INFLUENCE OF GUANIDINE, IMIDAZOLE, AND SOME HETEROCYCLIC COMPOUNDS ON DISSOLUTION RATES OF AMORPHOUS SILICA

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Abstract—Guanidine and imidazole are important functional molecules that constitute the side chain of basic amino acids (arginine and histidine); these molecules are capable of interacting with mineral surfaces. However, little information is available about the effect of these molecules on mineral dissolution, including amorphous silica. In this study, to evaluate the effect of these organic molecules on the dissolution rates of amorphous silica, dissolution experiments were performed in solutions containing these molecules and other related heterocyclic compounds. The dissolution experiments were conducted by the batch method using 0.1 g of amorphous silica and 100 mL of 0.1 mM NaCl solution with 0.0, 0.1, 1.0, and 10.0 mM of guanidine, imidazole, pyrazole, or pyrrole at pH values of 4, 5, and 6. The results demonstrated that these compounds can enhance the dissolution rate of amorphous silica, depending on their ionic speciation in the following order: guanidine = imidazole > pyrazole > pyrrole. When 10.0 mM solutions were used, both guanidine and imidazole greatly increased the dissolution rate with an enhancement factor of 5.5−6.5, pyrazole exhibited a smaller change in the dissolution rate with an enhancement factor of 1.5−2.4, and pyrrole exhibited no significant enhancement. *ChemEQL* calculations confirmed that guanidine (pK = 13.6) and imidazole (pK = 6.99) are fully protonated and mostly present as cationic species in a pH range of 4−6; therefore, these compounds are capable of interacting with the $>SiO^-$ sites of amorphous silica. Pyrazole (pK = 2.61) and pyrrole (pK = 0.4), however, existed mostly as neutral forms. The concentrations of cationic species of pyrazole and pyrrole were at least one and three orders of magnitude lower than those of fully protonated compounds, respectively; therefore, pyrazole and pyrrole were less reactive than the fully protonated compounds on the surfaces of amorphous silica.

Key Words—Amorphous Silica, Dissolution Rate, Guanidine, Imidazole, Pyrazole, Pyrrole.

INTRODUCTION

The interaction of organic molecules with mineral surfaces plays an important role in a wide range of mineralogical and geochemical processes in soils, sediments, and various aquatic environments (Barker *et al.*, 1997; Ullman and Welch, 2002). Proteins and proteinaceous materials such as polypeptide and various enzymes are important high-molecular-weight organic compounds released from bacterial cells by continuous secretion and also by cell lysis after their death. These compounds are normally present as dissolved and/or adsorbed forms with concentrations ranging from several µg/g to mg/g in soils and sediments (Bonmati *et al.*, 1998; Murase *et al.*, 2003; Weintraub and Schimel, 2005), and on the order of ~mg/L in freshwater and seawater environments (Tanoue *et al.*, 1996; Lu *et al.*, 2003; Jones *et al.*, 2004; Elliott *et al.*, 2006; Yamada and Tanoue, 2006). Such proteinaceous compounds have a strong adsorption affinity for the surfaces of various minerals, including clay minerals and oxide or hydroxide minerals; this affinity fundamentally originates from the functional properties of amino acid residues such as acidic and basic amino acids that can

carry negative or positive charges, respectively (Quiquampoix and Ratcliffe, 1992; Ding and Henrichs, 2002; Quiquampoix *et al.*, 2002; Quiquampoix and Burns, 2007; Stievano *et al.*, 2007; Norén *et al.*, 2008). With regard to adsorption on amorphous silica, proteins have been reported to adsorb and interact with the silica surfaces, possibly because of electrostatic interaction of the positively charged side-chain functional groups of basic amino acid residues with the negatively charged silica surfaces (Norde and Favier, 1992; Fukuzaki *et al.*, 1996). The interactions have been confirmed to contribute to the enhancement of dissolution rates by one order of magnitude depending on the solution pH (Kawano and Hwang, 2010). Several previous studies demonstrated that basic amino acids (arginine, histidine, and lysine) can adsorb on the surfaces of amorphous silica by forming outer-sphere complexes, depending on the degree of protonation of the basic functional groups (Vlasova and Golovkova, 2004; Liu *et al.*, 2005; Rezwan *et al.*, 2005; O'Connor *et al.*, 2006). Those studies also found that surface complexation led to an increase in the dissolution rates of amorphous silica as the concentrations of cationic species increased (Kawano and Obokata, 2007; Kawano *et al.*, 2009). In the protein structure, the main-chain functional groups (amino and carboxyl groups) of each amino acid residue are linked together by peptide bonds. Additional basic functional groups located in the side-

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chain should, therefore, play an important role in the interaction with the surfaces of amorphous silica. However, no experimental studies have confirmed the effects of side-chain functional groups of basic amino acids on the dissolution of amorphous silica.

In the present study, experiments on dissolution of amorphous silica in solutions containing guanidine, imidazole, pyrazole, or pyrrole were performed to evaluate the effects of these organic compounds on the dissolution rates of amorphous silica. Guanidine and imidazole are side-chain components of arginine and histidine; both guanidine and imidazole tend to be protonated over a wide pH range as expressed by their pK values of 13.6 and 6.99, respectively. Pyrazole and pyrrole are five-membered heterocyclic compounds similar to imidazole, but they exist mostly as neutral ionic forms except in highly acidic solutions. These two heterocyclic compounds were used to compare the effects of the ionic states on the interaction of these compounds with the surfaces of amorphous silica, and also on the enhancement of dissolution rates.

EXPERIMENTAL METHODS

Materials

The amorphous silica used in this study was split from the same sample used in earlier dissolution experiments (Kawano *et al.*, 2009; Kawano and Hwang, 2010). The sample was prepared from a SiO_2 reagent obtained from Kanto Chemical Co., Inc (Tokyo). The reagent was ground in an agate mortar, and $5-100$ μm-sized grains were separated by hand dry-sieving. The powdered sample was cleaned ultrasonically to remove adhering ultrafine particles and was washed at least five time with 0.1 M HCl and deionized-distilled water. This sample was then freeze dried and stored for the dissolution experiments. The surface area of the sample, determined by the BET method (degassing at 200ºC for 2 h), was 294 m^2/g.

Guanidine (CH_5N_3) and three other heterocyclic compounds, imidazole ($C_3H_4N_2$), pyrazole ($C_3H_5N_3$), and pyrrole (C_4H_5N), were used in the present study. All the compounds were guaranteed chemical reagent grade, purchased from Nacalai Tesqu, Inc. (Kyoto, Japan). The organic molecules dissolved easily in water and protonated depending on the solution pH (Figure 1). The pK values for the protonation are guanidine: pK = 13.6 (Dawson *et al.*, 1986), imidazole: pK = 6.99 (Dean, 1985), pyrazole: pK = 2.61 (Dean, 1985), and pyrrole: pK = 0.4 (Hall, 1930).

Experiment and analysis

Experiments on the dissolution of amorphous silica were performed by the batch method using a 100 mL Pyrex glass flask sealed with aerated caps at 25ºC for 10 days with no shaking or stirring. Four systems (A, B, C, and D) consisting of 0.1 g of amorphous silica grains

and 100 mL of 0.1 mM NaCl solution with 0.1, 1.0, and 10.0 mM of organic compounds were prepared (Table 1). System A consisted of nine flasks containing 0.1, 1.0, and 10.0 mM of guanidine with a solution pH of ~6, 5, and 4 (runs A61 to A43, Table 1). Systems B, C, and D were prepared in a similar manner using imidazole, pyrazole, and pyrrole instead of guanidine (runs B61 to B43, C61 to C43, and D61 to D43, respectively, Table 1). Experiments containing no organic compounds with a solution pH of ~6, 5, and 4 were also performed as controls (R60, R50, and R40).

Throughout the dissolution experiments, a glass electrode was used to measure the solution pH of each flask every 2 days, after which an aliquot of 0.5 mL was removed and filtered using 0.2 μm Minisart membranes for chemical analysis of Si and organic compounds. The dissolution rates of amorphous silica were calculated from changes in Si concentrations with time. The effect of guanidine and heterocyclic compounds on the dissolution rate of amorphous silica was estimated by the enhancement factor (k), which is defined as follows:

$$k = R_o/R_c \quad (1)$$

where R_o and R_c are the dissolution rates of amorphous silica in the solutions containing organic compounds and those in the controls, respectively. The measurement of Si concentrations was carried out using the post column
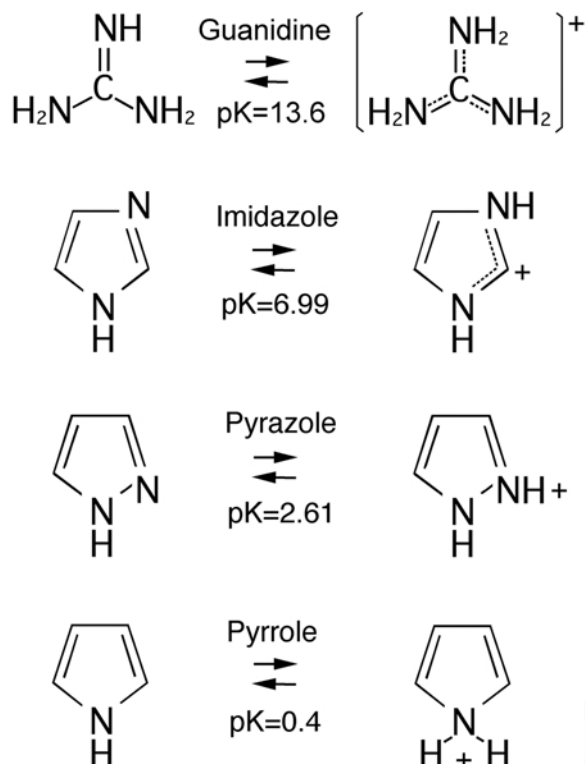

Figure 1. Schematic structures of organic compounds (guanidine, imidazole, pyrazole, and pyrrole) used in this study.

Table 1. Experimental conditions of dissolution of amorphous silica in systems A to D.

System	Run	Organic molecule	pH (initial)
Control	R60	–	6.04
(Total Na	R50	–	4.99
= 0.1 mM)	R40	–	3.92
System A	A61	0.1 mM	6.02
Guanidine	A62	1.0 mM	6.00
(Total Na	A63	10.0 mM	6.05
= 0.1 mM)	A51	0.1 mM	5.01
	A52	1.0 mM	5.02
	A53	10.0 mM	5.00
	A41	0.1 mM	3.98
	A42	1.0 mM	4.00
	A43	10.0 mM	4.01
System B	B61	0.1 mM	6.03
Imidazole	B62	1.0 mM	6.01
(Total Na	B63	10.0 mM	6.00
= 0.1 mM)	B51	0.1mM	5.04
	B52	1.0 mM	5.02
	B53	10.0 mM	5.02
	B41	0.1 mM	4.01
	B42	1.0 mM	4.02
	B43	10.0 mM	3.99
System C	C61	0.1 mM	5.99
Pyrazole	C62	1.0 mM	5.99
(Total Na	C63	10.0 mM	5.99
= 0.1 mM)	C51	0.1 mM	4.99
	C52	1.0 mM	5.00
	C53	10.0 mM	4.99
	C41	0.1 mM	4.00
	C42	1.0 mM	3.99
	C43	10.0 mM	4.00
System D	D61	0.1 mM	6.01
Pyrrole	D62	1.0 mM	6.00
(Total Na	D63	10.0 mM	6.01
= 0.1mM)	D51	0.1 mM	4.98
	D52	1.0 mM	5.00
	D53	10.0 mM	5.01
	D41	0.1 mM	3.95
	D42	1.0 mM	3.97
	D43	10.0 mM	3.99

pH buffer HPLC method, which is a modification of the procedure proposed by Li and Chen (2000). The HPLC instrument used for this method was an Hitachi LaChrom Elite system equipped with an electrical conductivity (EC) detector and an ion-exclusive column of TSKgel OApak-A. To separate H_4SiO_4 ions, 1.0 mM H_2SO_4 solution was used for the mobile phase, with a flow rate of 1.0 mL/min. Subsequently, 0.1% diethyl-aminoethanol was mixed with the mobile phase at a flow rate of 0.75 mL/min to increase the solution pH to ~10, thereby enabling detection of Si as the $H_3SiO_4^-$ anion using an EC detector. The relative error in this method is ±5%.

To confirm the interaction of the organic compounds with the amorphous silica surfaces, adsorption experiments were carried out by the batch method using a Pyrex glass flask containing 100 mL of 0.1 mM NaCl solution with 0.1 g of amorphous silica and 1.0 mM of each of the organic compounds. The initial solutions were adjusted to pH 2−10 by using 1.0 mM HCl or NaOH. The flasks were incubated at 25ºC for 1 day with continuous shaking at 100 rpm, after which the solution pH and concentration of each organic compound were measured. The concentrations of guanidine, imidazole, and pyrazole were measured with the Hitachi HPLC instrument equipped with a cation-exchange column of TSKgel IC-Cation I/II HR using the mobile phase of 1.0 mM HNO_3 solution, with a flow rate of 1.0 mL/min. Concentrations of pyrrole were determined by UV-vis spectrophotometry at an absorbance of 210 nm using a Shimadzu UV-1650PC spectrophotometer. The attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of selected amorphous silica samples used in the adsorption experiments were measured using a Shimadzu FTIR-8400S instrument equipped with an ATR module of *MIRacle*™A (a ZnSe prism; incident angle = 45º; one time reflection) to confirm the adsorption of the organic compounds and evaluate the surface-complexed structures of the adsorbed molecules.

RESULTS AND DISCUSSION

Throughout the dissolution experiments for 10 days, the solution pH remained constant at initial values of ~6, 5, and 4 in each system. The Si concentrations in all the systems increased linearly with time depending on the solution pH and the organic compounds (Figure 2). System A demonstrated that the Si concentrations of each run increased more rapidly with increasing concentrations of guanidine at each pH condition. System B, which contained imidazole, showed similar increasing trends for the Si concentrations to those of system A, indicating that both guanidine and imidazole exhibited a large enhancement of amorphous silica dissolution depending on their concentrations. However, system C indicated that pyrazole showed lesser enhancement than those of guanidine and imidazole. No enhancement was observed in system D, which contained pyrrole. These observations indicate that the guanidine and the heterocyclic compounds, including imidazole, appear to significantly affect the dissolution rates of amorphous silica; however, the effectiveness is strongly dependent on their chemical characteristics.

The dissolution rates of amorphous silica in systems A, B, C, and D were plotted against the solution pH (Figure 3), together with previously published data of 0.1, 1.0, and 10.0 mM NaCl solutions with no organic compounds (Kawano and Obokata, 2007). The dissolution rates of amorphous silica and the enhancement factors of the rates in each dissolution run (Table 2,
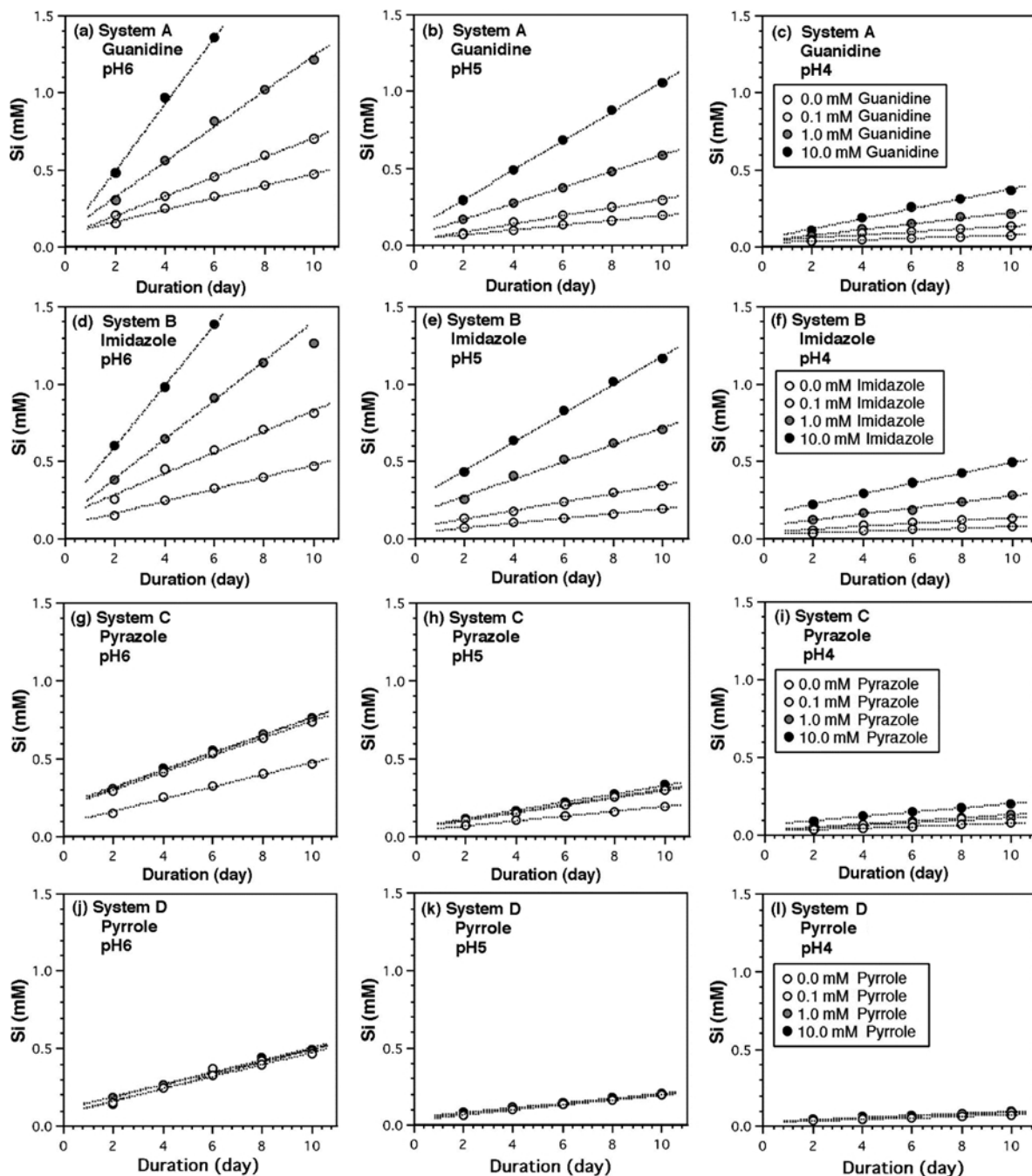
Figure 2. Concentrations of Si during dissolution of amorphous silica in systems A, B, C, and D at 25ºC.

Figure 3) revealed that the dissolution rates in all the systems tended to increase with increasing solution pH, which could be attributed to the increase in negatively charged sites ($>SiO^-$) on the amorphous silica surfaces with increased solution pH. The dissolution rates in solutions containing no organic compounds were consistent with those of amorphous silica in a 0.1 mM NaCl solution as plotted on the dotted line in Figure 3.

However, the dissolution rates increased progressively with increasing concentrations of organic compounds except in system D. The dissolution rates in system A increased considerably with enhancement factors of 5.7, 6.5, and 5.9 in solutions of pH 6, 5, and 4, respectively, with increasing concentrations of guanidine as compared with the controls (Table 2). System B also demonstrated similar enhancement factors of 5.5, 6.5, and 6.1 in
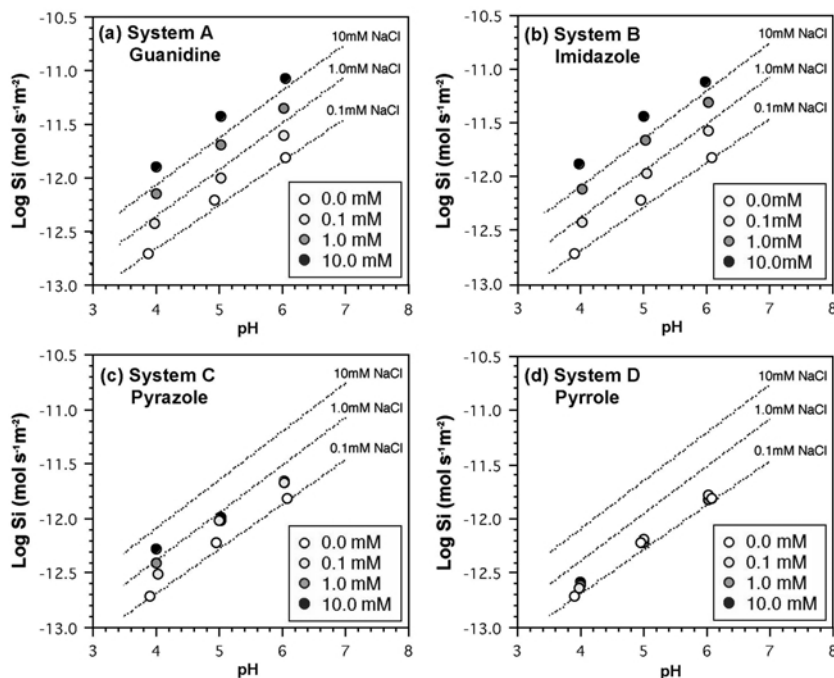
Figure 3. Dissolution rates of amorphous silica in systems A, B, C, and D at 25ºC, plotted as a function of average solution pH. The dotted lines indicate the dissolution rates of amorphous silica in a solution containing 0.1, 1.0, and 10 mM NaCl (Kawano and Obokata, 1997).

solutions containing 10 mM imidazole at pH 6, 5, and 4, respectively. On the other hand, system C showed a smaller enhancement than those of systems A and B, giving maximum enhancement factors of 1.5, 1.8, and 2.4 in each pH condition. Notably, the enhancement factors tended to increase with decreasing solution pH, indicating that the effect of pyrazole on the dissolution rate of amorphous silica was significantly larger in solutions of lower pH. In the case of system D, pyrrole exhibited no significant effect on the dissolution rate (Figure 3d). Thus, the organic compounds guanidine and imidazole were clearly effective in the enhancement of amorphous silica dissolution, while pyrazole was less effective than guanidine and imidazole. Pyrrole had no significant effect on the dissolution.

The dissolution rate of amorphous silica is known to be enhanced by the interaction of alkali and alkaline earth cations such as Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, and Ba^{2+} (Barker *et al.*, 1994). The listed cations may also be complexed with the negatively charged surface sites of amorphous silica, which would destabilize the framework of $Si-O-Si$ bonds and decrease the energy needed to break these bonds. The hydrolysis of the amorphous silica surfaces with H_2O molecules, therefore, proceeds readily in the presence of these cations. Similarly, organic molecules such as basic amino acids (histidine (pI 7.59), lysine (pI 9.74), and arginine (pI 10.76)), which exist mainly in cationic form under conditions where pH < pI, are capable of enhancing the dissolution rates by about one order of magnitude in the pH range of 4–6 due to the

complexation of the cationic species with the amorphous silica surfaces. However, neutral amino acids are less effective for increasing the dissolution rates, because these molecules exist mostly as neutral species, which are less effective in such interactions (Kawano *et al.*, 2009). In the case of the organic compounds used in the present study, the concentrations of cationic species of guanidine, imidazole, pyrazole, and pyrrole as a function of solution pH were calculated by *ChemEQL* (Müller, 1996), using their pK values for the protonation. The results of the calculations indicated that guanidine and imidazole were fully protonated and present mostly as cationic species in the range of pH $\sim< 6$ (Figure 4). However, the concentrations of cationic species of pyrazole were about three and one orders of magnitude smaller than those of guanidine and imidazole at pH 6 and 4, respectively. Pyrrole exhibited much lower concentrations of cationic species and was present mainly as a neutral species in these pH conditions. Thus, guanidine and imidazole are likely to interact strongly with the negatively charged surfaces of amorphous silica over a wide range of solution pH, which may contribute to greater enhancement of the dissolution rates of amorphous silica. The lower concentrations of cationic species of pyrazole tend to weaken the effective interaction, depending on the concentrations of the cationic species. The enhancement effect of pyrazole is thus less than that of guanidine and imidazole, and also becomes less effective in solutions of pH 6 compared to pH 4. The much lower concentrations of cationic species of pyrrole

Table 2. Dissolution rates of amorphous silica in systems A to D.

System	Run	Organic molecule	pH (Average)	Log rate (mol s^{-1} m^{-2})	Enhancement factor, k
Control (Total Na = 0.1 mM)	R60	−	6.06	−11.81	−
	R50	−	4.94	−12.21	−
	R40	−	3.90	−12.71	−
System A Guanidine (Total Na = 0.1 mM)	A61	0.1 mM	6.04	−11.60	1.67
	A62	1.0 mM	6.04	−11.34	3.06
	A63	10.0 mM	6.05	−11.06	5.73
	A51	0.1 mM	5.04	−12.00	1.72
	A52	1.0 mM	5.04	−11.68	3.57
	A53	10.0 mM	5.03	−11.43	6.45
	A41	0.1 mM	3.98	−12.42	1.76
	A42	1.0 mM	4.01	−12.14	3.28
	A43	10.0 mM	4.00	−11.89	5.88
System B Imidazole (Total Na = 0.1 mM)	B61	0.1 mM	6.03	−11.57	1.79
	B62	1.0 mM	6.03	−11.30	3.38
	B63	10.0 mM	5.97	−11.11	5.50
	B51	0.1mM	5.05	−11.97	1.82
	B52	1.0 mM	5.01	−11.66	3.84
	B53	10.0 mM	5.00	−11.44	6.49
	B41	0.1 mM	4.02	−12.42	1.70
	B42	1.0 mM	4.02	−12.11	3.48
	B43	10.0 mM	3.98	−11.88	6.10
System C Pyrazole (Total Na = 0.1 mM)	C61	0.1 mM	6.02	−11.66	1.48
	C62	1.0 mM	6.02	−11.65	1.53
	C63	10.0 mM	6.02	−11.66	1.48
	C51	0.1 mM	5.00	−12.02	1.70
	C52	1.0 mM	5.02	−12.01	1.71
	C53	10.0 mM	5.01	−11.98	1.85
	C41	0.1 mM	4.02	−12.50	1.42
	C42	1.0 mM	4.00	−12.40	1.80
	C43	10.0 mM	4.00	−12.27	2.43
System D Pyrrole (Total Na = 0.1 mM)	D61	0.1 mM	6.03	−11.78	1.11
	D62	1.0 mM	6.03	−11.82	1.02
	D63	10.0 mM	6.04	−11.81	1.03
	D51	0.1 mM	4.99	−12.19	1.16
	D52	1.0 mM	4.99	−12.22	1.08
	D53	10.0 mM	5.00	−12.22	1.07
	D41	0.1 mM	3.98	−12.63	1.09
	D42	1.0 mM	3.99	−12.61	1.15
	D43	10.0 mM	4.01	−12.58	1.20

give no significant enhancement effect on the dissolution in the pH range of 4−6. From the relationship between the enhancement factors of amorphous silica, dissolution due to interaction of organic compounds, and the logarithmic concentrations of the cationic species (Figure 5), the enhancement effect of these organic compounds obviously appeared at concentrations of cationic species approximately >10^{-5} M, and increased progressively with increasing concentrations.

Measurement of the concentrations of organic compounds of each system indicated that the adsorption of these organic compounds was very small and less than a few percent for guanidine and imidazole, while no significant adsorption was observed for pyrazole or pyrrole at a pH range of 4−6. To confirm the adsorption of these organic compounds over a wide range of pH, an adsorption experiment in solutions of approximately pH 2−10 was performed using 1.0 mM solutions of the organic compounds. The results of the experiment demonstrated that the guanidine adsorption was <1% (10 mM/g) at pH 4−6, but increased progressively with increasing solution pH (Figure 6), which is comparable to the variations in negative surface charge of amorphous silica as a function of pH (Vlasova and Golovkova, 2004). Imidazole exhibited similar adsorption behavior to that of guanidine for pH < 8.5; however, the adsorption % decreased gradually for pH > 8.5. Adsorption of pyrazole and pyrrole on the surfaces of
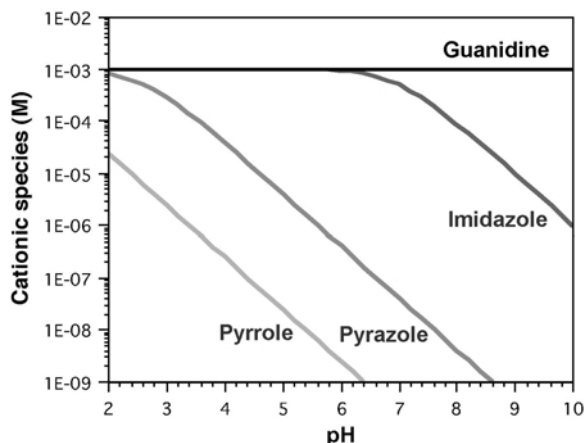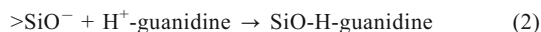
Figure 4. Concentrations of cationic species of organic compounds as a function of solution pH calculated with the geochemical program *ChemEQL*.

Figure 6. Adsorption (%) of organic compounds on the surface of amorphous silica as a function of solution pH at 25ºC for 1 day.

amorphous silica could not be detected in this experiment. Thus, adsorption of these organic compounds may occur through the electrostatic binding between the negatively charged silanol group ($>SiO^-$) of the amorphous silica surfaces and the cationic species of the organic compounds. Guanidine is present mainly as a cation in the pH range 2−10 (Figure 4), leading to progressive adsorption with increasing solution pH by forming outer-sphere complexes as might be expressed by the following reaction:

$$>SiO^- + H^+\text{-guanidine} \rightarrow SiO\text{-H-guanidine} \qquad (2)$$

Imidazole can also adsorb in a similar manner; however, concentrations of the cation decrease gradually from pH > ~7, which is attributable to the decrease in adsorption % of imidazole at pH > 8.5. Pyrazole and pyrrole are present mainly as neutral species, except in

highly acidic conditions, which makes electrostatic binding of the compounds to the $>SiO^-$ group difficult. ATR-FTIR absorption spectra of the amorphous silica used in the adsorption experiments of guanidine at pH 8.1, 9.0, and 9.5 in the frequency range 1200−2000 cm^{-1} (Figure 7) are shown together with the spectra of guanidinium ions (10.0 M solution at pH 6.8) and H$_2$O (pure water). The ATR-FTIR spectrum of amorphous silica at pH 8.1 contained no significant absorption band for guanidine, whereas a broad absorption band around 1660 cm^{-1} assigned to the C−N stretching of guanidine (Goto *et al.*, 1957) and a small band around 1640 cm^{-1} attributed to OH bending of adsorbed H$_2$O were observed in the spectra at pH 9.0 and 9.5. These C-N adsorption bands are not significantly different from those of free guanidinium ions, indicating that guanidine molecules bind weakly to the silica surfaces, possibly by intermolecular hydrogen bonding. Thus, guanidine and imidazole may adsorb in a manner similar to other basic monomers of organic molecules, such as amino acids (*e.g.* histidine, lysine, and arginine), and heterocyclic compounds (*e.g.* piperidine) to the negatively charged amorphous silica surfaces through electrostatic interaction by forming outer-sphere complexes (Vlasova and Golovkova, 2004; Liu *et al.*, 2005; Kitadai *et al.*, 2009).

In natural environments, guanidine and imidazole are abundantly present as a side-chain component of basic amino acids such as arginine and histidine, respectively. Most proteins, therefore, also contain these side chains as important reactive functional groups. Previous studies (Kawano and Obokata, 2007; Kawano *et al.*, 2009) reported that basic amino acids (histidine, lysine, and arginine) were capable of enhancing the dissolution rates of amorphous silica by ~8 to 8.5 fold compared with an amino acid-free control, possibly due to the complexation of the cationic species of the amino acid molecules with the negatively charged $>SiO^-$ sites of amorphous silica. These basic amino acids contain three functional
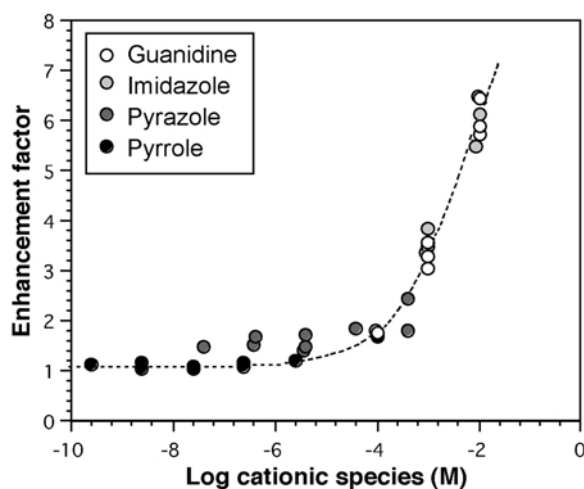

Figure 5. Variations in enhancement factors of dissolution rates of amorphous silica as a function of logarithmic concentrations of cationic species.
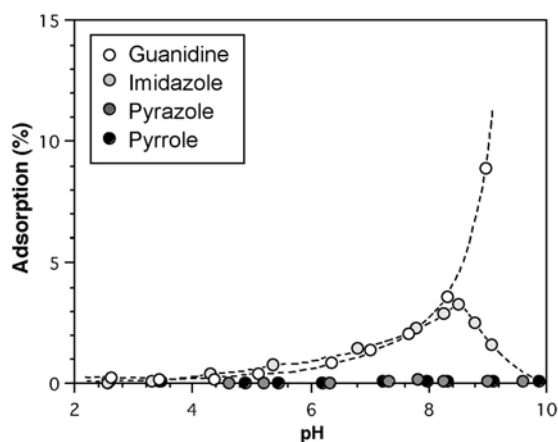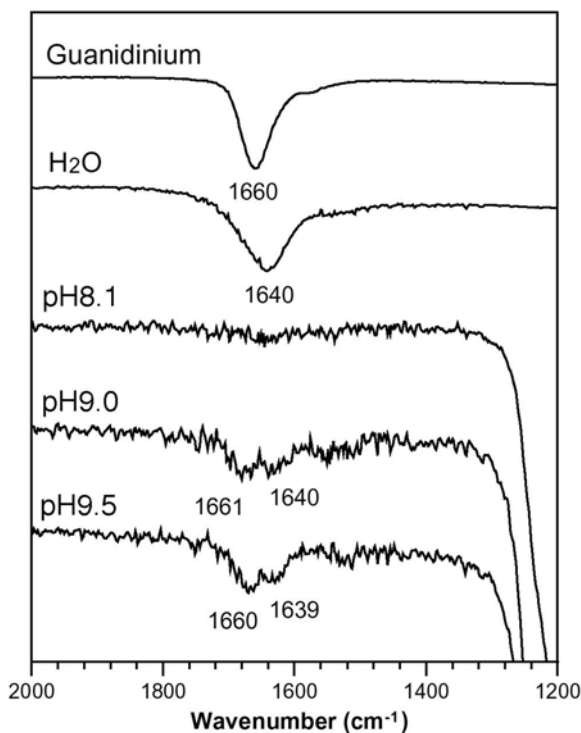
Figure 7. ATR-FTIR spectra of amorphous silica used in adsorption experiments of guanidine at pH 8.1, 9.0, and 9.5, and guanidinium ions (10.0 mM solution at pH 6.8) and H_2O (pure water).

groups: carboxyl (COO^-) groups, amino (NH_3^+) groups, and side-chain basic functional groups. Thus, achieving the interaction of the functional groups in both the main and side chains with the surfaces of amorphous silica may be possible. The present results confirm that the side-chain functional groups of arginine (guanidine) and histidine (imidazole) can interact with amorphous silica surfaces and enhance the dissolution rates of amorphous silica, depending on the degree of protonation.

CONCLUSIONS

In the present study, the dissolution rates of amorphous silica by the interaction of guanidine, imidazole, pyrazole, and pyrrole in 0.1 mM NaCl solutions at pH 4−6 were examined. The results demonstrated that these compounds can enhance the dissolution rate of amorphous silica in the following order: guanidine = imidazole > pyrazole > pyrrole. When 10.0 mM solutions were used, both guanidine and imidazole increased the dissolution rate by an enhancement factor of 5.5−6.5 whereas pyrrole exhibited no significant enhancement effect on the dissolution rate. The chemical speciation of these compounds suggested that both guanidine and imidazole are fully protonated and exist mostly as cations; the concentrations of cationic species of pyrazole and pyrrole were at least

one and three orders of magnitude smaller than that of guanidine and imidazole, respectively. The cationic species of these compounds were capable of forming outer-sphere surface complexes with the $>SiO^-$ sites of amorphous silica. The complexation is likely to contribute to the enhancement of the dissolution rate of amorphous silica by the mechanism of ligand-promoted dissolution.

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