Zinc isotope fractionation during sorption onto kaolinite

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Supplementary information

Number of pages: 19

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Number of figures: 7

Number of table: 1

Supplementary information 1

Potentiometric titration of kaolinite KGa-2

Acid-base titrations of kaolinite were realized in a Titrando unit (Metrohm) at 22 ± 2 °C. Two burettes were filled with KOH 0.10 M and HCl 0.10 M respectively. Experiments were carried out in glass vessel isolated by a constant flux of N_2 gas and previously equilibrated with NaOH, milliQ water and $NaNO_3$ solutions. Measurement of pH potential was realized using a combination of glass (6.0133.100, Metrohm) and Ag/AgCl (6.0726.107, Metrohm) reference electrodes. A potential-pH calibration was achieved with 4.01, 7.01 and 10.01 pH buffers before and after each batch of titration. Previous to kaolinite titration, a blank titration with $NaNO_3$ was performed to subtract the electrolyte contribution to H^+ sorption. Kaolinite at 20 g/L was equilibrated overnight with the $NaNO_3$ electrolyte solution. Blank and kaolinite titrations were done twice with KOH 0.10 M from -200mV to +200 mV and reversely with HCl 0.10 M. Points were recorded when drift was smaller than 0.1 mV/min or after 30 min if drift criteria was not reached. Experiments were performed at three different ionic strengths (0.005 M, 0.01 M and 0.1 M $NaNO_3$). Results (dots) are presented on fig S1 and fitted with our two-site model (lines).
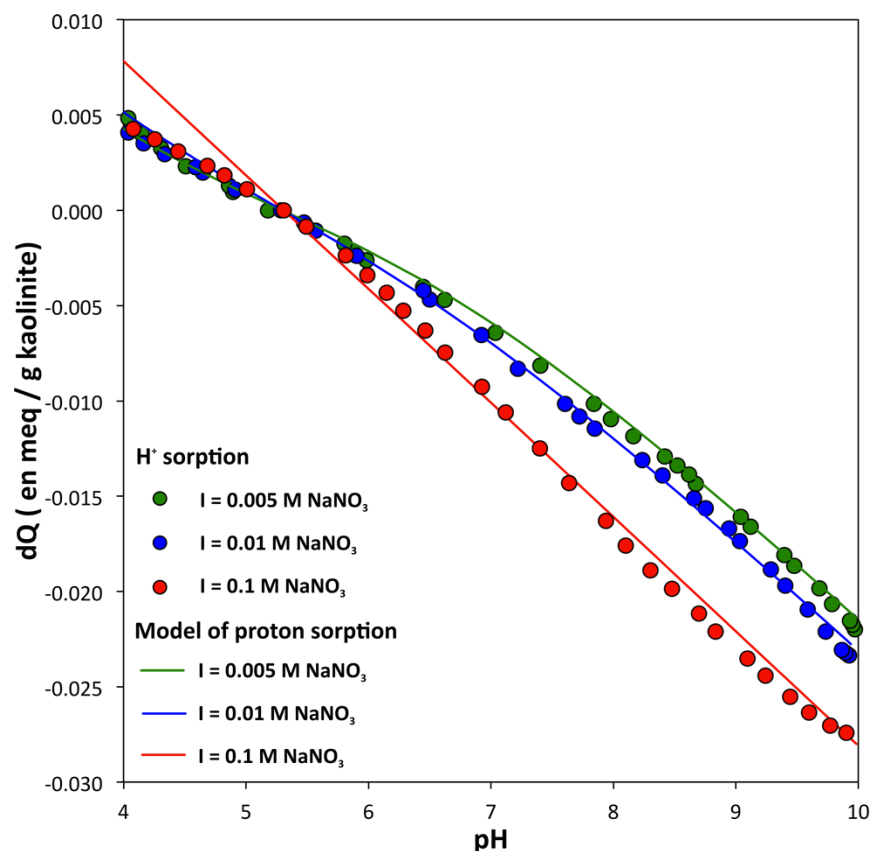
Figure S1: Proton binding to kaolinite. Dots and lines report measurements and models respectively.

Supplementary information 2

Instrumental mass bias correction using power law

To correct for the mass bias occurring during zinc isotope measurement with MC-ICP-MS Neptune Plus, a Cu-doping technique was adopted. A Cu solution with known isotopic ratio $(^{65/63}Cu = 0.44574)$[1] is added to the sample and the standard solutions. The chosen exponential law correction was previously used by different authors for Zn and Cu isotope analysis[2-4] and is expressed here for $^{66/64}Zn$ and $^{65/63}Cu$ ratios.

It is based on the empirical observation that β, the isotope fractionation factor, depends on the difference of masses between the two considered isotopes:

$$\left(\frac{^{66}Zn}{^{64}Zn}\right)^{meas}_{sple} = \left(\frac{^{66}Zn}{^{64}Zn}\right)^{true}_{sple} * \left(\frac{^{66}M}{^{64}M}\right)^{\beta_{Zn}} \qquad \text{for Zn} \quad (SI.\,1)$$

$$\left(\frac{^{65}Cu}{^{63}Cu}\right)^{meas}_{sple} = \left(\frac{^{65}Cu}{^{63}Cu}\right)^{true}_{sple} * \left(\frac{^{65}M}{^{63}M}\right)^{\beta_{Cu}} \qquad \text{for Cu} \quad (SI.\,2)$$

where meas and true refer to the measured and true ratios. ^{63}M, ^{64}M, ^{65}M and ^{66}M are atomic masses for ^{63}Cu, ^{64}Zn, ^{65}Cu and ^{66}Zn isotopes. Each sample measurement is bracketed by the measurement of an in-house standard solution with known Cu and Zn isotopic ratios ($^{66/64}Zn$ = 0.56505 and $^{65/63}Cu$ = 0.44574)[1]. From the repeated measurement of this standard solution the linear relationship between β_{Zn} and β_{Cu} is determined:

$$\beta_{Zn} = a\,\beta_{Cu} + b \qquad \text{were a and b are adjusted constant values} \quad (SI.3)$$

For each sample and standard measurement, the β_{Cu} factor is calculated from the measured and true values (eq. 2) and the $\beta_{Zn_{corr.}}$ is determined from eq. SI.3.

$$\beta_{Zn\,corr.} = a\,\beta_{Cu} + b \qquad (SI.4)$$

For each standard and sample, a mass-bias corrected $^{66/64}Zn$ is calculated

$$\left(\frac{^{66}Zn}{^{64}Zn}\right)^{corr.}_{sple} = \left(\frac{^{66}Zn}{^{64}Zn}\right)^{meas}_{sple} * \left(\frac{^{66}M}{^{64}M}\right)^{-\beta_{Zn\,corrected}} \qquad (SI.\,5)$$

Standard-sample bracketing measurement is triplicated, which allows for the determination of five distinct values of $\delta^{66}Zn$ following:

$$\delta^{66}Zn = \left(\frac{\left(\frac{^{66}Zn}{^{64}Zn} \right)_{sample.1}}{\left(\left(\frac{^{66}Zn}{^{64}Zn} \right)_{std.1} + \left(\frac{^{66}Zn}{^{64}Zn} \right)_{std.2} \right)/2} - 1 \right) * 1000 \quad (SI.6) \text{ for standard bracketing}$$

$$\delta^{66}Zn = \left(\frac{\left(\left(\frac{^{66}Zn}{^{64}Zn} \right)_{sample.1} + \left(\frac{^{66}Zn}{^{64}Zn} \right)_{sample.2} \right)/2}{\left(\frac{^{66}Zn}{^{64}Zn} \right)_{std.2}} - 1 \right) * 1000 \quad (SI.7) \quad \text{for sample bracketing}$$

Measurement reproducibility is calculated as the 2SD value of these 5 measurements[5].

To insure that Zn isotope ratios are correctly measured, a 3-isotopes diagram is reported in fig. S2. If the instrumental mass bias has been correctly corrected, and no mass independent fractionation is expected, two isotopic ratios from the same element (here $^{66/64}$Zn and $^{67/64}$Zn, and $^{66/64}$Zn and $^{68/64}$Zn) should follow a linear mass-dependent relationship. At equilibrium, the theoretical slope is dependent on the mass ratio of the three isotopes involved in the relationship and is expressed as $K_{equilibrium}$ notation as:

$$K_{equilibrium} = \left(\frac{\frac{1}{m_1} - \frac{1}{m_2}}{\frac{1}{m_1} - \frac{1}{m_3}} \right) \qquad \text{with } m_1 < m_2 < m_3 \quad (SI.8)$$

For δ^{66}Zn and δ^{67}Zn, $\mathbf{\delta^{67}Zn = 1.477 * \delta^{66}Zn}$

and for δ^{66}Zn and δ^{68}Zn, $\mathbf{\delta^{68}Zn = 1.942 * \delta^{66}Zn.}$

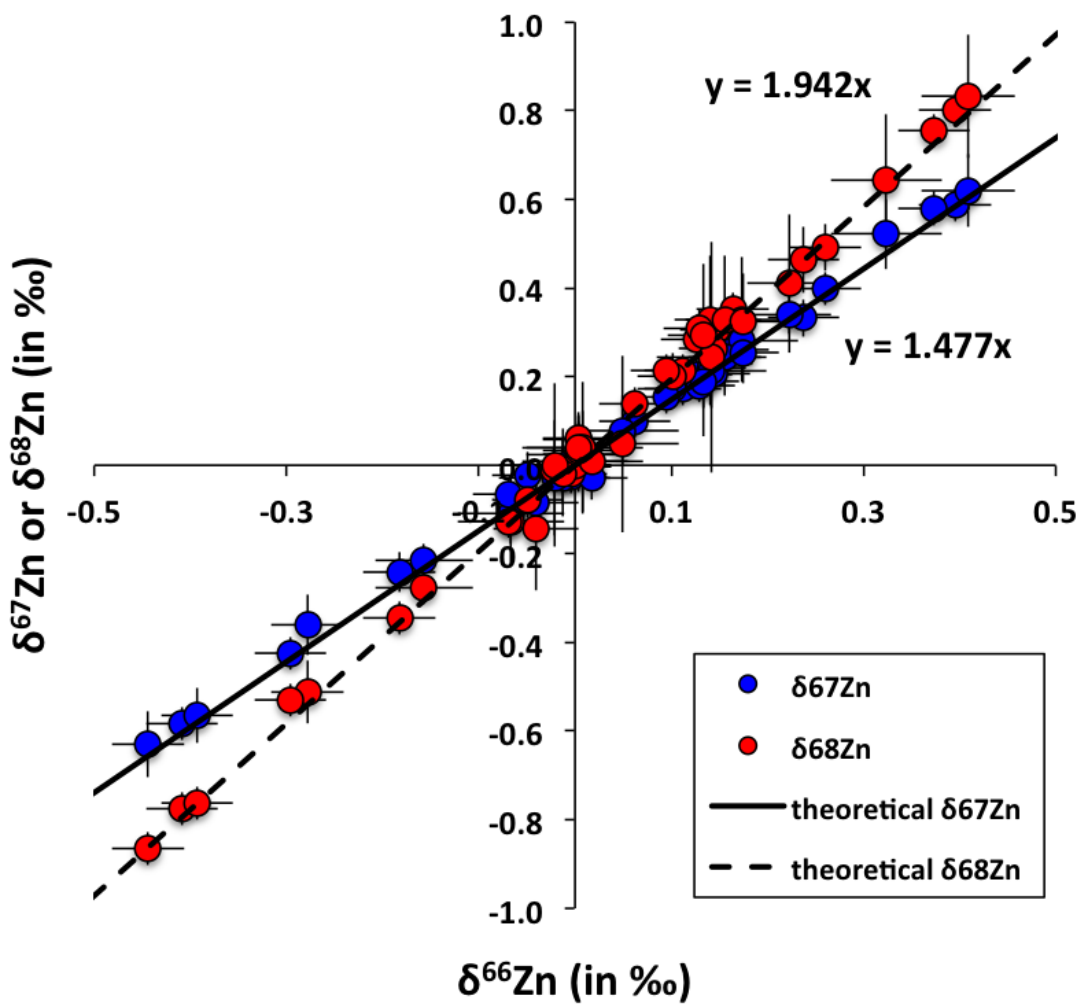These theoretical regressions are reported in fig. S2 and corroborate perfectly the measurements.

Figure S2: Three-isotopes diagram with all data measurements from this study and corrected from instrumental bias by the [65/63]Cu ratio and the exponential law. Theoretical mass dependent lines δ^{66}Zn vs. δ^{67}Zn and δ^{66}Zn vs. δ^{68}Zn are reported as straight and dotted lines respectively.

Supplementary information 3: Data table of sorption experiments:

Table S1: Data summary of Zn sorption experiments presented in this study. * refers to $\delta^{66}Zn$ sorbed corrected for crystalline Zn present in kaolinite. ** the respective 2σ value for both $\delta^{66}Zn$ measured in dissolved and particle phases was propagated for isotopic mass balance calculation.

Experiment	[kaol.] (in g/L)	pH	Initial [Zn] (µM)	[Zn]eq. solution (µM)	[Zn] sorbed (µmol Zn /m² kaol)	Sorbed Zinc (%)	1σ (%)	Crystalline Zn (µg)	% of Zn cryst. rel. to total solid Zn (%)	Dissolved $\delta^{66}Zn$ (‰)	2σ (%)	n	Sorbed $\delta^{66}Zn$ (‰)*	2σ (‰)	n	$\Delta^{66}Zn$ part.-diss. (‰)	Isotope mass balance (%)	2σ (‰)**	[Al]eq. solution (µM)
Sorption isotherm pH 4 IS=0.01N NaNO₃	5.00	4.09	5.5	3.0	0.024	45.43	1.88	1.53	48.4	0.02	0.04	3	0.34	0.05	3	0.32	0.17	0.06	<LOQ
	4.97	4.05	24.4	15.4	0.088	36.88	0.87												<LOQ
	4.87	4.08	46.2	33.5	0.126	27.46	0.53												<LOQ
	4.84	4.05	116.9	94.4	0.224	19.23	0.33												<LOQ
	4.75	4.02	161.3	136.4	0.253	15.44	0.24	1.54	8.8	0.00	0.04	3	0.10	0.04	3	0.10	0.02	0.06	<LOQ
	4.84	4.00	249.6	221.6	0.280	11.23	0.20	1.79	7.8	0.02	0.06	3	0.13	0.04	3	0.11	0.03	0.07	1.5
	4.81	4.04	371.9	340.2	0.319	8.53	0.12												<LOQ
	4.80	3.95	419.6	386.4	0.334	7.91	0.07												<LOQ
	4.69	4.04	542.3	513.0	0.302	5.41	0.07	1.86	7.5	0.01	0.04	3	0.01	0.06	3	0.00	0.01	0.07	2.4
	4.60	4.01	776.3	742.5	0.355	4.36	0.05												0.5
	4.55	4.00	979.2	938.1	0.436	4.19	0.04	1.47	4.8	0.00	0.04	3	0.11	0.04	3	0.11	0.00	0.06	0.2
	4.28	3.89	1443.2	1401.3	0.474	2.91	0.03												
Sorption isotherm pH 6 IS=0.01N NaNO₃	4.94	5.94	5.4	1.6	0.037	70.57	2.47	1.59	38.3	-0.07	0.06	3	0.21	0.06	3	0.28	0.13	0.08	<LOQ
	4.99	5.94	24.9	10.1	0.143	59.35	0.73												<LOQ
	4.97	5.97	49.5	25.0	0.238	49.49	0.56												<LOQ
	4.88	6.04	96.2	62.0	0.339	35.59	0.34	1.51	6.6	-0.02	0.06	3	0.15	0.06	3	0.17	0.04	0.08	<LOQ
	4.87	5.92	165.5	120.2	0.449	27.36	0.21	2.11	5.2	-0.05	0.04	3	0.13	0.04	3	0.18	0.00	0.06	<LOQ
	4.79	6.06	199.7	157.9	0.422	20.94	0.15	1.48	5.0	-0.04	0.04	3	0.14	0.05	3	0.18	0.00	0.06	0.3
	4.76	5.93	297.6	245.9	0.524	17.37	0.12	1.71	3.8	0.00	0.05	3	0.18	0.04	3	0.18	0.02	0.06	<LOQ
	4.67	5.97	393.7	338.2	0.562	14.08	0.10												<LOQ
	4.60	5.99	590.9	521.1	0.721	11.81	0.08	2.09	3.2	-0.02	0.04	3	0.22	0.04	3	0.24	0.00	0.06	<LOQ
	4.52	5.99	787.8	714.6	0.768	9.29	0.07												<LOQ
		5.96	976.3	906.0	0.751	7.20	0.06												
	4.25	5.99	1447.4	1363.3	0.957	5.81	0.04												
Sorption edge IS=0.01N NaNO₃	4.90	2.96	51.1	44.0	0.069	13.74	0.11	1.48	28.3	0.00	0.04	3	0.18	0.04	3	0.18	0.02	0.04	2.0
	4.85	3.58	49.3	39.8	0.094	19.19	0.13												0.4
	4.91	3.98	51.8	35.9	0.157	30.75	0.34	1.30	14.9	-0.01	0.04	3	0.05	0.05	3	0.06	0.01	0.05	<LOQ
	4.89	4.55	49.7	31.6	0.178	36.30	0.35												<LOQ
	4.85	5.05	49.2	29.2	0.200	40.76	0.43												<LOQ
	4.84	5.73	49.3	26.7	0.226	45.93	0.50	1.48	9.9	-0.07	0.04	6	0.13	0.04	3	0.20	0.03	0.05	0.0
	4.83	5.66	49.4	24.5	0.249	50.41	0.50												<LOQ
	4.84	6.09	49.3	19.3	0.300	60.88	0.77												<LOQ
	4.80	6.37	48.3	15.2	0.333	68.51	0.83	1.35	7.4	-0.18	0.04	3	0.10	0.04	3	0.28	0.01	0.05	<LOQ
	4.77	6.81	48.2	8.1	0.406	83.19	1.26	1.32	5.7	-0.30	0.04	3	0.07	0.04	3	0.37	0.01	0.04	<LOQ
	4.86	7.53	47.8	2.0	0.455	95.84	1.47	1.52	6.3	-0.41	0.04	3	0.08	0.04	3	0.49	0.06	0.04	0.0
	4.72	7.84	48.0	0.9	0.482	98.22	1.77												0.2
	4.74	8.66	48.2	0.2	0.490	99.66	2.44												
Sorption edge IS=0.1N NaNO₃	5.03	3.61	50.3	49.2	0.010	2.04	0.01	1.52	55.1	-0.01	0.04	3	0.31	0.04	3	0.32	0.00	0.03	3.6
	4.98	3.98	49.8	49.5	0.003	0.60	0.00												1.0
	4.99	4.45	51.6	49.3	0.023	4.53	0.03												0.3
	4.96	4.96	49.6	47.4	0.021	4.41	0.02												<LOQ
	4.66	5.33	46.6	44.4	0.023	4.84	0.03												<LOQ
	4.17	5.82	41.7	37.1	0.053	10.97	0.07	1.66	17.5	-0.16	0.05	3	0.35	0.04	3	0.51	-0.02	0.06	<LOQ
	4.71	6.33	46.8	34.2	0.129	26.89	0.23	1.68	9.4	-0.28	0.04	3	0.21	0.04	3	0.49	-0.01	0.06	<LOQ
	4.69	6.82	46.4	20.9	0.263	55.05	0.37												0.1
	4.86	6.88	49.4	15.2	0.339	69.14	0.27												0.1
	4.78	7.10	49.8	9.6	0.406	80.71	0.34	1.46	6.3	-0.39	0.04	3	0.13	0.04	3	0.52	0.03	0.03	0.0
	4.80	7.51	49.1	3.3	0.461	93.28	0.21	1.28	5.6	-0.44	0.04	3	0.04	0.04	3	0.48	0.01	0.03	0.1
	4.86	8.57	49.4	0.2	0.489	99.57	1.82												0.3
	4.78	8.74	48.6	0.1	0.490	99.73	1.64												

Supplementary information 4: Statistical tests of significance for sorption model:

To test our two-site model of sorption, we plotted the correlation between modeled and measured [Zn] adsorbed onto kaolinite, in order to obtain the best agreement between these values, the slope the closest to 1 (0.96) and the lowest p-value (p < 0.00001).
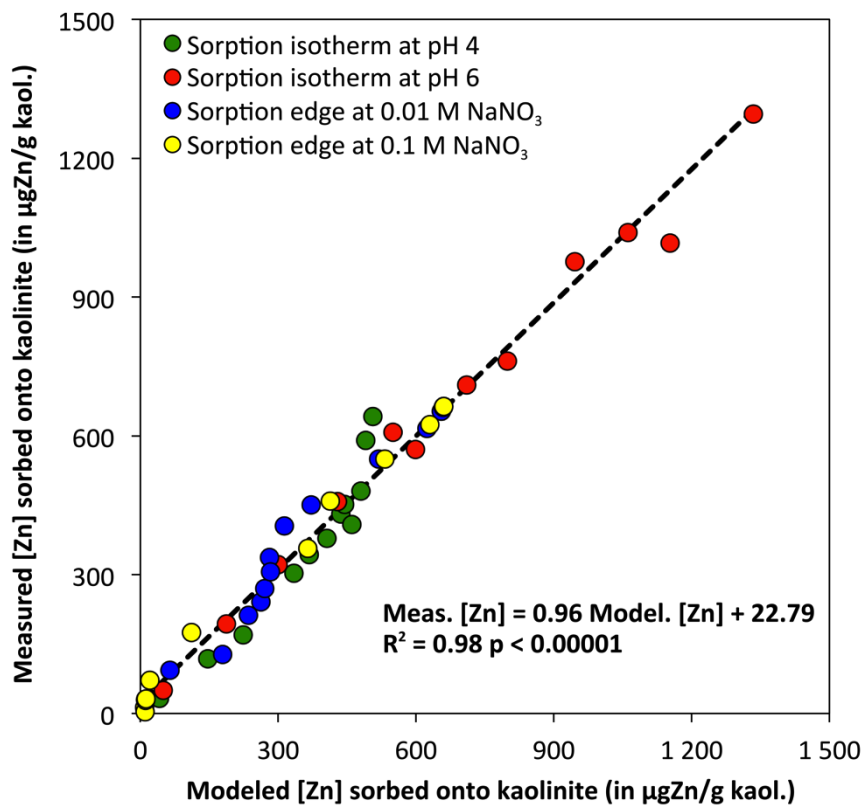

Figure S3: Cross-correlation between measured and modeled Zn concentration sorbed on kaolinite surface for the four experiments (sorption edges and isotherms).

Supplementary information 5: Equilibrium or Rayleigh distillation fractionation:

In natural systems, isotopes can be fractionated between two or more reservoirs. In our batch experiments, two phases (solid and solution) are interacting in a closed system. In most cases, Zn isotope signature will evolve at equilibrium between solid and solution. If the system evolves out of equilibrium, a Rayleigh distillation model can explain the instantaneous isotope compositions of solid and solution Zn.

Considering an initial $\delta^{66}Zn_{stock\text{-}solution}$ in the solution, the dissolved Zn isotopic ratio $\delta^{66}Zn_t$ at a time t may be calculated as:

$$\delta^{66}Zn_t = \delta^{66}Zn_{stock-solution} - \frac{1000\,f\,(\alpha_{adsorbed-solution}-1)}{(1-f+(f\,\alpha_{adsorbed-solution}))} \quad (in\ ‰) \quad \text{for equilibrium model} \quad (SI.9)$$

$$\delta^{66}Zn_t = (1000 + \delta^{66}Zn_{stock-solution})(1-f)^{(\alpha_{adsorbed-solution}-1)} - 1000 \quad (in\ ‰)\ \text{for Rayleigh model} \quad (SI.10)$$

where $\delta^{66}Zn_{stock\text{-}solution}$ refers to the initial zinc isotope signature in solution (0.00 ± 0.04 ‰), f is the fraction of zinc sorbed and $\alpha_{adsorbed\text{-}solution}$ is the isotopic fractionation factor between solid and solution. This latter represents the ratio of $^{66/64}Zn$ in solid over the $^{66/64}Zn$ ratio in solution. For the equilibrium model, it has been determined as 1.00018 for Zn sorption on exchange sites and 1.00049 for Zn sorption on edge sites (see discussion part of the paper).

The corresponding $\delta^{66}Zn_{sorbed}$ on the kaolinite surface at each time may be defined in both cases by:

$$\delta^{66}Zn_{adsorbed} = \alpha_{adsorbed-solution}\,(\delta^{66}Zn_t + 1000) - 1000 \quad (in\ ‰) \quad (SI.11)$$

$$\text{or } \delta^{66}Zn_{adsorbed} = \delta^{66}Zn_t + \Delta^{66}Zn_{adsorbed-solution} \quad (SI.12)$$

Figures S4A and S4B present the theoretical evolution of $\delta^{66}Zn$ in solution and for Zn sorbed on kaolinite for both equilibrium and Rayleigh models in comparison with experimental results.

As reported in the manuscript, for the equilibrium model, the dissolved $\delta^{66}Zn_t$ is the balance of the two distinct $\delta^{66}Zn_t$ during sorption on exchange and edge sites, respectively. The proportion of each binding site in Zn sorption allows the determination of $\delta^{66}Zn_{t-average}$ as:

$$\delta^{66}Zn_{t-average} = \delta^{66}Zn_{t,exchange} * p_{X2Zn} + \delta^{66}Zn_{t,edge} * p_{SOHZn1.5+} \quad (SI.13)$$

with $\delta^{66}Zn_{t-exchange}$ and $\delta^{66}Zn_{t-edge}$ the respective calculated isotope signature linked to exchange and edge binding in solution. p_{X2Zn} and $p_{SOHZn1.5+}$ are the proportions of each binding site involved at a time t of the sorption edge.

Combination of equations (SI.9) and (SI.13) with $\delta^{66}Zn_{stock-solution} = 0.00$ ‰ lead to equation (10) of the paper:

$$\delta^{66}Zn_{t-average} = -1000f\left(\frac{p_{X2Zn}(\alpha_{X_2Zn}-1)}{1-f+f\alpha_{X_2Zn}} + \frac{p_{SOHZn1.5+}\left(\alpha_{SOHZn1.5+}-1\right)}{1-f+f\alpha_{SOHZn1.5+}}\right) \quad (SI.14)$$

with α_{X_2Zn} and $\alpha_{SOHZn1.5+}$ the fractionation coefficients associated to exchange and edge sites, respectively.

Similarly, $\delta^{66}Zn_{adsorbed-average}$ is calculated from equation (SI.13) with both $\delta^{66}Zn_{adsorbed-X2Zn}$ and $\delta^{66}Zn_{adsorbed-SOHZn1.5+}$ as:

$$\delta^{66}Zn_{adsorbed-average} = \delta^{66}Zn_{adsorbed-X2Zn} * p_{X2Zn} + \delta^{66}Zn_{adsorbed-SOHZn1.5+} * p_{SOHZn1.5+} \quad (SI.15)$$

that can also be written as in Equation (11) of the paper:

$$\delta^{66}Zn_{adsorbed-average} = \delta^{66}Zn_{t-average} + p_{X2Zn} * \Delta_{X_2Zn} + p_{SOHZn1.5+} * \Delta_{SOHZn1.5+} \quad (SI.16)$$
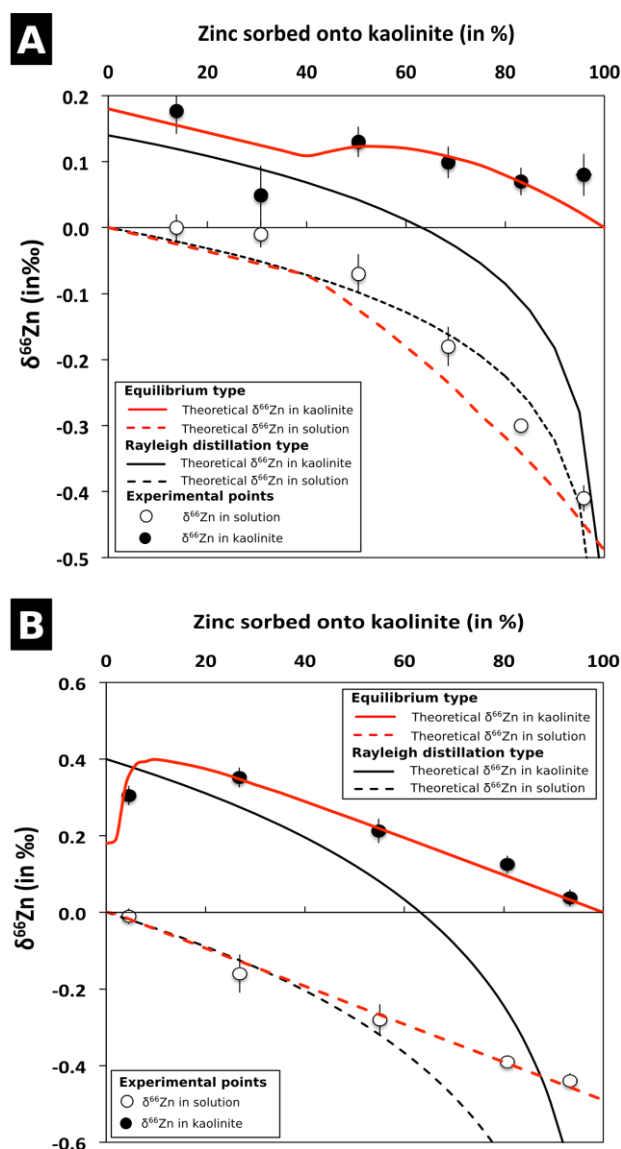
Figure S4: Zn isotope evolution as a function of zinc sorbed at A) low ionic strength (0.01 M NaNO$_3$) and B) high ionic strength (0.1M NaNO$_3$). Red lines refer to a theoretical isotope evolution at equilibrium for Zn sorbed on kaolinite (straight line) or in solution (dotted line). Black lines depict a theoretical Rayleigh model for kaolinite (straight line) or dissolved phases (dotted line). Rayleigh-type model does not fit the experimental points, whereas equilibrium type is non-linear due to the combination of two different $\alpha_{adsorbed-solution}$ at equilibrium onto basal and edge sites respectively.

For the Rayleigh model, several tests were realized with the two distinct $\alpha_{adsorbed-solution}$ associated with the two different binding sites. This however did not improve the fit of the model to the measured values compared to the use of only one $\alpha_{adsorbed-solution}$ for both low and high ionic strength cases (Fig. S4). So, a contradiction exists between the two type of Zn binding on kaolinite clay and the unique $\alpha_{adsorbed-solution}$ used for Rayleigh model. The best-fitted $\alpha_{adsorbed-solution}$ is 1.00014 for low (Fig. S4A) and 1.00040 for high ionic strength sorption edges (Fig. S4B), respectively. This difference of $\alpha_{adsorbed-solution}$ calculated for the two-sorption edges validates that a Rayleigh model of fractionation is not appropriate to describe these Zn isotope signals.

For both sorption edges (Fig. S4), the theoretical equilibrium model of zinc isotope fractionation matches with measured experimental points. The sorption edge at lower ionic strength reveals a more complex behavior. According to the pH, the binding sites involved are not the same. The two different $\alpha_{adsorbed-solution}$ (1.00018 and 1.00049 for exchange and edge site binding, respectively), combined in various proportions, explain the non-constant $\Delta_{adsorbed-solution}$ observed from low to high amount of Zn sorbed (red lines).

Supplementary information 6: Impact of crystalline Zn on $\delta^{66}Zn_{adsorbed}$ determination

$\delta^{66}Zn_{adsorbed}$ was calculated in this study by correcting the $\delta^{66}Zn_{solid}$ from the structural Zn initially present in the mineral lattice ($[Zn]_{struct.} = 37 \pm 5$ ppm (n=2) and $\delta^{66}Zn_{struct.} = 0.47 \pm 0.02$ ‰ (n=2)). The discussion part of the paper reports isotopically unbalanced samples (between solid and solution, see Supp Info 8), characterized by higher $\delta^{66}Zn_{adsorbed}$ than expected from the model, and low percentage of Zn adsorbed on kaolinite surface.

In Fig. S5, we plotted the difference between modeled and measured $\Delta^{66}Zn_{adsorbed-solution}$ in function of crystalline Zn proportion relatively to the total adsorbed Zn. When the crystalline Zn represents more that 35 % of the total adsorbed Zn, the uncertainty that exists on the $[Zn]_{cryst.}$ may explain the higher measured $\delta^{66}Zn_{adsorbed}$ compared to the theoretical one. Indeed, if the kaolinite lattice contained more Zn than the measured 37 ppm, the structural Zn correction will be underestimated and $\delta^{66}Zn_{adsorbed}$ corrected from the structural Zn will be too high, tending to increase the difference between $\Delta^{66}Zn_{adsorbed-solution}$ from the model and $\Delta^{66}Zn_{adsorbed-solution}$ measured. This under-correction of structural Zn may account for two or three samples (blue area in Fig. S5) but cannot explain the disagreement between modelled and measured $\Delta^{66}Zn_{adsorbed-solution}$ for the samples with a proportion of crystalline Zn under 35 %.
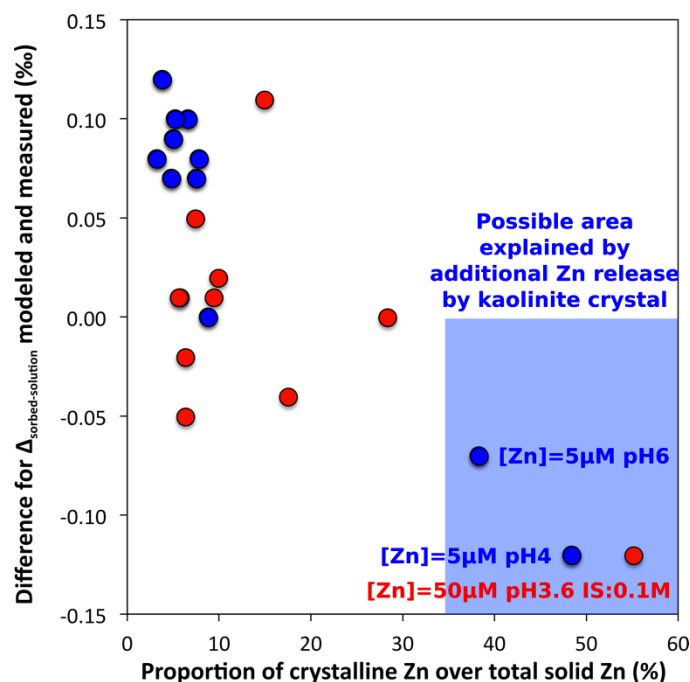
Figure S5 Difference in $\Delta^{66}Zn_{adsorbed-solution}$ from the model and measured relatively to the crystalline Zn proportion of the total solid Zn (adsorbed + crystalline). Red dots figure sorption edge experiments whereas blue dots depict sorption isotherm experiments. Only for 3 samples with the lowest $[Zn]_{solid}$ can the $\Delta^{66}Zn_{adsorbed-solution}$ shift observed between modelled and measured be explained by an underestimation of the structural Zn correction to the measured $\delta^{66}Zn_{adsorbed}$ (blue area).

Supplementary information 7: Zinc speciation in the dissolved phase

Speciation of Zn was evoked as a possible source of Zn isotope fractionation in the solution. This hypothesis is tested here, through a modeling of Zn species in $NaNO_3$ solutions (ECOSAT v.4.7). The main Zn species and their proportions according to pH in $NaNO_3$ 0.1 and 0.01N, and according to $[Zn]_{diss.}$ for sorption edge experiments are reported in Figure S6.

Even if $ZnNO_3^+$ is present in non-negligible amount for 0.1 M $NaNO_3$ sorption edge (Fig. S6A), the isotopic results obtained at 0.01 M $NaNO_3$ with less $ZnNO_3^+$ (Fig. S6B) corroborate those at high ionic strength and exclude a possible effect of in-situ Zn isotopic fractionation in solution. We also note the significant presence of $Zn(OH)^+$ and $Zn(OH)_2$ at pH > 6 and 7, respectively. As $Zn(OH)_2$ is negligible below pH 7 and because the fit is correctly realized up to pH 8.5 with Zn^{2+} sorption, $Zn(OH)_2$ is unlikely to be adsorbed and can be ruled out similarly to $ZnNO_3^+$. Finally, the steep increase of Zn sorption in sorption edges in Figure 1A and 1B coincides well with the first Zn hydrolysis constant, and thus the increasing $[Zn(OH)^+]$. A similar statement as for $ZnNO_3^+$ or $Zn(OH)_2$ is not allow. This issue is discussed in the "Molecular clues for Zn isotope fractionation process" part of the main text.

Besides, Visual Minteq's calculations indicate that zincite precipitation is thermodynamically unlikely at the kaolinite surface. However, as reported in the paper, Zn-Al-LDH precipitates can occur on kaolinite surface during sorption experiments with high [Zn] and long aging time[6]. Preliminary analysis of three different samples in X-ray Absorption Spectroscopy shows an absence of Zn-precipitates at the kaolinite surface for pH 4, $[Zn]_{ini}$ of 0.8 mM and 39-day-aging time. Incipient precipitation was observed for similar conditions at pH 6 and Zn precipitates are easily detectable at pH 8. These precipitations were observed after a long aging time compared to the lasting of our experiments (2 days), and with high $[Zn]_{ini}$. Zn-Al-LDH precipitates in our

experiments are thus highly improbable, even for the most concentrated samples of the sorption isotherms ($[Zn]_{ini}$ max of 1.5 mM). However, additional XAS spectra on samples submitted to short aging time and low $[Zn]_{ini}$ may be useful to confirm this assumption.
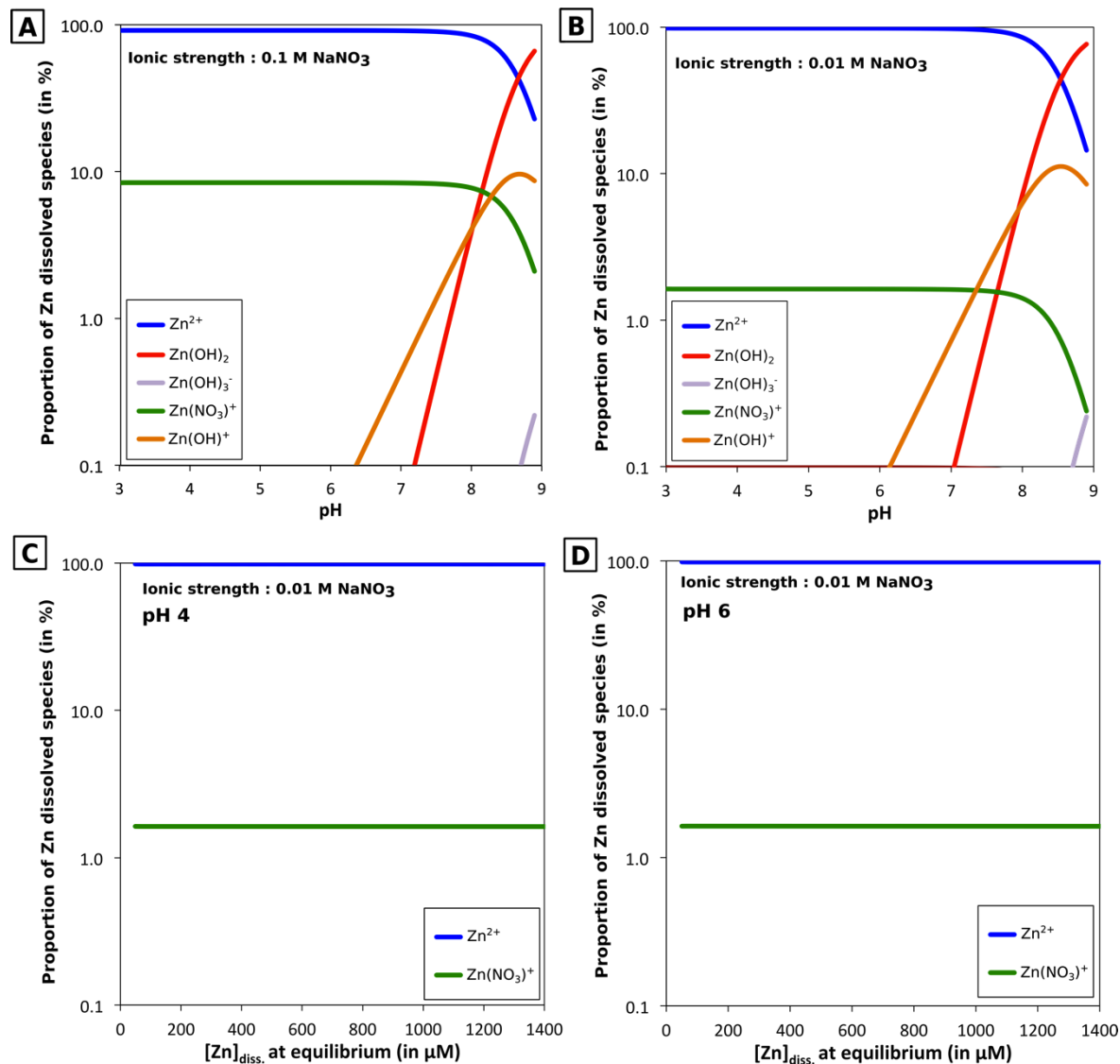

Figure S6: Speciation of dissolved Zn for sorption edges at 0.1 M NaNO$_3$ (A) and 0.01 M NaNO$_3$ (B); and for sorption isotherms at pH 4 (C) and pH 6 (D)

Supplementary information 8: Isotope mass balance in sorption experiments

We calculated a Zn isotope mass balance for all of our data points according to the following relation: $\delta^{66}Zn_{balance} = pZn * \delta^{66}Zn_{solution} + pZn_{adsorbed} * \delta^{66}Zn_{adsorbed}$

where $pZn_{solution.}$ and $pZn_{adosrbed.}$ are the proportion of Zn in solution and sorbed to kaolinite, respectively. $\delta^{66}Zn_{solution}$ and $\delta^{66}Zn_{adorbed}$ are the $^{66}Zn/^{64}Zn$ ratios in solution and on kaolinite surface; the latter being corrected from crystalline Zn. Results of the mass-balance calculations for each point of the sorption edge and isotherm experiments are presented in Figure S7.

For most of the samples, the isotopic mass balance is verified, within the 0.04‰ uncertainty (2SD) of the initial Zn added ($\delta^{66}Zn = 0.00 \pm 0.04$ ‰). However, for the first sample of each isotherm $\delta^{66}Zn_{balance}$ is clearly more positive than expected (0.17 ‰ and 0.13 ‰). In those cases, adsorbed [Zn] is relatively low and similar to [Zn] from the crystal lattice of kaolinite. As explained in the discussion, as well as in Suppl. Info 6, the uncertainty about [Zn] in kaolinite (37 ± 5 ppm) can result in an underestimation of the correction of $\delta^{66}Zn_{solid}$ and lead to a too high $\delta^{66}Zn_{adsorbed}$, explaining the imbalance.
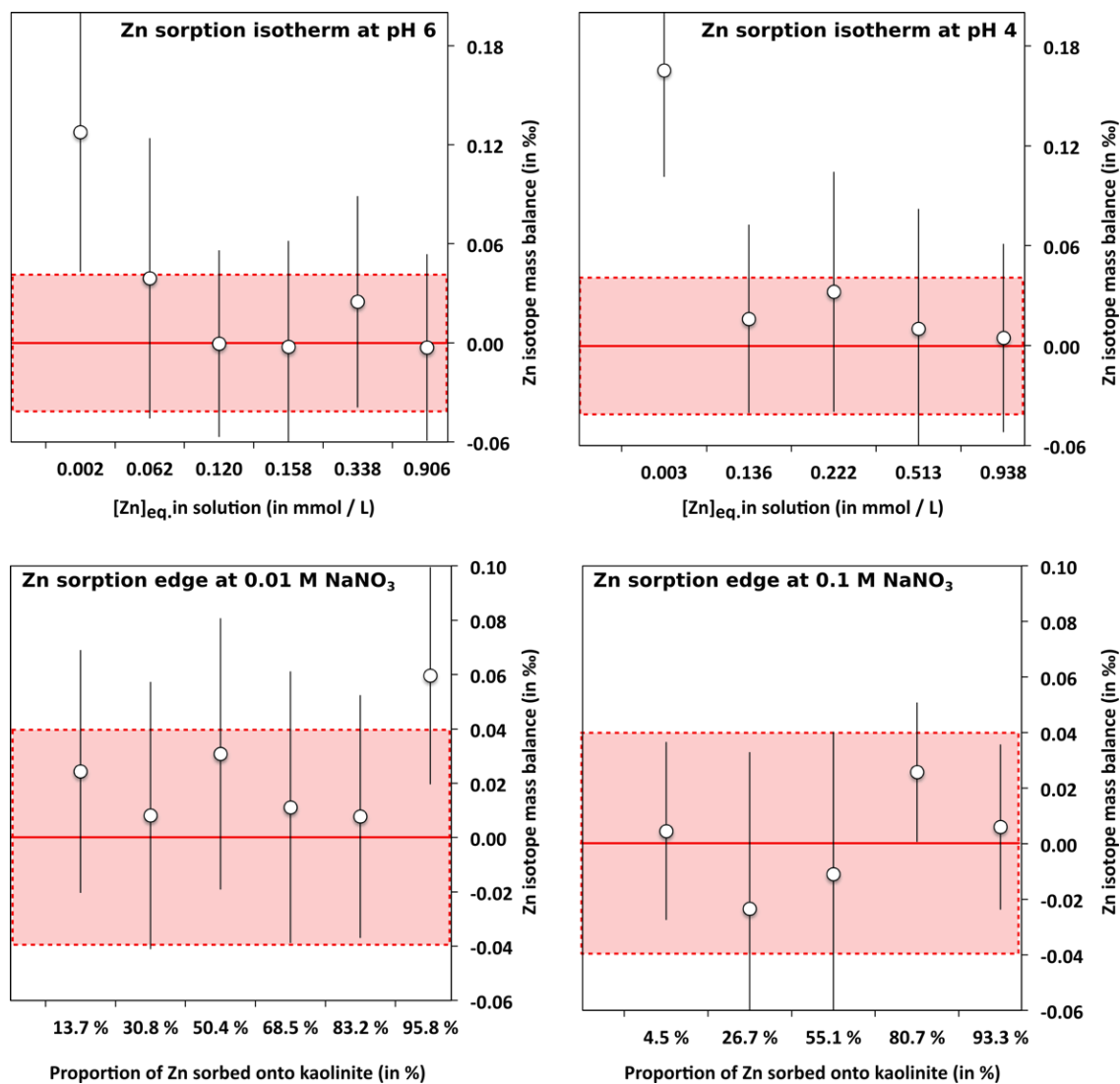
Figure S7: Zn isotope mass balance for sorption isotherms on top of the figure (pH 6: left and pH 4: right) and sorption edges at bottom part (0.01 M NaNO₃: left and 0.1 M NaNO₃: right).

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