Chemistry of Salt-Affected Soils

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Saline environments occur predominantly in arid and semiarid regions of the world. Saline soils occur less frequently in humid environments, primarily due to marine intrusions and anthropogenic inputs. The chemistry of these soils differs significantly from those present in non-saline, predominantly humid environments. Among the important differences are mineralogy (such as predominance of smectites over kaolinite), typically neutral to elevated pH, and base saturation of cation exchange sites. Salt affected soils usually contain calcite and less frequently gypsum. These soils typically contain high concentrations of exchangeable Na, consistent with the principles governing ion exchange as well as the relative solubility of Na as compared to Ca salts. It is necessary to measure all major dissolved species when examining solubility controls or constraints of any ion in solution.

ORIGIN OF SALTS

Various processes either singularly or in combination lead to the development of saline soils. A necessary condition is of course limited drainage. Ultimately the source of salts is directly linked to the development of liquid phase water on earth; the volcanic outgassing of water and other gases over geologic time and the corresponding weathering of silicate rocks. Since the early development of the earth surface, salts have been recycled into sedimentary rocks and redistributed via the hydrologic cycle.

Weathering

Mineral weathering is an important aspect of the development of saline soils. Primary aluminosilicate minerals, formed under high temperature and pressure, are almost all unstable under earth surface conditions. Weathering may consist of selective leaching of ions, such as base cations and resultant alteration into a secondary weathered mineral, such as feldspar alteration to smectite or formation of kaolinite and x-ray amorphous silica. These dissolution or weathering rates are very slow, thus soluble reaction products (salts) accumulate only under conditions that com-

bine high evapotranspiration, and or low rainfall with limited drainage. Low rainfall, moderate pH and presence of soluble salts all reduce the weathering process.

It is rare that saline soils develop in situ from weathering of igneous or metamorphic rock. More commonly, weathering processes in high precipitation areas (and in lower pH and salinity environments) result in dilute stream and ground water that carry soluble ions to more arid environments in low-lying areas. In this manner the transported dissolved salts become concentrated in areas with little or no drainage. A well documented case is the development of saline, high pH salt deposits in depressions east of the Sierra Nevada Mountains in California. Silicate weathering along the eastern slope of the Sierra range results in dilute solutions in stream flow. Deposition of this stream water into the depressions in the very arid eastern valleys, combined with the hot summer climate, results in very concentrated brines. Depending on the ion ratios present in the initial dilute water, distinctly different water compositions result upon concentration and precipitation. The evolutionary paths of waters undergoing concentration are discussed later in this chapter.

In contrast to igneous and metamorphic rock, sedimentary rocks form under ambient or slightly elevated temperature. Most of the minerals in the rock are either primary unweathered minerals from parent materials or altered minerals such as clays, formed as a result of weathering. If the sediments were deposited in marine or shallow saline inland seas, reactive saline minerals may be present, primarily, calcite, dolomite, and gypsum. In some instances marine shales may have other evaporite minerals, such as halite or mirabilite, but this is relatively less common. In some instances the bulk rock may appear relatively unreactive.

Mancos Shale formed under shallow inland seas during the Cretaceous Age, apparently under hot, dry conditions. Fresh rock samples contain calcite, sulfide minerals and/or elevated concentrations of organic matter, and high exchangeable Na and Mg concentrations on the clay minerals. When reacted overnight in water these rock samples generate a relatively non-saline solution. Long term weathering results in release of acid from sulfide mineral oxidation, dissolution of calcite, exchange of the released Ca with Na and Mg and ultimately a high pH, high sulfate, Mg and Na, saline solution.

Atmospheric Deposition

Atmospheric deposition of salts consists of both inputs from rain and dry deposition–redistribution from other land surfaces during wind storms. Salt deposition in rain is greatest in coastal areas. Rain from high energy storms that develop over the oceans, such as hurricanes, can be quite saline but rain is generally in the range of electrical conductivity (EC) of 0.01 to 0.05 dS m^{-1}. The salinity of rain generally decreases as a storm moves inland, with a more rapid decrease in the concentrations of the larger ions, Na and Cl. Average annual deposition of salts ranges from 10–20 kg ha^{-1} in continental interiors to 100–200 kg ha^{-1} in coastal environments (Mason, 1964).

During recent geologic time, large portions of the Australian continent were covered by deep rooted vegetation, such as eucalypts. These trees were able to use almost all of the rainfall. The lack of deep percolation resulted in concentration of

salts in the unsaturated zone (at and below the lower portion of the root zone). The highly weathered Australian landscape lacks salt-containing sedimentary rocks, in contrast to other saline regions of the world. Based on chemical and hydrological studies, these subsurface dissolved salts in Australia are attributed to concentration of salts present in rain (predominately Na and Cl).

Deposition of wind blown salts is also another important input of salts. Among these is the transport of calcite-containing dust into soils free of sedimentary pedogenic carbonates. These soil carbonates exert a major influence on the overall chemistry of the soil, inasmuch as it elevates soil pH and increases the base cation saturation of the soil. Most arid zone soils, even if classified as noncalareous, contain trace quantities of calcite that exert a large effect on the soil solution chemistry.

Anthropogenic Factors

The areal extent of saline soils has expanded as a result of human land use. Among the human land uses, the most influential has been introduction of irrigation into areas with insufficient drainage. Under high water table conditions salts are not leached downward and can accumulate due to surface evaporation. Most irrigated areas throughout the world contain saline soils, many of these saline regions developed as a result of irrigation.

Salinity also may develop in non-irrigated areas as a result of land use practices, such as conversion of eucalypt forests to wheat fields or conversion of prairie land into wheat fields with fallow rotations. In Australia the conversion to wheat increased subsurface recharge, displacing saline subsurface water into receiving streams, thus resulting in increased salinity in the rivers and in downstream irrigation projects. In the Northern Plains states and southern Canadian plains, fallowing had the desired effect of increasing soil moisture in years when wheat was planted, thereby decreasing crop failures, but it also had the effect of increasing recharge. Increased subsurface flow, combined with poor deep drainage resulted in lateral movement of naturally saline subsurface water and saline drainage water into low-lying areas, resulting in saline seeps, which are surface discharges. Continued discharge into low-lying areas, coupled to further salt concentration by evaporation, results in moist, high salinity soils.

Other anthropogenic inputs that cause soil salinization include surface discharge of brines from oil and natural gas operations, overgrazing soils underlain by saline formations, resulting in erosion and surface exposure of the saline materials, surface stockpiling of tailings from mining operations, and discharge of waste water from domestic water softeners.

Measurement of Soil Salinity

Various methods are used for reporting of salinity data. Total dissolved solids (TDS) refers to the dissolved material that remains upon evaporating a fixed volume of water. The values are commonly reported as mg L^{-1} TDS, but also may be reported as mg kg^{-1}, in this instance weight per kg of solution (corresponding to the molal scale). Under saline conditions the assumption that the molal concentration scale (moles per kg of water) can be approximated by concentrations in the

molar scale (moles L^{-1} of solution) is not valid. As TDS measurements are time consuming, requiring sample filtration and evaporation of the solutions, salinity is commonly reported in terms of the solution's specific electrical conductivity. Total soluble salts (TSS) is generally reported as the sum of the concentrations of the soluble ions, expressed as $mmol_c$ L^{-1}.

The conductance of a solution is proportional (non linearly) to the concentration of ionizing salts, and is measured in units of reciprocal ohms (mhos), or siemens (S) in the SI system. Measurement is made by generating a potential across two electrode surfaces (generally Pt) and determining the resistance. After correction for the cell constant (related to the cell geometry used) the data are reported as Specific Conductance (EC or SpC) per unit volume of solution (most commonly in units of dS m^{-1}). As a rough approximation TSS can be estimated from EC by using the relationship

$$\text{TSS (mmol}_c\ L^{-1}) = 10 \times \text{EC}\ (dSm^{-1}) \tag{1}$$

At elevated salinity, the approximate conversion value decreases (8.2 at a TSS value of 100 $mmol_c$ L^{-1} and 6.8 at TSS = 1000), based on saturation extracts of soils analyzed at the Salinity Laboratory (U.S. Salinity Laboratory Staff, 1954). The following empirical relationship (Marion and Babcock, 1976)

$$\log C = 0.955 + 1.039 \log EC \tag{2}$$

provides better accuracy but is limited in application since C in this instance was calculated based not on total concentration as earlier but on concentrations of individual species (corrected for ion pairs), thus requiring use of a chemical speciation program. If the chemical analysis of the sample is known very accurate calculations of EC can be done using the published data on EC relationships for either various single salt solutions and ion speciation, or calculations of individual ion conductances. The error in all of the approximation equations increases with increasing salinity, and is increasingly dependent on the specific ion composition of the water.

The detrimental effects of salinity on plant growth are primarily attributed to osmotic effects. Expression of salinity in terms of osmotic pressure is thus preferred to the alternative electrical conductivity or concentration expressions. Osmotic pressure can be estimated from electrical conductivity by the approximate relationship

$$\Pi\ (kPa) = 40\ \text{EC}\ (dSm^{-1}) \tag{3}$$

where Π is the osmotic pressure in kPa and EC is at 25°C. A more accurate representation is presented in the thermodynamics section.

Measurement of soil salinity is commonly made using the analysis of the extract from a saturated paste. This method provides a reference condition that minimizes sample dilution (there is no free standing water in the paste) and relates to water content in the field (usually a 1.5 to 1.8 dilution relative to "field capacity" water content). This provides a general reference state suitable for salinity assess-

ment in irrigated lands. A disadvantage of this method, in addition to dilution, is that there is not a fixed soil/water ratio in the extract. Other extraction methods such as 1:2 and 1:5 soil/water extracts have fixed soil water ratios, but result in greater dilution than saturation paste extracts, and thus the analyzed solutions deviate even further from the in situ soil solution composition.

Addition of water to a soil sample beyond the amount present under field conditions makes quantitative interpretation of the analysis difficult. Addition of water is undesirable because for saline soils, the assumption that concentrations can be simply corrected back to field water content is not correct, due to the processes of cation exchange, desorption, and dissolution reactions. The greater the dilution factor the greater the chemical changes from the in situ water composition. Dilution in the presence of exchangeable cations, results in release of Na to solution and loss of Ca and Mg from solution. If calcite or gypsum is present mineral dissolution will occur upon dilution. Use of computer models are useful in refining the estimated composition of in situ water at a given water content based on an extract analysis and the field water content and the extract water content.

The SAR (sodium adsorption ratio) is often reported in analyses of waters used for irrigation and soil water extracts. This ratio defined as

$$SAR = \frac{(Na^+)}{\left[\dfrac{(Ca^{2+} + Mg^{2+})}{2}\right]^{0.5}} \qquad [4]$$

where concentrations are expressed in $mmol_c \ L^{-1}$. The SAR is a useful water quality parameter since it relates to the exchangeable sodium percentage (ESP), which is the percentage of the cation exchange capacity (CEC) occupied by Na (where CEC is expressed as $mmol_c \ kg^{-1}$.

The relationship between SAR and ESP can be estimated from the relationship

$$ESP = \frac{100(-0.0126 + 0.01475 \ SAR)}{1 + (-0.0126 + 0.01475 \ SAR)} \qquad [5]$$

developed by the Salinity Laboratory Staff (1954), from a series of analyses of saturation extracts and exchangeable cations. The equation can be further simplified without much loss of accuracy to the relation

$$ESP = \frac{100 \ (0.1475 \ SAR)}{(1 + 0.01475 \ SAR)} \qquad [6]$$

Adjustment to the SAR is sometimes made to correct for the increase in SAR associated with degassing of a ground water when exposed to atmospheric conditions and the resultant decrease in Ca caused by precipitation of calcite. The use of SAR adjustment using pH_c is to be avoided as it results in large errors, exceeding the errors associated with no adjustment, however other adjustment methods are suitable (Suarez, 1981).

Thermodynamics of Soil Solution

Thermodynamic calculations are essential when considering soil chemistry but as often stated, these calculations provide us with knowledge of what reactions can occur, and not, what reactions are occurring. Thermodynamic calculations enable us to determine the solute composition of water in equilibrium with selected solid phases. These calculations also can be used to enable a comparison between water analyses and the equilibrium concentrations, to determine saturation status and the potential for selected phases to be controlling solution composition. Thus the equilibrium model is a useful reference, indicating which processes or specific reactions are possible and merit further consideration. In some instances these calculations also may serve to predict natural water compositions. This later application is frequently not satisfactory due to kinetic considerations. Models such as WATEQ, PREEQEE, MINTEQ, and GEOCHEM. provide the ability to calculate saturation status. Some of these models also have the capability to predict the solution composition that a given water would have in equilibrium with specified solid phases.

The reasons for kinetic controls are complex and varied; however for highly soluble chloride and sulfate salts, equilibrium calculations may serve to provide upper boundaries for solution concentrations. These calculations are generally not suitable for predictions of solution concentrations of heavy metals and many sparingly soluble salts, where supersaturation is prevalent, nor for silicate minerals whose reactivity is low at 25°C, thus almost always undersaturated. Specific examples will be presented in later sections.

For dilute solutions it is reasonable to assume that the commonly used molarity (moles of solute L^{-1} of solution), can be substituted for the thermodynamically required molality (moles of solute kg^{-1} of water). For saline waters this is clearly not a reasonable assumption, and molarity must be converted to molality, the following equation can be used:

$$m = M \ \frac{W_{solution}}{(W_{solution} - W_{solute}) \, d} \quad\quad [7]$$

where W is the weight (kg), and d is the density (kg dm^{-3}).

Calculation of Ion Activities

Activity Coefficients

Non-ideal behavior of soluble ions is accounted for in calculation of activities from the concentrations and activity coefficients. Under non saline to moderate saline conditions the single ion activity approach is commonly used. Using this approach the free ion activity is calculated from the ion concentration and the ionic strength. The model assumption is that there are no specific interactions among free ions in solution and the activity can be predicted from the ionic strength. The ionic strength, I is defined by,

$$I = 1/2 \sum_{i=1}^{c} C_i Z_i^2 \quad\quad [8]$$

where C is the molal ion concentration and z is the charge on the ion. Two approaches are most common, the Davis equation, and various versions of the Debye-Huckel equation. The Debye-Huckel limiting law is given as

$$\log \gamma = -Az^2 \sqrt{I} \qquad [9]$$

where $A = 1.82 \times 10^6 \, (\varepsilon T)^{-3/2}$, equal to 0.509 at 25°C, and z is the charge of the ion, and ε is the dielectric constant. This equation is suitable only for dilute solutions($<0.005 \, M$). The Davis equation, is given as (Stumm and Morgan, 1995)

$$\log \gamma = -Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \qquad [10]$$

This equation is listed by Stumm and Morgan (1995) as approximately applicable to 0.5 M, but generates significant errors above 0.1 M and is overly simplified in that it does not consider ion specific parameters, i.e., all ions of the same charge are treated equally. The second term in the equation is sometimes given as 0.2 instead of 0.3. An extended version of the Debye-Huckel equation is given by

$$\log \gamma = -Az^2 \, \frac{\sqrt{I}}{1 + Ba \sqrt{I}} \qquad [11]$$

where $B = 50.3 \, (\varepsilon T)^{-3/2}$, or 0.33 at 25°C, and a is an adjustable corresponding to the hydrated ion radius, calculated from experimental data. This equation appears useful from 0.1 to 0.2 M, depending on the electrolyte composition.

A further extension of the Debye Huckel equation was developed by Truesdell and Jones, 1974,

$$\log \gamma = - \frac{Az^2 \sqrt{I}}{1 + BA \sqrt{I}} + bI \qquad [12]$$

where, a and b are empirical adjustable parameters. Truesdell and Jones (1974) fit the parameters to salt solutions. These fits were made using the experimental data available from a series of mean molal activity coefficients of numerous salts. Single ion activity coefficients were obtained by first assuming that $\gamma_{K^+} = \gamma_{Cl^-}$ and calculating γ_{K^+} and γ_{Cl^-} from mean salt data for KCL up to 4.0 M. From these data and mean salt activity coefficients for other salts (e.g., $CaCl_2$), activity coefficients are obtained for all other ions (e.g., Ca^{2+}).

Application of these fits to mixed salt solutions is based on the assumption that there are no specific ion–ion interactions, other than the ion pairs used. Excellent fits were made to 4 M, indicating that these activity coefficients are accurate for the salts that were fit (predominantly Cl salts) but this does not ensure that they can be used under mixed salt environments, especially those with high concentrations of SO_4 or alkalinity. Equation [12] is thus useable up to 0.3 M and as high as 4.0 M, depending on ion composition of the solution. Use of different activity calculation models results in significant discrepancies in the prediction of single ion activities (Suarez, 1999).

Activity of water cannot be assumed equal to one for concentrated solutions. An approximate value is obtained using the empirical correction (Garrels and Christ, 1965)

$$a_{H_2O} = 1 - 0.017 \sum_{i=1}^{m} m_i \qquad [13]$$

where a is the activity, Σm_i is the sum of the molalities of dissolved anions, cations, and neutral species. The equation yields reasonable values if Σm_i is less than one molal. At higher concentrations it is necessary to consider osmotic coefficients and the expression given by Felmy and Weare (1986) can be used.

The osmotic pressure can be determined using the following equation from Robinson and Stokes (1965)

$$\Pi = \frac{-\nu RTW_A}{1000V_A} \phi m \qquad [14]$$

where Π is the osmotic pressure, R is the gas constant, T is absolute temperature, m is the molality, W is the molecular weight of the solvent (18 g mole^{-1} for water), V_a is the partial molal volume of the water and ϕ is the osmotic coefficient.

Pitzer Expressions

Under high ionic strength ($>0.3\ M$) activity coefficients cannot be represented solely by ionic strength expressions and ion–ion interactions must be considered. Pitzer (1979) described activity coefficients using a viral-type expansion

$$\ln \gamma_i = \ln \gamma_i^{DH} + \sum_j B_{ij}(I)\, m_j + \sum_j \sum_k C_{ijk}\, m_j m_k + \dots \qquad [15]$$

where γ^{DH} is a modified Debye-Huckel expression and B_{ij} and C_{ij} are specific coefficients for each ion interaction. Felmy and Weare (1986) have reported the coefficients for the major ions and numerous minor species (cations, anions, and neutral species). Use of this model has required consideration of only a few complex species. Application of this model requires use of a thermodynamic database consistent with the activity calculations and selection of ion complexes. Under saline conditions ions exhibit non-ideal behavior.

Complexation, Ion Pairs, and Equilibrium Constants

Some ion interactions are sufficiently strong as to form bonds that are detectable with spectroscopic methods. The concentrations of these complexes are subtracted from the total ion concentrations before calculating individual ion concentrations. In some instances it has been observed that the calculated ionic activities do not correctly predict the solubility of a salt under increasing ionic strength. Using these solubility calculations and specific conductance data it has been inferred that other species, ion pairs, must exist, reducing the free ion concentration and activity and reducing the specific conductance of a solution. The Pitzer model does not

include these ion pairs as separate chemical entities but rather represents the ion activity data by consideration of the ion–ion interactions.

Stability constants have been developed for a large number of ion pairs. In most instances there is no physical evidence for these species, and they are constructs to enable accurate predictions with the single ion model. The free ion activity is thus calculated from the total dissolved concentration of the element, activity coefficient of the single ion, association constants for the ion pairs and the activity coefficients of the individual ion pairs. In the case of Ca the total Ca concentration in solution is given by

$$Ca_T = Ca^{2+} + CaSO_4^0 + CaHCO_3^+ + CaCO_3^0 + CaOH^+ \ldots \qquad [16]$$

In some models $CaCl^+$ is also considered. Each species also has an associated single ion activity coefficient. A chemical speciation computer program is essential for calculation of individual ion activities and distribution of the concentrations of individual species.

Calculation of stability constants require accurate calculation of ion activities, thus of activity coefficients of both the major ions and of the complex. The stability constants based on solubility studies are thus dependent on the model used for activity coefficients and stability of ion complexes in solution. Several models, including the thermodynamic model PREEQEEC (Parkhurst, 1995), and the transport model UNSATCHEM (Suarez and Simunek, 1997) have the option of using these activity calculation routines.

Solubility products for various minerals have been calculated from both calorimetric and solubility studies. In the case of solubility studies it is important to note that these calculations depend on the accurate calculation of ion activity. Use of different sets of activity coefficients and, ion pair species and stability constants for the ion pair species, all result in discrepancies in the activity of the free ion species, thus in the reported solubility product. As a result it is important that these solubility constants be used only with the activity coefficient model, ion pair species and ion pair dissociation constants with which the constant was determined. These errors increase in importance under saline conditions, as the activity coefficient values of the different models diverge and the complexes and ion pairs become an increasing percentage of the total dissolved salts. There are important differences in ion calculations and in solubility predictions among the most commonly used models, PREEQEC (Parkhurst, 1995), GEOCHEM (Sposito and Mattigod, 1977), and MINTEQA2 (Allison et al., 1990).

Mineral Solubility

General Concepts

For a given solid phase of composition AB that dissolves, the equilibrium expression is given by

$$K = \frac{[A^+][B^-]}{[AB]} \qquad [17]$$

where brackets represent activity of a species. Using the convention that the activity of the pure thermodynamically stable well crystallized solid phase equals one then the solubility product, K_{sp} at specified temperature is

$$K_{sp} = [A^+][B^-] \tag{18}$$

In this case the activities represent the activities of the species that would be in equilibrium with the solid phase. An evaluation of the saturation status of a water with respect to a mineral phase can be made by calculating the activities of the ions of interest from the water analysis and ion speciation program and then comparing the ion activity product wit the K_{sp} value. The IAP, given as

$$IAP = [A^+][B^-] \tag{19}$$

is based on the calculated activities from measured concentrations.

If temperature dependent data are available then the dependence on temperature can be fit with a power function (Truesdell and Jones, 1974) In the absence of this information and for moderate changes in temperature the Van't Hoff equation is often used

$$\log K_T = \log K_{Tr} - \frac{\Delta H_{Tr}}{2.3R}\left(\frac{1}{T} - \frac{1}{Tr}\right) \tag{20}$$

where T is the absolute temperature of interest, T_r is the reference temperature (298 K), R is the gas constant and ΔH_{Tr} is the enthalpy of reaction and K_{tr} is the equilibrium constant at the reference temperature. This equation is generally suitable for the small temperature range encountered by aqueous solutions at ambient pressure.

Processes Affecting the Chemistry of Saline Waters

Solid Phases

Calcite, $CaCO_3$, is almost always present in saline soils, the exception being in acid, saline soils. It is considered to be relatively insoluble, however its solubility is enhanced by the presence of elevated concentrations of CO_2, as occurs in most soils. It is generally the first mineral to precipitate in an evaporating sequence, resulting in loss from solution of Ca and alkalinity (in most instances HCO_3^- and CO_3^{2-}) The solubility expression is given by

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-} \tag{21}$$

however, CO_3^{2-} is rarely the dominant carbonate species in solution. The carbonate species are not conservative since they depend on CO_2 partial pressure, as seen by the following set of equations. The partial pressure of CO_2 is related to the concentration of carbonic acid by the Henry's Law expression

$$[H_2CO_3^*] = P_{CO_2} K_H \qquad [22]$$

where $H_2CO_3^*$ denotes the sum of dissolved CO_2 gas and the aqueous species H_2CO_3. The summed expression $H_2CO_3^*$, decreases with increasing temperature since dissolved CO_2 gas is the major component. The concentration of $H_2CO_3^*$ depends only on the CO_2 partial pressure, temperature and to a minor extent, the ionic strength of the solution. The dissociation of carbonic acid is given by

$$[HCO_3^-] = \frac{H_2CO_3^* K_{a1}}{[H^+]} \qquad [23]$$

with a K_{a1} value of $10^{-6.35}$ at 25°C. As shown by Eq. [22] and [23], increasing the CO_2 partial pressure results in a decrease in pH and an increase in HCO_3^-. Carbonate ion is related to bicarbonate by the second dissociation expression

$$[CO_3^{2-}] = \frac{[HCO_3^-] K_{a2}}{[H^+]} \qquad [24]$$

with the constant K_{a2} equal to $10^{-10.33}$ at 25°C. In the absence of any additional reactions the change in CO_2 has no change on the net alkalinity since the change in H^+ (ΔH^+) = $\Delta HCO_3^- + \Delta CO_3^{2-} + \Delta OH^-$, expressed in $mmol_c L^{-1}$.

Under most commonly encountered conditions (pH 6.5–9.5) HCO_3^- is the dominant solution carbonate species. Based on the above reasoning it is more realistic to consider the following overall reaction for calcite dissolution and precipitation.

$$CaCO_3 + CO_2(g) + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^- \qquad [25]$$
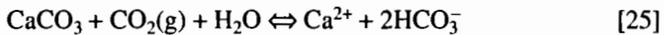
and thus the overall equilibrium expression is given by

$$[Ca^{2+}][HCO_3^-]^2 = K_{SP}^C \frac{K_{CO_2} K_{a1} P_{CO_2} (H_2O)}{K_{a2}} \qquad [26]$$

Where K_{SP}^C is the solubility constant for calcite. Analysis of this equation indicates that an increase in CO_2 results in an increase in the solubility of calcite.

Under acid, saline conditions dissolution of calcite is represented by the following equation

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3 \qquad [27]$$

Calcite is thus useful to neutralize acidity in acid sulfate soils, without further increasing the salinity.

Magnesium substitutes into the calcite structure, generally in the range of 2 to 5%, providing a minor sink term for Mg. Under high Mg/Ca ratios this substitution may increase to 8 to 12%; however, this is not usually observed in pedogenic calcite.

Soil solutions and shallow ground waters in arid environments are supersaturated with respect to calcite if calcite is present and concentrating processes such as evaporation and plant water uptake occur. This supersaturation, on average three fold (Suarez, 1977, Suarez et al., 1992), corresponds to the supersaturation level in the presence of dissolved organic matter at which nucleation stops and only crystal growth occurs (Lebron and Suarez, 1996). Soil solutions in arid zones thus contain substantially higher concentrations of calcium than predicted by equilibrium speciation models.

Dolomite, $CaMg(CO_3)_2$, is often present in saline soils but is derived from the soil parent materials rather than formed pedogenically. Dissolution of dolomite under non acid conditions is generally very slow, nonetheless over time it provides a source of Mg to solution. Dolomite dissolution is represented by the following reaction

$$CaMg(CO_3)_2 + 2CO_{2(g)} + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \qquad [28]$$
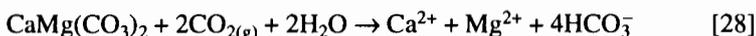
Dolomite solubility is roughly comparable to that for calcite $K_{sp} = 10^{-17}$ and as with calcite almost all arid soils are supersaturated. Kinetic constraints prevent precipitation under earth surface temperature and pressures (even under clean and controlled laboratory conditions). Under high degrees of supersaturation a mixture of hydrated magnesium carbonate and calcite may form, sometimes called protodolomite. Since it is a mixture of two phases, it is preferable to consider the solubility and formation of the phases as separate entities.

Gypsum, $(CaSO_4 \cdot 2 H_2O)$, is generally the second most common precipitated phase in arid soils, and may occur in acid as well as alkaline soils. Dissolution and precipitation of gypsum is represented by

$$CaSO_4 \cdot 2H_2O \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \qquad [29]$$
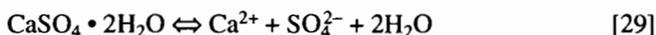
Saline acid soils are derived from the oxidation of sulfide minerals, generating sulphuric acid that reacts with the existing soil minerals. Gypsum will precipitate in these soils if small amounts of carbonates and other calcium source minerals are present. These soils typically occur in coastal areas, for example resulting from draining coastal wetland areas that were formerly under anaerobic conditions.

Gypsum readily precipitates and dissolves, thus gypsiferous soils can usually be assumed to be at equilibrium with respect to gypsum. The following solubility expression is applicable.

$$K_{SP}^G = [Ca^{2+}][SO_4^{2-}][H_2O]^2 \qquad [30]$$

where K_{SP}^G is the solubilty constant for gypsum. Due to high solubility, most gypsiferous soils are high in dissolved Ca, however, in some instances more soluble sulfate salts may be present and $SO_4^{2-} >> Ca^{2+}$.

Magnesium Carbonates

Magnesite, $(MgCO_3)$ is often considered the thermodynamically most stable magnesium carbonate mineral with a solubility comparable to that for calcite;
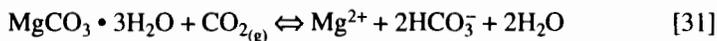
however, magnesite can generally be ignored as a mineral of interest in saline soils as it is not formed under earth surface temperature and pressure conditions and is rare, existing primarily as a hydrothermal mineral. The mineral is kinetically slow to dissolve.

The carbonate minerals potentially limiting Mg in solution are hydromagnesite and nesquehonite, both highly soluble and both able to readily precipitate when the solubility is exceeded. Use of these minerals in predictive models provides for an upper limit to magnesium in solution, and in combination with calcite, provides a mixed mineral phase material that is called protodolomite, as discussed above. Nonetheless these minerals, as well as the mixed phase protodolomite, are rare in saline soils.
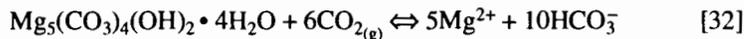
The predicted ratio of Mg/Ca based on simultaneous equilibrium with magnesium carbonate and calcite, is roughly 1,000/1, well above values commonly seen in natural waters. More typically, saline waters have Mg/Ca ratios that range from 1 to 10, suggesting that other minerals or processes either control or limit Mg in solution. Seawater has a Mg/Ca ratio of 5, also suggesting other Mg removal processes.

As waters concentrate, the SAR increases proportionally with the square root of the concentration, thus in the absence of other reactions, Ca and Mg would be released from clays exchange sites into solution; however, precipitation of Ca results in additional removal of Ca from exchange sites and is often sufficient to result in Mg loss from solution and adsorption onto the clay exchange sites despite the increasing SAR. In the case of freshwater sediments, upon reaction with seawater there is a depletion of Mg from seawater (Sayles and Manglesdorf, 1977).

Loss of Mg from solution during the process of concentration is attributed to cation exchange and minor substitution of Mg into precipitated calcite, as discussed with seawater chemistry above. Magnesium carbonate minerals such as nesquehonite, $MgCO_3\,3H_2O$, and hydromagnesite, rarely occur but if the solution concentration is above the saturation level, they will readily precipitate. Their rare occurrence indicates that other less soluble phases may control Mg in solution. The reaction of nesquehonite and hydromagnesite are represented by,

$$MgCO_3 \bullet 3H_2O + CO_{2_{(g)}} \Leftrightarrow Mg^{2+} + 2HCO_3^- + 2H_2O \qquad [31]$$

and,

$$Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O + 6CO_{2_{(g)}} \Leftrightarrow 5Mg^{2+} + 10HCO_3^- \qquad [32]$$

respectively. Additional unaccounted for sinks may include Mg uptake into silicate minerals, including precipitation of sepiolite, formation of palygorskite or Mg diffusion into silicate minerals. These processes also impact terrestial saline waters.

Magnesium Silicates

Precipitation of sepiolite is possible under earth surface conditions and serves to put an upper limit on Mg concentrations in solution. Precipitation–dissolution of amorphous sepiolite can be represented by,

$$Mg_2Si_3O_{7.5}(OH) \cdot 3H_2O) + 4.5H_2O + 4CO_{2(g)}$$
$$\Leftrightarrow 2Mg^{2+} + 3H_4SiO_4 + 4HCO_3^- \qquad [33]$$
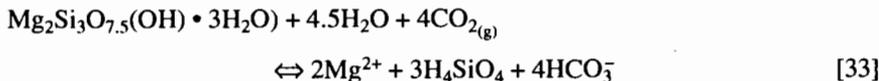
Mg silicates may provide a sink for Mg, however in soil with sulfate dominant solution conditions, Mg in surface salt crusts is found in mixed Na–Mg sulfate hydrated salts, bloedite, and konyaite (Kohut and Dudas, 1993).

Cation Exchange

Cation exchange is a major process affecting the chemistry of saline soils. Cation exchange can be represented by the following reaction for $Ca^{2+} - Na^+$,

$$2NaX + Ca^{2+} \rightarrow 2Ca_{0.5}X + 2Na^+ \qquad [34]$$
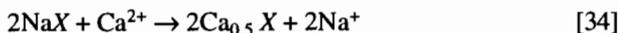
where the exchanger site can be expressed in the units of mol_c, in this case generating an expression similar to the commonly applied Gapon equation. The Gapon equation considers concentrations rather than activities of both the solid and solution phase,

$$k_G = \frac{(Ca^{2+})^{0.5}(NaX)}{(Na^+)(Ca_{0.5}X)} \qquad [35]$$

This equation is often applied due to the relative stability of the selectivity value. A true thermodynamic expression is rarely used because the solid phase activity coefficients are not independently determined. Alternatively, if we write the exchange reaction in terms of moles of species rather than moles of charge we obtain an expression such as

$$2NaX + Ca^{2+} \rightarrow CaX_2 + 2Na^+ \qquad [36]$$

The exchange expression for this reaction,

$$k_V = \frac{(Na^+)^2(CaX)}{(NaX)^2(Ca^{2+})} \qquad [37]$$

is called the Vanselow equation. This equation is not as commonly used, probably due to the greater variation in the selectivity constant.

Evolution of Saline Waters

A representation of the chemical evolutionary path of saline waters upon concentration is shown in Fig. 15–1. This figure has been modified from representations of closed basin evaporation shown by Eugster and Jones (1979), among others. These processes and changes in water composition are directly applicable to changes in saline soil waters, with several exceptions.

As shown in Fig. 15–1, the most important determinant of the change in a water composition upon concentration is the ratio of Ca +Mg to alkalinity (expressed
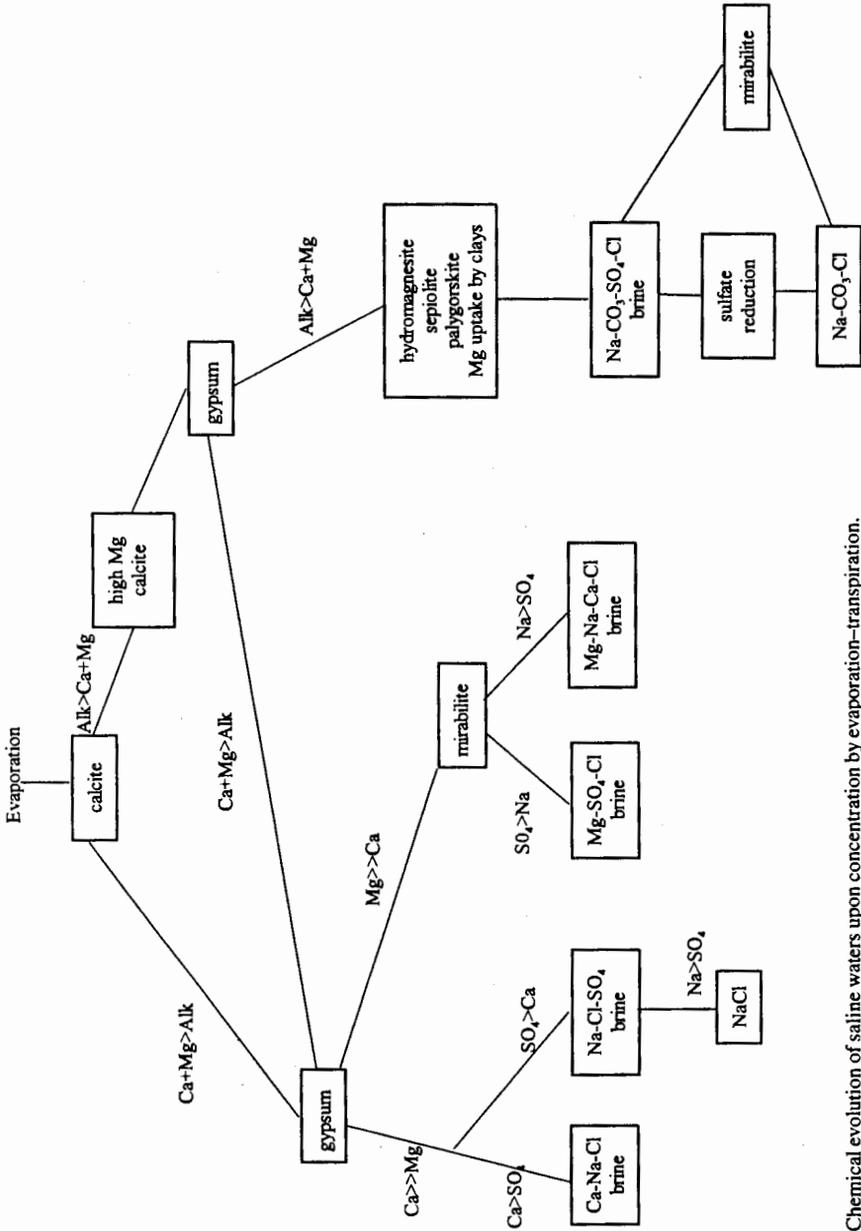
Fig. 15–1. Chemical evolution of saline waters upon concentration by evaporation–transpiration.

in $mmol_c$ L^{-1}). Typically the origin of the dissolved salts in the soil is not primarily from silicate weathering, thus Ca+ Mg usually exceeds alkalinity. For example dissolution of silicate minerals can be represented by release of cations (Ca, Mg, Na, and K) precipitation of a Al oxide and release of silica, in the form of silicic acid, with the counter anion being HCO_3^-. A representation for dissolution of Na feldspar (albite) is given by

$$NaAlSi_3O_8 + 8H_2O + CO_2 \rightarrow$$

$$Na^+ + Al(OH)_3 + 3H_4SiO_4 + HCO_3^- \qquad [38]$$
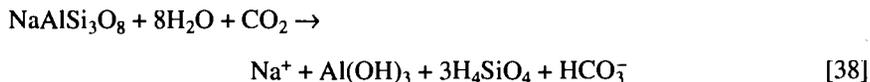
In many instances a more realistic reaction includes the formation of kaolinite as a weathering product such as

$$2NaAlSi_3O_8 + 11H_2O + 2CO_2 \rightarrow$$

$$Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2Na^+ + 2HCO_3^- \qquad [39]$$

From these reactions it follows that for the release of every base cation (Ca^{2+}, Mg^{2+}, Na^+, and K^+) there is a formation of one or more HCO_3^- ion, thus (in mol_c L^{-1}) Ca^{2+} + Mg^{2+} + Na^+ + K^+ = HCO_3^- and Ca < HCO_3.

When the (Ca+Mg)/alkalinity ratio is less than one the water evolves upon evaporation and/or transpiration to a high pH, high alkalinity and Ca and Mg depleted water. Waters of this composition are observed in the saline soils of the eastern Sierra Mountains. They are generally low in sulfate and the dissolved salts are derived from granitic weathering. Among the suite of minerals expected are calcite, which is almost always the first mineral to precipitate. With increasing concentration and continued calcite precipitation, Ca becomes increasing depleted in solution.

The cation exchange process exerts an important effect on the soil solution composition. As the water increases in salinity upon concentration, there is a decreasing preference for divalent as opposed to monovalent ions (see Eq. [35]. Upon concentration of the water this process serves to release Ca and Mg to solution and remove Na from solution. This process thus serves to buffer changes in the cation composition of the soil water, since Ca and Mg are being removed by precipitation. In some instances the Ca and Mg release may be sufficient to change the ratio of Ca+Mg to alkalinity to a value greater than one, thus moving the evolutionay path to the alkalinity depleted left side of Fig. 15–1. Cation exchange prevents the use of Na ratios as an indicator of the degree to which a water has been concentrated.

Upon further concentration of these waters where Ca+Mg exceeds alkalinity, gypsum may precipitate if sulfate is sufficiently elevated. Further concentration and precipitation of Mg minerals is often observed, however, the process may be more prevalent than reported as these minerals are relatively x-ray amorphous. With increasing concentration exchange sites become almost completely Na saturated with release of Mg to solution (at this stage Ca concentrations in solution and on exchange sites are very low). The waters are now enriched in Na sulfate and alka-

linity, and mirabilite. a hydrated Na sulfate mineral, may also precipitate. Over long time scales there also is Mg substitution into clay mineral structures.

When Ca+Mg exceeds alkalinity, the waters evolve to a low alkalinity and reduced pH condition. Calcite and then gypsum will be the precipitating minerals. In almost all instances Mg will exceed Ca and if the waters are further concentrated, will evolve to either a Mg SO_4–Cl or Mg Na Ca Cl brine. With depleted alkalinity Mg minerals remain highly soluble.

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