Supporting Information

Adsorption behavior of metasilicate on N-methyl D-glucamine functional groups and associated silicon isotope fractionation

Wei Wang, [†] Hai-Zhen Wei, *[,‡] Shao-Yong Jiang, *[,†,‡] Christopher J. Eastoe, [§]

Qi Guo, [†] Yi-Bo Lin[†]

[†] *State Key Laboratory of Geological Processes and Mineral Resources, Faculty of Earth Resources, China University of Geosciences, Wuhan 430074, PR China*
[‡] *State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing 210023, PR China*
[§] *Department of Geosciences, University of Arizona, Tucson, AZ 85721, USA*

* Author to whom correspondence should be addressed:
Prof. Shao-Yong Jiang, Email address: shyjiang@nju.edu.cn
Dr. Hai-Zhen Wei, Email address: haizhenwei@nju.edu.cn

Table of Contents

S1. Batch experiments for adsorption behaviors **2**

S2. Evaluation of adsorption thermodynamics, kinetics, capacity **3, 4, 5**

S3. Characterization of bonding configuration of Si-L complexes **3, 5, 6**

S1. Batch experiments

The experimental information on batch experiments for adsorption behaviors, evaluation of adsorption thermodynamics, kinetics and capacity, and characterization of bonding configuration of Si-L complexes were given in the Supporting Information Table S1.

Table S1. Experimental conditions for adsorption kinetic and thermodynamic mechanism of metasilicate with N-methyl-D-glucamine

Group A. Different initial silicon concentrations

No.	Temperature (K)	$[Si]_{initial}$ (ppm)	Resin mass (g)	Solution volume (mL)	Initial pH
A-1	298	5.6	2	50	10.53
A-2	298	11.2	2	50	10.83
A-3	298	16.8	2	50	10.98
A-4	298	22.4	2	50	11.02
A-5	298	28	2	50	11.20
A-6	298	42	2	50	11.36
A-7	298	56	2	50	11.48

Group B. Different solution temperatures

No.	Temperature (K)	$[Si]_{initial}$ (ppm)	Resin mass (g)	Solution volume (mL)	Initial solution pH
B-1	293	2.95	5	50	10.02
B-2	303	3.78	5	50	10.47
B-3	313	3.78	5	50	10.47
B-4	323	3.78	5	50	10.47

Group C. Cumulative adsorption amount of silicon on 5g of IRA -743 resin

No.	Temperature (K)	$[Si]_{initial}$ (ppm)	Resin mass (g)	Solution volume (mL)	Adsorption time (h)
C-1	293	126	5	5	2
C-2	293	126	5	10	4
C-3	293	126	5	10	4

C-4	293	126	5	25	24
Sum				50	34

Group D. Different molar ratio of silicate to L

No.	C_{si} (M)	Si: L ratios	Solution volume (mL)	C_L (M)	Mass of L (g)
D-1	1	1:2	10	2	4
D-2	1	1:1	10	1	2
D-3	1	2:1	10	0.5	1
D-4	1	1:0	10	0	0

S2. Estimation of adsorption capacity, thermodynamics and kinetics

On the basis of an assumption that all resin beads are uniform in size, the volume of resin and a single bead were calculated using Eq. S1 and Eq. S2, respectively. Thus, the surface area (S) of a single bead and the total resin were calculated using Eq. S4 and Eq. S5, correspondingly.

$$V_{total} = \frac{m}{\rho} \quad \text{(Eq. S1)}$$

$$V_{single} = \frac{4}{3}\pi r^3 \quad \text{(Eq. S2)}$$

$$n = \frac{V_{total}}{V_{single}} = \frac{3m}{4\pi\rho r^3} \quad \text{(Eq. S3)}$$

$$S_{single} = 4\pi r^2 \quad \text{(Eq. S4)}$$

$$S_{total}(dm^2) = \frac{3m}{\rho r} \cdot 10^{-2} \quad \text{(Eq. S5)}$$

where m (g) is the resin mass, ρ (g cm^{-3}) is the density of 0.68 g cm^{-3} for the IRA-743 resin. r (cm), the average bead radius of 0.052 cm.

Typical adsorption isotherms (e.g. Freundlich model (Eq. S6), Temkin model (Eq. S7), Langmuir model etc.) were employed to evaluate the adsorption process.

$$\Gamma = kC_0^{1/n} \quad \text{(Eq. S6)}$$

$$\Gamma = \frac{RT}{a}\ln(A_0 C_0) \qquad \text{(Eq. S7)}$$

where Γ (mol dm^{-2}) is the equilibrium silicon surface concentration corresponding to each concentration of silicon (C_0, mol L^{-1}) in the bulk solution. The terms of *K*, *n*, *a*, A_0 are constants at a certain temperature. R is the gas constant, 8.3145 J mol^{-1} K^{-1}, and T is the temperature in K.

Table S2. Surface concentration of adsorbed silicon on the IRA-743 resin in different bulk solution at 298 K

Sample No.	C_0 (ppm)	C_0 (M)	C_e (ppm)	Γ (mol dm^{-2})
Group A-I				
A-I-1	5.6	0.0002	1.60	4.20×10^{-6}
A-I-2	11.2	0.0004	4.38	7.17×10^{-6}
A-I-3	16.8	0.0006	4.30	1.31×10^{-5}
A-I-4	22.4	0.0008	11.88	1.11×10^{-5}
A-I-5	28.0	0.0010	6.02	2.31×10^{-5}
A-I-6	42.0	0.0015	12.31	3.12×10^{-5}
A-I-7	56.0	0.0020	16.52	4.15×10^{-5}
Group A-II				
A-II-1	5.6	0.0002	1.99	3.80×10^{-6}
A-II-2	11.2	0.0004	2.93	8.68×10^{-6}
A-II-3	16.8	0.0006	4.48	1.29×10^{-5}
A-II-4	22.4	0.0008	11.81	1.10×10^{-5}
A-II-5	28.0	0.0010	7.87	2.11×10^{-5}
A-II-6	42.0	0.0015	9.18	3.45×10^{-5}
A-II-7	56.0	0.0020	16.66	4.13×10^{-5}

Note: C_0 and C_e are silicon concentrations in the initial solution and the final solution after reaching equilibrium

Table S3. Accumulative adsorption of silicon on 5 grams of IRA 743 resin

No.	Temperature (K)	$[Si]_{initial}$ (ppm)	V(mL)	C_i (ppm)
C-1	293	126	5	1.01
C-2	293	126	10	4.58
C-3	293	126	10	11.14
C-4	293	126	25	21.35
Sum		6300 μg		696 μg
Adsorption capacity ($\mu mol \cdot g^{-1}$)			40.03	

Table S4. Variation of silicon concentration in parent solution with reaction time at different temperatures

Time (min)	Silicon concentration ($[C_{mean}]$ ppm, 2σ)			
	B-1 (293K)	B-2 (303K)	B-3 (313K)	B-4 (323K)
0	2.950	3.780	3.780	3.780
20	2.520 (0.135)	0.910 (0.026)	2.692 (0.099)	1.412 (0.285)
40	2.191 (0.126)	0.676 (0.053)	2.419 (0.177)	0.732 (0.029)
60	1.310 (0.135)	0.285 (0.022)	0.802 (0.095)	0.374 (0.043)
80	0.913 (0.015	0.246 (0.019)	0.507 (0.040)	0.225 (0.031)
100	0.694 (0.013)	0.376 (0.053)	0.452 (0.055)	0.209 (0.028)
120	0.440 (0.038)	0.103 (0.060)	0.373 (0.041)	0.192 (0.062)
240	0.203 (0.012)	0	0.152 (0.051)	0.056 (0.022)
360	0.015 (0.003)	0	0	0

Table S5. Variation of surface concentration of silicon on Amberlite IRA-743 resin with reaction time at different temperatures

Time (min)	Surface concentration Γ(mol·dm^{-2})			
	B-1 (293K)	B-2 (303K)	B-3 (313K)	B-4 (323K)
0	0	0	0	0
20	4.90×10^{-7}	1.21×10^{-6}	4.57×10^{-7}	9.95×10^{-7}
40	3.31×10^{-7}	1.31×10^{-6}	5.72×10^{-7}	1.27×10^{-6}
60	6.86×10^{-7}	1.47×10^{-6}	1.24×10^{-6}	1.42×10^{-6}
80	8.47×10^{-7}	1.48×10^{-6}	1.36×10^{-6}	1.48×10^{-6}
100	9.36×10^{-7}	1.43×10^{-6}	1.38×10^{-6}	1.49×10^{-6}
120	1.04×10^{-6}	1.54×10^{-6}	1.41×10^{-6}	1.50×10^{-6}
240	1.13×10^{-6}	1.58×10^{-6}	1.50×10^{-6}	1.55×10^{-6}
360	1.20×10^{-6}	1.58×10^{-6}	1.56×10^{-6}	1.57×10^{-6}

Table S6. Variation of surface coverage of silicon on Amberlite IRA-743 resin with reaction time at different temperatures

Time	B-1 (293K)		B-2 (303K)		B-3 (313K)		B-4 (323K)	
(min)	Surface coverage	2σ	Surface coverage	2σ	Surface coverage	2σ	Surface coverage	2σ
0	0	0	0	0	0	0	0	0
20	0.00113	0.00053	0.00756	0.00010	0.00286	0.00039	0.00622	0.00112
40	0.00201	0.00048	0.00815	0.00021	0.00357	0.00068	0.00800	0.00012
60	0.00427	0.00014	0.00916	0.00008	0.00774	0.00036	0.00893	0.00016
80	0.00527	0.00006	0.00926	0.00007	0.00849	0.00016	0.00931	0.00013
100	0.00582	0.00004	0.00893	0.00020	0.00863	0.00020	0.00935	0.00010
120	0.00646	0.00014	0.00961	0.00023	0.00882	0.00015	0.00939	0.00022
240	0.00704	0.00005	0.00986	0.00000	0.00937	0.00019	0.00972	0.00007
360	0.00750	0.00001	0.00986	0.00000	0.00974	0.00001	0.00986	0.00001

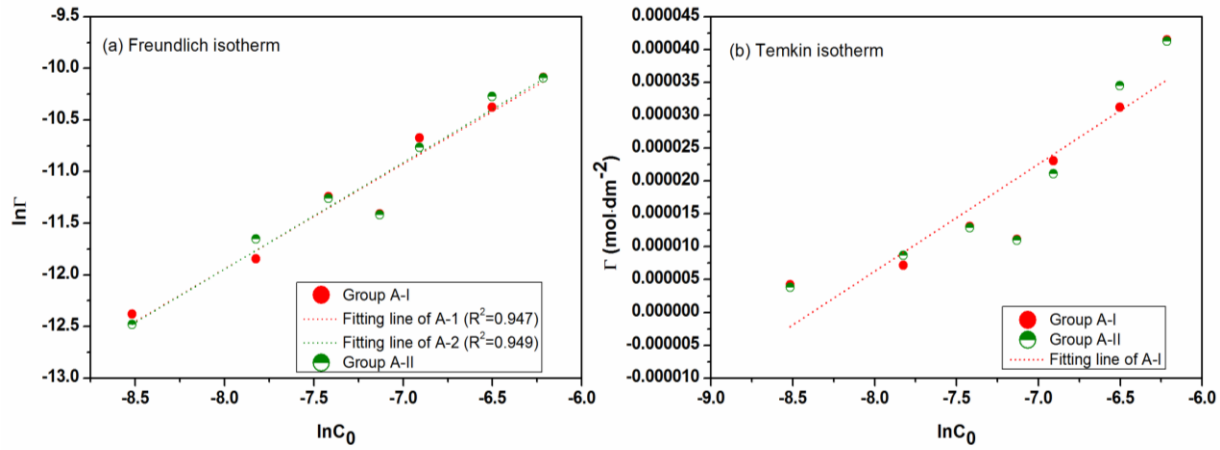


Figure S1. Adsorption isotherm of silicon on the IRA-743 resin evaluated by a Freundlich model (a) and a Temkin model (b).

S3. Characterization of bonding configuration of silicon-L complexes

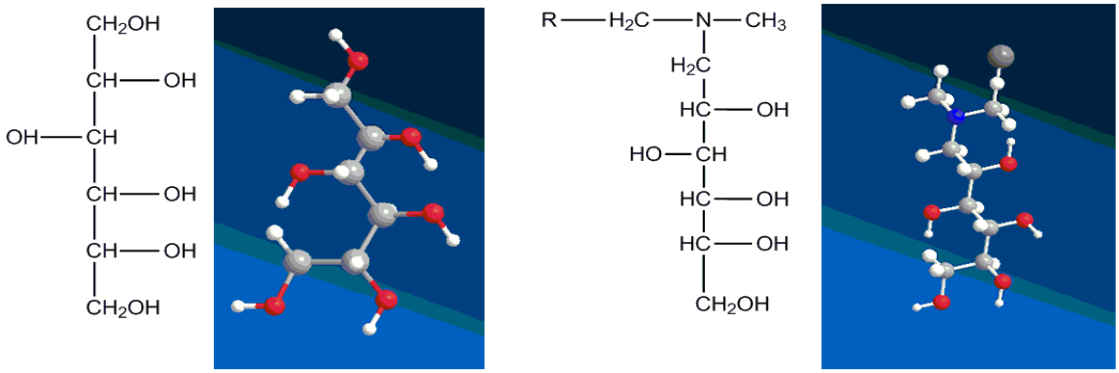
Table S7. ^{29}Si resonance position (δ) for Si-L complexes

Alkaline solution	δ (ppm)
C (Si):C (L) =1:0	-72, -79, -82, -87, -89, -95
C (Si):C (L) = 1:1	-72, -79, -82, -87, -89, -95, -97, -143.7, -144.4, -145.0
C (Si):C (L) = 2:1	-72, -79, -82, -87, -89, -95, -97, -145
C (Si):C (L) = 1:2	-72, -79, -82, -87, -89, -95, -97, -102.3, -143.7, -144.3,-145.0

Table S8. FTIR spectra of the Amberlite IRA-743 resin

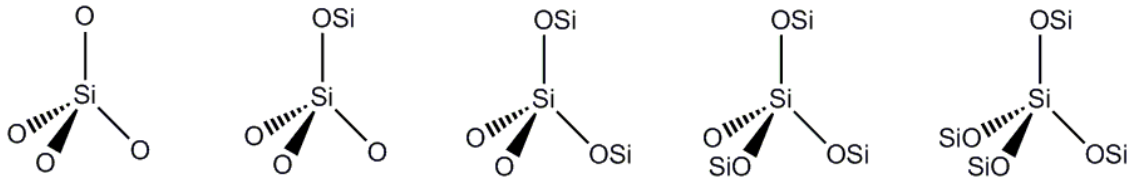
Band	Wavenumbers (cm^{-1})	Assignments
1	~3397	ν O-H and ν N-H
2	~3024	ν C-H of benzene ring
3	~2928	ν CH2

4	~1636.0, ~1610.6,~1511.6	ν C-C of benzene ring
5	~1453	δ CH2
6	~1371	δ CH3
7	~1276	δ C-C of benzene ring
8	~1193	ν C-N
9	~1083	ν C-O
10	~1043	δ C-H of benzene ring
11	~850.8, ~816.0, ~703.0	1,3-substituted
12	~659-769	δ O-H



(a) Sorbitol (b) N-methylglucamine in IRA 743 resin

Figure S2. The plane and stereo structure of the sorbitol (a) and N-methylglucamine (b). The larger grey sphere is a benzene ring. The atoms of C, N, O, H are illustrated in light gray, blue, red, white, respectively.



(a) (b) (c) (d) (e)

Figure S3. The possible structures for tetracoordinated silicates: Q0 (a), Q1 (b), Q2 (c), Q3 (d), Q4 (e), respectively

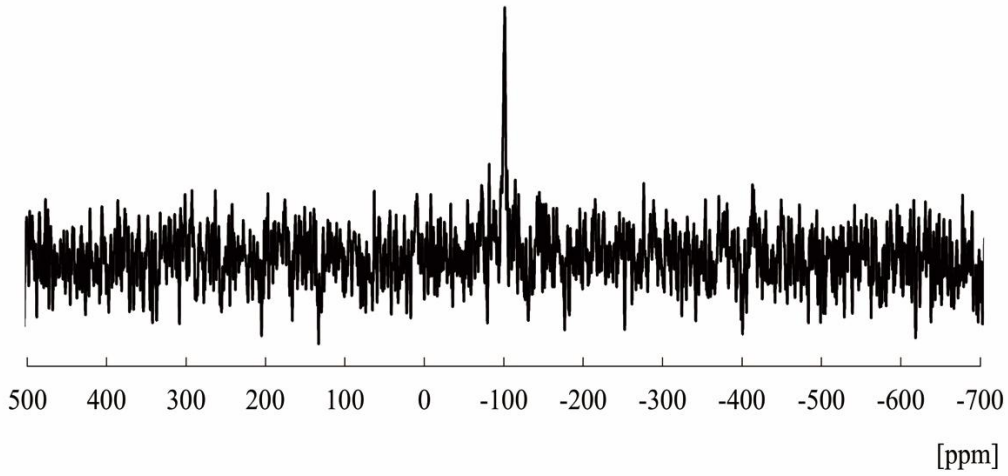


Figure S4. The MAS-29Si NMR spectrum of the IRA 743 resin with saturated attachment of silicate species.

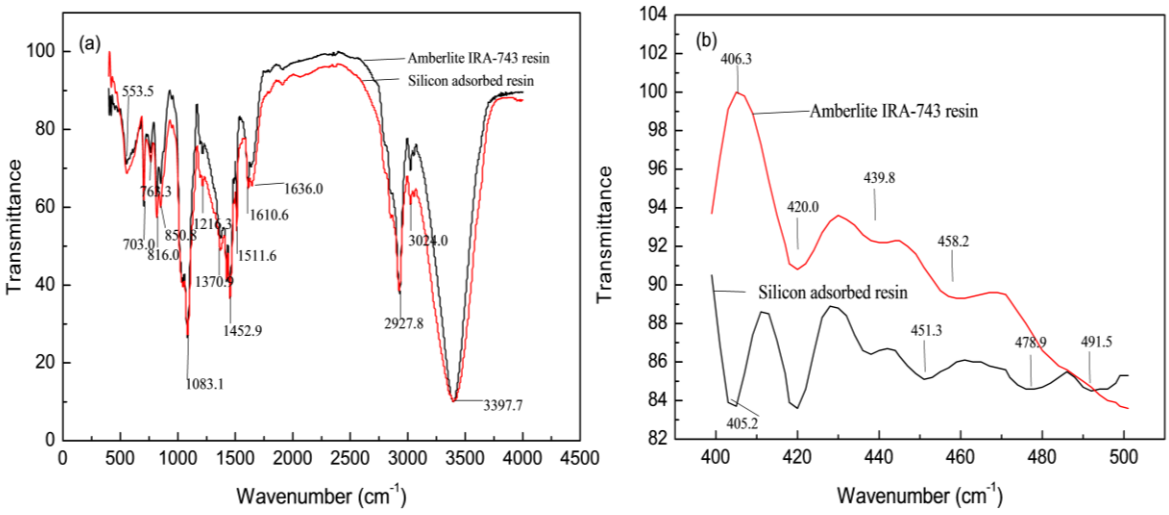


Figure S5. FTIR spectra of the Amberlite IRA-743 resin and silicon adsorbed resin: (a) vibration band from 0~4000 cm^{-1}; (b) vibration band from 400~500 cm^{-1}.