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ENHANCEMENT OF DISSOLUTION RATES OF AMORPHOUS SILICA BY INTERACTION WITH AMINO ACIDS IN SOLUTION AT pH 4

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Abstract—Amino acids are present in various geochemical environments and they interact with mineral surfaces. To evaluate the effects of amino acids on mineral dissolution at pH conditions less than their isoelectric points (pI), dissolution experiments of X-ray amorphous silica in solutions containing 10.0 mmol/L of various amino acids (cysteine, asparagine, serine, tryptophan, alanine, threonine, histidine, lysine, and arginine) at pH 4 were performed. The results confirmed that basic amino acids (histidine, lysine, and arginine) produce an 8- to 8.5-fold enhancement of the rate of dissolution of amorphous silica compared with an amino acid-free control. Neutral amino acids (cysteine, asparagine, serine, tryptophan, alanine, and threonine) enhanced rates of dissolution by a factor of ~3 to 3.5. The rate-enhancement effects of amino acids are controlled by concentrations of the amino acid's cationic species which interact with the negatively charged $>SiO^-$ sites at the surface of the amorphous silica.

Key Words—Amino Acids, Amorphous Silica, Cationic Species, Dissolution Rate, Rate Enhancement.

INTRODUCTION

Mineral-dissolution processes in natural geochemical environments involve various biochemical catalytic factors which enhance rates of dissolution of minerals (Barker *et al.*, 1997; Ullman and Welch, 2002). Many organic molecules produced by biological activity, such as organic acids, polysaccharides, amino acids, polypeptides, enzymes, and various molecular-sized proteins, are known to enhance the rates of dissolution of minerals by an organic-ligand dissolution process (Barker *et al.*, 1997). Of these organic molecules, 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, 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). Such amino acids are present in various geochemical environments, including weathered sediments such as soils (Szajdak *et al.*, 2003; Chen *et al.*, 2004; Amelung *et al.*, 2006), coastal and deep-sea marine sediments (Burdige and Martens, 1988, 1990; Andersson *et al.*, 2000; Takano *et al.*, 2003), and aquatic environments such as rivers and seas (Jennerjahn and Ittekkot, 1999; Dittmar *et al.*, 2001; Dittmar and Kattner, 2003; Gupta and Kawahata, 2003; Ingalls *et al.*, 2003; Chen *et al.*, 2004). In spite of such abundance, the effects of amino acids on mineral dissolution are not well known.

Amino acids are amphoteric and behave as cations, anions, or neutral ions by dissociation of two or three functional groups, including carboxyl and amino groups. The net charge of an amino acid molecule varies depending on the degree of dissociation, which is controlled by the solution pH. The isoelectric points (pI) of amino acids vary over a considerable range from 2.7 for aspartic acid to 10.8 for arginine (Dawson *et al.*, 1986). Generally, amino acids can be divided into three groups based on the pI values: acidic, neutral, and basic. In a pH solution below or above the pI value, the net charge of an amino acid molecule is positive or negative, respectively. Thus, amino acids, present as cations and/or anions, would interact with the mineral surface and affect dissolution rates. Kawano and Obokata (2007) reported on the rate-enhancement effects of amino acids on the dissolution of amorphous silica by interaction with basic and neutral amino acid groups in near-neutral pH solutions, and showed that basic amino acids such as histidine, lysine, and arginine affect dissolution rates. The rates of dissolution were enhanced by one order of magnitude in 10.0 mM basic amino acid solutions with pH ranging from 6.0 to 6.4 (Kawano and Obokata, 2007), while neutral amino acids showed no significant effect on the rates of dissolution in similar solution conditions. This difference in rate-enhancement effects of amino acids is attributed to the different concentrations of cationic species in the basic and neutral amino acids. In the Kawano and Obokata (2007) study, the concentrations of cationic species were calculated using

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the geochemical code *ChemEQL* (Müller, 1996) as 10^{-3} to 10^{-2} M for basic amino acids and $<10^{-6}$ M for neutral amino acids. Thus, different concentrations of cationic species may markedly affect amorphous silica dissolution rates in near-neutral solutions.

In order to confirm the above interpretations, dissolution of X-ray amorphous silica powder in solutions containing amino acids at pH 4 was studied. Amorphous silica has a point of zero charge at a pH of ~2.0 (Dove and Rimstidt, 1994), indicating that the surface charge of amorphous silica in solution at pH 4 would be negative. However, the pI values of neutral amino acids are greater than this pH value. Thus, neutral amino acids are likely to be present as cationic species in this acidic solution. Consequently, cationic species of neutral amino acids may be capable of enhancing the rates of dissolution of amorphous silica by interacting with negatively charged sites on the surface of the amorphous silica.

EXPERIMENTAL

Materials and methods

Amorphous silica was purchased from Kanto Chemical Co., Inc (Tokyo, Japan). Samples were ground in an agate mortar and grains with a size of 5−100 µm were separated by dry sieving. These were cleaned ultrasonically to remove adhering ultrafine particles and washed (at least five times) with 0.1 mM HCl and deionized-distilled water. The amorphous silica grains were freeze-dried prior to use. The sample surface area, determined by the BET method, was 294 m^2/g. This amorphous silica sample was the same material used in the study by Kawano and Obokata (2007). The amino acids used 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 were guaranteed, reagent-grade chemicals supplied by Nacalai Tesqu, Inc. (Kyoto, Japan). Cys, Asn, Ser, Trp, Ala, and Thr are neutral amino acids, while His, Lys, and Arg are basic amino acids.

Dissolution was performed using batch reactors consisting of polyethylene bottles containing 0.1 g of amorphous silica grains and 100 mL of 0.1 mM NaCl solution. The reaction system (system E) consisted of ten individual runs (Table 1). Run E0 contained no amino acid, while each run from E1 to E9 contained 10.0 mmol/L of a different amino acid (Cys, Asn, Ser, Trp, Ala, Thr, His, Lys, and Arg). The initial pH of each run was adjusted to ~4 using HCl (Table 1) so that each bottle contained the same Na concentration (0.1 mM). The bottles were sealed with an aerated polyethylene cap and incubated at 25ºC for 10 days without shaking.

Analysis

During dissolution, the pH values of each solution were measured every 2 days using a glass electrode. In addition, 0.5 mL of each solution was collected and filtered using 0.2 µm Minisart membranes in order to measure the Si concentrations. The measurement was made using the post-column pH-buffer HPLC method which is a modified version of the procedure proposed by Li and Chen (2000). The HPLC instrument used in this method was a Shimadzu LC-10 system equipped with an electrical conductivity (EC) detector and an ion exclusive TSKgel OApak-A column. The mobile phase of a 1.0 mM H_2SO_4 solution was used to separate H_4SiO_4 ions. Subsequently, a pH-buffer solution of 0.1% diethylaminoethanol was mixed with the mobile phase to increase the pH value for detection of Si ions as $H_3SiO_4^-$ anions using an EC detector. The relative error in this method is 5%. The dissolution rates of amorphous silica were calculated using Si concentrations in the initial linear stages for 2−10 days.

RESULTS AND DISCUSSION

The measurements of Si concentrations and solution pH during dissolution of amorphous silica over 10 days are shown in Figure 1. The Si concentrations in all runs increased linearly with time, and the concentrations in runs containing amino acids increased more rapidly than that in the NaCl run, which contained no amino acids

Table 1. Experimental conditions of dissolution of amorphous silica in system E.

System	Run	Solution	Initial pH
System E (Total Na = 0.1 mM)	E0	0.1 mM Na (NaCl + HCl)	3.92
	E1	10.0 mM cysteine + 0.1 mM Na (NaCl)	3.91
	E2	10.0 mM asparagine + 0.1 mM Na (NaCl + HCl)	3.95
	E3	10.0 mM serine + 0.1 mM Na (NaCl + HCl)	3.98
	E4	10.0 mM tryptophan + 0.1 mM Na (NaCl + HCl)	3.91
	E5	10.0 mM alanine + 0.1 mM Na (NaCl + HCl)	3.94
	E6	10.0 mM threonine + 0.1 mM Na (NaCl + HCl)	3.93
	E7	10.0 mM histidine + 0.1 mM Na (NaCl + HCl)	3.94
	E8	10.0 mM lysine + 0.1 mM Na (NaCl + HCl)	3.94
	E9	10.0 mM arginine + 0.1 mM Na (NaCl + HCl)	3.91

(Figure 1a). The solution pH remained constant at ~4 throughout each run (Figure 1b), suggesting no significant effect of pH on the rates of dissolution of amorphous silica in these runs. Table 2 summarizes the logarithmic dissolution rates and average solution pH over 2−10 days, together with the published pI value and dissociation constants for each amino acid. These dissolution rates were plotted in Figure 2 as a function of the average solution pH together with previously published data measured at pH 6 (Kawano and Obokata, 2007). The dissolution rate of the NaCl run containing no amino acid was compatible with those of amorphous silica in a 0.1 mM NaCl solution as plotted on dotted line A in Figure 2. The runs containing amino acids showed much greater rates of dissolution than the NaCl run, *e.g.* His, Lys, and Arg runs exhibited rates which were 8−8.5 times faster, while Cys, Asn, Ser, Trp, Ala, and Thr were 3−5 times quicker. Brady and Walther (1990), Dove (1999), and Icenhower and Dove (2000) also reported that Na ions are effective promoters of dissolution rates in amorphous silica. No effect of Na ions on the enhancement rate was expected in this study, however, because all runs contained the same Na ion concentration (0.1 mM). Therefore, the observed increases in dissolution rates of amorphous silica, using various amino acids, is probably attributed to different interactions of the amino acid with the amorphous silica surface in a similar manner to that observed in cations of alkali and alkaline earth metals (Tadros and Lyklema, 1969; Dove and Nix, 1997; Dove and Crerar, 1990).

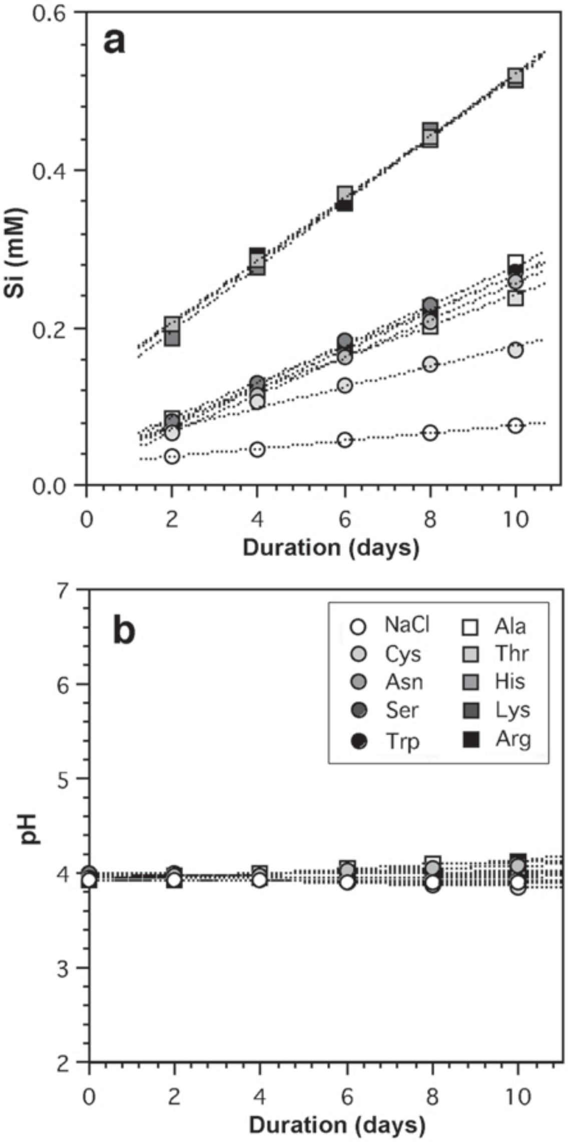

Figure 1. Concentrations of Si during dissolution of amorphous silica in system E at 25ºC, and variation of their solution pH.

In a previous study at pH 6 (Kawano and Obokata, 2007), basic amino acids (His, Lys, and Arg) produced a rate-enhancement effect of ~1 order of magnitude, similar to that at pH 4 (Figure 2). However, at pH 6, neutral amino acids (Cys, Asn, Ser, Trp, Ala, and Thr) showed no significant effect on the rates of dissolution of amorphous silica, while the present study showed a marked effect. At these pH levels, the surface charge of amorphous silica should be negative, based on the dissociation of silanol groups (>SiOH) to negatively charged >SiO$^-$ sites, because the point of zero charge of amorphous silica is at a pH of ~2 (Dove and Rimstidt, 1994). On the other hand, the pI values of the basic amino acids including His, Lys, and Arg are >7, leading to the formation of cationic species that are capable of

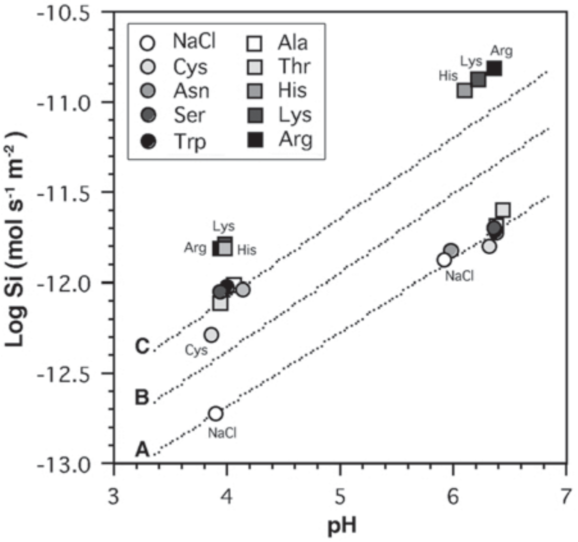

Figure 2. Dissolution rates of amorphous silica in system E containing 10.0 mmol/L of amino acids at 25ºC plotted as a function of average solution pH. The dotted lines A, B, and C imply dissolution rates of amorphous silica in an amino acid-free system with 0.1, 1.0, and 10.0 mM NaCl, respectively. The dissolution rates plotted in the pH 6 region are from Kawano and Obokata (2007).

interacting electrostatically with the negatively charged amorphous silica surface sites at pH 6. However, the pI values of neutral amino acids, such as Cys, Asn, Ser, Trp, Ala, and Thr, are <pH 6, and these amino acids exhibit mainly neutral ions with smaller concentrations of negative species, both of which are less effective at interacting with the negatively charged surface sites of amorphous silica. In the present study, at pH 4, the neutral amino acids showed a significant effect on the rates of dissolution (Figure 3). The pI values of these amino acids (pI = 5.07–6.16) are greater than the solution pH values (pH = 3.86–4.15), a difference that promotes protonation of amino acids and production of the positively charged cationic species. Therefore, at pH 4, neutral amino acids were capable of interacting electrostatically with the negatively charged surface sites of amorphous silica. These net electrostatic charges originate from compensation of negative charges of deprotonated carboxyl groups (COO^-), positive charges of protonated amino groups (NH_3^+), and additional basic groups, such as imidazole for His and guanisine groups for Arg, contributing to an increase in the net positive charge on the molecule. The positively charged functional groups, such as NH_3^+, tend to interact electrostatically with the negatively charged $>SiO^-$ of the amorphous silica surface and are reported to produce monodentate outer-sphere complexes (Vlasova and Golovkova, 2004). This interaction weakens Si–O–Si bonds in the structural framework, thereby leading to enhancement of the dissolution rates in a manner similar to that reported for cations of alkali and alkaline earth metals (Dove and Nix, 1997).

To confirm the chemical speciation of 10.0 mM amino acid solutions at pH 6 and 4, geochemical calculations were carried out using *ChemEQL* (Müller, 1996) (see Table 2 for the dissociation data). The calculation results in terms of molar concentrations of both cationic and anionic species of the amino acids as a function of their pI values (Table 2) revealed that the basic amino acids (His, Lys, and Arg) appear to be predominantly present as cationic species at pH 6 (His, Lys, Arg $>0.98 \times 10^{-2}$ M) and pH 4 (His = 0.41×10^{-2}, Lys, Arg $>0.99 \times 10^{-2}$ M). However, neutral amino acids (Cys, Asn, Ser, Trp, Ala, and Thr) remained in a neutral ionic state with very small amounts of cationic species ($<2.6 \times 10^{-6}$ M) at pH 6, but the concentrations of cationic species increased to between 0.12×10^{-3} and

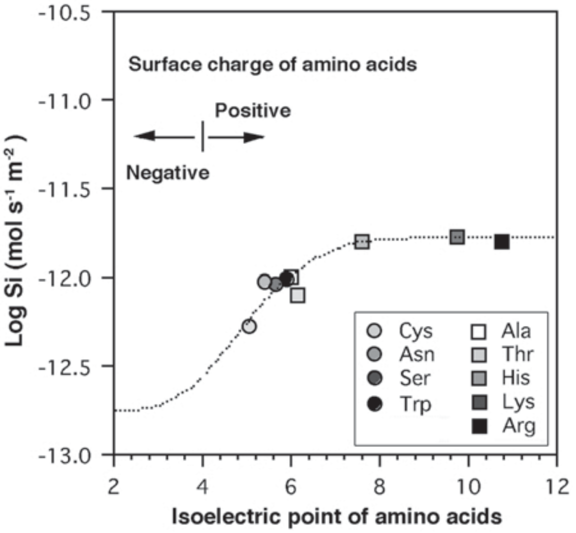

Figure 3. Dissolution rates of amorphous silica in system E containing 10.0 mmol/L of amino acids in solution at pH 4 and 25ºC plotted as a function of the isoelectric point of each amino acid.

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

Amino acids	pH (Average)	log rate (mol/s/m^2)	pI	logK_1	logK_2	logK_3	Ref.
NaCl	3.90	−12.71	–	–	–	–	–
Cys	3.86	−12.29	5.07	8.85	8.25	2.40	1
Asn	4.15	−12.03	5.41	8.95	2.38		2
Ser	3.93	−12.05	5.68	9.15	2.42		2
Trp	4.00	−12.02	5.89	9.34	2.31		3
Ala	4.05	−12.00	6.00	9.70	2.40		2
Thr	3.94	−12.10	6.16	9.04	2.45		2
His	3.98	−11.81	7.59	8.75	5.84	1.68	4
Lys	3.98	−11.78	9.74	11.16	9.50	2.31	5
Arg	3.94	−11.81	10.76	12.48	8.99	1.82	6

NaCl: control experiment without amino acids.
Data of isoelectric point (pI) and dissociation constants (K_1, K_2, K_3) were obtained from the following references:
(1) Apruzzese *et al.*, (2002); (2) Koseoglu *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:
$K_1 = [LH]/[L^-][H^+]$, $K_2 = [LH_2^+]/[LH][H^+]$, and $K_3 = [LH_3^{2+}]/[LH_2^+][H^+]$, where L stands for amino acid.

0.26×10^{-3} M at pH 4 (Figure 4a). These larger concentrations of cationic species in neutral amino acids are likely to enhance the dissolution rates of amorphous silica at pH 4. The anionic species of these amino acids exhibited an opposite tendency, *i.e.* the concentrations decreased with increasing pI values from Cys = 0.56×10^{-4} M to Arg = 0.34×10^{-11} M at pH 6 and from Cys = 0.55×10^{-6} M to Arg = 0.33×10^{-15} M at pH 4 (Figure 4b). The effect of anionic ions, including organic acids, on the dissolution rates of silica minerals, including amorphous silica, is not well understood, though anionic ions, except for some organic acids such as citrate and oxalate, have been reported to be less effective at enhancing dissolution rates (Bennett *et al.*, 1988; Bennett, 1991; Knauss and Copenhaver, 1995; Blake and Walter, 1999). Therefore, apparently the dissolution rates of amorphous silica at pH 4 are controlled mainly by the interaction of cationic species of amino acids with the negatively charged $>SiO^-$ sites of the amorphous silica surface.

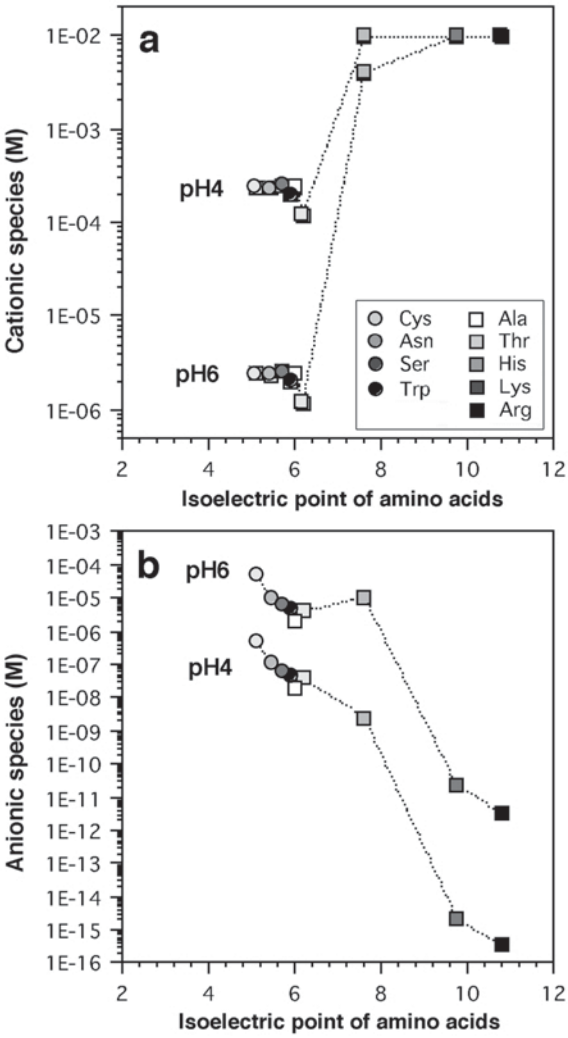

Figure 4. Concentrations of cationic and anionic species of amino acids at 10.0 mM calculated with geochemical program *ChemEQL* using dissociation data listed in Table 2. The labels pH 4 and 6 indicate the solution pH value.

In natural geochemical environments including soils, terrestrial and marine sediments, and various aquatic environments, variable amounts of organic molecules such as organic acids, polysaccharides, amino acids, proteins, enzymes, and various organic compounds produced and released by microorganisms are present. Among these organic molecules, organic acids and polysaccharides are known to enhance mineral dissolution by complexation of negatively charged COO^- sites with metal ions such as Al and Fe on the mineral surfaces (Ullman and Welch, 2002). These molecules, except for citric and oxalic acids, are much less effective at dissolution of silica minerals such as quartz because they are present, fundamentally, as anionic species in natural solutions by deprotonation of carboxyl groups (Bennett, 1991). On the other hand, amino acids and proteins are known to complex with the mineral surfaces (Hedges and Hare, 1987; Ding and Henrichs, 2002; Vlasova and Golovkova, 2004). Their effects on mineral dissolution are not well known, however (Barker *et al.*, 1997). The results of the present study confirm that the cationic species of amino acids can greatly enhance the dissolution rates of silica minerals by interaction with the negatively charged $>SiO^-$ sites. The concentrations of amino acids in natural geochemical environments range from nM to μM (Dittmar *et al.*, 2001; Dittmar and Kattner, 2003; Gupta and Kawahata, 2003; van Hees *et al.*, 2005). Such concentrations are considerably less than that of the present experiments and so the effects of amino acids on mineral dissolution in natural environments would be less than those measured here. Amino acids are essential constituents of proteins, which are the main components of microbial cell surfaces and also the main product released into the surrounding environment (van Roosmalen *et al.*, 2004). Amino acids consisting of these proteins may also interact with silica minerals and affect dissolution rates, depending on their degree of dissociation.

CONCLUSIONS

Dissolution of amorphous silica in solutions containing 10.0 mmol/L of various amino acids at pH 4 showed that basic amino acids (His, Lys, and Arg) can enhance the rate of dissolution of amorphous silica by ~8–8.5 times compared with an amino acid-free control. Similarly, neutral amino acids (Cys, Asn, Ser, Trp, Ala, and Thr) showed 3- to 5-fold enhancement of the dissolution rate. The amino acid rate-enhancement effect is caused by interaction of cationic species with the negatively charged $>SiO^-$ sites at the surface of the amorphous silica. Thus, the rates of dissolution of amorphous silica are probably controlled by the concentrations of the cationic species of various amino acids. The concentrations of cationic species of basic and neutral amino acids in solution at pH 4 ranged from 0.41×10^{-2} to 0.99×10^{-2} M and from 0.12×10^{-3} to 0.26×10^{-3} M, respectively. The different concentrations of cationic species contribute to the difference in rate-enhancement effects of amino acids on the dissolution of amorphous silica.

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