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DISSERTATION

DISSOLUTION CHEMISTRY OF FINE-TEXTURED BASALTIC MATERIALS (LUNAR SIMULANTS)

Submitted By

James P. Oglesby

Soil and Crop Sciences Department

In partial fulfillment of the requirements
for the degree of Doctor of Philosophy
Colorado State University
Fort Collins, Colorado
FALL 1999

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED BY JAMES P. OGLESBY ENTITLED DISSOLUTION CHEMISTRY OF FINE-TEXTURED BASALTIC MATERIALS (LUNAR SIMULANTS) BE ACCEPTED AS FULFILLING IN PART THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Committee on Graduate Work

E. A. Kelly

Kenneth G. Doxtader

Robert E. Lee

P. N. Soltanpour
Advisor

Department Head

ABSTRACT OF DISSERTATION

DISSOLUTION CHEMISTRY OF FINE-TEXTURED BASALTIC MATERIALS (LUNAR SIMULANTS)

The dissolution chemistry of basaltic lunar-soil simulants in water, dilute acids, or dilute carboxylate solutions at near-neutral pH was explored. The silt-textured simulants examined include JLS-1 (Johnson Space Center Lunar Simulant-1) and MLS (Minnesota Lunar Simulant). JLS-1, i.e., JSC-1 (McKay et al., 1994), is similar to Apollo 14 Sample 14163 and is a simulant of basaltic materials of lunar highlands which are rich in K, rare earth elements, and P, i.e., KREEP basalts. MLS is similar to Apollo 11 Sample 10084 and is a simulant of Ti-rich lunar mare soils (Weiblen and Gordon, 1988).

Future dissolution studies of lunar simulants are proposed, which could support development of bioregenerative life support systems for a permanently inhabited lunar launch site and test bed for planetary exploration. The utility of comprehensive soil extraction tests like the AB-DTPA test (Soltanpour, 1991) in these studies is also discussed.

James P. Oglesby
Soil and Crop Sciences Department
Colorado State University
Ft. Collins, CO 80523
FALL 1999

ACKNOWLEDGEMENT

To people of many colors and genders
Who stepped forward and dug their heels in
Making it possible ultimately
For me to have this chance.

And, to Mother Earth
My guardian and confidant.

James P. Oglesby

DISSOLUTION CHEMISTRY OF FINE-TEXTURED BASALTIC MATERIALS (LUNAR SIMULANTS)

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DISSOLUTION CHEMISTRY OF FINE-TEXTURED BASALTIC MATERIALS (LUNAR SIMULANTS)

SUMMARY

DISSOLUTION CHEMISTRY OF FINE-TEXTURED BASALTIC MATERIALS (LUNAR SIMULANTS)

The dissolution chemistry of basaltic lunar-soil simulants in water, dilute acids, or dilute carboxylate solutions at near-neutral pH was explored. Lunar simulants are terrestrial materials with chemical composition, mineralogy, and particle size distribution similar to lunar soils. Plant nutritional and toxicity character of the simulants was evaluated. These activities are in keeping with interests of the space science community, in assessing and planning use of lunar soils in bioregenerative life support systems of a permanently inhabited lunar launch site and test bed for planetary exploration.

The simulants examined include JLS-1 (Johnson Space Center Lunar Simulant-1) and MLS (Minnesota Lunar Simulant). JLS-1 is similar to Apollo 14 Sample 14163 (see discussion in McKay et al., 1994). It is a simulant of basaltic materials of the lunar highlands which are rich in K, rare earth elements, and P, i.e., KREEP basalts. JLS-1 is manufactured from an Arizona basaltic ash, by sieving to the particle size distribution of the similar lunar soil. MLS is similar to

Apollo 11 sample 10084 and is a simulant of Ti-rich lunar mare soils (Weiblen and Gordon, 1988). It is ground from a hornfels rock material found in Minnesota.

Solubility controls were determined for JLS-1 suspensions (1:2, solid:solution, by weight) containing HCl to vary the pH, after equilibrating on an orbital shaker in the presence of gases at earth-atmospheric levels. The solubility controls at alkaline pH appeared to be a Ca,Mg-carbonate for Ca and Mg, and rhodochrosite for Mn. The carbonates could have precipitated in a process in which alkaline earths were released upon acidification, and alkalinity associated with subsequent silicate and oxide hydrolysis eventually precipitated the alkaline earths. The carbonate minerals were likely present even in suspensions of relatively unweathered MLS, but not in amounts required to support equilibrium dissolved levels. With respect to Mn, rhodochrosite is perhaps the predominant control in most aqueous environments. For Al, $Al(OH)_3(am)$ was often the control in suspensions to which small amounts of acid were added.

In another experiment, MLS was weathered in reactors containing 0.5 g of MLS, thymol disinfectant, and 25 ml 1 mM carboxylate: citrate, malate, oxalate, succinate, glycolate, acetate, propionate, butyrate, or valerate. Solution pH values were adjusted to neutral before adding MLS, to eliminate acidity effects. Statistical analysis of Si dissolution revealed three classes of carboxylates with significantly different members (α=0.10). They were (a) a volatile carboxylate class (butyrate, valerate), (b) a weak carboxylate class (oxalate, succinate, glycolate, acetate, propionate), and (c) a strong carboxylate class (citrate, malate). In spite of these differences, Si solubilities after 81 d were comparable in all suspensions and roughly equal to that for quartz, i.e., amounts of Si that dissolved in the period from 10 to 81 d were least in the suspensions containing the strongest carboxylates. Si dissolution kinetics were "parabolic" and appeared to approach linearity for the weakest carboxylates, and rectangularity for the strongest carboxylates. The Ca and Mg dissolution in the period from 10 d to 81 d paralleled the Si behavior. Solution Si-quartz appeared to limit their solubilities.

In contrast to the other carboxylates which behaved predictably based on their binding constants with multivalent cations, oxalate, which was expected to be a strong ligand, behaved comparably with weak ligands. This may have been due to limitations in surface reactivity that arise through its interactions with surfaces. Oxalate forms binuclear complexes with pairs of trivalent metals, which could essentially divide its binding affinity, and also oxalate precipitates with multivalent metals, like Ca^{2+}, perhaps to yield coatings which impede weathering.

Future dissolution studies with simulants could be valuable in engineering the bioregenerative life support systems (BRLSS) for a lunar launch site for planetary exploration, in particular to engineer the BRLSS soil subsystems. Simple experiments with simulants can be completed to develop methods for stabilizing lunar soils to make them like terrestrial materials, and for modifying or augmenting the soils so that they provide ample plant nutrition.

Based on AB-DTPA (ammonium bicarbonate-diethylenetriaminephenylacetate) extraction testing (Soltanpour, 1991) of JLS-1, a simulant for lunar highland KREEP basalts, lunar soils are expected generally to be deficient in K, and without use of KREEP materials, usually in P as well. Lunar soils are also likely to be deficient in micronutrient cations like Zn^{2+} and Cu^{2+} that have volatilized into and ultimately from the thin lunar atmosphere. Possible K sources include KREEP basalts, felsites, or granites, for which a K extraction procedure may need to be developed. In all cases, the extracted K could be loaded to exchangers that ensure timely availability. Substantial work has been accomplished on exchangers, e.g., zeolites manufactured from simulants (Ming, 1989). Additional work could develop methods for synthesizing other exchangers from simulants, and determine good conditions for synthesis. Micronutrient coprecipitates with P, e.g., apatite (Gruener, Ming, et al., 1997) or Si are possible sources for the potentially deficient micronutrients.

Extractants like AB-DTPA which are commonly used for testing agricultural soils would be valuable in assessing nutrient availability from BRLSS soil subsystems, and for determining optimum size of subsystem components, i.e., fertilizer solids and exchangers. The extractants could even be used to test the lunar soils from the Apollo missions, to provide information for selecting the initial lunar base site and checking the results of simulant research.

The usable products of these dissolution studies are protocols for screening lunar soils that might be used for preparing and monitoring the BRLSS soil subsystems when they are used for growing plants. The knowledge base from dissolution studies of simulants of lunar and planetary soils can provide decision-makers with some of the evidence to show that space exploration and inhabitation efforts would be successful.

INTRODUCTION AND MATERIALS/METHODS

1.0 INTRODUCTION

The goal of this work is to examine the dissolution chemistry of basaltic lunar-soil stimulants, which includes characterization of solubility controls for major elements. Lunar-soil simulants are terrestrial materials with chemical composition, mineralogy, and particle size distribution similar to lunar soils. When the solubility controls of simulants have been characterized, basalt solution compositions can be predicted with the aid of geochemical speciation models such as MINTEQA2, and these predictions perhaps related to lunar soil solutions.

Early parts of this work were funded by NASA (Lindsay and Sadeh, 1992; Oglesby, Lindsay, and Sadeh, 1996), with a goal of beginning to assess suitability and plan use of lunar regolith materials as plant growth media, for life support systems of a permanently inhabited lunar launch site and test bed for planetary exploration. Research in this area at Colorado State University (CSU) began with efforts by R. Baker and W.L. Lindsay in the early 1970's, to see if lunar soils could support plant growth (Fig. 1). Related efforts continued into the 1980's and 1990's with work by W.Z. Sadeh and his colleagues to conceptualize life support systems and structural components for a lunar base (Cornett, Sadeh et al., 1994; Sadeh et al., 1996). Early ideas of NASA scientists and collaborating academics on space agriculture and bioregenerative life support systems (BRLSS) are documented in Lunar Base Agriculture: Soils for Plant Growth (e.g., Ming et al., 1989). D.W. Ming, a CSU alumnus, has led NASA and contractor efforts over the last decade, to study soil and nutrient supply subsystems for the lunar BRLSS (e.g., Ming and Lofgren, 1989; Gruener, Ming et al., 1997). In keeping with these scientific interests, plant nutrition and toxicity are addressed in this work.

Dissolution effects of pH are examined, especially effects from addition of acid. Acidity is certainly one of the more important weathering and formative agents of soils, arising from the CO_2 and exudates of plant roots and soil microbes. Dissolution effects of carboxylate ligands at near-neutral pH are also examined. Carboxylates/carboxylic acids are generally the major organic exudates by roots and soil microbes. The number of carboxylates is large, and grouping them into statistical classes based on similarities in extent of weathering could have the benefit of systematizing research.

Much of the baseline used in this work for the inorganic chemistry of terrestrial soils is found in Willard Lindsay's Chemical Equilibria in Soils (1979). This classic work documents what was known by earth scientists about soils in the late 1970's and early 1980's, and presents some concepts that have become important theories, as well. These include phosphate equilibria (Lindsay, 1979), metal chelate equilibria (Lindsay, Hodgson, and Norvell, 1967), and pe+pH as a redox parameter (Sadiq and Lindsay, 1978). Lindsay's book has presented a unified schema that allows soils to be examined systematically. One of the purposes of this work is to see if basaltic simulants have similar solubility controls to those documented or hypothesized by Lindsay, for soils.

The elements addressed in this work include major mineral elements (>0.1 wt. %): Ca, Mg, Si, Al, Fe, Mn, and trace elements important to plant nutrition, including Zn and Cu. Cr and Ni were also considered, since lunar soils contain high levels relative to terrestrial soils (Hossner and Allen, 1989).

The carboxylates considered include citrate, malate, oxalate, succinate, propionate, butyrate, valerate, acetate. Citrate, malate, succinate, and acetate are citric-acid-cycle intermediates, and oxalate is an important microbial exudate, especially from fungi. Propionate, butyrate, and valerate are fermentation products commonly present in sites of decomposition. Little is documented on the dissolution effects of these carboxylates.

Artificial ligands, e.g., DTPA, were also considered. The utility of an extraction method, like the AB-DTPA test

(Soltanpour, 1991), as a systems analysis tool for study of soil systems for growing plants, is discussed. Extractions can reveal availability and toxicity of elements that normally have solubilities below or near detection limits of analytic instruments, e.g., inductively coupled plasma spectrometers. Extraction tests have special merit in study of regenerative life support systems for space exploration, since they allow screening of soil-medium components, sizing of these components, and monitoring of soil-medium quality. This great utility as a systems engineering aid is possible because the tests are simple but comprehensive, and only small amounts of soil are required.

The succeeding chapters include discussion of simulant materials (Ch. 2), general methods (Ch. 3), dissolution results and expectations for lunar materials (Ch. 4,5,6), and suggestions for future simulant dissolution work (Ch. 7), with space exploration goals in mind. Some of the results and discussions are presented in the form of papers. Tables, figures, and references are located at the end of each chapter, and a complete bibliography is given at the end of this work.

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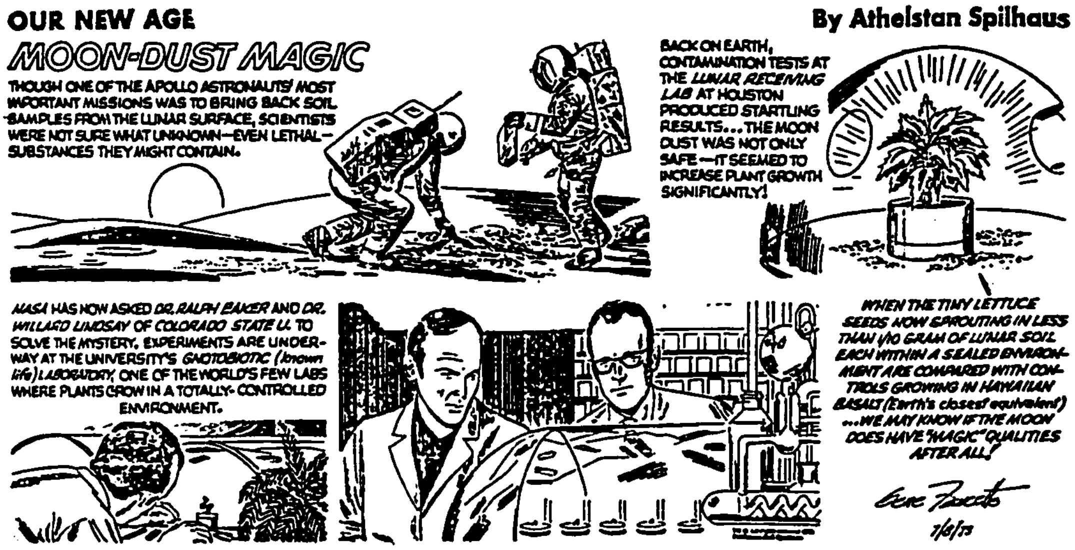

Fig. 1.1 Lunar Soil for Growing Plants: Early Work at Colorado State University

2.0 SIMULANT MATERIALS

2.1 Characteristics

Simulants have been used in dissolution studies since lunar soils are considered national treasures and limited in availability. Simulants are manufactured from terrestrial materials with chemical and mineralogical characteristics similar to lunar soils, typically by grinding and sorting to matching particle size distributions. Some of the simulants that have been used in geochemical or plant nutrition research relating to lunar soils include Minnesota Lunar Simulant (MLS), Lunar Basaltic Glass Simulant (LBGS), and Johnson Space Center Lunar Simulant-1 (JLS-1). MLS and JLS-1 were used in this work.

MLS is similar to Apollo 11 Sample 10084 and other lunar mare soils, which often have high Ti contents (>5 wt.%) (Weiblen and Gordon, 1988) (Table 2.1). This simulant is manufactured from a basaltic hornfels of the Duluth Complex in Minnesota. Major minerals in the hornfels include plagioclase (42 wt.%), pyroxene (27%), magnetite-ilmenite (14%), and olivine (6%) (Goldich, 1970). Biotite is also present in small amounts (Weiblen and Gordon, 1988).

LBGS is produced by Corning Company, by heating batch materials at temperatures near 1500°C in a nitrogen-purged furnace to maintain reducing conditions (Eick et al., 1996a). It has a basaltic chemical composition and high Ti content, like MLS. As with MLS and JLS-1, or any relatively unweathered basaltic material, the Fe in LBGS is primarily in the ferrous state.

JLS-1 (i.e., JSC-1; McKay et al., 1994) is an analog for Apollo 14 Lunar Sample 14163 and other low-Ti basaltic materials (<<5 wt.%). (See Table 2.1.) It is produced from ash of the San Francisco Volcanic Field near Flagstaff, Arizona. Approximately 50% of JLS-1 volume is glass. Glass content of most lunar soils is roughly similar; they typically contain 25 to 30 volume percent agglutinates and 5 percent glass particles. (See data in McKay et al., 1991.) The nonglass volume of JLS-1 is comprised largely of plagioclase, pyroxene, olivine, oxides including ilmenite, and small amounts of clay (McKay et al., 1994). JLS-1 is relatively rich in K and P like the lunar highland soils and rocks that have been classified as KREEP materials. (KREEP is a composite acronym for elements present at elevated levels: K, Rare Earth Elements, and P.) McKay et al. (1994) categorize JLS-1 as a simulant for mare soils, which is questionable since JLS-1 is more like highland KREEP basalts.

JLS-1 has been altered by weathering processes much more substantially than MLS, and as a result, contains measurable amounts of oxidized elements and calcite. JLS-1 could be considered a simulant of lunar soils that are altered in oxidizing, CO_2-charged environments.

2.2 Differences Between Simulants and Lunar Materials

Simulants and lunar soils have important differences which should be considered in interpretating dissolution study results. These include differences in chemical content, stability, and redox state.

Simulant compositions of major (wt.%>1.0) and minor elements (0.1<wt.%<1.0) are for the most part similar to those of their lunar counterparts. One exception is that simulant alkali metals are relatively elevated (Table 2.1). Also, some trace cationic elements (wt%<0.1) are enriched, e.g., Zn and Cu (Table 2.1). These apparently enriched levels are actually typical for the terrestrial materials; they are higher than those for lunar soils in which volatilization processes have caused major depletions. A substantial fraction of alkali metals escaped during the high-temperature events that formed the moon (Haskin and Warren, 1991) and also presumably in the subsequent micrometeoroid bombardment events and even in the interim periods. The trace elements are depleted to the extent that their content in lunar materials is in the µg/g or ng/g level. Haskin and Warren (1991) classify these trace elements (Cu, Zn, As, Se, Ag, Cd, In, Te, Hg, Tl, Pb, Bi, and the halogens) as "vapor-mobilized elements". Of these, K and Zn are commonly in short supply as plant nutrients from calcareous terrestrial soils, even without substantial volatilization. Nutritional shortages of these elements then, in lunar soils, could be potentially severe.

Simulants are more weathered than lunar soils. This is evident in the presence of substantial proportions of oxidized elements, and trace amounts of secondary minerals, including carbonates and phyllosilicates. JLS-1 is the most weathered, and could be considered a simulant of lunar soil altered in an oxidizing, CO_2-charged environment, as mentioned previously. JLS-1 contains roughly $10^{-2.0}$ moles of carbonate per kg, measured in this work with CO_2 entrapment methods. These measurements are discussed in Chapter 4. Ca-carbonate minerals like these are expected with weathering of lunar soils in CO_2-charged environments, since they are rich in Ca. Highland soils contain an average of 10% Ca as oxide equivalent, and mare soils, 8% (Haskin and Warren, 1991).

Because they are more weathered, the simulants are more stable than lunar soils would be initially in oxidizing, CO_2-charged environments. Lunar soils are considered highly unstable when wetted under these conditions, because they are glass-rich, radiation-altered, and highly reduced (Whitney, 1991). Alteration by radiation includes effects of bombardment by solar-wind particles, solar-flare particles, and galactic cosmic rays (McKay et al., 1991). Solar-wind particles, i.e., plasma emissions from the sun, cause the most change, rendering grain surfaces amorphous to depths of several hundred nanometers.

Simulants are more oxidized than lunar soils. Simulants contain substantial amounts of Fe(III), which is absent from lunar materials. Lunar materials are rich in Fe(II) and also contain small amounts of Fe metal. Titanium in simulants is limited primarily to the IV state, while lunar soils contain as much as 30-40% in the III form (Papike et al., 1991). Similarly, most simulant Cr is in the III state, while a substantial fraction of lunar Cr can be in the II form (Papike et al., 1991) much present as a substituent in olivines and pyroxenes. Even with these differences, the minerals that precipitate and ultimately control solubility in moderately oxidizing solutions can be the same. For example, ferrihydrite is the expected Fe-oxyhydroxide, if reduced Fe dissolves in slightly alkaline solutions containing small amounts of dissolved Si or organic matter. (See discussion on Fe solids in Schwertmann and Taylor, 1988).

Sulfur contents of simulants and lunar soils can be similar, e.g., between 0.1 and 0.2% (wt) for MLS and its lunar counterpart (Goldich, 1970), but the S in the lunar materials is more reduced. Even so, the amounts of reduced S, mostly in FeS (troilite) (Papike et al., 1991) are typically small relative to sulfide amounts required to generate acid-sulfate soils. Most often, unstable silicates and oxides of lunar soils are expected to set the initial dissolution pH at basic values. This expectation is supported by dissolution results for actual lunar soil, by Keller and Huang (1972). In their work, dissolution in water yielded slightly alkaline pH values even when the amount of carbonate acidity was relatively great. The dissolution results for MLS which follow are also corroborative of the expectation for basicity in the most common case.

2.3 Previous Simulant Dissolution Studies

Most of the works to investigate dissolution properties of lunar soils have utilized simulants. Several early dissolution studies utilized actual lunar soils (Keller and Huang, 1971; Mason et al., 1970).

2.3.1 Previous Dissolution Studies of Lunar Soils

The study of Keller and Huang (1971) examined dissolution of small amounts of lunar soil in suspensions containing water equilibrated with atmospheric CO_2, over an 81-d period. Suspensions were diluted to a low value, 1:500 (solid:water wt.), since amounts of available lunar soil were very limited, and presumably since dilution allows examination of reaction kinetics, rather than equilibria. pH increased from the original slightly acid values associated with water, to slightly alkaline final values near 7.4. As mentioned previously, apparently the basicity from dissolution of silicates and oxides exceeded the acidity from carbonic acid and from oxidation of Fe and S. Near-equilibrium was reported for relatively insoluble minerals, e.g., kaolinite (Al), whereas this condition was not attainable for soluble minerals like calcite (Ca). Total dissolution amounts for each of the major cations after 81 d were somewhat similar to amounts dissolved from a pulverized terrestrial basalt of the same texture.

In other suspensions of lunar soil or terrestrial basalt, which contained 0.01 M acetic acid or 0.01 M salicylic acid, lunar dust dissolution was greater than that for a pulverized basalt, by roughly 2.5 times. Based on their experiments, the authors concluded that nutrients would be readily available from lunar soils.

In other research, Mason et al. (1970) added lunar soil to water and found that large amounts of Ca dissolved, relative to the other elements. This is expected since the lunar soils are unstable glasses derived predominantly from Ca-rich feldspars, in which the Ca has not been stabilized by weathering processes such as carbonation.

2.3.2 LBGS and MLS

Dissolution studies for LBGS are documented in Eick et al. (1996a). The work examined dissolution kinetics over a 1-year period in suspensions buffered at pH 3, 5, and 7, and in suspensions containing 2 or 20 mM oxalate or citrate at pH 7. Rates of Si release relative to that at pH 7 (without carboxylates) appeared to be roughly 5 times greater at pH 5, and 10 times greater at pH 3. Oxalate and citrate ligands at the 20 mM level at pH 7 each enhanced Si dissolution rates comparably with the acidity in suspensions of pH 5, i.e., by roughly 5 times. Dissolution kinetics in organic solutions were found to be parabolic (i.e., rate directly proportional to the square root of time), while kinetics in inorganic acid suspensions were initially parabolic and linear in the long term, in the period after 1 to 2 months. Similar results which include rate constants are reported for MLS in Eick et al. (1996b).

In the work by Golden et al. (1994), solids from LBGS suspensions in water (pH=7.0) or 0.05 M HCl (pH=1.3) were examined after a 3.5-year incubation period with use of Fourier transform infrared spectroscopy, scanning electron microscopy, electron microprobe analysis, x-ray diffraction, and high resolution transmission electron microscopy. No new mineral phases were observed. Smectites and zeolites were evident, however, in solids of suspensions subject to hydrothermal conditions.

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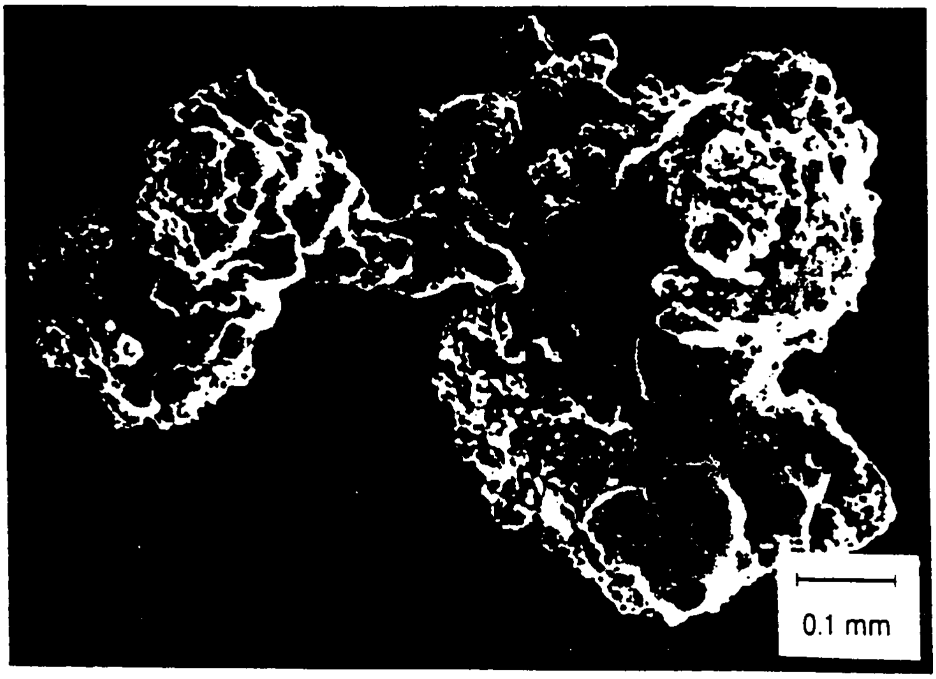

Fig. 2.1 Lunar Soil: Agglutinate Particle

(from McKay et al., 1991)

Table 2.1 Composition of Simulants and Lunar Soils from Apollo Missions

(a) Major Element (>1.0 wt.%) and Minor Element (>0.1%, <1.0%) Content

Weight Percentage

	JLS-1 a)	Apollo 14 14163 b)	Apollo 14 S&B c)	MLS d)	Apollo 11 10084 d)	Apollo 11 S&B c)
SiO_2	48.2	48.0	48.1	43.9	42.6	42.0
Al_2O_3	15.2	17.6	16.7	13.7	13.5	12.6
FeO	7.4	10.4	9.5	13.4	15.2	16.4
CaO	10.5	11.2	10.7	10.1	12.0	11.7
MgO	9.1	9.2	10.2	6.7	8.0	7.9
TiO_2	1.6	1.8	1.5	6.3	7.7	7.9
Fe_2O_3	3.5	0.0	0.0	2.6	0.0	0.0
Na_2O	2.7	0.7	0.7	2.1	0.4	0.5
K_2O	0.8	0.6	0.4	0.3	0.1	0.2
MnO	0.2	0.1	0.1	0.2	0.2	0.2
P_2O_5	0.7	0.5	0.4	0.2	0.1	0.1
TOTAL	99.9	100.1	98.3	99.5	99.8	99.5

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a) McKay et al., 1994. Loss on ignition subtracted.

b) Morris et al., 1983.

c) Haskin and Warren, 1991. S&B = soils and breccias. Apollo 14 data for SiO_2, Al_2O_3, FeO, CaO, MgO, TiO_2, and Na_2O is for breccias only.

d) Weiblen and Gordon, 1988.

(b) Content of Selected Trace Elements

ppm

	JLS-1 a),b)	Apollo14 S&B c)	MLS d)	Apollo 11 S&B c)
Cr	277 (274)	1496	173	1986
Sr	910 (860)	184	212	163
Zn	197 (NA)	27	122	25
Ni	191 (137)	411	97	199
Cu	90 (NA)	NA	445	12

NA = not available

a) Analysis of digest

b) Values enclosed in parentheses from McKay et al., 1994.

c) Haskin and Warren, 1991. Cu value is average of 2 values.

d) Weiblen and Gordon, 1988.

3.0 GENERAL METHODS

General methods are discussed in this section, while variations and additional procedures are given in sections which follow.

3.1 Dissolution Experiments to Examine Solubility Controls

All dissolution experiments were completed with use of batch reactors which were shaken on an orbital shaker at 3 cps. One part simulant and two parts water, by weight, were added to the reactors, which were then shaken, usually in the the presence of CO_2 and O_2 at near earth-atmospheric levels. The partial pressure of CO_2 was calculated from alkalinity titrations, discussed later in this chapter. The one-to-two ratio has been used by Lindsay and his coworkers over several decades (e.g., Workman and Lindsay, 1990), with experimental results often showing near-equilibrium for solubility controls of major elements, when the dissolution times were from days to weeks. Solution volumes were usually selected such that solids remained suspended during shaking. Reactors were covered with perforated parafilm, to prevent entry of particulates, while allowing entry of atmospheric gases, and water was added periodically to maintain suspension weights.

0.5N HCl was added in very small amounts to vary the pH of initial weathering suspensions, and suspensions were shaken for times up to 5 months. Three weeks was considered the reference time period for many of the experiments. Calculated CO_2 partial pressures for suspensions of different pH reached nearly constant values within this time.

3.2 Dissolution Experiments to Examine Kinetics

A low simulant-to-solid ratio (1:50, by weight) was used to examine simulant dissolution kinetics associated with carboxylates. This ratio is similar to those used in classical experiments in mineral weathering kinetics (e.g., 5.0:300 in Schott et al., 1981). Use of low ratios and gentle mixing maintains concentration gradients between weatherable surfaces and solution, so that rapid equilibration and precipitation of secondary solids is prevented, and dissolution behavior over time can be examined. The similarity or difference of these conditions from the natural ones should be considered in interpreting results.

A carboxylate concentration of 10^{-3} M was used. This concentration is within the range for many carboxylates in soil solution, 10^{-4} to 10^{-2} M (Huang and Violante, 1986).

The carboxylates selected for use included many commonly found as exudates: citrate, malate, oxalate, succinate, acetate, and glycolate (e.g., Riviere, 1960; Kraffczyk et al, 1984; Lee and Foy, 1986). Volatile carboxylates (propionate, butyrate, and valerate) were also included. The weathering effects of volatile carboxylates, which are often associated with sites of decomposition, have not been investigated as extensively as the other carboxylates. The binding affinities of these carboxylates for alkaline earths are significant; log stability constants of with alkaline earths (log(ML/M*L)) are typically greater than 1. (See Chapter 6.)

3.3 DTPA Extraction Tests

DTPA (diethylenetriaminepenta-acetic acid) soil tests were used to determine if simulants at various stages of weathering provide sufficient nutrients for plant growth. Initially, the test of Lindsay and Norvell (1978) was used for evaluation of Fe, Zn, Mn, and Cu, but later the AB-DTPA test of Soltanpour et al. (1977, 1979, 1991) was used, since it has been calibrated for additional elements including P and K, and is potentially useful for other solution species, including anions (Soltanpour, 1991; Miller and Donahue, 1990). The extracting solution for this test is 1.0 M NH_4HCO_3 and 0.005 M DTPA at pH 7.6.

3.4 Solution Analysis

To remove suspended solids prior to analysis, solution samples were centrifuged at approximately 5000 x g for 10 min and then filtered. This is adequate to sediment most particles with effective diameters less than 0.20 µm. Filters were Whatman cellulose-nitrate membrane filters with effective pore diameters of 0.20 µm. This is less than those of filters normally used for water and wastewater analysis, i.e., 0.45 µm (American Public Health Association et al., 1992). This procedure may not be adequate for settling out ferrihydrite particles, which are noted by Schwertmann and Taylor (1989) to be as small as several to tens of nm.

Solution elements of interest were analyzed with ICPS (inductively-coupled plasma spectroscopy). Detection limits for the elements of limited solubility were: Al (0.03 ppm), P (0.03), Cu (0.01), Zn (0.01), Mn (0.01), Ni (0.01), and Cr (0.01). Fe and Mn (0.01) can potentially be analyzed at much lower concentrations. Ca, Mg, and Si have low detection limits comparable with these elements, but did not need to be measured at levels below 0.10 ppm. (See Soltanpour et al., 1996, for a discussion about detection limits.) Activities of F^- and, in some cases, Ca^{2+}, were measured with Orion ion-selective electrodes. The detection limits given by Orion for F^- is near 1.0 ppm. The limit for Ca^{2+} can be lower than 1.0 ppm if electrodes are equilibrated for long periods and contamination is avoided. Sulfate was measured with ion chromatography or with turbidimetry (American Public Health

Association et al., 1992). Detection limits for these methods are approximately 1 ppm.

Inorganic alkalinity was calculated from the amounts of acid to titrate to pH 4.40 (Suarez et al., 1992). Contributions of silicic acid to alkalinity were also considered in these calculations.

3.5 Competitive Chelation Methods for Determining Free Metal Ion Activities

Competitive chelation methods have been used to estimate free metal ion activities in soil solutions. The early ideas that are the basis for these methods were conceived during collaborative efforts of Lindsay, Hodgson, and Norvell (1967) and later developed by Norvell and Lindsay (1982). Unfortunately, the host of researchers that worked with competitive chelation after Norvell and Lindsay (1982) did little to further develop this technique, with the possible exception of Vlek et al.(1974) who used dissolved elements to fix activities, e.g., dissolved Ca^{2+}, rather than added solids.

To complete the method, a constant amount of ligand (often EDTA or DTPA) loaded with varying mole fractions of the ion being estimated and a counterion with controlled solubility, is added to each of a series of pre-equilibrated solutions that contain the soil of interest. After several days to a week of shaking, the equilibrium mole fraction for the two ions is determined from a crossover point (Appendix

3.1). The equilibrium mole fraction is then used to compute the activity of the metal ion being estimated. These methods are thought to be especially useful for soil solutions in which activities are below detection limits of conventional instrumentation, or where a high degree of organic complexation prevents adequate speciation with geochemical models.

Though one of the original intents of this research was to utilize these methods, they were not used for several reasons. Weathering solution pH values in experiments were often in ranges from 4 to 9, so that activities below detection limits could sometimes be extrapolated from those which were just measurable at other pH values. Also, the extent to which natural, uncharacterized DOC complexes some of the metals of interest is known to be limited generally, so that geochemical speciation models can be used to estimate free metal ion activities. For example, Mn^{2+} complexes with DOC in very small proportion (e.g., Sunda, 1984), and Al only in large proportion at midrange pH values from 4.5 to 6.5, when DOC levels are high (>> 100 µmol C/L) (Driscoll, 1989). At alkaline pH values, Driscoll shows negligible proportions of dissolved Al complexed even with high C levels (1000 µmol C/L). This is consistent with work by La Zerte (1984) who showed Al-complexes unimportant to speciation in highly colored waters. Cu and Fe(III), in contrast to Mn and Al, are thought to be highly complexed with DOC in many natural waters, and are not likely to be accurately speciated with the geochemical models presently available.

Another reason that competitive chelation methods were not employed is that some important potential limitations in use of competitive chelation methods have not been explored (Oglesby, 1995; Appendix 3.1). When the dissolved molar amount of the metal of interest is orders of magnitude less than the amount of dissolved or adsorbed ligand, dissolved ligands or solids altered by adsorption can potentially be more important solubility determinants than the solids originally present. For example, DTPA, one of the more frequently used ligands, can be adsorbed in proportions as great as 50% in acid soils (Hill-Cottingham and Lloyd-Jones, 1958), and recent research suggests that DTPA adsorption by a soil can increase Cu solubility (Vulava et al., 1997).

3.6 Geochemical Modelling

MINTEQA2 (Lindsay and Ajwa, 1995; Allison et al., 1991) was used to calculate activities and concentrations of solution species, and saturation indices relative to common soil minerals. Input included component concentrations or activities, pH values, and ionic strengths. Ionic strengths were estimated from measured electrical conductivities with the formula of Griffin and Jurinak (1973):

I = 0.013 EC, where I = ionic strength in mol/L
EC = electrical conductivity in dS/m

Thermodynamic data for most solutions species and minerals are those screened and documented by Sadiq and Lindsay (1979) and Lindsay (1979). Important exceptions are noted in this work and summarized in Appendix A. Metal-carboxylate constants are taken directly from Smith and Martell (1977-1989), which in some cases required adjusting to "infinite dilution". Methods for this adjustment are discussed in Lindsay (1979).

3.7 Analysis of Weathered Solids

Weathered solids were, in some cases, analyzed for mineralogy with use of X-ray diffraction. Carbonate mineral amounts were estimated with a titration method. To obtain the solution for titrating, solid samples were acidified to release CO_2, which was trapped in 0.1 N NaOH over a 1 d period. CO_2 traps are discussed in Anderson (1982). Exchange capacities for alkaline soils were in some cases assessed with a variant of the method given in Rhoades, for calcareous soils (1996).

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DISSOLUTION OF SIMULANTS IN WATER AND HYDROCHLORIC ACID

4.0 DISSOLUTION OF SIMULANTS IN WATER AND HYDROCHLORIC ACID

This chapter discusses results of experiments in which MLS and JLS-1 were weathered in suspensions initially containing water or dilute HCl. Solubility controls for Ca, Mg, Al, Fe, and Mn are characterized and in some cases identified.

4.1 Possible Solubility Controls

Calcium

Calcium solubility can be controlled by calcite at alkaline pH and exchange solids at acid pH (Lindsay, 1979; Fig. 4.1). Calcite was expected to precipitate from the reaction of carbonate alkalinity with the Ca that dissolves from Ca-rich glassy materials and plagioclase of the simulants. Solutions of the simulants were expected to be supersaturated relative to calcite, which is the norm for soil waters and groundwaters. Numerous potential causes for this supersaturation have been documented. These include:

1) Evaporative concentration, release of carbonate alkalinity from organic matter decomposition, and inhibition of calcite precipitation by solution organics (Suarez et al., 1992)

2) Dissolution of high Mg-calcites which form under conditions of rapid precipitation (Busenberg and Plummer, 1989).

3) Carbonate alkalinity from dissolution of Mg/Na-silicates and equilibration of the associated base with atmospheric CO_2 (Levy et al., 1995)

4) Complexation of Ca with dissolved organics, which yields an increased apparent solubility when the complexation is not accounted for in modelling (Reddy et al., 1990). (Suarez et al. (1992) found Ca-organic complexes to be negligible.)

Magnesium

Activities of Mg^{2+} in calcareous soil solutions and groundwaters can often be plotted near a dolomite isotherm (Lindsay, 1979; Appelo and Postma, 1993). Since basaltic simulants have relatively high Mg contents compared to most weatherable materials that generate soils, greater Mg solubilities are perhaps attainable. A possible control with greater Mg solubility is amorphous sepiolite (Wollast, 1968; Christ et al., 1973; Levy, et al., 1995) a precursor of crystalline sepiolite. Sepiolite ($Mg_4Si_6O_{15}(OH)_2*6H_2O$) and a related Si mineral, palygorskite ($(Mg,Al,Fe)_4Si_8O_{20}*nH_2O$) are thought to form pedogenically under normal atmospheric conditions, from Mg-rich rocks, chiefly from primary minerals with chain structures (Singer, 1989). The simulants contain major amounts of pyroxenes, which are minerals of this type.

Manganese

Manganese solubility in alkaline weathering soil solutions under moderately oxidizing conditions is thought generally to be controlled by manganite (MnOOH) or rhodochrosite ($MnCO_3$) (Sadiq and Lindsay, 1978; Lindsay, 1979). The Mn solubility control which is favored depends on the pe+pH and the CO_2 partial pressure (Fig. 4.2), with manganite being favored at higher pe+pH and lower CO_2 partial pressure, and rhodochrosite otherwise.

Rhodochrosite may be less soluble than reported in Sadiq and Lindsay (1978) and Lindsay (1979)(-log K_{sp} = 10.1). Some commonly used constants are about 1 log unit less (Garrels et al., 1960; Robie et al., 1978). The value used in this research is -log K_{sp} = 11.0, selected by Garrels et al. (1960). Based on the notes found in Nordstrom et al. (1990), the -11.0 constant is associated with a crystalline carbonate, while the value reported by Lindsay (1979) is probably for a rapidly-precipitated synthetic carbonate.

Iron and Aluminum

The metals in trivalent form can be controlled by oxyhydroxides. Fe is the most difficult to speciate in alkaline waters, since it is often present primarily in complexes with organics which are not well-characterized. Al, in contrast, complexes proportionately much less with organics, particularly when the DOC level is low (Driscoll, 1989). (See the comments on Al speciation in Chapter 3.)

Fe solubility at alkaline pH can be controlled by ferrihydrite. Ferrihydrite is found where Fe(II) is oxidized and Si is moderately to strongly elevated (Schwertmann and Taylor, 1989), i.e., above 5 ppm or so, conditions evident in simulant suspensions.

Al solubility can be controlled by $Al(OH)_3$ in acidic to neutral natural waters. One of most comprehensive studies to show this is by Johnson et al. (1981), for surface waters of the Adirondak region. Numerous related analyses were subsequently completed by C.T. Driscoll and his colleagues, e.g., Driscoli and Bisgoni (1984), and widely reported.

At the alkaline pH values controlled by calcite and atmospheric CO_2, dissolved Al from $Al(OH)_3$ is not always detectable by ICP. Dissolution of gibbsite, for example in the absence of significant complexing at pH 8.3, can yield an equilibrium concentration of roughly 0.01 ppm, which is below ICP detection limits. $Al(OH)_3$(amorphous), on the other hand, is more than an order of magnitude more soluble and the dissolved Al is normally detectable.

4.2 Dissolution of MLS and JLS-1 in Water

4.2.1 XRD of MLS Solids

MLS, in contrast to JLS-1, is largely an unweathered material, ground from a Minnesota hornfels. MLS fines were examined with XRD to check for evidence of new secondary minerals. Fig. 4.3 shows XRD patterns for identical weights of MLS particles with effective diameters less than 85 µm, from suspensions equilibrated in water for 0 and 150 d. Peaks are evident for plagioclase, augite, ilmenite, and possibly magnetite, which are major original minerals. The peaks appear to decline in height over the 150 d period. Plagioclase peaks appear to decrease proportionately more than the augite peaks, which is consistent with the common observation that plagioclase weathers more rapidly than many common pyroxenes (Goldich, 1938; Birkeland, 1984).

No new peaks for secondary minerals are present, even after 150 d. Even so, some secondary minerals are likely present in greater amounts than originally, particularly carbonate and clay minerals. Consistent with low content of smectites, cation exchange capacities of JLS-1 and MLS remained at values less than 5 cmol/kg, which are typical of sandy soils (Miller and Donahue, 1990). Somewhat related results were reported by Golden et al. (1994) for a lunar glass simulant. No new mineral phases were detectable with XRD, after 3.5 years of dissolution in water at pH 7.0 (solid: solution = 1:100, by wt.).

4.2.2 Solubility

Solubility data for times up to 150 d are given in Table 4.1. A CO_2 partial pressure of 0.0003 atm is assumed. (Partial pressure was estimated in the other experiments in which pH was varied; they are discussed in pages which follow.)

Mg solubility from MLS was higher than from JLS-1 such that solubilities were eventually supersaturated relative to sepiolite(am), by roughly 0.5 log units. More data would be needed to check for stabilization of solubility. The major source of the Mg from MLS was perhaps Mg-olivine. Olivine is highly unstable, with weatherability comparable with fresh silicate glass (Dahlgren et al., 1993).

For both simulants, saturation indices relative to calcite appeared to stabilize at similar values associated with roughly 0.5 log units of supersaturation, and for JLS-1 the index relative to disordered dolomite appeared to stabilize. For MLS suspensions, equilibration relative to the carbonate minerals of interest appeared more rapid than for the silicate, sepiolite(am).

Fe concentrations (not shown in Table 4.1) ranged from 0.02 to 0.20 ppm. These concentrations can be shown roughly compatible with ferrihydrite solubility through use of MINTEQA2 modelling, if for example, -log K_{sp} is assumed to be 37.0, and organics are assumed to elevate Fe solubility by 100 times. This extent of organic complexing would be similar to that reported for Cu by Hodgson et al.(1966), i.e., an average factor of 99.0(std.dev.=0.8) for 20 soils. However, these solubility and complexation parameters may not be good approximations. Shwertmann and Taylor (1989) show -log K_{sp} values for ferrihydrite ranging widely from 37.0 to 39.4. And, the extent to which heterogeneous organics complex Fe is not known. The data only weakly support a hypothesis of ferrihydrite solubility control; another possibility is that unfiltered ferrihydrite particles yield the solution Fe.

4.3 Simulant Dissolution in Water or Acid

Weathering experiments were conducted in which initial pH values were varied in a series of dilute HCl solutions. After adding JLS-1, the suspensions were shaken for 3 weeks.

4.3.1 Calcium and Magnesium

Results for Ca and Mg dissolution from JLS-1 are shown in Fig. 4.4. The CO_2 partial pressure calculated from carbonate levels determined by titration is approximately 0.0005, for the points along the -2 slope. This value was calculated from the elevations in CO_3^{2-} activities relative to that expected for a CO_2 partial pressure of 0.0003. For the 4 rightmost points, the elevation is 0.21±0.04(std. dev.) log units.

The data in the figure suggests that the same Ca-carbonate mineral controls solution Ca, at the top and bottom of the -2 slope, from pH just greater than 8.0, to 8.5. For the rightmost points of pH 8.39 and 8.43, the latter associated with no acid addition, -log IAP values for $CaCO_3$ are 8.21 and 8.26. Based on the data in Busenberg and Plummer (1989) for $CaCO_3$ solubility, this Ca solubility is consistent with a high-Mg calcite having an Mg percentage, very roughly, in or near the range from 10 to 20%.

A percentage in this range seems to be in conflict with data of Fig. 4.4, since the rightmost points suggest about 40% Mg in a Ca,Mg-carbonate coprecipitate. However, the observation that the Mg points do not decline in parallel with Ca when its level begins to drop but do decline eventually, is more consistent with Mg adsorption to Ca carbonates, perhaps with limited coprecipitation. Preferential adsorption of Mg to a subset of carbonate particles could allow the Ca solubility control to remain the same over the pH range from 8.0 to 8.5. Observations of Miyamato and Pingitore (1992) are compatible with a hypothesis of this sort. Mg could be adsorbed to the larger carbonate particles. Smaller particles tend not to show Mg accumulations, which might be expected since Mg is an inhibitor of calcite precipitation.

Mg adsorption to calcite at alkaline pH is observed in seawater, which naturally has a pH near 8 (Berner, 1975). Mg adsorption could be expected to increase with pH at more alkaline values, as more Ca precipitates to form adsorbent, as amounts of solution Mg increase relative to Ca, and as Mg-carbonate complexation increases. Ca,Mg-solids formed in these processes in which Mg adsorption and coprecipitation increases with pH should show increasing Mg concentration away from centers of particles or coatings. This concentration gradient is in fact observed in electron microscopy observations, e.g., x-ray distribution maps of calcite particles reported by Miyamato and Pingitore (1992).

A process in which pH increases and Ca^{2+} activity decreases, and Mg^{2+} as well presumably, is shown in Fig. 4.5. Ca^{2+} activities in JLS-1 suspensions were measured at different times over 3 weeks, with an ion selective electrode. The top two set of points are associated with addition of HCl initially. Hydrolysis of silicates and oxides gradually increased the pH and alkalinity over time. With pH and HCO_3^- concentration increases, Ca^{2+} activities declined, as they approached the mineral carbonate line, and carbonate mineral precipitated. This type of trajectory is likely associated with important natural mechanisms for generating carbonate minerals. An example would be the flow of acidified rhizosphere solution to more alkaline regions, away from the rhizosphere. Another would be the flow of soil solution to more alkaline materials at greater depths.

The bottom set of points are associated with a suspension in water. The pH after 1 d is strongly alkaline. Hydrolysis associated with silicates or hydroxides is the important process initially controlling pH, more important than the countering processes that generate net acidity, e.g., oxidation of reduced S. Influx of CO_2 and the eventual buffering of pH with carbonate alkalinity did however decrease the pH as the solution composition approached equilibrium with calcite and carbon dioxide.

The carbonate mineral content of JLS-1, was quantified with a procedure in which acidification and CO_2 entrapment were utilized (Appendix 4.1). CO_2 entrapment is often used for soil "respiration" measurements (Anderson, 1982). The carbonate mineral content in JLS-1 was found to be approximately $10^{-2.0}$ mole/kg. This amount is equivalent to a solution concentration of $10^{-2.3}$ M, if the carbonate were to dissolve completely in a suspension containing one part solid and 2 parts solution.

Based on these results, Ca^{2+} activities at acid values (Fig. 4.4) reflect to large extent the complete dissolution of carbonates. The leveling and the activity limit between $10^{-2.0}$ and $10^{-2.5}$ are consistent with values of much more mature acid soils (Fig. 4.1) for which relatively constant Ca^{2+} activities are most often attributed to exchange (e.g., Lindsay, 1979).

The experiments with simulant dissolution in water, which were over longer time periods than these experiments with JLS-1, suggest that near-equilibrium with a carbonate mineral, i.e., Mg-calcite, is transitory (Table 4.1). In time, Ca^{2+} activities would reflect an increasingly supersaturated state. This would be from gradual pH increase with generation of base via the hydrolysis of silicates, and lack of precipitation, due to inhibitory factors, which include low concentrations of dissolved organics. Dissolved organics are strong inhibitors of calcite precipitation; for example, Inskeep and Bloom (1986) found concentrations greater than 0.15 mM C (approximately 2 ppm DOC) to be inhibitory. The level in a JLS-1 suspension equilibrated in water for 3 weeks (5 ppm) was greater than the threshold value. In this work causes for supersaturation relative to calcite appear to have included dissolution of metastable Ca carbonates and inhibition of calcite precipitation.

Results for MLS are shown in Fig. 4.6. Ca and Mg dissolved congruently. In contrast to the plot for JLS-1, a slope of -2 associated with a carbonate mineral is not apparent. Based on the previous discussion of Fig. 4.4 and 4.5, development of a -2 slope would require considerable acidification and release of alkaline earths, followed by reaction with alkalinity from weathering, to yield carbonate precipitate.

4.3.2 Aluminum

Calculated activities of Al^{3+} for JLS-1 are shown in Fig. 4.7. MLS results are limited to several values in the pH range from 4 to 5 (Appendix 4.2).

The values represented by X's in the pH range from 4 to 6 are not corrected for Al-Si complexation. Al^{3+} activities are consequently overestimated by up to 0.5 log units. The overestimation occurs in the pH range noted by Browne and

Driscoll (1992) over which complexation with Si can be proportionately most substantial.

Al solubilities at acidic pH values can be controlled by Al-sulfates, esp. jurbanite ($AlOHSO_4*5H_2O$) and alunite ($KAl_3(SO_4)_2(OH)_6$) (Nordstrom, 1982). The reference line for alunite included in Fig. 4.7 is based on a solubility reported in Nordstrom (1982), with $pK^+ + 2pSO_4^{2-} = 12$.

Al^{3+} activities were near the $Al(OH)_3(am)$ isotherm (Fig. 4.7) at pH values greater than 6. For some suspensions of similar pH values near and above neutral, Al was not detectable, suggesting that $Al(OH)_3$ may be created by acid addition. Reaction of dissolved Al and $Al(OH)_3(am)$, e.g., to form secondary Al-silicates, may normally depress Al^{3+} activities relative to $Al(OH)_3(am)$.

The $Al(OH)_3$ created by adding acid is likely in addition to amounts already present, since $Al(OH)_3$ is perhaps ubiquitously present in rapidly weathering materials, like JLS-1. Recent works show that $Al(OH)_3$ can be found on rapidly weathering surfaces, e.g., a feldspar in the study by Kawano and Tomita (1996).

pH can be varied to determine natural solubilities, but results for trace elements at low concentrations should be interpreted such that the possibility of artifactual controls is considered. Adding a small amount of acid may dissolve a small amount of Al so that $Al(OH)_3(am)$ precipitates.

Furthermore, abrupt or localized acid addition might yield precipitation which on the other hand might not occur with gradual or well-distributed addition.

4.3.3 Manganese

The Mn solubility plot for JLS-1 (Fig. 4.8) appears similar to that for Ca, with a -2 slope at alkaline pH values and a leveling in free metal ion activity at the lower pH values. The reference lines for Mn solubility at alkaline pH are for rhodochrosite, based on the solubility reported by Garrels (1960) ($-\log K_{sp} = 11.0$) and CO_2 partial pressures of 0.0003 and 0.0005 atm. The depression of points relative to the rhodochrosite isotherm is perhaps due in part to limited precipitation, in amounts which cannot support equilibrium dissolution levels.

The plot suggests that the solubility control at alkaline pH is rhodochrosite. At the higher pH values, the slope appears to decrease below -2, particularly at pH values greater than 8. This decrease could be due to coprecipitation of rhodochrosite with the Ca carbonate, which begins to precipitate measurably at pH values greater than 8 (Fig. 4.4). Similar to the behavior of Ca and Mg, the leveling at acid pH is due presumably largely to complete dissolution of the Mn secondary mineral.

If the Garrels constant is correct, rhodochrosite is a more common Mn solubility control than originally suggested by

Sadiq and Lindsay (1978b) and Lindsay (1979) (Fig. 4.2). With this constant, the pe+pH below which rhodochrosite would predominate over manganite is 15.0 when the partial pressure of CO_2 is 0.0005, and 16.0 when the CO_2 is elevated by an order of magnitude.

pe+pH values can be derived with the equations which follow. The assumption is a rhodochrosite-manganite system; manganite is present even when it is not predominant. The equation to calculate the pe+pH is

$$pe+pH = 18.3 + \log CO_2$$

which is derived from the following:

$MnOOH(s) + 3H^+ + e^- <-> Mn^{2+} + 2H_2O$ log K = 25.3 (Lindsay, 1979)

$Mn^{2+} + CO_2(g) + H_2O <-> MnCO_3 + 2H^+$ log K = -7.0 (Garrels, 1960)

$MnOOH(s) + H^+ + e^- + CO_2(g) <-> MnCO_3(s) + H_2O$ log K = 18.3

(The -7.0 value is equivalent to $-\log K_{sp} = 11.0$ for rhodochrosite, which accounts for the transformation of CO_2 to carbonate.)

Since most soil solutions have pe+pH values less than 16.0, the calculated 16.0 value for 0.005 atm CO_2 suggests that $MnCO_3$ may generally be the predominant mineral in soil systems in which biota are respiring. (The data of Sadiq and Lindsay (1978) shows pe+pH values from 16.0 to 16.5 to be extremes in Fe and Mn redox systems.)

Summary

The solubility controls for JLS-1 suspensions at alkaline pH appear to be metastable carbonate minerals for Ca and Mg, and perhaps rhodochrosite for Mn. $Al(OH)_3(am)$ can be the control for Al in slightly acidified solutions. These are somewhat different from those that could be predicted based on Lindsay (1979), i.e., calcite, ordered dolomite, manganite, and kaolinite. Metastable carbonates and $Al(OH)_3(am)$ are likely present ubiquitously in association with rapidly weathering silicate materials, often as controls of solubility for Ca, Mg, and Al. $Al(OH)_3$ is perhaps generally important as a control within and near the rhizosphere, where acidity is continually generated via biotic activity. Rhodochrosite is probably a more common control for Mn solubility than previously recognized by Sadiq and Lindsay (1978). It is perhaps the predominant control in most aqueous soil environments.

These solids are likely to form even in association with relatively unweathered materials like MLS, but are present initially in limited amounts that cannot support solution levels associated with equilibrium. To reach these levels would require extensive weathering.

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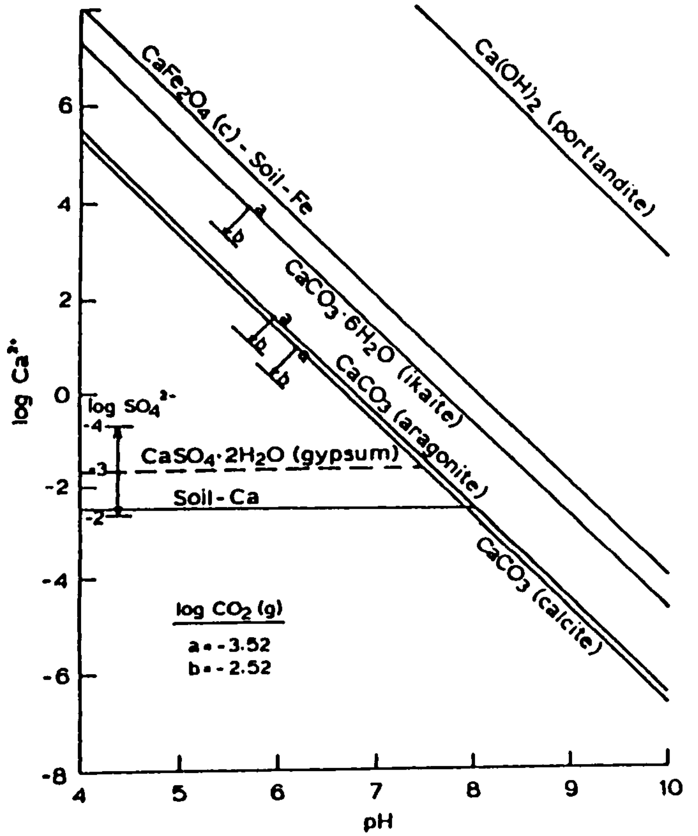

Fig. 4.1 Possible Ca Controls in Soils
(from Lindsay, 1979)

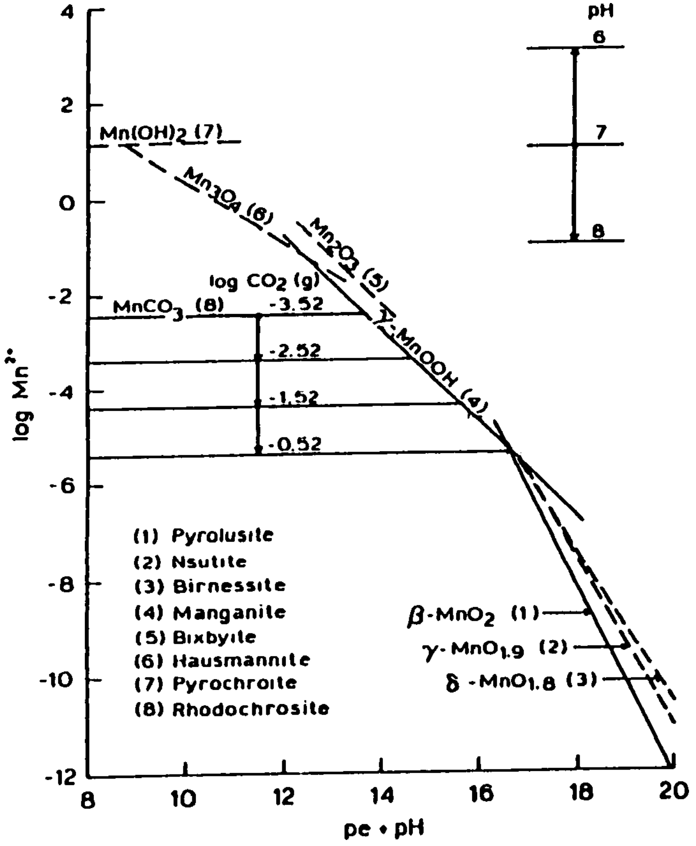

Fig. 4.2 Possible Mn Controls in Soils
(from Lindsay, 1979)

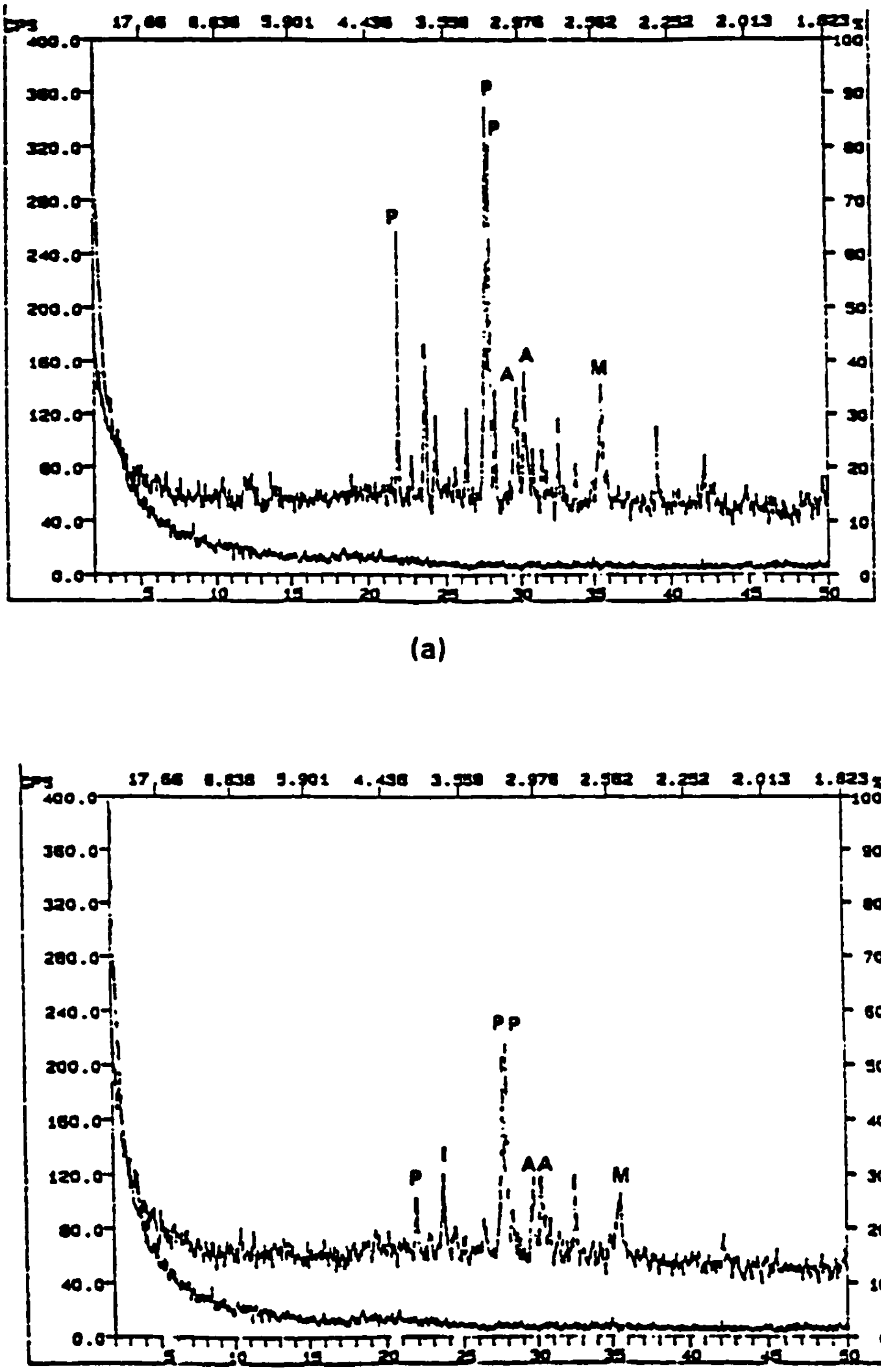

Fig. 4.3 X-ray Diffraction Patterns for MLS after (a) 0 d and (b) 150 d in Water
(P=plagioclase, A=augite, I=ilmenite, M=magnetite/other)

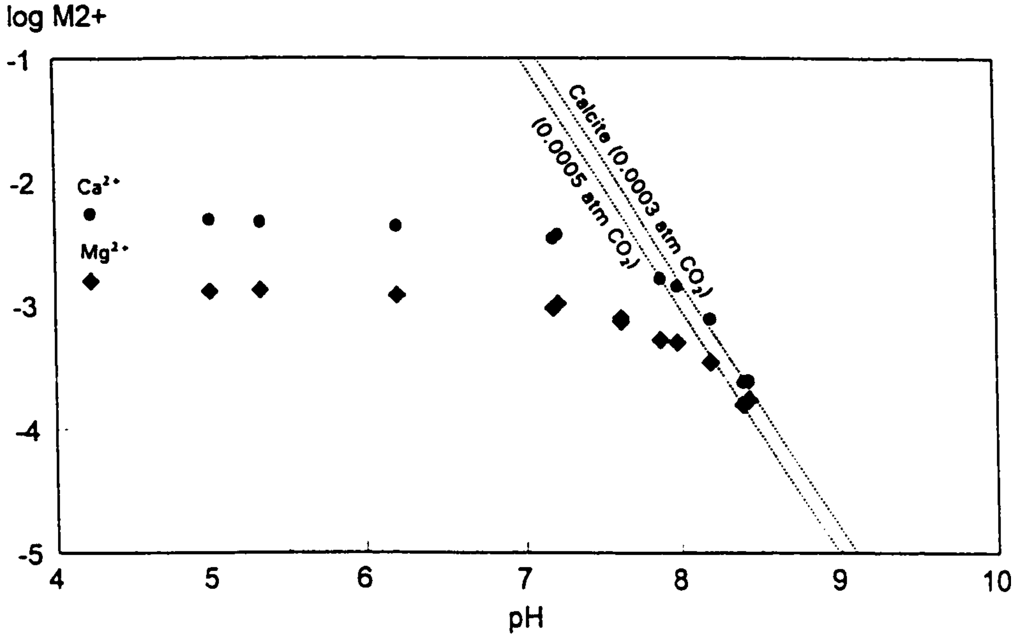

Fig. 4.4 Ca, Mg Solubility from JLS-1 after 3 Weeks
(2 experiments, n=2 for each point)

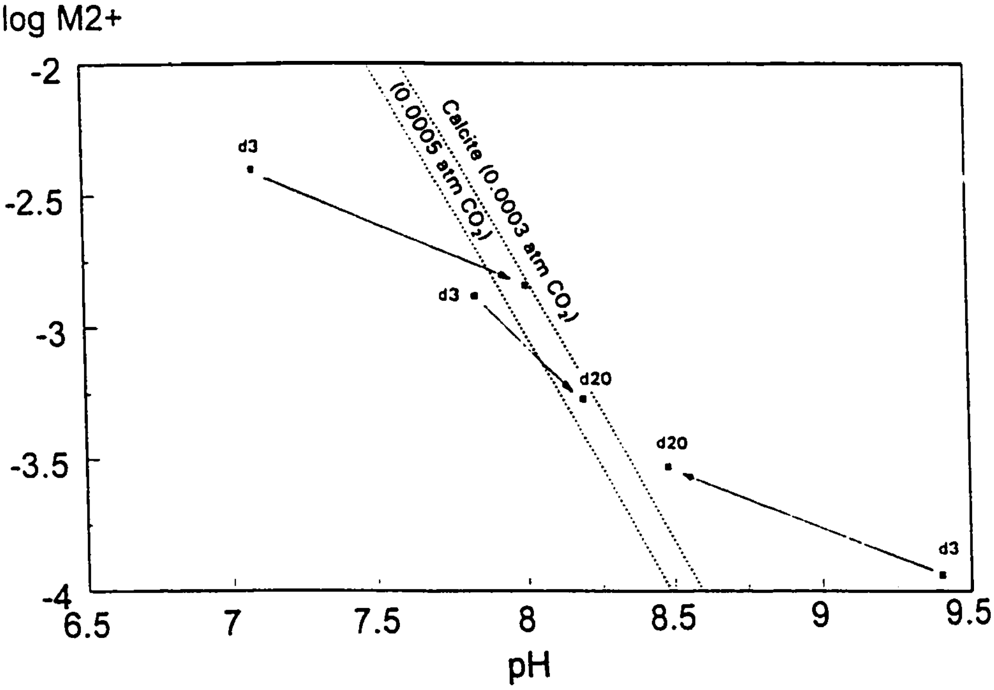

Fig. 4.5 Ca Solubility from JLS-1 During a 3-Week Period

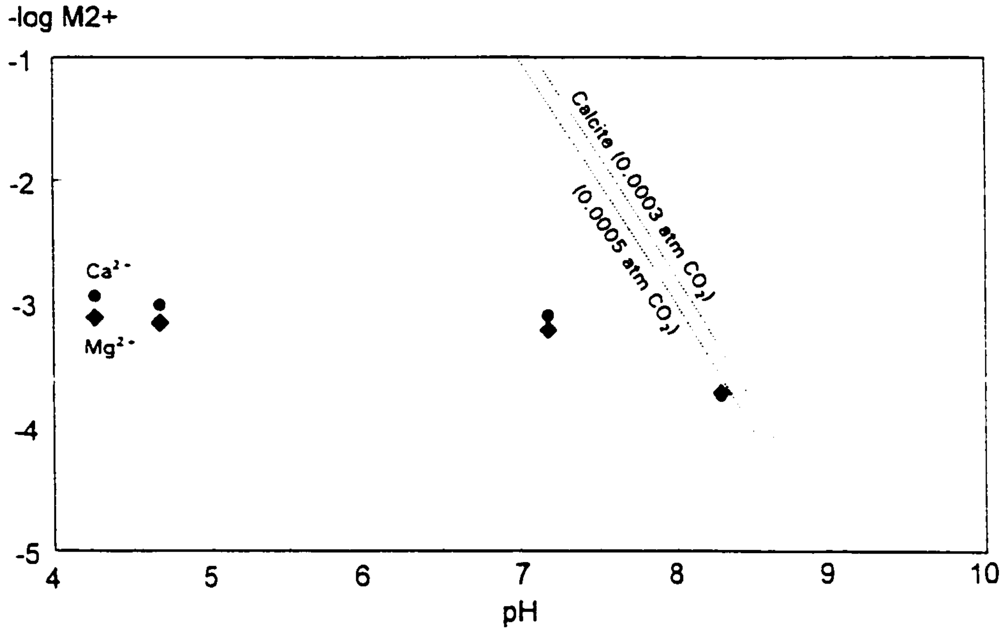

Fig. 4.6 Ca, Mg Solubility from MLS after 3 Weeks
(n=2 for each point)

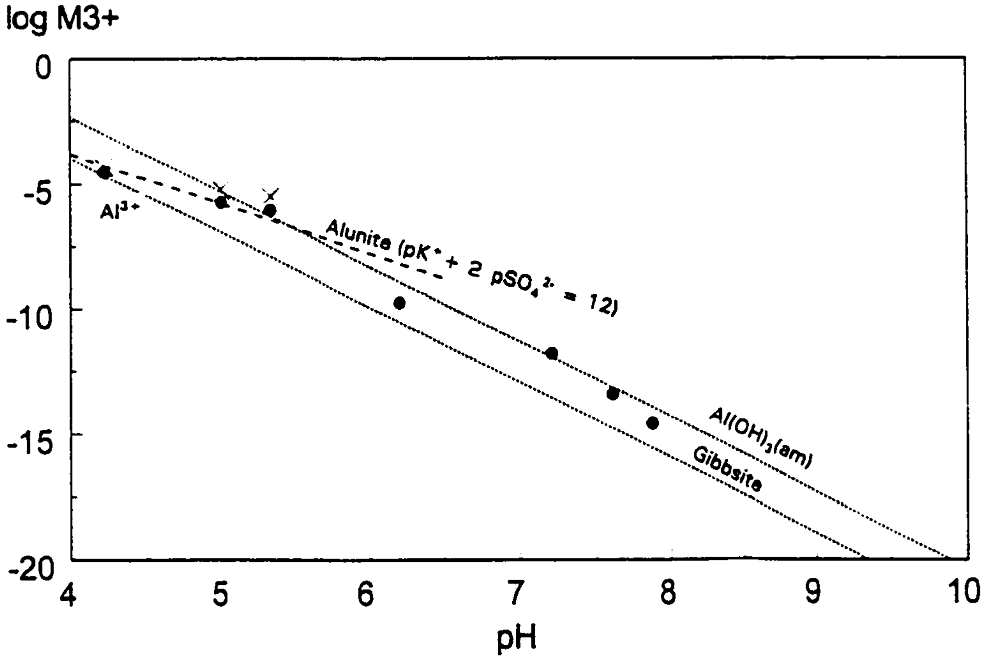

Fig. 4.7 Al Solubility from JLS-1 after 3 Weeks
(2 experiments, n=2 for each point)

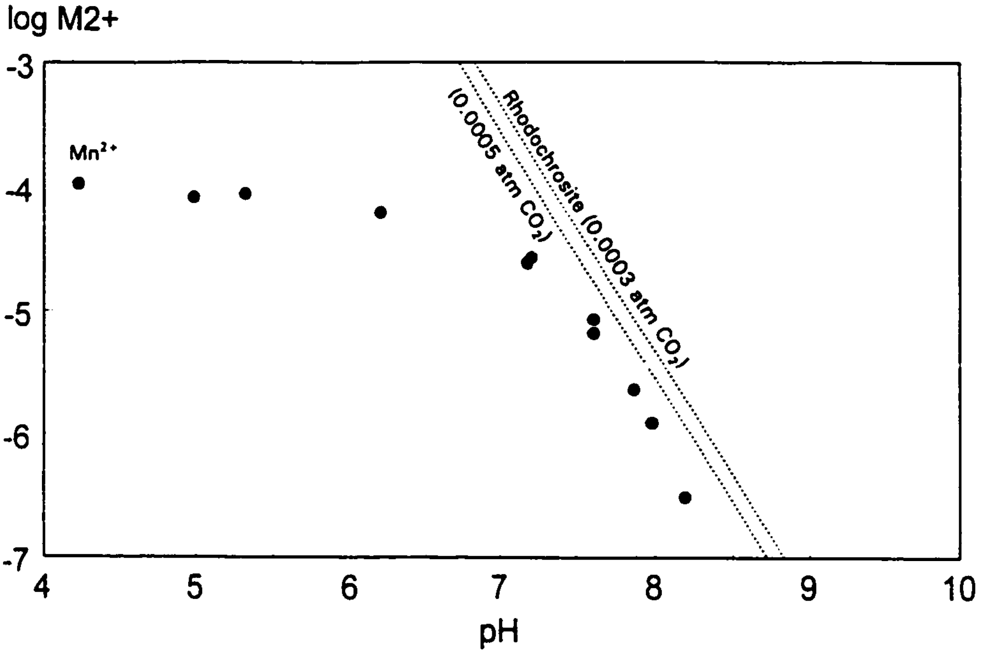

Fig. 4.8 Mn Solubility from JLS-1 after 3 Weeks
(2 Experiments, n=2 for each)

Table 4.1 Dissolution of MLS and JLS-1 in Water
(SI = saturation index, NA = not available)

MLS

	2d	14d	67d	150d
log (Ca^{2+})	-3.80	-3.62 (0.02)	-4.05 (0.06)	-4.13 (0.04)
(Mg^{2+})	-3.50	-2.99 (0.02)	-2.92 (0.04)	-2.88 (0.04)
($H_4SiO_4^0$)	-4.05	-3.80 (0.01)	-3.67 (0.04)	-3.56 (0.04)
pH	8.5	8.5 (0.0)	8.9 (0.1)	9.0 (0.1)
SI (calcite)	-	0.17 (0.02)	0.45 (0.08)	0.56 (0.11)
SI (disordered dolomite)	-	1.02 (0.04)	2.07 (0.18)	2.41 (0.21)
SI (sepiolite)	-	-2.19 (0.07)	-0.25 (0.10)	0.55 (0.18)

(a)

JLS-1

log (Ca^{2+})	-3.75 (0.02)	-3.60 (0.03)	-3.49 (0.05)	-3.60 (0.01)
(Mg^{2+})	-3.85 (0.04)	-3.73 (0.02)	-3.53 (0.04)	-3.60 (0.02)
($H_4SiO_4^0$)	-4.02 (0.07)	-3.72 (0.02)	-3.59 (0.02)	NA
pH	8.3 (0.2)	8.6 (0.0)	8.6 (0.0)	8.7 (0.1)
SI (calcite)	-	0.35 (0.05)	0.54 (0.06)	0.57 (0.10)
SI (disordered dolomite)	-	0.60 (0.13)	1.14 (0.09)	1.18 (0.21)
SI (sepiolite)	-	-3.10 (0.19)	-2.14 (0.04)	NA

(b)

PREDICTIONS ON THE INORGANIC DISSOLUTION CHEMISTRY OF STABILIZED LUNAR SOILS

5.0 PREDICTIONS ON THE INORGANIC CHEMISTRY OF STABILIZED LUNAR SOILS

Predictions about the chemistry of lunar soils can be made, based on results of work with simulants and knowledge about related terrestrial soils. An assumption is that lunar soils will be stabilized initially with CO_2 and O_2, in processes similar to those that naturally alter earth-surface basalts and ashes to make them young andisols. In the most general case when amounts of sulfides are limited (e.g., 0.1 to 0.2 wt.%), the soils that form are expected to be slightly calcareous, with solution pH values between 7 and 9. And, the soil solution redox potential should be moderately oxidizing, after gaseous O_2 oxidizes and limits dissolution of surface elements which are initially reduced.

Based on the results shown previously, expected solubility controls include the metastable minerals, Ca-carbonate for Ca and Mg, and Al-hydroxide for Al. Even though Mg is controlled by adsorption/desorption from Ca,Mg-carbonate most weathered Mg is likely to be found in secondary silicates, from which Mg is less soluble. Rhodochrosite is the predicted control for Mn, but the pool of secondary minerals will also include manganite and birnessite, which will increase in content through oxidative processes. Fe(III) is expected to be controlled by ferrihydrite, which is common in basaltic ash soils from which Fe(II) and Si are easily weathered.

With respect to major/minor mineral elements needed for plant nutrition, lunar soils are expected generally to be deficient in K, even if lunar KREEP basalts are used as soils. This is suggested by an AB-DTPA assessment of nutrient availability from JLS-1, a simulant for the KREEP basalts which has 0.8% K_2O by weight. (These results are reported in Chapter 7.) K would need to be supplemented, e.g., via exchangers loaded with K that is extracted with methods not yet determined. In addition to the deficiency in K, lunar soils could be deficient in P, if KREEP or other phosphate-rich materials are not used as soils or fertilizers.

Deficiencies are also expected for micronutrient metals that have volatilized from lunar soils, such as Zn^{2+} and Cu^{2+}. Corrective measures will be needed to obtain needed amounts, e.g., use of fertilizers or artificial ligands that extract the metals. Fertilizers could include silicate or phosphate coprecipitates with micronutrient metals. Since only small amounts of micronutrient metals or ligands would be needed, they could be transported with launches from earth, perhaps even as coprecipitates. Fe and Mn, in contrast to the volatile micronutrients, are expected to be at least moderately available, since the source minerals including silicates, are highly weatherable and have substantial contents of these metals. This ample availability is suggested by the AB-DTPA test of JLS-1.

Cr toxicity is not likely to be important. The natural content of reduced elements in lunar soils and solutions should keep Cr of lunar soil surfaces in the III state, with solubility controlled by Cr(III)-oxyhydroxides. This is the natural state of Cr for young terrestrial soils with high content of unweathered materials. Potential problems with Cr have likely been overstated in documented discussions on lunar base agriculture, e.g., Hossner and Allen (1989) and Ming (1989).

Ni solubility, on the other hand, could be a problem if surficial lunar soils are used for growing plants, since Ni is present in high content in meteoroid-deposited metal. Subsoils which are more similar to terrestrial materials in their Ni content, could be used for growing plants.

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DISSOLUTION OF MINNESOTA LUNAR SIMULANT (MLS) IN DILUTE CARBOXYLATE SOLUTIONS

6.0 DISSOLUTION OF MINNESOTA LUNAR SIMULANT (MLS) IN DILUTE ORGANIC ACIDS

6.1 Summary

A silt-textured basalt was weathered in suspensions containing 0.5 g of the basalt, thymol disinfectant, and 25 ml 1 mM carboxylate: citrate, malate, oxalate, succinate, glycollate, acetate, propionate, butyrate, or valerate (n=4). Solution pH values were adjusted to neutral before adding the basalt, to prevent acidity effects, and the suspensions were shaken on a rotary shaker and sampled at 10 d and 81 d.

Three different classes were evident (α=0.10) in Si dissolution data after 10d: (a) a volatile carboxylate class (butyrate, valerate), (b) a weak carboxylate class (oxalate, succinate, glycolate, acetate, propionate), and (c) a strong carboxylate class (citrate, malate). The three classes are also apparent in a plot of dissolved Si versus log K of stability constants for divalent cation-carboxylate complexes.

The plot for 10 d dissolution shows a continuum of weathering action. Si dissolution is least for volatile carboxylates with the greatest number of alkane carbons and correspondingly, the smallest K values. The function at greater K values shows two steps, one with slightly increasing Si from log $K_{Ca\text{-}carboxylate}$ = 1.0 to 2.0 (weak carboxylates), and another perhaps similar-appearing step at K values greater

than 2.0 (strong carboxylates). Most of the height in the first step is actually the result of Mg-silicate (1:1, Mg:Si, molar) dissolution, and the slight increase from K = 1.0 to 2.0 is the result of variable action by carboxylates having different affinities for the Mg of the silicate surface. The main Si source in the suspensions containing volatile and weak ligands was the Mg-silicate. Feldspar Si dissolved substantially only in the suspensions containing strong ligands.

In spite of dissolution differences between the carboxylates, Si solubilities after 81 d were found to be comparable in all suspensions and roughly equal to that for quartz, i.e., amounts of Si that dissolved in the period from 10 to 81 d were least in the suspensions containing the strongest ligands. The corresponding kinetics for Si release over the 81 d period were "parabolic", appearing to approach rectangularity for the strongest carboxylates, and linearity for the weakest carboxylates. The Ca and Mg dissolution in the period from 10 to 81 d paralleled the Si behavior. Solution Si-quartz appears to limit solubility ultimately, in any case.

Oxalate behavior as a weak ligand was incongruous with the other carboxylates, for which Si dissolution amounts appeared to be functionally related to log K for carboxylate-metal complexes. The difference from expected may be due to its contrasting properties relative to the other carboxylates.

Oxalate can form binuclear complexes with pairs of trivalent metals. This could limit its capacity to pull single trivalent metals into solution. Furthermore, the solution data indicates precipitation of Ca-oxalate, which could have acted as a barrier to limit dissolution.

6.2 Introduction

Organic ligands present in microenvironments within and near plant root rhizospheres include carboxylates, amino acid ions, and phenolics. Of these, carboxylates or their acids are present at the greatest concentrations, at levels from 0.0001 to 0.01 M (Huang and Violante, 1986). An intermediate concentration of 0.001 M was used in this work.

The carboxylates can include citric-acid-cycle intermediates (citrate, malate, succinate, fumarate, acetate) as well as the more volatile species often associated with decomposition (propionate, butyrate, valerate). Oxalate is also an important exudate from plant roots or microbes, especially fungi. These carboxylates or their acidic forms (Table 6.1) are among those commonly observed in weathering studies (e.g., Riviere, 1960; Kraffczyk et al., 1984; Lee and Foy, 1986). Based on their pK_a values (Table 6.1), the wholly deprotonated carboxylate species predominate at neutral to alkaline pH values.

The number of carboxylates is far greater than the number shown in Table 6.1, which complicates the process of generalizing from experimental results. The study of weathering processes could benefit by more systematization in which carboxylates are divided into classes of members which weather rock materials to similar degrees. Factors which potentially affect these groupings not only include the numbers of carboxylate moieties, but also numbers of alcohol groups and alkane carbons, and molecular stereochemistries relative to weathering surfaces. An alcohol group on a carbon adjacent to a carboxylate moiety increases the carboxylate affinity for cationic metals, while an alkane group in the same position has the opposite effect. These differences are apparent in formation constants, e.g., for Ca-carboxylate (Table 6.1). Presence of a hydroxyl group makes malate a stronger ligand than succinate, and glycolate stronger than acetate. An alkane group on the other hand, e.g., makes propionate a weaker ligand than acetate.

Major matrix elements in basaltic silicates include Si, Al, Fe, Ca, and Mg, of which Si is dominant (Table 6.2). Of the non-Si elements, carboxylates tend to bind to greatest extent with the trivalent metals, Al and Fe(III), and to lesser extent with the divalent metals. The difference in binding affinity between trivalent and divalent metals is most pronounced for the multidentate carboxylates, which have very high affinities for trivalent metals (Table 6.1).

Presently, dissolution of cations from primary aluminosilicates at pH values near neutral, particularly of feldspars and pyroxenes, is thought to be associated with very thin cation-depleted, Si-rich, leached layers, i.e., leached layers (Blum and Stillings, 1995). Blum and Stillings (1995) describe these layers on feldspars, as depleted of cations and Al to depths typically less than 20 Å. In the presence of carboxylates in solutions of near-neutral pH, these thicknesses could be greater; this needs to be checked. At more acidic pH values, leached layers can be much thicker, e.g., near 1000Å at pH 4 for labradorite, and 2000 Å at this pH when oxalic acid is present (Muir and Nesbitt, 1997).

Based on early kinetics research, e.g., Wollast (1967), leached layer barriers were originally thought to be important in causing "parabolic" kinetics, in which dissolution rates are proportional to the square root of time. Often in the literature, curvlinear kinetics are referred to as "parabolic", even if they do not strictly meet this criteria. Other works have claimed that the parabolic behaviors are a result of rapid dissolution of fines and damaged particle surfaces from sample preparation (e.g., Petrovic et al., 1976). A different mechanism is suggested in this work, i.e., that mineral impurities or heterogeneities can cause parabolic behavior, too.

In the leached-layer model, the Si-rich layer grows initially, and the parabolic behavior results with the constraint for cations to diffuse from greater depths, until the diffusion rate is equal to the dissolution rate for the layer. Then the dissolution becomes linear and stoichiometric. In opposition with this view, some relatively recent works suggest that leached layers are not particularly important in the kinetics of dissolution (e.g., Westrich et al., 1989; Casey et al., 1989); this could be considered one of the most popular views presently. Some recent works still explain dissolution kinetics with use of the leached-layer model, e.g., Muir and Bennett (1997).

In addition to the work with leached layers, some which considers them as kinetic controls, some workers have investigated the control by solution species, in particular the role of Si and Al. The reports to date suggest that Al is important but Si is not (Brantley and Chen, 1995; Blum and Stillings, 1995). For example, Chou and Wollast (1985) in a study of albite at pH 3, found Al to inhibit dissolution rates, while the effects of Na and Si were very weak. Also, Gautier (1994) in a work with feldspars at pH 9 found that Si had no effect on dissolution rate.

The initial objective of this work was not related to investigation of leached layers. The objective was to see if carboxylates could be separated into distinct groups, with members that dissolve basaltic matrix elements to similar extents. Particular attention was given to Si, the major matrix element. Distinct groups of carboxylates were apparent, and the differences in kinetics of Si dissolution were relatable to differences in binding affinities of carboxylates for cationic matrix elements. The results were also revealing in the controversial area of leached-layer hypotheses; they showed solution Si-quartz to be a limiter of dissolution.

6.3 Materials and Methods

The basaltic material used is Minnesota Lunar Simulant (MLS), a simulant of lunar soil materials which has been used in space-related research (Weiblen et al., 1988; Oglesby et al., 1993; Eick et al, 1996). The major element composition of MLS and a similar lunar soil is shown in Table 6.2. MLS is manufactured from a basaltic hornfels found in the Duluth Complex in Minnesota, by grinding and sorting to the silt-textured distribution of lunar soils. Major minerals in MLS include plagioclase (labradorite) 42 wt.%, pyroxenes 27%, magnetite-ilmenite 14%, and olivine 6% (Goldich, 1970). Hydrous minerals, especially biotite, are also present in small amounts.

To complete the dissolution experiment, Nalgene tubes (50 ml), 4 per carboxylate, were each filled with 20 ml of solution, which included 100 mg/l thymol and 10^{-3} M carboxylic acid, and NaOH to adjust the pH to 7.0. This ensured that carboxylates were almost wholly deprotonated, and allowed ligand dissolution effects to be examined. Thymol was used to prevent microbial growth (Block et al., 1991) and carboxylate decomposition. Its strong, phenolic smell was apparent for the duration of the 81-d dissolution period. 0.5 g of MLS was added after the pH adjustment, and the tubes were shaken on a rotary shaker at 3 cps. The solid:solution ratio of 1:50 is similar to those used in classical experiments in mineral weathering kinetics (e.g., 1.5:300 to 5.0:300 in Schott et al., 1981) to prevent rapid equilibration.

Solutions were sampled at 10 and 81 d, and analyzed for Si, Fe, Al, Ca, and Mg with ICPS. Results for the 9 different carboxylate and control suspensions were compared for differences with t-statistics, assuming variances to be different, i.e., the Behrens-Fisher problem (Hines and Montgomery, 1980). Solutions were speciated with use of the MINTEQA2 biogeochemical model (Allison et al., 1990).

Equilibrium constants for metal-carboxylate complexes were obtained from Smith and Martell (1977-1990), all adjusted to standard "infinite dilution".

6.4 Results and Discussion

Dissolution in 10 d

Dissolution data for 10 d are given in Table 6.3a, in which the carboxylates are ordered based on their affinity for Ca. pH values in solutions were near neutral, ranging from 7.1 to 7.7. Major dissolved elements included Al, Fe, Si, Ca, and Mg. Al and Fe dissolution were measurable with ICPS only in the solutions containing the strongest multidentate ligands, citrate and malate, while Si, Ca, and Mg dissolution were measurable in all solutions, including blanks.

Table 6.3b shows differences in the amount of Si dissolved after 10 d, at significance levels of 0.10 and 0.05. Based on the results for the 0.10 level, carboxylates can be divided into three classes:

citrate, malate ($Si = 5.1\text{-}6.3*10^{-5}$ M)>

oxalate, succinate, glycolate, acetate, propionate

($Si = 2.4\text{-}3.0*10^{-5}$ M) >

butyrate, valerate ($Si = 1.9\text{-}2.0*10^{-5}$ M)

Carboxylates in each class are significantly different from those of the other classes. The carboxylates listed above are in order, from those dissolving the most Si, to those dissolving the least. In addition to the significant differences between members of different classes, the end members of the the middle group, oxalate and propionate are significantly different at the 0.10 level. More separation of the carboxylates is perhaps possible if sample sizes larger than 4 are used. This is suggested strongly by the smooth increases or decreases in the functional relations of K shown in Fig. 6.1.

Not surprisingly, the number of carboxylate functional groups is the most important factor determining extent of Si dissolution, separating the carboxylates into groups. Less important are the effects associated with carboxylate hydroxyls, which increase Si dissolution, and with saturated carbons, which decrease dissolution.

The behavior of oxalate is incongruous with those of the other carboxylates. It was expected to behave like other strong ligands since its binding constant with Al and Fe(III) is comparable with malate, yet the amount of Si dissolved was relatively low. Oxalate's low ranking may relate to its interaction with weathering surfaces. Oxalate can form binuclear complexes with pairs of Al or Fe(III) atoms that are separated by oxygen atoms; the process for Fe oxides is discussed in Schwertmann et al.(1986). This binding contrasts with the behavior of other ligands of comparable strength, which would tend to bring the trivalent metals into solution, with Si. In effect, the adjacency of trivalent metals partially inactivates oxalate, by dividing its binding capacity between two sites.

Returning to Table 6.3a, which was introduced earlier, inspection of the Mg and Si columns indicates that the Si source in the initial 10 d is primarily an Mg-silicate, possibly the pyroxene in MLS, i.e., $MgSiO_3$. The molar amounts of Mg and Si dissolved are equal or roughly so for valerate, butyrate, propionate, acetate, succinate, and the blank. Actually, the amount of Si dissolved increases slightly in the sequence from propionate to succinate, perhaps due to an increasing affinity of carboxylate functional groups for Mg (Table 6.1).

The Mg dissolved is relatively low for glycolate, even though the Si concentration appears compatible in the sequence for the other weak and volatile carboxylates. This can be explained with a hypothetical adsorption mechanism. Glycolate carboxylate groups adsorb to trivalent metal sites, e.g., of feldspars, while the dangling hydroxyl groups (α-hydroxyls) provide exchange sites that have affinity for cations like Mg^{2+}. This exchange mechanism could also be important for some of the other ligands, e.g., malate and citrate.

For the volatile and weak carboxylates, an implication of the observations of Mg and Si dissolution in a 1-to-1 molar ratio is that Ca is dissolving from feldspars without release of significant amounts of Si (Table 6.1). Furthermore, the dissolved Ca amounts increase with the carboxylate binding affinities, for butyrate, propionate, acetate, and succinate.

Glycolate is the exception, associated with a relatively depressed Ca solubility, due potentially to the exchange mechanism mentioned previously. Also, Ca solubility in oxalate suspensions appears to be limited by Ca-oxalate precipitation. (log K_{sp} was -8.8 and log $[Ca^{2+}]$ was -5.3.)

Fig. 6.1a shows a plot of Si concentration at 10 d versus logarithms of equilibrium constants for Ca-carboxylates. Instead of Ca^{2+}, the selected cation could have been other Si-matrix cations, Mg^{2+}, Fe^{2+}, Fe^{3+}, or Al^{3+}, and somewhat similar functional behavior might be expected in each case. Ca^{2+} and Mg^{2+} curves in particular would be very similar. Complete sets of constants were available for Ca^{2+} and Mg^{2+}, but this was not so for trivalent metals. The constants that are available for trivalent metals are likely far less accurate than those for divalents, since the constants for trivalents are more sensitive to errors in pH measurement, and more uncertain if multiple hydrolysis constants are used to calculate their values.

The functional relation between log K for Ca-carboxylates and Si dissolution (Fig. 6.1a) is suggestive of a two-step function, the lower step associated with weak ligands and the upper one with strong ligands. The lower step appears clearly defined by the data points, and increases slightly over the range of K values from 1 to 2. As mentioned previously, the absolute level is determined in large part by the dissolution of Si from an Mg-silicate, and the smooth, continuous increase perhaps by differing affinities of carboxylates for the Mg of this silicate. The smooth increase suggests that significant differences between the weak ligands are likely discernable in experiments which utilizes larger sample sizes. The curve inflects upward sharply to a less well-defined upper level at K values greater than 2, where complexation and removal of trivalent metals begins to be important. This removal yields Si sites that can be protonated and dissolved, which in turn yields other Al sites more open to attack.

Dissolution Between 10 d and 81 d

Fig. 6.1b contains an additional function, the amount dissolved between 10 and 81 d. The total Si dissolved after 81 d, which is the sum of the values of the two functions shown, is relatively constant at roughly 10^{-4} M, which is the solubility of quartz.

An interesting observation about kinetics can be made about the curves of Fig. 6.1b. In all cases, the kinetic functions of concentration versus time are curvlinear (parabolic). The smallest equilibrium constants are associated with dissolution kinetics which approach linearity, while the largest constants are associated with kinetics approaching rectangularity, i.e., a step function. The greatest binding constants are not only associated with the strongest binding; they are associated with the most rapid initial Si dissolution, as well. Considering separate contributions, the dissolution via strong carboxylates includes release of Si from Mg-silicates and feldspars, which was mentioned previously.

The function for the Ca (and Mg) dissolved in the period from 10 to 81 d (Fig. 6.1c) is similar to that for Si (Fig. 6.1b). This similarity between elements was not evident in the initital 10 d period. The Si dissolution curve for this period appears to be constrained ultimately by quartz solubility, and similarity in the plots for Ca (and Mg) suggest that quartz controls the dissolution of Ca and Mg. This is notable, since other workers have documented that solution Si does not tend to limit solubilities, as mentioned in the introduction. It may be important that the earlier studies on feldspars (Chou and Wollast, 1985; Gautier, 1995) were at acid or alkaline pH values, where quartz or silica could be more unstable, so that Si solubilization is less restricted. At alkaline pH, Si is more soluble, and at acid pH, more weathering agents are present in solution.

6.5 Concluding Remarks

Three carboxylate groups were apparent in the dissolution data for MLS, a fine-textured basaltic material, at near-neutral pH: volatile, weak and strong carboxylates. Si dissolution kinetics were found to be slightly "parabolic" in the case of weak ligands, and almost rectangular in the case of strong ligands. Si dissolution and ultimately release of Ca and Mg appeared to be controlled by quartz. In the case of volatile and weak ligands, most of the dissolved Si was from Mg-silicates. For strong ligands, feldspars also contributed.

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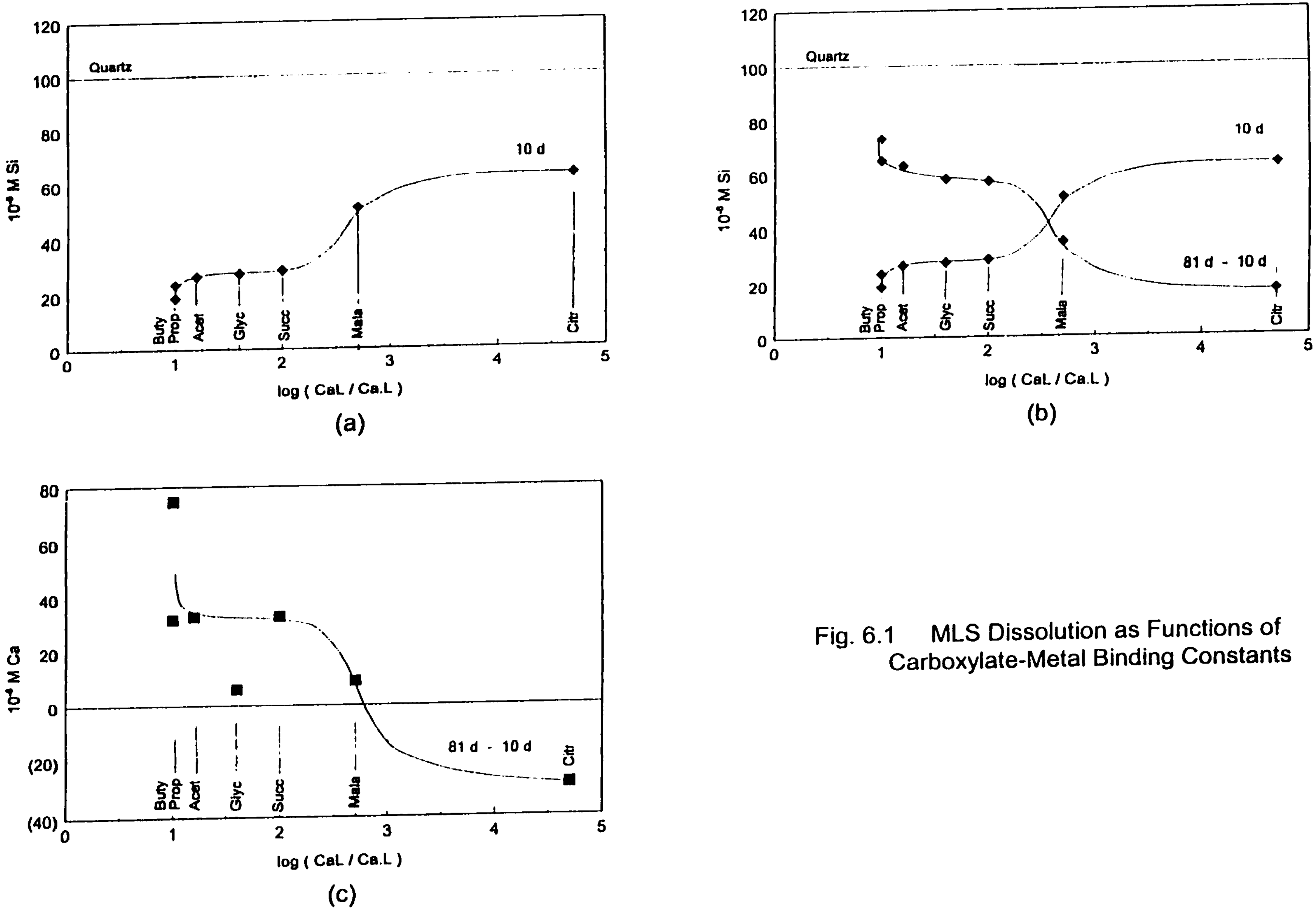

(a)

(b)

(c)

Fig. 6.1 MLS Dissolution as Functions of Carboxylate-Metal Binding Constants

Table 6.1 Carboxylates of This Study

Carboxylate	Protonated Form	log (CaL)/(Ca)(L)	log (HL)/(H)(L)
Citrate	 $HOOC\text{-}CH_2\text{-}\overset{COOH}{C}OH\text{-}CH_2\text{-}COOH$	6.4	4.7
Malate	$HOOC\text{-}CH_2\text{-}CHOH\text{-}COOH$	5.1	2.7
Oxalate	$HOOC\text{-}COOH$	4.3	3.0
Succinate	$HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH$	5.6	2.0
Glycolate	$HOCH_2\text{-}COOH$	3.8	1.6
Acetate	$H_3C\text{-}COOH$	4.8	1.2
Propionate	$H_3C\text{-}CH_2\text{-}COOH$	4.9	1.0
Butyrate	$H_3C\text{-}CH_2\text{-}CH_2\text{-}COOH$	4.3	1.0
Valerate	$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$	*	*

* Not available

Table 6.2 Composition of Minnesota Lunar Simulant (MLS) and Apollo 11 Sample 10084

Oxide	Weight Percentage	
	MLS	10084
SiO_2	43.9	42.6
Al_2O_3	13.7	13.5
FeO	13.4	15.2
CaO	10.1	12.0
MgO	6.7	8.0
TiO_2	6.3	7.7
Fe_2O_3	2.6	0.0
Na_2O	2.1	0.4
K_2O	0.3	0.1
MnO	0.2	0.2
P_2O_5	0.2	0.1
Cr_2O_3	< 0.1	< 0.1
S	0.1	0.1
TOTAL	99.6	99.9

* Percentages from Weiblen and Gordon (1988) except for S, which is from Goldich (1970)

Table 6.3 Dissolution of MLS in 0.001 M Carboxylate Suspensions, 10d (Solid : Solution = 1 : 50 (wt.), ± Standard Deviation)

(a)

	pH	10^{-6} M Si	Ca	Mg	Fe	Al
Blank	7.1	22 ± 5	21 ± 8	19 ± 5		
Citrate	7.7	63 ± 10	49 ± 10	24 ± 4	118 ± 15	17 ± 3
Malate	7.3	51 ± 15	24 ± 5	18 ± 3	20 ± 13	
Oxalate	7.7	30 ± 4	5 ± 2	18 ± 1		
Succinate	7.4	29 ± 10	47 ± 12	27 ± 5		
Glycolate	7.4	28 ± 6	28 ± 6	20 ± 3		
Acetate	7.3	27 ± 5	38 ± 12	24 ± 4		
Propionate	7.4	24 ± 2	37 ± 10	23 ± 2		
Butyrate	7.1	19 ± 3	32 ± 8	20 ± 3		
Valerate	7.3	20 ± 3	25 ± 2	19 ± 1		

(b)

Si Dissolution, Significant Differences: α = 0.10 (0.05)

	Blank	Citrate	Malate	Oxalate	Succinate	Glycolate	Acetate	Propionate	Butyrate	Valerate
Blank		-	-	-		(-)	(-)			
Citrate	+			+	+	+	+	+	+	+
Malate	+			+	+	+	+	+	+	+
Oxalate	+	-	-					+	+	+
Succinate		-	-						(+)	(+)
Glycolate	(+)	-	-						+	+
Acetate	(+)	-	-						+	+
Propionate		-	-	-					+	+
Butyrate		-	-	-	(-)	-	-	-		
Valerate		-	-	-	(-)	-	-	-		

LUNAR SIMULANT DISSOLUTION STUDIES TO SUPPORT DEVELOPMENT OF LIFE SUPPORT SYSTEMS

7.0 LUNAR SIMULANT DISSOLUTION STUDIES TO SUPPORT DEVELOPMENT OF LIFE SUPPORT SYSTEMS

7.1 Summary

Lunar soils can be used as plant growth media in the bioregenerative life support systems (BRLSS) of a lunar base (Ming et al., 1989) which serves as launch site and test bed for human missions to Mars and beyond. Use of this site would allow the launching of large payloads without the weight restrictions normally imposed by the earth's atmosphere. The use of lunar soils as plant growth media for the BRLSS can be explored and developed with dissolution studies of lunar simulants. Simulants are terrestrial materials with particle size distribution, chemical composition, and mineralogy similar to lunar soils.

If lunar soils are stabilized with CO_2 and O_2 prior to their use, their properties are expected to be similar to newly-formed terrestrial basaltic soils, which are slightly calcareous. The stabilization neutralizes the base from initial hydrolysis of silicates and oxides, and limits the solubility of elements which initially are highly reduced. Dissolution experiments with simulants could provide data which quantifies consumption of the stabilizing gases, CO_2 and

O_2, which are scarce resources on the moon.

Studies with simulants can be used to develop the BRLSS soil subsystem. Some of these studies could include

a) synthesis of exchange materials from simulants of heterogeneous lunar soils

b) development of methods for extracting nutrients, e.g., to load to exchangers

c) synthesis or identification of fertilizer materials

d) sizing of exchanger and fertilizer amounts for good plant nutrition

e) testing of soil subsystems containing parent soil materials, exchangers, and fertilizers

f) development of improved soil testing methods

Based on extraction testing of a simulant for highland KREEP basalts (JLS-1), lunar soils are expected generally to be deficient in K, and without use of KREEP materials, deficient in P, as well. Lunar soils are also likely to be deficient in micronutrient cations like Zn^{2+} and Cu^{2+} that have volatilized during cooling following lava flows and meteoroid bombardment events. Possible K sources include KREEP basalts, for which a K extraction procedure could be developed, or alternatively, felsites or granites. The K is expected to be extracted and loaded to exchangers that would ensure timely availability for plant growth. Much of the work on exchangers manufactured from simulants has been with zeolites (Ming, 1989). Additional work is needed to synthesize other exchangers, e.g., clays, from simulants, and to determine good conditions for synthesis. Micronutrient coprecipitates with P, e.g., apatite (Gruener, Ming et al. 1997) or Si are possible fertilizer sources for potentially deficient micronutrients.

Extractants like AB-DTPA, which are commonly used for assessing terrestrial agricultural soils, would be valuable in assessing nutrient availability from BRLSS soil subsystems, and for determining optimal size of subsystem components, e.g., fertilizers and exchangers. The extractants could even be used to test the lunar soils from the Apollo missions, to provide information for selecting an initial lunar base site and to check simulant research results.

Products of dissolution studies include protocols for use by space scientists, for locating soils and fertilizers on the lunar surface, setting up BRLSS soil subsystems, and monitoring their quality. The knowledge base from dissolution studies of simulants of lunar and planetary soils can ultimately provide decision-makers with some of the evidence to show that space exploration and inhabitation efforts would be successful.

7.2 Introduction

Dissolution studies of lunar-soil simulants can aid scientists in planning the use of lunar soils for bioregenerative life support systems (BRLSS) of a lunar base (Ming et al., 1989). A lunar base is an ideal launch site for human missions to Mars and beyond, as a platform to allow launching of large payloads without the weight restrictions normally imposed by the earth's atmosphere. It is also important as a testbed for completing experiments to prepare for human presence in low-pressure planetary environments, e.g., 0.6 kPa (0.09 psi) for Mars (Sadeh et al., 1996). With space exploration pursued in earnest, long-term inhabitation of a lunar base could be important for success of missions.

The BRLSS which allows this long-term inhabitation is envisioned to have plant modules in which lunar soils are the growth medium, or the source of extractable nutrients for hydroponic systems. Soil-medium methods are perhaps the most important to develop in the long-term (Sadeh and Criswell, 1996), since they are potentially more useful in extraterrestrial plant growth systems that are large in scale. Currently, however, the NASA research emphasis is on hydroponics (e.g., Erickson and Shah, 1997).

A symposium in 1989 covered many of the important technical variables for lunar plant growth systems and lunar soils (Ming et al., 1989). Elements obviously in short supply are the lighter elements, H, C, N, and O. H, C, and N are obtainable by heating regolith fines, in which they have accumulated via solar-wind impingement (Vaniman et al., 1991). O_2 and H_2O can be produced from Ti-rich rocks, through reductive dissolution processes (Gibson and Knudsen, 1985). Alternatively, H_2O may be obtainable directly from ice, which may be present at the lunar poles (Nozette et al., 1996; Astronomy, 1997).

Lunar soils can be defined as the fine-grained fraction of lunar regolith at the lunar surface (McKay et al., 1991). The silt-textured soils are secondary products of rock materials initially deposited by volcanic activity and subsequently altered through meteoroid bombardment and cooling processes. Due to the heating from meteoroid impact, a large fraction of soil particles are agglutinates (Fig. 7.1), i.e., aggregates of rock and mineral fragments cemented in glassy matrices. Based on the data of McKay et al. (1991), "average" lunar soils contain 25 to 30% agglutinates, by volume, and 5% pure glass particles.

7.3 Simulants of Lunar Soils

If lunar soils are to be used as plant growth media, or as sources of extractable nutrients, their dissolution chemistry needs to be understood. Simulants have been used in dissolution studies, since the lunar soils gathered in Apollo missions are very limited in availability and considered national treasures. The simulants are manufactured from terrestrial materials with chemical and physical characteristics similar to lunar soils, typically by grinding and sorting to matching particle size distributions.

Some of the simulants that have been used in plant nutrition research include Minnesota Lunar Simulant (MLS), Lunar Basaltic Glass Simulant (LBGS), and Johnson Space Center Lunar Simulant-1 (JLS-1). MLS is similar to Apollo 11 Sample 10084 and other lunar mare basalts, which typically have high Ti contents (>5 wt.%) (Weiblen and Gordon, 1988)(Table 7.1). LBGS is produced from batch materials by heating at temperatures near 1500°C, in a nitrogen-purged furnace to maintain reducing conditions (Eick et al., 1996). It has a high Ti content like MLS. JLS-1 (i.e., JSC-1, McKay et al., 1994) is similar to Apollo 14 Sample 14163 and other low-Ti basaltic lunar soils of the lunar highlands. It is a KREEP (K-Rare Earth Element-P) material, relatively rich in K, rare earth elements, and P (Table 7.1). JLS-1 is produced from ash of the San Francisco Volcanic Field near Flagstaff, Arizona. Approximately 1/2 of its volume is glass.

Differences Between Simulants and Lunar Soils

Even though simulants are like lunar soils in content of most elements (Table 7.1) and particle size distribution, they can be different in content of some elements and in other characteristics that relate to dissolution chemistry. In contrast to lunar soils, simulants have been stabilized to some extent by the actions of water and atmospheric gases (Whitney, 1991). Lunar materials are inherently more unstable, since they are damaged by meteoroid bombardment and radiation, and contain greater content of reduced elements.

With these characteristics, the lunar soils are expected to yield highly alkaline solutions upon initial dissolution in water (Helmke and Corey, 1989; Oglesby et al., 1996) due chiefly to hydrolysis of silicates and oxides. Since lunar soils usually have relatively low content of reduced S (0.1 to 0.2%, Haskin and Warren, 1991) which is true for most earth surface materials too, oxidation and weathering typically yields alkaline pH, and in the presence of gaseous CO_2, ultimately a mineral-carbonate-buffered pH. A carbonation process can be used to stabilize lunar soils (Oglesby et al., 1996), so that carbonate-buffered pH values are reached rapidly, and oxygen can be introduced to limit solubility of reduced elements after the pH has decreased.

The process in which carbonation reduces alkaline pH associated with dissolution of silicates and hydroxides can be seen in dissolution data for JLS-1 (Fig. 7.2). The figure shows Ca^{2+} activities in weathering suspensions allowed to equilibrate with earth-atmospheric gases, measured with an ion selective electrode. The bottom set of points are associated with a suspension in which the initial solution is water. The pH after 1 d is strongly alkaline. Hydrolysis of silicates or oxides to generate hydroxyls is the important process controlling pH at first, more important than the countering processes that generate acidity, e.g., oxidation of reduced Fe and S. Eventually however, the pH decreased with influx of CO_2 and the buffering of pH with carbonate alkalinity. For the top 2 sets of points, associated with addition of small amounts of HCl, Ca^{2+} and other cations were released initially by exchange with H^+, then hydrolysis of silicates increased the pH and alkalinity over time. With the increase in carbonate alkalinity, mineral carbonates eventually precipitated and Ca^{2+} activities declined.

Returning to the topic of simulant-lunar soil differences, simulant elements that can have variable redox states tend to be more oxidized than their counterparts in lunar soils. Simulants contain substantial amounts of Fe(III), which is absent from lunar materials. Lunar materials are rich in Fe(II) and contain small amounts of native Fe, which is not detectable in simulants. Titanium in simulants is limited primarily to the IV oxidation state, while lunar soils contain as much as 30-40% in the III form (Papike et al., 1991). Similarly, most simulant Cr is in the III state, while a substantial fraction of lunar Cr is in the II form (Papike et al., 1991). If water is added to lunar soils, the reduced elements are likely to be very soluble initially, especially the Fe from Fe metal, unless lunar soil is stabilized, e.g., with oxygen, before use. After this stabilization, the redox potential is expected to be moderately oxidizing as in oxygenated terrestrial soil solutions.

Simulants contain relatively large amounts of many elements that have volatilized from lunar soils. The volatilization from lunar materials occurred during cooling after lava flows (Haskin and Warren, 1991), and presumably after meteoroid bombardment and in the long-term, as well. The elements volatilized in the greatest amounts are the alkali metals; K^+ is the important nutrient affected. Some divalent trace metals have been volatized substantially, too, including Zn^{2+} and Cu^{2+}. The extent of depletion of the volatile divalent trace metals, relative to otherwise comparable terrestrial materials, can approach an order of magnitude. This is evident in the Zn and Cu data shown in Table 7.1.

Simulants contain small amounts of Cr and Ni relative to lunar soils, in which these elements are enriched. Lunar soils typically contain several thousand ppm of Cr, mostly in spinel minerals (Papike et al., 1991). Ni is found ubiquitously in soils to which it has been added via meteoroid bombardment, and at high concentrations in the sparsely distributed dunite rocks of highland areas (Haskin and Warren, 1991). From the data of Haskin and Warren (1991) Ni concentration extremes in surface soils can be near 1000 ppm.

Past Dissolution Studies

In spite of the great interest in space exploration in recent years, the number of studies on the dissolution chemistry of lunar simulants is still very limited. These include preliminary work by Oglesby et al. (1993, 1994, 1996), and works by Tan and Henninger (1993), Eick et al. (1996a, 1996b), and Sutter et al. (1996). A few studies with actual lunar soils were conducted in the 1970's (Mason et al., 1970; Keller and Huang, 1971). These studies with simulants and lunar soils dealt mostly with geochemistry, with little attention given to plant nutrition. More can be gleaned at present to predict plant nutritional properties of lunar soils from the body of agricultural research on young volcanic soils, than from the studies of simulants and lunar soils.

The works of Eick et al. (1996a, 1996b) deal primarily with dissolution kinetics in the presence of miscellaneous organic acids and reports rates for citrate and oxalate. The importance of knowing rates of weathering for soils of soil-medium systems is questionable, if nutrient availabilities over plant life cycles can be assessed with simple extractions, e.g., DTPA extraction tests. Extractions are a standard means for soil evaluation used by agriculturalists, and potentially useful for evaluating lunar soils, as well. The work on kinetics is probably of more value for considerations relating to hydroponic systems, in which nutrients would be extracted from lunar soils and rock materials.

Many of the other works listed above could be considered corroborative research, with findings similar to those reported for terrestrial basaltic materials. Some of the observations are that lunar simulants, which are rich in Fe/Al oxides, retain large fractions of added P (Sutter et al., 1996), and that simulants adsorb high-molecular-weight organics, forming a coating which limits dissolution of trace metal cations and weathering in general (Tan and Henninger, 1993). More research is needed that relates specifically to differences between simulants and lunar soils, particularly those that affect dissolution chemistry and plant nutrition/toxicity.

7.3 Predicted Plant Nutritional and Toxicity of Lunar Soils

As mentioned previously, the baseline dissolution behavior of lunar soils can be assumed similar to that for slightly weathered, terrestrial basalts. Potentially deficient nutrients of lunar soils include K, P, and some micronutrient cations. K and P deficiencies are common in newly-forming terrestrial volcanic soils, due to K fixation by aluminosilicates (Yamada and Shoji, 1982; Shoji et al., 1993) and P fixation by Al and Fe (Miller and Donahue, 1990; Nanzyo et al., 1993). Multivalent micronutrient cations, e.g., Zn^{2+}, Mn^{2+}, Cu^{2+}, and Fe^{3+}, tend to be limited in availability in many terrestrial alkaline soils, since they precipitate under basic conditions. Volatilization from lunar soils is expected to further limit the availability of K^{+} and some micronutrients, e.g., Zn^{2+} and Cu^{2+}.

Nutrient availabilities from JLS-1 were evaluated with the AB-DTPA test (Table 7.2). JLS-1 was found to have low K and moderate P availability. If comparable lunar soils were used for growing plants, additional K would have to be provided, presumably from exchangers (Ming, 1989) loaded with K extracted from mineral or rock sources. P may need to be provided also, if lunar soils other than KREEP materials are used, e.g., mare basalts. Mare basalts contain an average of 0.2% P as P_2O_5 compared to JLS-1, which contains approximately 0.7%. (The 0.2% was calculated with data reported by Papike et al., 1991.)

Availabilities of the micronutrients, Fe, Mn, Zn, and Cu, from JLS-1 were also assessed with the same AB-DTPA extraction test of Soltanpour, 1991 (Table 7.2). The extracted amounts suggest adequately available micronutrients from comparable lunar soils: medium for Zn, and high for Fe, Mn, and Cu. Moderate to high availability is perhaps the norm for young basaltic soils, which can be more weatherable than older calcareous soils. However, the Zn and Cu of lunar soils could be expected deficient, since these elements have been substantially depleted via volatilization, as mentioned before. Other extraction data (Oglesby et al., 1993) with an alternative test (Lindsay and Norvell, 1978) show somewhat similar extracted micronutrient levels for JLS-1 and MLS, with the exception of Cu, which is extractable in much greater amounts from MLS presumably because the content is much greater.

As noted previously, Cr and Ni have been noted as potentially toxic elements (Hossner and Allen, 1989; Ming et al., 1989; McKay and Ming, 1989), since the content of these elements in lunar soils is high. Even so, Cr is unlikely to be problematic, and Ni toxicity can be avoided.

Cr solubility from lunar soils is likely to be controlled by insoluble Cr(III)-hydroxides under most conditions. These solids are the controls in most terrestrial soils (Rai et al., 1984) even in moderately oxidizing environments, presumably due to presence of reduced elements in parent materials which dissolve to limit the solution redox potential, and keep Cr(III) from oxidizing. Likely for similar reasons, agricultural soils amended with Cr(III)-rich sludges show low Cr extractabilities (e.g., Berti and Jacobs, 1996; Tisdell and Breslin, 1995).

However, Cr oxidation is perhaps possible with extreme conditions. Cr(III) is potentially oxidized to Cr(VI) by O_2 oxidizing agent, during the initial wetting periods in which pH values are highly elevated. To avoid this, Oglesby et al. (1996) suggested that the initial wetting be performed anoxically. This may be an important design constraint for a carbonation process to stabilize lunar soils.

Nickel, in contrast to Cr, can be relatively soluble at at alkaline pH values, particularly when the controls are hydroxides. Potential problems with Ni mobility are suggested by studies in which Ni-rich sludges are added to soils (e.g., Berti and Jacobs, 1996; Tisdell and Breslin, 1995). Retention and reactivity with soil components is low, and extracted amounts are high. To avoid Ni toxicity problems, subsurface lunar soils could be used for growing plants. These subsurface soils have been less "reworked" and contaminated with Ni through meteoroid bombardment than the overlying materials, and have Ni levels much more comparable with typical terrestrial materials. Or, methods can be developed for stabilizing the Ni in lunar surface materials.

7.4 Future Dissolution Studies

Future dissolution studies of simulants could emphasize areas with direct application to use of lunar soils as a plant growth medium. Some important research areas might be:

1. Development of protocol for stabilizing lunar soils
2. Manufacture of exchangers from lunar materials
3. Fertilizers and fertlization with K, P, and micronutrient sources, e.g., for Zn, Cu
4. Engineering of soil subsystems for the BRLSS
5. Development of AB-DTPA extraction tests/protocols for use in selection of lunar base sites and assessment of soil subsystems
6. Evaluation and control of Ni solubility from lunar soils

Stabilization of lunar soils with CO_2 will consume CO_2, i.e., lunar soils are a C sink. This is important since C is a scarce lunar resource. As noted previously, it is confined to soil surfaces, where it accumulates through solar wind impingement. Large lunar soil volumes will need to be processed to obtain the C that is needed for the BRLSS. Estimates of the C amounts in the plants and mineral carbonates of the soil-medium will be required to determine these volumes. The changes in soil mineral carbonate amounts over time might be evaluated, for use in timing processes to recycle carbonate-C from soil, e.g., acidification. Assessing the extent to which lunar soils used for plant growth will be an O sink is perhaps less important than for C, since O is generally a major element in lunar regolith materials. Simulants to accomplish the research on lunar soils as sinks for C and perhaps O should be rich in reduced glassy materials, like LBGS.

Lunar soils which are expected to be highly alkaline initially could be stabilized rapidly with processes that introduce carbon dioxide and water, as liquid or vapor. Processes have been developed for highly alkaline terrestrial materials to accomplish this very task. CO_2 has been used to transform extremely alkaline oil-shale wastes in pressure vessels, to carbonate-rich materials with pH between 8.5 to 9.5 (Reddy et al., 1991). A similar process could be employed to stabilize basaltic glass simulants, metering the CO_2 input and measuring the amount fixed, since C is a scarce resource.

Another important research area is production of exchangers such as zeolites, which buffer nutrient levels so that they are available at critical times, and over entire plant growth cycles. Exchangers need to be developed because the exchange capacity of lunar soils is expected to be low (Ming, 1989). The work of Ming and his colleagues in this area over the last decade has concentrated on zeolites. For example, in the work of Ming and his colleagues (Ming, 1989; Ming and Lofgren, 1989) zeolites were produced from glassy simulants with the aid of pressurizing equipment. Additional research on exchangers is needed to synthesize other materials, e.g., clays, from simulants, and to determine good conditions for synthesis.

As mentioned previously, lunar soils are expected to be deficient in K and micronutrient cations, especially the volatile ones. K is likely to be provided from exchange materials loaded with extracted K. The rock or mineral source of the K, and the method for its extraction need to be developed. If adequate K cannot be extracted from KREEP basalts, then alternative materials richer in K are needed, e.g., felsites or granites. Ideally perhaps, a single KREEP material could provide adequate extractable K, P, and adsorbed metal micronutrients, and could also be used as the raw material for synthesizing exchangers. JLS-1, the KREEP basalt simulant, is one material that could be used in research of this sort. Furthermore, the lunar counterpart for JLS-1, Apollo 14 Sample 14163 is one of the largest lunar samples (7.8 kg), so that some testing of Sample 14163 could be conducted to check development results from simulant work.

Simulants for metal micronutrient fertilizers need to be identified or synthesized. They could include materials similar to the orange-colored glass from Apollo 17 flights, which is enriched in relatively volatile metals (Haskin and Warren, 1991). Or, they could include phosphates as the carriers for the micronutrients. Work in this area is being conducted by D. Ming and his colleagues (Gruener et al., 1997), with apatite as the carrier. Another possibility is to use heterogeneous KREEP materials as the carrier.

Solubilities of deficient micronutrients could also be increased by adding artificial ligands (e.g., DTPA or EDTA). Quite often, the ligands tend to depress activities of the free metal ions needed for nutrition, but increase the bulk flow of metals to the root surface so that more is ultimately available. Since low ligand concentrations (10^{-4} to 10^{-5} M) can be used to accomplish the solubility increase, several kg of ligand might satisfy long-term operational requirements for a lunar base. However, use of these ligands might decrease nutrient availability over several plant growth cycles, since the soils have low micronutrient content initially. That is, soil fertility might not be sustainable if ligands are used.

To effectively study deficiencies and fertilization in dissolution experiments, methods are needed to test nutrient availability from soil-medium systems, or more accurately, from subsystems of the BRLSS. Assessments of nutrient availability are readily accomplished with simple extractive tests which have been the mainstay of agricultural workers for several decades, e.g., the AB-DTPA test (Soltanpour, 1991). The utilization of the AB-DTPA test in particular is increasing greatly, because of its utility in testing comprehensively for multiple cationic and anionic nutrients

(Soltanpour, 1991; Miller and Donahue, 1990). Extractants like AB-DTPA can be considered important systems analysis tools for studying plant growth options, allowing plant growth systems to be assessed conveniently, without having to grow the plants. The simplicity of extractions allow sensitivity analyses to be performed easily, so that amounts of soil-medium components, e.g., exchangers and fertilizers, that provide ample nutrient availability can be determined. Simulants are especially useful in conducting sensitivity analyses of this sort, when they are often available for research in relatively large amounts.

Assessments with extractants could also include evaluations of the soils gathered from lunar missions, as an aid to select a lunar base site and to identify potential fertilizer sources. Since these materials are considered national treasures, the samples analyzed could be small. Each extraction might, for example, utilize 1 g sample and 2 ml of extractant, instead of the normal 10 g and 20 ml for the AB-DTPA extraction. The 2 ml extracted could provide a minimal amount of solution for inductively coupled spectrometry (ICPS) analysis, and perhaps ion exchange analysis, too, if desired. A soil sample analyzed in parallel might be extracted with water.

In addition to nutrients, studies of plant toxicants are needed. As mentioned previously, Cr and Ni have been noted as potentially toxic. Recent research and solubility considerations suggest that Cr is unlikely to be problematic. Ni on the other hand is potentially toxic, and its solubility from lunar soils still needs to be measured. If Ni is still thought to be potentially toxic, the soil subsystems developed without considering Ni specifically could be tested to see if they can buffer dissolved Ni at nontoxic levels. Or, a suitable simulant might be identified or synthesized, for use in experiments in which methods are developed for limiting Ni dissolution.

7.5 Concluding Remarks

Dissolution studies of simulants can be used to plan the processes for transforming lunar soils into productive media for growing plants in the BRLSS. Some of the major tasks to accomplish this include development of soil stabilization methods, identification or synthesis of fertilizers, synthesis of exchangers, sizing of soil subsystem components, and evaluation of alternative soil subsystems. Some dissolution work with actual soils from Apollo missions could be valuable in validating findings from simulant research and in selecting a site for the initial lunar base.

The product of the dissolution studies are protocols for use by space scientists, for screening lunar soils and fertilizers for use in the soil subsystems, and for preparing and monitoring them, too. The knowledge base from dissolution studies of simulants of lunar and planetary soils can provide decision-makers with important evidence to show that space exploration and inhabitation efforts would be successful.

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Fig. 7.1 Lunar Soil: Agglutinate Particle
(McKay et al., 1991)

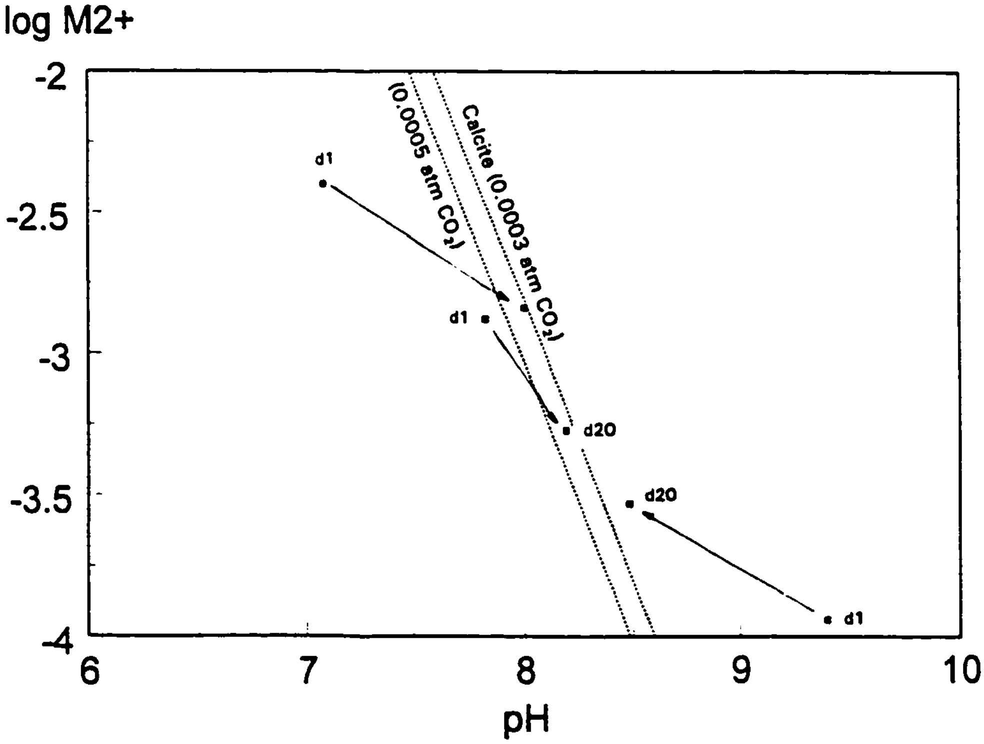

Fig. 7.2 Ca Solubility from JLS-1

Table 7.1 Composition of Simulants and Lunar Soils from Apollo Missions

(a) Major Element (>1.0 wt.%) and Minor Element (>0.1%, <1.0%) Content

Weight Percentage

	JLS-1	Apollo 14 14163	Apollo 14 S&B	MLS	Apollo 11 10084	Apollo 11 S&B
	a)	b)	c)	d)	d)	c)
SiO_2	48.2	48.0	48.1	43.9	42.6	42.0
Al_2O_3	15.2	17.6	16.7	13.7	13.5	12.6
FeO	7.4	10.4	9.5	13.4	15.2	16.4
CaO	10.5	11.2	10.7	10.1	12.0	11.7
MgO	9.1	9.2	10.2	6.7	8.0	7.9
TiO_2	1.6	1.8	1.5	6.3	7.7	7.9
Fe_2O_3	3.5	0.0	0.0	2.6	0.0	0.0
Na_2O	2.7	0.7	0.7	2.1	0.4	0.5
K_2O	0.8	0.6	0.4	0.3	0.1	0.2
MnO	0.2	0.1	0.1	0.2	0.2	0.2
P_2O_5	0.7	0.5	0.4	0.2	0.1	0.1
TOTAL	99.9	100.1	98.3	99.5	99.8	99.5

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a) McKay et al., 1994. Loss on ignition subtracted.

b) Morris et al., 1983.

c) Haskin and Warren, 1991. S&B = soils and breccias. Apollo 14 data for SiO_2, Al_2O_3, FeO, CaO, MgO, TiO_2, and Na_2O is for breccias only.

d) Weiblen and Gordon, 1988.

(b) Content of Selected Trace Elements

ppm

	JLS-1	Apollo14 S&B	MLS	Apollo 11 S&B
	a),b)	c)	d)	c)
Cr	277 (274)	1496	173	1986
Sr	910 (860)	184	212	163
Zn	197 (NA)	27	122	25
Ni	191 (137)	411	97	199
Cu	90 (NA)	NA	445	12

NA = not available

a) Analysis of digest

b) Values enclosed in parentheses from McKay et al., 1994.

c) Haskin and Warren, 1991. Cu value is average of 2 values.

d) Weiblen and Gordon, 1988.

Table 7.2 AB-DTPA Extraction of JLS-1

Diagnostic ranges from Soltanpour, 1991

Element	K	P	Fe	Mn	Zn	Cu
ppm	44.0	7.5	15.2	1.8	1.0	1.6
Std. Dev.	3.2	0.5	0.9	0.1	0.2	0.3
Low	0-60	0-3	0-2.0	0-0.5	0-0.5	0-0.2-
Moderate	61-120	4-7	2.1-4.0	0.6-1.0	0.6-1.0	0.2
High	120+	8-11+	4.0+	1.0+	1.0+	0.2+

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APPENDICES

Appendix 3.1 Problems with Competitive Chelation Methods for Estimating Free Metal Ion Activities

J.P. Oglesby. 1996. Competitive-chelation methods for estimating free metal ion activities. Soil Science Society of America Journal 59: 959.

Competitive-Chelation Methods for Estimating Free Metal Ion Activities

Several articles have been published during the past decade on competitive-chelation methods for estimating activities of free metal ions in soil solutions (Workman and Lindsay, 1990; Ma and Lindsay, 1990, 1993; El-Falaky et al., 1991). Each method utilizes a well-characterized ligand (e.g., ethylenediaminetetraacetic acid [EDTA]) that binds mostly with two ions: the free metal ion being estimated and a competing ion from a carbonate mineral. The carbonate mineral is selected to "fix" the activity of the competing ion.

To complete the method, a constant amount of ligand, with varying mole fractions of the two ions, is added to each of a series of preequilibrated solutions that contain the soil of interest and the carbonate mineral providing the competing ion. After several days to a week of shaking, the equilibrium mole fraction for the two ions is determined graphically from a crossover point, as shown in Fig. 1. The equilibrium mole fraction can then be used to compute the activity for the free metal ion being measured.

Two key implicit assumptions for these methods have not been discussed or tested. The first assumption is that the ligand used in the chelation method does not significantly change the solubility control for the free metal ion being estimated. The assumption should be tested to demonstrate that the estimated activity is not associated with an artifactual solubility control created by adding ligand to the soil solution. In my opinion, two types of artifacts are possible. The first is a new amorphous solubility control, which precipitates with weathering of soil minerals during the shaking period following ligand addition. The second is a modified solubility control, which results from ligand adsorption to the original solubility control. Since the ligand is selected to have high affinity for the free metal ion being estimated, it probably has high adsorptive affinity for the original solubility control as well. Norvell and Lindsay (1982), in early work related to competitive chelation, showed that a significant amount of EDTA was adsorbed. Changes in solubility controls can result in large changes in free metal ion activities. The range associated with crystalline to related amorphous minerals can be several orders of magnitude.

The second assumption of the chelation methods is that the carbonate mineral providing the competing ion is at equilibrium with atmospheric CO_2 at a partial pressure of 0.0003 atm. Partial pressures of CO_2 in soil solution can vary by several orders of magnitude depending on the extent of microbial activity. Unless CO_2 levels are known and controlled, carbonates are poor selections for minerals to provide competing ions.

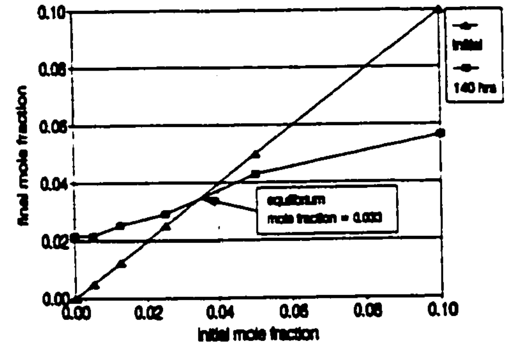

Fig. 1. Changes in $CdL/(CdL + PbL)$ mole fractions after reacting solutions with the Harland soil for 140 h. The intersections of the two lines gives the $CdL/(CdL + PbL)$ mole fraction that reflects equilibrium conditions (from Workman and Lindsay, 1990).

If the assumptions discussed are not true, actual free metal ion activities may differ from those estimated by several to many orders of magnitude.

Dep. of Agronomy
Colorado State Univ.
Ft. Collins, CO 80523

JAMES OGLESBY

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Appendix 4.1 Estimate of the Carbonate Amount in JLS-1

1. Samples A,B — 10 g JLS-1 + 25 ml 0.1 N HCl
   3 ml 0.1 N NaOH as CO_2 trap

   Samples C,D — Same, but no JLS-1

2. mls 0.1 N HCl to titrate 1 ml of NaOH from trap

Sample A	0.98
Sample B	1.20
Sample C	1.80
Sample D	1.70
Avg. A,B	1.09
Avg. C,D	1.75

3. Calculation

$$\frac{3(1.75-1.09)\ \text{ml HCl}}{0.01\ \text{kg JLS-1}} \times \frac{1\ \text{ml NaOH}}{1\ \text{ml HCl}} \times \frac{0.10\ \text{mole NaOH}}{1000\ \text{ml NaOH}} \times \frac{0.5\ \text{mole } CO_3^{2-}}{\text{mole NaOH}}$$

$$= 0.01\ \text{mole } CO_3^{2-}\ /\ \text{kg JLS-1}$$

Appendix 4.2 Mn and Al Solubility from MLS After 3 Weeks (Means and Standard Deviations, n=2)

pH	log Mn^{2+}	log Al^{3+}
8.28±0.05	-6.33±0.09	-
7.17±0.07	-4.44±0.04	-
4.66±0.02	-3.84±0.16	-5.28±0.11
4.26±0.13	-3.72±0.02	-4.81±0.20

APPENDIX A
SELECTED EQUILIBRIUM CONSTANTS

Appendix A. Selected Stability Constants, Relative to MINTEQA2 Components

Mineral/Complex	log K°	Source/Notes
$AlOH^{2+}$	-5.0	Nordstrom and May (1989)
$Al(OH)_2^+$	-10.1	
$Al(OH)_4^-$	-22.7	
$Al(OH)_3^0$	-16.8	
$Mg_2Si_3O_{7.5}(OH)*3H_2O$ Sepiolite(am)	-18.8	Wollast (1968)
$Al(OSi(OH)_3)^{2+}$	-1.1	Browne and Driscoll (1992)
$CaMg(CO_3)_2$ Disordered dolomite	17.0	Helgeson (1969)
$MnCO_3$	11.0	Garrels et al. (1960)
$CaC_2O_4*H_2O$	8.6	Harrison and Thyne (1991)
Ferrihydrite	-5.0	Schwertmann and Taylor (1989)/ extreme of -2.6 to -5.0
Ca-oxalate	3.0	Smith and Martell (1977-1989)
Ca-succinate	2.0	
Ca-glycolate	1.6	
Ca-acetate	1.2	
Ca-propionate	1.0	0.50 = log K(0.2M)
Ca-butanoate	1.0	0.51 = log K(0.2M)
Ca-citrate	4.7	
Ca-malate	2.7	
$AlOHSO_4*5H_2O$ Jurbanite	3.8	Nordstrom (1982)
$KAl_3(SO_4)_2(OH)_6$ Alunite	-0.6	Nordstrom (1982)/ extreme of 1.4 to -0.6
H-oxalate	4.3	Smith and Martell (1977-1989)
H-succinate	5.6	
H-glycolate	3.8	
H-acetate	4.8	
H-propionate	4.9	
H-butanoate	4.8	
H-citrate	6.4	
H-malate	5.1	

Mineral/Complex	log K°	Source/Notes
Mg-oxalate	3.4	Smith and Martell (1977-1989)
Mg-succinate	2.1	
Mg-glycolate	1.3	
Mg-acetate	1.3	
Mg-propionate	1.1	0.54 = log K(0.2M)
Mg-butanoate	1.0	0.53 = log K(0.2M)
Mg-citrate	4.7	3.37 = log K(0.1M)
Mg-malate	2.6	1.70 = log K(0.1M)

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