

MINERALOGICAL AND CHEMICAL PROPERTIES OF
AGRICULTURALLY ACIDIFIED SOILS IN COMPARISON WITH
NATURALLY ACIDIC SOILS

by

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ABSTRACT

Agricultural soils that have been rapidly acidified may be in pseudo-equilibrium or non-equilibrium states wherein minerals that were stable at higher pH may dissolve and release a suite of ions unlike those found in soils acidified by natural weathering (pedologically acidic soils). Acidification and accelerated mineral weathering as a result of N fertilization may result in solution silica activity that favors the formation of short-range-order aluminosilicates, thereby sequestering Al. Furthermore, soils formed in alluviums of differing lithology may partition Al^{3+} into different solid-phase pools. One hypothesis examined in this thesis was that parent material silica content of agriculturally acidified soils controls solution silica levels and short-range-order aluminosilicate formation, thereby controlling solution Al^{3+} activity. Because the rhizosphere is a zone of altered pH and Al solubility, it follows that parent material silica content can also affect the composition of pore water extracts from the rhizosphere. Therefore, it was hypothesized that roots via their effect on solution composition influence soil mineralogy. To test the first hypothesis, the mineral assemblages in non-acidified, agriculturally-acidified and naturally-acidic soils formed in sialic, mafic, and mixed alluvium were compared. To test the second hypothesis porewater from the rhizosphere of three different parent materials growing fescue and tomato was extracted and analyzed. X-ray diffraction analysis revealed that the clay fraction bulk mineralogy of agriculturally-acidified soils is similar to their non-acidified counterparts but is quite different from the pedogenically weathered soils. A combination of selective dissolution and CEC

measurements suggested that interlayering of smectites and precipitation of short-range-order aluminosilicates are the main mechanisms that control solution Al, but details vary among the three parent materials. Agriculturally-acidified soil from sialic parent material exhibited increased oxalate-extractable Al (acid-ammonium-oxalate; Al_o), without a concomitant increase in Si. This plus a modest increase in KCl-extractable Al (Al_{KCl}), suggested that the largest Al pool in the acidified sialic soil was a short-range-order hydroxy-Al. This pool may be associated with interlayers of vermiculite, although x-ray diffraction detected only minor amounts of vermiculite and did not strongly indicate the presence of hydroxy-interlayered-material (HIM). X-ray diffraction analysis of mafic soils indicated that clay fractions of the non-acidified and agriculturally-acidified soils are dominated by smectite. These smectites have a high d-spacing shoulder that could be a result of interlayer hydroxy-Al and/or hydroxy-aluminosilicate. Analysis did not unequivocally identify hydroxy-aluminosilicate in the interlayer; the high d-spacing shoulders may also indicate a low charge smectite. Acidification of the mafic soil resulted in increased Al_o and Si_o concentrations. Together with the lack of increased Al_{KCl} , this increased Al_o and Si_o suggested the presence of a short-range-order aluminosilicate pool in the agriculturally-acidified soil. Non-acidified and agriculturally-acidified clay fractions with mixed lithology are dominated by vermiculite and HIM. Acidification of these soils: (i) increased Al_{KCl} ; (ii) increased Al_o without a Si_o increase; and (iii) caused CEC_7 to decrease. These changes suggest that hydroxy-Al interlayering is the main Al sink. These results partly support the hypothesis that short-range-order aluminosilicates play some

role in controlling soil solution Al activity. These results suggest more strongly that interlayering of 2:1-type phyllosilicates by hydroxy-Al and/or aluminosilicates represents the largest Al and Si sink in the agriculturally-acidified soils regardless of the mineralogy. Comparison of the rhizosphere soil solutions to stability diagrams representing the dominant clay fraction mineralogy shows that the solutions generally reflect the dominant mineralogy of the clay fraction and that the solutions are not at equilibrium with the solid phases chosen for the stability diagrams. Among samples from the rhizosphere, the dicot (tomato) generally increased rhizosphere solution Si more than the monocot (fescue). Comparison of stability indexes for dominant clay minerals in the mafic soil rhizosphere solutions suggests a montmorillonite to beidellite to kaolinite transformation. In the sialic soil, a hydroxy-interlayer-material phase may be present and undetectable by x-ray diffraction. In soils derived from a mixed lithology, composition of the rhizosphere tended to move toward equilibrium with HIM. In the non-acidified and naturally-acidic mixed lithology soils, tomato increased silica more than fescue, but in the agriculturally-acidified soils the fescue was equal to or greater than tomato with respect to increasing silica in the rhizosphere. Generally, solutions extracted from samples of tomato rhizosphere were displaced from equilibrium more than were samples from the bulk soil. The rhizosphere (defined here as soil subjected to repeated cropping) effects are varied and depend on soil mineralogy and the type of plants grown. Generally, rhizosphere samples are less acidic than bulk soil in acid soils and less alkaline than alkaline bulk soils.

TABLE OF CONTENTS

| | |
|--|----|
| Introduction..... | 1 |
| Materials and Methods | 3 |
| Field | 3 |
| Lab | 4 |
| Results and Discussion..... | 6 |
| Sialic Parent Material..... | 6 |
| Mafic Parent Material..... | 7 |
| Mixed Parent Material..... | 10 |
| Summary..... | 12 |
| References..... | 13 |
| Introduction..... | 24 |
| Materials and Methods..... | 27 |
| Field - Collection of Soil Samples..... | 27 |
| Lab and Greenhouse..... | 27 |
| Generation of Rhizosphere Soil (Study #1)..... | 28 |
| Cropping Intensity Study (Study #2)..... | 29 |
| Results and Discussion..... | 31 |
| Cropping Intensity – Rhizosphere Soil Development..... | 31 |
| Clay Fraction Mineral Stabilities..... | 31 |
| Sialic Parent Material..... | 31 |
| Mafic Parent Material..... | 34 |
| Mixed Parent Material..... | 38 |
| Conclusions..... | 38 |
| References..... | 40 |
| Appendix..... | 52 |
| Solution Activities | 52 |
| Stability Calculations..... | 53 |
| Soil Iron..... | 53 |

| | |
|------------------------------------|----|
| | vi |
| Quartz..... | 54 |
| Amorphous Silica..... | 55 |
| Gibbsite..... | 56 |
| Kaolinite..... | 57 |
| Montmorillonite..... | 58 |
| Beidellite..... | 59 |
| Hydroxy-Interlayer-Material..... | 60 |
| Montmorillonite to Beidellite..... | 61 |

LIST OF TABLES

| | |
|--|----|
| Table 1-1.1. Classification, location, current crop and modal pH of soils used in the study. | 21 |
| Table 1-1.2. Selected soil properties for the soils used in the study. | 22 |
| Table 1-1.3. Selective dissolution chemistry of the soils used in the study. | 23 |
| Table 2-2.1. Classification, location and current crop grown on soils used in study. | 47 |
| Table 2-2.2. Thermodynamic values used to construct stability-equilibrium lines. | 48 |
| Table 2-2.3. Solution activities determined from cropping intensity (Study #2) and used in stability-equilibrium diagram.†..... | 48 |
| Table 2-2.4. Mineralogy of the clay fraction from soils used in this study. | 49 |
| Table 2-2.5. Solution activity increase or decrease in rhizosphere samples relative to bulk soil in Study #1. | 50 |
| Table 2-2.6. Saturation index [$\log(\text{IAP}/\text{KSP})$] for solutions extracted from bulk and rhizosphere soils with different parent materials (0=equilibrium, >0 is super-saturated, and <0 is under-saturated)..... | 51 |

LIST OF FIGURES

| | |
|--|----|
| Figure 1-1.1. Clay fraction ($< 2 \mu\text{m}$) x-ray diffractograms from soils formed in sialic alluvium. | 18 |
| Figure 1-1.2 Clay fraction ($< 2 \mu\text{m}$) x-ray diffractograms from soils formed in mafic alluvium..... | 19 |
| Figure 1-1.3 Clay fraction ($< 2 \mu\text{m}$) x-ray diffractograms from soils formed in mixed alluvium. | 20 |
| Figure 2-2.1. Stability diagram for solutions extracted from samples of tomato rhizosphere soil. The growth media was a sialic non-acidified soil. Bars are standard error of mean. Some error bars fall within the size of the symbol..... | 43 |
| Figure 2-2.2. Stability diagrams for solutions from non-acidified, agriculturally-acidified and naturally-acidic soils formed in sialic alluviums. The symbols are B = Bulk soil (uncropped); rhizosphere tomato (T), and rhizosphere fescue (F). The numeric values are average solution pH. Bars are standard error of mean. Some error bars fall within the size of the symbol..... | 44 |
| Figure 2-2.3. Stability diagrams for solutions from non-acidified, agriculturally-acidified and naturally-acidic soils formed in mafic alluviums. The symbols are B = Bulk soil (uncropped); rhizosphere tomato (T), and rhizosphere fescue (F). The numeric values are average solution pH. Bars are standard error of mean. Some error bars fall within the size of the symbol. | 45 |
| Figure 2-2.4. Stability diagrams for solutions from non-acidified, agriculturally-acidified and naturally-acidic soils formed in mixed alluviums. The symbols are B = Bulk soil (uncropped); rhizosphere tomato (T), and rhizosphere fescue (F). The numeric values are average solution pH. Bars are standard error of mean. Some error bars fall within the size of the symbol. | 46 |

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Chapter 1

MINERALOGICAL COMPARISON OF AGRICULTURALLY-ACIDIFIED AND NATURALLY-ACIDIC SOILS

Introduction

Soils acidified as a result of natural pedogenic processes generally are marked by depressed cation exchange capacity, lower potential for alkaline earth and alkali metal (base) cation releases, and increased influence of acidic cations, particularly Al (Foy, 1984; Thomas and Hargrove, 1984). Soil acidification resulting from fertilization practices may produce soil pH similar to the pH of naturally-acidic soils. Agricultural N amendment practices utilizing ammonium or urea sources cause release of protons during nitrification, which can result in clay mineral degradation and reduced mineral cation exchange capacity (Barak et al., 1997; Blake et al., 1999; Blevins et al., 1977; Bouman et al., 1995; Schwab et al., 1989). In the western USA, the acidification effect may be magnified by sulfur-supplying fertilizers and direct elemental S additions (Jackson and Reisenauer, 1984; Stallings, 1991). Weathering of the clay fraction minerals to low activity clays is one possibility and prominence of these clays is represented in the latter stages of Jackson's and Sherman's (1953) relative degree of soil development. In less weathered soils, chloritization can account for cation exchange capacity reductions (Barnhisel and Bertsch, 1989). Additionally, Al freed as a result of primary mineral weathering competes more effectively for exchange sites (Rampazzo and Blum, 1992;

Thomas and Hargrove, 1984). Jackson and Reisenauer (1984), however, contended that soils in the western USA acidified by agricultural practices have less Al contributing to exchangeable acidity than naturally acidic soils.

Rampazzo and Blum (1992) compared x-ray diffractograms from very acidic soil (pH ~3) affected by acid rain to non-acidic soils and reported alterations in clay fraction minerals. They documented Al loss from Al-hydroxy-interlayers in chlorite and a sharper vermiculite x-ray diffraction peak. Conversely, in laboratory experiments at less acidic conditions (pH 4.07-4.46) Lou and Haung (1988; 1994) and Sakurai and Haung (1998) reported adsorption of hydroxy-aluminosilicates and hydroxy-aluminum into montmorillonite interlayer spaces. Vermiculite also incorporates hydroxy-aluminosilicates in the interlayer (Inoue and Satoh, 1992; Lou and Huang, 1995). Alteration of clay minerals is often coincident with formation and persistence of x-ray amorphous hydroxy-aluminosilicate products (Hem et al., 1973).

Selective dissolution is widely used to estimate the x-ray amorphous, short-range-order allophane and imogolite pools and Al and Fe in metal-humus complexes in soils with andic and spodic properties (Dahlgren, 1994; Parfitt and Kimble, 1989; Southard and Southard, 1989), but the extractions are equally applicable to characterization of short-range-order compounds in other soils.

The hypothesis was that lithology affects the partitioning of acidic Al cations into different solid-phase pools. In silic alluvium, acidification and accelerated soil mineral weathering by N-fertilization may produce enough silica to favor formation of short-

range-order aluminosilicates that incorporate and thereby sequester Al. Soils formed in mafic alluvium, with less Si, are not expected to exhibit Al sequestered in the short-range-order pool as strongly as sialic materials. Soils formed in alluvium of mixed lithology, and silica content, are expected to exhibit intermediate behavior bounded by sialic and mafic parent materials.

By comparing non-acidified members of soils formed in sialic, mafic and mixed alluvium to naturally-acidic and agriculturally-acidified soils, the objective was to assess the effect of mineralogy on the partitioning of Al among various solid-phase pools. It was hypothesized that Al sequestration in a short-range-order pool would be greatest in agriculturally-acidified soils formed in sialic alluvium and least in soils from mafic alluvium.

Materials and Methods

Field

All soils are located in California in a xeric soil moisture regime and a thermic soil temperature regime. Soils were sampled to represent non-acidified (NA), naturally-acidified (acidic) and agriculturally-acidified (AA) members from sialic, mafic and mixed (not dominantly sialic or mafic) parent material (Table 1-1.1). The AA members sampled in tree crop locations were sampled in the drip basins of fertigation emitters. In tree crop sampling locations of the mafic and mixed soils, the NA and AA samplings occurred within 1 to 3 m of each other. Where possible B horizon samples were used to reduce

effects from organic matter and residual surface amendments, but for the AA and NA mafic soils, samples were collected from surface horizons.

Mixed AA soil received application of either ammonium sulfate or calcium nitrate at 800 kg ha⁻¹ for two years followed by 200 kg ha⁻¹ N as ammonium sulfate since 1991.

Nitrogen application in these research plots sampled for this study (800 kg N ha⁻¹) exceeds those typically applied to commercial almond orchards (200-300 kg N ha⁻¹), and fertilizer materials were applied to the drip irrigation basins, which occupy about 1 % of the area (Zasoski et al. 1997). Application rates and types for amendments for the mafic and silic soils are unknown.

Lab

Soils were air dried, sieved to pass through a 2- mm sieve and analyzed for particle size distribution, pH, extractable cations, selective dissolution of Fe, Al, and Si and clay mineralogy. Particle size distribution was determined by pipet method as described by Gee and Bauder (1986). Carbon was determined with a Fisons NA1500NC (Fisons Instruments, Beverly, MA) by dry combustion and infra-red detection of evolved CO₂ (Nelson and Sommers, 1982).

Soil reaction was determined in water (1:1 soil to water), 0.01 M CaCl₂ (1:2 soil:solution), and in a saturated soil paste (McLean, 1982; National Soil Survey Center, 1996).

Extractable cations were measured by displacement with 1 M BaOAc pH 7. Cation exchange capacity (CEC) was measured by ICP spectrometry by the difference in solution Ca following displacement of the Ba by Ca from a 0.58 M CaSO₄ · 2H₂O solution

(Janitzky, 1986; Rible and Quick, 1960) and by unbuffered 1 M NH_4Cl (National Soil Survey Center, 1996).

Extractable Al (Al_{KCl}) was extracted with 1 M KCl after 30-minute equilibration with agitation and vacuum filtration (National Soil Survey Center, 1996). The Al concentrations were measured with ICP spectrometry.

The clay-size ($<2 \mu\text{m}$) fraction was separated from the fine-earth fraction by repeated centrifugation following dispersion in dilute $\text{Na}_6(\text{PO}_3)_6$. No pretreatment to remove iron or organic matter was performed. Clays were washed with MgCl_2 or KCl salt solutions, rinsed with deionized water to remove excess salts, and mounted as oriented aggregates on glass slides. X-ray analyses were made with a Diano XRD 8000 diffractometer (Diano Corporation, Woburn, MA) producing Cu $\text{K}\alpha$ radiation. After the initial diffraction analysis the MgCl_2 treated samples were treated with glycerol and formamide and reanalyzed. The KCl samples were reanalyzed after 350°C and 550°C heat treatments (Whittig and Allardice, 1986).

Air-dry materials from the fine-earth fraction were extracted with sodium pyrophosphate, ammonium oxalate, and citrate-dithionite using the methods of the National Soil Survey Center (1996). Extracts were analyzed for Al, Si and Fe concentrations using ICP spectrometry. Initial oxalate-extractable Fe (Fe_o) was higher than dithionite-extractable Fe (Fe_d) for the NA and AA soils derived from sialic and mafic alluvium, suggesting the presence of magnetite. The presence of magnetite was confirmed in the magnetic fraction of these soils by x-ray diffraction. Oxalate dissolution was performed

sequentially after citrate dithionite treatment to estimate the Fe_0 fraction attributable to magnetite and deducted from Fe_0 reported in Table 1-1.3.

Results and Discussion

Across the range of soils and parent materials, agricultural practices have produced acidification (Table 1-1.2). In all soils except the mafic acidic sample, pH increased with dilution and decreased with salt addition, suggesting that negatively charged clays dominate the soil exchange properties (Thomas and Hargrove, 1984). Only in the mafic acidic sample are the soil properties dominated by oxyhydroxides.

The CEC measured by unbuffered salt (CEC_{NH_4Cl}) decreases with acidification. This is particularly relevant in the mafic and mixed lithology soils since they are pairs collected only a few meters apart. If the calculated CEC to clay ratio is considered, the decrease of the exchange capacity is extended through the acidic soil with each lithology (Table 1-1.2).

Sialic Parent Material

Clay fraction diffractograms of soil derived from sialic alluvium show a dominance of mica (persistent 1.0 nm peak), kaolinite (0.72 nm peak disappears with 550°C heat treatment), and a minor amount of vermiculite (1.4 nm peak collapses to 1.0 nm with heat). The AA soil shows a broad low shoulder between 1.4 and 1.0 nm that could be some incipient interlayering of the vermiculite resulting in incomplete closure to 1.0 nm with heat. Kaolinite content, based on peak intensities and CEC:clay ratios, is greater in

the acidic than in the NA and AA soils (Table 1-1.3). Even in the acidic soil the clay fraction was dominated by mica.

Selective dissolution results are shown in Table 1-1.3. The total "pedogenic" Fe content (citrate-dithionite; Fe_d) and short-range-order (acid-ammonium-oxalate; Fe_o) generally increases from NA, through AA, to the acidic soil. This pattern suggests that acidification of the soil by fertilization may enhance the weathering of Fe-bearing minerals and mimics the longer-term weathering processes.

The Al distribution shows that dithionite-extractable Al (Al_d) and organically bound Al (pyrophosphate extractable; Al_p) both increase from the NA to the acidic soils. The Al_p is as great as Al_d in the NA and AA soils suggesting that citrate-dithionite is extracting primarily organically bound Al (Table 1-1.3). Extractable Al (Al_{KCl}) increased in the AA soil but is lower in the acidic soil despite Al_d and short-range-order fraction (Al_o) increases (Table 1-1.3). Since the short-range-order Si pool (Si_o) did not increase as Al_o increased in the AA soils, the Al is most likely in a hydroxy-Al pool. This hydroxy-Al pool could be associated with the interlayers of the 2:1 mineralogy, but polymerization of the hydroxy-Al is not of great enough extent to be detectable by x-ray diffraction as a distinct peak or well-formed shoulder.

Mafic Parent Material

The clay fractions of soils derived from mafic alluvium are dominated by smectite (1.56 nm Mg-saturated peak that expanded with glycerol solvation) with a minor amount of kaolinite (0.72 nm peak disappears with heating to 550°C) in the NA and AA soils.

Acidified soil clay mineralogy resembles that of NA despite the acidified soil's strongly acid reaction class (Table 1-1.2). The acidic soils are dominated by halloysite (0.73 nm and 0.445 nm peak shifting to higher d-spacing with formamide treatment and disappearing with heating to 550°C), gibbsite (0.489 nm and disappearing with heating to 550°C), and goethite (0.415 nm and disappearing with heating to 550°C) (Figure 1-1.1). In the NA and AA mafic lithology soils, the resistance to collapse with K-saturation and residual higher d-spacing shoulder with heat treatment indicates interlayering of smectite. Lou and Huang (1994) and Sakurai and Huang (1998) showed that XRD diffractograms of hydroxy-Al interlayered smectite have lower K-saturated 25°C peak d-spacings than hydroxy-aluminosilicate interlayered smectite. The mafic NA and AA x-ray diffractograms do show large K-saturated d-spacing peaks at 25°C, and the decrease in CEC indicates that exchange sites, probably interlayer, are partially blocked or occupied by non-exchangeable cations. Alternately, the higher d-spacing could indicate a low charge smectite as suggested by the large Mg-saturated d-spacing. Our data did not allow us to unequivocally identify interlayer hydroxy-aluminosilicate.

Increases in Fe_d and Fe_o from NA through AA to the acidic soil were similar to the sialic lithology and suggest acidification by fertilization enhances weathering of the Fe bearing minerals. The acidic mafic soil shows the greatest Al_d . This pattern follows that of Fe_d , and for the mafic and mixed acidic soils may reflect the isomorphous substitution of Al for Fe in goethite (Norrish and Taylor, 1961). At least four other sources of Al_d are possible. First, the representation of the Al substitution in Fe-oxyhydroxides, $Al_d-Al_p/$

($Al_d-Al_p + Fe_d-Fe_p$), assumes that all of the Al_d-Al_p , up to 22%, is extracted from the Fe-oxhydroxides. Goethite was abundant enough, or sufficiently crystalline, to be identified by XRD and $Al_d > Al_o$ in the mafic acidic soil. Because goethite was not detected by XRD, it is difficult to argue for Al-substituted goethite in the other soils. It is possible, however, that Al substitution in ferrihydrite contributed to the Al_o pool or that goethite, present in amounts too small to be detected by XRD, contributed to the Al_d pool.

Second, increases in Al_d-Al_p may also arise from isomorphically substituted Al in crystalline 2:1 phyllosilicates minerals (Sridhar and Jackson, 1974). Citrate-dithionite, however, is considered a poor extractor of Al from these sources (Wada, 1989). Third, contributors to the Al_d-Al_p pool could include hydroxy-aluminosilicates (allophane- and imogolite-like materials), as dithionite-citrate may dissolve some of these components (Dahlgren, 1994; Parfitt and Childs, 1988). Finally, Al extracted from interlayers of 2:1 materials may also contribute to the Al_d and perhaps the Al_o pool. McKeague and Day (1966) found XRD pattern enhancement (sharper peaks) after both citrate-dithionite and acid-ammonium-oxalate treatments of HIM and expansion with glycerol of artificially prepared Al-chloritized bentonite. Iyengyr et al. (1981) attributed Al interlayer extraction by citrate-dithionite and acid-ammonium-oxalate to interlayer stability as evidenced by XRD peak intensity shifts, or lack thereof, from 1.4 nm to 1.0 nm, and concluded that acid-ammonium-oxalate was less aggressive than citrate-dithionite.

The acidic mafic soil has no 2:1 phyllosilicates detectable by XRD. Therefore, the Al_d in the acidic mafic soil is attributed to non-interlayer sources. The nature of the Al_d pools in

the NA and AA mafic soils is not as clear. Unlike the silic soil, AA mafic soil extractable Al (Al_{KCl}) did not increase, despite a drop in pH and an increase in the Al_d and Al_o pools from the NA to AA soil (Table 1-1.2). The increase in Al_o and Si_o from the NA to AA mafic soil shows an increase in the short-range-order aluminosilicate pool. The Al_d increase is less than the Al_o increase, and dithionite is assumed to be more aggressive than oxalate at removing interlayers (Iyengar et al., 1981). The $(Al_o - Al_p)/Si_o$ values (0.4 – 2.7) for the mafic NA and acidic soils suggest the occurrence of a non-interlayer, short-range-order aluminosilicate similar to allophane.

If interlayer hydroxy-aluminosilicate polymers are responsible for the high d-spacings in the diffractograms, they behave differently than those described by Iyengar et al. (1981). In their work interlayer polymers were not soluble in oxalate. The mafic soil results were interpreted to mean that the combination of a very low charge smectite and poorly polymerized interlayer hydroxy-aluminosilicates allow the interlayer phase to dissolve in oxalate.

Mixed Parent Material

The NA and AA soils derived from mixed alluvium contain mostly vermiculite (1.4 nm collapses to 1.0 nm) and hydroxy-interlayered material (HIM, 1.4 nm collapses to 1.17 nm), plus minor amounts of mica (persistent 1.0 nm) and kaolinite. The mixed acidic soil is dominated by kaolinite and contains only a minor amount of mica and goethite (Figure 1-1.3). In this case, the clay mineralogy of the AA soil most closely resembles that of the NA soil.

The decrease of CEC from NA to AA soil as measured by unbuffered salt (CEC_{NH_4Cl} , Table 1-1.2) may be the result of non-exchangeable aluminum on the exchange complex or further pillaring in the interlayer, thereby blocking exchange sites presumably as hydroxy-Al polymers. The increase of CEC_7 in the AA soil is interpreted as the increase in pH dependent charge and decrease in permanent charge with hydroxy-Al interlayering (Inoue and Satoh, 1992).

Inoue and Satoh (1992) found that the reduction of negative charge by interlayering in HIM was more pronounced in vermiculites than in smectites. They further noted that the CEC decrease caused by interlayering was diminished as the Si_o/Al_o-Al_p content of the interlayers approached that of allophane ($Si_o/Al_o-Al_p = 0.5$) presumably due to the lower positive charge of a hydroxy-aluminosilicate polymer compared to hydroxy-Al.

The CEC decrease with agricultural acidification is greater in the mixed soil (29%) than in the mafic soil (13%), a pattern consistent with a Si_o/Al_o-Al_p decrease from NA (0.50) to AA (0.25) in the mixed lithology soil and little change in the mafic soil (0.52 to 0.58).

The Al_{KCl} in the mixed lithology AA soil increased, showing that some of the Al released is not polymerized, but probably occurs as Al^{3+} on exchange sites. The increase in both the Al_o and Al_p extractable pools with a smaller increase in the Si_o suggests that hydroxy-Al is the Al sink in the AA mixed soils. It is not clear how this pool is distributed between interlayer and free phases.

Summary

Results show that acidification associated with N-fertilization tends to increase short-range-order pools in all soils and these pools may be associated with interlayers of 2:1 layer silicate minerals, either with hydroxy-Al or hydroxy-aluminosilicates. In none of the cases did acidification greatly alter the bulk soil mineralogy. This trend was similar for all three parent materials, suggesting that these short-range-order aluminosilicates may not be in equilibrium with the solid crystalline phases. These results partially support the hypothesis that silica content of the parent material affects the partitioning of Al, but the presence of 2:1 minerals also plays a major role in determining the sink for Al upon acidification.

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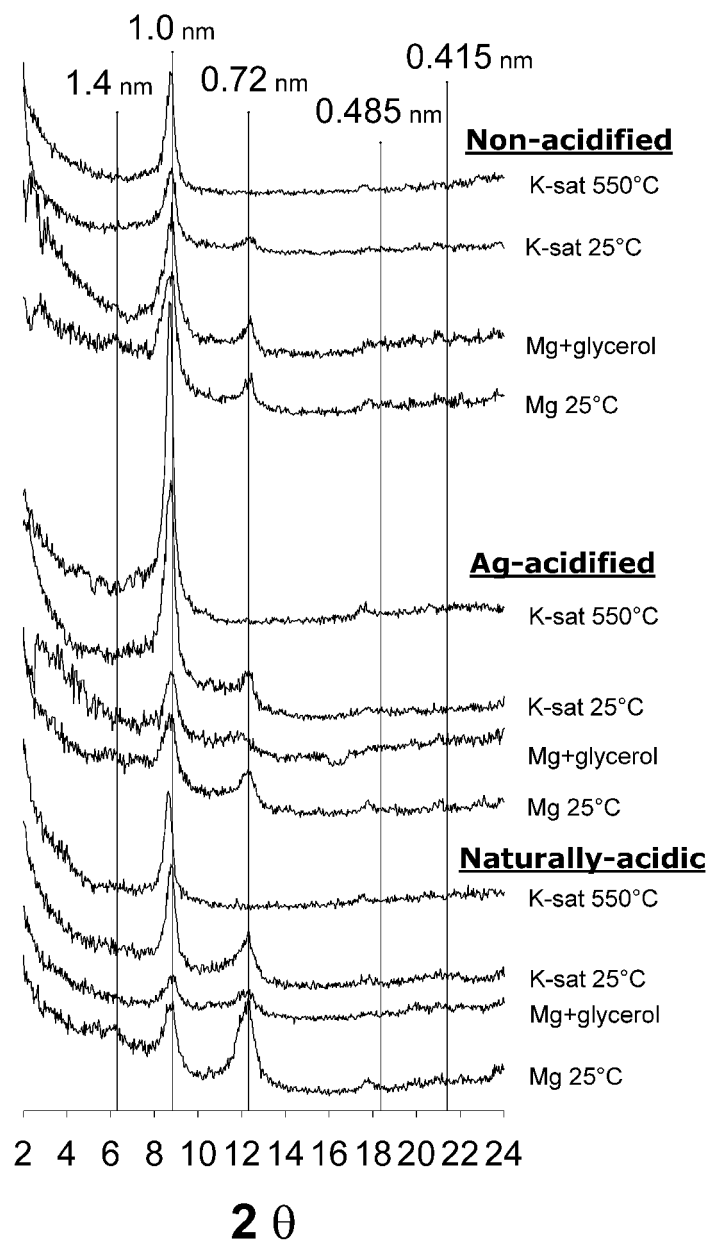


Figure 1-1.1. Clay fraction (< 2 μm) x-ray diffractograms from soils formed in sialic alluvium.

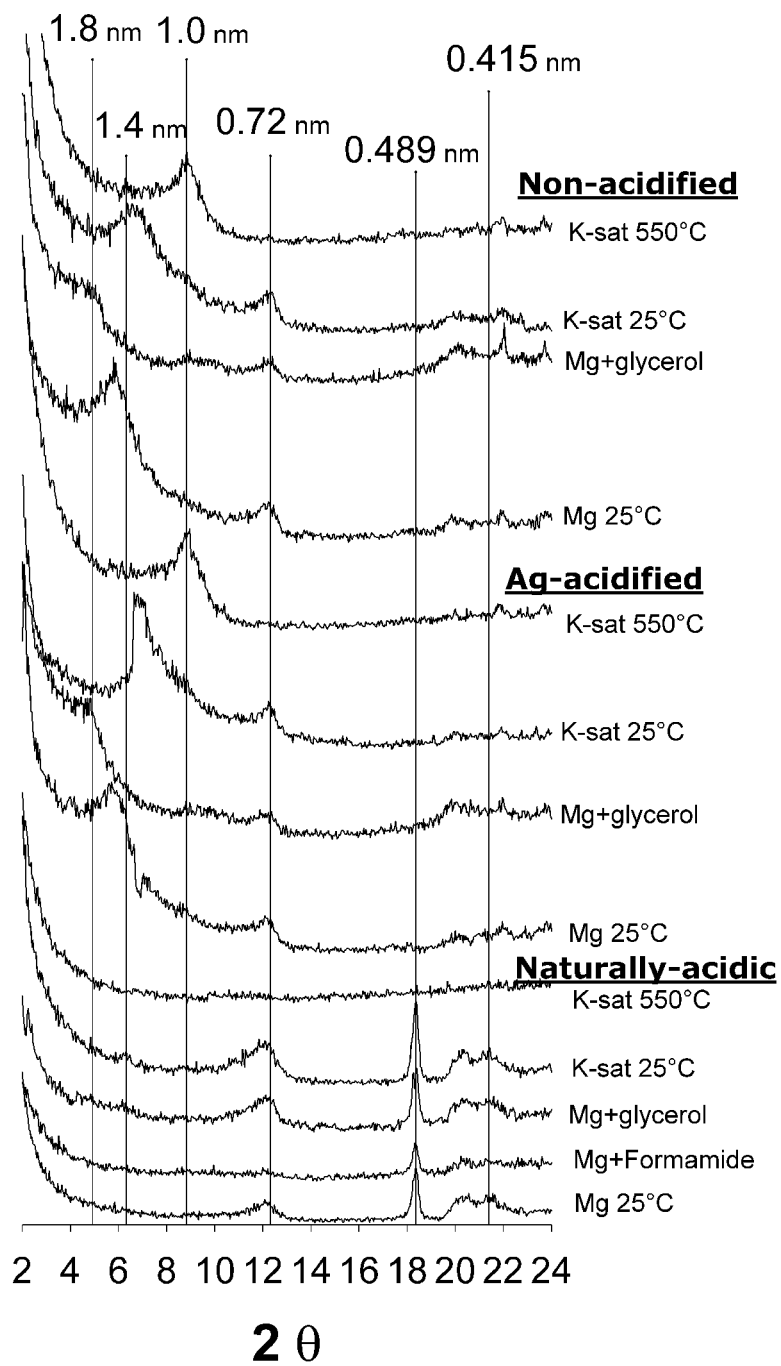


Figure 1-1.2 Clay fraction (< 2 μm) x-ray diffractograms from soils formed in mafic alluvium.

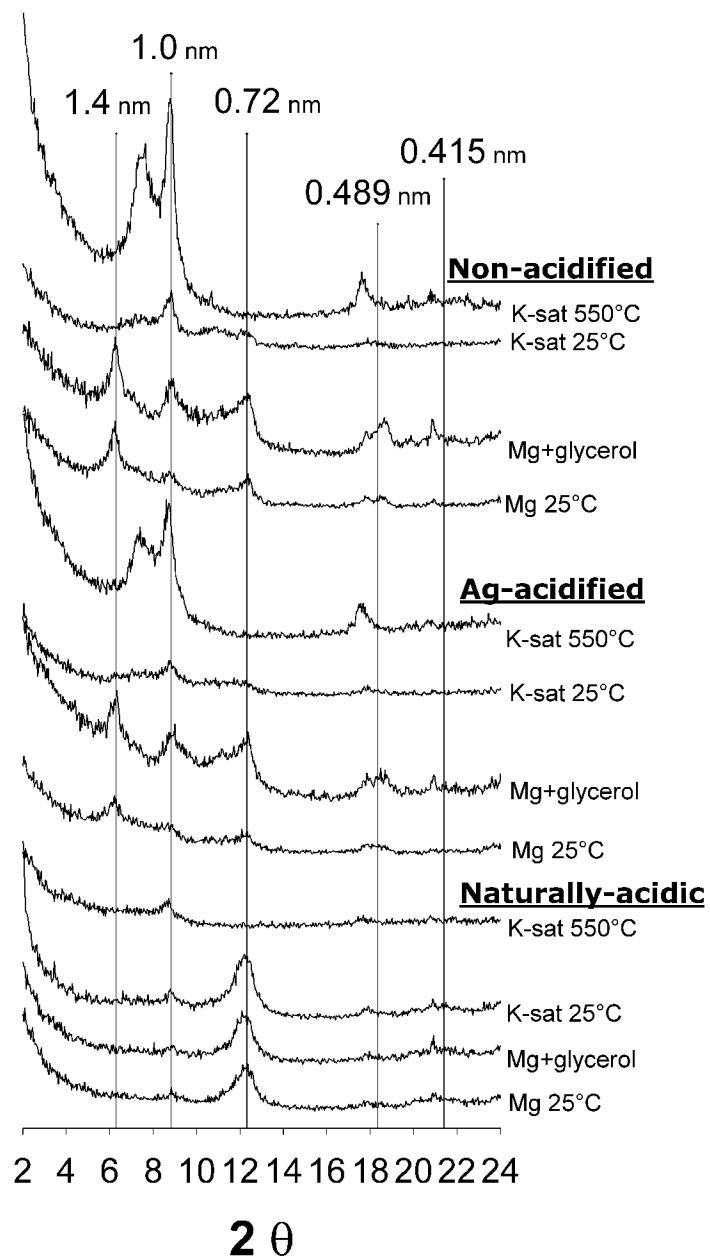


Figure 1-1.3 Clay fraction (< 2 μm) x-ray diffractograms from soils formed in mixed alluvium.

Table 1-1.1. Classification, location, current crop and modal pH of soils used in the study.

| Soil Mapped-As-Classification | Location/ County | Parent Material | Current Vegetation | Condition | Modal pH [†] |
|---|---------------------|--------------------|-----------------------|------------------------------|--------------------------|
| Dinuba series Coarse-loamy, mixed, superactive, thermic Typic Haploxeralf | Stanislaus | Sialic | Row crops | Non-acidified | 6.8 - 7.0 |
| Hilmar series Sandy over loamy, mixed, superactive, calcareous, thermic Aeric Halaquept | Stanislaus | Sialic | Almonds | Agriculturally -acidified | 7 |
| Montpellier series Fine-loamy, mixed, superactive, thermic Typic Haploxeralf | Stanislaus | Sialic | Annual grasses | Acidic | 6 |
| Vina series Coarse-loamy, mixed, superactive, thermic Pachic Haploxeroll | Tehama | Mafic | Walnuts | Non-acidified | 7 |
| Vina series Coarse-loamy, mixed, superactive, thermic Pachic Haploxeroll | Tehama | Mafic | Walnuts | Agriculturally -acidified | 7 |
| Sites series Fine, parassequic, mesic Xeric Haplohumult | Plumas | Mafic | Mixed conifer | Acidic | 5.3 |
| Arbuckle series Fine-loamy, mixed, superactive, thermic Typic Haploxeralf | Colusa | Mixed | Almonds | Non-acidified | 6.2 |
| Arbuckle series Fine-loamy, mixed, superactive, thermic Typic Haploxeralf | Colusa | Mixed | Almonds | Agriculturally -acidified | 6.2 |
| Red Bluff series Fine, kaolinitic, thermic Ultic Palexeralf | Shasta | Mixed | Pasture | Acidic | 5 |

Table 1-1.2. Selected soil properties for the soils used in the study.

| Series | Modal pH [#] | pH [†] | pH [‡] | pH [§] | Extractable Cations | | | | CEC ₇ | CEC _{NH₄Cl} | CEC:Clay [¶] | Sand | Silt | Clay | C _{total} |
|----------------------------------|--------------------------|-----------------|-----------------|-----------------|------------------------|-----|-----|-----|------------------|---------------------------------|-----------------------|------|--------------------|------|--------------------|
| | | | | | K | Ca | Mg | Na | | | | | | | |
| -----cmol kg ⁻¹ ----- | | | | | | | | | | | ----%<2 mm---- | | g kg ⁻¹ | | |
| Sialic | | | | | | | | | | | | | | | |
| NA | 6.8 - 7.0 | 7.8 | 7.3 | 7.1 | 1.1 | 4.7 | 0.6 | 0.7 | 5.5 | 2.9 | 1.19 | 90.1 | 7.5 | 2.4 | 5.3 |
| AA | 7 | 5.4 | 4.5 | 4.8 | 0.1 | 0.4 | 0.1 | <0. | 3.5 | 1.3 | 0.92 | 91.4 | 7.2 | 1.4 | 1.4 |
| Acidic | 6 | 5.2 | 4.6 | 4.8 | 0.3 | 2.1 | 0.4 | <0. | 6.0 | 3.8 | 0.75 | 70.7 | 24.1 | 5.1 | 10.8 |
| Mafic | | | | | | | | | | | | | | | |
| NA | 7 | 6.3 | 5.7 | 6.0 | 1.5 | 9.7 | 4.8 | <0. | 22.5 | 14.7 | 1.14 | 50.1 | 37.0 | 12.9 | 22.6 |
| AA | 7 | 5.6 | 4.6 | 5.2 | 0.6 | 5.4 | 4.0 | 0.2 | 17.5 | 12.1 | 1.08 | 54.5 | 34.3 | 11.2 | 0.8 |
| Acidic | 5.3 | 4.6 | 4.8 | 5.9 | 0.1 | 0.1 | 0.1 | <0. | 9.5 | 7.0 | 0.20 | 20.3 | 44.5 | 35.3 | 4.4 |
| Mixed | | | | | | | | | | | | | | | |
| NA | 6.2 | 6.5 | 5.7 | 6.0 | 0.1 | 5.2 | 2.1 | 0.1 | 12.0 | 6.3 | 0.43 | 56.4 | 28.8 | 14.8 | 2.7 |
| AA | 6.2 | 3.9 | 3.4 | 3.9 | 0.1 | 5.1 | 2.1 | 0.1 | 13.0 | 4.5 | 0.34 | 53.2 | 33.5 | 13.3 | 3.0 |
| Acidic | 5 | 4.7 | 4.3 | 4.5 | 0.4 | 0.6 | 2.1 | <0. | 8.5 | 7.7 | 0.25 | 34.3 | 35.2 | 30.5 | 8.1 |

[#] The pH of soil material as reported in official soil series description (soil series type location) at the depth corresponding to sampling.

[†] pH in 1:1 soil:water.

[‡] pH in 1:2 soil:0.01M CaCl₂.

[§] Saturated paste extract.

[¶] CEC_{NH₄Cl}

NA=Non-acidified

AA=Agriculturally-acidified

Acidic=Naturally acidic

Table 1-1.3. Selective dissolution chemistry of the soils used in the study.

| Soil | Fe _d [†] | Fe _o [†] | Fe _p [†] | Al _d [†] | Al _o [†] | Al _p [†] | Si _o [†] | Al _{KCl} [†] | Al _o ⁻ | Al _d ⁻ | Al _o -Al _p / | Al _o ⁻ | (Al _d -Al _p)/ |
|---------------|-------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|--------------------------------|------------------------------|------------------------------|------------------------------------|-------------------------------|---|
| | -----g kg ⁻¹ ----- | | | | | | | | | | | Al _d / | ((Al _d -Al _p)+ |
| | | | | | | | | | | | | Si _o ^{††} | (Fe _d -Fe _p) ^{††} |
| | | | | | | | | | | | | | % |
| Sialic | | | | | | | | | | | | | |
| NA | 2.37 | 1.64 | 0.07 | 0.03 | 0.11 | 0.04 | 0.13 | 0.006 | 0.07 | - | 0.5 | 0.6 | - |
| AA | 2.97 | 1.60 | 0.13 | 0.09 | 0.31 | 0.08 | 0.08 | 0.015 | 0.22 | 0.01 | 3.1 | 2.9 | 0.6 |
| Acidic | 7.67 | 2.04 | 0.27 | 0.16 | 0.40 | 0.10 | 0.19 | 0.006 | 0.29 | 0.05 | 1.6 | 1.3 | 1.5 |
| Mafic | | | | | | | | | | | | | |
| NA | 13.77 | 7.13 | 0.69 | 0.99 | 1.76 | 0.50 | 2.47 | 0.010 | 1.26 | 0.50 | 0.4 | 0.3 | 7.3 |
| AA | 14.32 | 5.21 | 0.82 | 1.20 | 2.43 | 0.65 | 2.95 | 0.010 | 1.78 | 0.55 | 0.6 | 0.4 | 7.8 |
| Acidic | 99.66 | 4.75 | 0.11 | 14.24 | 4.01 | 0.68 | 1.29 | 0.001 | 3.33 | 13.56 | 2.7 | - | 22.0 |
| Mixed | | | | | | | | | | | | | |
| NA | 10.54 | 1.50 | 0.14 | 0.08 | 0.46 | 0.12 | 0.15 | 0.008 | 0.35 | - | 2.4 | 2.6 | - |
| AA | 13.37 | 1.83 | 0.73 | 0.24 | 1.59 | 0.82 | 0.19 | 0.255 | 0.77 | - | 6.3 | 7.1 | - |
| Acidic | 21.77 | 4.21 | 0.84 | 2.27 | 2.01 | 0.89 | 0.25 | 0.138 | 1.11 | 1.38 | 4.7 | - | 12.0 |

‡ Mole basis.

† d subscript: citrate-dithionite-extractable. o subscript: acid-ammonium-oxalate-extractable. p subscript: pyrophosphate-extractable. KCl subscript: KCl-extractable.

NA=Non-acidified.

AA=Agriculturally-acidified.

Acidic=Naturally acidic

Chapter 2

RHIZOSPHERE EFFECTS ON SOIL SOLUTION COMPOSITION AND MINERAL STABILITY

Introduction

Investigations of rhizosphere soil properties are numerous, and considerable attention has been focused on rhizosphere pH (Chung and Zasoski, 1994; Marschner et al., 1986; Nye, 1981; Rollwagen and Zasoski, 1988; Walker, 1960). Changes in rhizosphere pH gradients normal to and along the root axes have been noted by several authors (Blancher and Lipton, 1986; Haussling et al., 1985; Marschner, 1983; Ruiz and Arvieu, 1990).

Because cation uptake often exceeds anion uptake, it is easy to assume that the rhizosphere soils and solutions becomes more acidic than the bulk soil. Research has also shown that the rhizosphere can become less acidic than bulk soil. Increases in rhizosphere pH are attributed primarily to NO_3^- uptake in excess of cation uptake. The roots must maintain charge balance and they exude organic anions (Marschner et al., 1986; Nye, 1981; Riley and Barber, 1969; Youssef and Chino, 1989). Independent of nitrogen supply, soil solution nutrient status can also affect rhizosphere pH gradients (Marschner, 1995 p.542). Despite being grown in acidic soils, increased pH has been demonstrated in the apical zone of roots (Marschner, 1995 p.542).

Solid-phase Al generally dissolves as H^+ increases (Kerlew and Boulden, 1987; Marschner, 1995 p.538; Thomas and Hargrove, 1984). Furthermore, solution Al activity

is of concern since it may be phytotoxic (Thomas and Hargrove, 1984). While changes in rhizosphere properties are known, collection of rhizosphere samples is not without its difficulties.

Rhizosphere soil is often collected by agitating plant roots and their associated volume of soil. Soil adhering strongly to the roots (that left after agitation) is considered to be rhizosphere soil and the easily removed soil is designated as bulk soil (Riley and Barber, 1969; Riley and Barber, 1971).

Although care is taken to perform the mechanics of this separation uniformly, reproducibility from one researcher to the next is not guaranteed. Differences in the volume of soil adhering to the roots strongly influence the ion concentrations, as solute concentrations in the rhizosphere exhibit steep concentration gradients (Kuchenbuch and Jungk, 1982; Youssef and Chino, 1989). Water content of the soil at root removal influences how much soil adheres to the root. This moisture content is critical and often not reported.

Solution extracts from rhizosphere soil sampled by this method may not be at moisture contents expected *in situ*, and solution concentration can effect cation exchange selectivity including Al (Chung and Zasoski, 1994; Chung et al., 1994; Kerlew and Boulden, 1987).

To avoid dilution artifacts produced by unrealistically high water contents large quantities of rhizosphere soil need to be collected. Collection of large volumes of rhizosphere soil can be troublesome, particularly in acidic soils where soluble Al can hamper root development. In the case of Al toxicity, lower root mass will limit the volume of rhizosphere soil.

Rhizosphere soil is an average in time and space. For example, soil initially at the root apex is associated with zones of elongation, maturation and finally mature regions as root growth progresses. Rhizosphere soils sampled as described by Riley and Barber (1969; 1971), are averages that homogenize gradients that were present radially and longitudinally. Differences in soil pH found from root apices through the mature zone and between primary and lateral roots are also averaged in this method. Clearly the rhizosphere is a zone of altered soil properties that are distinct from bulk soil, but collecting samples by agitating extracted roots obscures or averages gradients that may exist. None-the-less differences between bulk and rhizosphere soil should affect mineral weathering and stability.

Kittrick (1969) proposed the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system as one that encompasses a large percentage of minerals in soils and noted that mineral weathering influences the soil solution, which in turn influences secondary mineral formation. In chapter 1 it was suggested that hydroxy-interlayering of 2:1 phyllosilicate minerals plays a large role in sequestration of Al in agriculturally-acidified soil, over a broad range of parent material lithology. The effects of acidification was measurable by selective dissolution and cation exchange studies, but alteration of clay fraction minerals in the acidified soils was not detectable by XRD.

Given the fact that the rhizosphere is a zone of altered pH and that Al solubility is strongly pH dependent, can the effects of roots on soil mineralogy be elucidated from soil solution composition?

To answer this question, solutions extracted from rhizosphere and bulk soil samples collected from agriculturally-acidified, naturally-acidic, and non-acidified soils were examined. These samples were collected from soils formed in alluvium derived from dominantly sialic, mafic and mixed lithology. Since plant interactions with mineralogy may influence the Al solubility in the rhizosphere, we hypothesized that rhizosphere soil solution Al and Si chemistry would be different from bulk soil solution. Further, we hypothesized that because of greater nutrient uptake, dicots (tomato) will have a greater rhizosphere effect than do monocots (fescue).

Materials and Methods

Field - Collection of Soil Samples

Soils were sampled to represent non-acidified, naturally acidified and agriculturally acidified members from sialic, mafic and mixed alluvial parent material (Table 2-2.1). Agriculturally-acidified members sampled in tree crop locations were generally sampled in fertigation emitter basins; however, in the case of the sialic soil, samples were collected from the area between trees within the tree row. In tree crops on the mafic and mixed soils the non-acidified and agriculturally-acidified soils were sampled within 1 to 3 m of each other. Subsurface B horizon samples were used, where possible, to reduce effects from organic matter and residual surface amendments. Agriculturally-acidified and non-acidified mafic soils were collected from surface horizons.

Lab and Greenhouse

The fine-earth fractions of the soils were air-dried, lightly crushed, and separated from the coarse fraction by passing through a 2-mm sieve. Water contents were determined

for the air-dry fraction and by the pressure plate method at 33 or 10 kPa (National Soil Survey Center, 1996). Initial soil reaction was determined in water (1:1 soil to water). Clay fraction mineralogy was determined by x-ray diffraction as described in Chapter 1 and summarized in Table 2-2.4.

Generation of Rhizosphere Soil (Study #1)

Each of the soils in Table 2-2.1 was planted to tomato (*Lycopersicon lycopersicum*) and Zorro Fescue (*Vulpia myuros*) in twenty-one 140-cm³ pots and grown for 8 weeks in the greenhouse until the roots completely exploited the soil volume. No fertilizer was applied and the plants were watered with deionized water. After each cropping, the soil was allowed to dry and the roots were separated from the soil. The soil was replanted, for a total of three croppings. This method that allowed the plant to repeatedly exploit the same soil volume and generate a rhizosphere-like soil throughout the pot. This technique was employed rather than the agitation method in order to generate sufficient quantities of soil. The assumption was that the entire soil volume was at some time “in intimate contact” with the plant root and, therefore, could be considered as rhizosphere soil.

After the final cropping, the soil was air-dried and placed in a perforated nylon holdup cup with Whatman #1 filter paper and brought to 33 or 10 kPa water content (a proxy for field capacity), covered loosely with plastic and allowed to equilibrate for 24 hours. After equilibration the holdup was fitted to a nylon receiving cup and centrifuged in a GSA rotor at 9,500 rpm (14,680 G, ~ 31 MPa) for 120 minutes to force solution from the bottom of the upper unit into the lower collection vial.

Cropping Intensity Study (Study #2)

The silicic, non-acidified soil was used in a cropping intensity study. This study was designed to examine changes in bulk soil properties with successive croppings. The premise was that as cropping intensity increased bulk soil would become more “rhizosphere like.” Twelve pots were planted with tomato for three croppings. After one cropping, 4 pots were removed, and soil separated from the roots. Subsequently the remaining 8 pots were recropped and finally the last 4 pots were cropped a third time. All soils were equilibrated with water, and pore solution extracted as described above. Cropping intensity rhizosphere soils experienced greater desiccation times between root/soil separation and equilibration/extraction than did the general rhizosphere soil production in study #1. The intensity cropping samples were processed together at the end of all croppings.

Pore water pH was measured 12 and 16 hours after extraction to allow time for CO₂ to equilibrate with the soil solutions. Total dissolved silicon and Al concentrations were measured using ICP spectrometry. Solution Al was speciated using MINEQL3+ (Schecher and McAvoy, 1994).

Mineral stability relationships between the solid and solution phases were based on techniques developed by Kittrick (1969). Thermodynamic values (ΔG_f°) used for soil minerals are presented in Table 2-2.2. Gibbsite solubility is expressed as

$$\text{pH} - 1/3\text{pAl} = 2.69 \quad 2-2.1$$

and kaolinite solubility as

$$\text{pH} - 1/3\text{pAl} = 1.43 + 1/3\text{pH}_4\text{SiO}_4 \quad 2-2.2$$

Iron activity was assumed to be controlled by the relationship

$$p\text{Fe}^{3+} = 3\text{pH} - 0.44 \quad 2-2.3$$

using Norvell and Lindsay's value for $\text{Fe}(\text{OH})_3$ [soil iron] (1981).

The common log of averaged solution concentration values for Ca, Mg and K extracted from the bulk soils were 2.4, 2.68 and 1.78, respectively (Table 2-1). These concentrations were used for montmorillonite, hydroxy-interlayered-material (HIM) and beidellite stability diagrams. Montmorillonite is expressed as

$$\text{pH} - 1/3\text{pAl}^{3+} = 0.73 + 0.096\text{pMg}^{2+} + 0.043\text{pFe}^{3+} + 0.74\text{pH}_4\text{SiO}_4 - 0.3\text{pH} \quad 2-2.4$$

The calculated hydroxy-interlayered material (Karathanasis et al., 1983) solubility is expressed as

$$\text{pH} - 1/3\text{pAl}^{3+} = 1.74 + 0.286\text{pH}_4\text{SiO}_4 + 0.021\text{pK}^+ + 0.0071\text{pCa}^{2+} + 0.021\text{pFe}^{3+} + 0.0177\text{pMg}^{2+} - 0.134\text{pH} \quad 2-2.5$$

The calculated beidellite solubility is expressed as

$$\text{pH} - 1/3\text{pAl}^{3+} = 1.27 + 0.0024\text{pMg}^{2+} + 0.52\text{pH}_4\text{SiO}_4 - 0.047\text{pH} \quad 2-2.6$$

Using the relationships presented above and the measured solution levels the saturation index for the selected minerals depicted in the stability-equilibrium diagrams were calculated and are presented in Table 2-2.6.

Statistical analysis was performed using a one-way ANOVA for each dominant soil parent material and acidification type. Tests for the interactions were performed using ANOVA and a post-hoc Fisher's least-significant-difference test was used for pair-wise

comparisons among means. All statistical analyses were performed at a $p = 0.05$ significance level using SYSTAT for Windows, Version 9 (SYSTAT Inc., Chicago, IL).

Results and Discussion

Cropping Intensity – Rhizosphere Soil Development

Figure 2-2.1 and Table 2-2.3 show that after each cropping in the sialic, non-acidified soil pH-1/3pAl decreased. This method of rhizosphere soil generation and collection was particularly advantageous as we were able to equilibrate the soil at field capacity water content, and extract and analyze this solution without dilution beyond reasonable field conditions. Research by Kirlew and Bouldin (1987), Chung et al. (1994) and Chung and Zasoski (1994) has suggested that soil moisture contents can affect cation exchange Ca-Al selectivities in the rhizosphere. Therefore, field capacity moisture content was used to assess Al and Si solubility in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system.

Clay Fraction Mineral Stabilities

Sialic Parent Material

The XRD analysis revealed that kaolinite and mica were the dominant clay minerals in the soils formed in sialic alluvium (Table 2-2.4). Therefore, stability diagrams for these soils have kaolinite, gibbsite, quartz and amorphous Si stability-equilibrium lines.

Interlayering of vermiculite by hydroxy-Al to form hydroxy-interlayer-material (HIM), though not detected by x-ray diffractometry in the sialic soils is a possibility. HIM pH 6.54 and pH 4 equilibrium lines have also been added as references. These lines represent equilibrium with HIM at 1:1 soil:water pH of the non-acidified and agriculturally-acidified samples, respectively, from the mixed lithology soils. HIM was

identified by x-ray diffractometry in the mixed lithology soils and used in the sialic stability diagrams for visual consistency (Figure 2-2.2).

It appears that sialic non-acidified bulk and rhizosphere solutions are super-saturated with respect to kaolinite [above the stability-equilibrium line] (Figure 2-2). In the case of the tomato rhizosphere solution, the saturation index for kaolinite and HIM are less positive than the solution extracted from fescue samples (Table 2-2.6). Tomato rhizosphere solution contains more Si than the bulk soil solution but this increase was not significantly greater. The tomato rhizosphere solution has significantly greater H^+ and Al^{3+} activity than fescue (Table 2-2.5).

In contrast to the Si increase in the rhizosphere in study 1 (Figure 2-2), solution Si decreased with croppings in the intensity experiment [study 2] (Figure 2-1). The soil experienced longer periods of air-dry soil moisture conditions in the cropping intensity experiment (study 2). Desiccation of the soil between the growth periods may have led to the development of an amorphous Si phase no longer soluble in the porewater given the equilibration time allotted. With few exceptions this increased Si concentration with rhizosphere production (study 2) was observed in all lithologies and type of acidification. The soils were not leached with watering during rhizosphere production. Therefore, silica released by weathering remained in the system.

The non-acidified rhizosphere soil extracts plot in the same stability field as the bulk soil and are under-saturated with respect to kaolinite (Figure 2-2). The saturation index for both fescue and tomato become more negative for kaolinite, gibbsite and HIM.

The naturally-acidic soil solutions in the sialic lithology soils (study 1) are under-saturated with respect to kaolinite and HIM (Figure 2-2). Rhizosphere soil solutions of agriculturally-acidified soils are farther from kaolinite equilibrium values than the bulk soil (Figure 2-2.2 & Table 2-2.6). In the naturally-acidic rhizosphere solutions the saturation indices (SI) are closer to kaolinite equilibrium than the bulk soil. Solutions from the naturally-acidic fescue treatments have a particularly less negative SI with respect to both kaolinite and HIM. Tomato and fescue rhizosphere solution Al^{3+} activity increased while H^+ activity decreased in the fescue rhizosphere. This is counter to the notion that Al^{3+} activity may be directly coupled to H^+ activity and argues that gibbsite is not controlling solution Al levels.

One explanation for H^+ activity decrease could be that fescue is preferentially taking up N from a NO_3^- pool. The possibility of preferential N uptake in the form of NO_3^- by fescue growing in the naturally-acidic soils is not directly addressed. Plant root charge balance, however, necessitates anion exudates (or reducing H^+ exudates) from the root to maintain charge balance with NO_3^- uptake and would explain an increased rhizosphere pH in treatments growing fescue and the lower degree of acidification in the other fescue rhizospheres.

However in most cases, acidification of the rhizosphere soil leads to greater Al^{3+} solubility as expected. While x-ray diffraction analysis did not detect differences in clay mineralogy, the solutions are progressively further from equilibrium with the influence of the rhizosphere as the degree of acidification increases (Table 2-2.6). Overall in soils with sialic lithology the solution from the tomato rhizosphere had higher levels of soluble Al^{3+}

and H^+ than solutions from the fescue rhizosphere (Table 2-2.5). In chapter 1 it was suggested that acidification produced a hydroxy-Al pool and speculated that at least some of the hydroxy-Al may be associated with vermiculite interlayers. Formation of hydroxy-Al interlayers should buffer the Al^{3+} levels. Decreasing SI values as soils become more acidic may be further evidence for hydroxy-Al interlayering with acidification. These data seem to suggest that tomato would lead to a greater interlayering potential of vermiculite than fescue.

Mafic Parent Material

Smectite is the dominant mineral phase in the clay fractions of non-acidified and agriculturally-acidified bulk soils (Table 2-2.4). Therefore, montmorillonite was added as a solid-phase component in Figure 2-2.3 in addition to the solids in the non-acidified panel of Figure 2-2.2. The lines for montmorillonite at pH 6.26 and pH 5.55 represent the calculated value for montmorillonite given a 1:1 soil:water pH for the non-acidified and agriculturally-acidified bulk soils, respectively. Additionally, beidellite at pH 6.26 and pH 5.5 is another solid-phase component that was added to the non-acidified and agriculturally-acidified panel of Figure 2-3.

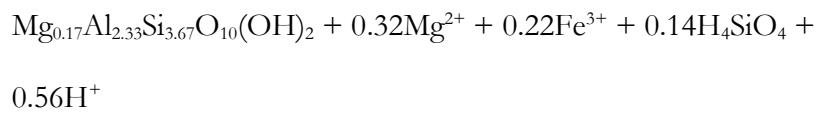
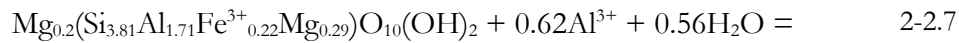
The non-acidified bulk clay fraction mineralogy was dominated by smectite; kaolinite was subdominant (Table 2-2.4). The montmorillonite SI shows that, while under-saturated, montmorillonite is near equilibrium. The solution is also under-saturated with respect to kaolinite and further from equilibrium than is montmorillonite (Table 2-2.6).

The rhizosphere soils have greater Al^{3+} activity than the bulk soil. Increases in Al^{3+} offset pH decreases and move the points representing the solution in Figure 2-3 up with respect

to the $\text{pH}-1/3\text{pAl}$ axis. The SI for montmorillonite increases and the rhizosphere solutions are super-saturated with SI values greater than the bulk solution. The beidellite saturation index decreases in the rhizosphere solutions relative to bulk soil and approaches equilibrium. This will be discussed later together with the agriculturally-acidified soil (Table 2-2.6).

Figure 2-3 depicts the agriculturally-acidified bulk solution extractions as super-saturated with respect to montmorillonite. Rhizosphere solutions were super-saturated with respect to montmorillonite but under-saturated with respect to beidellite (Figure 2-1 & Table 2-2.6). Solution Si in the tomato rhizosphere sample increased compared to the bulk soil, but the increase was not as pronounced as in the non-acidified soil. These rhizosphere solutions, as with the non-acidified rhizosphere solutions, exhibited increased Al^{3+} activity while the H^+ activity decreased (Table 2-2.5).

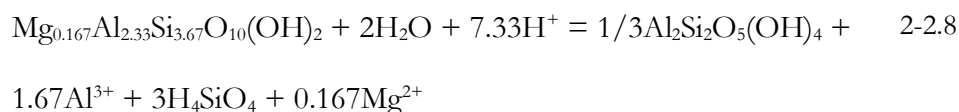
Solutions extracted from the mafic soils generally had a decreased H^+ activity in the rhizosphere solutions relative to bulk solutions. This lower H^+ activity was observed despite an increase in the solution Al^{3+} activity. As was observed for the silic soils, the solution Si activity increased in the rhizosphere. The formation of a short-range-order (SRO) aluminosilicate was proposed in chapter 1 as a mechanism for controlling solution Al and Si activities in acidified soils. Karathanasis and Hajek (1983) proposed a montmorillonite \rightarrow beidellite \rightarrow kaolinite transformation in acid soil systems. The alteration of smectite from montmorillonite to beidellite requires an increase in structural Al; a reasonable alteration in acidic soils and is represented by:



The standard free energy of change (ΔG_r°) for the montmorillonite to beidellite transformation using the thermodynamic data in Table 2-2 is positive (28.4 kJ) suggesting the transformation is not spontaneous.

The thermodynamic data used to calculate equilibria for smectite in this paper are not specific to the soils used and are undoubtedly not correct for the smectite present in our soil. In evaluating smectite stability in naturally acidic soils Karathanasis and Hajek (1983; 1984) described a soil (Lee) that exhibited different apparent equilibria in the B and C horizons. The more stable smectite was associated with the C horizon and the less stable smectite associated with the B horizon. Contributions of Si from mineral dissolutions in overlying horizons can increase smectite stability if Si activity is increased in underlying horizons. Leaching the growth pots was avoided in the production of rhizosphere soil. Therefore, we did not simulate field conditions with respect to Si loss. It is reasonable to assume that the non-acidified and agriculturally-acidified solutions have somewhat greater H_4SiO_4 activities than experienced *in situ* as the soil materials were collected from surface horizons, which would likely be leached in the field during irrigation.

The transformation from beidellite to kaolinite proposed by Karathanasis and Hajek (1983), adapted to the beidellite formula used in this manuscript, is H^+ consuming and results in the release of Si^{4+} and Al^{3+} according to the equation:



The data appear to support a transformation similar to this in the rhizosphere of the mafic soil. This would explain the H^+ activity decrease with an Al^{3+} activity increase. The SI of the rhizosphere solutions for montmorillonite becomes more positive while the SI for beidellite and kaolinite approach zero. Solutions extracted from tomato rhizosphere samples yield data that plots close to the kaolinite/beidellite equilibrium (Table 2-2.6). Smectite transformed from montmorillonite to beidellite becomes less stable as the pH decreases. Equations representing smectite equilibria are sensitive to pH change (montmorillonite more so than beidellite). Higher pH favors smectite stability (Figure 2-2.2). Barshad (1964, p.48) proposed that active cation uptake by plants might favor kaolinite formation while inactivity would favor montmorillonite. Therefore, differences in cation accumulation by plant roots causing soil solution composition to vary and to favor either montmorillonite or kaolinite stability. Tomato growth altered the solution chemistry more than fescue growth with respect to bulk soil mineralogy (Table 2-2.6). These results suggest that this soil would be a good candidate for further work regarding smectite-kaolinite transformations.

Clay fraction mineralogy in the naturally-acidic mafic soil is dominated by halloysite, gibbsite and goethite (Table 2-4). Calculated data for all naturally-acidic solutions are under-saturated with respect to gibbsite. Compared to the bulk soil, the rhizosphere solutions have increased silica content and the SI values for gibbsite are less negative. As with the non-acidified and agriculturally-acidified soil, the H^+ activity decreased as the

Al^{3+} activity increased. An increase in Si activity is assumed to be derived from the dissolution of adsorbed Si in Fe and Al hydroxide coatings though dissolution of small pools of allophane could contribute to increased Si activity. Given this assumption, formation of short-range-order aluminosilicates or extension of the existing halloysite minerals could account for the H^+ activity decrease and Al^{3+} activity increase from the bulk to rhizosphere soils. Solutions extracted from soils growing tomato had a more negative SI for gibbsite and kaolinite (and by extension halloysite) than did solutions from soils growing fescue. The potential influence of tomatoes on clay mineral stability was greater than the influence of fescue.

Mixed Parent Material

Clay fraction mineralogy of the mixed lithology soils is dominated by HIM, along with vermiculite and mica in the non-acidified and agriculturally-acidified soils (Table 2-2.4). The naturally-acidic soil had no vermiculite or HIM detectable in the clay fraction, and was dominated by kaolinite, with a small amount of mica. In Figure 2-2.4 the HIM pH 6.54 and pH 4 lines represent the equilibrium of HIM at 1:1 soil:water pH in the non-acidified and agriculturally-acidified soils, respectively.

Generally the solutions are under-saturated with respect to kaolinite and HIM (Figure 2-2.4 & Table 2-6). In acidified and acidic soils the rhizosphere solutions are generally nearer HIM equilibrium than the bulk soil (Table 2-2.6).

Conclusions

The rhizosphere soil solutions are altered with respect to the bulk soil. These solutions are generally under- or over-saturated and not in apparent equilibrium with common clay

minerals. However, they generally reflect the dominant mineralogy of the clay fraction.

Rhizosphere soil solutions were commonly enriched in Si with respect to the bulk solutions and solution extracted from tomato rhizosphere samples generally had higher Si concentration than solutions extracted from fescue rhizospheres.

Rhizosphere soil solution composition generally reflected the dominant clay mineralogy of the bulk soil, but with increased solution silica. Increased Si levels should favor the stability of minerals with higher silica content; however, mafic soil rhizosphere solutions suggest a montmorillonite-beidellite-kaolinite transformation. In the silic soil, a HIM phase that is as yet undetectable by XRD may be the potential sink for Al^{3+} and in soils with mixed mineralogy, the rhizosphere solutions tended toward equilibrium with HIM. Tomato increased silica activity more than fescue growth in the non-acidified and naturally-acidic soils; but in the agriculturally-acidified soils the solution extracted from fescue samples had solution Si that was as much or more than solutions from tomato samples. Generally, rhizosphere tomato solutions were further from equilibrium with bulk soil mineralogy. This study also identified the non-acidified and agriculturally-acidified mafic soil (Vina series) as a potential candidate for future investigation of smectite-kaolinite transformations.

Our results show that rhizosphere (as defined here through repeated cropping) effects on soil solution composition are varied and depend on soil mineralogy and the type of plants grown. Generally, the rhizosphere moderates the rooting environment, making acidic soils less acidic and lowering the pH of more alkaline soils. These changes affect mineral stability relative to bulk soil.

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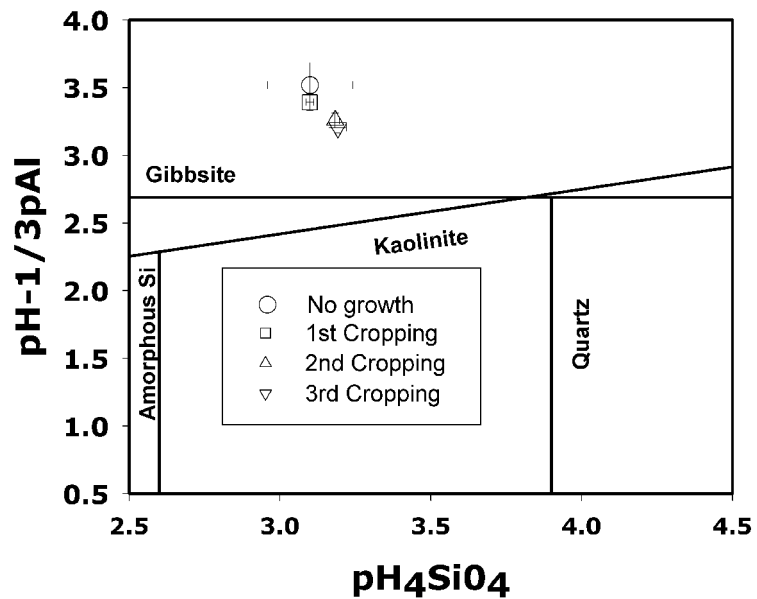


Figure 2-2.1. Stability diagram for solutions extracted from samples of tomato rhizosphere soil.

The growth media was a silicic non-acidified soil. Bars are standard error of mean. Some error bars fall within the size of the symbol.

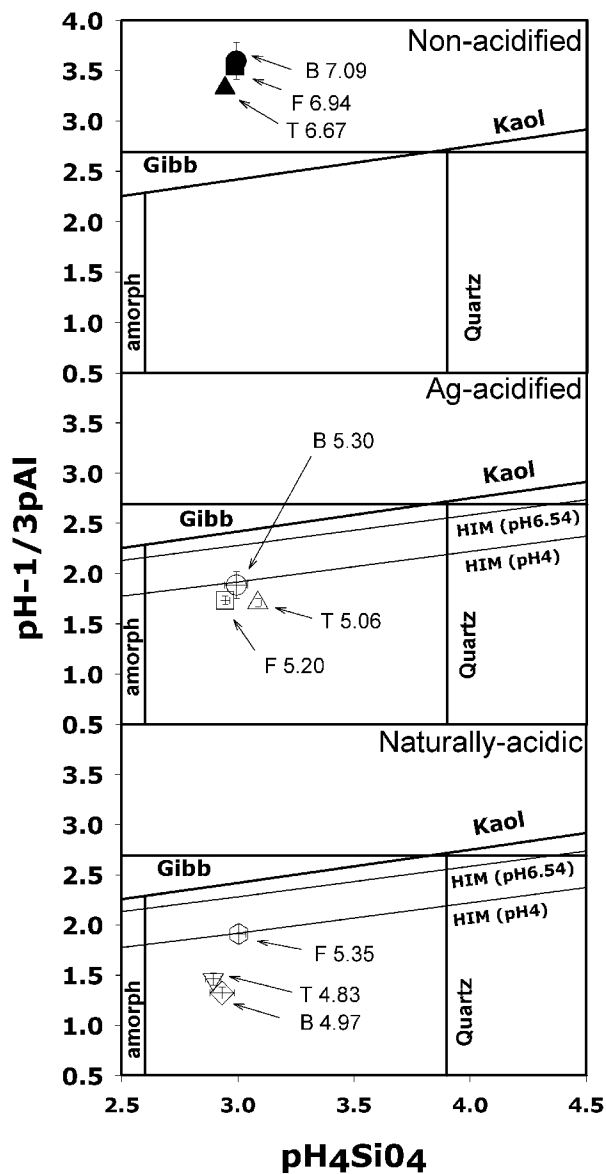


Figure 2-2.2. Stability diagrams for solutions from non-acidified, agriculturally-acidified and naturally-acidic soils formed in silicic alluviums. The symbols are B = Bulk soil (uncropped); rhizosphere tomato (T), and rhizosphere fescue (F). The numeric values are average solution pH. Bars are standard error of mean. Some error bars fall within the size of the symbol.

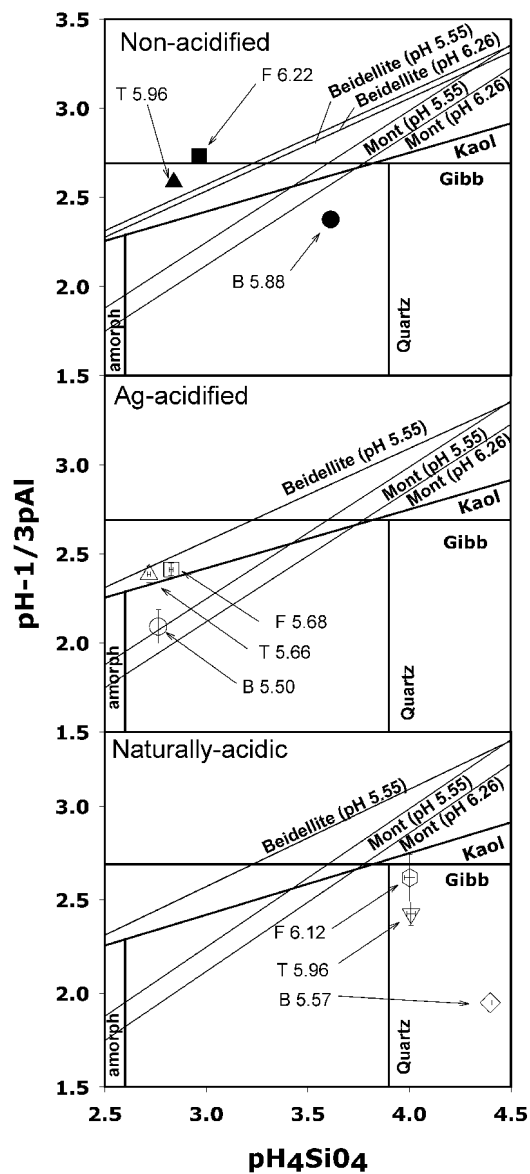


Figure 2-2.3. Stability diagrams for solutions from non-acidified, agriculturally-acidified and naturally-acidic soils formed in mafic alluviums. The symbols are B = Bulk soil (uncropped); rhizosphere tomato (T), and rhizosphere fescue (F). The numeric values are average solution pH. Bars are standard error of mean. Some error bars fall within the size of the symbol.

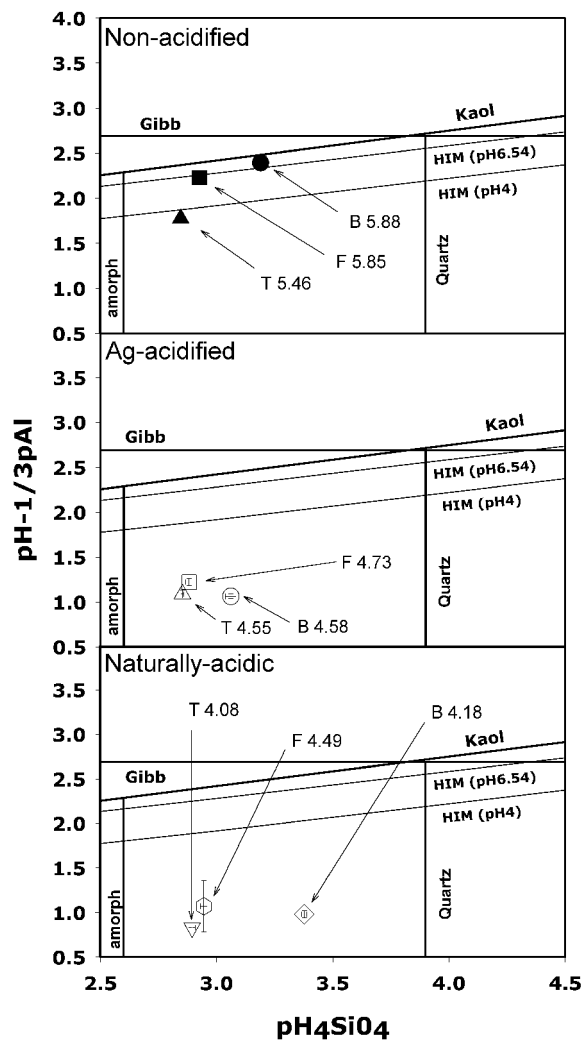


Figure 2-2.4. Stability diagrams for solutions from non-acidified, agriculturally-acidified and naturally-acidic soils formed in mixed alluviums. The symbols are B = Bulk soil (uncropped); rhizosphere tomato (T), and rhizosphere fescue (F). The numeric values are average solution pH. Bars are standard error of mean. Some error bars fall within the size of the symbol.

Table 2-2.1. Classification, location and current crop grown on soils used in study.

| Soil Mapped As Classification | County | Parent Material | Current Vegetation | Condition | pH 1:1 soil:water |
|---|------------|-----------------|--------------------|---------------------------|-------------------|
| Dinuba series Coarse-loamy, mixed, superactive, thermic Typic Haploxeralf | Stanislaus | Sialic | Row crops | Non-acidified | 7.78 |
| Hilmar series Sandy over loamy, mixed, superactive, calcareous, thermic Aeric Halaquept | Stanislaus | Sialic | Almonds | Agriculturally -acidified | 5.35 |
| Montpellier series Fine-loamy, mixed, superactive, thermic Typic Haploxeralf | Stanislaus | Sialic | Annual grasses | Naturally-acidic | 5.23 |
| Vina series Coarse-loamy, mixed, superactive, thermic Pachic Haploxeroll | Tehama | Mafic | Walnuts | Non-acidified | 6.26 |
| Vina series Coarse-loamy, mixed, superactive, thermic Pachic Haploxeroll | Tehama | Mafic | Walnuts | Agriculturally -acidified | 5.55 |
| Sites series Fine, parasitic, mesic Xeric Haplohumult | Plumas | Mafic | Mixed conifer | Naturally-acidic | 4.55 |
| Arbuckle series Fine-loamy, mixed, superactive, thermic Typic Haploxeralf | Colusa | Mixed | Almonds | Non-acidified | 6.54 |
| Arbuckle series Fine-loamy, mixed, superactive, thermic Typic Haploxeralf | Colusa | Mixed | Almonds | Agriculturally -acidified | 3.94 |
| Red Bluff series Fine, kaolinitic, thermic Ultic Palexeralf | Shasta | Mixed | Pasture | Naturally-acidic | 4.67 |

Table 2-2.2. Thermodynamic values used to construct stability-equilibrium lines.

| Formula | ΔG^0 (kJ/mole) | Source |
|---|---------------------------|-----------------------------|
| Al ³⁺ | -489.4 | (Robie et al., 1978) |
| Ca ²⁺ | -553.5 | (Robie et al., 1978) |
| K ⁺ | -282.5 | (Robie et al., 1978) |
| Fe ³⁺ | -4.6 | (Robie et al., 1978) |
| Mg ²⁺ | -454.8 | (Robie et al., 1978) |
| H ₂ O | -237.2 | (Robie et al., 1978) |
| Fe(OH) ₃ (soil) | -713.4 | (Norvell and Lindsay, 1981) |
| H ₄ SiO ₄ | -1308.0 | (Robie et al., 1978) |
| Al(OH) ₃ gibbsite | -1154.9 | (Robie et al., 1978) |
| SiO ₂ amorphous | -848.9 | (Helgeson et al., 1978) |
| SiO ₂ quartz | -856.3 | (Robie et al., 1978) |
| Al ₂ Si ₂ O ₅ (OH) ₄ Kaolinite | -3783.2 | (Kittrick, 1966) |
| K _{0.24} Ca _{0.08} (Si _{3.24} Al _{3.77} Fe _{0.24} Mg _{0.20})O ₁₀ (OH) _{5.79} HIV | -6846.0 | (Karathanasis et al., 1983) |
| Mg _{0.2} (Si _{3.81} Al _{1.71} Fe ³⁺ _{0.22} Mg _{0.29})O ₁₀ (OH) ₂ | -5254.3 | (Weaver et al., 1971) |
| Montmorillonite | | |
| Mg _{0.167} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂ Beidellite | -5332.5 | (Nesbitt, 1977) |

Table 2-2.3. Solution activities determined from cropping intensity (Study #2) and used in stability-equilibrium diagram.[†]

| Soil | pH | pAl | pSi | pH-1/3pAl |
|--------|----------------|----------------|---------------|----------------|
| Bulk | 7.08 ± 0.18 c | 10.46 ± 0.45 d | 2.99 ± 0.06 c | 3.60 ± 0.37 b |
| Crop 1 | 7.57 ± 0.24 b | 12.55 ± 0.52 c | 3.10 ± 0.03 b | 3.39 ± 0.06 ab |
| Crop 2 | 7.75 ± 0.10 ab | 13.47 ± 0.17 b | 3.18 ± 0.03 a | 3.26 ± 0.11 a |
| Crop 3 | 7.92 ± 0.07 a | 14.15 ± 0.12 a | 3.19 ± 0.04 a | 3.20 ± 0.08 a |

[†] Means (±standard deviation) of a given element followed by the same letter are not significantly different; $\alpha = 0.05$.

Table 2-2.4. Mineralogy of the clay fraction from soils used in this study.

| Soil | Dominant Mineral | Sub-dominant Mineral |
|--------------------------|------------------|----------------------|
| Sialic | | |
| Non-acidified | MI, KK | VR |
| Agriculturally-acidified | MI, KK | VR |
| Naturally-acidic | MI, KK | VR |
| Mafic | | |
| Non-acidified | SM | KK |
| Agriculturally-acidified | SM | KK |
| Naturally-acidic | KH, GI, GE | - |
| Mixed | | |
| Non-acidified | VR, HIM | MI |
| Agriculturally-acidified | VR, HIM | MI |
| Naturally-acidic | KK | MI |

MI = mica, KK = kaolinite, KH = halloysite, SM = smectite, VR = vermiculite, HIM = hydroxy-interlayered material, GI = gibbsite, GE = goethite.

Table 2-2.5. Solution activity increase or decrease in rhizosphere samples relative to bulk soil in

Study #1.

| Soil | pH | pAl | pSi |
|--------------------------|----|-----|-----|
| Sialic | | | |
| Non-acidified | | | |
| Fescue | 0 | 0 | 0 |
| Tomato | + | + | 0 |
| Agriculturally-acidified | | | |
| Fescue | 0 | 0 | 0 |
| Tomato | + | 0 | - |
| Naturally-acidic | | | |
| Fescue | - | + | 0 |
| Tomato | 0 | + | 0 |
| Mafic | | | |
| Non-acidified | | | |
| Fescue | - | 0 | + |
| Tomato | 0 | 0 | + |
| Agriculturally-acidified | | | |
| Fescue | - | + | - |
| Tomato | - | + | + |
| Naturally-acidic | | | |
| Fescue | - | 0 | + |
| Tomato | - | 0 | + |
| Mixed | | | |
| Non-acidified | | | |
| Fescue | 0 | - | + |
| Tomato | + | - | + |
| Agriculturally-acidified | | | |
| Fescue | 0 | 0 | + |
| Tomato | 0 | 0 | + |
| Naturally-acidic | | | |
| Fescue | 0 | 0 | + |
| Tomato | 0 | 0 | + |

+ significantly different increase; $\alpha = 0.05$.- significantly different decrease; $\alpha = 0.05$.0 not significantly different; $\alpha = 0.05$.

Table 2-2.6. Saturation index [$\log(\text{IAP}/K_{\text{SP}})$] for solutions extracted from bulk and rhizosphere soils with different parent materials (0=equilibrium, >0 is super-saturated, and <0 is under-saturated).

| Soil | Kaolinite | Montmorillonite | Beidellite | HIM | Gibbsite |
|--------------------------|-----------|-----------------|------------|------|----------|
| Sialic | | | | | |
| Non-acidified | | | | | |
| Bulk | 7.0 | 9.0 | 7.3 | 1.4 | 2.7 |
| Fescue | 6.7 | 8.6 | 6.8 | 1.4 | 2.6 |
| Tomato | 5.5 | 7.4 | 5.4 | 1.2 | 1.9 |
| Agriculturally-acidified | | | | | |
| Bulk | -3.2 | -1.5 | -5.3 | -0.4 | -2.4 |
| Fescue | -4.1 | -2.3 | -6.3 | -0.5 | -2.9 |
| Tomato | -4.5 | -3.0 | -6.9 | -0.6 | -2.9 |
| Naturally-acidic | | | | | |
| Bulk | -6.5 | -4.5 | -9.1 | -1.0 | -4.1 |
| Fescue | -3.1 | -1.4 | -5.2 | -0.4 | -2.3 |
| Tomato | -5.6 | -3.8 | -8.1 | -0.8 | -3.7 |
| Mafic | | | | | |
| Non-acidified | | | | | |
| Bulk | -1.6 | -0.8 | -4.0 | 0.0 | -0.9 |
| Fescue | 1.9 | 3.8 | 1.0 | 0.5 | 0.2 |
| Tomato | 1.3 | 3.3 | 0.4 | 0.4 | -0.3 |
| Agriculturally-acidified | | | | | |
| Bulk | -1.5 | 0.6 | -2.9 | -0.1 | -1.8 |
| Fescue | 0.2 | 2.2 | -0.9 | 0.2 | -0.8 |
| Tomato | 0.3 | 2.5 | -0.7 | 0.2 | -0.9 |
| Naturally-acidic | | | | | |
| Bulk | -5.7 | -6.3 | -10.0 | -0.7 | -2.2 |
| Fescue | -0.8 | -0.8 | -3.6 | 0.1 | -0.2 |
| Tomato | -2.1 | -2.0 | -5.1 | -0.1 | -0.8 |
| Mixed | | | | | |
| Non-acidified | | | | | |
| Bulk | -0.6 | 0.9 | -2.3 | 0.1 | -0.9 |
| Fescue | -1.0 | 1.0 | -2.5 | 0.0 | -1.4 |
| Tomato | -3.6 | -1.4 | -5.5 | -0.4 | -2.7 |
| Agriculturally-acidified | | | | | |
| Bulk | -8.3 | -6.7 | -11.6 | -1.3 | -4.9 |
| Fescue | -7.0 | -5.0 | -9.7 | -1.1 | -4.4 |
| Tomato | -7.7 | -5.8 | -10.6 | -1.2 | -4.8 |
| Naturally-acidic | | | | | |
| Bulk | -9.5 | -8.7 | -13.5 | -1.5 | -5.1 |
| Fescue | -8.0 | -6.3 | -11.1 | -1.3 | -4.8 |
| Tomato | -9.4 | -7.8 | -12.8 | -1.5 | -5.6 |

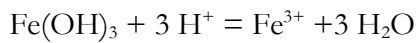
Appendix

Solution Activities

Activities used to construct rhizosphere solution stability-equilibrium diagrams.[†]

| Soil | pH | pAl | pSi | pH-1/3pAl |
|--------------------------|--------------------|----------------------|--------------------|--------------------|
| Sialic | | | | |
| Non-acidified | | | | |
| Bulk | 7.09 ± 0.09 (4) b | 10.46 ± 0.32 (4) b | 2.99 ± 0.03 (4) a | 3.60 ± 0.18 (4) b |
| Fescue | 6.94 ± 0.02 (18) b | 10.18 ± 0.09 (18) ab | 2.99 ± 0.02 (18) a | 3.54 ± 0.09 (18) b |
| Tomato | 6.67 ± 0.04 (17) a | 10.02 ± 0.07 (17) a | 2.94 ± 0.03 (17) a | 3.33 ± 0.05 (17) a |
| Agriculturally-acidified | | | | |
| Bulk | 5.30 ± 0.12 (6) b | 10.22 ± 0.09 (6) ab | 2.99 ± 0.05 (6) b | 1.89 ± 0.13 (6) ab |
| Fescue | 5.20 ± 0.04 (24) b | 10.39 ± 0.06 (24) b | 2.95 ± 0.02 (24) b | 1.73 ± 0.04 (24) b |
| Tomato | 5.06 ± 0.02 (31) a | 10.03 ± 0.08 (31) a | 3.08 ± 0.02 (31) a | 1.71 ± 0.04 (31) a |
| Naturally-acidic | | | | |
| Bulk | 4.97 ± 0.10 (7) a | 10.92 ± 0.28 (7) b | 2.93 ± 0.05 (7) ab | 1.32 ± 0.06 (7) a |
| Fescue | 5.35 ± 0.09 (14) b | 10.32 ± 0.13 (14) a | 3.00 ± 0.03 (14) b | 1.91 ± 0.10 (14) b |
| Tomato | 4.83 ± 0.06 (16) a | 10.09 ± 0.08 (16) a | 2.89 ± 0.03 (16) a | 1.46 ± 0.06 (16) a |
| Mafic | | | | |
| Non-acidified | | | | |
| Bulk | 5.88 (1) | 10.52 (1) | 3.61 (1) | 2.37 (1) |
| Fescue | 6.22 ± 0.03 (19) b | 10.43 ± 0.08 (19) b | 2.97 ± 0.01 (19) b | 2.73 ± 0.06 (19) b |
| Tomato | 5.96 ± 0.02 (16) a | 10.10 ± 0.05 (16) a | 2.84 ± 0.01 (16) a | 2.59 ± 0.03 (16) a |
| Agriculturally-acidified | | | | |
| Bulk | 5.50 ± 0.06 (6) a | 10.20 ± 0.19 (6) a | 2.76 ± 0.01 (6) c | 2.09 ± 0.09 (6) a |
| Fescue | 5.68 ± 0.02 (19) b | 9.79 ± 0.08 (19) b | 2.83 ± 0.01 (19) b | 2.41 ± 0.04 (19) b |
| Tomato | 5.66 ± 0.03 (16) b | 9.79 ± 0.09 (16) b | 2.72 ± 0.01 (16) a | 2.39 ± 0.05 (16) b |
| Naturally-acidic | | | | |
| Bulk | 5.57 ± 0.03 (6) b | 10.86 ± 0.10 (6) a | 4.40 ± 0.01 (6) b | 1.95 ± 0.03 (6) b |
| Fescue | 6.12 ± 0.08 (5) a | 10.48 ± 0.24 (5) a | 4.00 ± 0.26 (5) a | 2.62 ± 0.13 (5) a |
| Tomato | 5.96 ± 0.02 (18) a | 10.61 ± 0.07 (18) a | 4.01 ± 0.02 (18) a | 2.43 ± 0.06 (18) a |
| Mixed | | | | |
| Non-acidified | | | | |
| Bulk | 5.88 ± 0.04 (5) b | 10.43 ± 0.12 (5) b | 3.19 ± 0.03 (5) a | 2.39 ± 0.05 (5) b |
| Fescue | 5.85 ± 0.03 (17) b | 10.83 ± 0.09 (17) a | 2.93 ± 0.01 (17) b | 2.23 ± 0.05 (17) b |
| Tomato | 5.46 ± 0.03 (14) a | 11.03 ± 0.07 (14) a | 2.85 ± 0.02 (14) c | 1.78 ± 0.04 (14) a |
| Agriculturally-acidified | | | | |
| Bulk | 4.58 ± 0.00 (3) a | 10.54 ± 0.09 (3) a | 3.06 ± 0.02 (3) b | 1.06 ± 0.02 (3) ab |
| Fescue | 4.73 ± 0.04 (19) a | 10.50 ± 0.04 (19) a | 2.88 ± 0.01 (19) a | 1.22 ± 0.04 (19) b |
| Tomato | 4.55 ± 0.04 (17) a | 10.36 ± 0.04 (17) a | 2.85 ± 0.01 (17) a | 1.08 ± 0.05 (17) a |
| Naturally-acidic | | | | |
| Bulk | 4.18 ± 0.03 (4) ab | 9.59 ± 0.19 (4) ab | 3.38 ± 0.01 (4) b | 0.98 ± 0.04 (4) b |
| Fescue | 4.49 ± 0.47 (2) b | 10.23 ± 0.55 (2) b | 2.95 ± 0.02 (2) a | 1.07 ± 0.29 (2) b |
| Tomato | 4.08 ± 0.16 (2) a | 9.74 ± 0.49 (2) a | 2.90 ± 0.02 (2) a | 0.83 ± 0.00 (2) a |

[†] Means ± SE (*n*) in a given, parent material source, acidification status and element followed by the same letter are not significantly different; $\alpha = 0.05$.

*Stability Calculations*Soil Iron

$$\Delta G_f^0 = \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants}$$

$$= [(-4.60 \text{ kJ}) + 3(-237.1)] - [(-713.4 \text{ kJ})]$$

$$= -2.5 \text{ kJ}$$

$$\Delta G_f^0 = -RT \ln K$$

$$= -(2.30)RT \log K \quad | \quad T = 298.15 \text{ K and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$= -5.708 \text{ kJ} \log K$$

$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

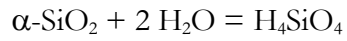
$$\log K = -(-2.5 \text{ kJ}) / 5.708 \text{ kJ}$$

$$\log K = 0.44$$

$$K = \frac{(\text{Fe}^{3+})}{(\text{H}^+)^3} = 10^{0.44}$$

$$\text{pFe}^{3+} = 3\text{pH} - 0.44$$

Quartz



$$\Delta G_f^0 = \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants}$$

$$= [(-1308 \text{ kJ})] - [(-856.3 \text{ kJ}) + 2(-237.1 \text{ kJ})]$$

$$= 22.5 \text{ kJ}$$

$$\Delta G_f^0 = -RT \ln K$$

$$= -(2.30)RT \log K \quad | \quad T = 298.15 \text{ K and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$= -5.708 \text{ kJ log K}$$

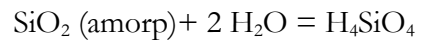
$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

$$\log K = -(22.5 \text{ kJ}) / 5.708 \text{ kJ}$$

$$\log K = -3.9$$

$$K = \text{H}_4\text{SiO}_4 = 10^{-3.9}$$

$$\text{pH}_4\text{SiO}_4 = 3.9$$

Amorphous Silica

$$\Delta G_f^0 = \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants}$$

$$= [(-1308 \text{ kJ})] - [(-848.9 \text{ kJ}) + 2(-237.1 \text{ kJ})]$$

$$= 15.1 \text{ kJ}$$

$$\Delta G_f^0 = -RT \ln K$$

$$= -(2.30)RT \log K \quad | \quad T = 298.15 \text{ K and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$= -5.708 \text{ kJ} \log K$$

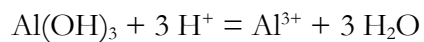
$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

$$\log K = -(15.1 \text{ kJ}) / 5.708 \text{ kJ}$$

$$\log K = -2.6$$

$$K = \text{H}_4\text{SiO}_4 = 10^{-2.6}$$

$$\text{pH}_4\text{SiO}_4 = 2.6$$

Gibbsite

$$\begin{aligned} \Delta G_f^0 &= \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants} \\ &= [(-489.4 \text{ kJ}) + 3(-237.2 \text{ kJ})] - [(-1154.9 \text{ kJ})] \\ &= -46.1 \text{ kJ} \end{aligned}$$

$$\Delta G_f^0 = -RT \ln K$$

$$\begin{aligned} &= -(2.30)RT \log K \quad | \quad T = 298.15 \text{ K and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1} \\ &= -5.708 \text{ kJ log K} \end{aligned}$$

$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

$$\log K = -(-46.07 \text{ kJ}) / 5.708 \text{ kJ}$$

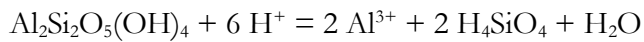
$$\log K = 8.07$$

$$K = \frac{(\text{Al}^{3+})}{(\text{H}^+)^3} = 10^{8.07}$$

$$\log \text{Al}^{3+} + 3 \text{pH} = 8.07$$

dividing by 3

$$\text{pH} - 1/3\text{pAl}^{3+} = 2.69$$

Kaolinite

$$\Delta G_f^0 = \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants}$$

$$= [2(-489.4 \text{ kJ}) + 2(-1308 \text{ kJ}) + (-237.2 \text{ kJ})] - [(-3783.2 \text{ kJ})]$$

$$= -48.8 \text{ kJ}$$

$$\Delta G_f^0 = -RT \ln K$$

$$= -(2.30)RT \log K \quad | \quad T = 298.15 \text{ K and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$= -5.708 \text{ kJ} \log K$$

$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

$$\log K = -(-48.8 \text{ kJ}) / 5.708 \text{ kJ}$$

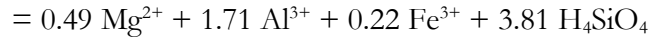
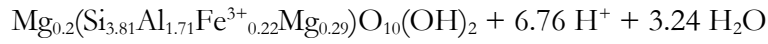
$$\log K = 8.6$$

$$K = \frac{(\text{Al}^{3+})^2 (\text{H}_4\text{SiO}_4)^2}{(\text{H}^+)^6} = 10^{8.6}$$

$$8.6 = 2 \log \text{Al}^{3+} + 2 \log \text{H}_4\text{SiO}_4 + 6 \text{pH}$$

Dividing through by 6

$$\text{pH} - 1/3\text{pAl}^{3+} = 1.43 + 1/3\text{pH}_4\text{SiO}_4$$

Montmorillonite

$$\Delta G_f^0 = \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants}$$

$$= [0.49(-454.8 \text{ kJ}) + 1.71(-489.4 \text{ kJ}) + 0.22(-4.6 \text{ kJ}) + 3.81(-1308 \text{ kJ})] - [(-5254.3 \text{ kJ}) + 3.24(-237.2 \text{ kJ})]$$

$$= -21.39 \text{ kJ}$$

$$\Delta G_f^0 = -RT \ln K$$

$$\Delta G_f^0 = -(2.30)RT \log K$$

$$\text{Where } T = 298.15 \text{ K}$$

$$\text{and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$\Delta G_f^0 = -5.708 \text{ kJ} \log K$$

$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

$$\log K = -(-21.95 \text{ kJ}) / 5.708 \text{ kJ}$$

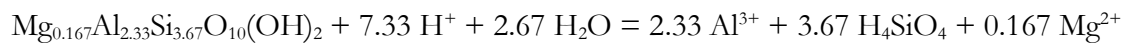
$$\log K = 3.75$$

$$K = \frac{(\text{Mg}^{2+})^{0.49} (\text{Al}^{3+})^{1.71} (\text{Fe}^{3+})^{0.22} (\text{H}_4\text{SiO}_4)^{3.81}}{(\text{H}^+)^{6.76}} = 10^{3.75}$$

$$3.75 = 0.49 \log \text{Mg}^{2+} + 1.71 \log \text{Al}^{3+} + 0.22 \log \text{Fe}^{3+} + 3.81 \log \text{H}_4\text{SiO}_4 + 6.76 \text{pH}$$

Rearranging & dividing by 5.13

$$\text{pH} - 1/3 \text{Al}^{3+} = 0.73 + 0.096 \text{pMg}^{2+} + 0.043 \text{pFe}^{3+} + 0.74 \text{pH}_4\text{SiO}_4 - 0.3 \text{pH}$$

Beidellite

$$\Delta G_f^0 = \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants}$$

$$= [2.33*(-489.4 \text{ kJ}) + 3.67*(-1308 \text{ kJ}) + 0.167*(-454.8 \text{ kJ})]$$

$$- [(-5332.5 \text{ kJ}) + 2.67*(-237.2 \text{ kJ})]$$

$$= -50.8 \text{ kJ}$$

$$\Delta G_f^0 = -RT \ln K$$

$$= -(2.30)RT \log K \quad | \quad T = 298.15 \text{ K and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$= -5.708 \text{ kJ log K}$$

$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

$$\log K = -(-50.8 \text{ kJ}) / 5.708 \text{ kJ}$$

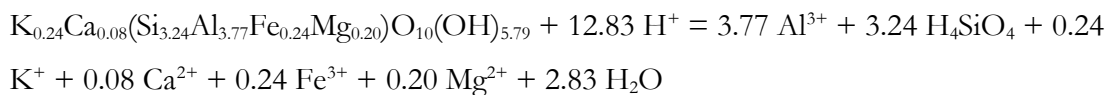
$$\log K = 8.9$$

$$K = \frac{(\text{Mg}^{2+})^{0.167} (\text{Al}^{3+})^{2.33} (\text{H}_4\text{SiO}_4)^{3.67}}{(\text{H}^+)^{7.33}} = 10^{8.9}$$

$$8.9 = 0.167 \log \text{Mg}^{2+} + 2.33 \log \text{Al}^{3+} + 3.67 \log \text{H}_4\text{SiO}_4 + 7.33 \text{pH}$$

Rearranging & dividing through by 7:

$$\text{pH} - 1/3\text{pAl}^{3+} = 1.27 + 0.0024\text{pMg}^{2+} + 0.52\text{pH}_4\text{SiO}_4 - 0.047\text{pH}$$

Hydroxy-Interlayer-Material

$$\begin{aligned} \Delta G_f^0 &= \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants} \\ &= [3.77(-489.4 \text{ kJ}) + 3.24(-1308 \text{ kJ}) + 0.24(-282.5 \text{ kJ}) + 0.08(-553.5 \text{ kJ}) + 0.24(-4.6) + \\ &0.20(-454.8 \text{ kJ}) + 2.83(-237.2 \text{ kJ})] - [(-6846 \text{ kJ})] \\ &= -112.4 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta G_f^0 &= -RT \ln K \\ &= -(2.30)RT \log K \quad | \quad T = 298.15 \text{ K and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1} \\ &= -5.708 \text{ kJ} \log K \end{aligned}$$

$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

$$\log K = -(-112.4 \text{ kJ}) / 5.708 \text{ kJ}$$

$$\log K = 19.7$$

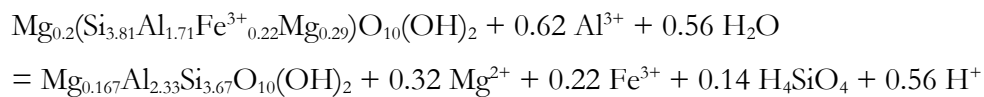
$$K = \frac{(\text{Al}^{3+})^{3.77} (\text{H}_4\text{SiO}_4)^{3.24} (\text{K}^+)^{0.24} (\text{Ca}^{2+})^{0.08} (\text{Fe}^{3+})^{0.24} (\text{Mg}^{2+})^{0.2}}{(\text{H}^+)^{12.83}} = 10^{19.8}$$

$$19.7 = 3.77 \log \text{Al}^{3+} + 3.24 \log \text{H}_4\text{SiO}_4 + 0.24 \log \text{K}^+ + 0.08 \log \text{Ca}^{2+} + 0.24 \log \text{Fe}^{3+} + 0.2 \log \text{Mg}^{2+} + 12.83 \text{pH}$$

divide by 11.31

$$1.75 = 0.33 \log \text{Al}^{3+} + 0.286 \log \text{H}_4\text{SiO}_4 + 0.021 \log \text{K}^+ + 0.0071 \log \text{Ca}^{2+} + 0.021 \log \text{Fe}^{3+} + 0.0177 \log \text{Mg}^{2+} + 1.134 \text{pH}$$

$$\begin{aligned} \text{Rearranging: } \text{pH} - 1/3 \text{pAl}^{3+} &= 1.74 + 0.286 \text{pH}_4\text{SiO}_4 + 0.021 \text{pK}^+ + 0.0071 \text{pCa}^{2+} + \\ &0.021 \text{pFe}^{3+} + 0.0177 \text{pMg}^{2+} - 0.134 \text{pH} \end{aligned}$$

Montmorillonite to Beidellite

$$\Delta G_f^0 = \sum \Delta G_f^0 \text{ products} - \sum \Delta G_f^0 \text{ reactants}$$

$$= [(-5332.5 \text{ kJ}) + 0.32(-454.8 \text{ kJ}) + 0.22(-4.6 \text{ kJ}) + 0.14(-1308 \text{ kJ})]$$

$$- [(-5254.3 \text{ kJ}) + 0.62(-489.4 \text{ kJ}) + 0.56(-237.2 \text{ kJ})]$$

$$= 28.4 \text{ kJ} > 0 \text{ will not go!}$$

$$\Delta G_f^0 = -RT \ln K$$

$$= -(2.30)RT \log K \quad | \quad T = 298.15 \text{ K and } R = 8.3145 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$= -5.708 \text{ kJ} \log K$$

$$\therefore \log K = -(\Delta G_f^0) / 5.708 \text{ kJ}$$

$$\log K = -(28.4 \text{ kJ}) / 5.708 \text{ kJ}$$

$$\log K = -5$$

$$K = \frac{(\text{Mg}^{2+})^{0.32} (\text{Fe}^{3+})^{0.22} (\text{H}^+)^{0.56} (\text{H}_4\text{SiO}_4)^{0.14}}{(\text{Al}^{3+})^{0.62}} = 10^{-5}$$

$$-5 = 0.32 \log \text{Mg}^{2+} + 0.22 \log \text{Fe}^{3+} - 0.62 \log \text{Al}^{3+} + 0.14 \log \text{H}_4\text{SiO}_4 + 0.56 \text{pH}$$