

THE EFFECT OF AMINO ACIDS ON THE DISSOLUTION RATES OF AMORPHOUS SILICA IN NEAR-NEUTRAL SOLUTION

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Abstract—Amino acids are ubiquitous in the Earth's surface environments as reactive biological molecules produced by every living thing including bacteria. To evaluate the effects of amino acids on mineral dissolution and to reveal the mechanism by which they interact with the mineral surface, we performed dissolution experiments of X-ray amorphous silica in solution containing 0.1 mmol Na with 10.0 mmol amino acids such as cysteine, asparagine, serine, tryptophan, alanine, threonine, histidine, lysine and arginine in near-neutral solutions. Dissolution experiments in solutions of 0.1, 1.0 and 10.0 mmol NaCl without amino acids were also conducted as amino acid-free controls. The results of this study indicate that basic amino acids such as histidine, lysine and arginine can interact more strongly with the negatively charged surface of amorphous silica than other non-basic amino acids due to their greater dissociation, thus forming cationic species. This electrostatical interaction enhanced dissolution rates of amorphous silica by approximately one order of magnitude compared with amino acid-free controls. In contrast, no significant effect on the dissolution rates of amorphous silica was observed in solutions containing cysteine, asparagine, serine, tryptophan, alanine and threonine because of lesser interaction with the surface of amorphous silica.

Key Words—Amino Acids, Amorphous Silica, Biological Molecule, Dissolution Rate, Mineral Dissolution.

INTRODUCTION

Amino acids are widespread biological molecules present in the Earth's surface including terrestrial weathered sediments such as soils (Szajdak *et al.*, 2003; Chen *et al.*, 2004; Amelung *et al.*, 2006), marine sediments of coastal regions to the deep sea (Burdige and Martens, 1988, 1990; Andersson *et al.*, 2000; Takano *et al.*, 2003), aquatic environments such as river and seawater (Jennerjahn and Ittekkot, 1999; Dittmar *et al.*, 2001; Dittmar and Kattner, 2003; Gupta and Kawahata, 2003; Ingalls *et al.*, 2003; Chen *et al.*, 2004) and various other geochemical environments. In these environments, amino acids are mainly produced by decomposition of proteinaceous materials such as dead cells of microorganisms, extracellular proteins including bacterial enzymes (Ladd and Butler, 1972; Lipson *et al.*, 1999, 2001), various types of organic matter (Trubetskaya *et al.*, 1998) and by fermentation of some bacteria (Umerie *et al.*, 2000; Tryfona and Bustard, 2005). These amino acids are present as dissolved free molecules in aqueous solutions, including porewater of soils and sediments and also as adsorbed forms on the surface of minerals, especially clays. There are many studies of amino acids centered around environmental

biology, involving distribution, production and cycling because they play an important role in supporting the biological ecosystems as a source of bioavailable nitrogen (Lipson *et al.*, 2001; Berthrong and Finzi, 2006); however, there are not many studies on interactions with mineral surfaces, especially the effects of amino acids on the dissolution rates of minerals.

As previously documented, many biological molecules released into the environment have significant ability to enhance the rate and extent of mineral dissolution by complexation with specific reactive sites on the mineral surfaces and also with the dissolved metal ions in solutions (Barker *et al.*, 1997). For example, organic acids such as oxalic, acetic, lactic and formic acids, which are produced by most bacteria, are known to enhance mineral dissolution by more than one order of magnitude faster by decreasing the solution pH and interacting with the mineral surfaces as well as dissolved metal ions (Bennett *et al.*, 1988; Welch and Ullman, 1993; Vandevivere *et al.*, 1994; Drever and Stillings, 1997; Welch and Ullman, 1999). Similarly, polysaccharides, which are a major component of extracellular polymers of bacteria, can greatly enhance mineral dissolution, depending on the amount of acid functional groups which are capable of metal-organic ligand complexation (Welch and Vandevivere, 1994; Welch *et al.*, 1999). These biological molecules contain reactive functional groups such as carboxyl groups that can be deprotonated to form negatively charged sites in near-neutral solutions. These deprotonated carboxyl groups

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serve as a reactive site to bind with positively charged sites on mineral surfaces such as aluminol groups as well as cationic metal ions in solutions (Stumm and Morgan, 1996). The effects of amino acids on mineral dissolution are poorly understood despite their abundance throughout the Earth's surface. Amino acids contain two or three functional groups, including a carboxyl group and an amino group. The net charges of amino acid molecules vary depending on the degree of dissociation of these functional groups, therefore amino acids have a wide range of isoelectric points (pI) from 2.7 for aspartic acid to 10.8 for arginine (Dawson *et al.*, 1986). Generally, these amino acids can be divided into three groups based on the pI values: acidic, neutral and basic amino acids. In near-neutral solution, the net charges of these groups are negative, neutral and positive, respectively. Thus, it can be predicted that some of the amino acids having negative and/or positive net charges would interact with mineral surfaces and have a significant effect on mineral dissolution.

In this study, we report rate-enhancement effects of amino acids on the dissolution of X-ray amorphous silica in near-neutral solutions. The point of zero charge of amorphous silica is ~ 2.0 , indicating that the surface charge of amorphous silica is negative in near neutral

conditions (Abendroth, 1970). Therefore, basic amino acids having positive net charges are capable of interacting electrostatically with the surface of amorphous silica. However, it has previously been reported that the dissolution rates of amorphous silica are strongly dependent on both solution pH and concentrations of alkali and alkaline earth cations present in solutions (Icenhower and Dove, 2000). To quantify the effects of amino acids, it is necessary to separate the effects of solution pH from those of concentrations of the background cations. Hence, we first measured the dissolution rates of amorphous silica in solutions under various pHs and in three different concentrations of Na ions with no amino acids. Then, dissolution rates of amorphous silica in a solution containing basic and other amino acids were determined and the effects of these amino acids on the dissolution rates were evaluated.

EXPERIMENTAL METHODS

Materials

Amorphous silica was purchased from Kanto Chemical Co., Inc. This sample was ground in an agate mortar and 5 to 100 μm size grains were separated by dry sieving. Then the powdered sample was cleaned ultrasonically in order

Table 1. Experimental conditions of dissolution of X-ray amorphous silica in the systems A–D.

System	Run	Solution	Initial pH
System A (Total Na = 0.1 mM)	A1	0.1 mM NaCl + 0.1 mM HCl	4.32
	A2	0.1 mM NaCl + 0.05 mM HCl	4.55
	A3	0.1 mM NaCl	5.62
	A4	0.05 mM NaCl + 0.05 mM NaOH	6.61
	A5	0.1 mM NaOH	8.48
System B (Total Na = 1.0 mM)	B1	1.0 mM NaCl + 0.2 mM HCl	4.02
	B2	1.0 mM NaCl + 0.1 mM HCl	4.34
	B3	1.0 mM NaCl + 0.05 mM HCl	4.76
	B4	1.0 mM NaCl	5.15
	B5	0.95 mM NaCl + 0.05 mM NaOH	6.55
	B6	0.9 mM NaCl + 0.1 mM NaOH	7.09
	B7	0.8 mM NaCl + 0.2 mM NaOH	8.04
System C (Total Na = 10.0 mM)	C1	10.0 mM NaCl + 0.2 mM HCl	3.86
	C2	10.0 mM NaCl + 0.1 mM HCl	4.16
	C3	10.0 mM NaCl + 0.05 mM HCl	4.47
	C4	10.0 mM NaCl	5.07
	C5	9.95 mM NaCl + 0.05 mM NaOH	6.34
	C6	9.9 mM NaCl + 0.1 mM NaOH	6.74
	C7	9.8 mM NaCl + 0.2 mM NaOH	7.95
System D (Total Na = 0.1 mM)	D1	10.0 mM cysteine + 0.1 mM Na (NaCl + NaOH)	6.01
	D2	10.0 mM asparagine + 0.1 mM Na (NaCl + NaOH)	5.49
	D3	10.0 mM serine + 0.1 mM Na (NaCl + NaOH)	6.00
	D4	10.0 mM tryptophan + 0.1 mM Na (NaCl + NaOH)	6.03
	D5	10.0 mM alanine + 0.1 mM Na (NaCl + NaOH)	6.01
	D6	10.0 mM threonine + 0.1 mM Na (NaCl + NaOH)	6.02
	D7	10.0 mM histidine + 0.1 mM Na (NaCl + HCl)	6.03
	D8	10.0 mM lysine + 0.1 mM Na (NaCl + HCl)	6.02
	D9	10.0 mM arginine + 0.1 mM Na (NaCl + HCl)	6.02

to remove adhering ultrafine particles and was washed with 0.1 mM HCl and deionized-distilled water more than five times. This X-ray amorphous silica sample was freeze dried and then used in this study. The surface area of this sample determined by the BET method was 294 m²/g. Amino acids used in this study were L-cysteine (Cys), L-asparagine (Asn), L-serine (Ser), L-tryptophan (Trp), L-alanine (Ala), L-threonine (Thr), L-histidine (His), L-lysine (Lys) and L-arginine (Arg), all of which are guaranteed-grade chemical reagents supplied by Nacalai Tesqu Inc.

Dissolution experiments

The dissolution experiments were performed using batch reactors of polyethylene bottles containing 0.1 g of X-ray amorphous silica and 100 mL of NaCl solution. First, in order to evaluate the effects of pH and concentrations of Na ions, three types of reaction systems (A, B and C) containing no amino acids were prepared. The concentrations of Na in these systems were 0.1, 1.0 and 10.0 mmol, respectively, and the pH of each system was adjusted in the range of ~4–8 using HCl or NaOH solutions (Table 1). Subsequently, reaction system D, containing 10.0 mmol amino acids and 0.1 mmol Na was also prepared. The pH of this system was adjusted to ~6 using HCl or NaOH as listed in Table 1. These bottles were sealed with an aerated polyethylene cap and incubated at 25°C for 20 days without shaking.

Analysis

During the dissolution experiments, the solution pH of each bottle was measured every 2 days using a glass electrode and then 0.5 mL of solution were collected and filtered using 0.2 µm Minisart membranes for chemical analysis of Si. The concentration of Si was measured by the molybdenum blue method with a Shimadzu UV-1650PC spectrophotometer at a wavelength of 390 nm. The dissolution rates of X-ray amorphous silica were calculated using the Si concentrations of initial liner stages for up to 10 days. For some of the systems exhibiting rapid dissolution such as those with relatively high pH, the Si concentrations of shorter reaction periods were used for calculation of the dissolution rates.

RESULTS AND DISCUSSION

Effect of pH and concentrations of Na

The Si concentrations of system A increased almost linearly with time throughout the reaction, whereas those of systems B and C increased more rapidly, corresponding to the solution pH and also concentrations of Na (Figure 1). Such dissolution-enhancing effects of pH and Na ions have been reported previously (Brady and Walther 1990; Dove, 1999; Icenhower and Dove, 2000); however, the increasing rates tended to decrease and the concentrations remained almost constant at ~2.0 mmol for subsequent reactions. Calculations by PHREEQC indicated that Si concentrations saturated with respect to

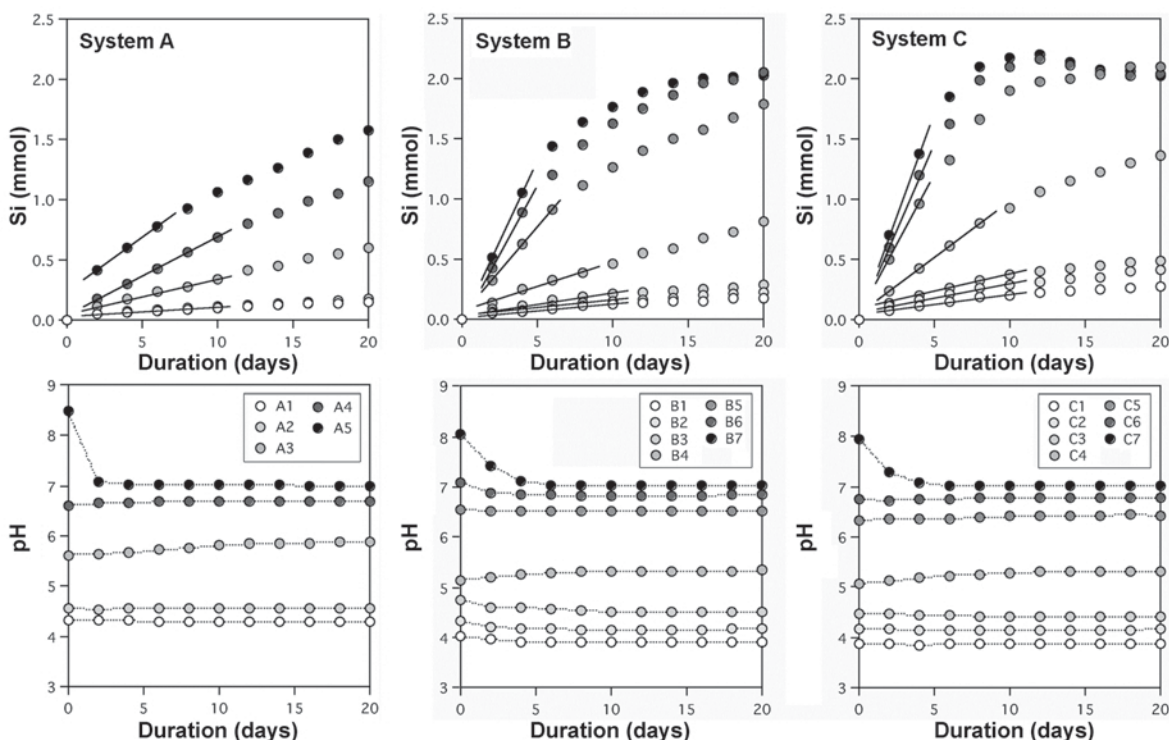


Figure 1. Concentrations of Si during dissolution of X-ray amorphous silica in the systems A, B and C at 25°C and variation of their solution pH. Systems A, B and C represent the experimental systems containing 0.1, 1.0 and 10.0 mmol NaCl, respectively.

X-ray amorphous silica were 1.9–2.0 mmol in the pH range 4–8. Thus, the decrease in Si release rate in systems B and C can be attributed to solutions approaching saturation with Si. To evaluate the effects of solution pH and Na concentrations on dissolution kinetics, dissolution rates calculated using Si concentrations in the reaction periods of initial linear stages up to 10 days were plotted as a function of solution pH, as shown in Figure 2. The dissolution rates yielded in these systems appear to increase linearly with solution pH, which is given by:

$$\text{System A: } R = 10^{-14.3}(\text{pH})^{-0.41} \quad (1)$$

$$\text{System B: } R = 10^{-14.1}(\text{pH})^{-0.44} \quad (2)$$

$$\text{System C: } R = 10^{-13.9}(\text{pH})^{-0.44} \quad (3)$$

These rate equations indicated that the dissolution rates of amorphous silica increased with pH dependence with a slope of ~ 0.4 in the pH range of ~ 4 –7. This is qualitatively compatible with the increase in negatively charged silanol groups ($>\text{SiO}^-$) on the surface of amorphous silica (Dove and Elston, 1992; Dove and Rimstide, 1994). The dissociation of silanol groups can be expressed by the following equation:



The effect of Na concentrations was also similar to the Langmuir-type isotherm expression reported by Dove and Crerar (1990), suggesting that the rates were enhanced by interaction of Na ions with negatively charged SiO^- sites. Dove and Nix (1997) reported that the rate-enhancing ability of alkali and alkaline earth cations by interactions with the quartz surface increased in the following order $\text{Ba}^{2+} > \text{K}^+, \text{Na}^+, \text{Li}^+, \text{Ca}^{2+} > \text{Mg}^{2+}$, which is consistent with the adsorption strength of these ions to the surface SiO^- sites. A similar tendency of

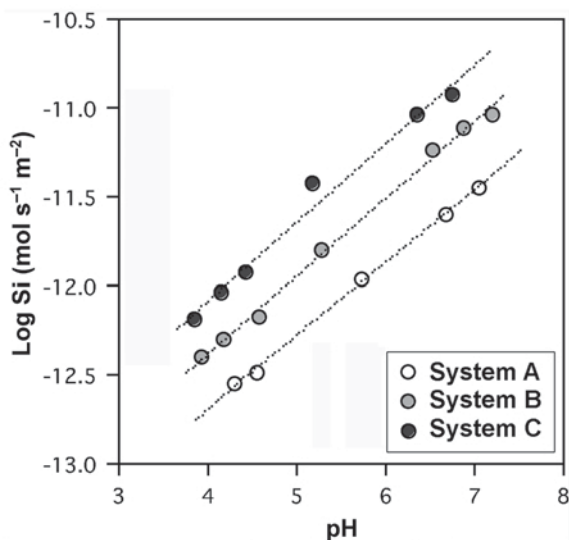


Figure 2. Dissolution rates of X-ray amorphous silica in the systems A, B and C at 25°C plotted as a function of average solution pH.

alkali cations to interact with the silica surface has also been reported previously (Tadros and Lyklema, 1969).

Effect of amino acids

Figure 3 shows the results of dissolution experiments of system D containing 10.0 mmol of various amino acids as listed in Table 1. The behaviors of Si concentrations in this system can be divided into two groups. Group I consists of the system containing Cys, Asn, Ser, Trp, Ala and Thr, all of which exhibited linear increases in Si concentrations with time, similar to the control experiment without amino acids labeled as NaCl in Figure 3a. Group II consists of the system containing His, Lys and Arg, which showed rapid increase in Si

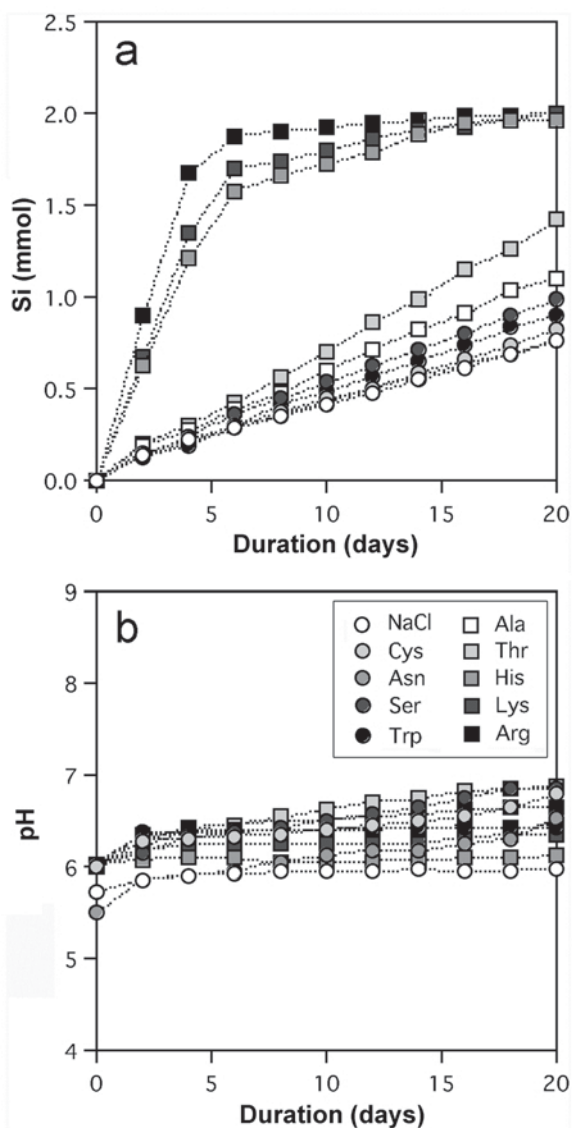


Figure 3. Concentrations of Si during dissolution of X-ray amorphous silica in the systems D containing 10.0 mM various amino acids at 25°C and variation of their solution pH.

concentrations up to saturation within the first several days and then remained almost constant during subsequent reactions. The pH values of these experiments were slightly different from each other as shown in Figure 3b, indicating a different strength of pH effect on Si release.

To separate such pH effects, dissolution rates of system D were plotted as a function of average solution pH together with dissolution rates of the systems A, B and C as shown in Figure 4, which clearly shows that the dissolution rates of group I were very close to those of system A, implying that the amino acids of group I, Cys, Asn, Ser, Trp, Ala and Thr have no significant effect on the dissolution rates of amorphous silica. In contrast, the dissolution rates of group II can be plotted on the area above system C. This indicates that His, Lys and Arg have a rate-enhancing effect on dissolution of approximately one order of magnitude at amino acid concentrations of 10.0 mmol and solution pH ranging from 6.0 to 6.4. Table 2 summarizes the dissolution rates and average solution pH of dissolution experiments of system D together with the published pI value and dissociation constant of each amino acid. In general, His, Lys and Arg are known as basic amino acids and their pI values are >7. Thus, these amino acids tend to protonate and exhibit positive net charge resulting in the predominance of cationic species in solution at pH 6.0–6.4. On the other hand, Cys, Asn, Ser, Trp, Ala and Thr have slightly negative or neutral net charges because their pI values are somewhat less than the solution pH. In addition, the surface charge of amorphous silica appears to be negative in these pH conditions because the point of zero charge of amorphous silica is ~pH 2.0 (Dove and Rimstidt, 1994). Consequently, it can be expected that His, Lys and Arg have the ability to interact electrostatically with the negatively charged

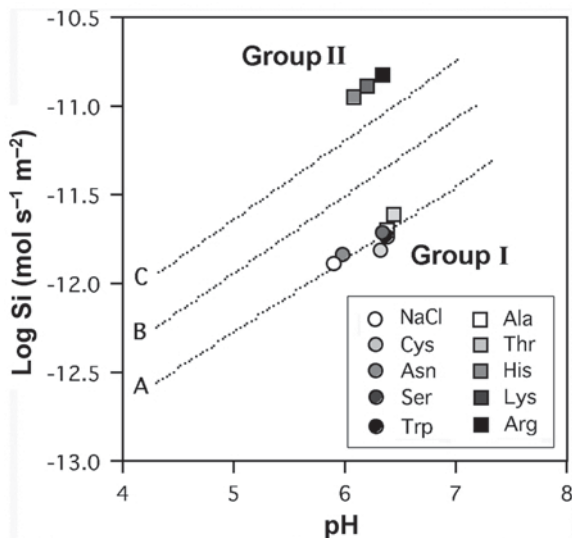


Figure 4. Dissolution rates of X-ray amorphous silica in the systems D containing 10.0 mM various amino acids at 25°C plotted as a function of average solution pH. The dotted lines A, B and C represent dissolution rates of amorphous silica in the systems A, B and C, respectively.

surface sites of amorphous silica. This interaction weakened Si–O–Si bonds of the structural framework leading to enhancement of dissolution rates in a manner similar to that of alkali and alkaline earth cations, as reported by Dove and Nix (1997). Such an interaction with the silica surface would be less effective for acidic and neutral amino acids including those in group I that have neutral or negative net charge leading to either a less significant or insignificant effect on dissolution rates of amorphous silica as illustrated in Figure 5. Previous adsorption experiments of amino acids on the surface of quartz demonstrated that the adsorption

Table 2. Dissolution rates of X-ray amorphous silica and average solution pH of system D with point of zero charge and dissociation constant of each amino acid.

Amino acids	pH (average)	log rate (mol s ⁻¹ m ⁻²)	pI	logK ₁	logK ₂	logK ₃	Ref.
NaCl	5.92	-11.88	—	—	—	—	—
Cys	6.32	-11.81	5.07	8.85	8.25	2.40	1
Asn	5.98	-11.83	5.41	8.95	2.38		2
Ser	6.36	-11.71	5.68	9.15	2.42		2
Trp	6.39	-11.74	5.89	9.34	2.31		3
Ala	6.38	-11.70	6.00	9.70	2.40		2
Thr	6.45	-11.61	6.16	9.04	2.45		2
His	6.10	-10.94	7.59	8.75	5.84	1.68	4
Lys	6.22	-10.88	9.74	11.16	9.50	2.31	5
Arg	6.36	-10.82	10.76	12.48	8.99	1.82	6

NaCl: control experiment without amino acids

* The isoelectric points (pI) and dissociation constants (K₁, K₂, K₃) were obtained from the following references:

(1) Apruzzese *et al.* (2002); (2) Köseoglu *et al.* (2000); (3) Dallavalle *et al.* (2001); (4) Dayde *et al.* (2002); (5) Stefano *et al.* (2000); (6) Dawson *et al.* (1986). The dissociation constants imply equilibrium constants of the following dissociation reactions: K₁ = [LH]/[L⁻][H⁺], K₂ = [LH₂⁺]/[LH][H⁺] and K₃ = [LH₃²⁺]/[LH₂⁺][H⁺], where L stands for amino acid.

properties of amino acids are strongly dependent on their pI values and that amino acids with higher pI values such as Lys (pI = 9.74) and Arg (pI = 10.76), are adsorbed much more strongly than acidic amino acids in near-neutral pH solution (Carter, 1978; Churchill *et al.*, 2004).

In order to confirm the concentrations of cationic species of these amino acids, chemical speciation calculation was performed with the geochemical program *ChemEQL* (Müller, 1996). In this calculation, the same concentration of amino acids (10.0 mmol) as those in the present dissolution experiments and in the dissociation constants listed in Table 2 was used. Figure 6 shows concentrations of cationic and anionic species obtained by *ChemEQL* calculation as a function of solution pH. Neutral species of these amino acids were not shown in this figure. In the pH range of 6.0 to 6.4, amino acids belonging to group I (Cys, Asn, Ser, Trp, Ala and Thr) exhibited mainly neutral species due to electrostatic compensation between the negatively charged COO⁻ group and positively charged NH₃⁺ group with <10⁻⁴ mol of anionic and <10⁻⁶ mol of cationic species (Figure 6a); however, higher concentrations of cationic species were confirmed for group II (His, Lys and Arg), *i.e.* >10⁻³ mol for His and ~10⁻² mol for Lys and Arg (Figure 6b). This is due to the protonation of additional basic groups such as the imidazole, amino and guanidine groups, respectively. These results are in agreement with the rate-enhancing effect of amino acids on the dissolution of X-ray amorphous silica. Therefore, these cationic species of His, Lys and Arg would interact electrostatically with the negatively charged SiO⁻ sites in the following reaction:



where *L* represents His, Lys and Arg. This reaction indicates the formation of monodentate outer-sphere complexes of amino acids on the surface of X-ray amorphous silica. In fact, Vlasova and Golovkova (2004) investigated adsorption of some amino acids on the surface of dispersed silica as a function of pH by acid-base titration and concluded that Lys and Arg form monodentate outer-sphere complexes with complexation constants of logK = 1.55 and 2.04, respectively. Therefore, basic amino acids have a significant rate-enhancing effect on the dissolution rate of X-ray amorphous silica by electrostatic interaction with the negatively charged SiO⁻ sites on the surface.

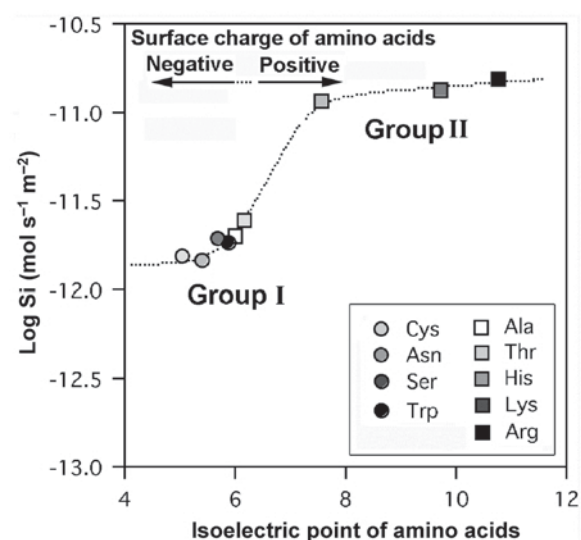


Figure 5. Dissolution rates of amorphous silica in the systems D containing 10.0 mM amino acids in solution pH5.98–6.45 at 25°C plotted as a function of the isoelectric point of each amino acid.

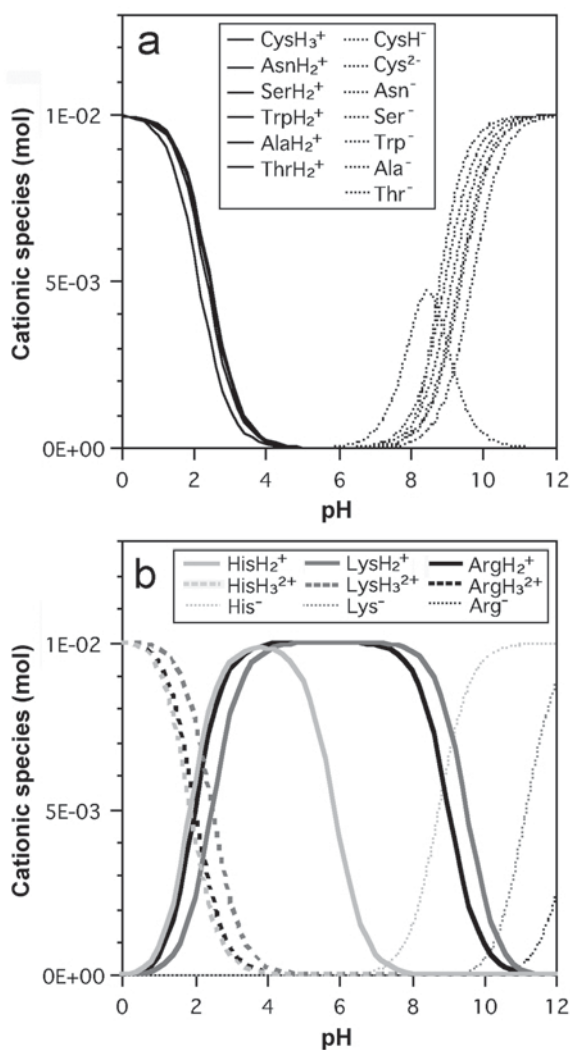


Figure 6. Concentrations of cationic and anionic species of 10.0 mmol amino acids calculated with the geochemical program *ChemEQL* using dissociation data listed in Table 2. (a) Group I (Cys, Asn, Ser, Trp, Ala and Thr); (b) Group II (His, Lys and Arg).

CONCLUSIONS

This study demonstrates the rate-enhancing effect of amino acids on the dissolution of X-ray amorphous silica in near-neutral solutions. The results of this study revealed that basic amino acids such as His, Lys and Arg can interact more strongly with the surface of X-ray amorphous silica than other amino acids in solutions with a pH range of 6.0 to 6.4, resulting in enhancement of dissolution rates by approximately one order of magnitude. In contrast, it was found that Cys, Asn, Ser, Trp, Ala and Thr have no significant effect on dissolution rates because of a lesser ability to interact with the surface of X-ray amorphous silica in this pH range. The greater reactivity of the basic amino acids is likely to be attributed to their higher pI values leading to greater dissociation of functional groups to form cationic species of amino acids.

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