In-depth characterization of phosphate intercalated MgAl Layered double hydroxides and study of the PO_4 release properties

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Supporting Information

Experimental section

Mg_2AlCl-LDH Synthesis

A 3.0 L solution of the metal salts with a total metal concentration of 2.5 M and the Mg/Al molar ratio equal to 2 was added by a peristaltic pump at a rate of 10 mL/min to 4 L deionized water in a large scale reactor (15 L). A nitrogen (N_2) atmosphere was used to minimize the carbonate contamination. The pH of the synthesis solution was kept constant (pH=10) by the simultaneous addition of a 5 M NaOH solution using a peristaltic pump that is monitored by a pHmeter connected to a pH electrode immersed in the reactor. Subsequently, the suspension was aged for 78 h at room temperature, then collected by centrifugation before the solid product was washed thrice with deionized water, dried at 40 °C and finally grinded to obtain a fine powder. 546 g of LDH were obtained in a homogenous one batch corresponding to a yield of 87 %.

Protocol of mineralization of solid samples for ICP-OES analysis

LDH matrices dosed by ICP-OES were first mineralized. 50.0 mg of powdered LDH were introduced into a hermetically sealed Teflon microwave reactor (MW5000 Anton Paar) in 2 mL HCl and 6 mL HNO_3. The reactors were placed in an Anton-Paar microwave oven and heated (10°C/min ramp) at 230°C for 30 min. The acidic solutions were then recovered and diluted in a 50 mL volumetric flask with deionized water. The solutions as well as some supernatants were dosed by ICP-OES (standard range from 0.01 mg/L to 50 mg/L), and in particular, the concentration of Mg, Al, P, and K in the supernatant were determined by ICP-OES.

Soil juice extraction

The procedure for extracting soil juice was inspired by the procedure for determining soil pH. The soil sample was dried at 40°C in an oven for 24 hours, then ground to obtain grains with a diameter of less than 2 mm. For the production of one liter of soil solution, 150 g of dry soil (Vsoil ~170mL) were introduced into a 1L flask and a volume of deionized water (V_{H2O}) equal to five times Vsoil were added. The closed flask was stirred for one hour on an orbital shaker, then the mixture was left to stand for an hour. The soil juice was then recovered by vacuum filtration (Büchner) after homogenization of the mixture (pH = 7.1). The elements of interest present in the soil juice were dosed to obtain a "blank" which was subtracted to calculate the release rate.

Pair Distribution function analysis

The simulated PDF for Mg_RAl hydroxide layers were calculated using PDFgui software[1] . Powder samples ground with a mortar were placed in glass capillaries of 0.7 mm diameter. An empty capillary of the same type was measured in the same way for background substraction. Data were recorded over the 1-145° 2θ range, which corresponds to an accessible maximum value for the scattering vector Q max of 21.4 Å−1. Data merging, background substraction, and Kα2 stripping were done using HighScore Plus software provided by PANalytical Corporation. It was also used to generate a corrected and normalized total scattering structure functions S(Q) and considering the bulk chemical

compositions given in Table 1. Finally, the PDF or G(r) were calculated from the Fourier transforms of S(Q) truncated at 21 Å−1. The comparison with Mg_2AlCO_3 (from a previous unpublished study) and Mg2AlCl reference samples clearly shows that phosphate intercalation leads to significant changes on the PDF. All the contributions of all pairs of atoms add up in the PDF and the integrated intensity of PDF peaks depends both on the number of atoms pairs occurring at the respective distances and on the X-ray scattering power of the atoms involved in these pairs. Here, the distance range examined is limited to the interlayer distance, thereby the peaks observed are mainly from distances of the hydroxide layer plus one interlayer. In the case of LDH, a major contribution is expected from the hydroxide layer on PDF peaks while the contribution of the interlayer species, which have weaker scattering and are subject to significant static and dynamic disorders (base of the peaks). Thus, the six main peaks labelled P1 to P6 are often considered as dominated by the contributions of M-OH and M-M pairs corresponding to the successive coordination shells around cations as shown in Figure S2B. The contributions of interlayer species can modify the intensity of M-OH pairs as shown here according to their scattering power.

[1] C L Farrow, P Juhas, J W Liu, D Bryndin, E S Božin, J Bloch, Th Proffen and S J L Billinge, PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals. J. Phys.: Condens. Matter 19 335219. DOI 10.1088/0953-8984/19/33/335219

Figures

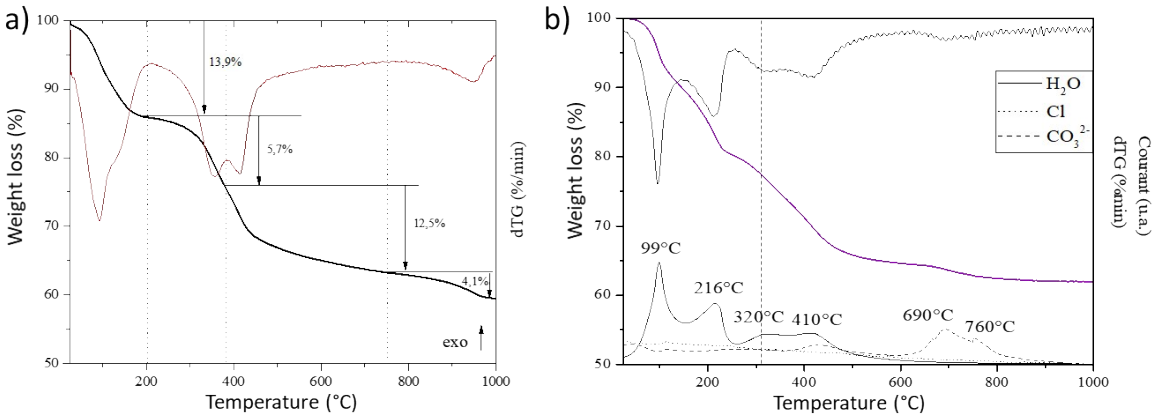


Figure S1. TGA and DTG analyses of Mg_2AlCl a) and Mg_2AlP b) in the case of the latter, the analysis was coupled with mass spectroscopy

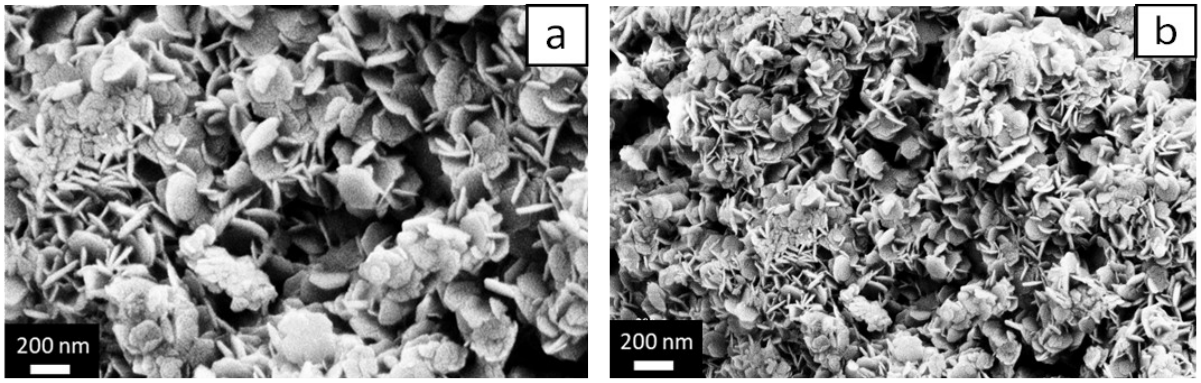
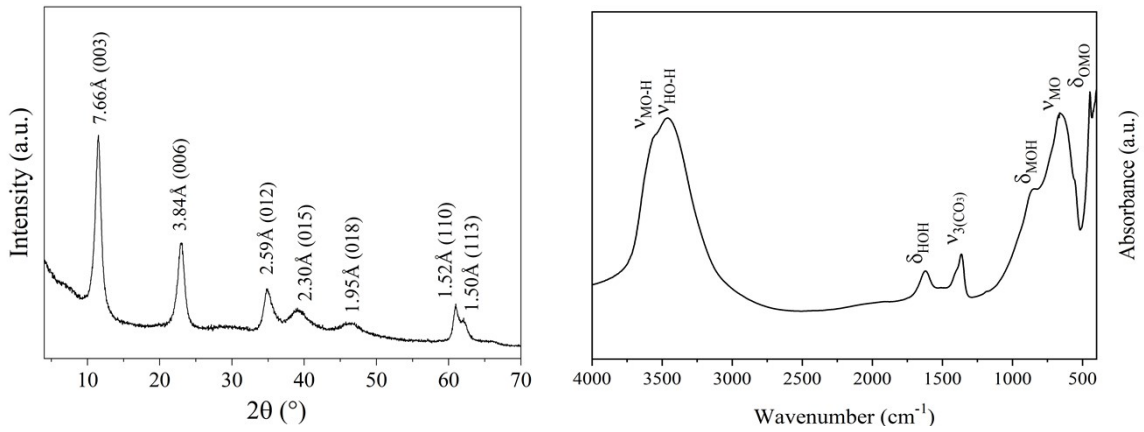


Figure S2. SEM images of Mg_2AlCl a) and Mg_2AlP b)



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72 Figure S3. XRD pattern of Mg_2AlCl (left), FTIR spectrum of Mg_2AlCl (right)

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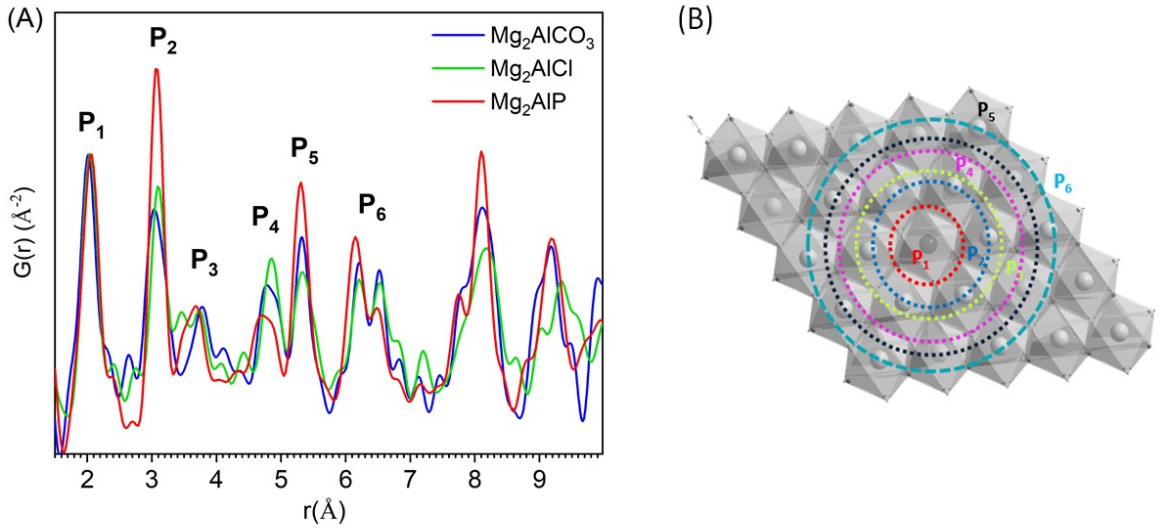

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76 Figure S4. Experimental pair distribution function (PDF) also known as G(r) for r < 10 Å for:
77 Mg_2AlCO_3 (blue line), Mg_2AlCl (green line), Mg_2AlP (red line) (A). Representation of the edge-
78 sharing octahedral layer where the contributions P1 to P6 are materialized (see text) (B).

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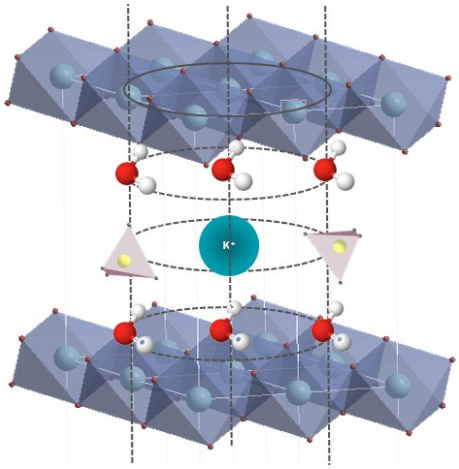


Figure S5. Schematic representation of the arrangement of interlayer species in sample Mg_2AlP on P2 coordination shell.

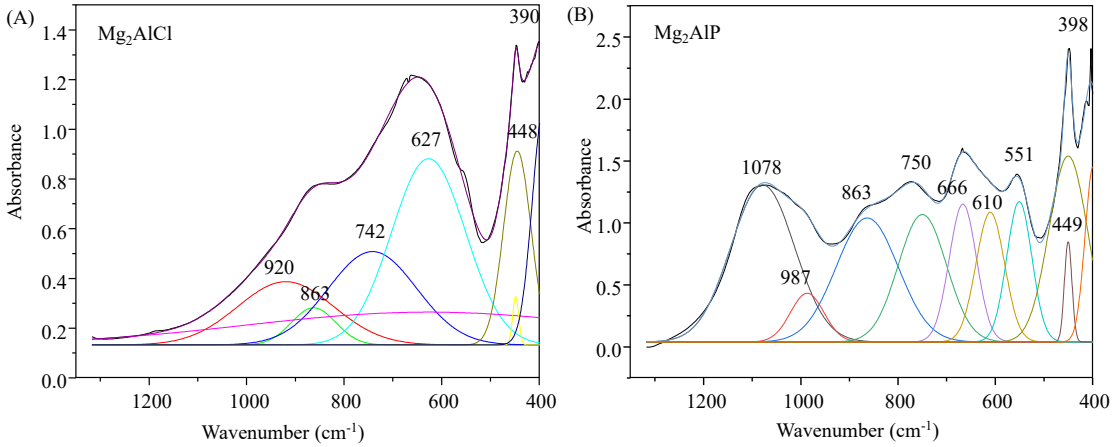
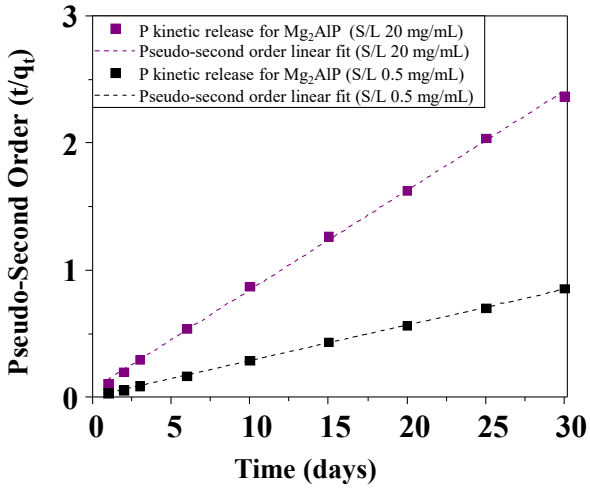


Figure S6. Deconvolution of FTIR spectra in the low energy domain of (A) Mg_2AlCl and (B) Mg_2AlP using Gaussian line shapes.



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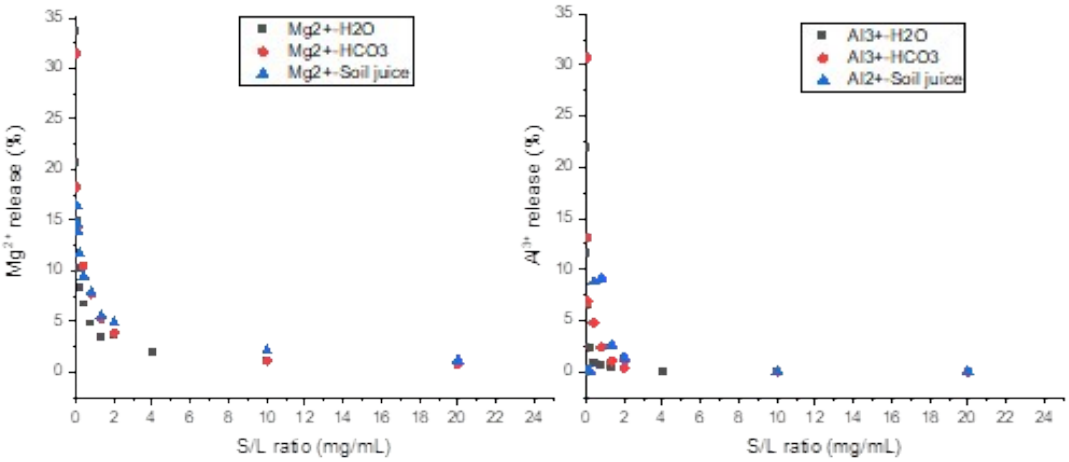
90 Figure S7. Kinetic of P release from Mg_2AlP at S/L at 20 mg/mL and 0.5 mg/mL (experimental data

91 points and fitted curves (dashed lines).



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93 Figure S8. Mg^{2+} and Al^{3+} released (%) by Mg_2AlP at different S/L ratios in water, HCO_3^- solution

94 and soil juice.

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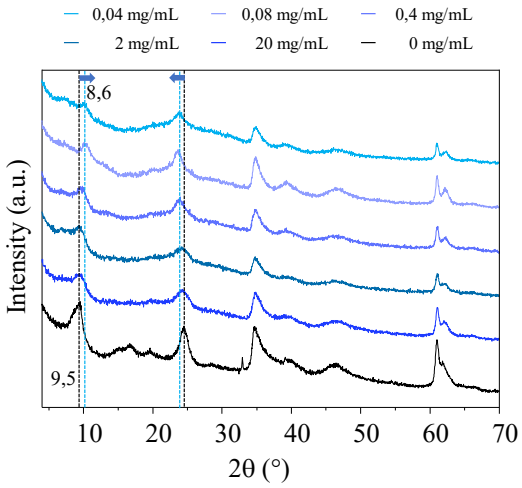

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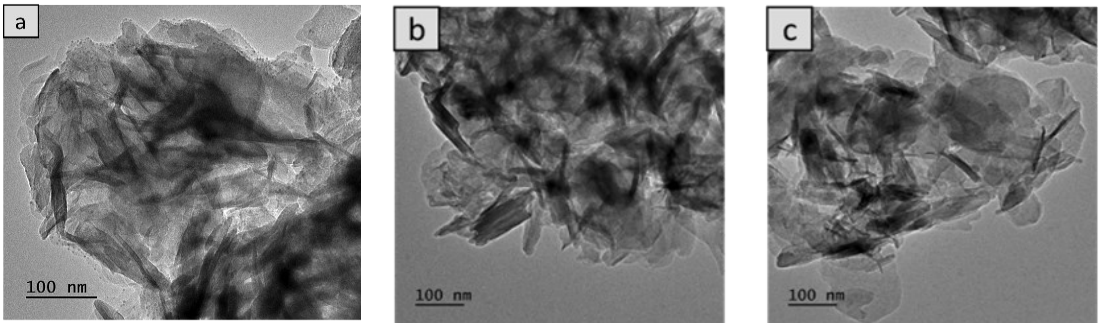
97 Figure S9. XRD of Mg_2AlP after 6 days release in H_2O at various S/L ratio.



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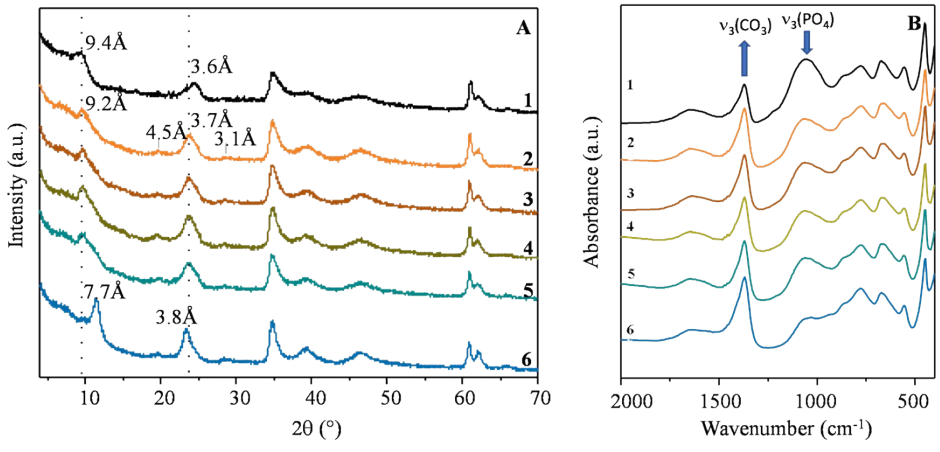
99 Figure S10. TEM images of a) Mg_2AlP and residues after release in water at b) S/L 20 mg/mL and c)

100 S/L 0.04 mg/mL.



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102 Figure S11. A) XRD patterns and B) FTIR spectra of Mg_2AlP (1) and solid residues after P release

103 trials (24h) at pH=4 (2), pH=6 (3), pH=8 (4), pH=10 (5), pH = 12 (6).

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105 **Table**

106 Table S1: Phosphorus loading for 100% phosphate exchanged on $Mg_2Al(OH)_6Cl.2H_2O$.

Phosphate species	PO_4^{3-}	HPO_4^{2-}	$H_2PO_4^-$
P loading (mgP/gLDH)	22.6	33.9	67.8

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108 Table S2: Release kinetic models.

Pseudo-second order model	Elovich model	Intraparticular diffusion model
$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^{\,2}} + \frac{1}{Q_e} t$	$Qt = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$	$Qt = k \times t^{1/2} + L$
t : time Q_t : [P] concentration at t Q_e : equilibrium concentration, k_2 : reaction rate constant	α : initial rate (mg.g-1.min-1) β : desorption constant as a function of release media, material surface and temperature	k : reaction rate constant L : limit layer thickness

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110 Table S3: ICP-OES chemical composition of soil solution.

Chemical element	Na	K	Mg	Ca	Fe	Al	P	Zn	humic acid
Concentration (ppm)	>35	20	3.4	>35	-	0.0	0.5	0.0	~ 10

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