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EFFECT OF ORGANIC LIGANDS AND HETEROTROPHIC BACTERIA ON WOLLASTONITE DISSOLUTION KINETICS

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ABSTRACT. Wollastonite ($CaSiO_3$) dissolution rates were measured at 25°C in 0.01 M NaCl using a mixed-flow reactor as a function of pH (5 to 12) and concentration of forty organic ligands. Mostly stoichiometric dissolution was observed at these conditions. For seven ligands (acetate, citrate, EDTA, catechol, glutamic acid, 2,4-dihydroxybenzoic acid, glucuronic acid), batch adsorption experiments and electrokinetic measurements performed as a function of pH and ligand concentration confirmed the interaction of ligands with $>CaOH_2^+$ sites and allowed quantification of their adsorption constants. The effect of investigated ligands on wollastonite dissolution rate was modeled within the framework of the surface coordination approach taking into account the adsorption of ligands on dissolution-active sites and the molecular structure of the surface complexes they form. A positive correlation between surface adsorption constant and the stability constant of the corresponding reaction in homogeneous solution was observed.

At neutral and weakly alkaline pH, the following total dissolved concentrations of ligands are necessary to double the rate of wollastonite dissolution: EDTA (10^{-4} M), phosphate ($1.5 \cdot 10^{-4}$ M), catechol ($3 \cdot 10^{-4}$ M), 8-hydroxyquinoline, gallic acid or adipate ($5 \cdot 10^{-4}$ M), 3,4-DHBA ($7 \cdot 10^{-4}$ M), PO_3^- ($7.5 \cdot 10^{-4}$ M), glutamate (0.002 M), citrate (0.003 M), malate or 2,4-DHBA (0.004 M), phthalate or succinate (0.005 M), tartrate (0.006 M), thioglycolate (0.008 M), aspartame (0.01 M), gluconate, ascorbate (> 0.01 M), malonate, diglycolate or lactate at pH 8.4 (0.02 M), formate or fumarate (0.05 M), oxalate (>0.05 M), bicarbonate (0.075 M), lactate at pH 5.6 (0.1 M), acetate (> 0.1 M), salicylate (0.15 M), humic acids (> 54 mg/L of dissolved organic carbon, DOC), gum xanthan (1.5-2.0 g/L). Sorbitol, mannitol, glucose, glucosamine, saccharose, fulvic acids and silica at pH ~ 7 exhibit weakly inhibiting or no effect up to concentration of 0.1 M. The presence of the following ligands leads to a decrease of dissolution rates by a factor of 2: silica at pH 10.7 ($2 \cdot 10^{-4}$ M), glucuronic acid (0.001 M), algae exudates (30 mg/L DOC), mannit (0.02 M), urea (>0.05 M), pectin (>15 g/L), alginic acid (> 2 g/L).

Overall, results of this study demonstrate that high concentrations (0.001-0.01 M) of organic ligands, whether they are originated from organic matter, enzymatic degradation or bacterial metabolic activity, are necessary to appreciably enhance wollastonite dissolution. This is further corroborated by batch experiments on live and dead cultures of soil bacteria *Pseudomonas aureofaciens* interaction with wollastonite. The release rates of both Ca and Si are only weakly affected by the presence of live or dead bacterial cells in inert electrolyte solution and in nutrient media: there is only ~20 percent-increase of dissolution rate in experiments with live cultures compared to dead cultures. However, the reproducibility of rate measurements in ligand-free solutions at $7 \leq pH \leq 8$ achieves ± 30 percent. Therefore, the effect of extracellular organic products on the weathering rate of Ca-bearing minerals is expected to be weak and the acceleration of "basic" silicate rocks dissolution in natural settings in the presence of soil bacteria is likely solely due to the pH decrease.

Key words: Wollastonite, Organic ligands, Rhizospheric bacteria, Dissolution, Kinetics.

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INTRODUCTION

It has been known for a long time that the weathering of basic rocks (Ca- and Mg-bearing silicates) controls the CO_2 uptake from the atmosphere and thus the climate of the earth at the long-term scale (for example, Berner, 1992; Dupré and others, 2003). Among the factors, controlling the intensity of this process, solution pH, pCO_2 and organic compounds produced during enzymatic degradation of vegetation litter or the exudates of soil bacteria and roots are believed to be the most important. While the effect of pH and pCO_2 on "basic" silicates dissolution kinetics is rather well characterized (Rimstiddt and Dove, 1986; Knauss and others, 1993; Oelkers and Schott, 2001; Pokrovsky and Schott, 2001; Golubev and others, 2005) the effect of organic ligands is still poorly understood (Grandstaff, 1977, 1986; Wogelius and Walther, 1991). At the same time, interaction of organic ligands with basic silicates and basalts turns out to be a very interesting proxy for paleo-weathering conditions (Neaman and others, 2005a; 2005b). Indeed, it has been argued (Antweiler and Drever, 1983; Drever, 1994) that the organic ligands should have much higher effect on the dissolution of basic silicates compared to aluminosilicates. However, this contradicts the observation of weak adsorption of organic ligands on Mg centers of brucite surface and their weak effect on this mineral's dissolution kinetics (Pokrovsky and others, 2005). This contrasts to strong interaction of organic ligands with aluminum, both at the mineral surface (Kummert and Stumm, 1980; Stumm, 1992) and in aqueous solution (Martell and others, 1997) leading to acceleration of aluminosilicates dissolution by organic matter (Heyes and Moore, 1992; Stillings and others, 1996; Oelkers and Schott, 1998). To resolve these contradictions, we attempted, in the present study, rigorous measurements of ligands-affected wollastonite ($CaSiO_3$) dissolution in which we were able to separate the effect of pH from that of organic ligands using a mixed-flow reactor system. Wollastonite was chosen as a simple and model mineral for basic silicates, frequently used as representative of silicates dissolution at the Earth surface (Peters and others, 2004). Besides, the calcium surface centers of this mineral can serve as proxies for Ca sites of other more complex silicates. Since hydrolysis of Ca—O bond is often the rate-limiting step for Ca-bearing mineral dissolution (Schott and others, 2009), understanding of ligand interaction with Ca sites of wollastonite may help to predict the reactivity of other Ca-bearing silicates.

It is known that, in addition to carbonic acid and simple carboxylic and aromatic compounds routinely identified in soil solutions (Kaurichev and others, 1963; Whitehead, 1964; Manley and Evans, 1986; Leyval and Berthelin, 1991), microbes can produce extracellular acid and neutral polysaccharides, uronic acids (galacturonic, guluronic), peptides and aminoacids (Ullman and others, 1996; Welch and others, 1999). Mycobionts such as lichens are known to exude various low molecular weight organic carboxylic acids (oxalic, citric, tartaric, gluconic, lactic) and polyphenolic compounds called "lichen acids" (Adamo and Violante, 2000). While the effects of simple and complex organic molecules and polymers on the dissolution of metal oxides (Sigg and Stumm, 1981; Bondietti and others, 1993; Biber and others, 1994; Kraemer and Hering, 1997; Kraemer and others, 1998; Axe and Persson and others, 2001; Duckworth and Martin, 2001) and aluminosilicates (Huang and Keller, 1970; Huang and Kiang, 1972; Manley and Evans, 1986; Lundstrom and Ohman, 1990; Ochs and others, 1993; Drever and Stillings, 1997; Welch and others, 1999; Welch and Ullman, 1999; van Hees and others, 2002), or on iron mobilization from silicates (Schalscha and others, 1967; White and Yee, 1985; Watteau and Berthelin, 1994; Liermann and others, 2000; Santelli and others, 2001; Bonneville and others, 2009) have been widely described, their interaction with Ca or Mg-bearing silicates is not well characterized except some works with olivine (Wogelius and Walther, 1991; Olsen and Rimstidt, 2008). In our previous works (Pokrovsky and others, 2005; Golubev and

Pokrovsky, 2006; Golubev and others, 2006), the influence of organic ligands on brucite, diopside and smectite dissolution has been modeled using a surface complexation approach. It has been demonstrated that very high concentrations of naturally-relevant organic ligands (0.01-0.1 M) are necessary to significantly enhance or inhibit brucite dissolution and thus the effect of extracellular organic products on the weathering rate of Mg-bearing minerals in natural settings is expected to be weak. The question remains how far this conclusion can be extended to other alkali-earth bearing minerals such as calcium silicates. The main goal of the present study, therefore, is to use wollastonite as a model to study the effect of naturally-occurring organic ligands and chemical analogs of bacterial metabolites and cell envelopes on all Ca-bearing silicates in aqueous solutions.

The second motivation for this work is to quantitatively access the effect of microbial activity on wollastonite dissolution. There are several recent studies dealing with quantifying the effect of bacteria on basalt and granite rock dissolution (Wu and others, 2007, 2008). However, due to the complexity of whole rock systems, assessing the elementary mechanisms that control the element release in the mineral–bacteria system is rather difficult. On the other hand, extensive studies on alumosilicates (Barker and others, 1997; Bennett and others, 2001) and calcite (Friis and others, 2003; Luttge and Conrad, 2004; Davis and others, 2007) dissolution in the presence of bacteria cannot be directly applied to basic silicates and wollastonite dissolution because of different reaction mechanisms involved in these interactions. The use of a pure mineral specimen with a reference culture of soil bacteria offers the possibility of directly testing, for the first time, the effect of live and dead bacteria on calcium and silica release rate from the silicate mineral. We choose a typical rhizospheric soil bacteria, *Pseudomonas aureofaciens,* which is relatively well studied from the viewpoint of metal adsorption and is known to produce or not abundant exopolysaccharides depending on the type of substrate they use for growth (Pokrovsky and others, 2008). It has been also shown that a soil strain of genera *Pseudomonas* is capable of producing 2-ketogluconic acid from glucose and thus dissolving Ca, Zn, Mg silicates, wollastonite, apophyllite and olivine via formation of Ca-2 ketogluconate (Webley and others, 1960; 1963) however, no quantitative parameters of the process were assessed.

MATERIALS AND METHODS

Materials

Natural wollastonite crystals characterized in previous work (Golubev and others, 2005) were used in this study. The ultrasonically-cleaned 100 to 200 μm size fraction having a specific surface area of 690 ± 30 cm^2/g was selected for dissolution rate measurements. For adsorption experiments, that required high surface area in solution, wollastonite fine powder <10 μm was ground in an agate mortar for 3 hours. To eliminate the surface defects produced by grinding, prior to the experiments this powder was heated at 550°C during 6 hrs and aged during 7 days under nitrogen atmosphere in a solution of pH=10.8. Its specific surface area was 4.7 m^2/g as measured by 3-point N_2 adsorption using the B.E.T. method. All solutions were prepared from 18 MΩ ultrapure water (MilliQ Plus system) having a blank of dissolved organic carbon < 0.05 ppm. The pH of the isoelectric point of this powder was 2.2 to 2.5 as determined by Oelkers and others (2009). Investigated inorganic and organic ligands were in the form of sodium salts or pure acids of analytical grade purchased from Fluka, Aldrich or Sigma. We used several families of organic compounds, representing both individual organic acids identified in soil solutions and groundwaters and chemical analogs of microbial exometabolites, functional groups of cell surface envelopes and various specific binding ligands. The ligands selected in this study can be considered as analogs of functional groups for dissolved organic matter,

bacterial cell envelopes and their exometabolites. They included monocarboxylic acids (acetate and formate), di(tri)carboxylic acids (lactate, malate, malonate, fumarate, succinate, tartrate, adipate, gluconate, oxalate, citrate and diglycolate) and chelates (EDTA and EGTA). Aromatic compounds used in this work can be considered as analogs of aromatic groups of natural polymers or extracellular microbial chelates [catechol, 8-hydroxychinolin, 2,4-Dihydroxybenzoic acid (2,4-DHBA), 3,4-Dihydroxybenzoic acid (3,4-DHBA), 4-Hydroxybenzoic acid, gallic acid, oxine, phthalate and salicylate], and polysaccharides (glucose, saccharose, D-mannit and xylose), aminoacids (aspartate, glutamate, glycine), alcohols (sorbitol, mannitol). In addition, miscellaneous compounds (ascorbate, thioglycolate and urea) and some inorganic ligands (phosphate, metaphosphate and carbonate) were also used. Besides these simple synthetic compounds, natural ligands such as soil humic and fulvic acids, phytoplankton exudates, commercial acid and neutral (that is, Welch and Vandevivere, 1994) polysaccharides such as bacterial gum xanthan, pectin from citrus peel, alginate from brown algae, and glucosamine as analogs of microbial extracellular polysaccharides and peptidoglycan were also tested with respect to their effect on wollastonite dissolution.

Bacterial Cultures

The bacterial strain of soil aerobic gram-negative bacteria *Pseudomonas aureofaciens* CNMN PsB-03 was obtained from laboratory of Plant Mineral Nutrition and Hydric Regime (Institute of Plant Genetics and Physiology, Moldovan Academy of Sciences, Chishinau, Moldova). The specific strain was isolated from soybean root-adhering (rhizosferic) soil for their capability of producing large amounts of gel-forming exopolysacharide (EPS) on a sucrose-peptone (SP) medium (Behrens and Ringpfeil, 1963). On sugar-poor medium (0.4% succinic acid, SA, Meyer and Abdallah, 1978), this strain provides only poor synthesis of EPS. The *Pseudomonas* sp. was maintained at 4°C in SA media (as broth and agar plate cultures). For biomass accumulation the strain was cultered in SP and SA media for 48 hrs at 28°C. Cells were harvested at the beginning of stationary phase. Two samples of *P. aureofaciens* PsB-03 biomass were used in the present study. First, cells were grown in nutritive medium with sucrose as a single carbon source, which yields an abundant EPS synthesis labeled "SP culture", and the second, cells were grown in nutritive medium with succinic acid as a single carbon source, which produces very poor EPS, called "SA culture". The chemical composition of growth media was as follows: SP, 40 g/L sucrose, 15 g/L peptone, 5 g/L NaCl and 1 g/L Na_2HPO_4; SA, 4 g/L succinic acid, 1 g/L $(NH_4)_2SO_4$, 0.6 g/L K_2HPO_4, 0.3 g/L KH_2PO4, 0.1 g/L $MgSO_4$. In addition to the differences in the amount of EPS produced on SP and SA media, the qualitative monosaccharide composition of produced exopolymers is also different (Emnova and others, 2007). In the EPS produced on SP media, fructose constituted 76 percent of total sugars, and the second dominant monosaccharide was glucose (11%). The monosaccharides from EPS produced on SA media are composed of 50 percent glucose, 22 percent fructose, and 14 percent mannose. Small amounts (<10% of total sugars) of rhamnose, ribose, xylose, and galactose were present in both EPS samples. These data indicate that the polysaccharide levan (polyfructan) is likely EPS of *P. aureofaciens* in medium SP, and glucan and some other heteropolymers are present in medium SA.

The biomass of live bacteria and diatom cell suspensions were quantified by measuring humid (centrifuged 15 min at 10,000 rpm) and dry (liophylized) weight. Before the inoculation, cells were rinsed twice in appropriate fresh culture media or sterile 0.01 M NaCl solution using centrifugation at 4500× g (~ 500 mL of solution for 1 g of wet biomass) to remove, as possible, the adsorbed metals and cell excudates from the surface. The conversion factors humid/dry(liophylised) weight for studied microorganisms were the following: EPS-rich (SP culture), 3.6; EPS-poor (SA culture), 5.0.

Typical live biomass concentration during batch experiment was in the range of 0.5 to 4 g humid/L. Dead cultures were prepared by autoclaving at 130°C during 30 min SA and SP cultures suspension collected at the stationary state. They were subsequently rinsed using appropriate sterile media or 0.01 M NaCl and diluted to final concentration of 1.5 g humid/L.

Ligand Sorption Experiments

Batch adsorption experiments were carried out in 30 mL polypropylene plastic vials. Solutions of 0.01 M NaCl were equilibrated with < 10 μm wollastonite powder (4.7 m^2/g, see Materials section) of 57 g/L producing 268 m^2/L total surface area in the reactor. Ligand (L) addition from 0.01 or 0.001 M stock solutions was made using a calibrated automatic pipette to achieve the initial ligand concentration of 70 ± 10 μM for all ligands except acetate for which the initial concentration was set at 450 μM in order to increase the adsorption yield. Suspensions were shaken in the thermostated chamber at 25 ± 0.5°C. Preliminary kinetic experiments demonstrated that the equilibrium distribution of two selected ligands (acetate and citrate) between solution and solid phase was achieved in less than 2 days, but two weeks was taken as final equilibration time for all ligands. Prior to the analysis, suspensions were centrifuged and solutions were filtered through a 0.22 μm Nylon filter.

Analyses

Solution pH was measured using a combination glass electrode calibrated on the activity scale with NIST buffers (pH = 4.002, 6.865, and 9.180 at 25°C). Precision of pH measurements was ± 0.002 units (0.1 mV). Total calcium ($[Ca^{2+}]_{tot}$) concentration was measured by flame atomic absorption spectrophotometry using a Perkin Elmer 5100 PC spectrometer equipped with an AS-90 autosampler, with an uncertainty of ± 0.5 percent and a detection limit of 0.5 μM. To achive such precision, we performed multiple replicates of the same sample (5 replicats) and completely calibrated the system after each 5 samples. Monomeric silica concentration was measured by automated spectrophotometry with molybdate blue using Technicon analyzer with an uncertainty of ± 1 percent and a detection limit of 0.3 μM. Alkalinity was determined following a standard HCl titration procedure with an uncertainty of ± 1 percent and a detection limit of $5 \cdot 10^{-5}$ M. Phosphate and acetate were analyzed using a Dionex HPLC equipped with a Gilson autoinjector with an uncertainty of ± 2 percent and a detection limit of 0.05 ppm. The concentration of organic ligands was measured as total dissolved organic carbon using a TOC Shimadzu 5000 analyzer with an uncertainty of 5 percent and a detection limit of 0.2 mg C_{org}/L.

The MINTEQA2 computer program (Allison and others, 1991) was used to calculate the equilibrium species distribution in the $CaSiO_3$-H_2O-NaCl-ligand system. This program combines interfaces and homogeneous solution equilibria and mass balance calculations. Stability constants for Ca^{2+}(aq) complexation with all ligands were taken from the Critical Database (Martell and others, 1997) and are listed in table 1.

Wollastonite Dissolution Experiments

Mixed-flow bacteria-free dissolution experiments.—Steady-state dissolution rates were obtained at 25.0 ± 0.2°C in 0.01 M NaCl and distinct solution compositions and pH using a thermostated mixed-flow reactor (see Pokrovsky and Schott, 2004 for details). Mechanical steady-state in reactor was achieved after 12 hrs of reaction, but the chemical steady state was typically attained after 24 hrs. Each experiment involved new wollastonite powder which was reacted with consequently increasing ligand concentrations. For each steady-state condition, 4 to 5 measurements of Ca concentration and pH and one flow rate measurement were performed and used for calculating the

TABLE 1

Ligands used in the present study and their acid-base (**pK°$_1$, pK°$_2$, pK°$_3$**) *and aqueous stability* (**log K° aq (Ca-L)**) *constants taken from the database*

Ligand	Chemical formula and description	pK°$_1$, pK°$_2$, pK°$_3$	log K° aq (Ca-L)	log K^*_{Ca-L}	$k^{\#}_L$ / $k^{\#}_{Ca}$	$k^{\#}_L$	$k^{\#}_{Ca}$
Acetic acid	CH_3COOH	3.745	1.18	1.74	0.7	$1.5\cdot10^{-13}$ (pH=6.7) $2.5\cdot10^{-14}$ (pH=10.7)	$2.5\cdot10^{-13}$ (pH=6.7) $3.2\cdot10^{-14}$ (pH=10.7)
Formic acid	HCOOH	3.75	1.43	1.48	2.0	$4.5\cdot10^{-13}$ (pH=6.7)	$2.3\cdot10^{-13}$ (pH=6.7)
Lactic acid	$CH_3CH(OH)COOH$	3.86	1.45	1.57	2.4-3.3	$1.1\cdot10^{-12}$ (pH=5.5) $3.3\cdot10^{-13}$ (pH=8.5)	$4.5\cdot10^{-13}$ (pH=5.5) $1.1\cdot10^{-13}$ (pH=8.5)
Oxalic acid	HOOC = COOH	1.25; 4.27	2.76	2.30	0.4-1.0	$3.0\cdot10^{-13}$ (pH=6.5) $1.0\cdot10^{-14}$ (pH=10.9)	$3.0\cdot10^{-13}$ (pH=6.5) $2.4\cdot10^{-14}$ (pH=10.9)
Fumaric acid	HOOCCH - CHCOOH	3.02; 4.48	2.00	2.30	2.2	$3.4\cdot10^{-13}$ (pH=7.0)	$1.6\cdot10^{-13}$ (pH=7.0)
Citric acid	$C_3H_5O(COOH)_3$	3.13; 4.76; 6.40	3.51	2.43	2.0-3.4	$1.2\cdot10^{-12}$ (pH=7.2) $5.3\cdot10^{-14}$ (pH=10.7)	$3.5\cdot10^{-13}$ (pH=7.2) $2.7\cdot10^{-14}$ (pH=10.7)
Malic acid	$HOOCCH_2CHOHCOOH$		2.72	2.26	3.7	$7.0\cdot10^{-13}$ (pH=6.5)	$1.9\cdot10^{-13}$ (pH=6.5)
Tartaric acid	$C_4H_6O_6$	3.04; 4.37	2.80	2.28	0.6-3.3	$2.6\cdot10^{-13}$ (pH=9.1) $1.4\cdot10^{-14}$ (pH=11.0)	$8.0\cdot10^{-14}$ (pH=9.1) $2.6\cdot10^{-13}$ (pH=11.0)
Phtalic acid	$C_6H_4(COOH)_2$	2.95; 5.41	2.45	2.24-2.40	1.2-3.1	$4.0\cdot10^{-13}$ (pH=6.9) $3.2\cdot10^{-14}$ (pH=10.9)	$1.3\cdot10^{-13}$ (pH=6.9) $2.7\cdot10^{-14}$ (pH=10.9)
Malonic acid	$CH_2(COOH)_2$	2.85; 5.70	2.43	2.40	2.6	$4.5\cdot10^{-13}$ (pH=7.0)	$1.7\cdot10^{-13}$ (pH=7.0)
Adipic acid	$(CH_2)_4(CO_2H)_2$	4.42; 5.42	2.19	2.24	4.7	$9.1\cdot10^{-13}$ (pH=6.7)	$1.9\cdot10^{-13}$ (pH=6.7)
D-gluconate	$HOCH_2(CHOH)_4COOH$	3.46#	1.21	2.00	3.7	$3.7\cdot10^{-13}$ (pH=8.4)	$1.0\cdot10^{-13}$ (pH=8.4)
Succinic acid	$C_4H_4Na_2O_4$	4.21; 5.64	2.00	2.08	4.3	$5.2\cdot10^{-13}$ (pH=8.4)	$1.2\cdot10^{-13}$ (pH=8.4)
D-glucuronic	5-carboxy-D-glucopyranose	12.04#	1.64	2.30	0.1	$2.0\cdot10^{-14}$ (pH=6.6)	$1.4\cdot10^{-13}$ (pH=6.6)
EDTA	$[CH_2N(CH_2CO_2H)_2]_2$	10.95; 6.27; 2.69; 2.00	10.65# for Ca-L 5.78 for Ca-HL 3.66 for Ca-H2L	3.48 4.70 4.30	14.7 (pH = 7.7) 62.5 (pH = 9.4) 8.7 (pH = 10.9)	2.2·10-12 (pH=7.7) 2.5·10-12 (pH=9.4) 2.6·10-13 (pH=10.9)	1.5·10-13 (pH=7.7) 4.1·10-14 (pH=9.4) 3.0·10-14 (pH=10.9)

TABLE 1
(continued)

Ligand	Chemical formula and description	pK°$_1$, pK°$_2$, pK°$_3$	log K° aq (Ca-L)	log K^{*}_{Ca-L}	$k^{\#}_{L}$ / $k^{\#}_{Ca}$	$k^{\#}_{L}$	$k^{\#}_{Ca}$
H_2EGTA^{2-}	$C_{12}H_{24}N_2O_{10}^{2-}$	9.40[#]; 8.79[#]; 2.70; 1.90	10.86 for Ca-L 3.81 for Ca-HL	3.70	4.7	$8.0\cdot10^{-13}$ (pH=6.1)	$1.7\cdot10^{-13}$ (pH=6.1)
H_2Catechol°	$C_6H_4(OH)_2$	9.45; 13.00	4.0	2.85 3.00	2.5 – 6.0	$1.5\cdot10^{-12}$ (pH=6.3) $5.3\cdot10^{-14}$ (pH=10.7)	$2.5\cdot10^{-13}$ (pH=6.3) $2.1\cdot10^{-14}$ (pH=10.7)
8-Hydroxyquinoline	C_9H_7NO	4.92; 9.82	3.27	2.70	4.4	$5.9\cdot10^{-13}$ (pH=8.3)	$1.35\cdot10^{-13}$ (pH=8.3)
H_2(2,4-DHBA$^-$)				2.48	3.3	$5.0\cdot10^{-13}$ (pH=7.0)	$1.5\cdot10^{-13}$ (pH=7.0)
[a]H_2(3,4-DHBA$^-$)				2.90	4.3	$1.52\cdot10^{-12}$ (pH=7.4)	$2.9\cdot10^{-13}$ (pH=7.4)
Gallic acid	$C_7H_6O_5$	4.44; 9.11; 11.40*		2.40	10.4	$1.45\cdot10^{-12}$ (pH=7.0)	$1.4\cdot10^{-13}$ (pH=7.0)
Ascorbic acid	$C_6H_7O_6$	4.02; 11.35	1.05 for Ca-HL	2.04	4.5	$5.0\cdot10^{-13}$ (pH=7.4)	$1.1\cdot10^{-13}$ (pH=7.4)
Orthophospate	$H_2PO_4^-$		2.66	3.00	16.7	$3.6\cdot10^{-12}$ (pH=6.9)	$2.15\cdot10^{-13}$ (pH=6.9)
Metaphosphate	$H_2PO_3^-$	2.05	3.47	2.60	7.3	$3.0\cdot10^{-12}$ (pH=7.3)	$4.1\cdot10^{-13}$ (pH=7.3)
[b]Humate (COO$^-$)		4.5; 9-10	2.0	2.6	5.6	$2.0\cdot10^{-12}$ (pH=6.75)	$3.6\cdot10^{-13}$ (pH=6.75)
[b]Fulvate (COO$^-$)		4.5; 9-10		2.7	0.5	$1.0\cdot10^{-12}$ (pH=6.4)	$2.0\cdot10^{-13}$ (pH=6.4)
Algae excudates		4.5; 6-7; 9-10		3.0	0.03	$7.0\cdot10^{-15}$ (pH=6.7)	$2.5\cdot10^{-13}$ (pH=6.7)
Salicylic acid	$C_6H_4(OH)COOH$	2.974; 13.7		1.30	2.8	$7.0\cdot10^{-13}$ (pH=6.5)	$2.5\cdot10^{-13}$ (pH=6.5)
Thioglycolate	SH-CH_2COO^-	3.64; 10.61		1.60	6.3	$1.45\cdot10^{-12}$ (pH=6.6)	$2.3\cdot10^{-13}$ (pH=6.6)
Oxydiacetate	$O(CH_2COOH)_2$	3.01; 4.36	4.28	2.48	2.6	$4.5\cdot10^{-13}$ (pH=7.3)	$1.75\cdot10^{-13}$ (pH=7.3)
Aspartic acid	$HO_2CCH(NH_2)CH_2CO_2H$	1.99; 3.90; 10.00	2.5	2.48	2.5	$1.4\cdot10^{-12}$ (pH=7.3)	$5.7\cdot10^{-13}$ (pH=7.3)
Glutamic acid	$C_5H_9NO_4$		2.06	2.78	2.9	$4.8\cdot10^{-13}$ (pH=7.1)	$1.6\cdot10^{-13}$ (pH=7.1)
Sorbitol	D-gluco-Hexitol, $C_6H_{14}O_6$			2.30	1.6	$6.0\cdot10^{-13}$ (pH=5.8)	$3.7\cdot10^{-13}$ (pH=5.8)
Mannitol	$C_6H_{14}O_6$			1.7	1.3	$5.9\cdot10^{-14}$ (pH=10.9)	$4.5\cdot10^{-14}$ (pH=10.9)
D(+)-Glucose	D-gluco-Hexose	12.28		1.48	2.0	$6.0\cdot10^{-13}$ (pH=6.1)	$3.0\cdot10^{-13}$ (pH=6.1)
Saccharose	β-D-Fructofuranosyl-α-D-glucopyranoside	12.57; 13.45		0.00	1.0	$1.2\cdot10^{-13}$ (pH=8.4)	$1.2\cdot10^{-13}$ (pH=8.4)

TABLE 1
(continued)

Ligand	Chemical formula and description	$pK°_1$, $pK°_2$, $pK°_3$	log K° aq (Ca-L)	log K^*_{Ca-L}	$k^{\#}_L$ / $k^{\#}_{Ca}$	$k^{\#}_L$	$k^{\#}_{Ca}$
D-Mannit				1.88	0.11	$2.5 \cdot 10^{-15}$ (pH=10.9)	$2.2 \cdot 10^{-14}$ (pH=10.9)
UREA	$(NH_2)_2CO$			2.48	0.6	$1.8 \cdot 10^{-14}$ (pH=11.0)	$3.0 \cdot 10^{-14}$ (pH=11.0)
Pectin[c]	1-4 α-galacturonic acid polymer methoxy groups comprised of 84% galacturonic acid and 10% methoxyl content	4.5 – 5.5	5.80	3.44	0.25	$9.0 \cdot 10^{-14}$ (pH=6.0) $2.5 \cdot 10^{-14}$ (pH=7.8)	$3.2 \cdot 10^{-13}$ (pH=6.0) $1.55 \cdot 10^{-13}$ (pH=7.8)
Gum Xanthan[d]	Microbial polysaccharide produced by *Xanthomonas campestris* comprised of D-glucosse, D-mannose, D-glucuronic acid, pyruvite.	4.5 – 5.5		2.30	25	$5.5 \cdot 10^{-12}$ (pH=7.5)	$2.2 \cdot 10^{-13}$ (pH=7.5)
Alginic acid	(M_r = 32 – 200 kD; 4 mM COO^-/g alginate)	4.5	3.40 ± 0.2 at pH = 6-7	2.3	0.6	$8.0 \cdot 10^{-14}$ (pH=7.0)	$1.4 \cdot 10^{-13}$ (pH=7.0)
Glucosamine	$C_6H_{13}NO_5$	7.58*	2.0	2.3	1.1	$2.4 \cdot 10^{-13}$ (pH=6.9)	$2.2 \cdot 10^{-13}$ (pH=6.9)

[a] Rogers and Bennett (2004); [b] 10 μeq COO^- per mg DOC; [c] Postulated M.W. = 65,000; [d] Postulated M.W. = 10,000.
The surface adsorption constants (K^*_{Ca-L}) are fitted from kinetic data.
[#] stands for I = 0.1 M.
All aqueous complexation constants are taken from Martell and others (1997) except for alginate (Gregor and others, 1996) and for pectine (Schlemmer, 1989).

average dissolution rate. We used a criterion of average Ca concentration at steady state as ± 3 percent at $[Ca^{2+}]_{tot} > 10^{-4}$ M and ± 7 to 10 percent at $[Ca^{2+}]_{tot} < 10^{-4}$ M, measured after achieving 3 times mechanical steady state. All experiments were performed at far from equilibrium conditions with respect to Ca-L insoluble salts with Ca ($\log \Omega_{Ca\text{-}L(s)} < -0.5$).

Batch dissolution experiments with bacteria.—The aim of these experiments was to compare, under identical solution conditions, the Ca and Si release rate from wollastonite placed in contact with dead and live bacterial cultures. The batch reactors used to study wollastonite–bacteria interaction consisted of sterile 500 mL polystyrene culture flasks with vented caps (Biosilico). All manipulations were conducted in sterile laminar hood box (class 100). For all experiments, 0.5 g of sterile 50 to 100 μm wollastonite (BET specific surface area of 1300 cm^2/g) were placed in 250 mL sterile solution producing a solid concentration of 2.5 g/L. We conducted eight experiments, four involving live SA and SP cultures, (in SA and SP nutrient solution and in 0.01 M NaCl solution), and four with dead (autoclaved) biomass (in SA, SP media and in 0.01 M NaCl). The exact chemical composition of succinic acid and sucrose-peptone culture media is given in the *Bacterial Cultures* section. The reactors were inoculated with 1 to 2 mL of fresh SA or SP cultures or the fixed amount of dead biomass and placed on rotative shaker (120 rpm) at 25 ± 1°C for 7 days. Sterile controls were routinely run both for nutrient media and 0.01 M NaCl solutions and did not demonstrate any bacterial contamination. Twice per day, 10 mL aliquots of homogeneous mineral suspension + bacteria were collected using sterile serological pipettes and transferred in sterile polystyrene vials for Ca, Si, pH and cell biomass measurements. The solid/fluid ratio remained constant during experiments and the concentration of bacteria was not affected by the sampling. Ca and Si were measured in 0.22 μm filtrates and pH and cell biomass were measured in unfiltered samples.

RESULTS AND DISCUSSION

Ligand Adsorption

Results of seven adsorption isotherms performed at far from surface sites saturation conditions are presented in figure 1. It can be seen that the surface concentration of all studied ligands decreases with increase of pH which suggests an anion-like adsorption behavior. Assuming the dominant species interacting with ligands at the wollastonite-H_2O interface are hydrated Ca centers $>CaOH_2^+$ and $>CaOH^\circ$ (Schott and others, 2002, 2009), whose protonation/deprotonation constants are given by

$$>CaOH^\circ + H^+ = >CaOH_2^+ \qquad K_1 \tag{1}$$

$$>CaOH^\circ = >CaO^- + H^+ \qquad K_2 \tag{2}$$

the surface concentration of a Ca-ligand complex, $>CaL^{1-n}$, can be deduced from its formation reaction:

$$>CaOH_2^+ + L^{n-} = >CaL^{1-n} + H_2O, \qquad K^*_{Ca\text{-}L} \tag{3}$$

with

$$K^*_{Ca\text{-}L} = \frac{\{>CaL^{1-n}\}}{\{>CaOH_2^+\}[L^{n-}]} \cdot \exp\left(\frac{zF\Psi_0}{RT}\right) \tag{4}$$

where $\{>i\}$ and $[L^{n-}]$ represent the surface concentration of the ith species and the aqueous concentration of ligand L, $zF\Psi_0$ is the electrostatic term with F standing for Faraday constant, and z and Ψ_0 being the species charge and wollastonite surface potential, respectively. A rigorous analytical expression of adsorbed ligand concentra-

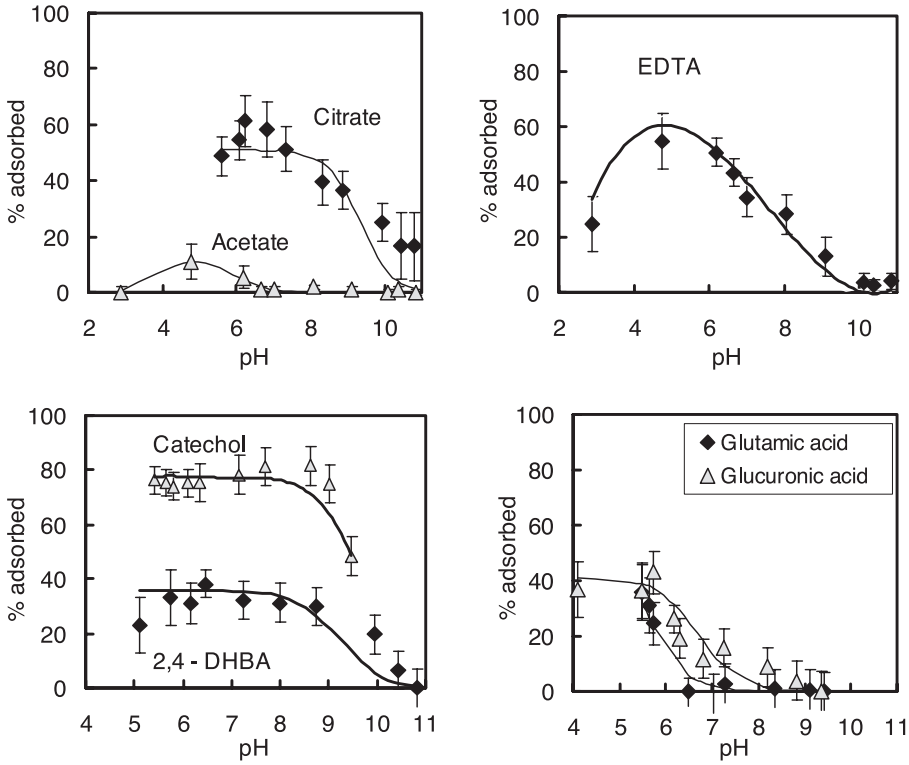

Fig. 1. Adsorption of acetate, citrate, EDTA, 2,4-DHBA, catechol, glutamic and glucuronic acids on wollastonite surface as a function of pH. Solid lines were generated using equation 6 with surface adsorption constants listed in table 2. Note that to fit the EDTA adsorption edge, we used different set of adsorption constants depending on pH, consistent with results of kinetic study (see *Modeling of Ligand-Affected Wollastonite Dissolution* section below).

tion as a function of pH and surface protonation/deprotonation or ligand adsorption constants leads to nonlinear equation with respect to adsorbed ligand concentration as a function of pH and requires precise knowledge of K_1 and K_2, not available at the present time due to the lack of wollastonite titration data (see Oelkers and other, 2009, for discussion). Therefore, in this study, numerical approach was used for fitting the percentage adsorbed ligand as a function of pH.

In our adsorption experiments, surface ligand concentrations are low and ionic strength variations are insignificant. As a result, ligand sorption does not yield a significant variation of the electrostatic term (eq 4). Within the Surface Complexation Model (SCM), total concentration of surface sites (S_T) is given by

$$S_T = \{>\mathrm{CaOH_2^+}\} + \{>\mathrm{CaOH^\circ}\} + \{>\mathrm{CaO^-}\} + \{>\mathrm{CaL^{1-n}}\} \quad (5)$$

Assuming that *i*) the concentration of $>\mathrm{CaO^-}$ being negligible at our experimental conditions and *ii*) the adsorption of organic anions and neutral molecules occurs on positively charged $>\mathrm{CaOH_2^+}$ sites, the pH-dependence of adsorption can be described as

$$\Gamma_{ads} = \{>CaL^{1-n}\} = \frac{S_T \cdot K^*_{Ca\text{-}L} \cdot [L^{n-}]}{1 + A + K^*_{Ca\text{-}L} \cdot [L^{n-}]} \quad (6)$$

TABLE 2

Experimental parameters of Eqn. 6 describing the adsorption of ligands on wollastonite surface. The value of K_2 is fixed at 10^{-12}. Experimental conditions: 25°C, 0.01 M NaCl, 50 g/L, 4.7 m^2/g.

Ligand	K_1	$K^*_{Ca\text{-}L}$ (experimental)
Acetate	10^6	55 ± 5
Glutamate	$1.5 \cdot 10^5$	650 ± 50
EDTA	10^6	200 - 50000 [#]
Glucuronic acid	$3 \cdot 10^6$	300 ± 50
Citrate	10^9	320 ± 30
Catechol	10^9	1600 ± 200
2,4-DHBA	10^9	250 ± 50

[#]—For EDTA, different $K^*_{Ca\text{-}L}$ were used depending on pH, because all three dominnat species—H_2EDTA^{2-}, $HEDTA^{3-}$ and $EDTA^{4-}$—can be adsorbed at the wollsatonite surface.

where

$$A = (K_2 + a_{H+})/(K_1 \cdot a_{H+}{}^2) \quad (7)$$

as follows from the mass balance consideration (eqs 1, 2, 3 and 5). Equation 6 allows us to model each of the experimental ligand's adsorption isotherms using acid-base constants of surface sites protonation/deprotonation, *K1* and *K2*, and ligand adsorption constant, $K^*_{Ca\text{-}L}$, as it is illustrated in figure 1 where the solid lines represent a fit of experimental data using equation. 6. Thus generated values of surface adsorption constants are listed in table 2. These constants should be considered only as fitted mathematical variables, given that the concentration of Ca and Si sites at the wollastonite surface is highly non-stoichiometric in the acidic and circumneutral pH range (Oelkers and others, 2009) and thus the mass balance equation (eq 5) may be not valid in the full range of ligand adsorption pH. Note, however, that the adsorption constants $K^*_{Ca\text{-}L}$ are comparable with corresponding values in aqueous solution while the surface protonation constants *K1* and *K2* are similar to those of Ca-bearing minerals such as calcite (Pokrovsky and others, 2001) and fluorapatite (Wu and others, 1991). The adjustable *K1* values for catechol, DHBA and citric acid adsorption are different from those for other ligands and from those used in the dissolution rate modeling (see below). It can be partially due to complexation of these ligands with surface silica centers, not taken into account in our adsorption model, like it is known in solution for DHBA (Rogers and Bennett, 2004), catechol–aqueous silica interaction and citrate–aqueous germanium interaction (Pokrovski and Schott, 1998).

To get further insights on macroscopic factors controlling organic ligand adsorption on wollastonite surface, electrophoretic measurements of zeta-potential were performed as a function of pH and organic ligand concentration (fig. A1, Appendix 1). It can be seen from this figure that the addition of 0.017 mM organic ligand shifts the zeta-potential to more positive values. This can be explained by adsorption of catechol on negatively-charged $>SiO^-$ groups and thus the decrease of overall negative surface potential, in accord with reaction 3. At the same time, addition of 1 mM of ligand does not induce any significant change in wollastonite zeta-potential at neutral pH although it is certain that the adsorption of these ligands on wollastonite surface at pH = 6–7 occurs (figs. 1B, 1C, and 1G). Therefore, it is most likely that this adsorption happens in the deep surface layers containing both $>CaOH_2^+$ and $SiOH^\circ$ groups. These layers are located beneath the first,

Ca-proton exchanged surface layer which is represented solely by >SiOH groups and which exerted an overall control on $CaSiO_3$ surface potential. A thorough discussion of exchanged layer composition and its impact on silicates zeta potential and surface charge is given in Oelkers and others (2009).

Wollastonite Steady-State Dissolution Kinetics in the Presence of Ligands

Results of ~400 steady-state dissolution experiments performed at $6 \leq pH \leq 11$ and far from equilibrium conditions are listed in the table A3 of the Appendix 3. Included in these tables are ligand concentrations, outlet fluid pH, $[Si]_{tot}$ and $[Ca^{2+}]_{tot}$, and logarithms of steady-state wollastonite dissolution rates. According to SEM observations of unreacted (fig. 2A) and reacted (figs. 2B-H) wollastonite's grains, the presence of ligands yields an etching of wollastonite edge surfaces (fig. 2D, catechol) and appearance of corrosion pits (2C, acetate and 2E, EDTA) oriented along the crystallographic axis. Pectin (fig. 2F) exhibiting inhibiting effect on dissolution leads to disaggregation of the fibers that, apparently, stabilizes the surface and prevents etch pits formation whereas the humic acid seems to attack preferentially some zones of the crystals (2G). Typically, the specific surface area of powder after 48 to 96 hrs of reaction increases by 20 to 30 percent. However, similarly to what is observed for proton- and ligand-promoted brucite dissolution (Pokrovsky and Schott, 2004; Pokrovsky and others, 2005), the flux of dissolved calcium in the course of experiments stays constant within ± 10 percent. As a result, dissolution rate values listed in Appendix 3 were normalized to the B.E.T. surface area of the initial powders.

Ligands investigated in this study can be distributed among two groups according to their influence on dissolution rates. This is illustrated in figure 3 where wollastonite dissolution rates are plotted as a function of free or total ligand concentration in solution. The addition of "catalysts" at neutral and weakly alkaline pH leads to an increase of the dissolution rate with the following relative effectiveness: EDTA > phosphate at pH 6.8; > gallic acid > metaphosphate PO_3^- > catechol > 8-hydroxyquinoline ~ adipate > 3,4-DHBA ≫ glutamate > citrate > malate ~ 2,4-DHBA > phthalate > tartrate > thioglycolate > gluconate ~ ascorbate ~ succinate > malonate ~ aspartame ≥ fumarate > ~ diglycolate ~ lactate at pH 8.4; > formate ≥ oxalate > bicarbonate > lactate at pH 5.6; ≥ acetate > salicylate > humic acids > gum xanthan. On the other hand, glucuronic acid, algae exudates, mannitol, urea, pectin and alginate at neutral pH and silica at pH 10.7 lead to a decrease of wollastonite dissolution rate (fig. 3). Sorbitol, glucose, saccharose, mannitol, glucosamine, fulvic acids and silica at pH ~ 7 exhibit weakly inhibiting or no effect up to concentration of 0.1 M.

In near-neutral and alkaline solutions investigated in the present study, wollastonite demonstrate a stoichiometric Ca and Si release, despite the fact that the linkages of silicate chains in wollastonite is influenced by underlying structure (Casey, 2008). In particular, wollastonite is known to form a near-surface amorphous region enriched in silicon and hydrogen, and depleted in calcium (Casey and others, 1993; Schott and others, 2009). However, the rates listed in table A3 and given in figure 3 are in most cases stoichiometric. Moreover, there is no systematic differences in R_{Ca} and R_{Si} as a function of ligand concentration for variety of ligands, from weakly-complexing carboxyaltes to chelates. A good example is catechol (exp. 28_1 to 28_6 and W33-W45 of table A3) which is known to form stable complexes with Si in aqueous solution (and, presumably, at the surface) but do not yield any differences in Si and Ca fluxes.

There are some cases when non-stoichiometric element release was observed, mostly at the highest concentration of ligand. For example, Ca oxalate and apatite precipitation could interfere with the rates measurements at elevated oxalate and phosphate concentrations. Enhanced Ca release compare to Si at elevated (0.01-0.03 M) citrate, tartrate, phtalate and urea concentrations (experiments in alkaline solutions, Appendix A3) is most likely linked to specific interaction of these ligands with Ca

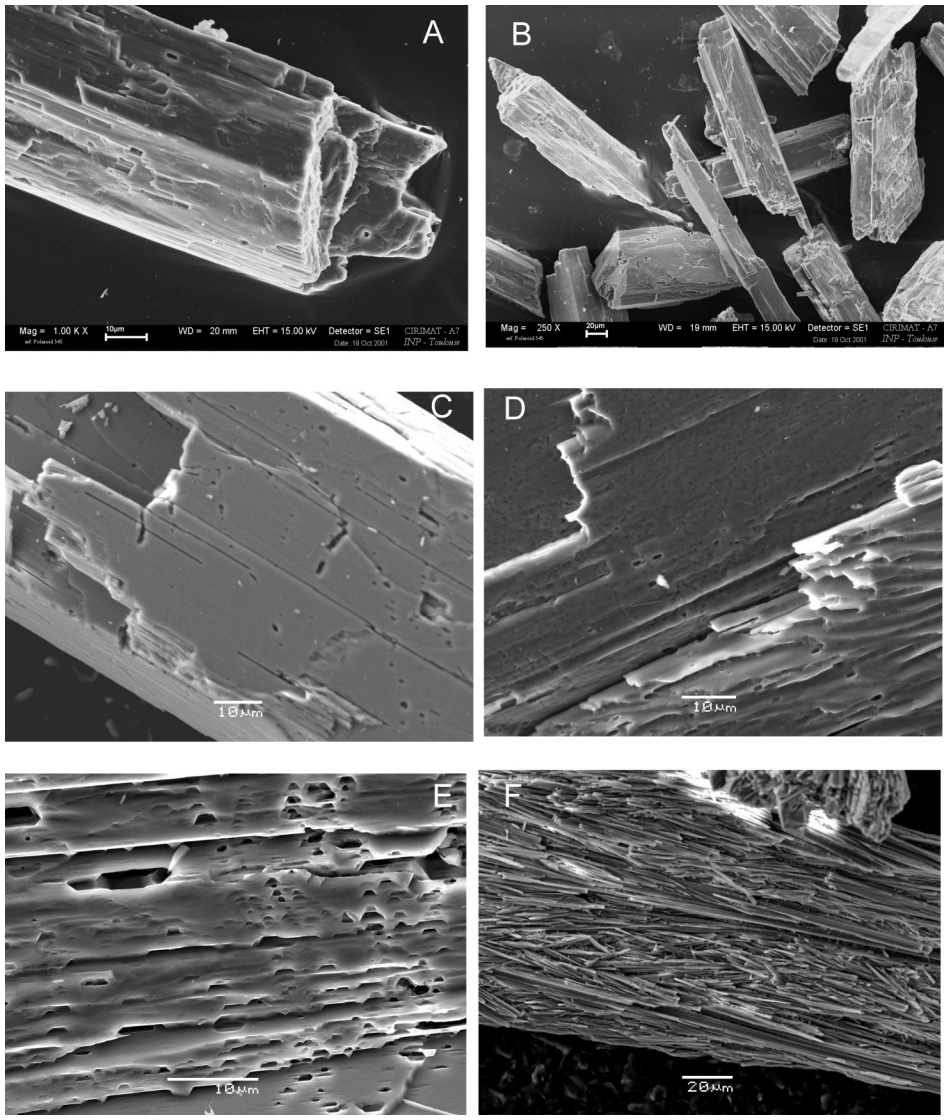

Fig. 2. Scanning Electron Microphotographs (SEM) of initial wollastonite grains (A), powder reacted at pH 7 in 0.01 M NaCl without ligands (B), grains reacted with acetate (exp 23_8, 0.1 M, pH = 7.3, 26 hrs) (C), catechol (exp W48, 0.05 M, pH = 10.7, 32 hrs) (D), EDTA (exp 27, 0.01 M, pH = 7.0, 24 hrs) (E), and pectin (exp W86, 50 g/L, pH = 7.8) (F).

site on the surface; however the exact geometry and molecular structure can be determined only by *in-situ* spectrosocpic techniques.

Modeling of Ligand-Affected Wollastonite Dissolution

The effect of ligands on wollastonite dissolution at neutral to basic conditions can be modeled within the framework of the surface coordination approach assuming the overall dissolution rate is the sum of all the different parallel dissolution reactions promoted at Ca centers by various reactants/ligands which compete for available

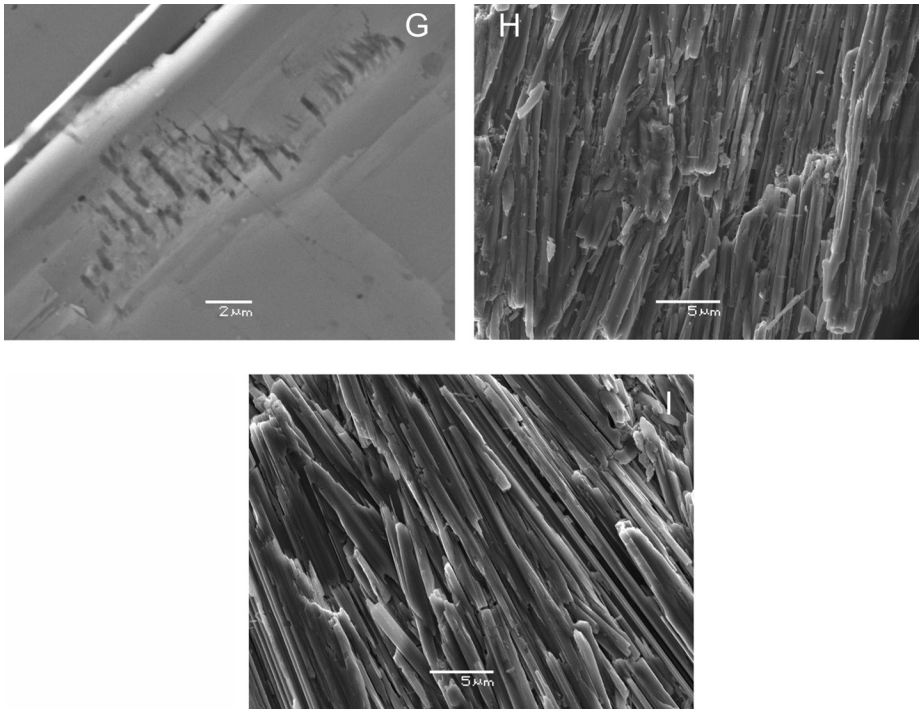

Fig. 2 continued. G: Effect of humic acid (experiment 34) on wollastonite dissolution at pH = 6.7, [DOC] = 53 mg/L, exposure time 36 hrs; H: Effect of alginate (experiment 60-7); I: Gallic acid, exp No 65.

surface sites (Wieland and others, 1988; Stumm, 1992). The effectiveness of ligands depends both on the nature of their functional groups, molecular structure and thermodynamic stability of the surface complexes they form. It is well known that especially efficient are ligands whose functional groups contain two or more oxygen donors and which can form bi- or multidentate mononuclear surface chelates (Stumm, 1992, 1997). In contrast, ligands forming bi- or polynuclear complexes, that can bridge two or more metal centers at the surface lattice, are known to slow down dissolution.

According to this scheme, the rate of ligand-controlled dissolution is proportional to the concentration of the surface metal complex $>CaL^{1-n}$ which can be deduced from reaction (4) stability constant. In the presence of a ligand, the wollastonite forward dissolution rate at neutral to basic pHs is thus the sum of H_2O- and ligand-controlled dissolution, similar to that of brucite (Pokrovsky and Schott, 2004) and carbonates (Jordan and others, 2007; Pokrovsky and others, 2009):

$$R_+ = k_{Ca} \cdot \{>CaOH_2^+\} + k_L \cdot \{>CaL^{1-n}\} \quad (8)$$

Combination of equations (4-8) yields

$$R_+ = k_{Ca} \cdot \left(\frac{S_T}{1 + A + K^*_{Ca\text{-}L} \cdot [L^{n-}]} \right) + k_L \cdot \frac{S_T \cdot K^*_{Ca\text{-}L} \cdot [L^{n-}]}{1 + A + K^*_{Ca\text{-}L} \cdot [L^{n-}]} \quad (9)$$

where A is given by equation 7 and k_{Ca} is a forward dissolution rate constant in the absence of ligands at a given ionic strength, k_L is a rate constant in the presence of ligand L, and $K^*_{Ca\text{-}L}$ stands for the adsorption constant of the ligand on wollastonite $>CaOH_2^+$ sites.

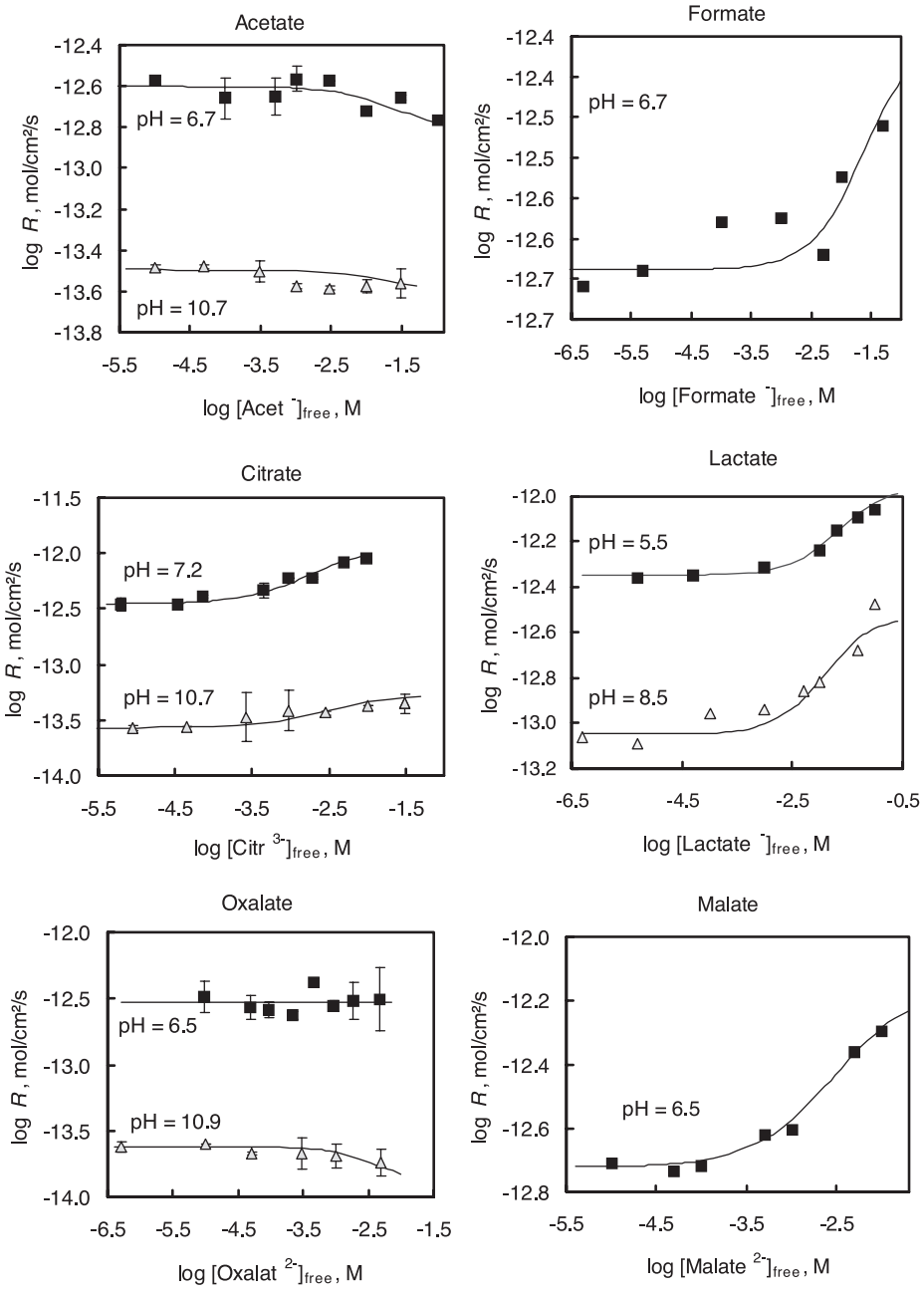

Fig. 3. Dissolution rate of wollastonite at 25°C, 0.01 M NaCl as a function of ligand concentration. The lines represent the model fit using equation 10. The uncertainties stem from the difference of Ca and Si release rate and are within the symbol size unless shown.

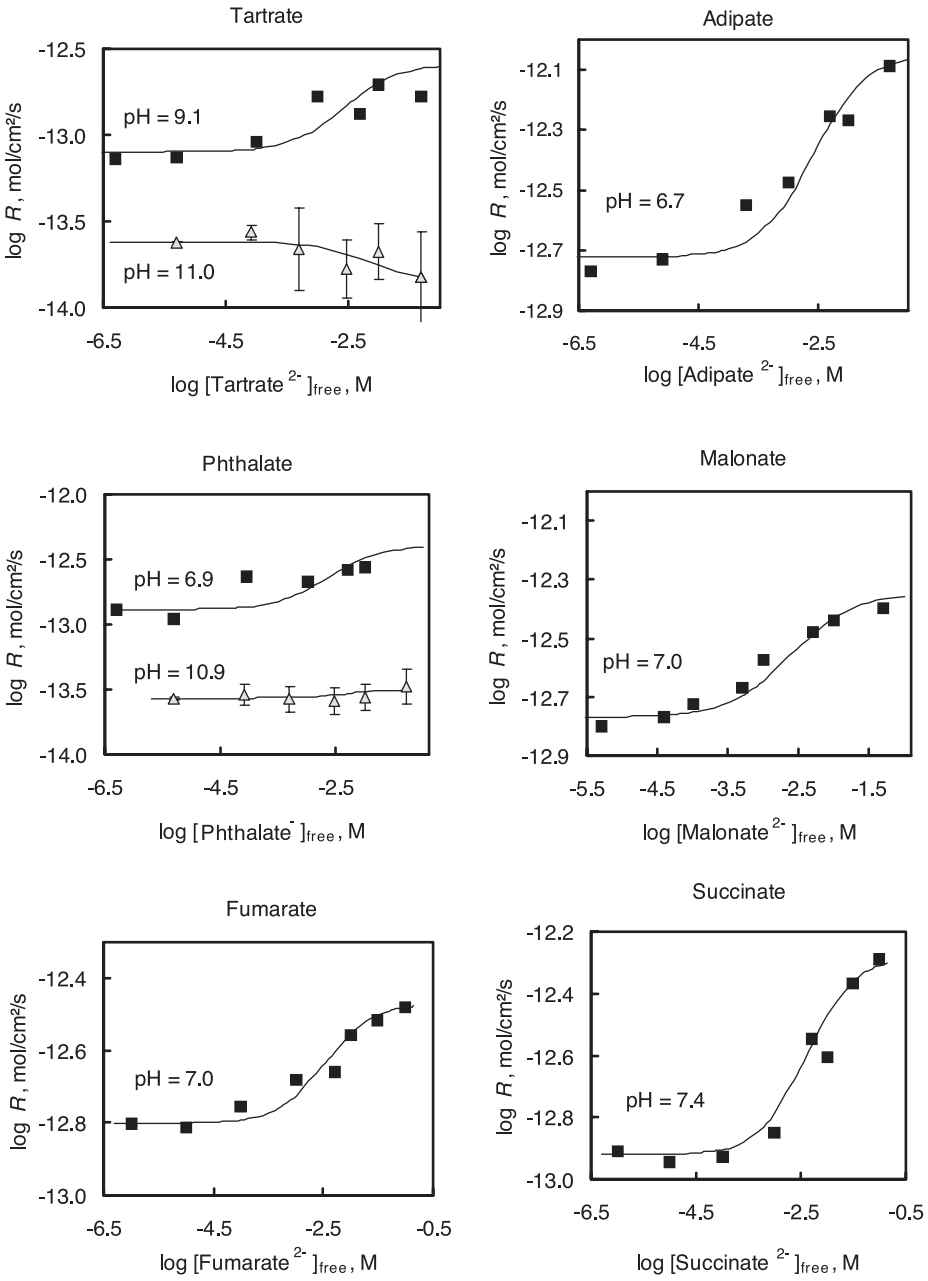

Fig. 3 (continued).

The number of data points obtained for a given ligand in this study (that is, typically 7-8 rate measurements corresponding to different concentrations) is not enough to constrain wollastonite surface speciation in the presence of ligand. However, equation (9) can be simplified assuming at the constant pH of our experiments that ligand sorption on mineral surface follows a Langmurian adsorption isotherm (*Ligand Adsorption* section) with $S_T \approx \{>CaOH_2^+\}^* + \{>CaL^{1-n}\}$:

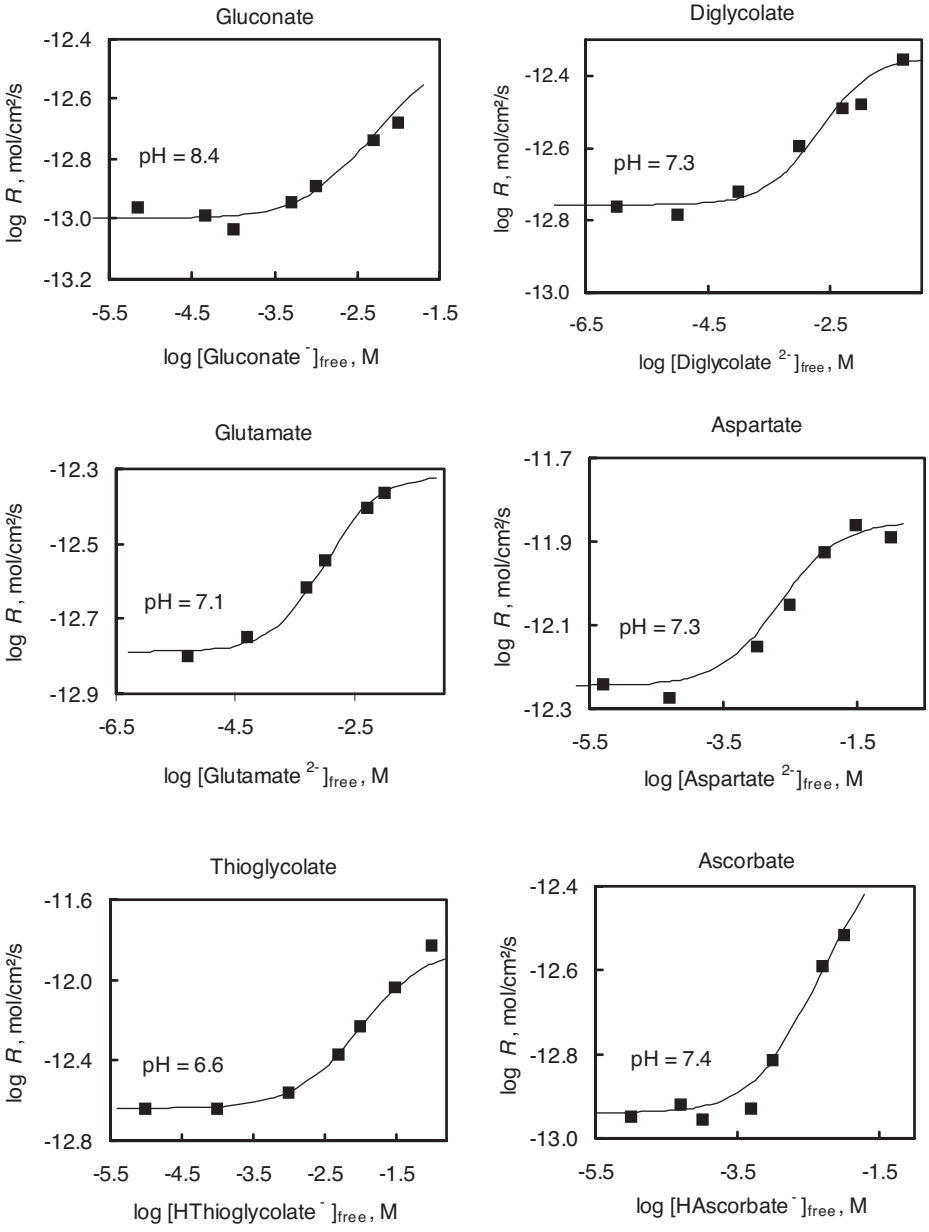

Fig. 3 (continued).

$$R_+ = k^{\#}_{Ca} \cdot \left(1 - \frac{K^{*}_{Ca\text{-}L} \cdot [L^{n-}]}{1 + K^{*}_{Ca\text{-}L} \cdot [L^{n-}]}\right) + k^{\#}_{L} \cdot \frac{K^{*}_{Ca\text{-}L} \cdot [L^{n-}]}{1 + K^{*}_{Ca\text{-}L} \cdot [L^{n-}]} \qquad (10)$$

In this equation, $k^{\#}_{Ca}$ and $k^{\#}_{L}$ are the apparent kinetic constants treated as fitting parameters. Strictly speaking, they depend on ionic strength and pH but can be considered constant given that all experiments were performed in 0.01 M Na(L)Cl

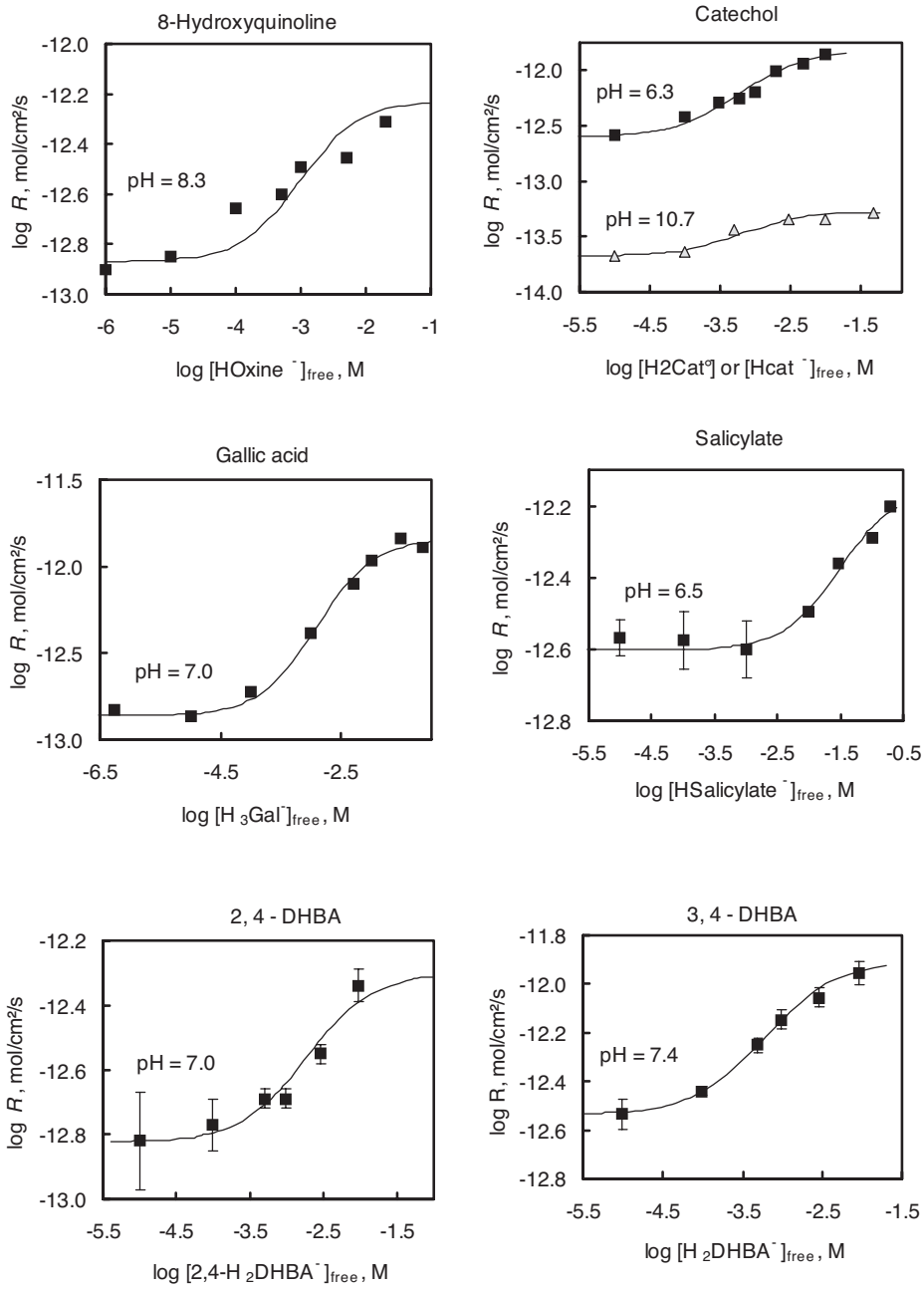

Fig. 3 (continued).

solutions and the pH value was kept constant in a series of experiments with each given ligand. Since the pH value varies among experiments with different ligands within 0.5 to 1 pH units, the variations of ± 0.2 to 0.3 log units for the $k^{\#}_{Ca}$ constant used to model were accepted. Note that these variations are within the range of experimental

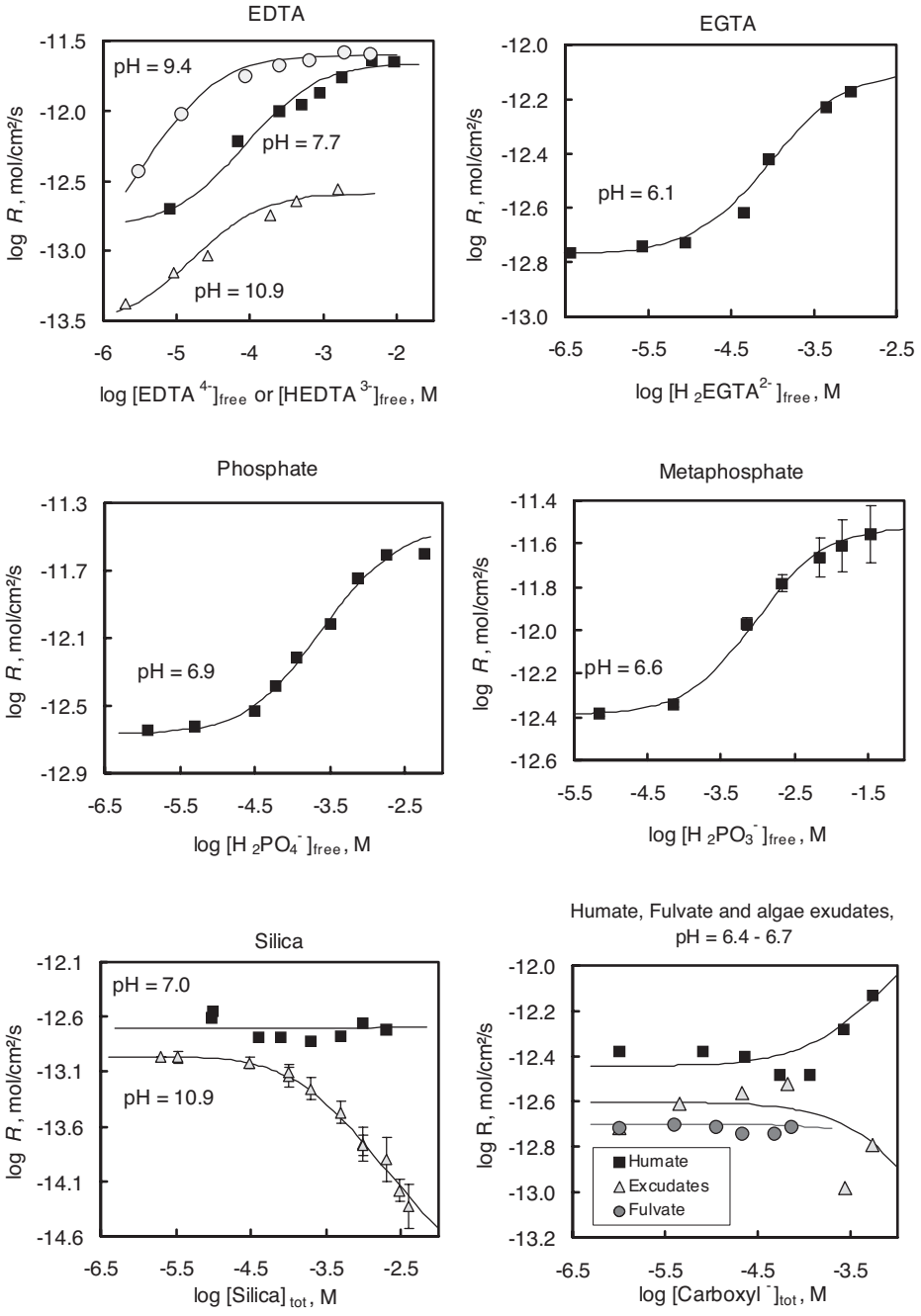

Fig. 3 (continued).

reproducibility of the dissolution rates measured in ligand-free system at neutral pHs (Appendix 2).

Application of eq (10) to model the experimental dependence of wollastonite dissolution on ligand concentration requires accurate values of $K^*_{Ca\text{-}L}$ for the ligands

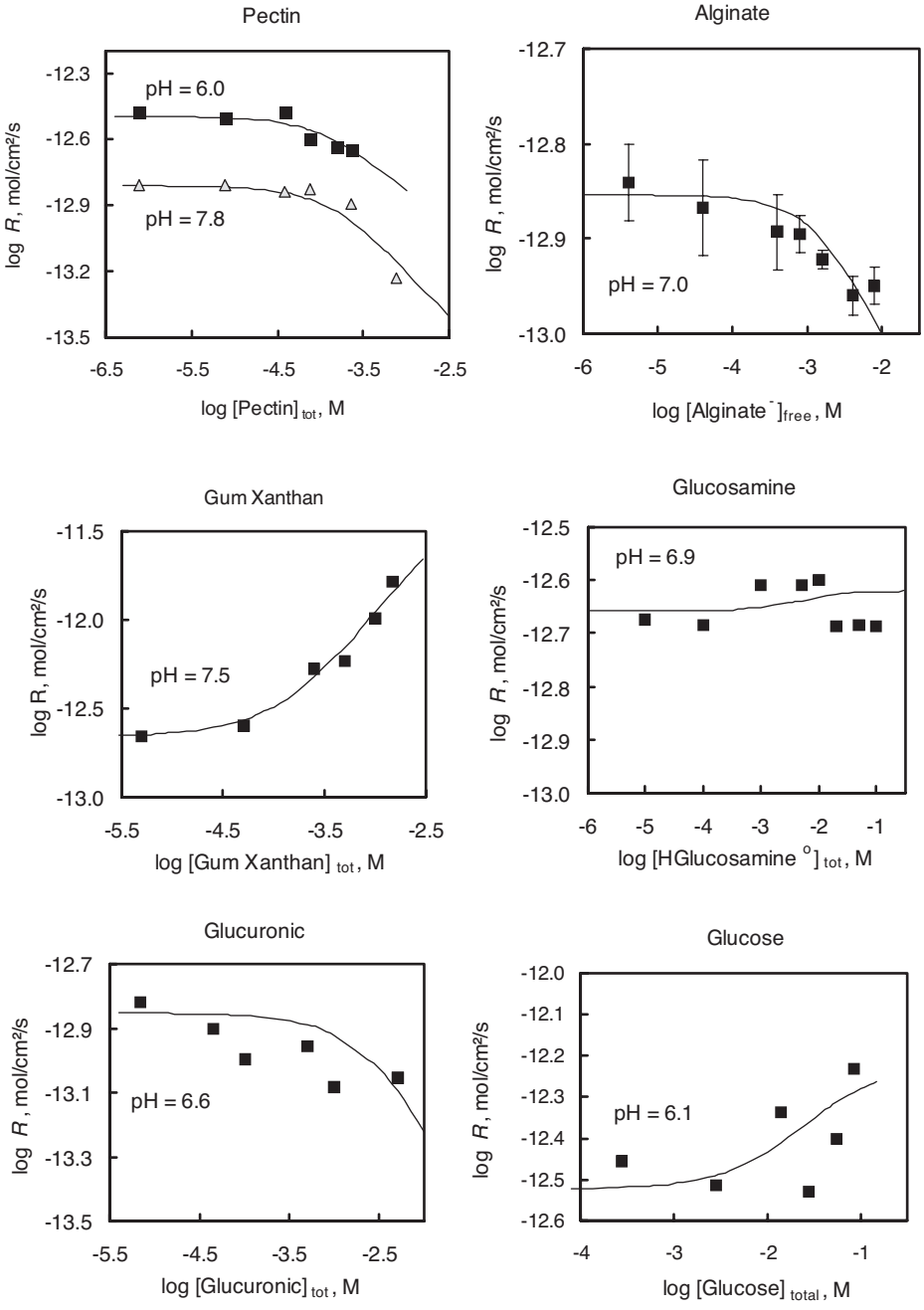

Fig. 3 (continued).

investigated in this study. For several ligands, these constants are available from the batch ligand adsorption experiments (*Ligand Adsorption* section). For other ligands, $K^{*}_{Ca\text{-}L}$ values were generated from the fitting of dissolution rate dependences on aqueous ligand concentrations. The fitting procedure performed by "trial and error"

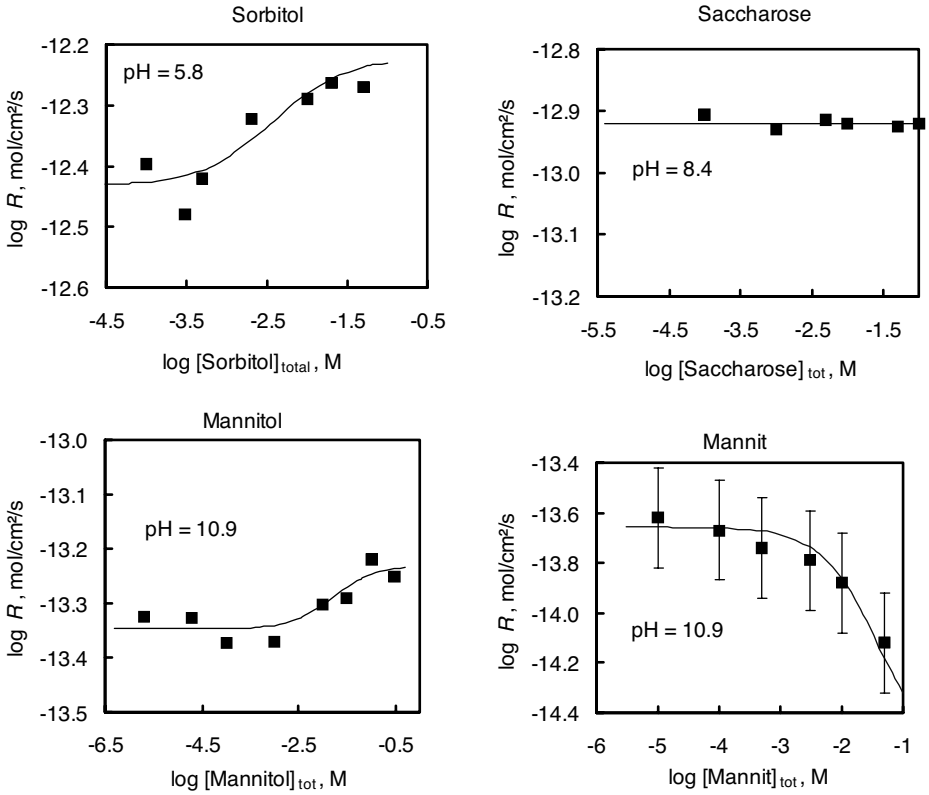

Fig. 3 (continued).

consisted in assuming that the values of the equilibrium constants for ligands adsorption were the same as the corresponding values for Ca-ligand association reactions in aqueous solution (Schindler and Stumm, 1987), table 1. The values of $k_L^{\#}$ were set first equal to $k_{Ca}^{\#}$ assuming no inhibition or catalyses occurs. Then, the values of rate constants $k_L^{\#}$ were allowed to increase/decrease in order to fit the experimental dependence of dissolution rate on ligand concentration using equation 10. The values of $k_{Ca}^{\#}$ at a given pH for each ligand were determined for the lowest ligand concentration; consistent with those determined in the absence of ligands as a function of pH (Appendix 2). When fitting was not possible with the selected value of $K_{Ca\text{-}L}^{*}$, it was allowed to vary within one order of magnitude from the initial settings. A $\leq$ 20 percent difference between measured and modeled (eq 10) rate values at each ligand concentration was taken as a criterion of goodness of fit. The final values of constants used in equation 10 are listed in table 1. The uncertainties attached to these values correspond to the range of best fits obtained by varying the $k_L^{\#}$ and $K_{Ca\text{-}L}^{*}$. The degree to which equation 10 can be used to describe the effect of investigated ligands on wollastonite dissolution rate can be assessed in figure 3. The solid curves depicted in these figures were computed with equation 10 using values of $K_{Ca\text{-}L}^{*}$, $k_L^{\#}$ and $k_{Ca}^{\#}$ listed in table 1. The close correspondence between the solid curves and experimental data for a very broad range of a ligand's aqueous concentration demonstrates the validity of equation 10. It is important to note that, the values of surface adsorption constants for acetate, citrate, EDTA, catechol, glucuronic, glutamic and 2,4-DHBA acids generated by fitting the rate data are in agreement with those directly measured in batch adsorption experiments.

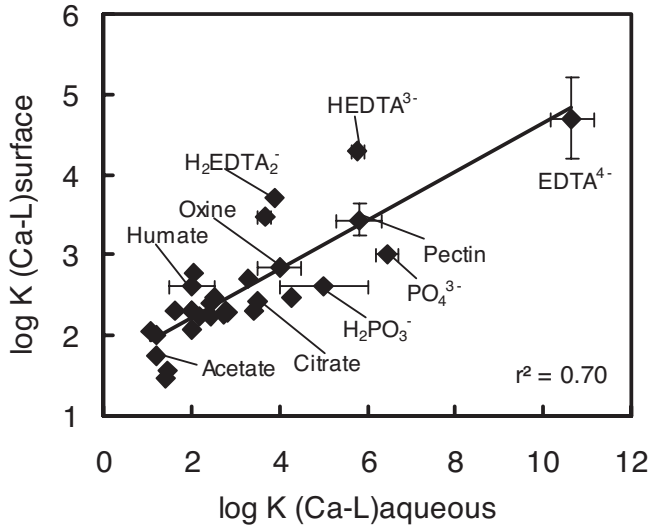

Fig. 4. Plot of stability constants at 25°C for $>CaOH_2^+$-ligand surface complexes (log $K(Ca\text{-}L)_{surface}$) vs. the stability constants of Ca-ligand aqueous complexes (log $K(Ca\text{-}L)_{aqueous}$). The values of aqueous complexes stability constants are from Martell and others, 1997, Table 1. Stability complexes for Ca^{2+}-H_2EDTA^{2-} and Ca^{2+}-$HEDTA^{3-}$ were assessed via linear correlation between acetate, oxalate, citrate and EDTA complexes of Ca^{2+}(aq) and NpO_2^+(aq), the constants for the latter are available from Pokrovsky and Choppin, 1997 and Pokrovsky and others, 1998. The solid line represents a linear regression.

It follows from the fitting procedure employed in this study that the stability constants for surface adsorption reactions correlate with corresponding values for association reactions in homogeneous aqueous solution as it is the case for other simple oxides (Schindler and Stumm, 1987; Ludwig and others, 1996; Pokrovsky and others, 2005). Such correlation is depicted in figure 4. High uncertainty for both surface and aqueous complex stability constants when log $K < 2$ explains some of the scatter in this correlation.

Since the limiting step of wollastonite dissolution seems to be the breaking of Ca—O bonds, the structure and stability of complexes that ligands form with surface reactive site. The reactivity of a given surface site depends on its chemical structure including *i*) hydroxylation or protonation of particular ion; *ii*) the number of coordinatively unsaturated bonds with mineral lattice, reflected in the site geometry, and *iii*) the length of the cation-anion bonds at the mineral surface (that is, Ganor and others, 2009). The sequence of rate constants listed in table 1 shows that carboxylic acids like acetate, lactate and formate, that are known to form monodendate surface complexes on oxides, promote dissolution to a much less extent than those that form surface chelates (citrate, EDTA). The catalyzing effect of bicarbonate at neutral pH observed in this study for wollastonite is in agreement with the results of Bruno and others (1992) and Pokrovsky and others (2005) for hematite and brucite, respectively. Natural polymers such as humic and fulvic acids at their concentrations typical for natural waters (10 ± 5 mg DOC/L) do not exhibit any measurable effect on wollastonite dissolution, although some increase of dissolution is observed in the presence of 30 to 50 mg DOC/L of humic acid, consistent with previous results for oxides (Hering, 1995). The catalyzing effect of $H_2PO_4^-$ at neutral pH is rather unusual and was not, to our knowledge, reported earlier in the literature, given that this ligand is notoriously known as being an inhibitor of dissolution of Ca-containing minerals such as calcite (Morse, 1974). It is possible that the distance Ca-SiO_3-Ca in wollastonite,

being much larger than Ca-CO_3-Ca in carbonates, does not allow phosphate to bridge two adjacent metal centers. At the same time, one or two hydrogen of $H_2PO_4^-$ molecule can be used for protonation of Ca centers thus increasing the reactivity of the whole mineral. Note that dihydrogen phosphate accelerated the dissolution of brucite in neutral solution but orthophosphate decreased the rates in alkaline solutions (Pokrovsky and others, 2005). Dihydrogen phosphate also increase the rate of magnesite dissolution at pH 7.8 (Jordan and others, 2007). For many ligands, the relations between their molecular structure and their effect on the reactivity of the brucite-water interface are the same as for goethite. Thus, dihydrogen phosphate accelerates the dissolution of goethite and iron oxy(hydr)oxides at pH<5 by increasing their surface protonation via the formation of mononuclear negatively charged complexes (Bondietti and others, 1993). In neutral and weakly alkaline solutions it is known to form binuclear or multinuclear surface complexes as shown by ATR (Tejedor-Tejedor and Anderson, 1986; Tejedor-Tejedor and others, 1990, 1992) and XAFS studies (Rose and others, 1996; 1997) and to inhibit goethite dissolution.

The strong effect of two hydroxyl-bearing ligands, ascorbate and citrate, can be understood in view of the marked affinity of their hydroxyl groups for surface Mg and Ca as is the case for calcite (Geffroy and others, 1999), dolomite (Pokrovsky and Schott, 2001), brucite (Pokrovsky and others, 2005) smectite (Golubev and others, 2006), and diopside (Golubev and Pokrovsky, 2006). Among the aliphatic ligands, tridentate citrate was also reported to have the greatest effect on elements release from granite and basalt (Neaman and others, 2005a, 2006). Finally, EDTA, EGTA, some aromatic compounds (oxine, catechol, DHBA) both of which being likely to form very stable five-membered chelate rings with surface Ca ions, present the strongest catalyzing effect on wollastonite dissolution. Among all aromatic ligands, gallic acid exhibit the strongest catalyzing effect because of highest steric symmetry of its molecule. Unusually strong effect of gallic acid on Ca-bearing mineral reactivity has been noted earlier in $CaCO_3$ precipitation experiments (Pokrovsky and Savenko, 1994). Gallate was also reported to increase the rate of granite and basalt dissolution to the greatest extent among aromatic ligands (Neaman and others, 2005a, 2006). Note that the values of surface adsorption and kinetic constants for wollastonite dissolution measured in the present study for acetate, lactate, oxalate, citrate, EDTA, catechol, oxine, ascorbate and dihydrogen phosphate are similar to those obtained earlier for ligand-promoted dolomite and brucite dissolution which is also controlled by the hydrolysis of alkali-earth metal surface centers (Pokrovsky and Schott, 2001; Pokrovsky and others, 2005, 2009).

The inhibiting effect of complex molecules considered as analogs of bacterial exudates and cell envelopes (alginate, pectin), can be understood following the approach developed by Welch and co-authors (Welch and Vandevivere, 1994; Welch and others, 1999) for ligand-affected alumosilicate dissolution. It has been established by these authors that, similar to wollastonite, long chain acid polysaccharides such as pectin, algae exudates, glucuronic and alginic acid and mannitol inhibit the dissolution rate of silicates because they bind "irreversibly" to multiple sites on the mineral surface thus forming multi-nuclear complexes. Though all the sugars have hydroxyl groups on adjacent carbon atoms, they are not able to form bidentate complexes with metal ions due to steric hindrance. Therefore, interactions of neutral polysaccharide molecules (sorbitol, mannitol, glucose, saccharose) with cations or mineral surfaces are limited to weak outer-sphere complexes and hydrogen bonding and thus they exhibit weak effect on wollastonite dissolution rates. This result corroborates previous works of Ullman and others (1996) on polymers of neutral sugars which demonstrated that starch, cellulose, polysucrose, and gum xanthan have no effect on alumosilicates dissolution rates up to concentrations of 1 g/L.

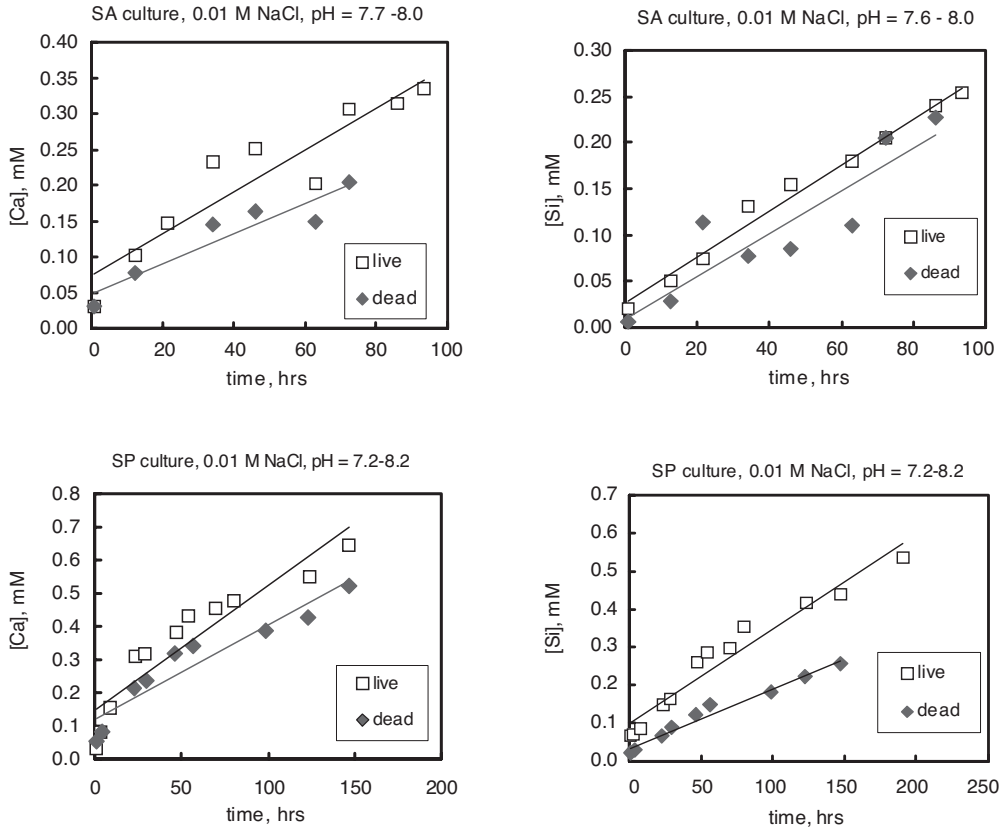

Fig. 5. Ca and Si release from wollastonite at 25°C in the presence of live and dead soil bacteria in inert electrolyte solution (0.01 M NaCl).

Calcium and Silica Release Rate in the Presence of Bacteria

Results of Ca and Si release from wollastonite in 0.01 M NaCl and in nutrient media in the presence of live and dead *Pseudomonas aureofaciens* are presented in figures 5 and 6, respectively. Concentrations of both Ca and Si increase quasi-linearly with time in all types of experiments. The pH varied within ± 0.2–0.3 units. The correlation coefficient varies from 0.9 to 0.99 with the exception of Si release in SP media (r^2 = 0.64-0.77). Taking into account that *1*) all solutions are strongly undersaturated with respect to wollastonite, all other possible Ca silicates and amorphous silica and *2*) there is no effect of aqueous Ca and Si concentration on wollastonite forward dissolution rates in neutral solution (Schott and others, 2009), one can quantify the far-from equilibrium dissolution rates for each individual experiment using the equation which can be rigorously applied over the whole duration of the experiment:

$$R = (d[\mathrm{Ca, Si}]_{\mathrm{tot}}/dt)/s \qquad (11)$$

where t (s) designates the elapsed time, $[\mathrm{Ca, Si}]_{\mathrm{tot}}$ (mol/L) stands for the concentration of calcium and silica released from the solid, and s (cm^2/L) is the powder B.E.T. surface area. Results are listed in table 3. The uncertainties on these rates can be evaluated as ± 20 percent. The rates measured in 0.01 M NaCl agree within ± 0.3 log units with those of abiotic experiments in mixed-flow reactor (fig. A2 of Appendix 2).

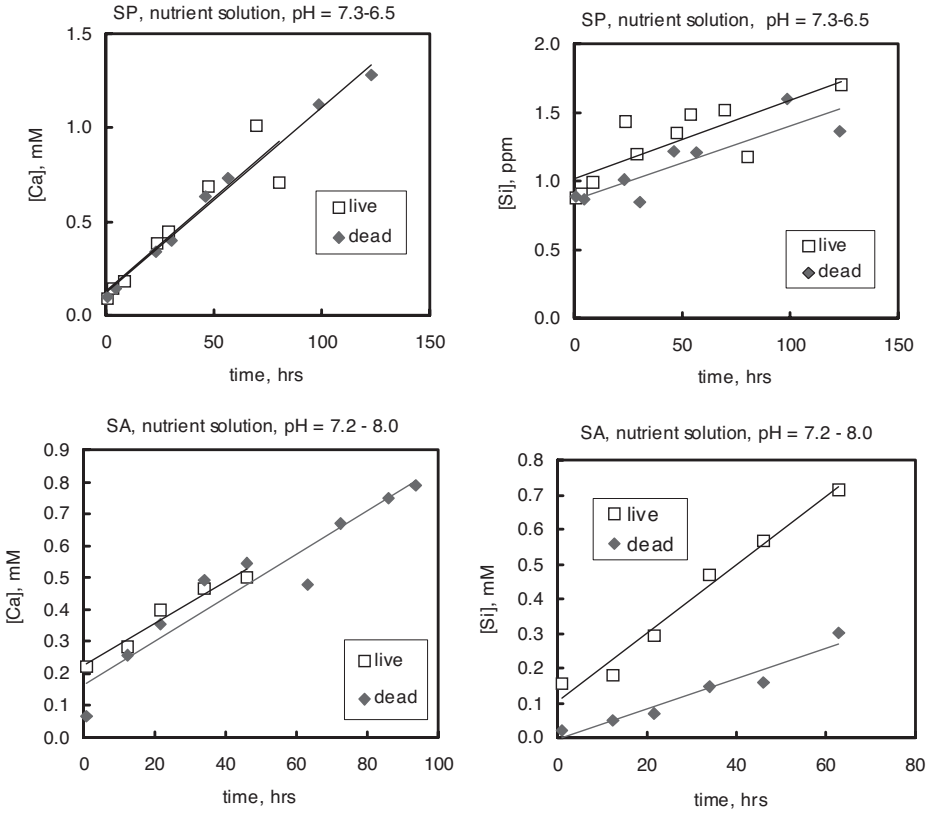

Fig. 6. Ca and Si release from wollastonite in the presence of live and dead soil bacteria in nutrient solution.

In the nutrient media, containing 40 g/L sucrose+15 g/L peptone and 0.01–0.007 M phosphate (SP) or 4 g/L succinic acid (SA), the rates are a factor of 2 to 3 higher than those in 0.01 M NaCl. Both solution pH (0.3 to 0.5 units lower in nutrient media compared to 0.01 M NaCl) and the presence of high concentration of organic matter and di-hydrogen phosphate can be responsible for this difference. At similar solution conditions (0.01 M NaCl or nutrient media, pH stable within ± 0.3 units), the presence of live bacteria accelerates the rates of Ca and Si release from wollastonite by 10 to 30 percent compared to the presence of dead bacteria. Two exceptions are Si release in SP (EPS-rich) and SA (EPS-poor) culture demonstrating, respectively, 37 and 55 percent higher rates for live cells compared to dead biomass. Taking into account results of all eight experiments and using statistical treatment, the silica and calcium release rates are 26 ± 24 percent and 12 ± 16 percent, respectively, higher for live cultures compared to dead biomass at similar solution conditions (pH, ionic strength, concentration of nutrients). Considering the absolute rate uncertainty in this pH range of ± 30 percent that stems both from the pH variation of ± 0.2 to 0.3 units during the course of an experiment and the rate reproducibility in mixed-flow reactor with ligand-free systems (see Appendix 2), we conclude that the ~20 percent difference between dead and live bacteria experiments is within the experimental uncertainty. Therefore, the effect of live bacteria on Ca and Si release rate from wollastonite is not significant. Note that the present result corroborates the recent work of Jacobson

Table 3

Wollastonite dissolution rates (mol/cm^2/s) in nutrient media and inert electrolyte solution (0.01 M NaCl) in the presence of dead and live Pseudomonas aureofaciens. Experimental conditions: 25°C, pH = 7.2–8.2, $CaSiO_3$ powder of 50–100 μm with SSA_{BET} = 1300 cm^2/g at concentration of 2.5 g/L, dead biomass concentration 1.5 g humid/L, duration 120–150 hrs.

Media and bacteria	log R_{Ca}	log R_{Si}
SP media, live	-12.07	-12.31
SP media, dead	-12.07	-12.34
SP culture, live, 0.01 M NaCl	-12.50	-12.63
SP culture, dead, 0.01 M NaCl	-12.62	-12.71
SA media, live	-12.25	-12.08
SA media, dead	-12.23	-12.43
SA culture, live, 0.01 M NaCl	-12.60	-12.67
SA culture, dead, 0.01 M NaCl	-12.74	-12.87

and Wu (2009) who demonstrated the similarity of calcite dissolution rate in biotic and abiotic experiments with heterotrophic *Burkholderia fungorum*. The main conclusion of these authors is that, depending on nutritient regime, the solution pH acts as the main governing factor of calcite dissolution in the presence of bacteria. Therefore, implementation of mineral–bacteria interaction in chemical weathering codes requires solely the information on solution chemistry that can be directly assessed from macroscopic measurements of interstitial soil solutions.

Effect of Organic Ligands and Bacteria on Ca, Mg-Bearing Silicates Weathering in Natural Environments

The concentration range of various carboxylic ligands (oxalic, citric, malonic, succinic, lactic, formic, acetic), detected in soil solutions, spans from 10^{-6} to 10^{-4} M (Hue and others., 1986; Hongve and others, 2000). Stevenson (1991) reported the ranges 10^{-3} to $4 \cdot 10^{-3}$ and $8 \cdot 10^{-5}$ to $3 \cdot 10^{-4}$ for aliphatic and aromatic organic ligands in contemporary soil solutions, respectively. In table 4, we calculated, based on results of the present study, the concentrations of ligands necessary to triple the rates of wollastonite at pH around 7. For most ligands, very high concentrations (0.001-0.1 M), are necessary to appreciably affect the rates. Threshold rate-affecting concentrations for strong complexants, aromatic compounds and chelates, are lower ($n \cdot 10^{-5} - n \cdot 10^{-3}$ M, table 4) but this is still an order or two of magnitude higher than those ever detected in soil solutions or groundwaters. Thus, for individual organic ligand such as carboxylic, amino acids, or aromatic compounds, the effect on mineral dissolution rates should be negligible under conditions of natural settings. While for simple carboxylic acids, direct comparison between ligands concentration in natural environments and in our laboratory experiments is possible, such a comparison is not straightforward for (*1*) typical functional groups of natural polyelectrolyte (humic or fulvic acids) and (*2*) microbial exudates and analogs of bacterial cell envelopes as we discuss below. In the first case, typical concentration of carboxylic groups in humic or fulvic acids is 10^{-4} mol per 10 μmol of DOC (Oliver and others, 1983) and the ratio between carboxylic and phenolic groups is 3.5:1 (Perdue and Ritchie, 2003). This suggests that for typical DOC level of surface continental waters (10 ± 5 mg DOC/L),

TABLE 4

Concentration of ligands necessary to triple (to increase log R by half an order of magnitude) the rates of wollastonite dissolution at 25°C and neutral pH

Ligands	Concentration
Acetate	> 0.1 M
Formate	> 0.05 M
Lactate	> 0.07 M
Malic acid	> 0.01 M
Malonate	> 0.05 M
Succinate	0.02 M
Fumarate	> 0.1 M
Tartrate	> 0.05 M
Adipate	0.05 M
Gluconate	> 0.05 M
Oxalate	> 0.01 M
Citrate	0.01 M
Salicylate	0.2 M
Phthalate	> 0.1 M
Ascorbate	> 0.05 M
Thioglycolic acid	0.02 M
Diglycolic acid	> 0.05 M
EDTA	30 μM
EGTA	50 μM
Live P. aureofaciens (SP media)	> 30 g humid/L
Live P. aureofaciens (SA media)	> 30 g humid/L
Catechol	0.0015 M
8-Hydroxychinolin	0.005 M
2,4-Dihydroxybenzoic acid	0.01 M
3,4-Dihydroxybenzoic acid	0.003 M
Gallic acid	0.002 M
Phosphate	30 μM
Metaphosphate	0.001 M
Aspartate	0.1 M
Glutamate	> 0.01 M
Sorbitol	> 0.1 M
Mannitol	> 0.3 M
Glucose	> 0.1 M
Saccharose	> 0.1 M
Humic acid	> 100 mg DOC/L
Exudates of algae	> 50 mg DOC/L
Gum Xanthan	7 g/L
Pectin	weakly inhibiting
D-mannit	inhibiting
Glucoronic acid	inhibiting
Alginic acid	inhibiting
Glucosamine	> 0.1 M
HCO_3^-	> 0.1 M

rather low concentrations of carboxylic (8 mM) or aromatic (~2 mM) acids reproduce the natural soil environments. It follows from the results of this study that these concentrations are at the lower limit that is necessary to appreciably affect the rates. Only in surface horizons of interstitial soil solutions, at the concentration level of 50 to 100 mg/L of DOC, the effect of organic matter on mineral dissolution should be detectable. However, unaltered minerals rarely present in the surface soil horizons, whereas the concentration of DOC in deep (mineral) soil horizons rarely exceeds 5 to 10 mg/L. The DOC level of groundwater is 2 to 3 times lower and thus the effect of organic matter on mineral dissolution is less likely. Note however, that although the bulk soils do not contain enough concentration of organic ligands to appreciably increase weathering rates, other specific environments, such as rhizosphore, at fungal hyphae, and near decaying organic matter, could support higher concentrations of organics. For this, high-resolution *in-situ* analysis of organic ligands in soil microenvironments are lacking.

For bacterial metabolites and components of cell envelopes, concentrations of 1 to 10 g/L are necessary to modify the rates (table 4). Mean concentrations of bacteria are 300 to 600, 2000 to 2500, and 1200 to 1600 millions of cell/g soil for taiga, podzol and step soils, respectively (Aristovskaya, 1965). Typical bacterial concentration in forest soil is around 4800 millions cell/cm^3 (Torsvik and others, 2002), while microbial abundance in deep subsurface environments ranges between 10^5 and 10^8 cells/cm^3 and does not decrease with depth (Balkwill, 1989). Assuming: *i*) the minimal bacterial cell volume of 1 μm^3, *ii*) specific density of cell biomass of ~1 g/cm^3, *iii*) cell envelopes constitute up to 60 percent of total cell mass, *iv*) water proportion in soil is 10 to 30 percent, one can calculate that concentration of bacterial organic matter in the form of extracellular polysaccharides (EPS) in soil water varies between 1 and 30 g/L. These EPS are known to be composed of sugars such as glucose, galactose, mannose, N-acetylglucosamine and sugar acids such as glucuronic and galacturonic acid (that is, Sutherland, 1977; Christensen and Characklis, 1990; Welch and Vandevivere, 1994). It follows from the results of this study that most of these compounds either do not affect or decrease the rates of wollastonite. Among all polysaccharides tested, only commercial gum xanthan produced by *Xanthomonas campestris* and comprised of glucose, mannose, glucuronic acid and pyruvite leads to dissolution rate increase, still, its effect is visible at concentration $\geq$ 2.5 g/L and up to 10 g/L of this substance is necessary to appreciably increase the rates. Therefore, although concentration of organic matter in soil is enough to affect the rates of wollastonite dissolution in the vicinity of microbial cells, it still remains to determine whether this effect is inhibiting like for pectin, glucuronic residues, alginate or accelerating like for gum xanthan. Our single example of EPS-poor and EPS-rich rhizospheric bacteria *P. aureofaciens* unambiguously demonstrates the weak or negligible effect of the live compared to dead cell presence on Ca and Si release from wollastonite in neutral solutions. In order to appreciably affect the rates, significant increase of bacterial concentration compared to the one used in our experiments is necessary. In fact, linear extrapolation of 20 percent rate increase in the presence of live bacteria (1-4 g humid/L in this work) to the 300 percent rate increase requires the live biomass concentration of 20 to 60 g humid/L. This is the maximal possible range of bacterial concentration in some specific microenvironments. It should be noted that the extrapolation from culture experiments to soil conditions also requires the knowledge of bacterial concentration on a mineral surface, which is not available at the moment. Besides, it remains to be tested whether *P. aureofaciens* can be representative for other soil and groundwater microorganisms. For example, another soil gram-positive bacteria (*Bacillus mucilaginosus*), are known to have the ability to dissolve silicates via their acidic exopolysaccharides (Belkanova and others, 1985, 1987); and it was shown that the adsorption of silicate ions on the EPS

macromolecules decreases Si concentration in solution and thus shifts the reaction towards its products (Malinovskaya and others, 1990). In this regard, a quantitative assessment of plants and microbial activity impact on basic rock weathering on a global scale (that is, Berner, 1992; Drever, 1994) will require detailed characterization and sufficient statistics both on concentration of microbial biomass and of their exometabilites produced in response to the change of environmental conditions.

CONCLUDING REMARKS

The present study corroborates previous works on organic ligands effect on "basic" (Ca, Mg)-bearing oxides and silicates dissolution and should help to better understand the weathering of these minerals in natural settings. As the breaking of Me—O bonds via the hydration of surface Me centers control the dissolution of many Mg-Ca oxides and silicates in neutral to alkaline solutions (periclase, Wogelius and others, 1995, Mejias and others, 1999; forsterite, Wogelius and Walther, 1992; Pokrovsky and Schott, 2000; orthosilicates, Casey, 1991, Casey and Westrich, 1992; chrysotile, Bales and Morgan, 1985; biotite, Malmstrom and Banwart, 1997; pyroxenes and amphiboles, Brantley, 2004 and Brantley and Chen, 1995), one can expect that the ligands-calcium surface sites interactions are similar for wollastonite and other divalent metal silicates. Indeed, the effect of organic ligands (ascorbate, phthalate, citrate and acetate) on forsterite and bronzite dissolution (Wogelius and Walther, 1991, 1992, and Grandstaff, 1977, 1986) and, as recently studied, effect of ~20 different ligands on diopside and smectite dissolution (Golubev and others, 2006 and Golubev and Pokrovsky, 2006) is quite comparable to that for wollastonite measured in the present study.

It follows from the results of this study that the effect of all studied organic ligands on wollastonite and, possibly, other Ca, Mg-bearing silicate dissolution at concentrations relevant to those found in natural soil environments should be quite weak. In order to increase wollastonite dissolution rate by a factor of ~3, very high concentrations of most organic ligands (0.01-0.1 M) and live bacteria (10-50 g humid/L) are required. Such concentrations can be met only in soil microenvironments built up around bacteria adhering to mineral surfaces (Ehrlich, 1981; Vandevivere and others, 1994). This is in contrast to aluminosilicates whose dissolution rates in bulk soil solutions are greatly enhanced in the presence of a minor amount of organic acids forming strong surface and aqueous complexes with aluminum (Amrhein and Suarez, 1988; Lundstrom and Ohman, 1990; Fein and others, 1995; Oelkers and Schott, 1998; Oelkers and Gislason, 2001).

Therefore, despite the huge variability of tested organic substances and various environmental conditions (pH from 6 to 12, live and dead bacteria), the effect of both microorganisms and their potential exometabolites on Ca and Si release rate from wollastonite is of second order importance compared to that of solution pH. Since soil solution pH is controlled by several complex reactions including both minerals and organic substances, only if the bacteria affect solution pH at the solid surface, then they should impact the dissolution. As a result, the overall effect of the presence of biota on Ca silicate dissolution may be much less than usually anticipated.

An important consequence of the relatively weak effect of bacterial cell components and microbial exometabolites on wollastonite (and, possibly, other Ca-Mg-bearing silicates) reactivity in aqueous solutions is that the impact of plants and biota on "basic" mineral chemical weathering in soils may be weaker than generally argued for (alumino)silicates. Indeed, the main factor controlling the aluminosilicates dissolution—aqueous activity of dissolution inhibitor Al^{3+}(aq)—is not important for Ca, Mg-bearing silicates since the far-from-equilibrium rates of the latter's are not controlled by the presence in solution of mineral constituents (Ca, Mg, Si, at least in the neutral pH range, Schott and others, 2009). The complexation of oranic ligands with

aqueous and surface Al and complexation of Al with bacterial surface will be the main mechanisms of bacterial influence on alumosilicates dissolution via aqueous Al^{3+} removal from solution thus decreasing its inhibiting effect and the supersaturation value with respect to secondary Al-phases. In contrast, speciation of Ca and Mg in solution is weakly affected by the presence of biota and the adsorption of organic matter on the surface of basic silicates is weak. As a result, the atmospheric CO_2 consumption on the land and Ca, Mg-associated transport of aqueous bicarbonate ions linked to basic silicates weathering is unlikely to be strongly influenced by the biological activity in soils.

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Appendix 1

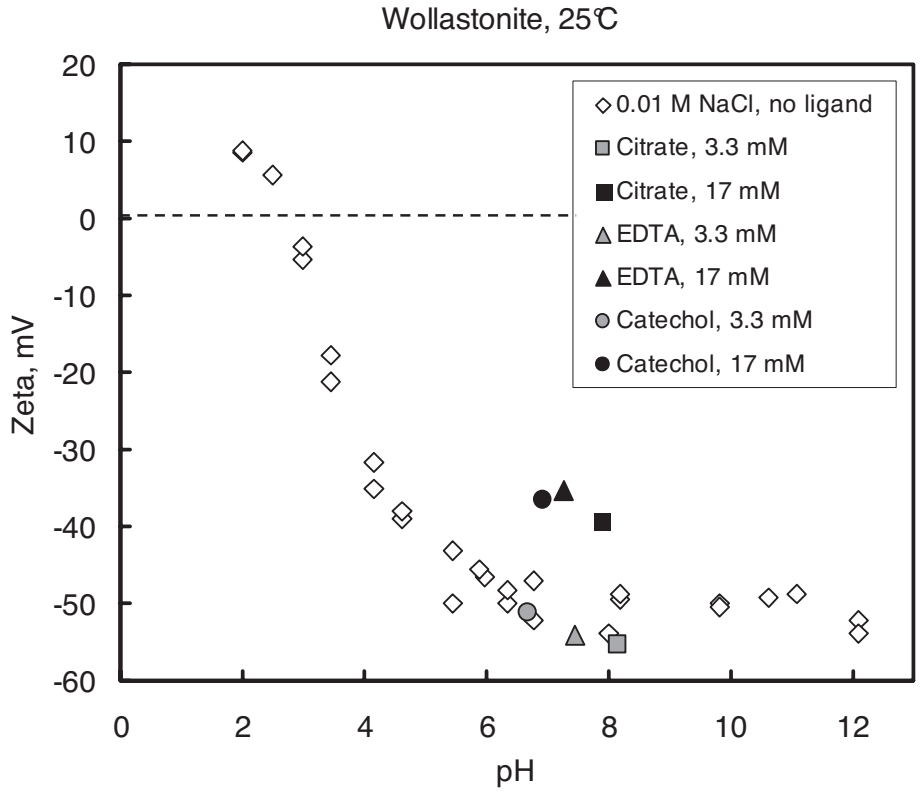

Fig. A1. Electrophoretic measurements of wollastonite zeta-potential in the presence of organic ligands.

Appendix 2

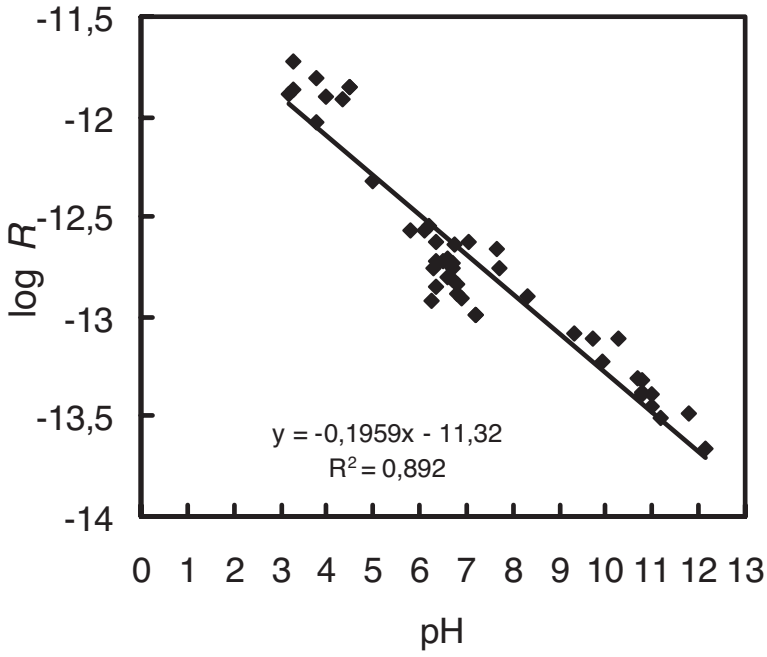

Fig. A2. Dissolution rate of wollastonite (R, mol/cm^2/s) as a function of pH in ligand-free system at 25°C and 0.01 M NaCl.

Appendix 3

Table A3

Summary of wollastonite powder dissolution experiments performed in the presence of different ligands. N.D. stands for not determined. R units are mol/cm^2/s.

N	ligand	[Ligand], M	[Ca], M	[Si], M	pH	log R_{Ca}	log R_{Si}	log R_{avg}
23_1	Acetate	1.00E-05	1.35E-05	1.27E-05	6.59	-12.56	-12.59	**-12.57**
23_2	Acetate	1.00E-04	1.37E-05	8.50E-06	6.68	-12.55	-12.76	**-12.66**
23_3	Acetate	5.00E-04	1.35E-05	8.90E-06	6.43	-12.56	-12.74	**-12.65**
23_4	Acetate	1.00E-03	1.54E-05	1.17E-05	6.47	-12.50	-12.62	**-12.56**
23_5	Acetate	3.00E-03	1.32E-05	1.34E-05	6.74	-12.58	-12.57	**-12.57**
23_6	Acetate	1.00E-02	N.D.	9.40E-06	6.98	N.D.	-12.72	**-12.72**
23_7	Acetate	0.03	1.06E-05	1.08E-05	6.67	-12.66	-12.65	**-12.66**
23_8	Acetate	0.1	8.40E-06	8.46E-06	6.74	-12.77	-12.77	**-12.77**
W11	Acetate	1.00E-05	1.50E-05	1.50E-05	10.8	-13.39	-13.38	**-13.39**
W14	Acetate	5.00E-05	1.20E-05	1.22E-05	10.6	-13.49	-13.47	**-13.48**
W17	Acetate	3.00E-04	1.30E-05	9.90E-06	10.8	-13.45	-13.56	**-13.51**
W20	Acetate	1.00E-03	9.50E-06	9.80E-06	10.8	-13.58	-13.57	**-13.58**
W23	Acetate	3.00E-03	9.20E-06	9.60E-06	10.7	-13.59	-13.58	**-13.59**
W26	Acetate	1.00E-02	9.00E-06	1.01E-05	10.7	-13.6	-13.55	**-13.58**
W29	Acetate	3.00E-02	1.50E-05	1.53E-05	10.8	-13.59	-13.73	**-13.66**
59-1	Formiate	1.00E-06	2.22E-05	2.57E-05	6.7	-12.69	-12.63	**-12.66**
59-2	Formiate	1.00E-05	3.06E-05	3.18E-05	6.5	-12.65	-12.63	**-12.64**
59-3	Formiate	1.00E-04	3.61E-05	3.68E-05	6.5	-12.58	-12.58	**-12.58**
59-4	Formiate	1.00E-03	3.91E-05	3.48E-05	6.5	-12.55	-12.60	**-12.58**
59-5	Formiate	5.00E-03	3.43E-05	3.29E-05	6.6	-12.61	-12.63	**-12.62**
59-6	Formiate	1.00E-02	4.09E-05	4.03E-05	6.7	-12.52	-12.53	**-12.53**
59-7	Formiate	5.00E-02	4.90E-05	4.71E-05	6.8	-12.45	-12.47	**-12.46**
55-1	Lactate	1.00E-06	1.43E-05	1.44E-05	8.5	-13.06	-13.06	**-13.06**
55-2	Lactate	1.00E-05	9.90E-06	9.80E-06	8.45	-13.09	-13.09	**-13.09**
55-3	Lactate	1.00E-04	1.38E-05	1.30E-05	8.4	-12.94	-12.97	**-12.96**
55-4	Lactate	1.00E-03	1.40E-05	1.46E-05	8.6	-12.95	-12.93	**-12.94**
55-5	Lactate	5.00E-03	1.81E-05	1.65E-05	8.6	-12.84	-12.88	**-12.86**
55-6	Lactate	1.00E-02	1.93E-05	1.80E-05	8.6	-12.80	-12.83	**-12.82**
55-7	Lactate	5.00E-02	2.44E-05	2.68E-05	8.7	-12.70	-12.66	**-12.68**
55-8	Lactate	1.00E-01	3.98E-05	4.10E-05	8.4	-12.48	-12.47	**-12.48**
46_1	Lactate	1.00E-05	1.15E-05	1.10E-05	5.38	-12.35	-12.37	**-12.36**
46_2	Lactate	1.00E-04	1.20E-05	1.16E-05	5.36	-12.34	-12.35	**-12.35**
46_3	Lactate	1.00E-03	1.30E-05	1.25E-05	5.35	-12.30	-12.32	**-12.31**
46_4	Lactate	0.01	1.52E-05	1.55E-05	5.53	-12.24	-12.23	**-12.24**
46_5	Lactate	0.02	1.80E-05	1.90E-05	5.32	-12.16	-12.14	**-12.15**
46_6	Lactate	0.05	2.10E-05	2.05E-05	5.54	-12.09	-12.10	**-12.10**
46_7	Lactate	0.1	2.36E-05	2.39E-05	5.55	-12.06	-12.06	**-12.06**
46_8	Lactate	0.2	2.82E-05	2.72E-05	5.52	-11.97	-11.98	**-11.98**
		$[Oxalat^{2-}]_{free}$						
24_1	10^{-5} M Oxalate	9.64E-06	2.03E-05	1.20E-05	6.47	-12.38	-12.61	**-12.49**
24_2	$5x10^{-5}$ M Oxalate	4.80E-05	1.60E-05	1.05E-05	6.45	-12.48	-12.66	**-12.57**
24_3	10^{-4} M Oxalate	9.30E-05	1.43E-05	1.09E-05	6.47	-12.53	-12.64	**-12.58**
24_4	$2x10^{-4}$ M Oxalate	2.18E-04	1.23E-05	1.06E-05	6.55	-12.60	-12.66	**-12.63**
24_5	$5x10^{-4}$ M Oxalate	4.60E-04	2.09E-05	1.96E-05	6.63	-12.37	-12.39	**-12.38**
24_6	0.001 M Oxalate	9.18E-04	1.24E-05	1.53E-05	6.45	-12.60	-12.51	**-12.55**
24_7	0.002 M Oxalate	1.84E-03	1.12E-05	2.05E-05	6.41	-12.65	-12.38	**-12.52**
24_8	0.005 M Oxalate	4.60E-03	9.08E-06	2.68E-05	6.43	-12.74	-12.27	**-12.51**
W35	Oxalate	5.00E-07	8.50E-06	9.80E-06	10.6	-13.66	-13.59	**-13.63**
W38	Oxalate	1.00E-05	9.70E-06	9.30E-06	10.8	-13.60	-13.61	**-13.61**
W41	Oxalate	5.00E-05	1.29E-05	6.55E-06	11	-13.67	-13.66	**-13.67**
W44	Oxalate	3.00E-04	1.07E-05	5.93E-06	11	-13.55	-13.8	**-13.68**
W47	Oxalate	1.00E-03	9.80E-06	6.15E-06	11.1	-13.60	-13.79	**-13.70**
W50	Oxalate	5.00E-03	5.90E-06	8.80E-06	11.05	-13.84	-13.64	**-13.74**
N	**ligand**	**$[Ligand^{n-}]_{free}$**	**[Ca], M**	**[Si], M**	**pH**	**log R_{Ca}**	**log R_{Si}**	**log R_{avg}**
25_1	10^{-5} M Citrate	6.15E-06	1.89E-05	1.39E-05	6.57	-12.39	-12.52	**-12.46**
25_2	$5x10^{-5}$ M Citrate	3.45E-05	ND	1.59E-05	6.71	ND	-12.46	**-12.46**
25_3	10^{-4} M citrate	7.09E-05	1.88E-05	1.83E-05	6.68	-12.39	-12.40	**-12.39**
25_4	$5x10^{-4}$ M Citrate	4.42E-04	2.40E-05	1.88E-05	7.12	-12.28	-12.39	**-12.33**
25_5	0.001 M Citrate	9.24E-04	2.78E-05	2.79E-05	7.27	-12.22	-12.22	**-12.22**
25_6	0.002 M Citrate	1.91E-03	2.79E-05	2.86E-05	7.64	-12.23	-12.21	**-12.22**
25_7	0.005 M Citrate	4.87E-03	4.04E-05	3.84E-05	7.67	-12.07	-12.09	**-12.08**
25_8	0.01 M Citrate	9.74E-03	4.67E-05	4.02E-05	7.67	-12.01	-12.07	**-12.04**
W12	Citrate	1.00E-05	1.28E-05	1.10E-05	10.7	-13.45	-13.50	**-13.48**
W15	Citrate	5.00E-05	1.05E-05	9.60E-06	10.6	-13.56	-13.57	**-13.57**
W18	Citrate	3.00E-04	2.01E-05	7.10E-06	10.9	-13.25	-13.70	**-13.48**
W21	Citrate	1.00E-03	2.10E-05	9.00E-06	10.75	-13.23	-13.60	**-13.42**
W24	Citrate	3.00E-03	1.45E-05	1.25E-05	10.7	-13.41	-13.46	**-13.44**
W27	Citrate	1.00E-02	1.55E-05	1.50E-05	10.7	-13.37	-13.37	**-13.37**
W30	Citrate	3.00E-02	2.65E-05	1.72E-05	10.7	-13.26	-13.44	**-13.35**
W2	Malate	1.00E-05	2.90E-06	3.40E-06	6.60	-12.75	-12.67	**-12.71**
W5	Malate	5.00E-05	2.70E-06	3.10E-06	6.40	-12.76	-12.71	**-12.74**
W8	Malate	1.00E-04	2.90E-06	3.10E-06	6.50	-12.74	-12.7	**-12.72**
W11	Malate	5.00E-04	3.90E-06	3.70E-06	6.55	-12.61	-12.63	**-12.62**
W14	Malate	1.00E-03	3.70E-06	4.10E-06	6.70	-12.63	-12.58	**-12.61**
W17	Malate	5.00E-03	5.60E-06	5.70E-06	6.60	-12.36	-12.36	**-12.36**
W20	Malate	1.00E-02	5.60E-06	5.80E-06	6.60	-12.30	-12.29	**-12.30**

TABLE A3
(continued)

N	ligand	$[Ligand^{n-}]_{free}$	[Ca], M	[Si], M	pH	log R_{Ca}	log R_{Si}	log R_{avg}
52-1	Tartrate	1.00E-06	8.20E-06	8.80E-06	9.2	-13.15	-13.12	**-13.14**
52-2	Tartrate	1.00E-05	1.04E-05	1.13E-05	8.9	-13.13	-13.16	**-13.13**
52-3	Tartrate	1.00E-04	9.90E-06	1.06E-05	9	-13.05	-13.02	**-13.04**
52-4	Tartrate	1.00E-03	1.83E-05	1.87E-05	9.2	-12.78	-12.77	**-12.78**
52-5	Tartrate	5.00E-03	1.64E-05	1.60E-05	9.1	-12.87	-12.88	**-12.88**
52-6	Tartrate	1.00E-02	2.14E-05	2.65E-05	9.2	-12.75	-12.66	**-12.71**
52-7	Tartrate	5.00E-02	3.21E-05	1.30E-05	9.1	-12.58	-12.97	**-12.78**
W34	Tartrate	1.00E-05	1.07E-05	1.06E-05	10.95	-13.62	-13.62	**-13.62**
W37	Tartrate	1.00E-04	1.15E-05	9.30E-06	10.85	-13.52	-13.61	**-13.57**
W40	Tartrate	5.00E-04	1.45E-05	4.80E-06	11.00	-13.42	-13.90	**-13.66**
W43	Tartrate	3.00E-03	1.05E-05	4.25E-06	11.00	-13.60	-13.95	**-13.78**
W46	Tartrate	1.00E-02	1.16E-05	5.50E-06	11.05	-13.51	-13.84	**-13.68**
W49	Tartrate	5.00E-02	2.05E-05	1.00E-05	11.05	-13.56	-14.09	**-13.83**
57-1	Phthalate	1.00E-06	1.50E-05	1.78E-05	6.8	-12.92	-12.85	**-12.89**
57-2	Phthalate	1.00E-05	1.35E-05	1.51E-05	6.8	-12.98	-12.93	**-12.96**
57-3	Phthalate	1.00E-04	3.09E-05	3.11E-05	6.5	-12.63	-12.63	**-12.63**
57-4	Phthalate	1.00E-03	2.40E-05	2.65E-05	6.9	-12.69	-12.65	**-12.67**
57-5	Phthalate	5.00E-03	3.47E-05	2.94E-05	6.8	-12.54	-12.62	**-12.58**
57-6	Phthalate	1.00E-02	3.54E-05	3.36E-05	7.0	-12.55	-12.57	**-12.56**
W52	Phthalate	1.00E-05	9.90E-06	1.10E-05	10.7	-13.55	-13.58	**-13.57**
W55	Phthalate	1.00E-04	1.34E-05	9.00E-06	11.0	-13.46	-13.62	**-13.54**
W58	Phthalate	5.00E-04	1.28E-05	7.82E-06	11.0	-13.47	-13.68	**-13.58**
W61	Phthalate	3.00E-03	1.24E-05	7.60E-06	10.9	-13.49	-13.69	**-13.59**
W64	Phthalate	1.00E-02	1.32E-05	8.26E-06	11.0	-13.46	-13.66	**-13.56**
W67	Phthalate	5.00E-02	1.70E-05	9.55E-06	11.0	-13.35	-13.61	**-13.48**
W44	Malonate	1.00E-05	7.00E-06	8.20E-06	6.95	-12.78	-12.82	**-12.80**
W46	Malonate	5.00E-05	7.80E-06	8.80E-06	7.05	-12.79	-12.75	**-12.77**
W48	Malonate	1.00E-04	6.90E-06	7.70E-06	6.70	-12.75	-12.70	**-12.73**
W50	Malonate	5.00E-04	8.20E-06	8.30E-06	6.85	-12.67	-12.67	**-12.67**
W45	Malonate	1.00E-03	9.90E-06	1.08E-05	6.90	-12.59	-12.56	**-12.58**
W47	Malonate	5.00E-03	1.20E-05	1.36E-05	7.10	-12.51	-12.45	**-12.48**
W49	Malonate	1.00E-02	1.40E-05	1.40E-05	7.15	-12.44	-12.44	**-12.44**
W51	Malonate	5.00E-02	1.70E-05	1.71E-05	7.05	-12.35	-12.45	**-12.40**
53-1	Adipate	1.00E-06	5.70E-06	5.70E-06	6.65	-12.78	-12.76	**-12.77**
53-2	Adipate	1.00E-05	7.40E-06	6.70E-06	6.80	-12.68	-12.75	**-12.73**
53-3	Adipate	2.00E-04	5.20E-06	5.40E-06	6.62	-12.55	-12.48	**-12.55**
53-4	Adipate	1.00E-03	1.14E-05	1.07E-05	6.66	-12.46	-12.49	**-12.48**
53-5	Adipate	5.00E-03	1.79E-05	1.64E-05	6.70	-12.24	-12.27	**-12.26**
53-6	Adipate	1.00E-02	1.43E-05	1.55E-05	6.75	-12.33	-12.30	**-12.27**
53-7	Adipate	5.00E-02	1.89E-05	2.18E-05	6.75	-12.11	-12.07	**-12.09**
64-1	Fumarate	1.00E-06	1.84E-05	1.37E-05	7.05	-12.74	-12.87	**-12.80**
64-2	Fumarate	1.00E-05	1.42E-05	1.50E-05	6.92	-12.82	-12.80	**-12.81**
64-3	Fumarate	1.00E-04	2.00E-05	1.51E-05	6.94	-12.69	-12.82	**-12.75**
64-4	Fumarate	1.00E-03	2.14E-05	1.75E-05	7.00	-12.64	-12.72	**-12.68**
64-5	Fumarate	0.005	2.15E-05	1.87E-05	6.93	-12.63	-12.69	**-12.66**
64-6	Fumarate	0.01	2.75E-05	2.64E-05	6.92	-12.55	-12.57	**-12.56**
64-7	Fumarate	0.03	2.79E-05	2.84E-05	7.13	-12.52	-12.51	**-12.52**
64-8	Fumarate	0.1	3.07E-05	3.19E-05	7.08	-12.48	-12.47	**-12.48**
63-1	Succinate	1.00E-06	1.05E-05	9.19E-06	7.40	-12.88	-12.94	**-12.91**
63-2	Succinate	1.00E-05	1.02E-05	8.60E-06	7.46	-12.91	-12.98	**-12.94**
63-3	Succinate	1.00E-04	1.18E-05	8.06E-06	7.44	-12.85	-13.01	**-12.93**
63-4	Succinate	1.00E-03	1.24E-05	1.04E-05	7.38	-12.81	-12.89	**-12.85**
63-5	Succinate	0.005	2.23E-05	2.40E-05	7.45	-12.56	-12.53	**-12.55**
63-6	Succinate	0.01	1.99E-05	2.03E-05	7.42	-12.61	-12.60	**-12.61**
63-7	Succinate	0.03	3.71E-05	3.31E-05	7.37	-12.34	-12.39	**-12.37**
63-8	Succinate	0.1	4.48E-05	3.94E-05	7.36	-12.26	-12.32	**-12.29**
W23	D-gluconate	1.00E-05	3.70E-06	4.10E-06	8.30	-13.01	-12.9	**-12.96**
W26	D-gluconate	5.00E-05	3.50E-06	4.30E-06	8.30	-13.03	-12.95	**-12.99**
W29	D-gluconate	1.00E-04	3.20E-06	4.00E-06	8.30	-13.08	-12.99	**-13.04**
W32	D-gluconate	5.00E-04	4.30E-06	4.70E-06	8.30	-12.97	-12.92	**-12.95**
W35	D-gluconate	1.00E-03	4.80E-06	5.00E-06	8.40	-12.90	-12.88	**-12.89**
W38	D-gluconate	5.00E-03	6.60E-06	7.50E-06	8.60	-12.77	-12.7	**-12.74**
W41	D-gluconate	1.00E-02	7.50E-06	7.90E-06	8.59	-12.70	-12.66	**-12.68**
W24	D-glucuronic	1.00E-05	7.50E-06	8.20E-06	6.60	-12.84	-12.80	**-12.82**
W27	D-glucuronic	5.00E-05	5.80E-06	7.30E-06	6.60	-12.95	-12.85	**-12.90**
W30	D-glucuronic	1.00E-04	5.70E-06	6.10E-06	6.65	-13.01	-12.98	**-13.00**
W33	D-glucuronic	5.00E-04	5.00E-06	6.20E-06	6.70	-13.00	-12.91	**-12.96**
W36	D-glucuronic	1.00E-03	4.20E-06	4.80E-06	6.60	-13.11	-13.06	**-13.09**
W39	D-glucuronic	5.00E-03	4.70E-06	4.80E-06	6.70	-13.06	-13.05	**-13.06**
		$[HEDTA^{3-}]$						
27_1	0.01 M NaCl	8.00E-06	9.46E-06	8.20E-06	7.52	-12.66	-12.73	**-12.70**
27_2	10^{-4} M EDTA	6.70E-05	2.68E-05	2.67E-05	7.15	-12.22	-12.22	**-12.22**
27_3	$3x10^{-4}$ M EDTA	2.50E-04	4.29E-05	4.50E-05	7.74	-12.02	-12.00	**-12.01**
27_4	$6x10^{-4}$ M EDTA	5.00E-04	4.91E-05	5.29E-05	7.70	-11.97	-11.94	**-11.95**
27_5	0.001 M EDTA	9.00E-04	6.17E-05	6.15E-05	7.73	-11.87	-11.87	**-11.87**

TABLE A3
(continued)

N	ligand	$[Ligand^{n-}]_{free}$	[Ca], M	[Si], M	pH	log R_{Ca}	log R_{Si}	log R_{avg}
		$[HEDTA^{3-}]$						
27_5	0.001 M EDTA	9.00E-04	6.17E-05	6.15E-05	7.73	-11.87	-11.87	**-11.87**
27_6	0.002 M EDTA	1.83E-03	8.00E-05	7.80E-05	7.73	-11.76	-11.77	**-11.76**
27_7	0.005 M EDTA	4.64E-03	1.07E-04	1.03E-04	7.70	-11.63	-11.65	**-11.64**
27_8	0.01 M EDTA	9.23E-03	1.05E-04	9.94E-05	7.55	-11.64	-11.66	**-11.65**
		$[EDTA^{4-}]$						
22_10	0.00001 M EDTA	1.00E-06	1.85E-05	1.63E-05	9.44	-12.40	-12.45	**-12.43**
22_11	0.0001 M EDTA	1.16E-05	4.37E-05	4.46E-05	9.04	-12.03	-12.02	**-12.02**
22_12	0.0005 M EDTA	8.66E-05	7.92E-05	8.28E-05	9.20	-11.77	-11.75	**-11.76**
22_13	0.001 M EDTA	2.48E-04	9.67E-05	9.80E-05	9.41	-11.68	-11.67	**-11.68**
22_14	0.002 M EDTA	6.50E-04	1.06E-04	1.08E-04	9.54	-11.64	-11.63	**-11.64**
22_15	0.005 M EDTA	0.00194	1.23E-04	1.21E-04	9.47	-11.58	-11.58	**-11.58**
22_16	0.01 M EDTA	0.00448	1.21E-04	1.18E-04	9.38	-11.58	-11.59	**-11.59**
W10	0.00001 EDTA	2.00E-06	1.70E-05	1.51E-05	10.8	-13.35	-13.40	**-13.38**
W13	0.00005 EDTA	9.00E-06	2.80E-05	2.55E-05	10.7	-13.14	-13.18	**-13.16**
W16	0.0001 EDTA	2.60E-05	3.80E-05	3.50E-05	10.8	-13.02	-13.05	**-13.04**
W19	0.0005 EDTA	1.87E-04	7.60E-05	7.70E-05	10.9	-12.75	-12.74	**-12.75**
W22	0.001 EDTA	4.30E-04	8.50E-05	9.10E-05	10.9	-12.66	-12.63	**-12.65**
W25	0.003 EDTA	1.62E-03	1.05E-04	1.11E-04	11.0	-12.57	-12.55	**-12.56**
		$[H_2EGTA^{2-}]$						
W3	0.000001 EGTA	4.00E-07	2.40E-06	2.40E-06	6.15	-12.76	-12.77	**-12.77**
W6	0.000005 EGTA	3.00E-06	2.30E-06	2.70E-06	6.10	-12.78	-12.70	**-12.74**
W9	0.00001 EGTA	1.00E-05	2.50E-06	2.90E-06	6.10	-12.76	-12.69	**-12.73**
W12	0.00005 EGTA	5.00E-05	3.90E-06	3.00E-06	6.10	-12.56	-12.67	**-12.62**
W15	0.0001 EGTA	1.00E-04	6.00E-06	5.30E-06	6.05	-12.39	-12.45	**-12.42**
W18	0.0005 EGTA	5.00E-04	1.41E-05	1.53E-05	6.20	-12.25	-12.21	**-12.23**
W21	0.001 EGTA	1.00E-03	1.05E-05	9.60E-06	6.13	-12.15	-12.19	**-12.17**
		$[H_2Cat^{o}]$						
28_1	0.01 M NaCl	1.00E-05	1.22E-05	9.20E-06	6.37	-12.52	-12.64	**-12.58**
28_2	10^{-4} M Catechol	1.00E-04	1.57E-05	1.53E-05	6.54	-12.42	-12.43	**-12.42**
28_3	$3x10^{-4}$ M Catechol	3.00E-04	2.12E-05	2.10E-05	6.49	-12.28	-12.29	**-12.28**
28_4	$6x10^{-4}$ M Catechol	6.00E-04	2.30E-05	2.33E-05	6.60	-12.25	-12.25	**-12.25**
28_5	10^{-3} M Catechol	1.00E-03	2.53E-05	2.63E-05	6.41	-12.20	-12.19	**-12.20**
28_6	$2x10^{-3}$ M Catechol	2.00E-03	4.01E-05	4.03E-05	6.35	-12.01	-12.01	**-12.01**
28_7	$5x10^{-3}$ M Catechol	5.00E-03	4.85E-05	4.88E-05	6.30	-11.94	-11.93	**-11.94**
28_8	0.01 M Catechol	1.00E-02	5.80E-05	5.96E-05	6.22	-11.86	-11.84	**-11.85**
		$[HCat^{-}]$						
W33	Catechol	1.00E-05	8.30E-06	7.60E-06	10.7	-13.66	-13.69	**-13.68**
W36	Catechol	1.00E-04	8.70E-06	6.40E-06	10.7	-13.64	N.D.	**-13.64**
W39	Catechol	5.00E-04	1.50E-05	1.25E-05	10.6	-13.41	-13.47	**-13.44**
W42	Catechol	3.00E-03	1.62E-05	1.85E-05	10.4	-13.37	-13.31	**-13.34**
W45	Catechol	1.00E-02	1.66E-05	1.78E-05	10.7	-13.36	-13.32	**-13.34**
W48	Catechol	5.00E-02	2.00E-05	N.D.	10.7	-13.28	N.D.	**-13.28**
		$[H\text{-}Oxine^{-}]$						
54-1	8-Hydroxyquinoline	0.000001	1.21E-05	1.28E-05	8.3	-12.92	-12.88	**-12.90**
54-2	8-Hydroxyquinoline	1.00E-05	1.84E-05	1.93E-05	8.5	-12.86	-12.84	**-12.85**
54-3	8-Hydroxyquinoline	1.00E-04	2.93E-05	2.95E-05	8.5	-12.69	-12.66	**-12.68**
54-4	8-Hydroxyquinoline	5.00E-04	3.89E-05	5.39E-05	8.2	-12.64	-12.56	**-12.60**
54-5	8-Hydroxyquinoline	1.00E-03	4.53E-05	4.70E-05	8.1	-12.50	-12.48	**-12.49**
54-6	8-Hydroxyquinoline	5.00E-03	4.77E-05	4.89E-05	8.2	-12.46	-12.45	**-12.46**
54-7	8-Hydroxyquinoline	2.00E-02	6.80E-05	6.50E-05	8.4	-12.30	-12.32	**-12.31**
		$[H_2DHBA^{-}]$						
W69	2,4 – Dihydroxybenzoic acid, 10^{-5} M	9.80E-06	6.90E-06	3.30E-06	7.0	-12.67	-12.97	**-12.82**
W72	2,4 – Dihydroxybenzoic acid, 10^{-4} M	9.80E-05	7.00E-06	4.50E-06	6.2	-12.68	-12.85	**-12.77**
W75	2,4 – Dihydroxybenzoic acid, $5x10^{-4}$ M	4.90E-04	7.00E-06	5.90E-06	6.3	-12.65	-12.72	**-12.69**
W78	2,4 – Dihydroxybenzoic acid, 10^{-3} M	9.50E-04	6.70E-06	6.80E-06	6.7	-12.71	-12.66	**-12.69**
W81	2,4 – Dihydroxybenzoic acid, $3x10^{-3}$ M	2.90E-03	8.50E-06	9.10E-06	7.4	-12.57	-12.52	**-12.55**
W84	2,4 – Dihydroxybenzoic acid, 0.01 M	9.23E-03	1.36E-05	1.56E-05	7.5	-12.38	-12.29	**-12.34**
		$[H_2DHBA^{-}]$						
W70	3,4 – Dihydroxybenzoic acid, 10^{-5} M	9.80E-06	8.80E-06	6.20E-06	6.9	-12.47	-12.6	**-12.54**
W73	3,4 – Dihydroxybenzoic acid, 10^{-4} M	9.80E-05	9.60E-06	9.36E-06	7.3	-12.45	-12.42	**-12.44**
W76	3,4 – Dihydroxybenzoic acid, $5x10^{-4}$ M	4.90E-04	1.55E-05	1.70E-05	6.9	-12.28	-12.22	**-12.25**
W79	3,4 – Dihydroxybenzoic acid, 10^{-3} M	9.50E-04	1.68E-05	1.91E-05	7.3	-12.18	-12.11	**-12.15**
W82	3,4 – Dihydroxybenzoic acid, $3x10^{-3}$ M	2.90E-03	2.22E-05	2.57E-05	7.5	-12.09	-12.02	**-12.06**
W85	3,4 – Dihydroxybenzoic acid, 0.01 M	9.23E-03	2.59E-05	3.08E-05	7.5	-12.00	-11.91	**-11.96**
		$[H_3Gal^{-}]$						
65-1	Gallic acid	5.50E-07	3.03E-05	2.25E-05	7.04	-12.76	-12.89	**-12.83**
65-2	Gallic acid	1.00E-05	2.75E-05	2.61E-05	6.94	-12.85	-12.87	**-12.86**
65-3	Gallic acid	1.00E-04	3.64E-05	3.38E-05	6.88	-12.71	-12.74	**-12.72**
65-4	Gallic acid	1.00E-03	7.67E-05	7.44E-05	7.05	-12.38	-12.39	**-12.38**
65-5	Gallic acid	0.005	1.36E-04	1.60E-04	6.81	-12.13	-12.06	**-12.10**
65-6	Gallic acid	0.01	1.80E-04	2.11E-04	6.85	-12.00	-11.93	**-11.97**
65-7	Gallic acid	0.03	2.20E-04	2.97E-04	6.95	-11.90	-11.77	**-11.84**
65-8	Gallic acid	0.07	2.05E-04	2.72E-04	7.09	-11.95	-11.83	**-11.89**

TABLE A3
(continued)

N	ligand	$[Ligand^{n-}]_{free}$	[Ca], M	[Si], M	pH	log R_{Ca}	log R_{Si}	log R_{avg}
		$[HAscorbate^-]$						
W1	10^{-5} M Ascorbic acid	1.00E-05	2.52E-06	2.80E-06	7.30	-12.97	-12.94	**-12.96**
W4	5 x10^{-5} M Ascorbic acid	5.00E-05	2.40E-06	2.88E-06	7.20	-12.96	-12.88	**-12.92**
W7	10^{-4} M Ascorbic acid	1.00E-04	2.32E-06	2.64E-06	7.30	-12.98	-12.93	**-12.96**
W10	0.0005 M Ascorbic acid	5.00E-04	2.16E-06	2.56E-06	7.30	-12.96	-12.9	**-12.93**
W13	0.001 M Ascorbic acid	1.00E-03	3.80E-06	3.90E-06	7.40	-12.82	-12.81	**-12.82**
W16	0.005 M Ascorbic acid	5.00E-03	6.10E-06	5.60E-06	7.35	-12.57	-12.61	**-12.59**
W19	0.01 M Ascorbic acid	1.00E-02	8.10E-06	6.00E-06	7.50	-12.45	-12.58	**-12.52**
		$[H_2PO_4^-]$						
31_1	1e-5 M PO_4	5.07E-06	2.30E-05	2.00E-05	7.05	-12.59	-12.65	**-12.62**
31_2	2e-5 M PO_4	1.19E-06	2.10E-05	2.08E-05	6.90	-12.65	-12.65	**-12.65**
31_3	5e-5 M PO_4	3.20E-05	2.60E-05	2.86E-05	6.80	-12.55	-12.51	**-12.53**
31_4	1e-4 M PO_4	6.00E-05	3.62E-05	3.90E-05	6.89	-12.40	-12.37	**-12.39**
31_5	2e-4 M PO_4	1.15E-04	5.24E-05	6.04E-05	6.93	-12.25	-12.19	**-12.22**
31_6	5e-4 M PO_4	3.20E-04	8.16E-05	1.02E-04	6.79	-12.06	-11.97	**-12.01**
31_7	1e-3 M PO_4	7.40E-04	1.15E-04	1.64E-04	6.61	N.D.	-11.75	**-11.75**
31_8	3e-3 M PO_4	1.80E-03	1.42E-04	2.31E-04	6.85	N.D.	-11.61	**-11.61**
31_9	0.01 M PO_4	5.79E-03	1.51E-04	2.39E-04	6.87	N.D.	-11.60	**-11.60**
		$[H_2PO_3^-]$						
39_1	10^{-5} M $NaPO_3$	7.00E-06	1.97E-05	1.91E-05	6.61	-12.38	-12.39	**-12.38**
39_2	10^{-4} M $NaPO_3$	7.00E-05	2.03E-05	2.11E-05	6.52	-12.35	-12.33	**-12.34**
39_3	10^{-3} M $NaPO_3$	7.00E-04	4.77E-05	5.30E-05	6.85	-11.99	-11.94	**-11.97**
39_4	0.003 M $NaPO_3$	2.10E-03	7.00E-05	8.60E-05	6.69	-11.83	-11.74	**-11.78**
39_5	0.01 M $NaPO_{3ez}$	7.00E-03	8.44E-05	1.27E-04	6.70	-11.75	-11.57	**-11.66**
39_6	0.02 M $NaPO_3$	1.40E-02	9.00E-05	1.53E-04	6.62	-11.72	-11.49	**-11.61**
39_7	0.05 M $NaPO_3$	3.50E-02	1.00E-04	1.75E-04	6.44	-11.68	-11.43	**-11.56**
32_1	2 x10^{-5} M $NaHCO_3$		2.21E-05	1.98E-05	6.90	-12.61	-12.66	**-12.63**
32_2	10^{-4} M $NaHCO_3$		1.63E-05	1.54E-05	7.02	-12.74	-12.76	**-12.75**
32_3	5 x10^{-4} M $NaHCO_3$		1.26E-05	1.34E-05	7.53	-12.85	-12.83	**-12.84**
32_4	0.001 M $NaHCO_3$		1.66E-05	1.75E-05	7.90	-12.74	-12.72	**-12.73**
32_5	0.002 M $NaHCO_3$		1.80E-05	1.86E-05	8.42	-12.71	-12.69	**-12.70**
32_6	0.005 M $NaHCO_3$		2.02E-05	1.96E-05	8.56	-12.66	-12.67	**-12.67**
32_7	0.01 M $NaHCO_3$		2.10E-05	2.15E-05	8.62	-12.64	-12.63	**-12.64**
32_8	0.05 M $NaHCO_3$		3.73E-05	3.78E-05	8.54	-12.39	-12.38	**-12.39**
32_9	0.1 M $NaHCO_3$		4.80E-05	5.16E-05	8.44	-12.29	-12.26	**-12.27**
33_1	0.001 M NaOH		1.33E-05	9.03E-06	11.08	-12.86	-13.03	**-12.95**
33_2	2 x 10^{-5} M Na_2CO_3		4.36E-06	4.26E-06	11.03	-13.36	-13.37	**-13.36**
33_3	5 x 10^{-5} M Na_2CO_3		3.95E-06	3.47E-06	10.52	-13.40	-13.45	**-13.42**
33_4	10^{-4} M Na_2CO_3		2.75E-06	3.35E-06	11.15	-13.56	-13.47	**-13.52**
33_5	2 x 10^{-4} M Na_2CO_3		2.60E-06	3.90E-06	11.16	-13.59	-13.41	**-13.50**
33_6	4 x 10^{-4} M Na_2CO_3		2.20E-06	2.60E-06	11.18	-13.66	-13.58	**-13.62**
33_7	10^{-3} M Na_2CO_3		2.00E-06	3.10E-06	11.17	-13.70	-13.51	**-13.60**
33_8	2 x 10^{-3} M Na_2CO_3		2.14E-06	3.62E-06	11.17	-13.67	-13.43	**-13.55**
33_9	5 x 10^{-3} M Na_2CO_3		(3.4±0.2)E-6	5.03E-06	10.93	-13.47	-13.30	**-13.38**
34_0	Humics, [DOC] = 0,1 mg/L	0.1	2.25E-05	2.00E-05	6.75	-12.36	-12.41	**-12.38**
34_1	Humics, [DOC] = 0,8 mg/L	0.8	2.31E-05	1.93E-05	6.80	-12.35	-12.42	**-12.38**
34_2	Humics, [DOC] = 2,24 mg/L	2.24	2.26E-05	1.83E-05	6.76	-12.36	-12.45	**-12.40**
34_3	Humics, [DOC] = 5,46 mg/L	5.46	1.75E-05	1.65E-05	6.74	-12.47	-12.49	**-12.48**
34_4	Humics, [DOC] = 11,3 mg/L	11.3	1.64E-05	1.64E-05	6.73	-12.48	-12.48	**-12.48**
34_5	Humics, [DOC] = 26,5 mg/L	26.5	2.63E-05	2.52E-05	6.80	-12.27	-12.29	**-12.28**
34_6	Humics, [DOC] = 53,8 mg/L	53.8	3.64E-05	3.72E-05	6.70	-12.13	-12.12	**-12.13**
36_6	0,01 M NaCl, [DOC] =0 mg/L	0.1	N.D.	8.64E-06	6.87	N.D.	-12.72	**-12.72**
36_1	Diatoms exudates, [DOC] = 0,45 mg/L	0.45	1.29E-05	9.45E-06	6.42	-12.54	-12.68	**-12.61**
36_2	Diatoms exudates, [DOC] = 2,1 mg/L	2.1	1.30E-05	1.15E-05	6.46	-12.54	-12.59	**-12.56**
36_3	Diatoms exudates, [DOC] = 6,7 mg/L	6.7	N.D.	1.38E-05	6.76	N.D.	-12.52	**-12.52**
36_4	Diatoms exudates, [DOC] = 27,4 mg/L	27.4	N.D.	4.50E-06	6.81	N.D.	-12.98	**-12.98**
36_5	Diatoms exudates, [DOC] = 54 mg/L	54	N.D.	7.40E-06	6.79	N.D.	-12.79	**-12.79**
35_6	0,01 M NaCl, [DOC] =0.1 mg/L	0.1	9.30E-06	8.46E-06	6.35	-12.70	-12.74	**-12.72**
35_1	Fulvics, [DOC] = 0.4 mg/L	0.4	1.10E-05	8.20E-06	6.37	-12.64	-12.76	**-12.70**
35_2	Fulvics, [DOC] = 1.1 mg/L	1.1	1.02E-05	8.50E-06	6.38	-12.67	-12.75	**-12.71**
35_3	Fulvics, [DOC] = 2.1 mg/L	2.1	9.20E-06	7.90E-06	6.41	-12.71	-12.78	**-12.74**
35_4	Fulvics, [DOC] = 4.8 mg/L	4.8	9.80E-06	7.60E-06	6.42	-12.68	-12.79	**-12.74**
35_5	Fulvics, [DOC] = 7.2 mg/L	7.2	1.05E-05	7.45E-06	6.40	-12.63	-12.78	**-12.71**

TABLE A3
(continued)

N	ligand	[Ligand]	[Ca], M	[Si], M	pH	log R_{Ca}	log R_{Si}	log R_{avg}
		[HSalicyl$^-$]						
38_1	10^{-5} M Salicylate	1.00E-05	1.40E-05	1.11E-05	6.76	-12.52	-12.62	**-12.57**
38_2	10^{-4} M Salicylate	1.00E-04	1.47E-05	1.05E-05	6.75	-12.50	-12.65	**-12.57**
38_3	10^{-3} M Salicylate	1.00E-03	1.45E-05	9.89E-06	6.75	-12.52	-12.68	**-12.60**
38_4	0.01 M Salicylate	0.01	1.55E-05	1.51E-05	6.51	-12.49	-12.50	**-12.50**
38_5	0.03 M Salicylate	0.03	2.14E-05	2.15E-05	6.65	-12.36	-12.36	**-12.36**
38_6	0.1 M Salicylate	0.1	2.51E-05	N.D.	6.45	-12.29	N.D.	**-12.29**
38_7	0.2 M Salicylate	0.2	3.10E-05	N.D.	6.52	-12.20	N.D.	**-12.20**
		[SH-CH_2COO^-]						
40_1	10^{-5} M Thioglycolate (SH-CH2COOH)	1.00E-05	1.17E-05	9.80E-06	6.76	-12.60	-12.68	**-12.64**
40_2	10^{-4} M Thioglycolate (SH-CH2COOH)	1.00E-04	1.24E-05	9.32E-06	6.75	-12.58	-12.70	**-12.64**
40_3	10^{-3} M Thioglycolate (SH-CH2COOH)	1.00E-03	1.44E-05	1.15E-05	6.75	-12.51	-12.61	**-12.56**
40_4	0.005 M Thioglycolate (SH-CH2COOH)	0.005	2.14E-05	1.86E-05	6.51	-12.34	-12.40	**-12.37**
40_5	0.01 M Thioglycolate (SH-CH2COOH)	0.01	2.73E-05	2.72E-05	6.65	-12.23	-12.23	**-12.23**
40_6	0.03 M Thioglycolate (SH-CH2COOH)	0.03	4.20E-05	4.31E-05	6.65	-12.04	-12.03	**-12.04**
40_7	0.1 M Thioglycolate (SH-CH2COOH)	0.1	6.90E-05	7.07E-05	6.62	-11.83	-11.82	**-11.83**
		[Oxydiacetate^{2-}]						
51-1	Diglycolic acid	1.00E-06	2.02E-05	2.02E-05	7.20	-12.76	-12.76	**-12.76**
51-2	Diglycolic acid	1.00E-05	1.86E-05	1.90E-05	7.35	-12.79	-12.78	**-12.79**
51-3	Diglycolic acid	1.00E-04	2.17E-05	2.21E-05	7.25	-12.72	-12.72	**-12.72**
51-4	Diglycolic acid	1.00E-03	2.86E-05	2.95E-05	7.25	-12.6	-12.59	**-12.60**
51-5	Diglycolic acid	5.00E-03	3.99E-05	3.83E-05	7.25	-12.48	-12.5	**-12.49**
51-6	Diglycolic acid	1.00E-02	3.97E-05	3.99E-05	7.30	-12.48	-12.48	**-12.48**
51-7	Diglycolic acid	5.00E-02	5.53E-05	5.18E-05	7.45	-12.34	-12.37	**-12.36**
		[Aspartam^{2-}]						
47_1	10^{-5} M Aspartate	5.00E-06	1.28E-05	1.24E-05	7.27	-12.23	-12.25	**-12.24**
47_2	10^{-4} M Aspartate	1.00E-04	1.22E-05	1.22E-05	7.23	-12.27	-12.27	**-12.27**
47_3	10^{-3} M Aspartate	1.00E-03	1.57E-05	1.70E-05	7.27	-12.17	-12.13	**-12.15**
47_4	0.003 M Aspartate	3.00E-03	2.10E-05	2.33E-05	7.26	-12.07	-12.03	**-12.05**
47_5	0.01 M Aspartate	0.01	2.88E-05	3.21E-05	7.27	-11.95	-11.90	**-11.93**
47_6	0.03 M Aspartate	0.03	3.52E-05	3.70E-05	7.31	-11.87	-11.85	**-11.86**
47_7	0.1 M Aspartate	0.1	3.51E-05	3.42E-05	7.34	-11.88	-11.90	**-11.89**
		[Glutamate^{2-}]						
W22	L-glutamic	5.00E-06	1.53E-05	1.55E-05	6.85	-12.80	-12.80	**-12.80**
W25	L-glutamic	5.00E-05	1.15E-05	1.15E-05	6.90	-12.75	-12.75	**-12.75**
W31	L-glutamic	5.00E-04	2.12E-05	2.39E-05	6.95	-12.64	-12.59	**-12.62**
W34	L-glutamic	1.00E-03	1.10E-05	1.16E-05	7.10	-12.56	-12.53	**-12.55**
W37	L-glutamic	5.00E-03	1.56E-05	1.53E-05	7.30	-12.40	-12.41	**-12.41**
W40	L-glutamic	1.00E-02	1.85E-05	1.64E-05	7.10	-12.34	-12.39	**-12.37**
		[Polysaccharide]$_{tot}$						
48_1	10^{-4} M Sorbitol	1.00E-04	1.10E-05	9.42E-06	5.87	-12.36	-12.43	**-12.40**
48_8	$3{\cdot}10^{-4}$ M Sorbitol	3.00E-04	8.51E-06	9.70E-06	5.77	-12.51	-12.45	**-12.48**
48_2	$5{\cdot}10^{-4}$ M Sorbitol	5.00E-04	1.02E-05	9.18E-06	5.81	-12.40	-12.44	**-12.42**
48_3	0.002 M Sorbitol	0.002	1.20E-05	1.25E-05	5.86	-12.33	-12.31	**-12.32**
48_4	0.01 M Sorbitol	0.01	1.31E-05	1.37E-05	5.9	-12.30	-12.28	**-12.29**
48_5	0.02 M Sorbitol	0.02	1.47E-05	1.44E-05	5.81	-12.26	-12.27	**-12.26**
48_6	0.05 M Sorbitol	0.05	1.47E-05	N.D.	5.81	-12.27	N.D.	**-12.27**
48_7	0.1 M Sorbitol	0.1	1.26E-05	N.D.	5.90	-12.34	N.D.	**-12.34**
G_1	2.8·10-4 M Glucose	2.80E-04	2.35E-05	2.51E-05	6.10	-12.47	-12.44	**-12.45**
G_2	0.0028 M Glucose	0.0028	1.65E-05	1.75E-05	6.05	-12.53	-12.50	**-12.51**
G_3	0.014 M Glucose	0.014	2.30E-05	2.25E-05	6.06	-12.33	-12.34	**-12.34**
G_4	0.028 M Glucose	0.028	6.63E-05	5.60E-05	6.20	-12.49	-12.57	**-12.53**
G_5	0.056 M Glucose	0.056	3.27E-04	3.16E-04	6.15	-12.39	-12.41	**-12.40**
G_6	0.084 M Glucose	0.084	1.59E-04	2.04E-04	6.20	-12.28	-12.18	**-12.23**
56-3	Saccharose	1.00E-04	1.62E-05	1.46E-05	8.5	-12.88	-12.93	**-12.91**
56-4	Saccharose	1.00E-03	1.53E-05	1.45E-05	8.5	-12.92	-12.94	**-12.93**
56-5	Saccharose	5.00E-03	1.59E-05	1.49E-05	8.4	-12.9	-12.93	**-12.92**
56-6	Saccharose	1.00E-02	1.50E-05	1.51E-05	8.4	-12.92	-12.92	**-12.92**
56-7	Saccharose	5.00E-02	1.47E-05	1.48E-05	8.3	-12.93	-12.92	**-12.93**
56-8	Saccharose	1.00E-01	1.49E-05	1.49E-05	8.2	-12.92	-12.92	**-12.92**
W51	D-mannit	1.00E-05	9.40E-06	7.80E-06	10.7	-13.6	-13.64	**-13.62**
W54	D-mannit	1.00E-04	1.31E-05	4.15E-06	11.1	-13.42	-13.92	**-13.67**
W57	D-mannit	5.00E-04	1.27E-05	3.20E-06	11.0	-13.44	-14.03	**-13.74**
W60	D-mannit	3.00E-03	1.05E-05	3.00E-06	10.9	-13.52	-14.06	**-13.79**
W63	D-mannit	1.00E-02	8.00E-06	2.70E-06	11.0	-13.64	-14.11	**-13.88**
W66	D-mannit	5.00E-02	6.60E-06	1.05E-06	10.9	-13.73	-14.51	**-14.12**
		[Carbamid$^-$]						
W53	Urea	1.00E-05	9.80E-06	1.04E-05	10.95	-13.56	-13.52	**-13.54**
W56	Urea	1.00E-04	1.44E-05	7.80E-06	11.0	-13.39	-13.64	**-13.52**
W59	Urea	5.00E-04	1.35E-05	6.95E-06	11.0	-13.41	-13.69	**-13.55**
W62	Urea	3.00E-03	1.10E-05	6.40E-06	11	-13.5	-13.73	**-13.62**
W65	Urea	1.00E-02	8.50E-06	6.00E-06	11	-13.61	-13.76	**-13.69**
W68	Urea	5.00E-02	7.80E-06	5.64E-06	11	-13.67	-13.78	**-13.73**

TABLE A3
(continued)

N	ligand	[Ligand]	[Ca], M	[Si], M	pH	log R_{Ca}	log R_{Si}	log R_{avg}
		[Mannitol]$_{tot}$						
62-1	Mannitol	2.00E-06	6.50E-06	8.50E-06	10.80	-13.38	-13.27	**-13.32**
62-2	Mannitol	2.00E-05	7.00E-06	7.40E-06	10.90	-13.34	-13.32	**-13.33**
62-3	Mannitol	1.00E-04	5.60E-06	7.68E-06	10.87	-13.44	-13.31	**-13.37**
62-4	Mannitol	1.00E-03	6.50E-06	6.70E-06	10.81	-13.38	-13.36	**-13.37**
62-5	Mannitol	1.00E-02	8.40E-06	7.09E-06	10.87	-13.27	-13.34	**-13.30**
62-6	Mannitol	0.03	9.00E-06	7.10E-06	10.84	-13.24	-13.34	**-13.29**
62-7	Mannitol	0.10	9.50E-06	ND	10.95	-13.22	ND	**-13.22**
62-8	Mannitol	0.30	8.40E-06	ND	10.88	-13.25	ND	**-13.25**
		[H-Glucosamine]. M						
61-1	Glucosamine	1.00E-05	3.00E-05	3.30E-05	7.07	-12.69	-12.65	**-12.67**
61-2	Glucosamine	1.00E-04	3.05E-05	3.23E-05	7.04	-12.70	-12.67	**-12.68**
61-3	Glucosamine	1.00E-03	4.19E-05	3.50E-05	7.02	-12.57	-12.65	**-12.61**
61-4	Glucosamine	5.00E-03	4.02E-05	3.76E-05	6.99	-12.59	-12.62	**-12.61**
61-5	Glucosamine	0.01	4.09E-05	4.06E-05	6.88	-12.60	-12.60	**-12.60**
61-6	Glucosamine	0.02	3.25E-05	3.47E-05	6.89	-12.70	-12.67	**-12.69**
61-7	Glucosamine	0.05	3.10E-05	3.30E-05	6.78	-12.70	-12.67	**-12.68**
61-8	Glucosamine	0.10	3.21E-05	3.42E-05	6.58	-12.70	-12.67	**-12.69**
		Carboxylic groups						
60-1	1 mg/L Alginate	4.00E-06	2.16E-05	1.81E-05	6.95	-12.80	-12.88	**-12.84**
60-2	10 mg/L Alginate	4.00E-05	2.18E-05	1.74E-05	6.95	-12.82	-12.92	**-12.87**
60-3	100 mg/L Alginate	4.00E-04	2.01E-05	1.66E-05	6.86	-12.85	-12.93	**-12.89**
60-4	200 mg/L Alginate	8.00E-04	1.94E-05	1.72E-05	6.95	-12.87	-12.92	**-12.90**
60-5	400 mg/L Alginate	1.60E-03	1.80E-05	1.70E-05	6.82	-12.91	-12.93	**-12.92**
60-6	1 g/L Alginate	4.00E-03	ND	6.18E-05	7.09	ND	-12.96	**-12.96**
60-7	2 g/L Alginate	8.00E-03	ND	1.32E-04	7.05	ND	-12.95	**-12.95**
		[Pectin]$_{tot}$. M						
P_1	50 mg/L Pectin	7.69E-07	1.74E-05	1.78E-05	5.96	-12.48	-12.47	**-12.48**
P_2	500 mg/L Pectin	7.69E-06	1.80E-05	1.72E-05	5.97	-12.49	-12.51	**-12.50**
P_3	2,5 g/L Pectin	3.85E-05	2.00E-05	2.12E-05	6.05	-12.49	-12.47	**-12.48**
P_4	5 g/L Pectin	7.69E-05	1.52E-05	1.72E-05	6.12	-12.62	-12.57	**-12.59**
P_5	10 g/L Pectin	1.54E-04	2.35E-05	2.18E-05	6.08	-12.61	-12.65	**-12.63**
P_6	15 g/L Pectin	2.31E-04	2.08E-05	2.02E-05	6.10	-12.64	-12.65	**-12.64**
	Pectin = Polygalacturonic acid methyl ester, Mr = 30,000-100,000: we postulate Mr = 65,000							
W71	0.05 g/L Pectin	7.69E-07	5.10E-06	3.10E-06	7.75	-12.71	-12.91	**-12.81**
W74	0.5 g/L Pectin	7.69E-06	4.90E-06	3.40E-06	7.65	-12.74	-12.87	**-12.81**
W77	2.5 g/L Pectin	3.85E-05	4.40E-06	3.70E-06	7.75	-12.83	-12.84	**-12.84**
W80	5 g/L Pectin	7.69E-05	4.30E-06	4.00E-06	7.85	-12.83	-12.82	**-12.83**
W83	15 g/L Pectin	2.31E-04	4.80E-06	4.40E-06	7.8	-12.89	-12.89	**-12.89**
W86	50 g/L Pectin	7.69E-04	9.90E-06	1.89E-05	7.85	-13.39	-13.07	**-13.23**
		[Gum_Xanthan]$_{tot}$. M						
X_1	50 mg/L Gum Xanthan	0.000005	1.00E-05	1.02E-05	7.64	-12.66	-12.65	**-12.66**
X_2	500 mg/L Gum Xanthan	0.00005	1.05E-05	1.30E-05	7.45	-12.64	-12.55	**-12.60**
X_3	2.5 g/L Gum Xanthan	0.00025	3.61E-05	3.15E-05	7.45	-12.25	-12.31	**-12.28**
X_4	5 g/L Gum Xanthan	0.0005	5.00E-05	4.40E-05	7.37	-12.21	-12.26	**-12.23**
X_5	10 g/L Gum Xanthan	0.001	2.44E-04	2.51E-04	7.41	-12.00	-11.98	**-11.99**
X_6	15 g/L Gum Xanthan	0.0015	3.15E-04	2.86E-04	7.50	-11.77	-11.81	**-11.79**
	Gum Xanthan from *Xanthomonas campestris*:; Mr = 10,000 is postulated							

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