oxy)hydroxides**

346   **Quantification protocols.** Because the unique peak shapes of Al sites in aluminum

347   (oxy)hydroxides and metastable alumina (due to their characteristic NMR parameters)

348   allows us to deconvolute (and simulate) the NMR spectra, the fraction of consisting

349   phases in the heat-treated samples was estimated from the NMR spectra (Figures 8-10).

350   To simulate the NMR spectra for highly-ordered crystalline phases (i.e., bayerite and

351   gibbsite), Q-mas 1/2 model in Dmfit software was used (e.g., Massiot et al., 2002; Lee et

352   al., 2009a; Park and Lee, 2019). In the current study, we simulated the bayerite and

353   gibbsite using well-established values of NMR parameters previously obtained by 2D

354   NMR. While the slight variation stems from the adjustment to match among

355   experimental and simulated spectra, the NMR parameters were well-reproduced within

356   the error range. The spectra for boehmite and metastable alumina were fitted (using

357   DMFIT software) using a Gaussian isotropic model distribution (GIM, case of d = 5 of the

358   more general Czjzek distribution) which assumes a statistical distribution of charges

359   around the observed nuclei (see references Le Caer and Brand, 1998; Neuville et al., 2004;

360   Lee et al., 2009a; Kim and Lee, 2013b for more detailed discussion on GIM and the

361   detailed parameterization to simulate the quadrupolar line shape with disorder and thus

362   the distribution of electronic field gradient tensors) (see SI-2 for details of simulation

363   using Dmfit).

364   In the current study, following protocol has been used to estimate the population

365   of aluminum (oxy)hydroxides and metastable alumina at varying temperature. First, the

366   ^{27}Al NMR spectra were simulated using the NMR parameters reported in the previous

367   studies (Pecharroman et al., 1999; Damodaran et al., 2002; Vyalikh et al., 2010; see Table 2;

368   Kim and Lee, 2013b). Then, these parameters are slightly adjusted to better reproduce the

369   overall spectra. Second, the constraints on the relative ratio between Al sites for each

370   phase were applied: boehmite is composed of a single disordered [6]Al site (Damodaran et

371   al., 2002), and bayerite and gibbsite have two crystallographic inequivalent [6]Al sites with

372   a ratio of 1:1 (Bastow et al., 1994; Damodaran et al., 2002; Vyalikh et al., 2010). For the

373   ideal structure of γ- and η-Al_2O_3, the [4]Al:[6]Al ratios are 25:75 and 38:62, respectively, as

374   shown in Table 1 (John et al., 1983; Zhou and Snyder, 1991). However, the ratio of [4]Al

375   and [6]Al of γ- and η-Al_2O_3 of the defected cubic (spinel) structure varies depending on the

376   distribution of defects on the Al sites (Levin and Brandon, 1998). In addition, it is difficult

377   to obtain pure γ- and/or η-Al_2O_3 phases from precursors (Lippens and De Boer, 1964;

378   Digne et al., 2002). Practically, the earlier NMR studies have shown that the [4]Al and [6]Al

379   fractions in model γ- and η-Al_2O_3 are ~30% and ~70%, respectively (Pecharroman et al.,

380   1999; Kim and Lee, 2013b; Chandran et al., 2019). The reported [4]Al and [6]Al ratios are in

381   between those for ideal structures of γ- (i.e., [4]Al:[6]Al = 25:75) and/or η-Al_2O_3 (i.e.,

382   [4]Al:[6]Al = 38:62). This suggests that γ- and η-Al_2O_3 often coexist. Thus, in the current

383   study, the [4]Al:[6]Al ratios for γ-/η-Al_2O_3 were constrained to be 3:7.

384   With the constraint of the intensity ratio of [4]Al and [6]Al for γ-/η-Al_2O_3, the

385   fractions of precursors and the coexisting γ-/η-Al_2O_3 were estimated (see below). As the

386   presence of [4]Al is exclusively accompanied with the metastable alumina, the fractions of

13

387 metastable alumina were obtained by the sum of [4]Al and the corresponding [6]Al

388 (i.e., $X_{[6]Al}^{\gamma\text{-}/\eta\text{-}Al_2O_3}$ = 7/3 * $X_{[4]Al}$). The remaining [6]Al intensity (e.g., total $X_{[6]Al}$ - 7/3 * $X_{[4]Al}$) is

389 thus attributed to the fraction of aluminum (oxy)hydroxide precursors, because the NMR

390 peak area directly represents the fraction of phase: for example, the boehmite annealed at

391 300 °C contains the 16±3%, 3±3%, and 36±3% of [4]Al, [5]Al, and [6]Al for γ-/η-Al_2O_3,

392 respectively, indicating that there are ~55% of γ-/η-Al_2O_3 and ~45% of boehmite in the

393 sample. The NMR parameters were allowed to vary slightly depending on the annealing

394 temperature. The estimated NMR parameters and the fractions for Al sites of each phase

395 at varying annealing temperature were shown in Tables 3-5. Note that the fraction of [n]Al

396 site for each phase shown in Tables 3-5 was obtained by calculating the ratio of the area

397 under the [n]Al for the specific phase to the total area in the ^{27}Al MAS NMR spectra. The

398 current NMR spectra were also simulated by considering the intensity of spinning

399 sideband stemming from the satellite transition (see SI-3 for details). Taking into

400 consideration the minor difference in the estimated fractions of each phase at given

401 temperature between simulation results with considering and without considering the

402 spinning sidebands (~1.5%), the contribution of satellite transition to quantification of the

403 relative fraction between Al sites is rather minor.

404 **Phase transformation from boehmite precursor.** Figures 8 and 9 show the simulated ^{27}Al

405 MAS NMR spectra at 11.7 T and 14.1 T using identical NMR parameters. Despite the

406 overlap, the [6]Al peak for γ-/η-Al_2O_3 and that from boehmite can be partly distinguished.

407 This is because of the higher C_q for [6]Al of γ-/η-Al_2O_3 (~4.8 MHz) than that of boehmite

408 (~2.7 MHz). Note that reported C_q values for [6]Al of boehmite varies from 1.8 MHz to 2.8

409 MHz (Damodaran et al., 2002; Chandran et al., 2019). The δ_{iso} of boehmite in the current

410 study (~10.8 ppm) is somewhat different from that reported previously between the

411 previous study (~12.6 ppm) (Damodaran et al., 2002). This because the NMR parameters

412 in the current study were obtained by simulation of 1D NMR spectra using Czjzek model.

413 In contrast, those in the previous study were obtained from center of gravity of peak in

414 the 2D NMR spectra (Damodaran et al., 2002). A minor [4]Al signal (~2%) is detected at a

415 temperature as low as ~50 °C. The [4]Al fraction gradually increases from ~2% at 50 °C to

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416   ~4% at 200 °C, and then increases rapidly to ~7% and ~16% at 250 °C and 300 °C,

417   respectively. The [5]Al fraction also increases from < 1% at 50 °C to ~2.3% at 300 °C.

418   **Phase transformation from bayerite precursor.** Figure 10A shows the simulation results

419   of the ^{27}Al MAS NMR spectra of bayerite heat-treated from 25 °C to 300 °C. Although the

420   two crystallographically inequivalent [6]Al sites in bayerite are not fully resolved in the

421   1D NMR spectra, the NMR parameters reported in earlier ^{27}Al NMR studies were used to

422   deconvolute NMR spectra (Bastow et al., 1994; Damodaran et al., 2002): for example, as

423   for bayerite, the δ_{iso}, C_q, and η values of [6]Al-1 are 9.8 ppm, 1.9 MHz, and 0.3,

424   respectively, and those of [6]Al-2 are 12.9 ppm, 1.7 MHz, and 0.8, respectively (Table 4).

425   As mentioned above (Figure 4), the bayerite transforms into boehmite + γ-/η-Al$_2$O$_3$. Thus,

426   the spectra were simulated above 200 °C using the multiple [4]Al and [6]Al components

427   corresponding to boehmite and γ-/η-Al$_2$O$_3$.

428   The simulation results show that there are ~14% of boehmite, ~39% of γ-/η-Al$_2$O$_3$,

429   and ~47% of bayerite at 200 °C. The [4]Al fraction rapidly increases to ~25% as the

430   temperature increases up to 250 °C, and then gradually up to ~27% at 300 °C, confirming

431   that the γ-/η-Al$_2$O$_3$ (~91%) is predominant at 300 °C. This drastic increase [4]Al fraction

432   indicates that the phase transformation occurs dramatically within narrow temperature

433   range between 200 °C and 250 °C.

434   **Phase transformation from gibbsite precursor.** Figure 10B presents the simulation

435   results for ^{27}Al MAS NMR spectra of gibbsite with varying annealing temperatures. The

436   NMR spectra of gibbsite at 25 °C, showing the coexistence of two different [6]Al sites, were

437   simulated with the two components. The ^{27}Al NMR parameters are δ_{iso} = 12.4 ppm, C_q =

438   4.5 MHz, and η = 0.4 for the [6]Al-1 site and δ_{iso} = 11.3 ppm, C_q = 2.3 MHz, and η = 0.8 for

439   the [6]Al-2 site (Table 5). These values are consistent with those obtained in the previous

440   ^{27}Al MAS NMR study (Vyalikh et al., 2010). As the temperature increases above 200 °C,

441   the peak shape of [6]Al changes gradually because the gibbsite is transformed into

442   boehmite. Note that the changes in [6]Al peak at 200 °C is not due to the formation of

443   metastable alumina, because the presence of [4]Al is not observed at 200 °C. Thus, the

444   spectrum at 200 °C was simulated using a single [6]Al peak for boehmite and two [6]Al

445   peaks for gibbsite. At 200 °C, the proportions of gibbsite and boehmite are ~88% and

15

446   ~12%, respectively. Above 250 °C, the [4]Al fraction of γ-/η-Al$_2$O$_3$ increases from ~2% at

447   250 °C to ~15% at 300 °C, suggesting that the phase transformation into γ-/η-Al$_2$O$_3$ occurs

448   at ~250 °C.

449

450   **Temperature-induced changes in the population of Al-(oxy)hydroxides and metastable**

451   **aluminas**

452   Figure 11 shows the variations in the [4,5]Al fractions in aluminum (oxy)hydroxides

453   and metastable alumina with varying temperatures. At 25 °C, boehmite has ~1% of [4]Al,

454   and the bayerite and gibbsite do not have detectable [4]Al and [5]Al. The temperature at

455   which the increase in [4,5]Al is first observed in the NMR spectra (i.e., the onset temperature

456   of the phase transformation into metastable alumina) depends on the type of precursor

457   hydroxide minerals. The presence of [4,5]Al peaks is observed in boehmite even at 50 °C

458   (~2.7%), and the [4,5]Al fraction steadily increases up to 300 °C (~18%). In contrast, in the

459   case of bayerite and gibbsite, the [4]Al peak intensity increases abruptly from 200 °C (~11%)

460   to 250 °C (~26%), and then increases gradually from 250 °C to 300 °C (~27%). As for gibbsite,

461   while the [4]Al fraction is not observed in the spectra up to 200 °C, the [4]Al fraction of ~2% is

462   observed in the spectra for 250 °C sample, and the [4]Al fraction increases rapidly to ~15% as

463   the temperature increases to 300 °C.

464   Taking the temperature-induced changes in [4]Al fraction into consideration, Figure

465   12 exhibits the transformation paths from boehmite (A), bayerite (B), and gibbsite (C) to γ-

466   /η-Al$_2$O$_3$. As shown in Figure 12A, the fraction of γ-/η-Al$_2$O$_3$ increases continuously from

467   ~8% at 50 °C to ~55% at 300 °C, suggesting that the phase transformation of boehmite → γ-

468   /η-Al$_2$O$_3$ occurs at a temperature as low as ~50 °C. The threshold temperature (~50 °C) is

469   much lower than that previously reported. These results suggest that the phase

470   transformation from boehmite to γ-/η-Al$_2$O$_3$ occurs in a wide temperature range than

471   previously reported. In contrast, as shown in Figure 12B, the population of bayerite

472   abruptly decreases from 100% (at 150 °C), through ~47% (at 200 °C), to 0% (at 250 °C),

473   indicating that the phase transition from bayerite to boehmite + γ-/η-Al$_2$O$_3$ occurs within a

474   narrow temperature range. Figure 12C shows the variations in the population among

475   gibbsite, boehmite, and γ-/η-Al$_2$O$_3$ with varying annealing temperatures. At 200 °C, the

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476 ~12% of boehmite. Above 250 °C, the fractions of both boehmite and γ-/η-Al_2O_3 increase. In

477 particular, the population of boehmite increases abruptly from ~12% to ~45% as the

478 temperature increases from 200 °C to 250 °C, and then increases gradually from ~45% at 250

479 °C to ~48% at 300 °C. The formation of γ-/η-Al_2O_3 (~9%) is observed at 250 °C, and the

480 fraction of γ-/η-Al_2O_3 increases dramatically from ~9% at 250 °C to ~52% at 300 °C. At 300

481 °C, the gibbsite is not observed. These results show that the threshold temperatures for

482 gibbsite (~200 °C) are higher than that from boehmite (~50 °C).

483 Although the further kinetic studies are certainly necessary (see below), the current NMR

484 results confirm that the onset temperature and paths of transformation from aluminum

485 (oxy)hydroxides to metastable alumina depend on the type of precursor minerals. In

486 particular, the phase transformation of boehmite $\rightarrow$ γ-/η-Al_2O_3 occurs at much lower

487 temperatures (~50 °C) than those of bayerite $\rightarrow$ boehmite + γ-/η-Al_2O_3 and gibbsite $\rightarrow$

488 boehmite + γ-/η-Al_2O_3 (~200 °C). The phase transformation associated with boehmite

489 occurs gradually within a broad temperature range. Furthermore, the NMR results show

490 that the presence of [5]Al is accompanied by the phase transformation of boehmite $\rightarrow$ γ-/η-

491 Al_2O_3, whereas the presence of [5]Al is not evident in the gibbsite-derived γ-/η-Al_2O_3. Note

492 that several previous studies have suggested that the [5]Al is located on the surface of γ-/η-

493 Al_2O_3 (e.g., Kwak et al., 2009; Lee et al., 2014 and references therein). Alternatively, the

494 earlier NMR studies of amorphous Al_2O_3-thin film indicated that the fractions of [5]Al

495 decrease with thickness (Lee et al., 2009b; Lee et al., 2010; Lee and Ahn, 2014). Based on

496 these results, the fraction of [5]Al in disordered/amorphous oxides is a proxy to the extent of

497 structural disorder for bulk materials (Lee and Ahn, 2014; Lee et al., 2016; Lee and Ryu,

498 2018). The current results confirm that the extent of disorder of the boehmite-derived γ-/η-

499 Al_2O_3 is higher than that of the gibbsite-derived γ-/η-Al_2O_3.

500 Therefore, the pronounced gradual phase transformation from boehmite to γ-/η-

501 Al_2O_3, which occurs from ~50 °C, results from the moderate degree of structural disorder in

502 boehmite, as also indicated from the wider X-ray diffraction peak. The difference in the

503 extent of disorder in γ-/η-Al_2O_3 associated with the types of precursor minerals result in the

504 difference in the stability of metastable alumina.

17

505   Note that it is difficult to determine the phase transition temperature under 300 °C,

506   because the phase transformation in the low-temperature range can be kinetically

507   broadened (e.g., Lee et al., 2020). Thus, further extensive study for kinetic nature of

508   dehydration is necessary. While the previous studies have shown that the heating for more

509   than ~2 h above 300 °C does not cause significant changes in the degree of phase

510   transformation and/or dehydration (e.g., Xu and Smith, 2012; Kim and Lee, 2013a, b; Lee

511   and Ryu, 2018 and references therein), the effect of annealing time on the dehydration in the

512   low-temperature range remains to be explored. Furthermore, the stability fields of

513   metastable aluminas are dependent on their physical properties (i.e., particle sizes,

514   permeability, and surface area) (Sun et al., 2008; Kim and Lee, 2013b; Karouia et al., 2016).

515   Thus, the additional kinetic study of transformation with varying properties of aluminum

516   (oxy)hydroxides remains to be considered. Nevertheless, the current results clearly

517   demonstrate that the transformation path to metastable alumina depends on the type of

518   precursor minerals.

519

520   **Implications**

521   The current ^{27}Al NMR results provide detailed information on the dehydration paths

522   from three different aluminum (oxy)hydroxides (i.e., boehmite, bayerite, and gibbsite) to

523   metastable alumina in the low-temperature range (≤ 300 °C). By quantifying the populations

524   of involving phases, the control of precursor minerals on the transformation paths have

525   been systematically explored. The results demonstrate that the temperature ranges of phase

526   transformation and the transformation paths (gradual *vs*. dramatic) depend on the extent of

527   disorder of precursor minerals.

528   The precursor-dependent structural evolution in the low-temperature range would

529   help to understand the geological processes involving metastable phases and their

530   dehydration on the Earth's surface environments as the phase transformation involving

531   metastable phases, such as γ-Al_2O_3, are common in the Earth's surface environments. For

532   example, the recent rotary shear experiment of quartzite showed that the friction-induced

533   melting at fault planes is partly controlled by the formation of metastable phase (such as

534   metastable β-quartz), contributing to an overall fault-weakening (Lee et al., 2017). The

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535 melting temperature (i.e., threshold temperature) of metastable phase is much lower than

536 the equilibrium transition temperature (Lee et al., 2017).

537 Furthermore, the reactivity of metastable oxides in contact with an aqueous solution

538 depends on the short-range structures (e.g., electronic environment and network topology)

539 (e.g., Phillips et al., 2000a; Phillips et al., 2000b; Lee and Stebbins, 2003; Lee and Weiss, 2008;

540 Li et al., 2010). The previous studies have shown that the [5]Al sites are known to control the

541 overall catalytic ability of metastable alumina (e.g., Kwak et al., 2007; Kwak et al., 2009; Lee

542 et al., 2010). Because the formation of metastable Al_2O_3 with [5]Al may be prevalent at low

543 temperature condition (~50 °C) as shown in the current study, the absorption of metal

544 elements including rare-earth elements (REEs) on bauxite can be controlled by the presence

545 of metastable alumina. It has been reported that the REEs are more enriched in boehmite-

546 rich bauxite than in gibbsite-rich bauxite (e.g., Boni et al., 2013; Hanilçi, 2013; Radusinović et

547 al., 2017). While speculative, this difference in REE contents may stem from the presence of

548 [5]Al (and thus its high catalytic activity) in the boehmite-derived metastable alumina at low

549 temperature.

550

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List of figure captions

789

790 **Figure 1|** Crystal structures of (A) boehmite, (B) bayerite, (C) gibbsite, and (D) γ-Al_2O_3. See

791   Table 1 for details of crystal structures.

792 **Figure 2|** (A) XRD patterns for boehmite with varying annealing temperatures up to 300

793      $^\circ$C. Red and blue vertical lines correspond to the peak positions and intensities of

794   boehmite (JCPDS file no. 00-021-1307), γ-Al_2O_3 (JCPDS file no. 01-079-1558), and η-

795   Al_2O_3 (JCPDS file no. 00-21-0010), respectively. ^{27}Al MAS NMR spectra for boehmite

796   with varying temperatures at 11.7 T (B) and 14.1 T (C).

797 **Figure 3|** The enlarged ^{27}Al MAS NMR spectra for boehmite with varying annealing

798   temperatures obtained at 11.7 T (left) and 14.1 T (right).

799 **Figure 4|** (A) XRD patterns for bayerite with varying annealing temperatures up to 300 $^\circ$C.

800   Black, red, and blue vertical lines correspond to the peak positions and intensities of

801   bayerite (JCPDS file no. 01-083-2256), boehmite (JCPDS file no. 00-021-1307) and η -

802   Al_2O_3 (JCPDS file no. 00-21-0010), respectively. (B) ^{27}Al MAS NMR spectra at 11.7 T for

803   bayerite with varying temperatures. (C) Comparison of ^{27}Al NMR spectra for bayerite

804   at 25 $^\circ$C (black line) and 300 $^\circ$C (red line). The enlarged ^{27}Al NMR spectra (D) are also

805   shown to manifest the evolution of [4]Al sites.

806 **Figure 5|** (A) XRD patterns for gibbsite with varying annealing temperatures up to 300 $^\circ$C.

807   Black, red, and blue vertical lines correspond to the peak positions and intensities of

808   gibbsite (JCPDS file no. 01-070-2038), boehmite (JCPDS file no. 00-021-1307), and γ-Al_2O_3

809   (JCPDS file no. 01-079-1558), respectively. (B) ^{27}Al MAS NMR spectra at 11.7 T for

810   gibbsite with varying temperatures. (C) Comparison of ^{27}Al NMR spectra for gibbsite at

811   25 $^\circ$C (black line) and 300 $^\circ$C (red line). The enlarged ^{27}Al NMR spectra (D) are also

812   shown to manifest the evolution of [4]Al sites.

813 **Figure 6|** ^{27}Al 3QMAS NMR spectra for boehmite with varying annealing temperature (as

814   labeled) at 9.4 T. The contour lines are drawn from 8 to 98% relative intensity with a 6%

815   increment. Four additional contour lines (1, 2.5, 4, and 6%) were added in [4,5]Al sites to

816   better show low-intensity peaks (see SI-1 for 2D spectra without noise removal)

817 **Figure 7|** (A) [6]Al peaks in ^{27}Al 3QMAS NMR spectra for boehmite with varying annealing

818   temperature up to 300 $^\circ$C. Contour lines are drawn from 8 to 98% of the relative

819   intensity with increment of 5%. (B) Expected center of gravity for boehmite and γ-/η-

820   Al_2O_3 calculated on the basis of the current simulation (open symbols) and previous

821   works [solid symbols, black circle (Damodaran et al., 2002); red triangle (Kraus et al.,

822   1996); red inverted-triangle (Pecharroman et al., 1999); red diamond (Perander et al.,

823   2007); red circle (Kim and Lee, 2013)]. Black and red symbols refer to boehmite and γ-

824   /η-Al_2O_3, respectively.

825   **Figure 8|** Simulation of ^{27}Al MAS NMR spectra obtained at 11.7 T for boehmite with

826   varying annealing temperatures up to 300 °C. Thick gray lines refer to the experimental

827   spectra, and thin black lines refer to the simulation results. Each component used in the

828   simulation is shown as labeled.

829   **Figure 9|** Simulation of ^{27}Al MAS NMR spectra obtained at 14.1 T for boehmite with

830   varying annealing temperatures up to 300 °C. Thick gray lines refer to the experimental

831   spectra, and thin black lines refer to the simulation results. Each component used in the

832   simulation is shown as labeled.

833   **Figure 10|** Simulation of ^{27}Al MAS NMR spectra obtained at 11.7 T for bayerite (left) and

834   gibbsite (right) with varying annealing temperatures up to 300 °C. Thick gray lines

835   refer to the experimental spectra, and thin black lines refer to the simulation results.

836   Each component used in the simulation is shown as labeled.

837   **Figure 11|** Variation in the [4,5]Al fraction for boehmite (blue squares), bayerite (red circles),

838   and gibbsite (black triangles) with varying temperatures. The smooth lines are to guide

839   the eye only.

840   **Figure 12|** (A) Variations in the populations of (A) boehmite and γ-/η-Al_2O_3, (B) bayerite

841   and γ-/η-Al_2O_3 + boehmite, and (C) gibbsite, boehmite and γ-/η-Al_2O_3 with varying

842   annealing temperatures. The smooth lines are to guide the eye only. The shaded areas

843   show the phase transformation temperature ranges from precursor minerals to

844   metastable alumina.

27

Tables

Table 1 | Crystallographic information of aluminum (oxy)hydroxide precursor minerals (i.e., boehmite, bayerite, and gibbsite) and metastable alumina (i.e., γ- and η-Al_2O_3)

	Boehmite	Bayerite	Gibbsite
Al coordination	[6]Al-1 100%	[6]Al-1 50%	[6]Al-1 50%
		[6]Al-2 50%	[6]Al-2 50%
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Cmcm	$P2_1/m$	$P2_1/m$
Lattice parameter (Å)			
A	2.8796	5.096	8.742
B	12.205	8.729	5.112
C	3.761	9.489	9.801
Density (g/cm^3)	3.04	2.42	2.38-2.42
Reference	Hill (1981)	Balan et al. (2008)	Balan et al. (2006)

	γ-Al_2O_3	η-Al_2O_3
Crystal system	Cubic (defect spinel)	Cubic (defect spinel)
Space group	$Fd\bar{3}m$	$Fd\bar{3}m$
Lattice parameter (Å)		
A (=B=C)	7.911	7.914
Idealized formula	$^{[4]}Al\square_{1/3}{}^{[6]}Al_{5/3}O_4$	$^{[4]}Al_{2/3}\square_{1/3}{}^{[6]}Al_2O_4$
[4]Al:[6]Al	1:3 (~25:75)	3:5 (~38:62)
Reference	Lippen and de Bohr (1964)	Zhou and Snyder (1991)

28

Table 2 | ^{27}Al NMR parameters for aluminum (oxy)hydroxides and metastable alumina

Reference	Method	Phase	Larmor frequency (MHz)	$^{[n]}$Al	δ_{iso} (ppm)[a]	$\Delta\delta_{iso}$[b]	C_q (MHz)[c]	η[d]	Site fraciton (%)
Damodaran et al. (2002)	MQMAS	Boehmite	130.3	$^{[6]}$Al	12.6	-	1.8-2.8	0.5-1.0	100
		Bayerite		$^{[6]}$Al-1	9.1	-	1.9 ± 0.1	0.25 ± 0.05	50
				$^{[6]}$Al-2	13.1	-	1.4 ± 0.1	0.80 ± 0.05	50
		Gibbsite		$^{[6]}$Al-1	11.6	-	2.2 ± 0.2	0.75 ± 0.05	50
				$^{[6]}$Al-2	17.2	-	4.7 ± 0.2	1.00 ± 0.05	50
Vyalikh et al. (2010)	MAS	Gibbsite	130.3	$^{[6]}$Al-1	11.3 ± 0.2	-	2.2 ± 0.2	0.7 ± 0.1	50 ± 5
				$^{[6]}$Al-2	13.6 ± 0.2	-	4.6 ± 0.2	0.4 ± 0.1	50 ± 5
Ferreira et al. (2001)	Theoretical Calculation	Boehmite	-	$^{[6]}$Al	11.7-12.4	-	2.1-2.3	0.5-0.7	100
Kim and Lee (2013)	MAS (Czjzek)	γ-Al$_2$O$_3$	130.3	$^{[6]}$Al	14.0 ± 1.0	6.5 ± 2.5	4.6 ± 1.0	-	68 ± 3
				$^{[4]}$Al	72.5 ± 1.0	10 ± 3	5.7 ± 1.0	-	32 ± 3
de Lacaillerie et al. (2008)	MAS (Czjzek)	γ-Al$_2$O$_3$	130.3	$^{[6]}$Al	13.8	-	-	-	67
				$^{[4]}$Al	73.8	-	-	-	33
Kraus et al. (1996)	MAS	γ-Al$_2$O$_3$	130.3	$^{[6]}$Al	9 ± 1	-	4.5 ± 0.5	0.3	-
				$^{[4]}$Al	67 ± 1	-	5.0 ± 0.5	0.3	-
Pecharroman et al. (1999)	MAS	η-Al$_2$O$_3$	104.3	$^{[6]}$Al	14.5 ± 0.2	-	3.9 ± 0.2	0.4 ± 0.1	69-78
				$^{[4]}$Al	76.5 ± 0.2	-	4.5 ± 0.2	0.7 ± 0.1	22-31
		γ-Al$_2$O$_3$	104.3	$^{[6]}$Al	15.2 ± 0.2	-	3.7 ± 0.2	0.4 ± 0.1	69-76
				$^{[5]}$Al	-	-	-	-	3-6.5
				$^{[4]}$Al	78.5 ± 0.2	-	4.7 ± 0.2	0.7 ± 0.1	21-26

[a] Isotropic chemical shift

[b] Full-width at half maximum of the distribution of the isotropic chemical shift in the Czjzek model

[c] Quadrupolar coupling constant

[d] Asymmetry parameter

Table 3| ^{27}Al NMR parameters for the simulation of the NMR spectra for boehmite with varying temperature at 11.7 T and 14.1 T.

Precursor mineral	T (^{o}C)	Phase	$^{[n]}$Al	δ_{iso} (ppm)[a]	C_q (MHz)[b]	$\Delta\delta_{iso}$[c]	$^{[n]}$Al fraction for each phase (%)[d,*]
Boehmite	25	Boehmite	$^{[6]}$Al	10.8 ± 1.5	2.7 ± 0.3	4 ± 2	99 ± 1
			$^{[4]}$Al	73.0 ± 1.5	5.0 ± 1.0	4 ± 2	< 1
	50	Boehmite	$^{[6]}$Al	10.5 ± 1.5	2.8 ± 0.3	4 ± 2	93 ± 3
		γ-/η-Al$_2$O$_3$	$^{[6]}$Al	11.4 ± 1.5	4.8 ± 0.5	6 ± 2	4 ± 3
			$^{[5]}$Al	41.3 ± 1.5	5.7 ± 1.0	6 ± 2	< 1
			$^{[4]}$Al	73.4 ± 1.5	5.1 ± 1.0	7 ± 2	2 ± 3
	110	Boehmite	$^{[6]}$Al	10.5 ± 1.5	2.8 ± 0.3	4 ± 2	92 ± 3
		γ-/η-Al$_2$O$_3$	$^{[6]}$Al	11.4 ± 1.5	4.8 ± 0.5	7 ± 2	5 ± 3
			$^{[5]}$Al	41.3 ± 1.5	5.7 ± 1.0	6 ± 2	< 1
			$^{[4]}$Al	73.6 ± 1.5	5.3 ± 1.0	7 ± 2	2 ± 3
	150	Boehmite	$^{[6]}$Al	10.2 ± 1.5	2.8 ± 0.3	4 ± 2	87 ± 3
		γ-/η-Al$_2$O$_3$	$^{[6]}$Al	11.1 ± 1.5	4.8 ± 0.5	7 ± 2	8 ± 3
			$^{[5]}$Al	41.0 ± 1.5	6.0 ± 1.0	6 ± 2	< 2
			$^{[4]}$Al	73.4 ± 1.5	5.6 ± 1.0	9 ± 2	3 ± 3
	200	Boehmite	$^{[6]}$Al	10.5 ± 1.5	2.8 ± 0.3	5 ± 2	85 ± 3
		γ-/η-Al$_2$O$_3$	$^{[6]}$Al	12.2 ± 1.5	4.8 ± 0.5	7 ± 2	9 ± 3
			$^{[5]}$Al	41.0 ± 1.5	6.0 ± 1.0	6 ± 2	< 2
			$^{[4]}$Al	73.9 ± 1.5	5.7 ± 1.0	10 ± 2	4 ± 3
	250	Boehmite	$^{[6]}$Al	10.1 ± 1.5	2.8 ± 0.3	5 ± 2	78 ± 3
		γ-/η-Al$_2$O$_3$	$^{[6]}$Al	11.8 ± 1.5	4.8 ± 0.5	7 ± 2	14 ± 3
			$^{[5]}$Al	41.2 ± 1.5	6.0 ± 1.0	6 ± 2	< 2
			$^{[4]}$Al	73.7 ± 1.5	5.7 ± 1.0	9 ± 2	6 ± 3
	300	Boehmite	$^{[6]}$Al	10.6 ± 1.5	2.8 ± 0.3	5 ± 2	45 ± 3
		γ-/η-Al$_2$O$_3$	$^{[6]}$Al	12.1 ± 1.5	4.8 ± 0.5	8 ± 2	36 ± 3
			$^{[5]}$Al	41.0 ± 1.5	6.0 ± 1.0	7 ± 2	< 3
			$^{[4]}$Al	73.9 ± 1.5	5.7 ± 1.0	10 ± 2	16 ± 3

Note: The ^{27}Al NMR spectra for boehmite at 25, 50, 110, 200, and 300 ^{o}C were simulated simultaneously at 11.7 T and 14.1 T.

[a] Isotropic chemical shift

[b] Quadrupolar coupling constant

[c] Full-width at half maximum of the distribution of the isotropic chemical shift in the Czjzek model

[d] $^{[n]}$Al fraction for each phase = $^{[n]}$Al for each phase/total area under NMR spectra

*The uncertainties of each Al site fraction stem from the deviation between experimental and simulated spectra (~1.5%), the contribution from the adjusted NMR parameters (~1.5%), the contribution of spinning sidebands (~1.5%), and phasing of the NMR spectrum (~1.5%). Considering these uncertainties, the total error bar of ±3% is estimated.

Table 4| ^{27}Al NMR parameters for the simulation of the NMR spectra for bayerite with varying temperature at 11.7 T.

Precursor mineral	Larmor frequency (MHz)	T (°C)	Phase	$^{[n]}$Al	δ_{iso} (ppm)[a]	C_q (MHz)[b]	η[c]	$\Delta\delta_{iso}$[d]	$^{[n]}$Al fraction for each phase (%)[e,*]
Bayerite	130.28	25	Bayerite	$^{[6]}$Al-1	9.8 ± 0.5	1.9 ± 0.3	0.3 ± 0.1	-	51 ± 3
				$^{[6]}$Al-2	12.9 ± 0.5	1.7 ± 0.3	0.8 ± 0.1	-	49 ± 3
		110	Bayerite	$^{[6]}$Al-1	9.8 ± 0.5	1.9 ± 0.3	0.3 ± 0.1	-	50 ± 3
				$^{[6]}$Al-2	13.0 ± 0.5	1.7 ± 0.3	0.8 ± 0.1	-	50 ± 3
		150	Bayerite	$^{[6]}$Al-1	9.8 ± 0.5	2.0 ± 0.3	0.3 ± 0.1	-	51 ± 3
				$^{[6]}$Al-2	12.9 ± 0.5	1.7 ± 0.3	0.8 ± 0.1	-	49 ± 3
		200	Bayerite	$^{[6]}$Al-1	9.9 ± 0.5	2.0 ± 0.3	0.3 ± 0.1	-	23 ± 3
				$^{[6]}$Al-2	13.1 ± 0.5	1.6 ± 0.3	0.8 ± 0.1	-	24 ± 3
			Boehmite	$^{[6]}$Al	11.2 ± 1.0	2.7 ± 0.5		4 ± 1	14 ± 3
			γ-/η-Al$_2$O$_3$	$^{[6]}$Al	13.5 ± 1.5	4.4 ± 0.5	-	5 ± 1	27 ± 3
				$^{[4]}$Al	73.0 ± 1.5	5.4 ± 0.5	-	8 ± 1	12 ± 3
		250	Boehmite	$^{[6]}$Al	10.9 ± 1.5	2.7 ± 0.5	-	4 ± 1	14 ± 3
			γ-/η-Al$_2$O$_3$	$^{[6]}$Al	13.5 ± 1.5	4.8 ± 0.5	-	5 ± 1	60 ± 3
				$^{[4]}$Al	72.8 ± 1.5	5.4 ± 0.5	-	8 ± 1	26 ± 3
		300	Boehmite	$^{[6]}$Al	10.9 ± 1.5	2.7 ± 0.5	-	4 ± 1	9 ± 3
			γ-/η-Al$_2$O$_3$	$^{[6]}$Al	13.2 ± 1.5	4.8 ± 0.5	-	5 ± 1	64 ± 3
				$^{[4]}$Al	72.8 ± 1.5	5.4 ± 0.5	-	8 ± 1	27 ± 3

[a] Isotropic chemical shift

[b] Quadrupolar coupling constant

[c] Asymmetry parameter

[d] Full-width at half maximum of the distribution of the isotropic chemical shift in the Czjzek model

[e] $^{[n]}$Al fraction for each phase = $^{[n]}$Al for each phase/total area under NMR spectra

*The uncertainties of each Al site fraction stem from the deviation between experimental and simulated spectra (~1.5%), the contribution from the adjusted NMR parameters (~1.5%), the contribution of spinning sidebands (~1.5%), and phasing of the NMR spectrum (~1.5%). Considering these uncertainties, the total error bar of ±3% is estimated.
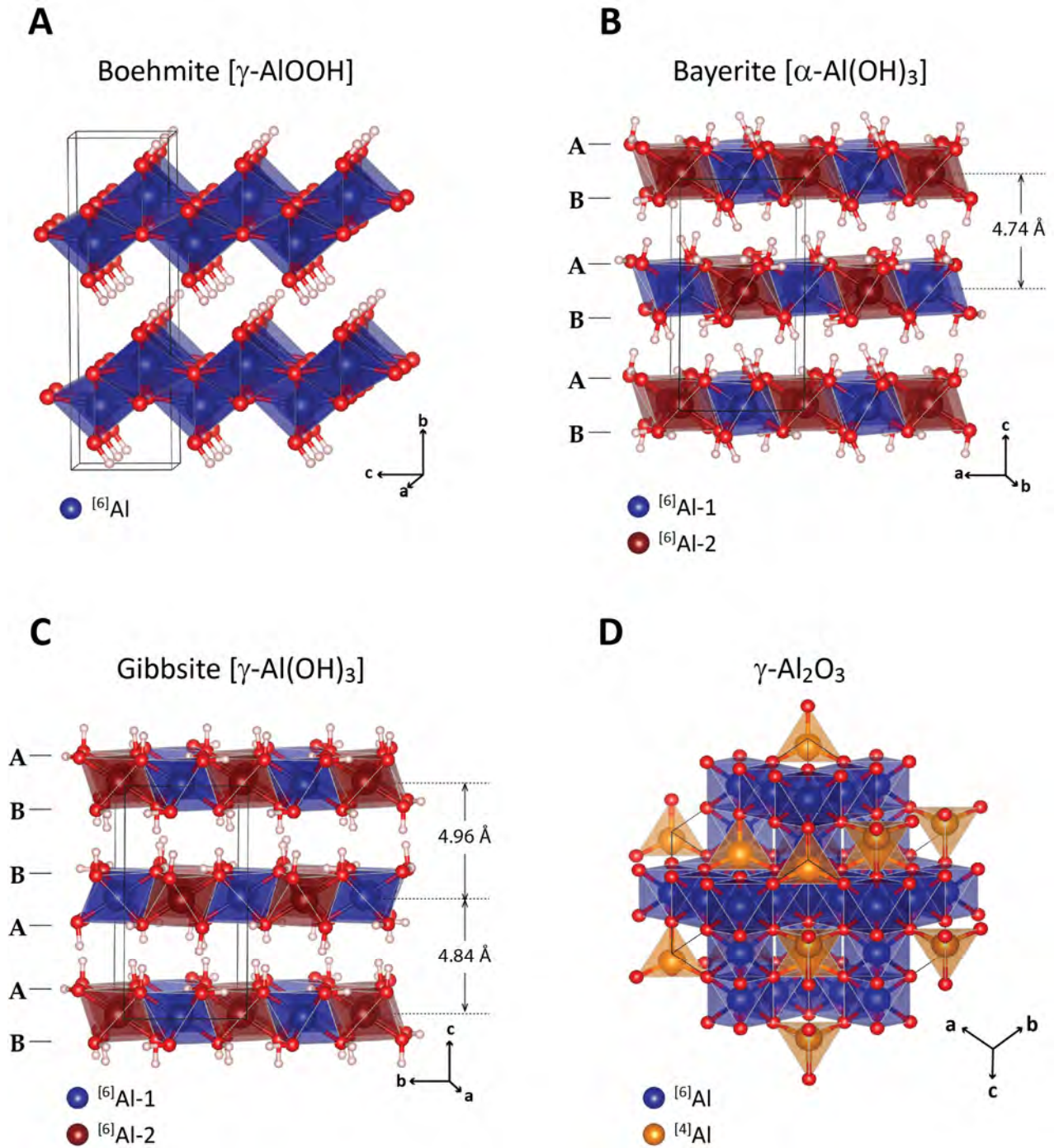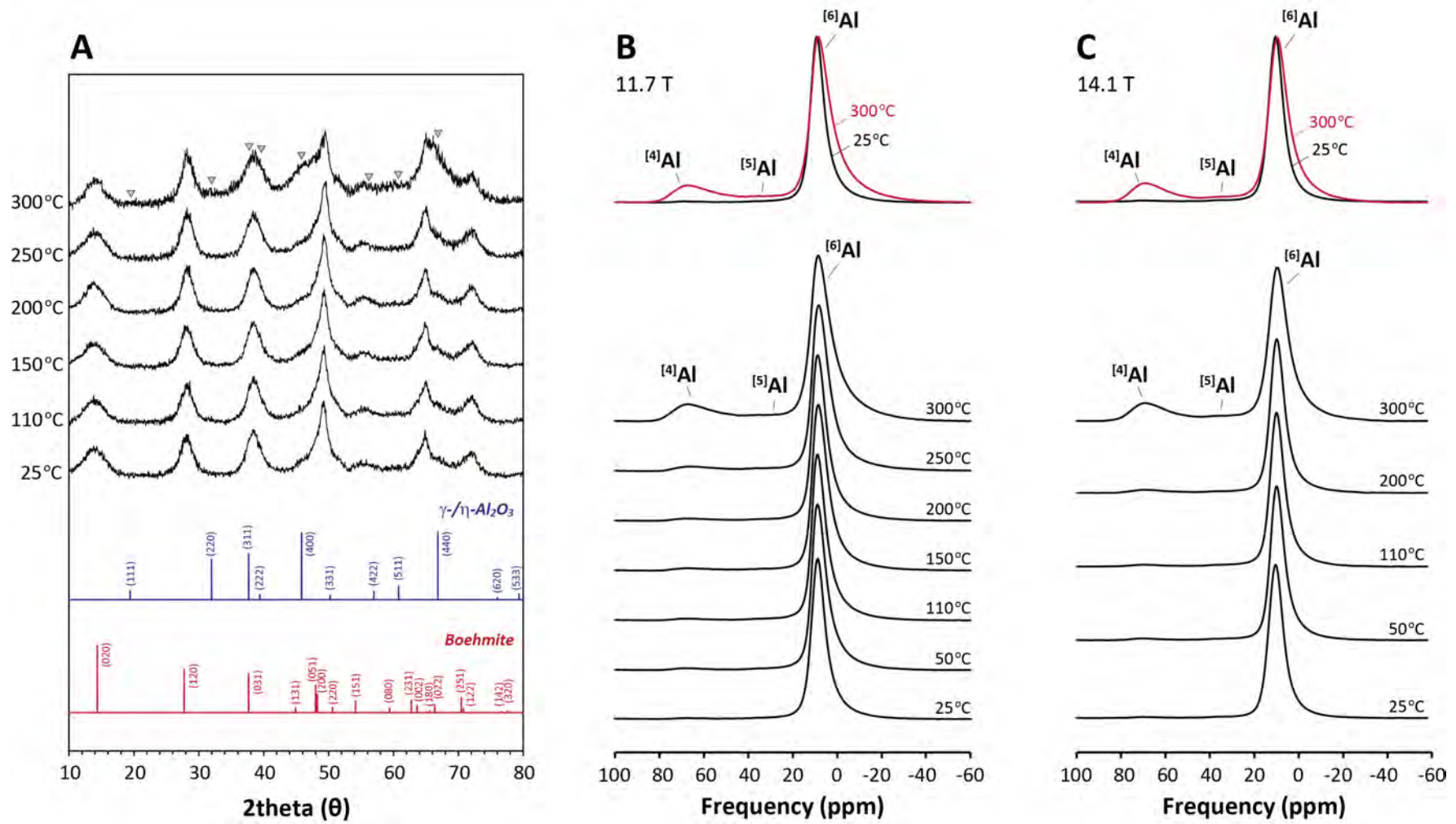
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Table 5 | ^{27}Al NMR parameters for the simulation of the NMR spectra for gibbsite with varying temperature at 11.7 T.

Precursor mineral	Larmor frequency (MHz)	T (°C)	Phase	$^{[n]}$Al	δ_{iso} (ppm)[a]	C_q (MHz)[b]	η[c]	$\Delta\delta_{iso}$[d]	$^{[n]}$Al fraction for each phase (%)[e,*]
Gibbsite	130.28	25	Gibbsite	$^{[6]}$Al-1	12.4 ± 1.0	4.5 ± 0.3	0.4 ± 0.1	-	50 ± 3
				$^{[6]}$Al-2	11.3 ± 1.0	2.3 ± 0.3	0.8 ± 0.1	-	50 ± 3
		110	Gibbsite	$^{[6]}$Al-1	12.5 ± 1.0	4.5 ± 0.3	0.4 ± 0.1	-	50 ± 3
				$^{[6]}$Al-2	11.3 ± 1.0	2.3 ± 0.3	0.8 ± 0.1	-	50 ± 3
		150	Gibbsite	$^{[6]}$Al-1	12.5 ± 1.0	4.5 ± 0.3	0.4 ± 0.1	-	50 ± 3
				$^{[6]}$Al-2	11.3 ± 1.0	2.3 ± 0.3	0.8 ± 0.1	-	50 ± 3
		200	Gibbsite	$^{[6]}$Al-1	13.4 ± 1.0	4.6 ± 0.3	0.4 ± 0.1	-	44 ± 3
				$^{[6]}$Al-2	11.3 ± 1.0	2.3 ± 0.3	0.8 ± 0.1	-	44 ± 3
			Boehmite	$^{[6]}$Al	11.9 ± 1.5	2.5 ± 0.3	-	7 ± 1	12 ± 3
		250	Gibbsite	$^{[6]}$Al-1	12.7 ± 1.0	4.5 ± 0.3	0.4 ± 0.1	-	23 ± 3
				$^{[6]}$Al-2	11.2 ± 1.0	2.4 ± 0.3	0.8 ± 0.1	-	23 ± 3
			Boehmite	$^{[6]}$Al	10.6 ± 1.5	2.7 ± 0.3	-	5 ± 1	45 ± 3
			γ-/η-Al$_2$O$_3$	$^{[6]}$Al	14.0 ± 1.5	4.6 ± 0.5	-	6 ± 1	7 ± 2
				$^{[4]}$Al	73.2 ± 1.5	5.5 ± 0.5	-	7 ± 1	2 ± 1
		300	Boehmite	$^{[6]}$Al	10.6 ± 1.5	2.7 ± 0.3	-	5 ± 1	48 ± 3
			γ-/η-Al$_2$O$_3$	$^{[6]}$Al	13.8 ± 1.5	4.6 ± 0.5	-	8 ± 1	37 ± 3
				$^{[4]}$Al	73.9 ± 1.5	5.5 ± 0.5	-	9 ± 1	15 ± 3

[a] Isotropic chemical shift

[b] Quadrupolar coupling constant

[c] Asymmetry parameter

[d] Full-width at half maximum of the distribution of the isotropic chemical shift in the Czjzek model

[e] $^{[n]}$Al fraction for each phase = $^{[n]}$Al for each phase/total area under NMR spectra

*The uncertainties of each Al site fraction stem from the deviation between experimental and simulated spectra (~1.5%), the contribution from the adjusted NMR parameters (~1.5%), the contribution of spinning sidebands (~1.5%), and phasing of the NMR spectrum (~1.5%). Considering these uncertainties, the total error bar of ±3% is estimated.

Figures

A — Boehmite [γ-AlOOH], [6]Al

B — Bayerite [α-Al(OH)$_3$], 4.74 Å, [6]Al-1, [6]Al-2

C — Gibbsite [γ-Al(OH)$_3$], 4.96 Å, 4.84 Å, [6]Al-1, [6]Al-2

D — γ-Al$_2$O$_3$, [6]Al, [4]Al

Figure 1.

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Figure 2.

Figure 3.

Figure 4.
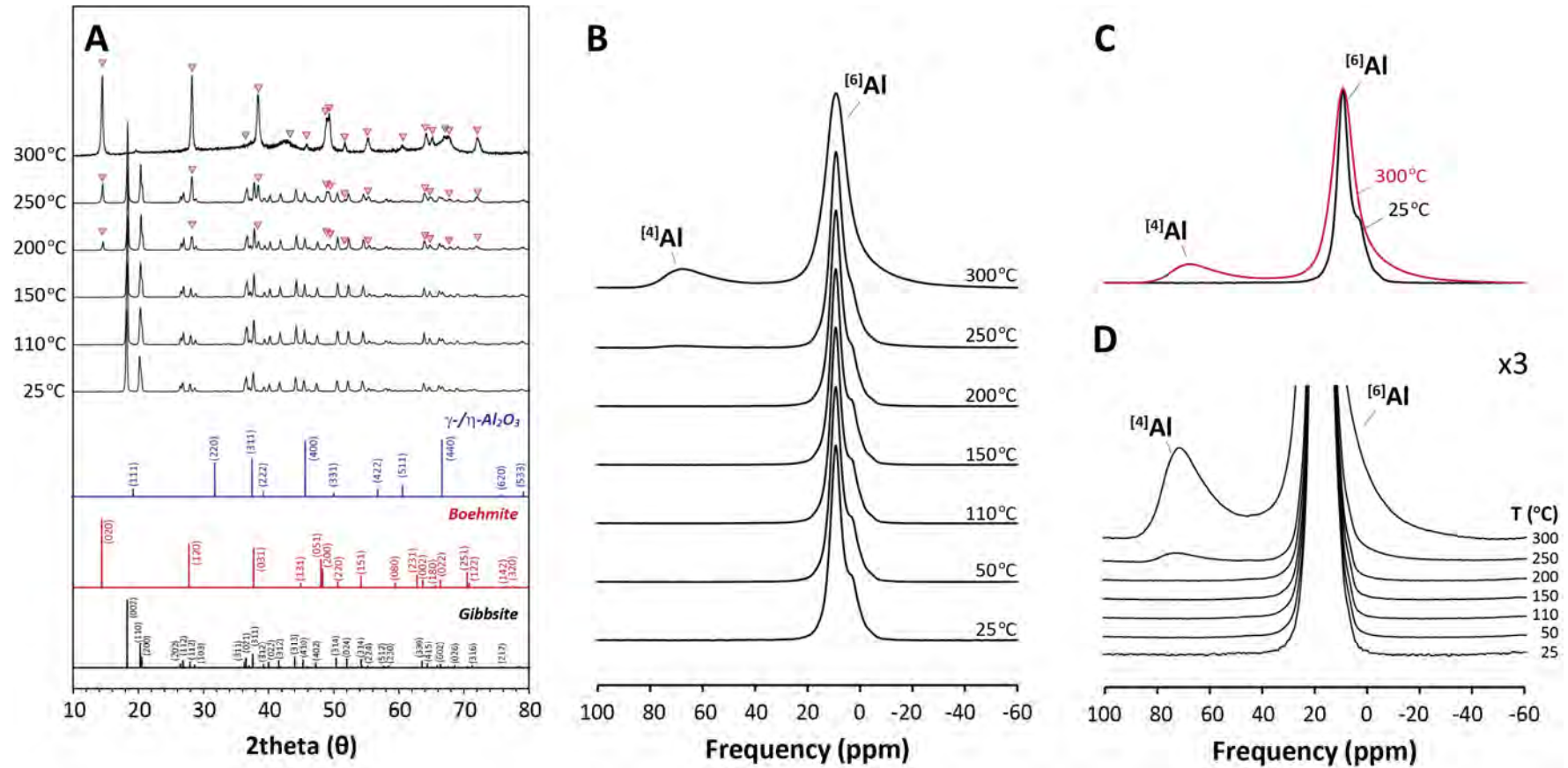
Figure 5.
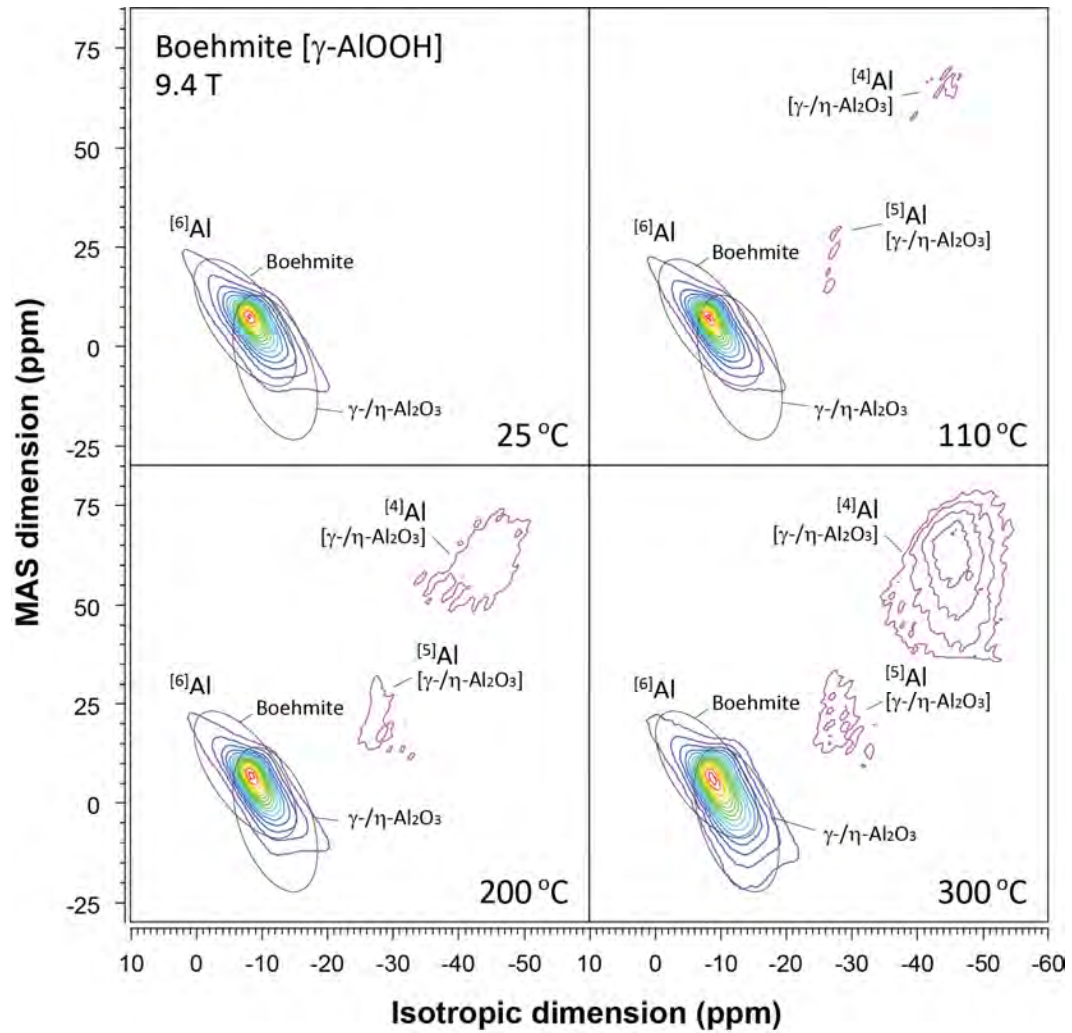
Figure 6.

Figure 7.

Figure 8.

Figure 9.

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Figure 10.

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Figure 11.

Figure 12.