

Supporting Information

for

Standard Protocol and Quality Assessment of Soil Phosphorus Speciation

by P K-edge XANES Spectroscopy

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Table S1. Comparison of Results of Linear Combination Fitting Performed on Phosphorus K-edge XANES Spectra of Three Exemplary Soil Samples Using Either (i) our Standard Protocol for Baseline-Correction and Edge-Step Normalization (Short Range Parameters) or (ii) Consistent, Traditional Baseline-Correction and Edge-Step Normalization Performed with ATHENA^{1a}

soil ^c	soil sample characteristics ^b							AlPO ₄	
	parent material	pH [CaCl ₂]	C _{org} [mg g ⁻¹]	C _{inorg} [mg g ⁻¹]	P _{tot} [mg g ⁻¹]	Fe _{ox} [mg g ⁻¹]	Al _{ox} [mg g ⁻¹]	new standard protocol	traditional method ATHENA
TUT topsoil	Limestone	7.4	108.00	37.23	1.12	2.31	3.14	0.00	0.00
MIT topsoil	Gneiss	3.8	74.51	0.00	0.88	10.33	3.28	0.00	0.00
BBR subsoil	Basalt	4.5	9.27	0.00	1.54	6.36	5.28	0.00	0.00

Table S1 cont.

FePO ₄		HydAp		PhyAc		χ^2		R factor	
new standard protocol	traditional method ATHENA	new standard protocol	traditional method ATHENA	new standard protocol	traditional method ATHENA	new standard protocol	traditional method ATHENA	new standard protocol	traditional method ATHENA
0.04	0.11	0.41	0.13	0.55	0.77	1.93	21.06	0.00331	0.06023
0.40	0.79	0.10	0.00	0.50	0.21	1.87	68.78	0.00299	0.13411
0.38	0.39	0.31	0.32	0.31	0.30	0.38	0.50	0.00062	0.00203

^aNote that the LC fitting improved, when using our new standard protocol (as seen from the fitting statistics: χ^2 and *R* factor).

^bSoil samples are characterized by parent material, pH, as well as concentrations of organic carbon (C_{org}), of inorganic carbon (C_{inorg}), total phosphorus (P_{tot}), and oxalate-extractable iron (Fe_{ox}) and aluminum (Al_{ox}).

^cSamples TUT, MIT and BBR are from a calcareous topsoil (Ah horizon) near Tuttlingen (Germany), an acidic topsoil (Ah) near Mitterfels (Germany), and an acidic subsoil (Bw) near Bad Brückenau (Germany), respectively.

Table S2. Optimized Ranges for Baseline-Correction and Edge-Step Normalization as Identified with our Standard Protocol for Different Ternary Mixtures Comprised of Aluminum Phosphate, Iron Phosphate, Hydroxyapatite, and Phytic Acid Diluted with Fine-Ground Quartz to a Total P Concentration of 2 mg g^{-1a}

mixture	baseline correction				normalization			
	lower limit		upper limit		lower limit		upper limit	
	long range	short range	long range	short range	long range	short range	long range	short range
1:1:1:0	-70.0	-29.0	-12.5	-17.0	+150.0	+34.0	+310.0	+69.0
2:1:1:0	-55.0	-37.0	-22.5	-18.0	+135.0	+36.5	+290.0	+63.0
1:2:1:0	-70.0	-34.0	-17.5	-18.0	+135.0	+35.0	+305.0	+63.0
1:1:2:0	-60.0	-41.0	-30.0	-13.0	+135.0	+35.5	+330.0	+60.0
1:1:0:1	-40.0	-30.0	-10.0	-13.0	+145.0	+34.0	+335.0	+64.0
2:1:0:1	-60.0	-36.0	-10.0	-11.0	+140.0	+34.5	+325.0	+66.0
1:2:0:1	-40.0	-28.0	-25.0	-16.0	+160.0	+35.5	+325.0	+63.0
1:1:0:2	-75.0	-47.0	-30.0	-14.0	+130.0	+35.0	+340.0	+60.0
1:0:1:1	-55.0	-28.0	-30.0	-13.0	+135.0	+37.5	+305.0	+60.0
2:0:1:1	-40.0	-46.0	-20.0	-17.0	+130.0	+35.5	+335.0	+65.0
1:0:2:1	-80.0	-45.0	-17.5	-10.0	+145.0	+34.5	+310.0	+67.0
1:0:1:2	-50.0	-40.0	-20.0	-18.0	+150.0	+36.0	+330.0	+63.0
0:1:1:1	-55.0	-32.0	-30.0	-18.0	+120.0	+36.5	+340.0	+61.0
0:2:1:1	-80.0	-29.0	-20.0	-15.0	+130.0	+33.5	+315.0	+67.0
0:1:2:1	-80.0	-28.0	-22.5	-16.0	+130.0	+38.5	+290.0	+60.0
0:1:1:2	-40.0	-34.0	-12.5	-18.0	+145.0	+36.0	+325.0	+66.0

^aMixture abbreviations represent proportions of P concentration, i.e., AlPO₄-P/FePO₄-P/HydAp-P/PhyAc-P. A longer and a shorter parameter range were tested. Range values are presented in eV with respect to the edge energy of the mixture spectrum, respectively.

Table S3. Simple Linear Regression Results (Slope, Intercept and Coefficient of Determination *R*²) of the Linear Combination Fitting Results Obtained Using our Standard Protocol for the Short Range Baseline-Correction and Normalization Parameters Versus the LC Fitting Results Obtained Using our Standard Protocol for the Long Range Baseline-Correction and Normalization Parameters for Every Standard (Aluminum Phosphate, Iron Phosphate, Hydroxyapatite, and Phytic Acid)^a

	slope	intercept	R^2
AlPO ₄	0.995	−0.0008	0.998
FePO ₄	1.004	0.0083	0.998
HydAp	0.995	0.0002	0.999
PhyAc	0.979	−0.0008	0.998

^a R^2 is generally high and the intercept small, indicating strong correlation. Note that the slope closely equals one in every standard.

Table S4. Phosphorus (P) Speciation of 16 Ternary Mixtures Comprised of Aluminum Phosphate, Iron Phosphate, Hydroxyapatite, and Phytic Acid Diluted with Fine-Ground Quartz to a Total P Concentration of 2 mg g^{−1} and Results of Linear Combination Fitting Conducted on Baseline-Corrected and Edge-Step-Normalized (Larger Energy Ranges) P K-edge XANES Spectra^a

mixture	portion of total P				LC fitting results (fraction of 1)				fitting statistics		deviation from total P (relative and mean of absolute)				
	AlPO ₄	FePO ₄	HydAp	PhyAc	AlPO ₄	FePO ₄	HydAp	PhyAc	χ^2	R factor	AlPO ₄	FePO ₄	HydAp	PhyAc	mean
1:1:1:0	0.35	0.32	0.34	0	0.27	0.35	0.34	0.05	0.09	0.00015	−0.08	+0.03	0.00	+0.05	0.04
2:1:1:0	0.52	0.23	0.25	0	0.39	0.33	0.27	0.01	0.11	0.00020	−0.13	+0.10	+0.02	+0.01	0.06
1:2:1:0	0.26	0.48	0.26	0	0.19	0.53	0.28	0.00	0.09	0.00016	−0.07	+0.05	+0.02	0.00	0.04
1:1:2:0	0.26	0.24	0.50	0	0.17	0.28	0.54	0.00	0.09	0.00015	−0.09	+0.04	+0.04	0.00	0.04
1:1:0:1	0.34	0.31	0	0.35	0.26	0.46	0.00	0.28	0.13	0.00021	−0.08	+0.15	0.00	−0.07	0.07
2:1:0:1	0.51	0.23	0	0.26	0.55	0.31	0.00	0.14	0.10	0.00016	+0.04	+0.08	0.00	−0.12	0.06
1:2:0:1	0.26	0.47	0	0.27	0.23	0.63	0.00	0.14	0.12	0.00019	−0.03	+0.16	0.00	−0.13	0.08
1:1:0:2	0.25	0.23	0	0.52	0.27	0.39	0.01	0.32	0.21	0.00036	+0.02	+0.16	+0.01	−0.20	0.10
1:0:1:1	0.33	0	0.32	0.35	0.30	0.02	0.42	0.27	0.09	0.00015	−0.03	+0.02	+0.10	−0.08	0.06
2:0:1:1	0.50	0	0.24	0.26	0.51	0.01	0.31	0.17	0.10	0.00018	+0.01	+0.01	+0.07	−0.09	0.04
1:0:2:1	0.25	0	0.49	0.26	0.18	0.00	0.52	0.29	0.14	0.00025	−0.07	0.00	+0.03	+0.03	0.03
1:0:1:2	0.25	0	0.24	0.51	0.21	0.01	0.32	0.47	0.10	0.00018	−0.04	+0.01	+0.08	−0.04	0.04
0:1:1:1	0	0.31	0.33	0.36	0.00	0.33	0.40	0.27	0.16	0.00028	0.00	+0.02	+0.07	−0.09	0.04
0:2:1:1	0	0.48	0.25	0.27	0.00	0.55	0.30	0.15	0.09	0.00015	0.00	+0.07	+0.05	−0.12	0.06
0:1:2:1	0	0.23	0.50	0.27	0.00	0.25	0.60	0.15	0.11	0.00018	0.00	+0.02	+0.10	−0.12	0.06
0:1:1:2	0	0.23	0.25	0.52	0.00	0.30	0.36	0.35	0.13	0.00021	0.00	+0.07	+0.11	−0.17	0.09

^aMixture abbreviations represent proportions of P concentration, i.e., AlPO₄–P/FePO₄–P/HydAp–P/PhyAc–P. Furthermore, LC fitting statistics (χ^2 and R factor) from the fitting procedure and relative deviations of the LC fitting results from the actual proportions are shown.

Table S5. Simple Linear Regression Results (Slope, Intercept and Coefficient of Determination R^2) of the Linear Combination Fitting Results Obtained Using our Standard Protocol for the Short Range Baseline-Correction and Normalization Parameters and of Fitting Results Obtained with ATHENA¹ with Traditional Consistent Normalization Parameters (Baseline from −40 to −10 eV and Normalization from +35 to +65 eV) Versus the Real Portions of P for Every Standard (Aluminum Phosphate, Iron Phosphate, Hydroxyapatite, and Phytic Acid)^a

	Slope		Intercept		R^2	
	new standard protocol	traditional method ATHENA	new standard protocol	traditional method ATHENA	new standard protocol	traditional method ATHENA
AlPO ₄	0.920	0.822	0.012	−0.038	0.925	0.722
FePO ₄	1.170	1.283	0.013	0.057	0.953	0.718
HydAp	1.129	1.135	0.014	0.011	0.976	0.969
PhyAc	0.728	0.686	0.005	0.001	0.884	0.828

^aNote that the correlation of the regression model, as seen by R^2 , increases when using our standard protocol. The error of the LC fitting decreases (i.e., the slope is closer to 1.0, compared to the respective slope of the traditional method) for every standard when applying the standard protocol. Intercepts are generally low and R^2 values also suggest strong relationships, especially for AlPO₄ and FePO₄ when using our standard protocol.

REFERENCES

(1) Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **2005**, 12, (4), 537–541.