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# Si stable isotope fractionation during adsorption and the competition between kinetic and equilibrium isotope fractionation: implications for weathering systems

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## Abstract

The adsorption of Si onto amorphous Al-hydroxides is the cause for the light Si isotope signature that secondary crystalline clay minerals in weathering systems carry. We propose this hypothesis from a series of adsorption experiments in which the light isotopes are being favored during Si adsorption onto crystalline gibbsite and in which the associated fractionation factor depends on the solution's initial Si concentration.

Three adsorption experiments were carried out at pH 7 with different initial Si concentrations of 0.36, 0.71 and 1.42 mmol/l Si start concentrations. As Al-hydroxide adsorbent, 30 g/l crystalline gibbsite were used to provide equal surface area in all experiments. Adsorption rates are higher with higher initial Si concentration. At the same time, calculated apparent isotope fractionation factors  $10^3 \ln \alpha_{\text{adsorbed/solution}}$  decrease from -1.8 to -3 ‰ with increasing initial Si concentration. As care was taken to avoid isotope fractionation during transport of dissolved Si to the gibbsite surface, the mass dependence

of the activation energy barrier at the interface is causing the kinetic isotope fractionation. Within the mass balance framework of DePaolo (2011) the shift in Si isotope fractionation with initial Si concentration is interpreted to be induced by different kinetic isotope fractionation factors associated with the forward reaction. Only after ca. two months do the isotope ratios begin to adjust to an equilibrium isotope fractionation factor that is close to 0 ‰. With such slow re-equilibration Si adsorption differs fundamentally from transition metals that re-equilibrate isotopically within hours after adsorption onto Fe and Mn oxide surfaces.

These observations may provide an explanation for the light Si isotope signature clay minerals formed during weathering carry: the light Si isotope composition is being inherited early on during Si adsorption onto amorphous Al-hydroxides and is potentially carried over during all further stages of transformation.

*Keywords:* isotope fractionation, stable silicon isotopes, silicon adsorption, kinetic fractionation, rate-dependence

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## 1 **1. Introduction**

2 Weathering of minerals and rocks releases elements into the ambient solution.  
3 Si and Al being the second and third most abundant elements in the Earth's  
4 crust, respectively, are both key players during weathering of silicates. While  
5 Al is almost insoluble under near neutral pH conditions and low dissolved  
6 organic carbon contents (Sposito, 1996), Si is partitioned in roughly equal  
7 proportions between the dissolved phase and into a solid secondary mineral  
8 phase during the dissolution of primary silicate minerals. In the last decade

9 Si stable isotopes have been increasingly used to trace weathering processes.  
10 One major finding of these Si isotope studies is the relative enrichment of  
11 heavy Si isotopes in the ambient soil solution. The isotopically lighter coun-  
12 terpart is found in secondary siliceous solid phases (Ziegler et al., 2005a,b;  
13 Georg et al., 2006a, 2007; Opfergelt et al., 2009; Bern et al., 2010; Opfergelt  
14 et al., 2011). Despite this consistent picture, the partitioning of Si isotopes  
15 in the presence of Al has not been explored in detail under controlled lab-  
16 oratory conditions. Determining the related isotope fractionation factors is  
17 critical as the reaction of Si and Al is likely to be the first crucial reaction  
18 occurring in weathering environments after releasing Al and Si from primary  
19 silicates.

20 In the present study, we explore Si isotope fractionation during adsorption  
21 of Si onto gibbsite at three different initial Si concentrations. We explain the  
22 resulting dependence of the Si isotope fractionation factor on adsorption rate  
23 within the conceptual mass balance framework of DePaolo (2011).

## 24 **2. Materials and Methods**

### 25 *2.1. Si source for adsorption experiments*

26 Dietzel (1993, 2002) showed that only monomeric silicic acid ( $\text{H}_4\text{SiO}_4$ ) is  
27 formed when tetraethylorthosilicate (TEOS;  $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ ) is used as Si source  
28 and that its behavior in adsorption experiments is identical to that found in  
29 monomeric silicic acid solutions prepared by alternative means. The advan-  
30 tage of using TEOS as Si source is that neither associated cations nor minor  
31 elemental amounts (released during the dissolution of silicates (e.g.  $\text{Na}_2\text{SiO}_3$ )  
32 or from alkaline standard solutions ( $\text{SiO}_2$  in 2% NaOH)) are present in the

33 solution, which then have to be removed to obtain pure silicic acid for exper-  
34 iments. Further monomeric silicic acid can be produced easily by a simple  
35 addition of small volumes of TEOS to aqueous solutions where TEOS con-  
36 verts to silicic acid via a hydrolysis reaction. The side product of TEOS  
37 hydrolysis is ethanol (a concentration of 261 ppm is calculated). The Si  
38 stock solution was prepared by adding 5.9 g (6 ml) TEOS (Merck®) to 20 l  
39 Milli-Q water (1.42 mmol/l Si).

40 To avoid formation of polysilicic acid the prepared starting solution was  
41 held below the solubility of amorphous silica. In addition, before using the  
42 starting solution we first analyzed the solution for the degree of polymer-  
43 ization of dissolved silicic acid and the presence of colloidal silica using the  
44  $\beta$ -silicomolybdate method (for details see Appendix B and Iler (1979) and Di-  
45 etzel (2000)). The amount of colloidal silica is determined by measuring the  
46 total Si concentration using ICP-OES minus the concentration of monosilicic  
47 acid determined by the  $\beta$ -silicomolybdate method. For all experiments both  
48 Si concentrations show that within the analytical precision of 5% no colloidal  
49 Si was present in the experiments. Furthermore, the reaction rate constant  
50 for the formation of the  $\beta$ -silicomolybdate complex can be used to evaluate  
51 the average polymerization degree of dissolved silicic acid. For the present  
52 stock solution a value of 2 min<sup>-1</sup> was calculated, which clearly indicates the  
53 sole presence of monomeric silicic acid.

## 54 *2.2. Adsorption experiments*

55 Adsorption experiments were carried out following a method adapted from  
56 Dietzel and Böhme (1997). The experimental solutions were prepared from a  
57 TEOS stock solution. Three distinct adsorption experiments were performed

58 with initial Si concentrations of 0.36, 0.71 and 1.42 mmol/l Si corresponding  
59 to concentrations of 10, 20 and 40 ppm, respectively. All experimental solu-  
60 tions were adjusted to 0.1 M NaCl by addition of NaCl (p.a. grade Merck<sup>®</sup>).  
61 Si concentrations were below the solubility limit of amorphous silica which  
62 is 1.93 mmol/l Si at 25°C and pH <8 (Gunnarsson and Arnorsson, 2000), to  
63 prevent polymerization and precipitation of amorphous silica.  
64 In each experimental run 30 g of gibbsite ( $\gamma$ -Al(OH)<sub>3</sub>; p.a. grade Merck<sup>®</sup>)  
65 with a given specific surface area of 1.18 m<sup>2</sup>/g (BET, N<sub>2</sub>-adsorption) was  
66 suspended in 1 l of the experimental solution containing Si in PE bottles.  
67 The pH of 7.0 was adjusted and kept constant during the experiment by  
68 the addition of diluted HCl or NaOH solution (pH were measured with pH  
69 meter WTW 330 and pH electrode WTW SenTix 41, calibrated using pH 4.0  
70 and 7.0 WTW standard buffer solutions). The variability of the pH values  
71 throughout the whole experimental runtime was  $\pm$  0.1 pH units. During the  
72 first 6 hours of the experiment, the gibbsite suspension was heavily agitated  
73 using a IKA RW 20 DZM stirrer at 500 rpm with a Teflon stirring staff. A  
74 parafilm cover prevented evaporation of the solution. Subsequently the closed  
75 PE bottles were placed in an overhead shaker. Experimental suspensions (15  
76 ml) were sampled with a syringe and filtered (0.45  $\mu$ m porosity, cellulose  
77 acetate) at several intervals; total maximum experimental run time was 1536  
78 hours (64 days). The sampled solutions were split: 10 ml were used for  
79 ICP-OES analyses (Varian 720-ES) and Si isotope measurements (Thermo  
80 Scientific NEPTUNE). The remaining solutions of 5 ml were immediately  
81 analyzed by UV-Vis (UV-VIS 641 Cary 100, Varian).

82 *2.3. Chemical separation and purification*

83 Chemical separation of Si was done following the method from Georg et al.  
84 (2006b). The filtered solutions were loaded onto pre-cleaned columns (1.5  
85 ml of BioRad DOWEX 50W-X8; 200-400 mesh) and Si was eluted with 5  
86 ml Milli-Q water and stored in pre-cleaned centrifuge tubes. It was assured  
87 for all samples that the Si yield was  $>95\%$ , which was checked by ICP-OES  
88 (Varian 720-ES).

89 *2.4. Mass spectrometry*

90 Silicon isotope composition was measured on a Thermo Neptune multi-collector  
91 inductively coupled mass spectrometer (MC-ICP-MS) equipped with an H-  
92 skimmer cone and the newly developed Thermo Scientific<sup>®</sup> Jet - interface in  
93 high-resolution mode ( $m/\Delta m > 5000$ ). The purified sample solutions were  
94 introduced into the plasma via a desolvation unit for dry plasma conditions  
95 (Apex, ESI<sup>®</sup>, no  $N_2$  addition, no further membrane desolvation) equipped  
96 with a  $120 \mu\text{l}/\text{min}$  nebulizer.

97 We used Mg doping combined with standard-sample-bracketing to correct  
98 for mass bias during measurements by using an exponential mass bias law  
99 (Cardinal et al., 2003). A magnesium solution was added to samples and  
100 standards to yield a final concentration of 1 ppm Mg. Sample solutions were  
101 diluted to 1 ppm Si concentration in 0.1 M HCl, which typically resulted in  
102 an intensity of  $\sim 15$  V/ppm on  $^{28}\text{Si}$  (using a  $10^{11}\Omega$  resistor).

103 Measurements were conducted on the interference-free low-mass side of the  
104 three Si isotopes. The most critical interference, caused by  $^{14}\text{N}^{16}\text{O}$  on the  
105  $^{30}\text{Si}$  signal, is usually below 5V which is resolvable from the  $^{30}\text{Si}$  signal in  
106 the high-resolution mode used. Each sample and standard was measured at

107 least 4 times during a sequence; each sample or standard was measured in  
 108 dynamic mode for 30 cycles with an integration time for each cycle of 4 s for  
 109 Si as well as for Mg with an idle time of 3 s after magnet switching. Pure  
 110 0.1 M HCl solutions were measured before and after each standard-sample-  
 111 standard block and were used for on-peak zero correction. Typical intensities  
 112 of  $^{28}\text{Si}$  in blank solutions were below 5 mV. We report Si isotope data relative  
 113 to the standard reference material NBS28 (quartz sand) in the delta notation  
 114 according to Coplen (2011) as  $\delta(^{29/28}\text{Si})_{\text{NBS28}}$  and  $\delta(^{30/28}\text{Si})_{\text{NBS28}}$  expressed  
 115 in per mill (‰) by multiplication of Equation 1 and 2 with a factor of  $10^3$ :

$$\delta(^{29/28}\text{Si})_{\text{NBS28}} = \left( \frac{\left( \frac{^{29}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left( \frac{^{29}\text{Si}}{^{28}\text{Si}} \right)_{\text{NBS28}}} - 1 \right) \quad (1)$$

$$\delta(^{30/28}\text{Si})_{\text{NBS28}} = \left( \frac{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{NBS28}}} - 1 \right) \quad (2)$$

116 All reported errors on delta values are the 95% confidence interval (CI) cal-  
 117 culated according to Eq.3 where  $\overline{\delta(^{30/28}\text{Si})_{\text{NBS28}}}$  is the mean of the measured  
 118 delta values for the sample or standard (at least n=4),  $t_{n-1}$  is a critical value  
 119 from tables of the *Student's t*-law and SE is the standard error of the mean.

$$\text{CI} = \overline{\delta(^{30/28}\text{Si})_{\text{NBS28}}} \pm t_{n-1} \times \text{SE} \quad (3)$$

120 The well-defined Si isotope reference material BHVO-2g, a basalt standard  
 121 (measured over a 12 months period of analysis ; including several individual  
 122 chemical separations as well as several digestions procedures;  $\delta(^{30/28}\text{Si})_{\text{NBS28}} =$

123  $-0.27 \pm 0.02$ ; n=73), was usually measured as control standard during mea-  
124 sured sequences.

### 125 *2.5. Analytical tests*

126 As it is mentioned in Section 2.1 the side product during monomeric silicic  
127 acid preparation using TEOS is ethanol. In a separate experiment using  
128 similar starting material (Oelze et al., 2014) it has been tested whether the  
129 remaining ethanol in the prepared solutions induces analytical artifacts dur-  
130 ing the preparation and measurement of Si isotopes. Pairs of solutions and  
131 the formed solid counterparts were measured. Applying a mass balance ap-  
132 proach showed that all fluid-solid pairs gave the isotopic composition of the  
133 starting solution. Hence no mass-spectrometric artifact was induced from the  
134 release of ethanol during preparation of Si-containing solutions using TEOS.  
135 A known limitation of using the sample purification method of Georg et al.  
136 (2006b) is that anions present in the samples remain in the purified Si so-  
137 lutions. As the Si adsorption experiments were conducted in the presence  
138 of 0.1 M NaCl and further HCl has been used to adjust the pH,  $Cl^-$  anions  
139 might have been present after purification and potentially might have caused  
140 matrix effects as their amounts are different between sample and bracketing  
141 standards. Therefore we tested whether different amounts of  $Cl^-$  anions in  
142 sample and bracketing standard causes matrix effects by measuring a “ $Cl^-$ -  
143 doped” standard against “pure” bracketing standards. In the estimated range  
144 of different  $Cl^-$  anion concentrations (difference between “doped” and “pure”  
145 of up to 20 %) no bias has been found.

### 146 **3. Results**

147 Si concentrations as well as  $\delta(^{29/28}\text{Si})_{\text{solution}}$  and  $\delta(^{30/28}\text{Si})_{\text{solution}}$  values are  
148 reported in the Appendix Table A.1.

#### 149 *3.1. Evolution of Si concentration*

150 During the adsorption experiments, a continuous decrease in Si concentra-  
151 tion with time is observed (Figure 1). In all experiments (0.36, 0.71 and  
152 1.42 mmol/l Si starting concentration) the major change of Si concentration  
153 occurs during the first 50 hours, and subsequently the changes slow down  
154 continuously. Over 60% of the total adsorption takes place during the first  
155 24 hours. Si adsorption rates (Figure 2) at the beginning of the experiments  
156 differ strongly between the conducted experiments. Adsorption rates for ex-  
157 periments with an initial Si concentration of 1.42 mmol/l are up to four times  
158 higher compared to solutions with an initial concentration of 0.36 mmol/l Si;  
159 the 0.71 mmol/l Si solution experiment yields intermediate adsorption rates.  
160 Using estimates from Karamalidis and Dzombak (2011) of 8 - 8.8 adsorption  
161 surface sites/nm<sup>2</sup> on gibbsite and the measured BET surface area of 1.18  
162 m<sup>2</sup>/g a maximum possible amount of adsorbed Si of 440 - 484  $\mu\text{g/g}$  (470 -  
163 520  $\mu\text{mol Si total}$ ) can be calculated. As the maximum Si amounts adsorbed  
164 (defined by the equilibrium constant of the adsorption reaction) were ca. 130,  
165 200, and 250  $\mu\text{mol}$  for the 0.36, 0.71, and 1.42 mmol/l experiment, respec-  
166 tively, in all adsorption experiments an excess of free adsorption surface sites  
167 was still available at the end of the experiments.

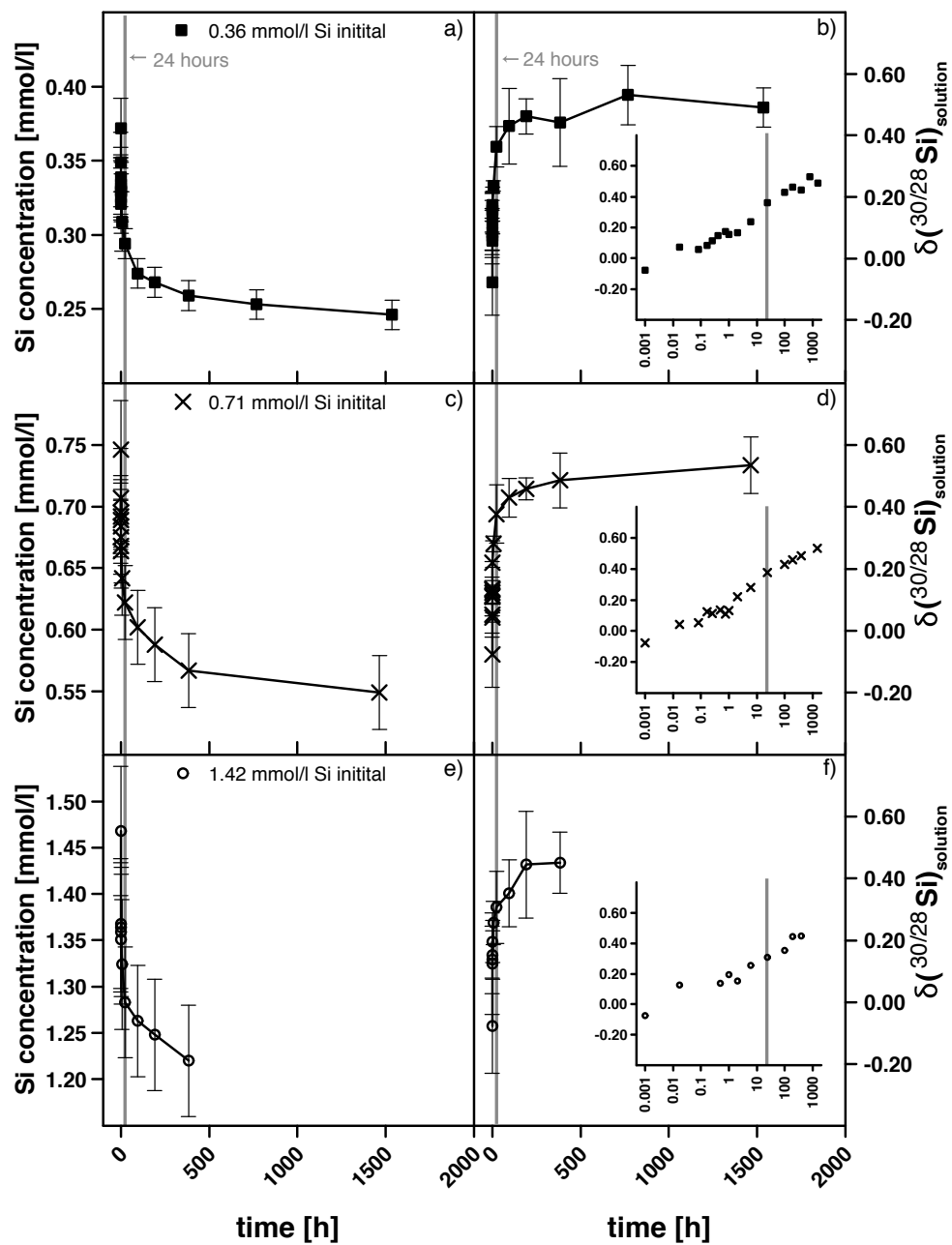


Figure 1: Evolution of Si concentration (panels a, c and e) and  $\delta(^{30/28}\text{Si})_{\text{solution}}$  (panels b, d and f) of the solution with time during adsorption experiments (30 g/l of gibbsite, pH 7.0). Squares, crosses and circles depict experiment with an initial Si concentration of 0.36, 0.71 and 1.42 mmol/l, respectively. Insets in panels b, d and f show the same isotopic datasets plotted vs. log time in hours.

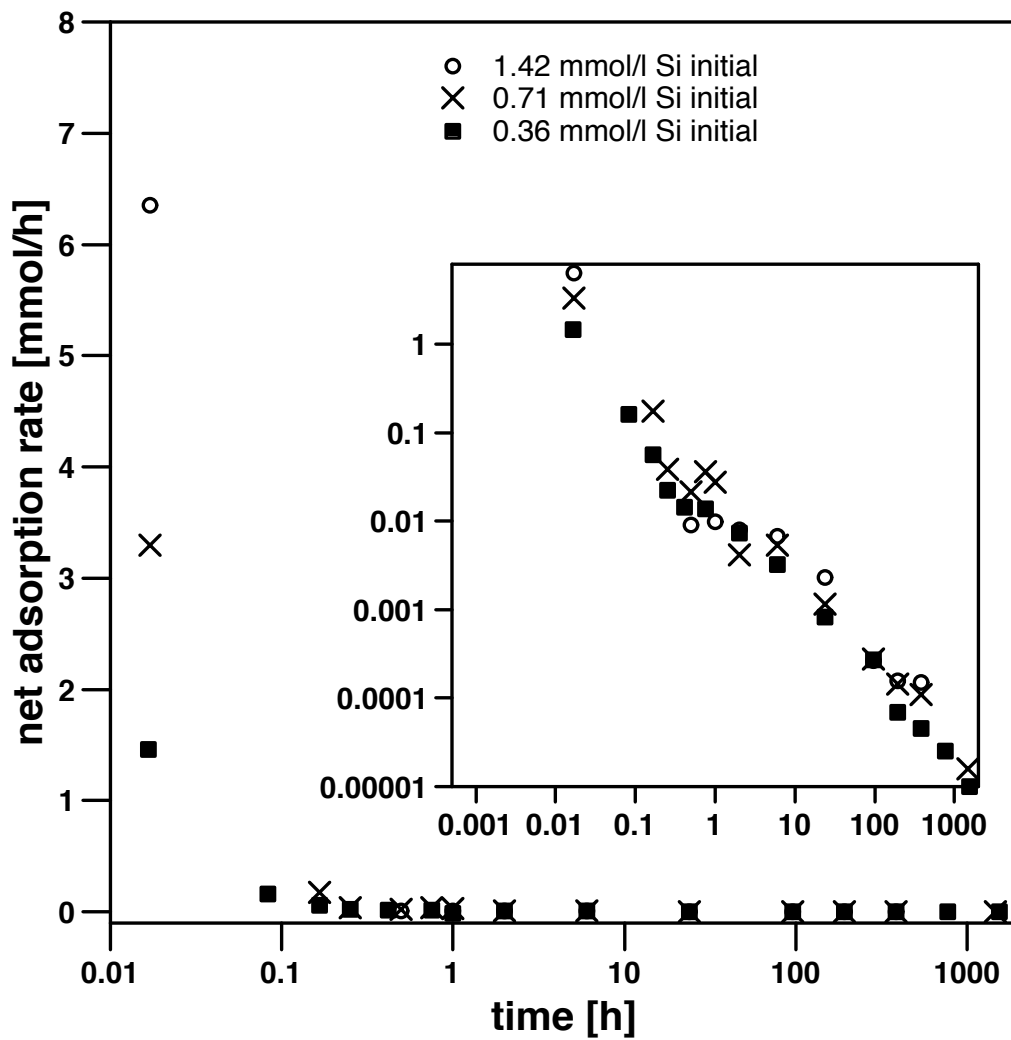


Figure 2: The net adsorption rate vs. time in a semi-log diagram (inset log-log scale). Net adsorption rate  $dq/dt$  is calculated as the difference between the amount adsorbed in mmol  $dq = q_{n+1} - q_n$  divided by the time elapsed in hours  $dt = t_{n+1} - t_n$ .

168 *3.2. Silicon isotopes*

169 We report measured  $\delta(^{30/28}\text{Si})_{\text{solution}}$  solution values (measured relative to  
170 NBS28) throughout this section. All three adsorption experiments (with  
171 initial Si concentrations of 0.36, 0.71 and 1.42 mmol/l) display a similar evo-  
172 lution of their  $\delta(^{30/28}\text{Si})_{\text{solution}}$  values. With increasing experimental runtime  
173 or decreasing fraction of Si remaining in solution ( $f_{\text{solution}}$ ), the dissolved Si  
174 becomes increasingly enriched in  $^{30}\text{Si}$ , which results in higher  $\delta(^{30/28}\text{Si})_{\text{solution}}$   
175 values (Figure 3). The largest changes in  $\delta(^{30/28}\text{Si})_{\text{solution}}$  are observable dur-  
176 ing the first 24 hours where also over 60% of the Si adsorption onto gibbsite  
177 takes place. After this initial period of rapid change in both Si concentration  
178 and  $\delta(^{30/28}\text{Si})_{\text{solution}}$ , the change in  $\delta(^{30/28}\text{Si})_{\text{solution}}$  is much slower. In fact  
179 in contrast to the continuously evolving Si concentrations  $\delta(^{30/28}\text{Si})_{\text{solution}}$   
180 values are almost constant. Finally a maximum  $\delta(^{30/28}\text{Si})_{\text{solution}}$  value is  
181 reached where Si concentration and  $\delta(^{30/28}\text{Si})_{\text{solution}}$  remain virtually con-  
182 stant (see Appendix Table A.1). We only used the data of the first 24  
183 hours to determine an apparent isotope fractionation factor  $\alpha_{\text{adsorbed/solution}}$   
184 for each of the experiments. We define  $\alpha_{\text{adsorbed/solution}}$  ( $\alpha_{\text{adsorbed/solution}} =$   
185  $(^{30}\text{Si}/^{28}\text{Si})_{\text{adsorbed}}/(^{30}\text{Si}/^{28}\text{Si})_{\text{solution}}$ ) as the isotope fractionation factor be-  
186 tween adsorbed Si and dissolved Si remaining in solution. However, the com-  
187 position of Si adsorbed onto gibbsite  $\delta(^{30/28}\text{Si})_{\text{adsorbed}}$  was calculated by mass  
188 balance, as the gibbsite remained in the experimental containers throughout  
189 the experiment. An “open-system” (Rayleigh mass balance) and a “closed-  
190 system” mass balance approach were applied to the data (Johnson et al.,  
191 2004). An “open-system” mass balance approach assumes that the product  
192 (here adsorbed Si) does not remain in contact with the starting material

193 (here dissolved Si) after formation. In this case the evolution of dissolved Si  
194 isotope composition is given by:

$$\frac{(1000 + \delta(^{30/28}\text{Si})_{\text{solution}})}{(1000 + \delta(^{30/28}\text{Si})_{\text{solution-initial}})} = f_{\text{solution}}^{(\alpha_{\text{adsorbed/solution}} - 1)} \quad (4)$$

195 In contrast, a “closed-system” approach assumes complete isotope exchange  
196 during removal of dissolved Si, leading to:

$$\delta(^{30/28}\text{Si})_{\text{solid}} = \delta(^{30/28}\text{Si})_{\text{solution-initial}} + 1000 * f * (\alpha_{\text{adsorbed/solution}} - 1) \quad (5)$$

197 As  $f_{\text{solution}}$  did not extend to values lower than 0.6, our data does not allow  
198 to identify whether the experiments follow “open-system” or “closed-system”  
199 behavior. We return to this question in section 4.1. Here we apply both  
200 types of mass balance models to our data, and obtain a reasonable fit for  
201 each experiment. Three distinct isotope fractionation factors are obtained  
202 for both mass balance approaches (see Figure 3 and Table 1).

Table 1: Resulting  $\alpha^{30/28}\text{Si}_{\text{adsorbed/solution}}$  and  $10^3\ln\alpha^{30/28}\text{Si}_{\text{adsorbed/solution}}$  values using adsorption data of the first 24 hours. To determine isotope fraction factors an open-system and a closed-system mass balance model has been applied to the experimental data. To fit the data we used the nlme-package (Pineiro et al., 2014) in R (R Core Team, 2014). We report the calculated standard error (SE) of  $\alpha^{30/28}\text{Si}$  and the standard error of the residuals (RMSD) calculated for each experiment.

“open-system” mass balance			
Experiment	$\alpha^{30/28}\text{Si}$	$10^3\ln\alpha^{30/28}\text{Si}$	RMSD
0.36 mmol/l Si initial	$0.998222 \pm 0.000050$	$-1.779 \pm 0.050$	0.022
0.71 mmol/l Si initial	$0.997669 \pm 0.000088$	$-2.334 \pm 0.088$	0.030
1.42 mmol/l Si initial	$0.996986 \pm 0.000102$	$-3.019 \pm 0.102$	0.023
“closed-system” mass balance			
Experiment	$\alpha^{30/28}\text{Si}$	$10^3\ln\alpha^{30/28}\text{Si}$	RMSD
0.36 mmol/l Si initial	$0.998071 \pm 0.000060$	$-1.931 \pm 0.060$	0.025
0.71 mmol/l Si initial	$0.997516 \pm 0.000100$	$-2.487 \pm 0.100$	0.033
1.42 mmol/l Si initial	$0.996827 \pm 0.000103$	$-3.178 \pm 0.103$	0.022

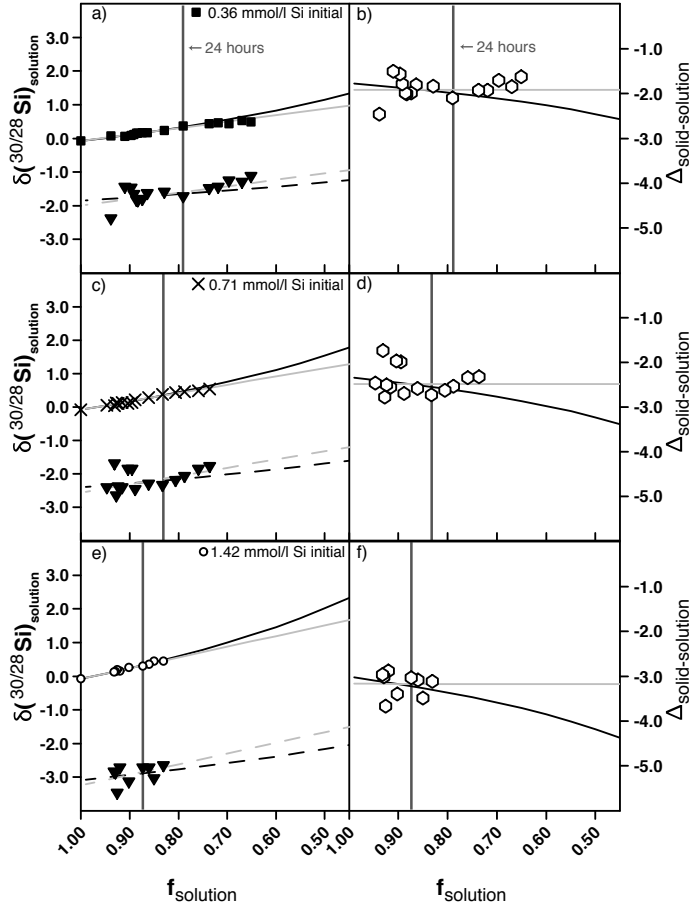


Figure 3: The left panels (a, c and e) show the  $\delta(^{30/28}\text{Si})_{\text{solution}}$  evolution of the measured solution and the corresponding calculated  $\delta(^{30/28}\text{Si})_{\text{adsorbed}}$  of the solid in the adsorption experiments, as a function of the fraction of Si remaining in solution ( $f_{\text{solution}}$ ). The open diamonds in the right panels (b, d and f), show the isotopic difference  $\Delta(^{30/28}\text{Si})_{\text{solid-solution}}$  between solid and solution as a function of the fraction of Si remaining in solution ( $f_{\text{solution}}$ ). In the left panels, squares, crosses and circles depict experiments with initial Si concentrations of 0.36, 0.71 and 1.42 mmol/l, respectively. The triangles depict  $\delta(^{30/28}\text{Si})_{\text{adsorbed}}$  calculated for the corresponding Si adsorbed onto solids for each individual experiment. Regression lines for the experimental data (first 24 hours) fitted according to the open-system mass balance approach (black lines; Eq. 4) and for the closed-system approach (gray lines; Eq. 5) are also shown (see Table 1 for obtained fractionation factors; error bars are smaller than symbol size).

## 203 4. Discussion

### 204 4.1. Si isotope fractionation during Si adsorption

205 During our adsorption experiments significant changes of Si concentration  
206 are associated with changes in the  $\delta(^{30/28}\text{Si})_{\text{solution}}$  values, where light isotopes  
207 are preferentially adsorbed onto the gibbsite surface. We further observe a  
208 higher Si isotope fractionation between adsorbed and dissolved Si the higher  
209 the initial Si concentration is.

210 We first explore whether isotope fractionation found between Si adsorbed  
211 onto solids and Si remaining in solution follows a “closed-system” behav-  
212 ior (Johnson et al., 2004). In our experiments the range of Si fractions  
213 remaining in solution (0.7 to 1.0) experienced does not allow one to dis-  
214 tinguish the “closed” system behavior from the “open” system case. There-  
215 fore, the observed pattern is compatible with a “closed-system” behavior and  
216 hence continuous contact and exchange between solids and solution. Such  
217 re-equilibration has been shown to be characterized by equilibrium isotope  
218 fractionation in previous adsorption experiments (Juillot et al., 2008; Wa-  
219 sylenki et al., 2008, 2011). However, we can rule out equilibrium isotope  
220 fractionation as the adsorption rate is high from hours 0 to 400, which ar-  
221 gues against attainment of chemical equilibrium - a prerequisite for isotopic  
222 equilibrium. Therefore we proceed to discuss our results in terms of the  
223 “open-system” behavior.

224 We next discuss the prevailing mechanism of adsorption of light isotopes  
225 onto the gibbsite surfaces. Any transport-induced isotope effect (e.g. isotope  
226 fractionation of Si through diffusion) can be ruled out, as the experimental  
227 solutions were constantly heavily stirred or shaken. Hence the occurrence

228 of Si isotope fractionation in our experiments can be explained by the ad-  
229 sorption process being “reaction-limited” i.e. the fractionation depends on  
230 the kinetics of the adsorption reaction when an activation energy barrier  
231  $E_a$  during formation or breaking of bonds has to be overstepped. The Ar-  
232 rhenius equation demands that reactions of light isotopes are preferred over  
233 those of heavy isotopes (Bigeleisen, 1965). Yet even this activation energy  
234 barrier model does not explain the dependence of  $\alpha_{\text{adsorbed/solution}}$  on the ini-  
235 tial Si concentration. As also Si adsorption rates differ significantly between  
236 our experiments, we next evaluate how reaction kinetics might affect isotope  
237 fractionation.

#### 238 *4.2. Kinetics of Si adsorption*

239 Adsorption reaction kinetics of Si onto gibbsite was often described as a first-  
240 order reaction, at least for some parts of the reaction (Hingston and Raupach,  
241 1967; Adu-Wusu and Wilcox, 1991; Dietzel, 2002). An attempt to explain the  
242 overall adsorption reaction with simple kinetic rate laws (first-order, second-  
243 order or first-order forward and backward reaction, see Appendix C) fails.  
244 The evolution of Si concentration follows a linear trend in a semi-log diagram  
245 (Figure 4) and therefore we apply the empirical equation:

$$[Si] = a \times \log(\text{time}) - b \quad (6)$$

246 In such a diagram the slope  $a$  is a coefficient describing the relative adsorption  
247 rate. For each adsorption experiment, the data describe a straight line but  
248 different slopes are obtained. This dependence can be interpreted to mean  
249 that distinct initial Si concentrations result in different Si adsorption rates.

250 The higher the initial Si concentration, the faster the adsorption (see Figure  
251 4).

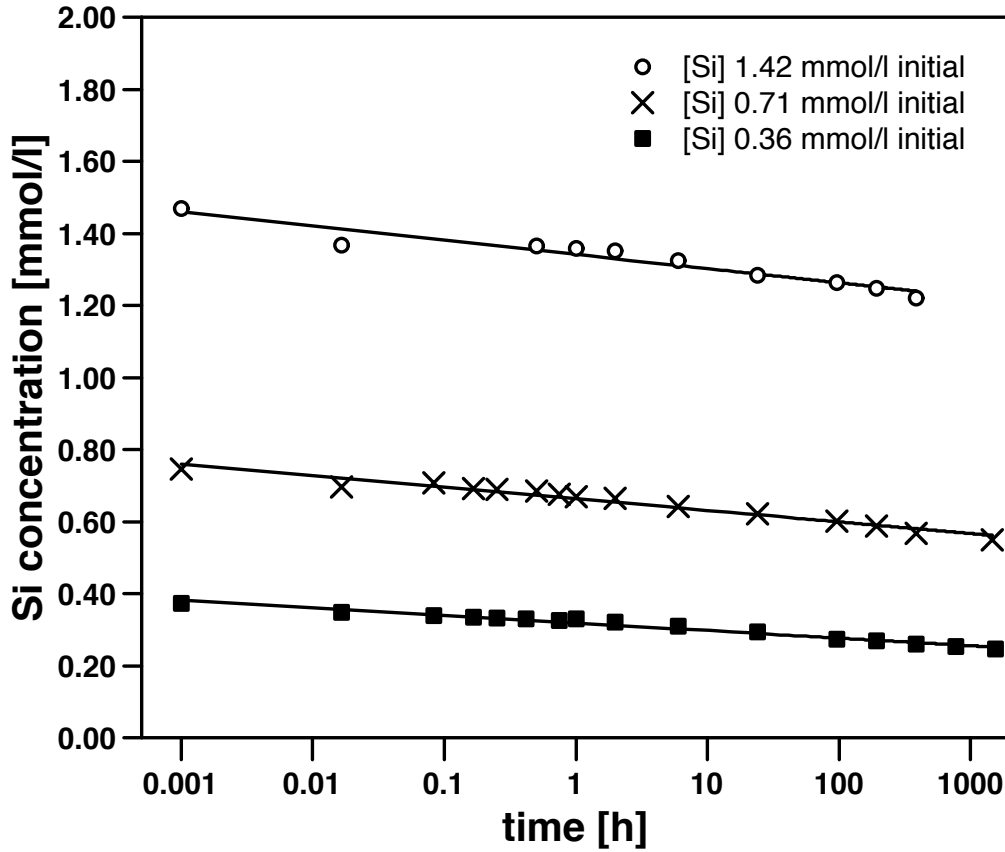


Figure 4: Si concentration vs. time (on log scale), where the slopes denotes the overall adsorption rate (Eq. 6) Squares depict the experiment with an initial Si concentration of 0.36 mmol/l, crosses depict experiment with 0.71 mmol/l and circles the experiment with 1.42 mmol/l initial Si concentration. Adsorption experiments with high initial Si concentration show steeper slopes than lower Si initial concentration experiments, which means the higher the Si initial concentration the higher the adsorption rate.

252 When for all three adsorption experiments the apparent Si isotope fractiona-  
253 tion factor (derived for the first 24 hours from the open-system mass balance  
254 model; see Table 1) is plotted against the slope obtained from the empiri-  
255 cal logarithmic relationship (Eq. 6) a strong linear relationship is obtained  
256 (see Figure 5). With increasing adsorption rate the determined fractionation  
257 factors decrease. Hence the Si isotope fractionation depends on adsorption  
258 rate.

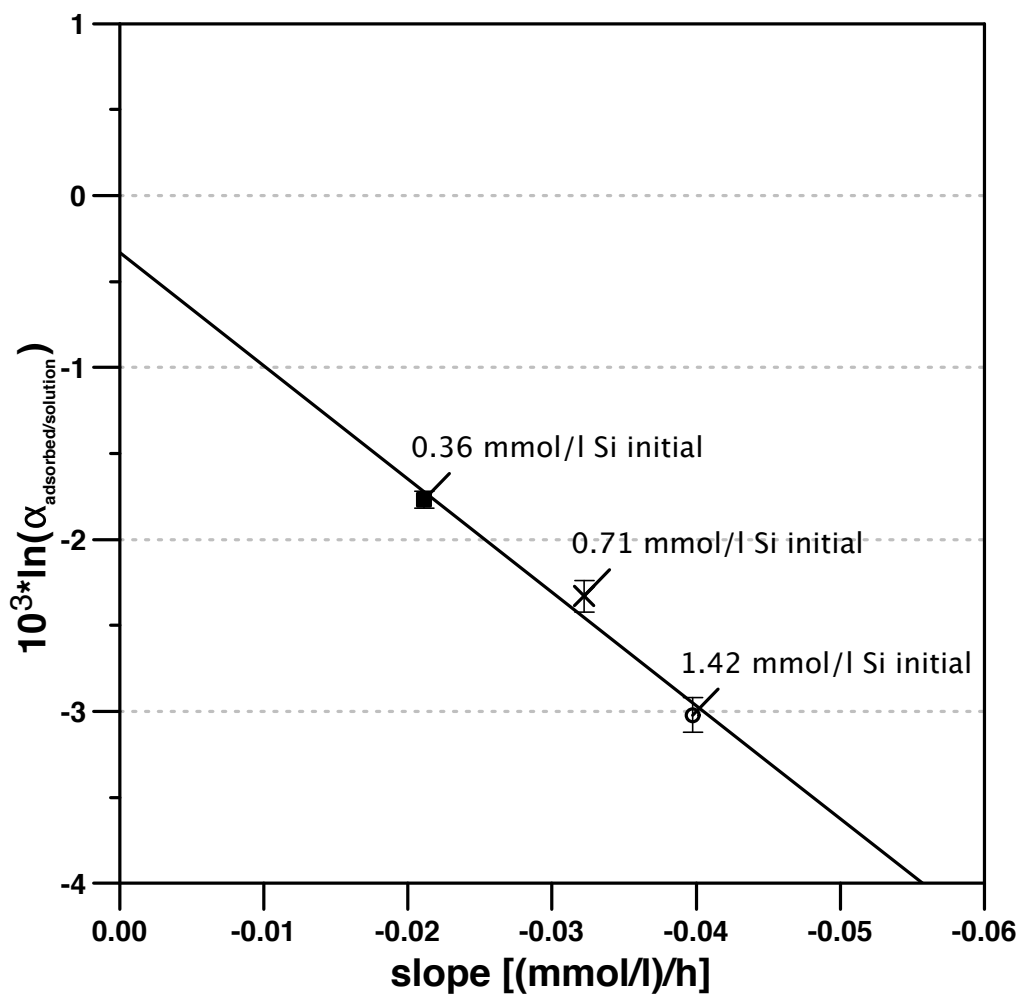


Figure 5: Fractionation factors as  $10^3 \ln(\alpha_{\text{adsorbed/solution}})$  deduced from applying an open-system mass balance to the first 24 hours of the individual adsorption experiments (Table 1) vs. the slope derived from applying the empirical logarithmic relationship (Eq. 6)

259 *4.3. The change of the isotope fractionation regime*

260 Two explanations can be invoked to explain the rate dependence of isotope  
261 fractionation factors between the three experiments. Given that the isotope-  
262 specific energy barrier of a chemical pathway does not depend on adsorption  
263 rate, the first explanation is that reactions pathways differ between experi-  
264 ments. The second explanation is that a significant relative rate of a back  
265 reaction and the associated isotope fractionation affects the experiments,  
266 differs between the experiments. A framework that relates isotope fractiona-  
267 tion to the ratio of backward to forward reaction rate has been developed by  
268 DePaolo (2011). This conceptual model is based on simple definitions of a  
269 forward reaction rate  $R_f$  (formation of new phases; here Si adsorption onto  
270 gibbsite), a backward reaction rate  $R_b$  (dissolution of newly formed phases;  
271 here Si desorption from gibbsite) and the net reaction rate  $R_p$  ( $R_p = R_f - R_b$ ).  
272 The forward and backward rates are associated with distinct kinetic isotope  
273 fractionation factors ( $\alpha_f$  and  $\alpha_b$ , respectively). An apparent fractionation  
274 factor  $\alpha_p$  arises from the  $R_p/R_b$  ratio (see Eq. 11 in DePaolo (2011)). The  
275 overall prediction is that if the net adsorption rate  $R_p$  is much larger than the  
276 backward rate  $R_b$ , the apparent isotope fractionation will be kinetically dom-  
277 inated (favoring light isotopes). By contrast if  $R_p$  is much smaller than  $R_b$ ,  
278 the system reaches isotopic fractionation at equilibrium. While at interme-  
279 diate regimes  $\alpha_p$  depends on the values of  $\alpha_f$ ,  $\alpha_b$  and  $R_p/R_b$ . On the low and  
280 on the high end of the  $R_p/R_b$  axis (Figure 6) plateaus in  $\alpha_p$  emerge. We can  
281 evaluate whether the dependence of the fractionation factor on adsorption  
282 rate can be interpreted within this framework.  
283 First, for a given experiment, net adsorption rates decrease abruptly over the

284 first 24 hours, hence it is most likely that the  $R_p/R_b$  ratio changes. However,  
 285  $\alpha^{30/28}\text{Si}_{\text{adsorbed/solution}}$  ( $\alpha_p$  in DePaolo (2011)'s terminology) remains constant.  
 286 This means that the early stage of our experiments cannot be interpreted  
 287 as being located at intermediate  $R_p/R_b$  values where  $\alpha_p$  is expected to be  
 288 strongly dependent on adsorption rate (Figure 6). Second, as there is net  
 289 adsorption during this early stage, the experiments cannot be interpreted  
 290 as operating near chemical and isotopic equilibrium, hence they are likely  
 291 not located on the low end of the  $R_p/R_b$  axis (Figure 6). Therefore, for the  
 292 first 24 hours in each experiment, the constant  $\alpha_p$  value while  $R_p/R_b$  ratios  
 293 change means that the experiments are located, on the "kinetic plateau".  
 294 There, at the high end of  $R_p/R_b$  values,  $\alpha_p \sim \alpha_f$ . The difference between  
 295 the apparent isotope fractionation factors then reflects different values of the  
 296 kinetic isotope fractionation factors associated with the forward reaction.  
 297 We therefore conclude that the observed dependence of Si isotope fractiona-  
 298 tion on the initial Si concentration can only be explained within the DePaolo  
 299 framework if  $\alpha_f$  values differ between the three experiments (Figure 6).  
 300 After 24 hours  $\delta(^{30/28}\text{Si})_{\text{solution}}$  and hence  $\alpha^{30/28}\text{Si}_{\text{adsorbed/solution}}$  changes. We  
 301 can interpret this second stage of the experiments within the DePaolo frame-  
 302 work as only then  $R_b$  increases at the cost of  $R_f$  and hence  $\alpha_p$  departs from  
 303 the kinetic plateau and evolves towards equilibrium. We can estimate the  
 304 equilibrium isotope fractionation factor from the linear correlation of the  
 305 overall net adsorption rate and the determined closed-system isotope frac-  
 306 tionation factors (see Figure 5). Extrapolated to a zero net adsorption rate,  
 307 an equilibrium isotope fractionation factor of  $\alpha^{30/28}\text{Si}_{\text{adsorbed/solution}} = 0.9997$   
 308 ( $10^3 \ln \alpha^{30/28}\text{Si}_{\text{adsorbed/solution}} = -0.3 \text{ ‰}$ ) results.

309 That  $\alpha_f$  values depend on Si concentrations is an unexpected conclusion that  
310 warrants an explanation. At the early stage of this finding we can only spec-  
311 ulate on its cause. We can exclude that our high-concentration experiments  
312 were limited in adsorption sites, such that the removal mechanism shifted  
313 from one of adsorption to one for example of precipitation (see section 3.1).  
314 The most likely process is hence adsorption onto monolayers in all three  
315 experiments. It is conceivable that a shift in surface complexation occurs  
316 with increasing Si concentration and that different complexes differ by the  
317 strength of their adsorption site and are hence associated with different  $\alpha_f$   
318 values (Lemarchand et al., 2007). However, this assumption is not supported  
319 by surface complexation models which are able to reconcile the evolution of  
320 Si adsorption onto gibbsite using only one surface complex (Karamalidis and  
321 Dzombak, 2011). We note that the poor fit and the small amount of usable  
322 data of that study does not allow to fully rule out this explanation either.  
323 A second possible explanation is the polymerization of silicic acid at the  
324 gibbsite surface and therefore the formation of Si-O-Si bonds that are prob-  
325 ably associated with different isotope fractionation factors. Yokoyama et al.  
326 (1982) reported the polymerization of Si at the surface of Al-hydroxides but  
327 only for much higher concentrations of dissolved Si. However, in a precip-  
328 itation experiment Oelze et al. (2014) observed a fractionation factor  $\alpha_p =$   
329 1 for polymerization of silicic acid. Therefore further studies on the exact  
330 adsorption process of Si onto Al-hydroxides are needed to resolves this issue.

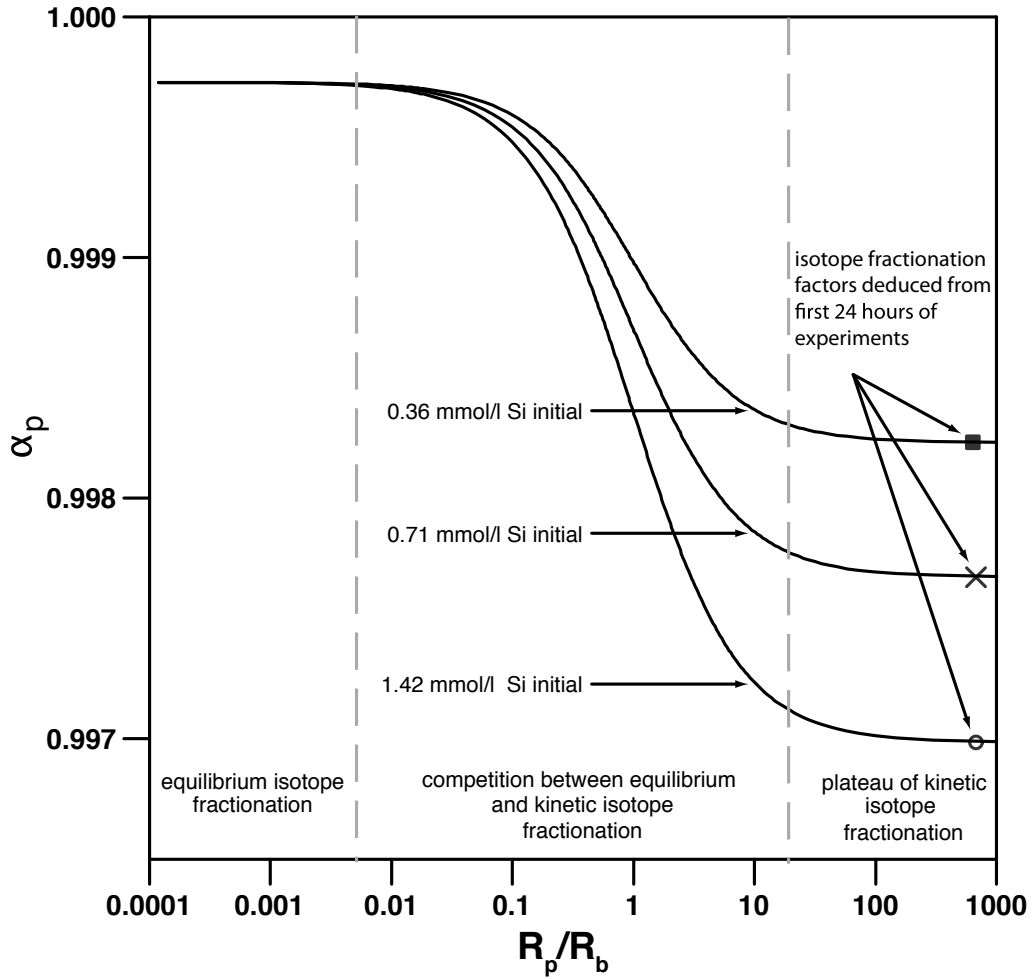


Figure 6: Model curve of  $\alpha_p$  vs.  $R_p/R_b$  using the “DePaolo-Model” (black lines) as a function of  $R_p/R_b$ . The  $\alpha_f$  values for different initial Si concentrations were deduced from the calculated closed-system isotope fractionation factor for the first 24 hours of the individual experiments (see Figure 2 and Table 1). The isotope fractionation factor at equilibrium is inferred from the linear correlation of the overall net adsorption rate and the closed-system isotope fractionation factors (see Figure 4). For a zero net adsorption rate the equilibrium isotope fractionation factor results to  $\alpha_{eq} = 0.9997$

331 *4.4. Si adsorption in natural systems*

332 Si adsorption onto gibbsite (this study) and onto Fe-oxides (Delstanche et al.,  
333 2009) both favor light Si isotopes while the remaining solution accumulates  
334 the heavy Si isotopes. Delstanche et al. (2009) computed fractionation fac-  
335 tors for Si adsorption onto Fe-oxides ( $10^3 \ln \alpha^{30/28} \text{Si}_{\text{ferrihydrite/solution}} = -1.05 \text{ ‰}$   
336 and  $10^3 \ln \alpha^{30/28} \text{Si}_{\text{goethite/solution}} = -1.56 \text{ ‰}$ ). These fractionation factors were  
337 shown to be independent of Si concentration (Delstanche et al., 2009). There  
338 are two ways to explain the contrasting behavior of Si isotope between these  
339 two series of experiments: (i) Delstanche et al. (2009) propose that the Si  
340 isotope fractionation during adsorption onto Fe-oxides is caused by the for-  
341 mation of a Fe oxide-monosilicate bi-dendate inner surface complex. The  
342 apparent isotope fractionation factor during Si adsorption is expected to de-  
343 pend in particular on the kinetics of the formation of this distinct surface  
344 complex. The formation rate of this surface complex might be independent  
345 of Si concentration and thus no dependence of Si concentration and isotope  
346 fractionation would be observed. (ii) We can also use the “DePaolo-Model”  
347 (DePaolo, 2011) to explain this behavior. If we assume that the net adsorp-  
348 tion rate is much higher than the backward rate, the resulting  $\alpha_p$  is firmly  
349 located within the kinetically dominated regime and is thus independent of  
350 small changes of  $R_p/R_b$  (see Figure 6). Both explanations are conceivable.

351 *4.5. Comparison to adsorption of transition metals*

352 The isotopic behavior of Si during adsorption differs fundamentally from  
353 that observed in studies of transition metals. The adsorption of molybde-  
354 num onto Mn-Oxide surfaces was shown to attain equilibrium within <10  
355 hours (Wasylenki et al., 2008). Adsorption of zinc onto ferrihydrite and

356 goethite surfaces attained isotopic equilibrium after <20 hours (Juillot et al.,  
357 2008). Adsorption of ferrous iron to surfaces of goethite, quartz, goethite-  
358 loaded quartz, and aluminium oxide resulted in attainment of equilibrium  
359 within <72 hours (Mikutta et al., 2008). Given such rapid equilibration time  
360 scales and the observed “closed-system” behavior, in natural environmental  
361 systems such transition metal results can be interpreted in terms of equilib-  
362 rium isotope fractionation. The opposite is observed for silica. The strong  
363 kinetic isotope fractionation accompanying Si adsorption and its sluggish re-  
364 equilibration, even after several months of experimental runtime, makes it  
365 likely that natural systems are dominated by kinetic isotope effects. This  
366 conclusion bears important implications for weathering systems that we ex-  
367 plore in the next section.

#### 368 *4.6. Implications for silicate weathering environments*

369 Many recent studies attribute the heavy Si isotopic signature of soil and  
370 stream water to the formation of secondary minerals containing the comple-  
371 mentary reservoir of light Si isotopes (Douthitt, 1982; de La Rocha et al.,  
372 2000; Basile-Doelsch et al., 2005; Ziegler et al., 2005a; Basile-Doelsch, 2006;  
373 Georg et al., 2006a, 2009; Opfergelt et al., 2011). However, the formation  
374 of secondary silicate minerals is sufficiently slow so that equilibrium isotope  
375 fractionation can be expected (Iler, 1979; Sposito, 1996). The Si isotope frac-  
376 tionation factors inferred from *ab initio* calculations (Méheut et al., 2009)  
377 and experimental studies (Oelze et al., 2014) show that  $^{28}\text{Si}$  will not be pref-  
378 erentially incorporated into the clay fraction if dissolved Si and crystalline  
379 silicates are in isotopic equilibrium. How then can the enrichment of  $^{28}\text{Si}$  in  
380 clays found in weathering systems be explained?

381 With increasing age and/or stage of silicate weathering the composition of  
382 secondary solids changes from one dominated by amorphous solids to one  
383 dominated by crystalline clay minerals (Ziegler et al., 2003; Joussein et al.,  
384 2005). For instance, a known transformation path is the reaction of plagioclase  
385 to amorphous aluminosilicates such as allophane, subsequently e.g. to  
386 halloysite, and finally to clay minerals such as kaolinite. It is indeed more  
387 likely that kaolinite is formed via thermodynamically less stable phases which  
388 act as precursor such as allophane and halloysite (Steefel and Van Cappellen,  
389 1990).

390 In any case, the first step is the release of Al and Si from primary minerals  
391 such as plagioclase. At pH values between 5 and 7 and at the low  
392 dissolved organic carbon concentrations typically prevailing in soils or in interstitial  
393 solutions, the solubility of  $\text{Al}(\text{OH})_3$  is extremely low (Sposito, 1996).  
394 Accordingly, Al precipitates as amorphous  $\text{Al}(\text{OH})_3$  or as crystalline solids  
395 such as gibbsite. The affinity of Si to adsorb onto these precipitated Al-  
396 hydroxides is high (Hingston and Raupach, 1967; Adu-Wusu and Wilcox,  
397 1991; Dietzel, 2002). As we have shown in this study, Si adsorption onto Al-  
398 hydroxides is associated with rather strong Si isotope fractionation, favoring  
399 light Si isotopes adsorbed onto the solid surface. In the next step, amorphous  
400 aluminosilicates like siliceous gels or colloids such as hydroxyaluminosilicate  
401 (HAS) are formed. Accordingly, Strekopytov et al. (2006) suggested that,  
402 for HAS formation, the reaction of Si with Al-hydroxides is a prerequisite.  
403 Such amorphous Al-Si phases can be re-arranged to structures with higher  
404 degrees of order, similar to allophane or imogolite (Sposito, 1996; Doucet  
405 et al., 2001). If the transformation from amorphous Al-Si phases without

406 any short range order to phases with distinct short range order like HAS  
407 or allophane takes place without substantial exchange of Si, the Si isotope  
408 signature of HAS/allophane will be inherited from the initial fast adsorption  
409 process of Si. With ongoing weathering, the halloysite content in the soil  
410 decreases, whereas the kaolinite content increases (Papoulis et al., 2004). As  
411 halloysite has the same structure and chemical compositions as kaolinite ex-  
412 cept for the higher water content in halloysite (Joussein et al., 2005), we can  
413 assume that during the transformation of halloysite to kaolinite no shift in Si  
414 isotope composition occurs, as Si will be neither lost nor added. Therefore,  
415 we suggest that the Si isotopic signature of crystalline clay minerals, such  
416 as kaolinite, is inherited from the kinetically-dominated process occurring  
417 during adsorption of Si onto a previously formed amorphous Al-hydroxide.  
418 Our model of inherited isotope signals has important implications for inter-  
419 preting element cycles in the different weathering regimes observed at the  
420 Earth surface. In the kinetically limited weathering regime (where supply  
421 into and erosion from the weathering zone is so fast that not all primary  
422 minerals are dissolved (West et al., 2005; Ferrier and Kirchner, 2008; Dixon  
423 et al., 2012) and solutions are at equilibrium concentrations (Maher, 2011)),  
424 the Si isotopic signature of soil or stream water will inevitably show heavy  
425 Si isotopic values, as in such regimes only fast processes like adsorption of Si  
426 occur and no light Si will be released from secondary minerals due to their  
427 short residence time in the weathering zone. In the supply-limited weath-  
428 ering regime (where supply and erosion of primary minerals is so slow that  
429 most primary minerals are exhausted (West et al., 2005; Ferrier and Kirchner,  
430 2008; Dixon et al., 2012) and solutions are diluted with respect to equilib-

431 rium concentrations (Maher, 2011)), the Si isotopic signature of the soil or  
432 stream water will be characterized by the degree of weathering, ranging from  
433 heavy Si isotopic signatures, where kinetically dominated Si adsorption is the  
434 major process, to light Si isotopic signatures where the system is governed  
435 by dissolution of clay minerals. This has been already shown for tropical  
436 supply-limited settings in the black-water rivers of the Amazon and Congo  
437 basin (Cardinal et al., 2010; Hughes et al., 2013). Where erosion rates of  
438 secondary minerals are low, it is also conceivable that adsorption of Si and  
439 dissolution of secondary minerals are balanced out which results then in an  
440 isotopic signature of soil and stream water indistinguishable from the par-  
441 ent material. The dissolution of previously formed secondary precipitates  
442 dominates and these minerals release their inherited light Si (Bouchez et al.,  
443 2013). Such temporal evolution has been observed from chronosequences in  
444 Hawaii (Ziegler et al., 2005a). These authors measured the isotopic signature  
445 of the soil solutions and observed an enrichment of heavy Si in solution with  
446 increasing age of the soil. In analogy, Opfergelt et al. (2011) clearly showed  
447 from allophane sequences in volcanic soils that the more weathered the soil,  
448 the older the allophane and the lighter the Si isotope signature is.

## 449 **5. Summary**

450 The adsorption of monomeric silicic acid onto gibbsite is accompanied by  
451 a significant kinetic Si isotope fractionation. In all adsorption experiments,  
452 light Si isotopes are preferentially adsorbed. By applying a closed-system  
453 mass balance model we calculate Si isotope fractionation factors that are de-  
454 pendent on the initial Si concentration. High initial Si concentrations result

455 in a strong kinetic Si isotope fractionation during adsorption. This initial ki-  
456 netic signature does begin to re-equilibrate only after ca. 2 months. With this  
457 sluggish behavior Si behaves fundamentally different from transition metals  
458 (e.g. Fe, Mo, Zn) that equilibrate isotopically within hours.

459 Application of the mass balance model of DePaolo (2011) requires the as-  
460 sumption of different isotope fractionation factors ( $\alpha_f$ ) associated with the  
461 forward reaction at different initial Si concentrations, rather than changes  
462 in forward to backward reaction rate. A minor shift in isotope ratios after  
463 24 hours of Si adsorption is explained by a change in the isotope fractiona-  
464 tion regime from kinetically dominated to dominated by equilibrium isotope  
465 fractionation. This behavior is compatible with a change from high net ad-  
466 sorption rates to low net adsorption rates (almost constant Si concentration  
467 at the end of experiments).

468 Our findings have major relevance for explaining Si isotope systematics dur-  
469 ing silicate weathering. We hypothesize that the light Si isotopes signatures  
470 commonly found in secondary siliceous minerals and amorphous solids are  
471 obtained from adsorption of Si onto Al-hydroxides during the early stages of  
472 weathering. When these amorphous phases slowly age to ordered structures  
473 and clay minerals, the low isotope ratio is passed on from the amorphous pre-  
474 cursors. The light isotope composition found in clays is therefore inherited  
475 from the early stages of primary mineral decomposition.

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637 **Appendix A. Tables**

Table A.1: Adsorption experiments; Si concentration ([Si]) (the relative uncertainty  $\epsilon$  has been estimated by the long term reproducibility to 5%); and  $\delta(^{29/28}\text{Si})_{NBS28}$  and  $\delta(^{30/28}\text{Si})_{NBS28}$  solution values as well as 95% confidence interval (CI) of the delta values; sample names: (pH)\_(sampling time [h])\_(Si-start-conc [mmol/l])

name	[Si]	$\delta(^{29/28}\text{Si})_{NBS28}$	CI	$\delta(^{30/28}\text{Si})_{NBS28}$	CI
	[mmol/l]	[‰]	[‰]	[‰]	[‰]
7_start_0.36	0.372± 0.019	-0.038	0.057	-0.078	0.106
7_0.02_0.36	0.349± 0.017	0.031	0.040	0.073	0.048
7_0.08_0.36	0.339± 0.017	0.016	0.034	0.057	0.074
7_0.17_0.36	0.334± 0.017	0.052	0.044	0.083	0.080
7_0.25_0.36	0.332± 0.017	0.058	0.068	0.114	0.102
7_0.42_0.36	0.330± 0.016	0.082	0.049	0.148	0.063
7_0.75_0.36	0.325± 0.016	0.071	0.072	0.173	0.016
7_1_0.36	0.329± 0.016	0.077	0.045	0.156	0.076
7_2_0.36	0.321± 0.016	0.080	0.018	0.168	0.046
7_6_0.36	0.309± 0.015	0.108	0.026	0.236	0.017
7_24_0.36	0.294± 0.015	0.206	0.052	0.363	0.066
7_96_0.36	0.274± 0.014	0.218	0.092	0.430	0.123
7_192_0.36	0.268± 0.013	0.249	0.040	0.462	0.057
7_384_0.36	0.259± 0.013	0.215	0.041	0.442	0.142
7_768_0.36	0.253± 0.013	0.248	0.057	0.531	0.096
7_1536_0.36	0.246± 0.012	0.256	0.032	0.490	0.064
7_start_0.71	0.746± 0.037	-0.038	0.057	-0.078	0.106
7_0.02_0.71	0.695± 0.035	0.023	0.014	0.042	0.063

Continued...

name	[Si]	$\delta(^{29/28}Si)_{NBS28}$	CI	$\delta(^{30/28}Si)_{NBS28}$	CI
7_0.08_0.71	0.707± 0.035	0.014	0.024	0.052	0.061
7_0.17_0.71	0.692± 0.035	0.070	0.033	0.123	0.038
7_0.25_0.71	0.689± 0.034	0.048	0.031	0.113	0.025
7_0.5_0.71	0.684± 0.034	0.075	0.007	0.135	0.088
7_0.75_0.71	0.675± 0.034	0.053	0.047	0.110	0.062
7_1_0.71	0.668± 0.033	0.069	0.026	0.131	0.073
7_2_0.71	0.664± 0.033	0.082	0.040	0.219	0.072
7_6_0.71	0.642± 0.032	0.119	0.032	0.281	0.025
7_24_0.71	0.622± 0.031	0.210	0.041	0.377	0.094
7_96_0.71	0.602± 0.030	0.221	0.024	0.430	0.063
7_192_0.71	0.588± 0.029	0.242	0.064	0.459	0.036
7_384_0.71	0.567± 0.028	0.264	0.062	0.486	0.088
7_1464_0.71	0.549± 0.027	0.275	0.037	0.535	0.091
7_start_1.42	1.468± 0.073	-0.054	0.072	-0.077	0.154
7_0.02_1.42	1.368± 0.068	0.049	0.077	0.125	0.165
7_0.5_1.42	1.364± 0.068	0.046	0.057	0.137	0.109
7_1_1.42	1.359± 0.068	0.076	0.024	0.195	0.068
7_2_1.42	1.351± 0.068	0.104	0.071	0.153	0.078
7_6_1.42	1.324± 0.066	0.107	0.103	0.256	0.070
7_24_1.42	1.283± 0.064	0.183	0.062	0.307	0.116
7_96_1.42	1.263± 0.063	0.174	0.121	0.352	0.108
7_192_1.42	1.248± 0.062	0.166	0.065	0.445	0.173
7_384_1.42	1.220± 0.061	0.247	0.053	0.451	0.099

638 **Appendix B. Determination of monosilicic acid using  $\beta$ -silicomolybdate**  
639 **method**

640 Using the  $\beta$ -silicomolybdate method (described in detail by Iler (1982) and  
641 Dietzel (2000)) we verified that the Si stock solution contains only monomeric  
642 silicic acid. This method is based on the reaction of molybdate with dissolved  
643 monomeric silicic acid to a yellow colored  $\beta$ -silicomolybdate aquocomplex,  
644 whose evolution is detected at 390 nm by spectrometry for 20 min (UV-VIS  
645 Cary 100, Varian). The reaction rate constant,  $k$ , for the unidirectional re-  
646 action of molybdate with dissolved monomeric silicic acid obtained by fitting  
647 a second-order reaction is  $2.1 \pm 0.2 \text{ min}^{-1}$  for the prepared solution. This  
648 measured range of  $k$  values clearly indicates that only monomeric silicic acid,  
649  $\text{Si}(\text{OH})_4$ , is present in solution as polymeric silicic acid induces  $k$  values of  
650  $0.03 \text{ min}^{-1}$  for dimeric and octameric silicic acid and for silica colloids with  
651 about 40 silicon atoms in its structure, respectively (e.g. Iler (1982)).

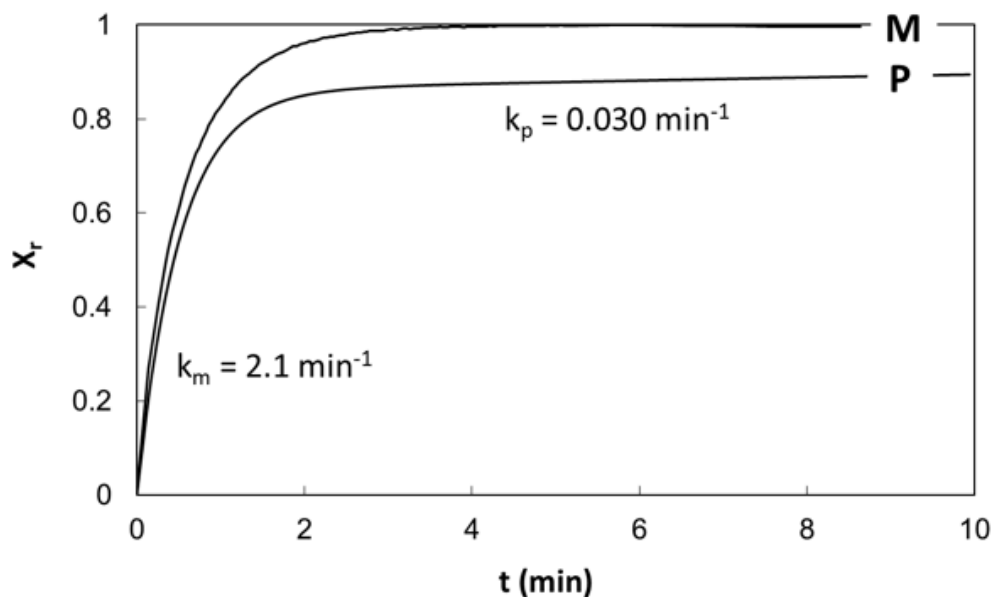


Figure B.1: Evolution of the  $\beta$ -silicomolybdate complex formation by the reaction of molybdate and dissolved monomeric silicic acid.  $t$ : reaction time of the measurement.  $X_r$ : molar fraction of total dissolved monomeric silicic acid that has reacted to the silicomolybdate complex (see Dietzel (2000) for details). M: monosilicic acid stock solution. P: solution containing both monosilicic (86%) and polysilicic acid (14%) (soil solution from Wonisch et al. (2008)). Polysilicic acid was not detected in our experimental solutions (evolution according to curve M).  $k_m$  and  $k_p$  denote the reaction rate constant for the reaction of monosilicic and polysilicic acid to the  $\beta$ -complex, respectively.

652 **Appendix C. Chemical kinetic rate laws applied to Si adsorption**  
653 **on gibbsite**

654 In an attempt to explain the evolution of Si concentration with time we tried  
655 to apply well-known chemical rates laws to our data. Here we show that  
656 first-order, second-order and first-order forward-backward reaction rate laws  
657 are not able to explain the data.

658 Reactions that follow first-order kinetics are only dependent on the concen-  
659 tration change of one reactant (A).

$$R = -\frac{d[A]}{dt} = k[A] \quad (\text{C.1})$$

660 The integrated form of this equation is:

$$\ln[A] = -kt + \ln[A]_0 \quad (\text{C.2})$$

661 If the reaction follows first-order rate kinetics a plot of  $\ln[A]$  vs.  $t$  should  
662 result in a straight line with a slope of  $-k$ . The adsorption of Si onto gibbsite  
663 does not follows a first-order rate law (Figure C.1).

664 If the adsorption reaction follows a second-order rate law of the form:

$$R = -\frac{d[A]}{dt} = k[A]^2 \quad (\text{C.3})$$

665 of which the integrated form is:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad (\text{C.4})$$

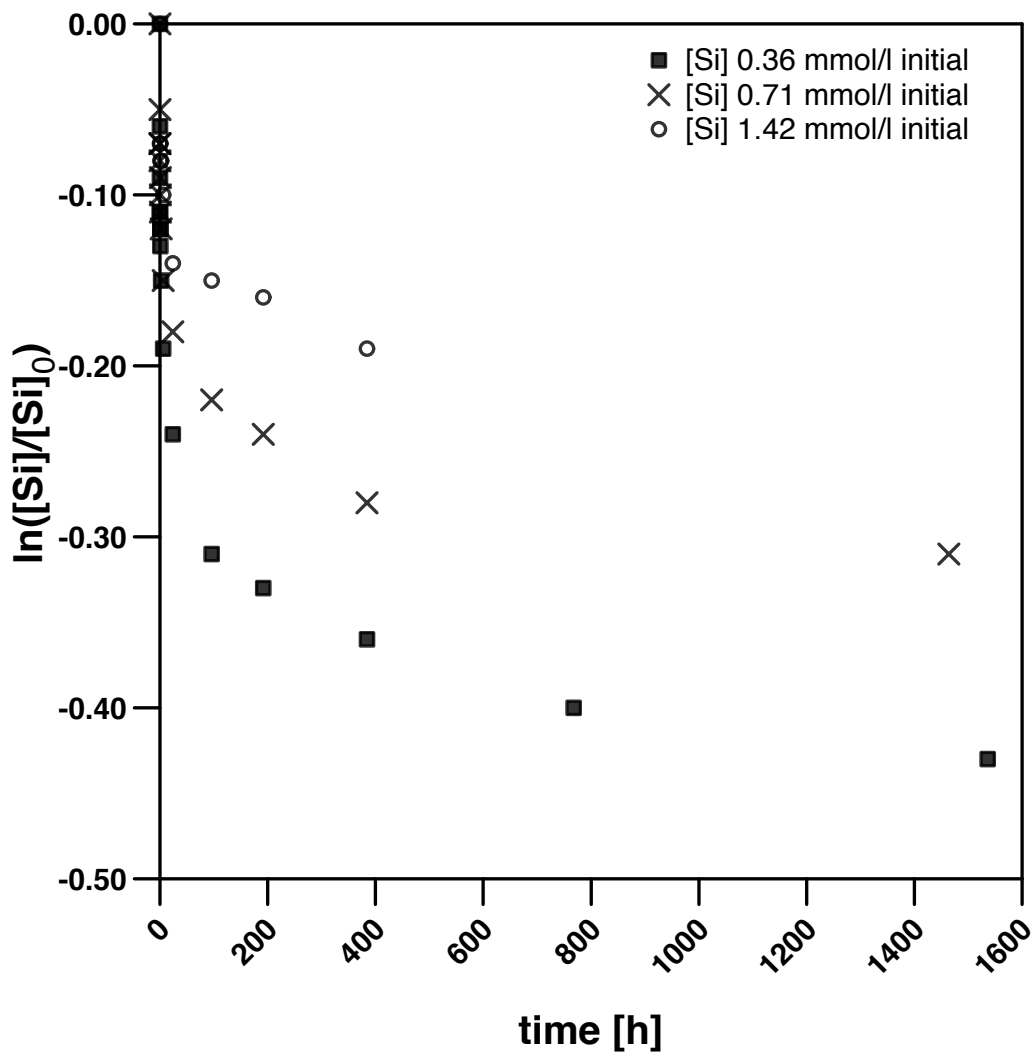


Figure C.1:  $\ln\left(\frac{[A]}{[A]_0}\right)$  vs. experimental runtime  $t$ . If the adsorption of Si onto gibbsite followed first-order rate kinetics the experimental data should plot on a straight line.

666 Then the experimental data of the adsorption experiments should fall on a  
 667 straight line in a plot of  $\frac{1}{[A]}$  vs.  $t$ , where the slope of this line would be the  
 668 reaction rate constant  $k$ . Figure C.2 shows obviously that the adsorption of

669 Si onto gibbsite surfaces does not follow a second-order rate law.

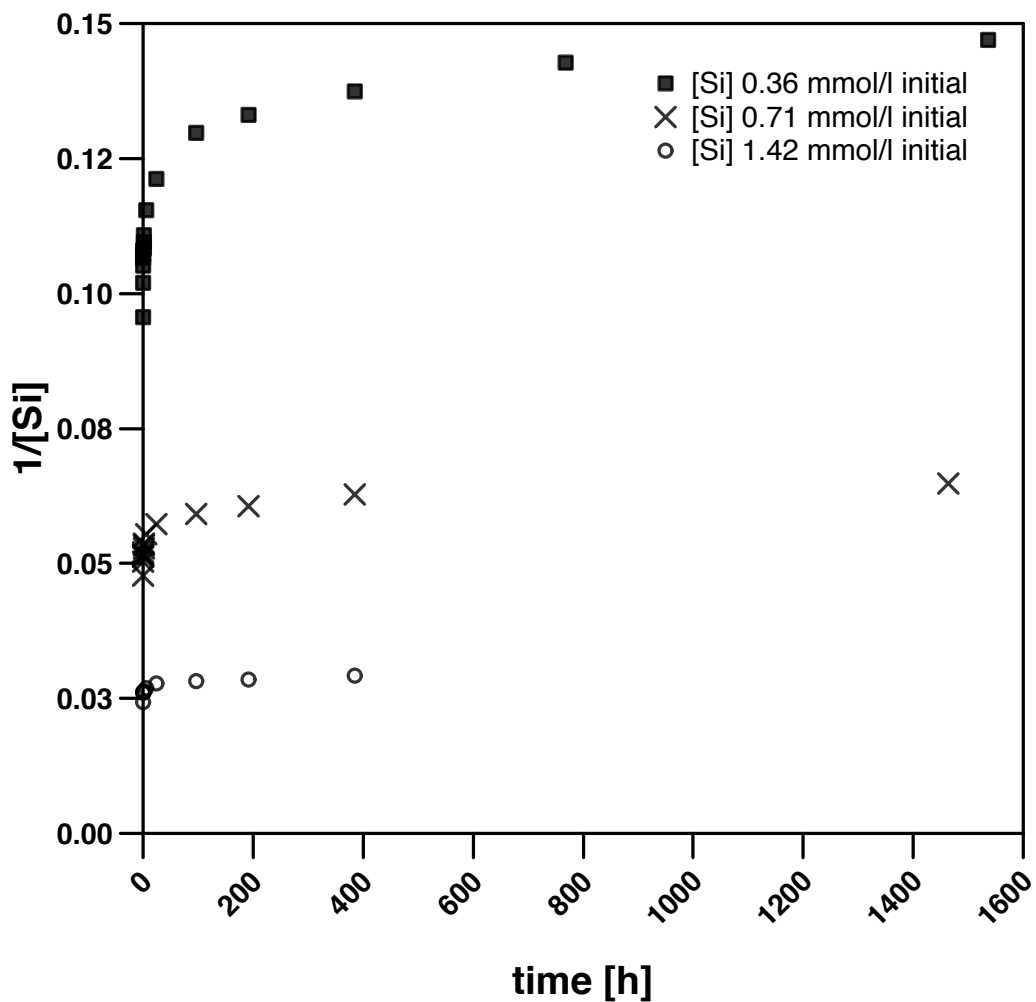


Figure C.2:  $\frac{1}{[A]}$  vs. experimental runtime  $t$ . If the adsorption of Si onto gibbsite followed second-order rate kinetics the experimental data should plot on a straight line.

670 The third attempt was to describe the adsorption kinetics of Si onto gibbsite  
671 as a forward-backward reaction (adsorption-desorption reaction). We assume  
672 that the individual reactions (forward and backward, respectively) following

673 a first-order rate law. Further we assume that at the beginning of the exper-  
674 iment no Si is adsorbed onto gibbsite. In such case the reaction rate would  
675 be:

$$R = -\frac{d[A]}{dt} = k_f[A]_t - k_b[B]_t \quad (\text{C.5})$$

676 Where  $k_f$  and  $k_b$  are the reaction rate constants for the forward (adsorption)  
677 and backward (desorption) reactions, respectively. The integrated form of  
678 this equation is:

$$\ln \left( \frac{([A]_0 - [A]_{eq})}{([A]_0 - [A]_{eq})} \right) = (k_f + k_b)t \quad (\text{C.6})$$

679 If the adsorption of Si onto gibbsite followed Eq. C.6, then all data should  
680 fall along a straight line with a slope of  $(k_f + k_b)$  in a plot of  $\ln \left( \frac{([A]_0 - [A]_{eq})}{([A]_0 - [A]_{eq})} \right)$   
681 vs. experimental runtime  $t$ . But figure C.3 shows that this assumption is  
682 not true for the adsorption of Si into gibbsite.

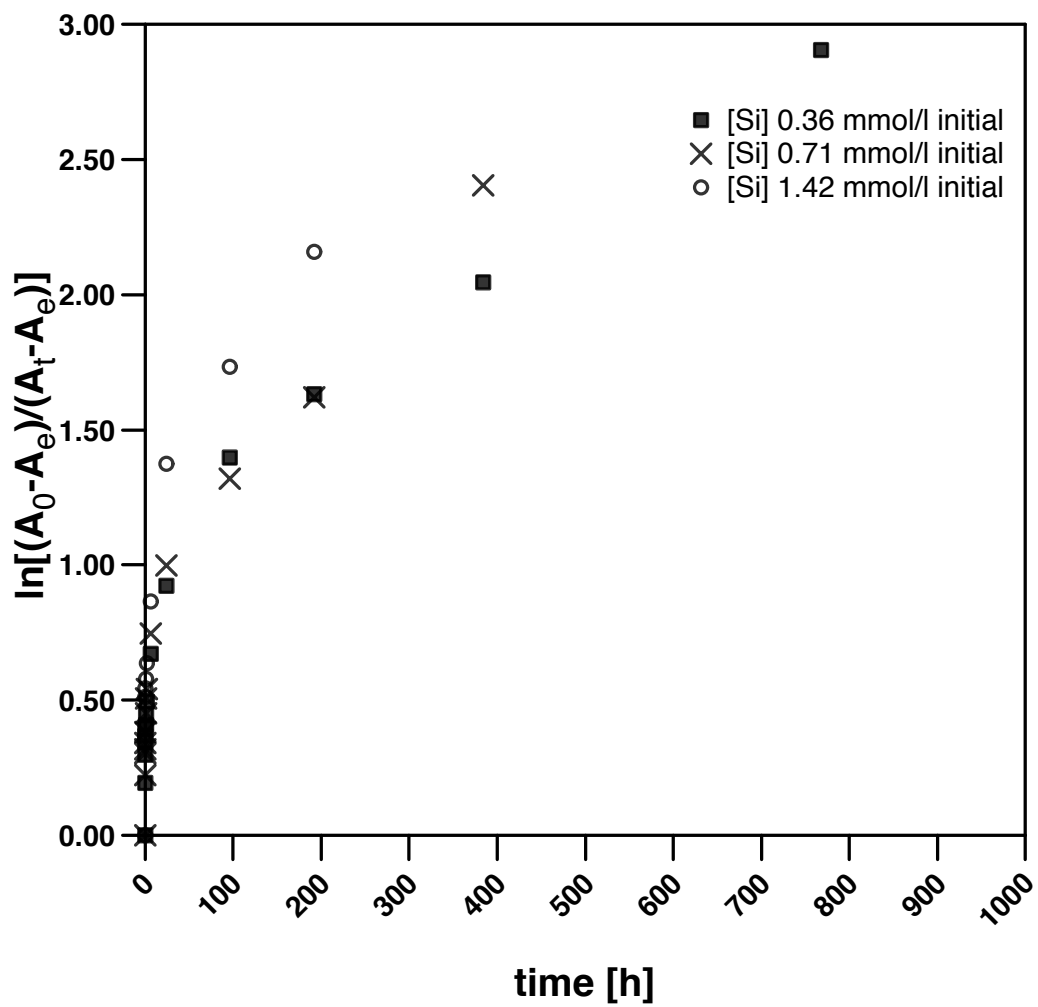


Figure C.3:  $\ln\left(\frac{([A]_0 - [A]_{eq})}{([A]_0 - [A]_{eq})}\right)$  vs. experimental runtime  $t$ . If the adsorption of Si onto gibbsite followed the assumption that Si adsorption onto gibbsite occurs via first-order forward and backward reactions the experimental data should plot on a straight line.