

CHANGES IN CHEMICAL PROCESSES IN SOILS CAUSED BY ACID PRECIPITATION

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INTRODUCTION

The acidification of precipitation is an accomplished fact. The only question that remains is whether the present trend of acidification is to continue into the future, and if so, to what degree. A related question is, are the consequences of acid precipitation reversible and to what extent, or over what time period? Research conducted over the last twenty years has been addressed to the problem of monitoring the composition of rainfall (and precipitation in general) (e.g. Cogbill and Likens, 1974). Except for the rather obvious and blatant examples of the effects of acid precipitation such as the dissolving of much of the inscription on Cleopatra's needle in Central Park, New York City (cited in many introductory geology texts) and the etching of surfaces in metropolitan areas, the more subtle and long term effects of acidified precipitation have been more elusive. Only recently have workers begun to appreciate the longer term effects that are occurring. Some of these effects may in fact be irreversible within the time span of modern "civilized" man.

Foliage damaged by isolated acid precipitation events may recover or be replaced within the same growing season. Lake ecosystems which have become nearly abiotic because of lowered pH may recover naturally in the space of a few years with the cessation of acid precipitation or their recovery may be accelerated with proper chemical treatment. However, certain processes, although capable of being arrested upon cessation of the acid precipitation, are essentially irreversible over a time scale of tens and even hundreds of years. For example, certain types of soils are readily leached of trace nutrients which reduces the productivity of those soils. The re-establishment of proper levels of nutrients within the appropriate levels of the soils may take either artificial fertilization or hundreds of years of chemical weathering and plant activity.

The most recent trend in research related to acid precipitation is oriented toward the predictive area, i.e., what projections can we make about the effects of prolonged acid precipitation on various components of the ecosystem.

This paper examines the changes in the nature of precipitation brought about by acid precipitation and the anticipated changes in mineral stability and element mobility in the rock-water chemical system.

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CHANGES IN PRECIPITATION CHEMISTRY

If the pH of water were controlled solely by the $\text{CO}_2 - \text{H}_2\text{O}$ system, the following equilibria prevail:



Under normal atmospheric pressure for CO_2 ($10^{-3.5}$ atm.) and at 25°C , the result of these relationships is a pH of 5.6 and the following concentrations of the carbon-bearing species:

$$\text{H}_2\text{CO}_{3aq} \approx 10^{-5} \text{ m/l} = 620 \text{ ppb.}$$

$$\text{HCO}_{3aq}^- \approx 10^{-5.6} \text{ m/l} = 153 \text{ ppb.}$$

$$\text{CO}_{3aq}^{=} \approx 10^{-10.45} \text{ m/l} = 0 \text{ ppb.}$$

$$\text{CO}_{2aq} \approx 10^{-4.9} \text{ m/l} = 553 \text{ ppb.}$$

However, it is probably a reasonable assumption that there are other naturally occurring acids present in precipitation. Hydrogen sulfide is generated in large amounts in many near surface environments and released to the atmosphere where it is subject to oxidation and conversion to sulfuric acid. Additionally, volcanic emanations contain appreciable quantities of sulfuric and hydrochloric acid. Lastly, gaseous and aerosol organic acids may constitute a significant fraction of the total acidity of precipitation. Although most of these organic acids are weak, they constitute a buffer mechanism much like the carbonate system. Thus, considering all natural sources of acidity in precipitation, we might reasonably expect the pH of rain to range from 5.7 down to perhaps 5.0 or somewhat lower.

Counteracting natural and unnatural acid loads in precipitation are particles intercepted by falling precipitation or acting as nuclei. Most inorganic particles in the atmosphere would tend to react with the acid and consume the acid. Thus pH's in the range 7 to 8 are not uncommon in areas where there is abundant windblown dust, particularly evaporitic salts, in the precipitation. Consequently the natural pH range for precipitation might range from about 5 to 8.

The best evidence for anthropogenic sources of acid in rain is based on the time studies of the Swedish and Norwegian workers (e.g. Oden, 1968) who have documented the pH of precipitation for several decades. Both the temporal and geographic variation of pH and the associated strong acids in the precipitation have been correlated with industrial sources. Similarly in the United States, although less well documented with respect to long term trends, the geographic relationship between pH and culture is well established (Cogbill and Likens, 1974).

The levels of SO_4^- and NO_3^- in rainwater suggest that the bulk of the excess acidity may be attributed to these two acids. For example, if we take representative values of $\text{SO}_4^- = 4.5$ ppm and $\text{NO}_3^- = 3.0$ ppm (Cogbill and Likens, 1974), the H^+ contribution from these two acids is $10^{-4.03}$ and $10^{-4.32}$ m/l respectively. This would lead to a pH of 3.86. In this situation the acid contribution of the $\text{CO}_2\text{-H}_2\text{O}$ system is negligible. Under these conditions where the pH is established by the strong acids, the carbonate equilibria are shifted such that HCO_3^- goes from the original value of $10^{-5.6}$ to $10^{-7.4}$ m/l. These relationships are shown graphically on Figure 1. Thus we have a drastic reduction in available HCO_3^- in water as a result of the shift in the pH. However, examination of Figure 2 shows that the other acid radicals are essentially not shifted in their abundance.

All other things being equal, there should be a tendency for rainfall to have a higher amount of dissolved solids with greater acidity. Although the largest part of dissolved material in precipitation is commonly composed of cyclical salts that are dominated by NaCl, the dissolved load in rainfall varies drastically. The sources of this variation is probably manifold, but one strong possibility is that in

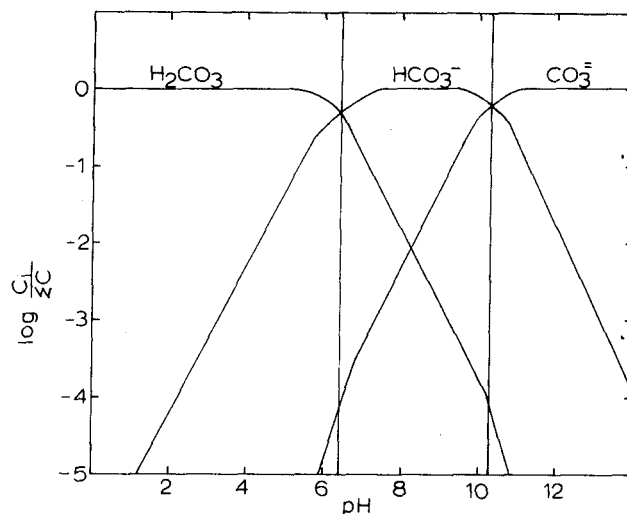


Figure 1. Concentration of carbon-bearing species in the system $\text{CO}_2\text{-H}_2\text{O}$ as a function of pH. Calculated for 25°C . Thermodynamic data from Garrels and Christ (1965).

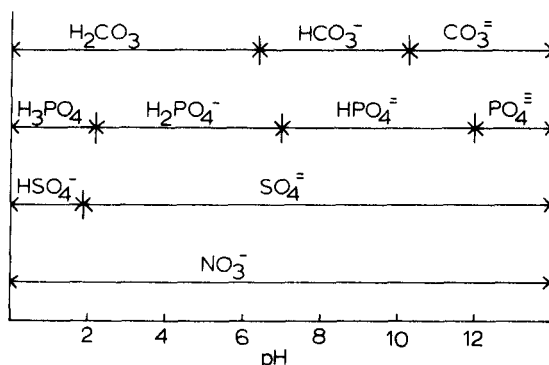


Figure 2. pH range for dominant species of various weak and strong acids. Calculated for 25°C . Thermodynamic data from Garrels and Christ (1965).

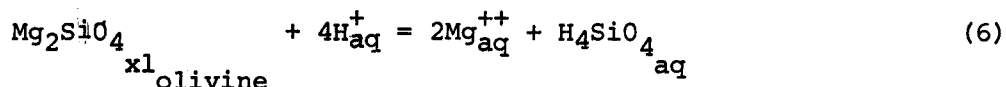
strongly acid rain, there is considerable incongruent and congruent solution of particulate material, particularly silicate minerals of various compositions. This would be an extremely difficult thing to document but undoubtedly it has and will continue to occur.

An interesting consequence of the increased load of $\text{SO}_4^{=}$ in precipitation is the increased capability of solutions to oxidize other material. Consider a solution saturated with respect to atmospheric oxygen pressure (0.20 atm) and containing about 12 ppm dissolved O_2 . This is equivalent to 0.75×10^{-3} m/l of oxygen atoms which correspond to 1.5×10^{-3} m/l of electrons if all the oxygen is reduced to the -2

valance by redox equilibria. For rain (and ultimately groundwater) containing 5 ppm $\text{SO}_4^{=}$, the equivalent oxidation capacity is 0.4×10^{-3} m/l electrons, or 25% of that of the dissolved oxygen. Stagnant groundwater or groundwater removed from contact with the atmosphere commonly has H_2S . The reduction from $\text{SO}_4^{=}$ to H_2S permits many redox equilibria to occur.

THE EXTENT OF CHEMICAL WEATHERING

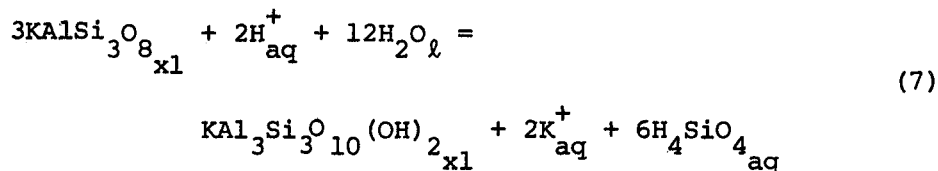
Except in situations where rainwater and/or groundwater is in contact with extremely soluble material, or is in contact with less reactive material for very long periods of time, equilibrium is generally not reached, only approached. This is suggested on several grounds. The equilibrium pH for most silicate-water reactions is generally in excess of 7 and groundwaters in temperate humid climates generally do not have pH's in excess of 7. Consider, for example, the following congruent equilibrium:



$$K = 10^{20.33}$$

For rainwater with an initial pH of 5.0 and no initial Mg^{++} or H_4SiO_4 , the final equilibrium pH (ignoring carbonate equilibria for simplicity) would be on the order of 8.7, $\text{Mg}^{++} = 10^{-4.7}$ m/l, and $\text{H}_4\text{SiO}_4 = 10^{-5}$ m/l. These collective values are seldom realized, commonly for kinetic reasons or because of competing reactions.

Alternatively, consider an incongruent reaction such as:



$$K = 10^{-8.47}$$

Under a regime of pH values from 5.0 to 8.0, Al is considered geochemically inert. Taking the initial pH of the rainwater to be 5.0 and K^+ and H_4SiO_4 to be = 0, if equilibrium prevails, the final values will be

$$\text{pH}_f \approx 13$$

$$K^+ \approx 10^{-5} \text{ m/l}$$

$$H_4SiO_4 = 3 \times 10^{-5} \text{ m/l}$$

Again, these values are not realized in nature for various reasons.

Considering reactions (6) and (7) under more acidic conditions, because the K's are not changed by a change in the initial pH, one can predict that (a) the reactions will proceed from left to right to a greater extent and (b) the final pH will not be as high in either case and (c) the reactions should be more rapid.

For equation (6) with $pH_0 = 4$

$$pH_f \approx 8.04$$

$$Mg^{++} \approx 10^{-4} \text{ m/l}$$

$$H_4SiO_4 = 3 \times 10^{-4} \text{ m/l}$$

and for equation (7) with $pH_0 = 4$

$$pH_f \approx 10.3$$

$$K^+ \approx 10^{-4} \text{ m/l}$$

$$H_4SiO_4 = 10^{-4} \text{ m/l}$$

Furthermore, the assumption that equation (7) is the proper reaction is no longer completely valid, as will be discussed in a subsequent section.

The extent to which mineral-water equilibria in the natural environment are affected by the acidification of precipitation can be precisely evaluated. Similarly the absolute amount of material which might be removed from soil can be evaluated. For example, when considering nutrient capital for the purposes of constructing nutrient budgets or cycles, the soil capital is commonly identified as the upper 30 cm of inorganic soil or the rooting zone.

Consider a rooting zone, 30 cm deep, consisting of material of granitic composition, with a bulk density of 1.5. We may ask the question, how long would it take for all the K, Na, and Ca to be leached from the soil? If we assume that solution is congruent and that these three elements are removed primarily by acid attack by downward percolating precipitation (100 cm per year, net), the following argument prevails:

- (1) There are 45g of inorganic material/cm² in the rooting zone

(2) Of this 45g, approximately 12g are K, Na, or Ca oxides and the approximate weighted atomic weight of these is 35. Therefore we have about 6g of elemental K, Na, and Ca (= 0.18 moles) or $\approx .24$ equivalents.

(3) If precipitation with pH 4.0 is allowed to displace these metals by acid attack, then each liter of precipitation will remove approximately 10^{-4} m of $\Sigma K + Na + Ca$. (This assumes that the pH goes from 4.0 to 6.0, or 99% of the acid is consumed).

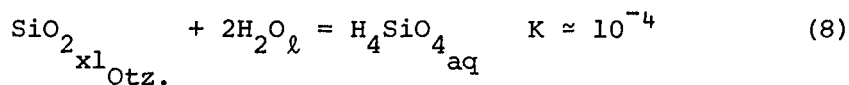
(4) Each liter/cm² corresponds to 10 years. 2.25×10^3 liters will remove all the K, Na, and Ca from the rooting zone in 2.25×10^4 years (22,500 years). A reduction in the initial pH to 3.0 yields a "time until impoverishment" of 2,250 years, still a long time.

This rather simplistic argument does demonstrate that for certain rock types, initially high in certain nutrients, impoverishment by acid rain is unlikely. However, many rock types are not so invulnerable. In the above model, I have ignored the solution of Mg (a similar argument would ensue). Similarly the solution of Al and Fe was ignored but will be treated below.

pH INSENSITIVE REACTIONS

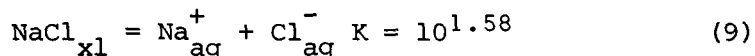
A number of reactions which are insensitive to pH values over a wide range occur in soils. Three types of reactions are common:

(1) No release of cations or anions during congruent solution: This type of reaction is illustrated by:



Only above a pH of 9 (Figure 3) does the solubility of quartz exceed 10^{-4} m/l. It should be pointed out that, for kinetic reasons, the amount of H_4SiO_4 in soil solutions or aqueous ecosystems is not determined by the solubility of quartz. The upper limit is established by the solubility of amorphous silica. The lower limit is established by siliceous organisms.

(2) Σ Cation charges released = Σ anion charges released: - with no H^+ or OH^- involved in the stoichiometry: An example of this type of reaction is the solubility of a salt:



However acid rain does have an effect on some equilibria of this type

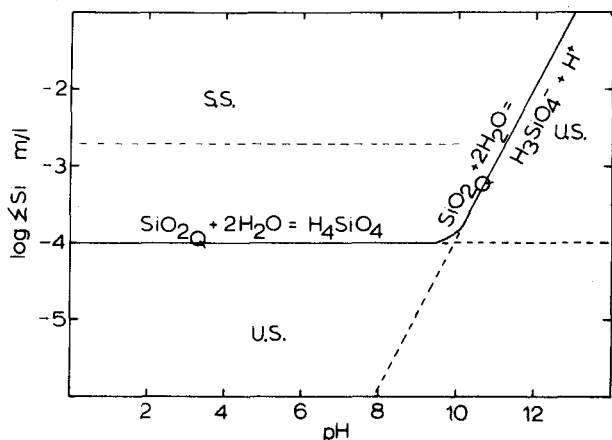
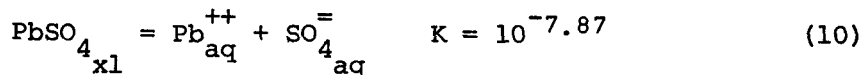


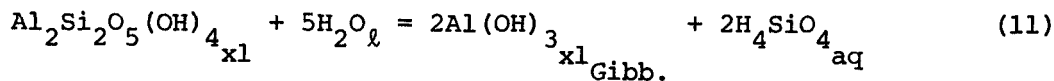
Figure 3. Solubility of quartz as a function of pH. Upper dashed line is the solubility of amorphous silica. S.S. = supersaturation. U.S. = undersaturation. Calculated for 25°C. Thermodynamic data from Garrels and Christ (1965).

because of the "common ion effect" ($\text{SO}_4^{=}$ and NO_3^-). For example:



With $\text{SO}_4^{=}$ levels approaching 10^{-4} m/l in most aqueous ecosystems, we are reducing the mobility of Pb to about 10^{-4} .

(3) No release of cations or anions during incongruent solution. An example of this type of reaction is the conversion of kaolinite to gibbsite:

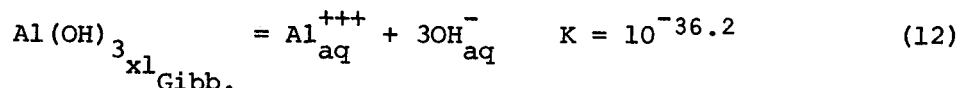


$$K = 10^{-4.67} = \text{H}_4\text{SiO}_4_{aq}$$

Again, one should note that there is a tacit assumption of no Al mobility.

pH SENSITIVE REACTIONS

Because of the dissociation equation for water (5), any reaction written so as to consume H^+ , can also be written so as to release OH^- , and vice versa. Thus the solubility of gibbsite at low pH may be written (Figure 4):



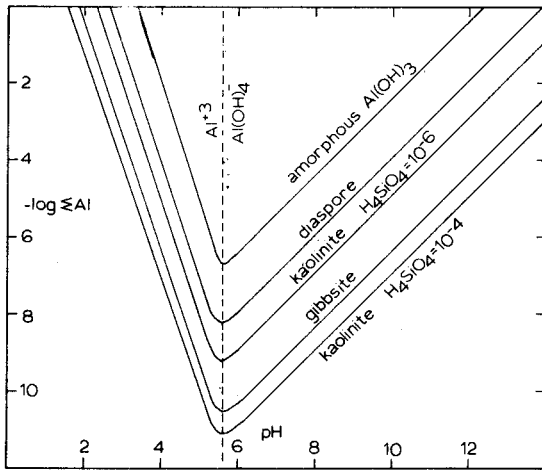
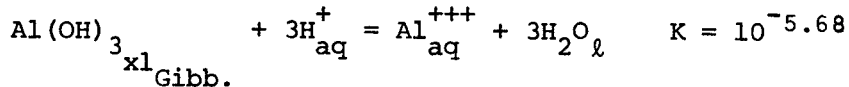
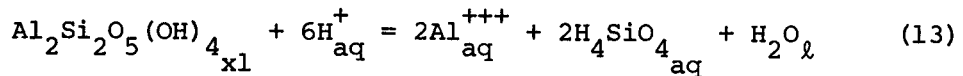


Figure 4. Solubility surfaces of gibbsite, $\text{Al}(\text{OH})_3$; amorphous $\text{Al}(\text{OH})_3$; diaspore, AlOOH ; and kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ for two $\text{H}_4\text{SiO}_{4\text{aq}}$ concentrations as a function of pH. Calculated for 25°C . Thermodynamic data from Garrels and Christ (1965).

or the equivalent



Similarly, aluminum silicate minerals may react either incongruently (equation 7) or congruently with acidified rain (equation 7 would be more typical of reactions with rain having $\text{pH}_0 \geq 5.0$), for example (see Figure 4):

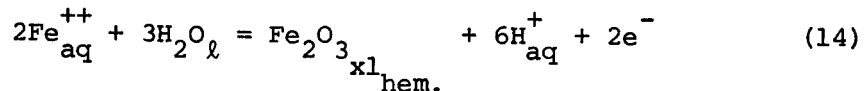


$$K = 10^{+2.05}$$

The congruent solubility of Al-bearing phases is a function of $(\text{H}_{\text{aq}}^+)^3$. Thus changes in pH sharply change the mobility of this element and Al-phases.

Eh SENSITIVE REACTIONS

Most oxidation-reduction equations in natural aqueous systems involve hydrogen ions (although not all!; see Figure 5). The one I wish to consider is the solubility of the mineral hematite (Fe_2O_3), the stability of which is nearly coincident with that of goethite (FeOOH), a common soil mineral. The solubility of hematite may be represented (written as an oxidation):



Inorganic Eh - pH Solubility Relationships (for metals)					
Oxidation State of Metals in Solid	Oxidation State of Metals in Solute	Charge on Solute	Example	ΔSol. with inc. in Eh	ΔSol. with inc. in pH
Red.	Red.	0	$As_2O_3_{xl} \rightarrow H_3AsO_3^{\circ}_{aq}$	0	0
Red.	Red.	+	$Fe^{++}Si_2O_7^{--}_{xl} \rightarrow Fe^{++}_{aq}$	0	Dec.
Red.	Red.	-	$As_2O_3_{xl} \rightarrow H_2AsO_3^{-}_{aq}$	0	Inc.
Red.	Ox.	0	$As_2O_3_{xl} \rightarrow H_3AsO_4^{\circ}_{aq}$	Inc.	Inc.
Red.	Ox.	+	$Fe^{++}Si_2O_7^{--}_{xl} \rightarrow Fe^{+++}_{aq}$	Inc.	Dec.
Red.	Ox.	-	$As_2O_3_{xl} \rightarrow H_2AsO_4^{-}_{aq}$	Inc.	Inc.
Ox.	Red.	0	$FeS^{-1}_{xl} \rightarrow Fe^{++}_{aq} + 2H_2S^{-2}_{aq}$	Dec.	Dec.
Ox.	Red.	+	$Fe_2O_3_{xl} \rightarrow Fe^{++}_{aq}$	Dec.	Dec.
Ox.	Red.	-	$Fe_2O_3_{xl} \rightarrow FeO(OH)^{-}_{aq}$	Dec.	0
Ox.	Ox.	0	$As_2O_5_{xl} \rightarrow H_3AsO_4^{\circ}_{aq}$	0	0
Ox.	Ox.	+	$Fe_2O_3_{xl} \rightarrow Fe^{+++}_{aq}$	0	Dec.
Ox.	Ox.	-	$As_2O_5_{xl} \rightarrow H_2AsO_4^{-}_{aq}$	0	Inc.

Figure 5. Changes in solubility of phases as a function of pH and Eh.

or

$$Eh = 0.72 - 0.059 \log [(Fe^{++})] - 0.177 \text{ pH}$$

This equation applies over almost all of Eh-pH space of interest on Figure 6.

As was the case for Al, the solubility of Fe-phases is dependent upon the $(H^+)^3$ value. An independent (of Eh) change in pH sharply changes the mobility of Fe and the stability of Fe-phases.

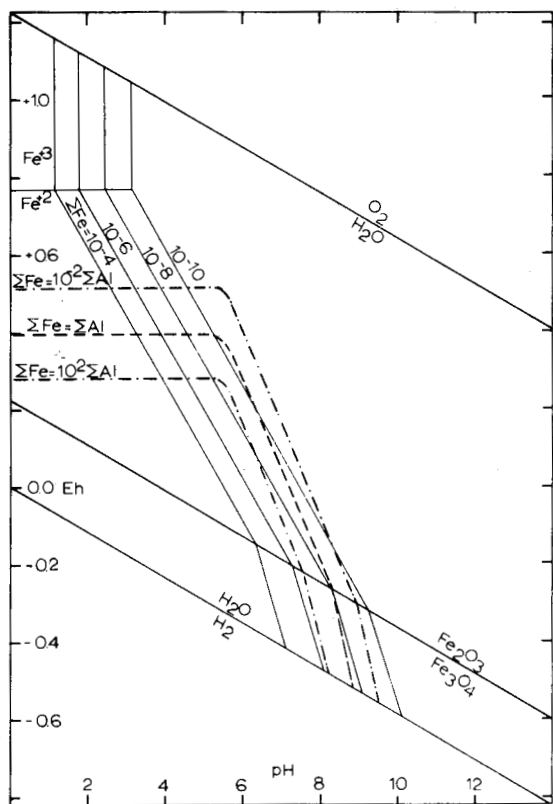
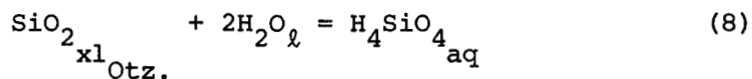


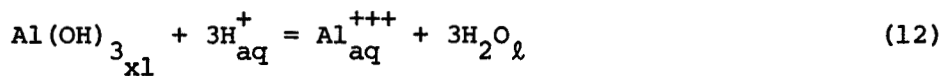
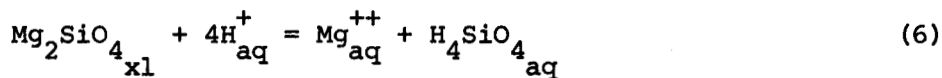
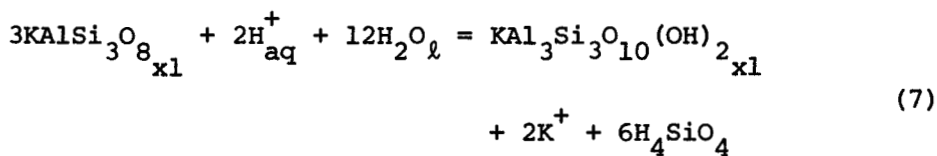
Figure 6. Solubility of hematite (Fe_2O_3) and magnetite (Fe_3O_4) as a function of pH and Eh. Calculated for 25°C. Thermodynamic data from Garrels and Christ (1965).

An independent (of pH) change in Eh will also change the mobility of Fe. As was pointed out earlier, the high $\text{SO}_4^{=}$ values in precipitation result in an Eh buffering capacity which is of the same order of magnitude as the oxygen dissolved in the precipitation.

RELATIVE MOBILITY OF ELEMENTS

One might consider the mobility of elements in a particular environment to be relatively constant over time. However, the change in mobility elicited by a change in the pH of rainwater will be related to the stoichiometry of the incongruent (or congruent where appropriate) solution of the phases that contain the elements in question. Consider for example the solubilities of quartz (SiO_2), orthoclase (a feldspar) (KAlSi_3O_8), olivine (Mg_2SiO_4), and gibbsite [$\text{Al}(\text{OH})_3$]. The respective solution equations are





It is clear that the potential effect of a decrease in pH from, e.g. 4 to 3 is to change the mobility by a factor of 10^0 , 10^1 , 10^2 , and 10^3 , respectively.

It is clearly possible to reverse relative mobility of certain elements. Consider Figure 7 on which are plotted solubility contours

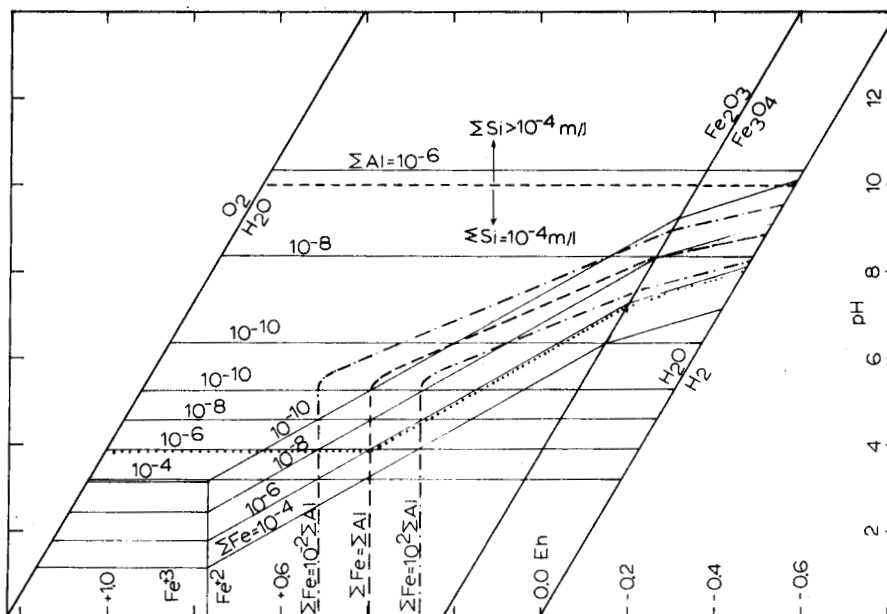
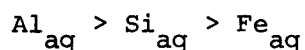
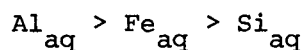


Figure 7. Solubility of quartz, SiO_2 ; gibbsite, $\text{Al}(\text{OH})_3$; and hematite, Fe_2O_3 , as a function of Eh and pH. All contours are in m/l. Calculated for 25°C. Thermodynamic data from Garrels and Christ (1965).

for the phases hematite (Fe_2O_3), gibbsite [$\text{Al}(\text{OH})_3$]- the most insoluble Al-bearing phase and thus the most stable Al-phase, and quartz (SiO_2). Slight variations in solution characteristics (Eh and pH) can result in



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.

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etc.

As pointed out previously, in nutrient-rich or non-essential element-rich substrate the absolute losses due to acid precipitation may be negligible over the short term. However, increases in the levels of dissolved elements may have significant impact in aqueous ecosystems. This would be true of essential elements in minerals (e.g. Fe^{++} from FeOOH) as well as the trace elements coprecipitated with or adsorbed on soil minerals (e.g. Mn^{++} adsorbed on or coprecipitated with FeOOH). Furthermore, because of the obvious increase in mobility of Al and consequent destruction of clay minerals, the cation exchange capacity of the soil may be altered over a long period of time.

CONCLUSIONS

The acidification of precipitation, primarily rain, causes several significant changes in the characteristics of rainfall. They are:

1. Decreased pH.
2. Increased H^+ buffering.
3. Increased Eh buffering (caused by SO_4^-).
4. Increased dissolved solids.

The possible results of this precipitation falling on soil are:

1. Increased mobility of most elements. The change in mobility is essentially: monovalent divalent trivalent cations.

2. Increased loss of existing clay minerals. However, this may under certain circumstances be compensated for by the production of clay minerals which do not have essential (stoichiometric) alkalis or alkali earths.

3. A change in cation exchange capacity - in some situations an increase, in others a decrease.

4. A general proportionate increase in the rate of removal of all cations from the soil. In initially impoverished or unbuffered soils the removal may be significant on the time scale of 10 to 100 years.

5. An increased flux of nutrients through ecosystems contiguous with the soil and through aquatic ecosystems "below" the soil zone.

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