

Supporting Information for:

**A New Chiral Uranyl Phosphonate Framework Consisting
of Achiral Building Units Generated from Ionothermal
Reaction: Structure and Spectroscopy Characterizations**

Tao Zheng,^{a,b} Yang Gao,^{a,b} Lanhua Chen,^{a,b} Zhiyong Liu,^{a,b} Juan Diwu,^{*,a,b} Zhifang Chai,^{a,b} Thomas
E. Albrecht-Schmitt,^c Shuao Wang^{*,a,b}

a School for Radiological and Interdisciplinary Sciences (RAD-X), Soochow University, Jiangsu 215123, China.

b Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Jiangsu 215123, China.

c Department of Chemistry and Biochemistry, Florida State University, 95 Chieftain Way, Tallahassee, Florida 32306, United States.

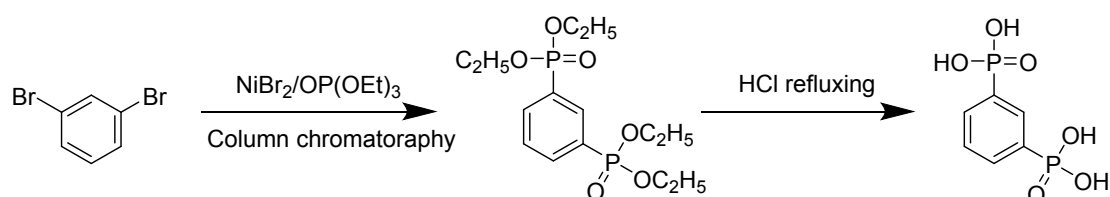
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exchange experiments of compound 1.**

S1. Synthesis of (1,3-phenylenebis(phosphonic acid) (1,3-pbpH₄)).

Materials: All chemicals used in the synthesis were obtained from commercial sources (J&K Chemical, Sinopharm Chemical Reagent) and used without further purification. Infrared spectra of chemicals were recorded on a Thermo Nicolet IS50 spectrophotometer in ATR mode. ¹H NMR were measured with Unity INOVA 400 instruments.



Scheme S1.

Tetraethyl 1,3-benzenediphosphonate. 1,3-dibromobenzene (19.5 g, 82.7 mmol) and 1,3-diisopropylbenzene (40 mL) were heated to 180 °C for 20 min under nitrogen atmosphere, with stirring. Nickel(II) bromide (2.34 g, 10.7 mmol) was added in the mixture. After 10 min, Triethyl phosphite (45 mL, 260.8 mmol) was added dropwise. After 1 ml was added, waiting for nearly 30 min, the color of mixture was change from near-black to turquoise, finally into yellow. The left triethyl phosphite was added in 5 h. The reaction was hold for 24 h, and then cooled to room temperature. The residue was extracted by ethyl acetate (100 mL) and water (100 mL) for triple times. The organic phase was collected and the volatile components (ethyl acetate, 1,3-diisopropylbenzene, and triethyl phosphite) were distilled off by vacuum. The brown oil-like residue was obtained. Chromatography of the residue was performed on a column of silica gel eluted with chloroform. Yellowish oil was finally obtained, with yield is 77.6 % (22.5g, 64.2 mmol). ¹H NMR(400 MHz, CDCl₃): δ 8.19-8.12 (1H, C₆H), 7.96-7.91 (2H, C₆H₂), 7.54-7.51 (1H, C₆H), 4.15-3.99 (8H, PO-CH₂-C), 1.28-1.25 (12H, PO-C-CH₃).

(1,3-phenylenebis(phosphonic acid) (1,3-pbpH₄)). A mixture of tetraethyl 1,3-benzenediphosphonate (10.0g, 28.6 mmol), concentrated hydrochloric acid (37 mL) was refluxed over a night. The solution was filtered and the filtrate was evaporated to yield **1,3-pbpH₄** (5.55g, 23.3 mmol) as a white solid. Yield: 81.5 %. ¹H NMR(400 MHz, D₂O): δ 8.08-8.02 (1H, C₆H), 7.92-7.86 (2H, C₆H₂), 7.61-7.57 (1H, C₆H),

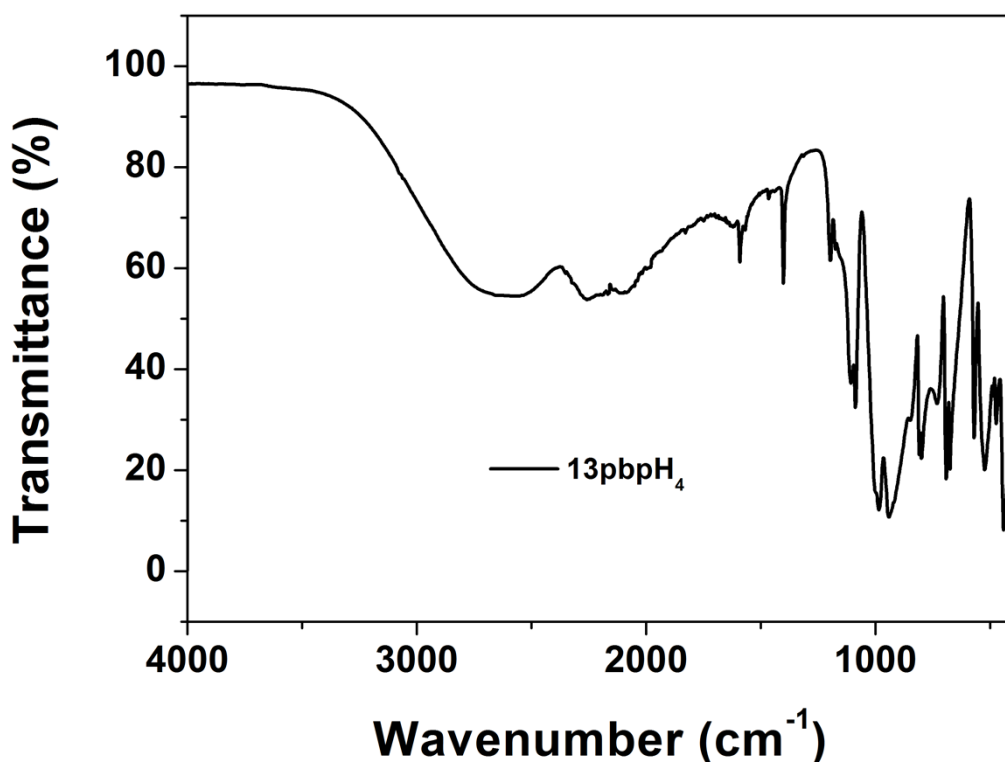
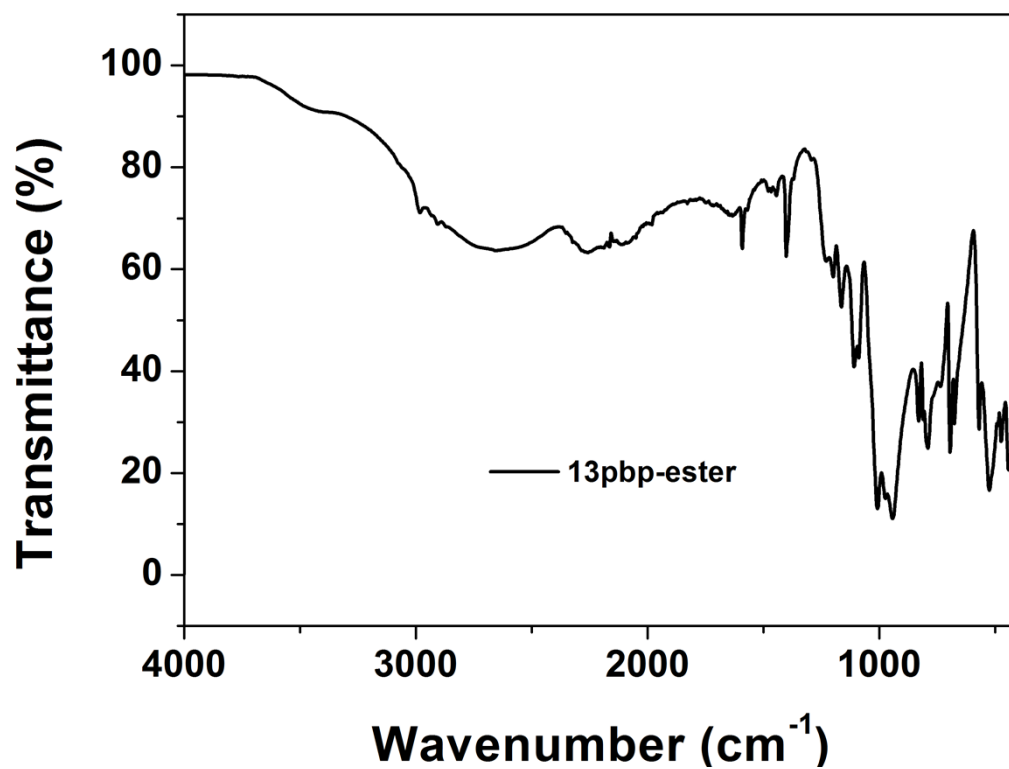


Fig. S1 IR of Tetraethyl 1,3-benzenediphosphonate (up) and 1,3-phenylenebis(phosphonic acid) (bottom).

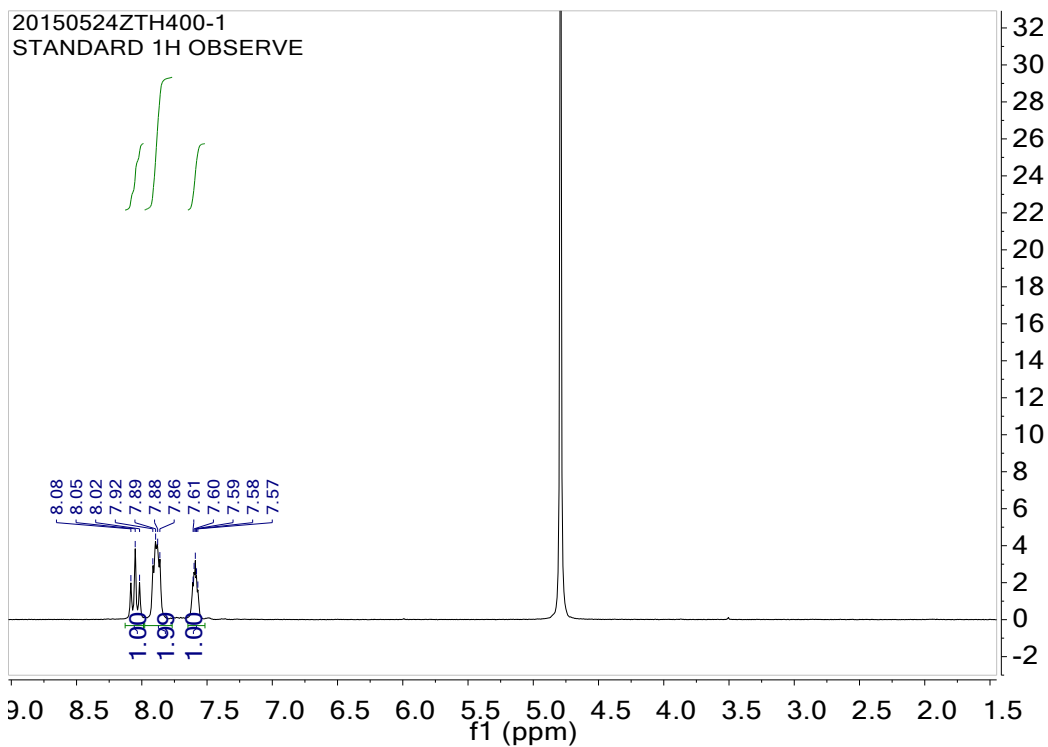
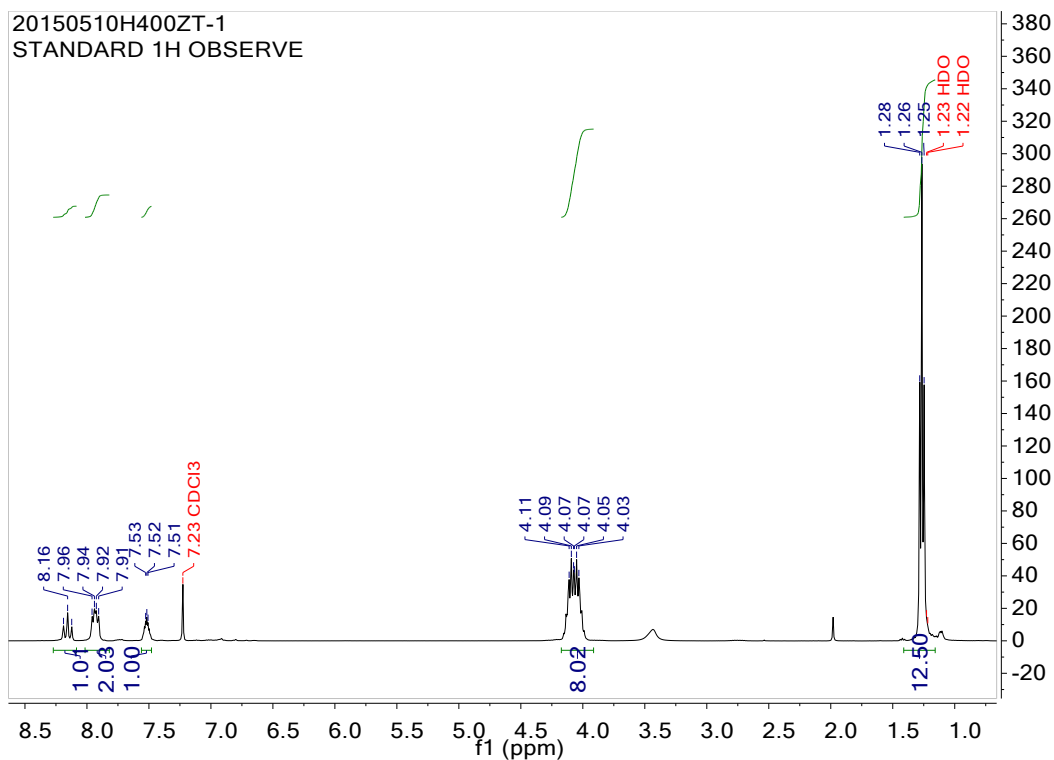


Fig. S2 ¹H NMR of Tetraethyl 1,3-benzenediphosphate (up) and 1,3-phenylenebis(phosphonic acid) (bottom).

S2. Circular Dichroism (CD) spectrum and Cs^+ and Sr^{2+} exchange experiments of compound 1.

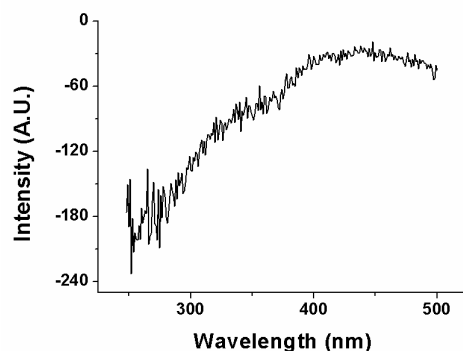


Fig. S3 Circular Dichroism of compound $[\text{C}_4\text{mim}][(\text{UO}_2)_2(\mathbf{1},\mathbf{3}\text{-pbpH})(\mathbf{1},\mathbf{3}\text{-pbpH})\cdot\text{Hmim}] (\mathbf{1})$.

Cs^+ and Sr^{2+} exchange experiments:

Cs^+ and Sr^{2+} exchange experiments were studied by soaking 2 mg of compound **1** in 0.5 M CsCl and SrCl_2 water solution, respectively, which were put on a shaker. The EDS spectra were performed on the samples for desired contacting time 1, 2, and 5 days for Cs^+ and 1, 3, and 5 days for Sr^{2+} . The EDS results show that the uptake of Cs^+ is higher than Sr^{2+} , under similar conditions (Fig. S4 and S5), suggesting a decent exchange selectivity towards Cs^+ possessed by compound **1**. The mechanism accounting for such an unexpected selectivity is under further investigation.

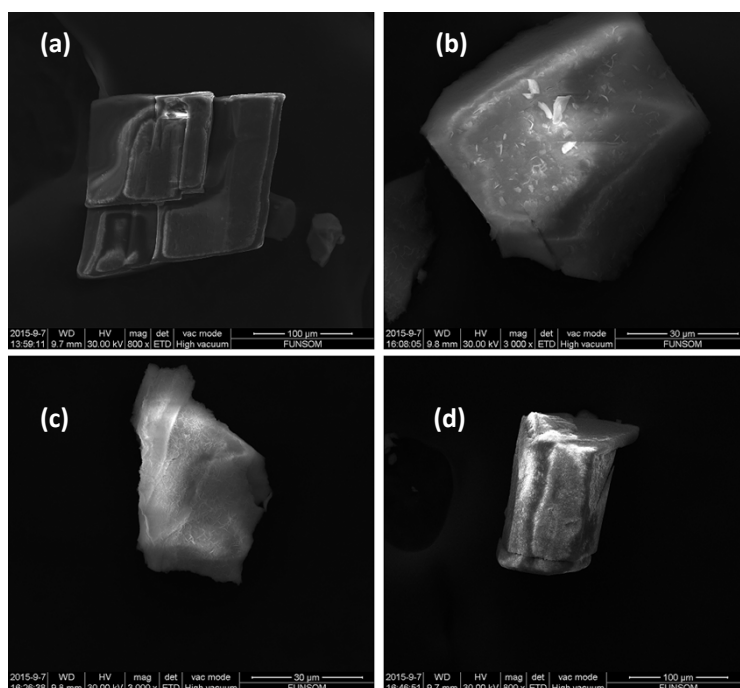


Fig. S4 SEM images for EDS spectra of compound **1** soaking in 0.5 M CsCl solution for 0 (a), 1 (b), 2 (c), and 5 (d) days.

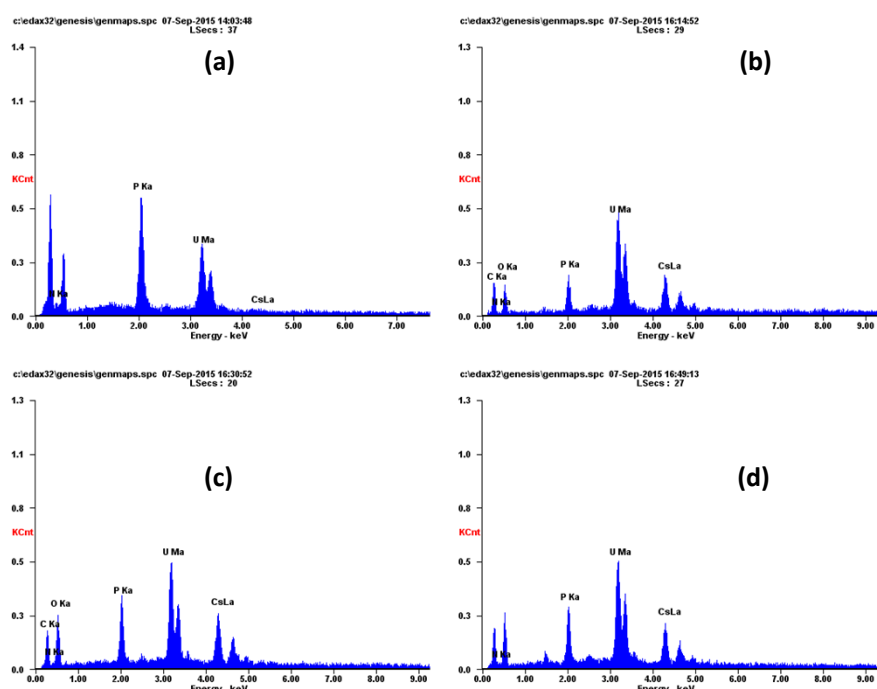


Fig. S5 EDS spectra from crystals of compound **1** soaking in 0.5 M CsCl solution for 0 (a), 1 (b), 2 (c), and 5 (d) days.

Table S1. Ratio of selected elements for Cs⁺ exchange experiments.

<i>Element</i>	<i>0 Day</i>		<i>1 Day</i>		<i>2 Day</i>		<i>5 Day</i>	
	<i>Wt%</i>	<i>At%</i>	<i>Wt%</i>	<i>At%</i>	<i>Wt%</i>	<i>At%</i>	<i>Wt%</i>	<i>At%</i>
<i>NK</i>	22.88	60.25	06.06	33.71	05.10	30.46	04.71	28.11
<i>PK</i>	26.56	31.62	12.95	32.58	12.19	32.90	13.16	35.49
<i>UL</i>	48.09	07.45	53.16	17.40	55.41	19.47	54.85	19.25
<i>CsL</i>	02.46	00.68	27.83	16.32	27.30	17.17	27.28	17.15
<i>Matrix</i>	Correction	ZAF						

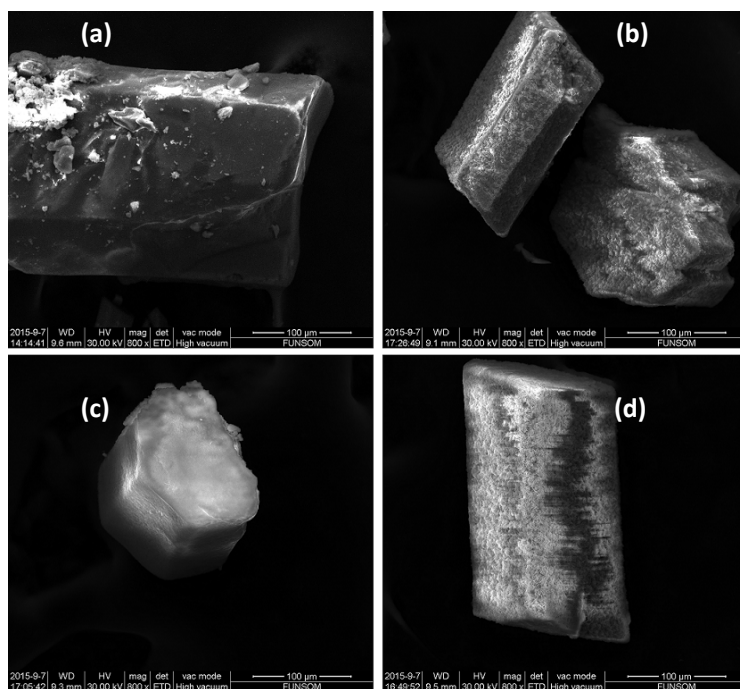


Fig. S6 SEM images for EDS spectra of compound **1** soaking in 0.5 M SrCl₂ solution for 0 (a), 1 (b), 3 (c), and 5 (d) days.

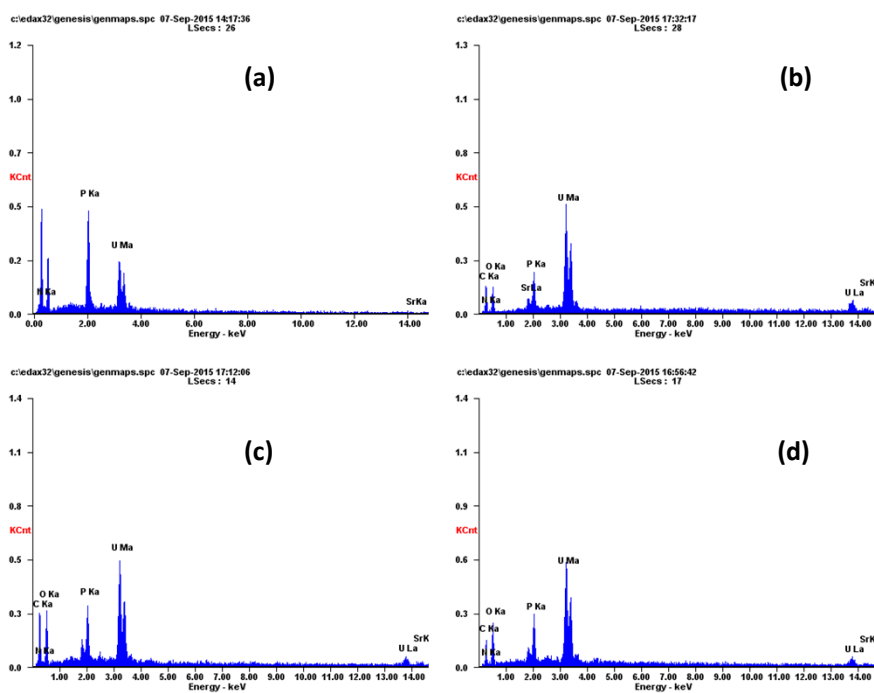


Fig. S7 EDS spectra from crystals of compound **1** soaking in 0.5 M SrCl₂ solution for 0 (a), 1 (b), 3 (c), and 5 (d) days.

Table S2. Ratio of selected elements for Sr²⁺ exchange experiments.

Element	0 Day		1 Day		3 Day		5 Day	
	Wt%	At%	Wt%	At%	Wt%	At%	Wt%	At%
NK	23.04	59.78	24.06	60.26	03.98	27.31	04.83	32.96
PK	27.27	32.00	26.31	29.81	10.16	31.58	08.34	25.73
UL	47.28	07.22	39.29	05.79	76.65	30.99	77.44	31.07
SrK	02.42	01.00	10.34	04.14	09.21	10.12	09.39	10.23
Matrix	Correction	ZAF						