

1 ***Supporting Information***

2

3 **Mechanism of *Myo*-inositol Hexakisphosphate Sorption on**
4 **Amorphous Aluminum Hydroxide: Spectroscopic Evidence for**
5 **Rapid Surface Precipitation**

6 Yupeng Yan,[†] Wei Li,^{‡,1} Jun Yang,[§] Anmin Zheng,[§] Fan Liu,[†] Xionghan Feng,^{*,†,‡} and

7 Donald L. Sparks[‡]

8 [†] Key Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze
9 River), Ministry of Agriculture, College of Resources and Environment, Huazhong
10 Agricultural University, Wuhan 430070, China

11 [‡] Environmental Soil Chemistry Group, Delaware Environmental Institute and
12 Department of Plant and Soil Sciences, University of Delaware, Newark, Delaware,
13 19716, United States

14 [§] State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics,
15 Wuhan Center for Magnetic Resonance, Wuhan Institute of Physics and Mathematics,
16 Chinese Academy of Sciences, Wuhan 430071, China

17 ¹ Key Laboratory of Surficial Geochemistry, Ministry of Education, School of Earth
18 Sciences and Engineering, Nanjing University, Nanjing 210093, China

19

20 *Corresponding author:

21 Xionghan Feng, Tel: +86 27 87280271; Fax: +86 27 87288618; E-mail:

22 fxh73@mail.hzau.edu.cn

23 **S1. Synthesis and Characterization of Amorphous Aluminum Hydroxide (AAH)**

24 **Synthesis of AAH.** AAH was prepared following a modified procedure described by
25 Shang et al.¹ and Guan et al.² A 0.167 M AlCl₃ solution was adjusted to and maintained at
26 pH 6.0 ± 0.1 with a 0.5 M sodium hydroxide solution under rapid stirring. After the
27 solution pH stabilized without any further addition of alkali, the solution was stirred at
28 room temperature for 48 hours. The suspension was centrifuged (16 000 g for 5 minutes)
29 and the supernatant was decanted.

30 **Poorly Crystalline Aluminum Phytate (Al-IHP) Synthesis.** To prepare Al-IHP, 30
31 mL of 0.3 M AlCl₃ (pH 2.0) was added to an equal volume of 0.05 M K₂IP₆ (pH 2.0). The
32 final pH of the reaction mixture was adjusted to 2.4 with 0.5 M KOH.³

33 **Zeta (ζ) Potential Measurements.** Variation of ζ potential of AAH over time after
34 sorbing *myo*-inositol hexakisphosphate (IHP) at various pHs was examined as follows.
35 The AAH suspensions (1.5 g L⁻¹) were prepared at desired pHs with IHP (522 μM P) in
36 0.1 M KCl. The suspensions were adjusted to the desired pH before and after IHP addition.
37 Aliquots were sampled at selected times for ζ determinations. The effect of IHP
38 concentration on ζ potential dynamics was also studied. Each sample was measured three
39 times with 12–30 runs for every measurement.

40 ***In situ* Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR)**

41 **Spectroscopy.** The ATR-FTIR spectra were recorded on a Bruker Vertex 70 FTIR
42 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector (Bruker
43 Optics Inc., Ettlingen, Germany). A single-reflection diamond ATR accessory (Pike
44 Technologies, Inc., Madison, WI, USA) was used to acquire spectra of wet samples.

45 Spectra were collected in the spectral range extending from 900 to 1300 cm^{-1} for an
46 average of 512 scans at an instrument resolution of 4 cm^{-1} . Prior to ATR-FTIR analysis,
47 10 mL of amorphous $\text{Al}(\text{OH})_3$ suspension was withdrawn and immediately filtered
48 through a 0.22 μm membrane filter. The wet sample paste was directly and uniformly
49 applied to the diamond ATR crystal. The sample-holding region was covered with a glass
50 lid to prevent water evaporation during measurements, and ATR-FTIR spectra were then
51 recorded immediately. To isolate the spectra of the solid, the paste spectra were subtracted
52 from the spectra of supernatants to remove strong contributions from the water bands.

53 **Powder X-ray Diffraction (XRD) Measurements.** The powder XRD patterns were
54 obtained on a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe,
55 Germany) equipped with a LynxEye detector using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda =$
56 0.15418 nm). The diffractometer was operated at a tube voltage of 40 kV and a current of
57 40 mA with a scanning rate of $10^\circ/\text{min}$ and at a step size of 0.02° .

58 **Solid-state NMR Spectroscopy.** Solid-state ^{27}Al and ^{31}P single-pulse MAS
59 (SP/MAS) NMR spectra of AAH-IHP sorption samples and standard samples were
60 collected on a 500 MHz Bruker AscendTM spectrometer (11.7 T). The ^{31}P and ^{27}Al
61 SP/MAS NMR spectra were collected at the operating frequencies of 202.6 and 130.4
62 MHz, respectively using a PH MASDVT 500WB BL 4 X/Y/F/H probe, with samples
63 contained in 4 mm (o.d.) ZrO_2 rotors at a spinning rate of 10 kHz. The ^{31}P chemical shifts
64 (δ_{P}) are reported relative to an external 85% H_3PO_4 solution. The ^{31}P SP/MAS spectra
65 were obtained with an excitation 30° pulse of 5.5 μs , with a 30-s relaxation delay. The
66 ^{27}Al chemical shifts (δ_{Al}) are reported relative to an external 1 M $\text{Al}(\text{NO}_3)_3$ solution set to

67 $\delta_{Al} = 0$ ppm. The pulse delay was optimized at 5 s, and approximately 200 scans were

68 collected for each spectrum to obtain an acceptable signal-to-noise ratio.

69

70

71 **Table S1.** Langmuir parameters for sorption of *myo*-inositol hexakisphosphate (IHP) on
 72 aluminum (oxyhydr)oxides (amorphous aluminum hydroxide, AAH; boehmite, γ -AlOOH;
 73 and α -alumina, α -Al₂O₃).

Aluminum (oxyhydr)oxides	$Q_{\max}^a/\mu\text{mol m}^{-2}$	$Q_{\max}^b/\mu\text{mol g}^{-1}$	Sorption affinity constant $K/L \mu\text{mol}^{-1}$	R^2
AAH	16.01 ± 0.78	1168.99	22.86	0.885
Boehmite	0.73 ± 0.06	83.77	0.95	0.877
α -Al ₂ O ₃	1.13 ± 0.06	10.53	7.03	0.932

74 ^aMaximum sorption density Q_{\max} ($\mu\text{mol m}^{-2}$) of IHP normalized to surface area as
 75 predicted by the Langmuir isotherm.

76 ^bMaximum sorption amount ($\mu\text{mol g}^{-1}$) of IHP normalized to mass.

77

78 **Table S2.** Stability constants of the complexes between *myo*-inositol hexakisphosphate

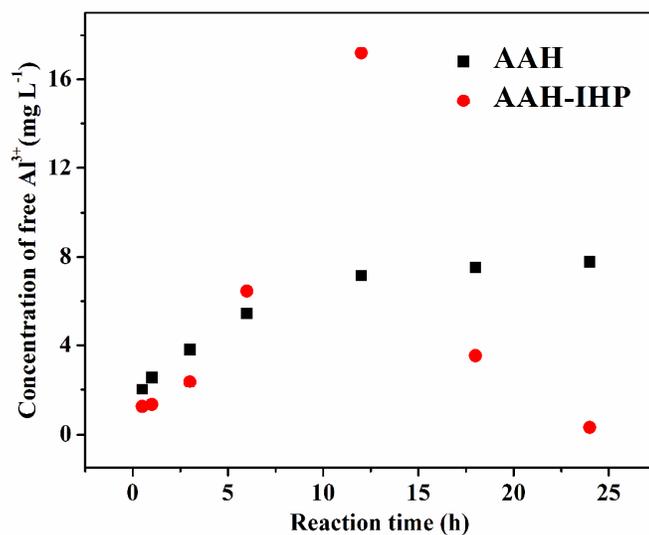
79 (IHP) and Al cation.⁴

Equilibrium	<i>K</i>
$\text{Al}^{3+} + \text{H}_2\text{L}^{10-} \leftrightarrow [\text{Al}(\text{H}_2\text{L})]^{7-}$	$10^{23.7}$
$\text{Al}^{3+} + \text{H}_3\text{L}^{9-} \leftrightarrow [\text{Al}(\text{H}_3\text{L})]^{6-}$	$10^{20.1}$
$\text{Al}^{3+} + \text{H}_4\text{L}^{8-} \leftrightarrow [\text{Al}(\text{H}_4\text{L})]^{5-}$	$10^{16.4}$
$\text{Al}^{3+} + \text{H}_5\text{L}^{7-} \leftrightarrow [\text{Al}(\text{H}_5\text{L})]^{4-}$	$10^{12.2}$
$\text{Al}^{3+} + \text{H}_6\text{L}^{6-} \leftrightarrow [\text{Al}(\text{H}_6\text{L})]^{3-}$	$10^{8.48}$

80

81

82



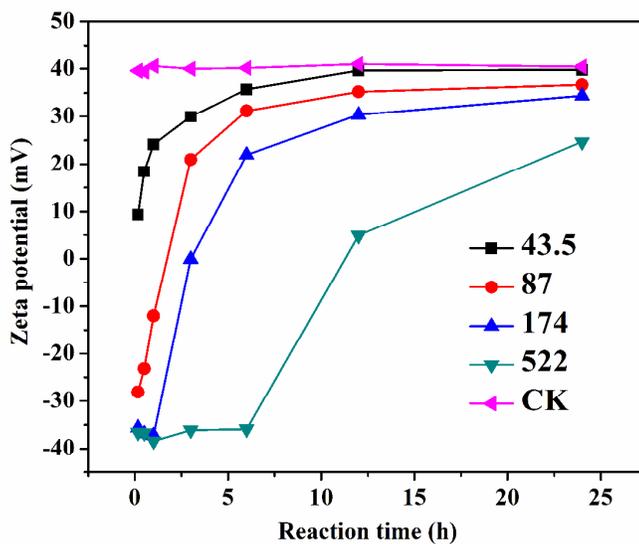
83

84 **Figure S1.** The amount of Al³⁺ ions released from amorphous aluminum hydroxide (AAH,

85 1.5 g L⁻¹) in the absence and presence of *myo*-inositol hexakisphosphate (IHP, 522 μM) in

86 0.1 M KCl at pH 5 as a function of time.

87



89

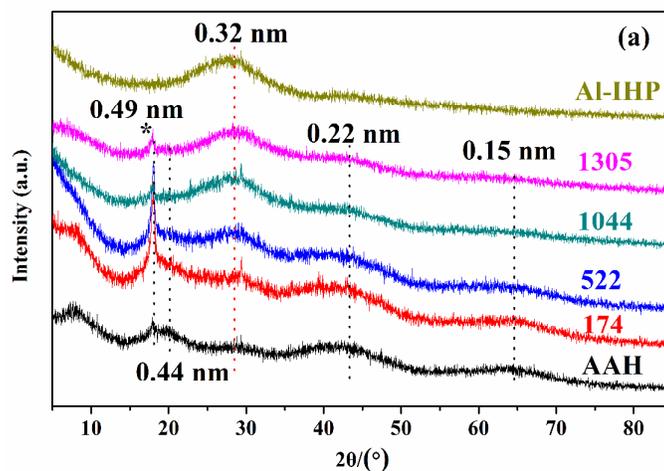
90 **Figure S2.** Zeta potential of amorphous aluminum hydroxide (AAH) reacted with phytate

91 over time at pH 5 with the initial *myo*-inositol hexakisphosphate (IHP) concentrations of

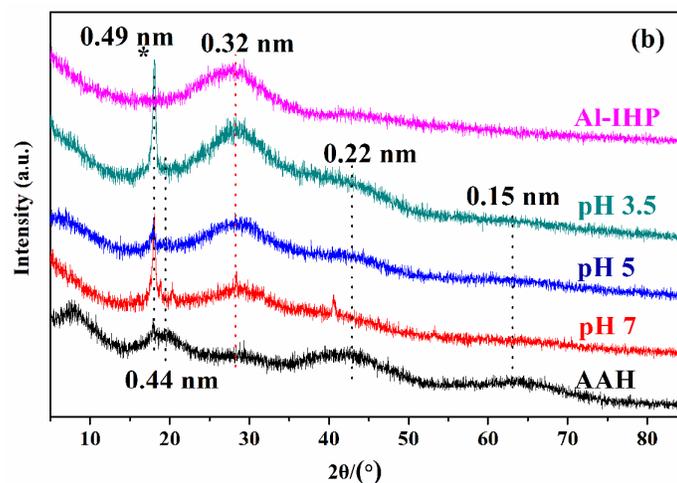
92 43.5, 87, 174, and 522 μM , 1.5 g L^{-1} AAH, and 0.1 M KCl.

93

94



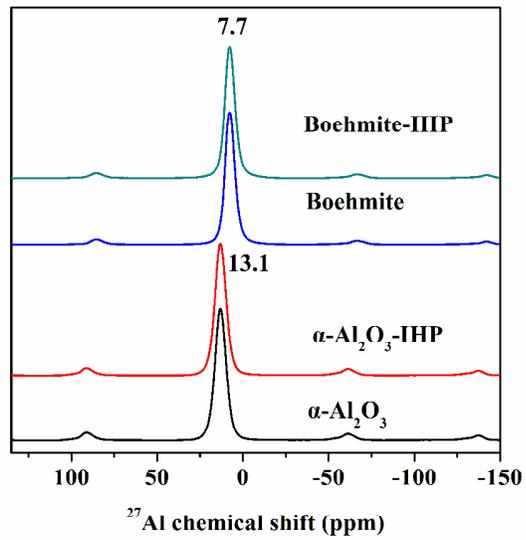
95



96

97 **Figure S3.** Comparison of XRD patterns of amorphous aluminum hydroxide (AAH)
98 sorbed with *myo*-inositol hexakisphosphate (IHP) at pH 5 as a function of IHP
99 concentration (174 to 1 305 μM) with reference materials (AAH and aluminum phytate,
100 Al-IHP) (a), and comparison of XRD patterns of AAH-IHP sorption solids (1 305 μM IHP)
101 as a function of pH with reference materials (AAH and Al-IHP) (b). Asterisk denotes the
102 characteristic peak (0.49 nm) of minor gibbsite impurity in AAH (JCPDS No.
103 00-002-0173).

104



105

106 **Figure S4.** Solid-state ²⁷Al single-pulse (SP) MAS NMR spectra for boehmite and
107 α -Al₂O₃ sorbed with *myo*-inositol hexakisphosphate (IHP) at pH 5. The spinning rate is 10
108 kHz and pulse delay is 5 s for ²⁷Al NMR.

109

110 **REFERENCES**

- 111 (1) Shang C.; Huang P. M.; Stewart J. W. B. Kinetics of adsorption of organic and
112 inorganic phosphates by short-range ordered precipitate of aluminum. *Can. J. Soil Sci.*
113 **1990**, *70*, 461–470.
- 114 (2) Guan, X. H.; Shang, C.; Zhu, J.; Chen, G. H. ATR-FTIR investigation on the
115 complexation of myo-inositol hexaphosphate with aluminum hydroxide. *J. Colloid*
116 *Interf. Sci.* **2006**, *293*, 296–302.
- 117 (3) He, Z.; Honeycutt, C. W.; Zhang, T.; Bertsch, P. M. Preparation and FT-IR
118 characterization of metal phytate compounds. *J. Environ. Qual.* **2006**, *35*, 1319–1328.
- 119 (4) Torres, J.; Dominguez, S.; Cerda, M. F.; Obal, G.; Mederos, A.; Irvine, R. F.; Diaz, A.;
120 Kremer, C. Solution behaviour of myo-inositol hexakisphosphate in the presence of
121 multivalent cations. Prediction of a neutral pentamagnesium species under
122 cytosolic/nuclear conditions. *J. Inorg. Biochem.* **2005**, *99*, 828–840.

123