Chapter 4
Chemical Weathering Processes on the Earth's Surface

Abstract The exhumation of rocks from the Earth's crust implies that they must adjust thermodynamically to the conditions existing on the surface, which are extremely different from those prevailing during their formation, with higher temperature, pressure, and often exposed to chemically aggressive fluids. The processes involved in chemical weathering, such as dissolution, hydrolysis, etc., are at the core of the adjustment mechanism, transforming solid, and usually refractory rock material, into particles-typically stripped from part of their original components and dissolved phases, both of which are amenable to be transported from the continents to the sea. Although anthropogenic actions have altered natural denudation rates, still a relatively minor portion of the material thus produced stays for a longer period on the continents, temporarily sequestered in depositional systems. The most important participants in the weathering scenario are mineral dissolution, silicate hydrolysis, and redox reactions.

Keywords Dissolution · Hydration · Carbonation · Hydrolysis · Redox processes · Oxidation · Reduction · Cation exchange · Regolith · Isotopes

4.1 Introduction

As seen in a previous chapter, physical weathering is a mechanical process which fragments rocks into smaller particles without a substantial change in chemical composition; in contrast, biological weathering exerts jointly a biophysical and biochemical effect. As an example of the synergism that dominates in rock weathering, these processes are very important in the exogenous cycle since they vastly increase the surface area of crustal material exposed to the agents of chemical weathering, i.e., air and water. A larger surface area means that more mineral matter will be accessible to react with fluids (Fig. 4.1). All weathering processes can be viewed as the adjustment of rocks and minerals formed at high temperature and pressure contrasting with the situation prevailing on the Earth's surface, where low temperatures and pressure prevails (e.g., Anderson et al. 2007).
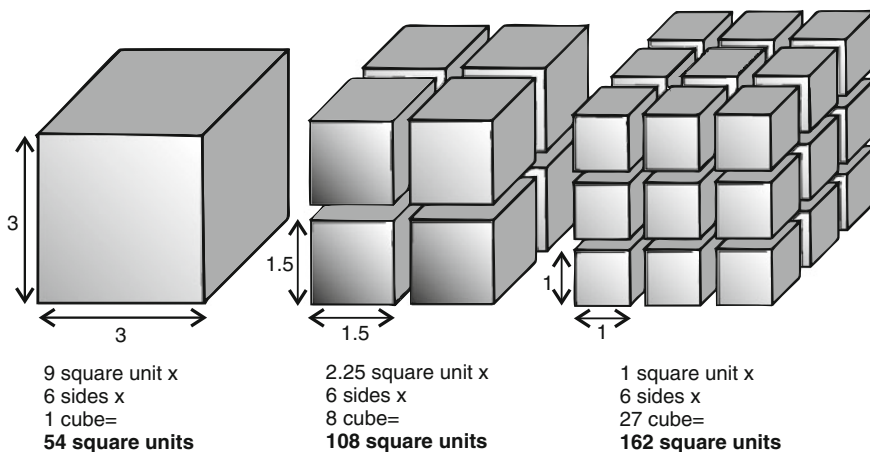
9 square unit x
6 sides x
1 cube=
54 square units

2.25 square unit x
6 sides x
8 cube=
108 square units

1 square unit x
6 sides x
27 cube=
162 square units

Fig. 4.1 The specific surface area (SSA) is the total surface area of a material per unit of mass, for example, $m^2 \ g^{-1}$. The figure illustrates the increase of the surface area as the size of particles decreases

Therefore, minerals adjust to the new set of conditions to recuperate stability; this adjustment may be relatively fast for a Ca-rich plagioclase, for example, or slow as in the weathering of some silicates, like alkali feldspar or muscovite.

Among the many factors that control rock weathering such as climate, relief, biota, time, and the properties of the rock itself, climate plays a major role determining water availability and reaction kinetics which jointly determine the extent of chemical leaching. A clear example was presented by Benedetti et al. (2003), which studied the response of weathering in a region exposed to extremely high precipitation (1.8 to 12 m yr^{-1}). Clearly, chemical weathering is set off by water (mostly water with slightly acid pH) and gases (e.g., oxygen), which attack minerals (e.g., Drever 2005). Some compounds and ions of the original mineral are removed in solution, percolating through mineral debris to feed groundwater, rivers, and lakes. A proportion of fine-grained solids may be washed away from the weathering site, leaving a modified solid residue (i.e., *regolith*) which forms the basis of soils.

4.2 Mechanisms of Chemical Weathering

Chemical weathering is essentially an intricate process not only because of the complexity of the chemistry involved—some of which remains unknown—but also because minerals react differently to the aggression of weathering agents (e.g., White and Brantley 1995). Diverse mechanisms of chemical weathering are recognized and a variety of combinations occur together during the breakdown of the majority of minerals and rocks.

4.2.1 Dissolution

The most straightforward weathering reaction is the **dissolution** of soluble minerals. The water molecule is efficient in separating ionic bonds, such as in the dissolution of halite that results in an electrolyte solution:

$$NaCl_{(s)} \leftrightarrow Na^+_{(aq)} + Cl^-_{(aq)} \tag{4.1}$$
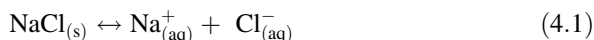
Halite's *solubility product* is $K_{sp} = 37.6$.

Clearly, halite is highly soluble; at 25 °C and a pressure of 100 kPa, its solubility is 6.15 mol kg^{-1} (~ 351 g L^{-1}). Since no hydrogen ions (H^+) are involved, the process is independent of pH. Due to a number of factors, like the remarkable abundance in seawater of the two ions involved, several authors have probed into the chemical characteristics of this simple mineral. For example, Gavrieli et al. (1989) studied the solubility of halite as a function of temperature in the highly saline brine system of the Dead Sea, and Alkattan et al. (1997) experimented on its dissolution kinetics.

Similarly, anhydrite, which is markedly less soluble than halite (i.e., its solubility is 0.67 g L^{-1}), is subjected to *congruent dissolution* when in contact with water;

$$CaSO_{4(s)} \leftrightarrow Ca^{2+}_{(aq)} + SO^{2-}_{4\ (aq)} \tag{4.2}$$
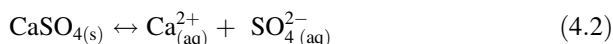
In contrast with halite, anhydrite's $K_{sp} = 2.4\ 10^{-5}$.

In some cases, the formation of a *hydrate* occurs with a definite number of molecules of water of crystallization;

$$CaSO_{4(s)} + 2H_2O \leftrightarrow CaSO_4 \cdot 2H_2O_{(s)} \tag{4.3}$$
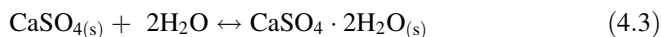
4.2.2 Hydration

The **hydration** of anhydrite to gypsum results in "bubbles," often discernible in *playas*, as a consequence of expansion and mechanical deformation. Anhydrite and gypsum, as well as halite, are typical minerals of saline lakes and playas, where they crystallize as a consequence of evaporation, following a sequence that is governed by their solubility product (Fig. 4.2). Moreover, these minerals, abundant in arid environments, are easily windblown and transported away from their source, thus contributing significantly to the chemical composition of raindrops. Likewise, ocean aerosols determine that most atmospheric precipitation is of the Na^+-Cl^-- type. As rainfall moves away from the sea coast, the continental chemical signature becomes more prominent (e.g., Forti Adolpho et al. 2012) due to the participation of windblown dust and soluble aerosols. It follows, then, that a
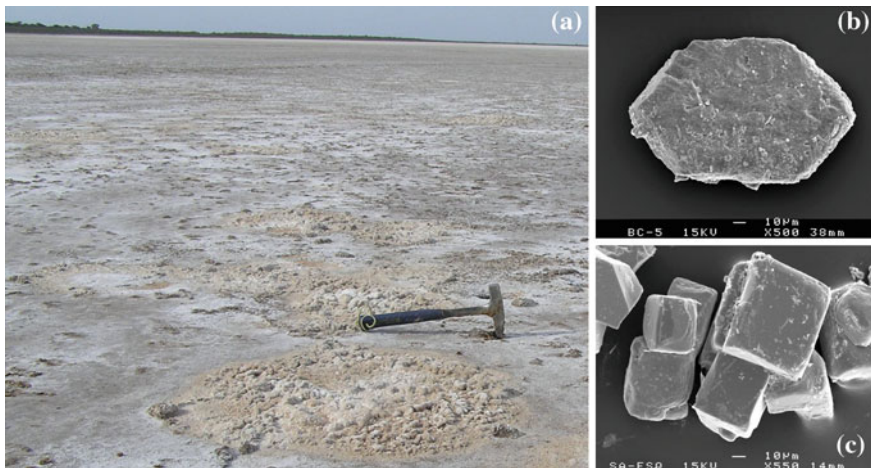
Fig. 4.2 **a** Typical playa basin (Salina de Ambargasta, $\sim 29°$ S $\sim 64°$ W), in the NW corner of Córdoba Province (Argentina), photographed during the desiccation stage (i.e., austral winter); the structure *left* by microbial mats can be clearly observed. **b** Pseudo-hexagonal gypsum crystal from Barranca Colorada (Salina de Ambargasta) obtained at 5 cm depth. **c** Cubic halite crystals from the surface salt crust at the playa basin of Salina de Ambargasta (Córdoba, Argentina) (Zanor et al. (2013). Photographs by G.A. Zanor

significant part of the dissolved phases in atmospheric precipitation are, in fact, recycled salts that originate in the sea and return to the sea after flowing over and through the outcropping continental crust, as rivers and aquifers. Many authors that have examined chemical denudation employed a methodology that allows correcting the contribution of chemical weathering, by subtracting the atmospheric input (e.g., Stallard and Edmond 1987; Gaillardet et al. 1999).

Silica is very abundant in the Earth's crust and, although it occurs naturally as eight distinct forms with uneven abundance, the species of real interest are ordinary quartz, opal-A, and amorphous silica (e.g., Wray 1997). Amorphous silica has a solubility of 60–80 mg L^{-1} at 0 °C, 100–140 mg L^{-1} at 25 °C, and about 300–380 mg L^{-1} at 90 °C (Krauskopf 1956; Krauskopf and Bird 1995). Clearly, silica solubility increases markedly with temperature. After its congruent dissolution, $Si(OH)_4^°$ is the most representative *monomer* and usually exists as the uncharged acid, H_4SiO_4 (Fig. 4.3). Wray (1997) has completed an extensive review on solutional weathering in sandstones, and Piccini and Mecchia (2009) have studied the solution weathering rate and the origin of *karst* landforms and caves in quartzites of Venezuela.
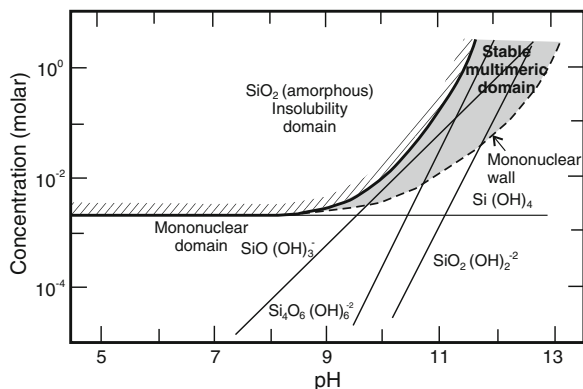
Fig. 4.3 Species in equilibrium with amorphous silica. In natural waters dissolved silica is present as monomeric silicic acid. The line surrounding the shaded area gives the concentration of maximum soluble silica. The mononuclear wall represents the lower concentration limit below which multinuclear silica species are not stable (Stumm and Morgan 1996). Reproduced with permission, John Wiley and Sons
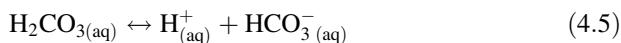
4.2.3 Carbonation

Carbonation is perhaps the Earth's commonest geochemical mechanism and is concerned with the weathering effects of CO_2 in aqueous solution and, particularly, the interaction with $CaCO_3$ that in some parts may give rise to peculiar karstic landscapes. Water in equilibrium with the atmosphere has a pH of ~ 5.6 due to presence of CO_2 but groundwater may be more acidic as the concentration of CO_2 can be 20 to 30 times higher than in the atmosphere due to the production of CO_2 by biological respiration and the resulting higher partial pressure in soil air. Microbes, moss, and fungi are significant producers of CO_2 (see Chap. 3) and plants respire about 40 % of their CO_2 through the root system. In tropical soils, the interstitial air may contain up to 11 % of CO_2 due to the exuberant biological activity.

The following equation is of significant importance in chemical weathering because it produces carbonic acid:

$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_{3(aq)} \tag{4.4}$$
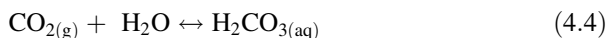
The weak carbonic acid can dissociate further:

$$H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO^-_{3\,(aq)} \tag{4.5}$$

Bicarbonate ion itself dissociates also

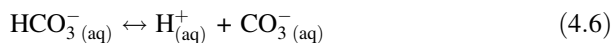$$HCO^-_{3\,(aq)} \leftrightarrow H^+_{(aq)} + CO^-_{3\,(aq)} \tag{4.6}$$

Fig. 4.4 Karstic "cenotes" in the Yucatán Peninsula (Mexico). The term derives from low-land Maya and refers to any location with accessible groundwater. It is a deep natural sinkhole that results from the collapse of limestone bedrock. In the Peninsula's N and NW, cenotes may be up to 100 m deep, with the water flow being more likely dominated by aquifer matrix and fracture flows. Conversely, the cenotes along the Caribbean coast often provide access to extensive underwater cave systems. **a** The so-called "sacred cenote" at the archeological area of Chichen Itzá (Wikimedia Commons). **b** A typical cenote (Chan Sinicché) at Cuzamá, on the eastern side of Yucatán (Wikimedia Commons)

Equations 4.5 and 4.6 clearly show the dependency of the system with the pH of the solution, as Bjerrum plots clearly show (e.g., Drever 1997). Moreover, the corresponding equilibrium constant for the above reactions and a detailed treatment of carbonate chemistry has been also presented by Stumm and Morgan (1996) and by Langmuir (1997).

Limestone is dissolved by water which contains dissolved CO_2 (or carbonic acid) and the reaction becomes:

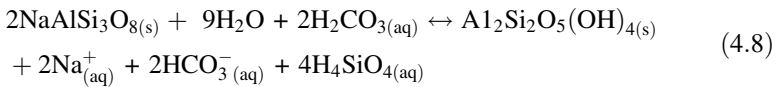$$CaCO_{3(s)} + H_2O + CO_{2(aq)} \leftrightarrow Ca^{2+}_{(aq)} + 2HCO^-_{3\,(aq)} \tag{4.7}$$
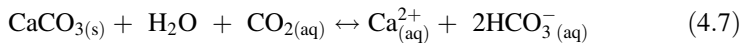
The reaction in Eq. 4.7 explains the formation of caves in calcareous terrains, like the extraordinary *cenotes* of the Mayan peninsula (Fig. 4.4). It is evident that if the equilibrium of Eq. 4.7 is displaced to the left-hand side of the chemical equation, due to Le Chatelier's principle, one mole of CO_2 is returned to the gaseous pool and another may be sequestered as calcite. At any rate, carbonation is a mechanism that exports alkalinity from the continents to the sea. Harmon and Wicks (2006) have brought together many case studies that deal with the geomorphologic, hydrologic, and geochemical aspects associated with carbonation processes.

4.2.4 *Hydrolysis*

Another significant mechanism in chemical weathering is the **hydrolysis** of minerals. It may occur under neutral, acidic, or basic conditions, with compounds in which either cations give rise to weak bases or anions give rise to weak acids, or both the cation and anion give rise to weak bases and acids. The suffix "-olysis" implies the chemical reaction or breaking down of a chemical compound, such as a silicate.

A typical acid hydrolysis, which is closely associated with the carbonation mechanism and which is of enormous significance in continental denudation is the *incongruent dissolution* of sodium feldspar to clay (i.e., kaolinite) by water saturated with CO_2:

$$2NaAlSi_3O_{8(s)} + \ 9H_2O + 2H_2CO_{3(aq)} \leftrightarrow Al_2Si_2O_5(OH)_{4(s)}$$
$$+ \ 2Na^+_{(aq)} + 2HCO^-_{3 \ (aq)} + 4H_4SiO_{4(aq)} \tag{4.8}$$

Gibbs free energy of formation values, which can be found in the literature (e.g., Faure 1998), allow to calculate $\Delta G^0 = 69.1$ kJ for the above reaction. The positive value of ΔG^0 means that the reaction is not energetically favored and, hence, it is not spontaneous. There is ample evidence, however, that it occurs. The corresponding equilibrium constant,

$$\log_{10}K = \Delta G^{\circ}/(2.303RT) = -12.1022 \tag{4.9}$$

R is a constant with the value of $8.314 \ JK^{-1}mol^{-1}$ and T is the temperature in degrees Kelvin; 2.303 is the conversion factor to transform $\ln K$ into $\log_{10} K$.

Therefore,

$$K \ = 7.9 10^{-13} \tag{4.10}$$

The value of K shows that a relatively large quantity of carbonic acid is needed for the reaction to occur. Hence, the scenario that comes into focus is one of an aqueous solutions moving away from the mineral surface under chemical attack and a significant replenish rate of fresh carbonated water coming into contact with the mineral surface, thus sustaining the continuous hydrolysis process. This chemical mechanism plays a key role in the transfer of major dissolved ions via riverine or groundwater pathways to the world's oceans (Meybeck 2005).

Many authors have probed into the significance of silicate hydrolysis in the overall picture of continental chemical weathering, (Fig. 4.5) and there are many examples that can be cited (e.g., Zakharova et al. 2005; Banks and Frengstad 2006; Zakharova et al. 2007; Rajamani et al. 2009) as important contributions to increase the present knowledge. At any rate, White (2005) has completed a valuable in-depth review on the natural weathering of silicate minerals.

Chemical weathering not only supplies major chemical components to the hydrosphere, like cations and anions. They are accompanied by numerous trace elements (i.e., concentrations lower than 1 ppm), which usually also are trace

Fig. 4.5 Dissolution rates of
different minerals as a
function of pH (25 °C). For
data, see Stumm and Morgan
(1996). Reproduced with
permission, John Wiley and
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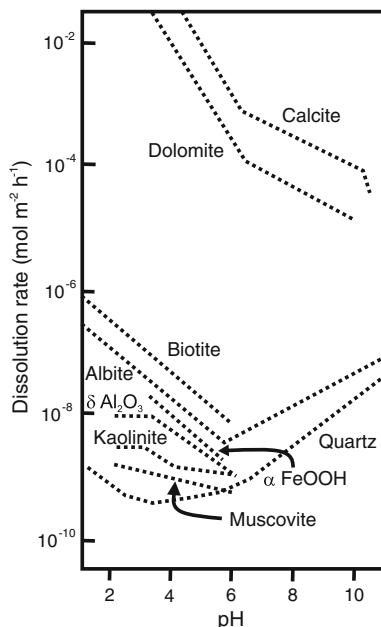
elements in rocks, although there are some exceptions: Fe, Al, and Ti are major
rock components but, due to their low solubility, occur as traces in natural waters
(Gaillardet et al. 2005). Of special interest among trace components are the group
or rare earths (REE), which are freed during weathering but are rapidly adsorbed
onto colloids and thus constitute valuable tracers of the original rock (e.g.,
Elderfield et al. 1990; Sholkovitz 1995) (Fig. 4.6).

4.2.5 Oxidation-Reduction Processes

Redox reactions are common in aqueous solution, whether as weathering reactions
or in the early stages of sediment diagenesis, in the water-mud interface (e.g.,
Potter et al. 2005). Although oxidation and reduction occur jointly, in weathering
processes one product may be more relevant than others, so the following treat-
ment of the subject matter is divided into oxidation (i.e., when oxidized products
are the significant part) and reduction (i.e., when reduced phases are the more
important byproducts). One interesting aspect of this weathering mechanism (it
also happens in early *diagenetic processes*) is that it is often mediated by microbes
(as seen in Chap. 3) and organic debris.

    Oxidation usually occurs with free oxygen (i.e., dissolved in water) as the
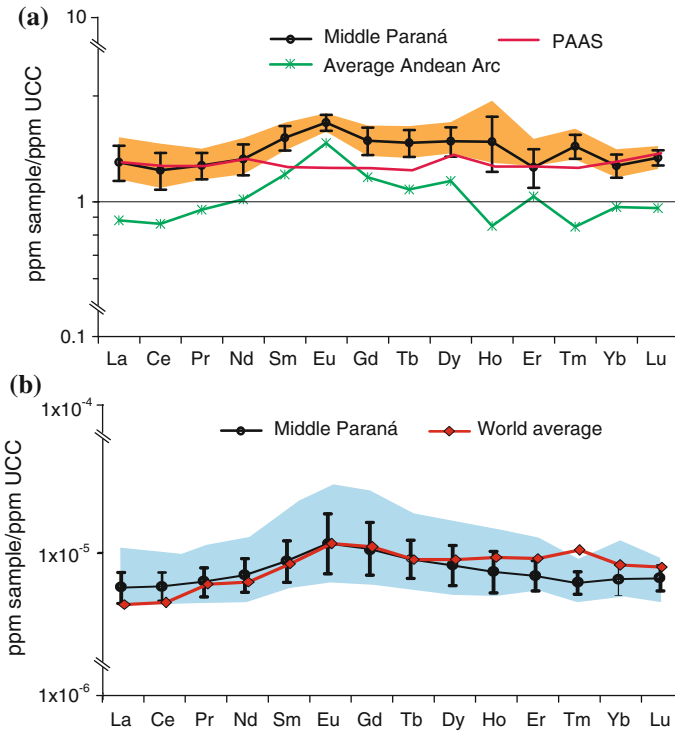oxidizing agent. For example, in the reaction:

Fig. 4.6 Upper continental crust (UCC)-normalized REE spidergrams for Paraná River. **a** Paraná total suspended sediments (shaded area, N = 35, data from Depetris and Pasquini 2007); Post Archean Australian shale (PAAS, Taylor and McLennan 1985); and Average Andean Arc (AAA, http://www.geokem.com/) normalized compositions are included for comparison. Note the pronounced Eu positive anomaly in the Paraná River and in the AAA. **b** Dissolved REE in the middle Paraná River (data from Depetris and Pasquini 2007); world average dissolved REE composition (Gaillardet et al. 2005) is included for comparison. Note that the dissolved fraction preserves the Eu positive anomaly observed in total suspended sediments

$$4FeO_{(s)} + O_{2(g)} \rightarrow 2Fe_2O_{3(s)} \tag{4.11}$$
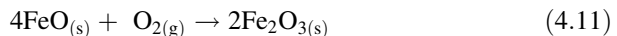
The corresponding value for $\Delta G^0 = -240$ kJ. The associated equilibrium constant for the reaction is $K = 1.08 \times 10^{42}$, thus indicating that the reaction will go practically to completion, as direct observation of rusting iron proves.

Sulfides are common in coal deposits, mineral veins, and mudrocks; for example, the oxidation of Fe(II) and S in pyrite generates sulfuric acid:

$$2FeS_{2(s)} + 7\tfrac{1}{2}O_{2(g)} + 7\ H_2O \rightarrow 2Fe(OH)_{3(s)} + 4H_2SO_{4(aq)} \tag{4.12}$$
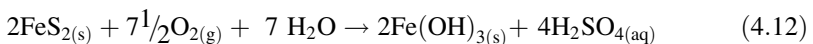
As was presented in Chap. 3, microorganisms play a very significant role and are closely involved in sulfide oxidation. The resulting acidity (e.g., pH may be as low as 1 or 2; according with Norstrom et al. (2000) it may be even negative in

natural environments) enhances the solubility of aluminum and other metals which causes toxicity in aquatic ecosystem. Clearly, this mechanism, when active, promotes mineral dissolution and chemical denudation. Another example of oxidation worth addressing is the one depicted by the reduced iron-bearing fayalite, the iron-rich olivine:

$$Fe_2SiO_{4(s)} + \tfrac{1}{2}O_{2(g)} + 5H_2O \rightarrow 2Fe(OH)_{3(s)} + H_4SiO_{4(aq)} \tag{4.13}$$
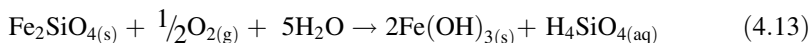
The products of this reaction are silicic acid and colloidal hydrated iron oxide which, after dehydration, yields a variety of iron oxides whose common occurrence reflects their insolubility under the oxidizing Earth surface conditions. Both phases—dissolved and solid—are common participants in global continental denudation.

In weathering processes, **reduction** is less significant than oxidation reactions. It occurs frequently in anaerobic environment-types, such as waterlogged soils whose greenish-grayish color is determined by reduced iron oxides. Organic matter typically operates as a reducing agent in weathering processes. Tissue or organic debris are oxidized to form CO_2, as seen above, or to form new organic compounds. SO_4^{2-} may be reduced by microbes which use the oxygen in the sulfate to oxidize organic material. The resulting sulfide (S^{2-}) can go on to react in various ways. One of them is the reaction that may take place:

$$2H_{(aq)}^+ + S_{(aq)}^{2-} \rightarrow H_2S_{(g)} \tag{4.14}$$

Besides entering the gas pool, sulfide can react with metals to precipitate, for example, FeS or MnS (Fig. 4.7).

In addition to their capability of alternately mobilizing or immobilizing metals associated with naturally occurring aquifer materials, redox processes can also

Fig. 4.7 A comparison between typical anoxic and oxic aqueous environments. T represents turbulence (Potter et al. 2005). Note the location of the sulfate reduction zone in both, anoxic and oxic environments; organic matter is better preserved in saline sulfate rich environments. Reproduced with permission from Springer Science
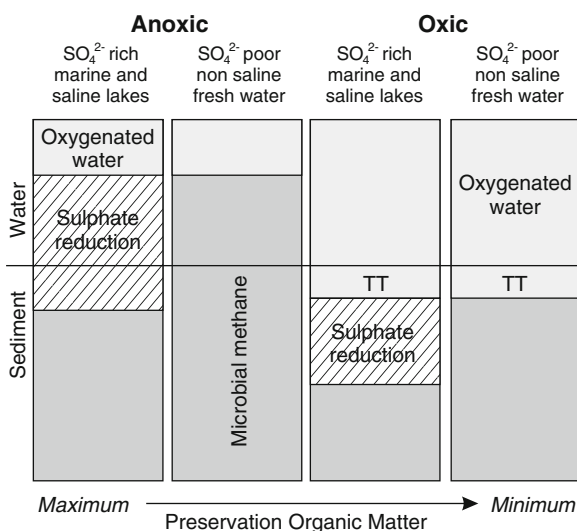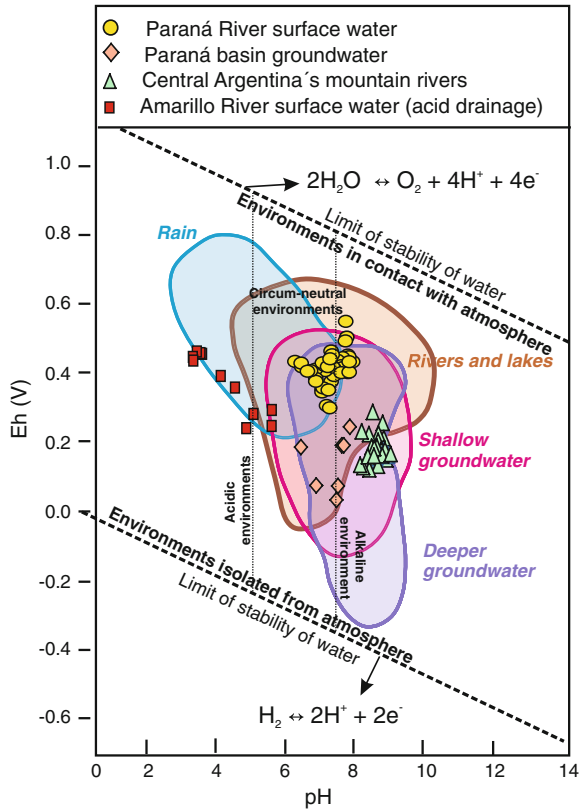
Fig. 4.8 pH-Eh (i.e., a measure of the redox state of a solution) diagram showing the fields for natural waters. Data from different environments have been added for comparison (Pasquini and Depetris 2012 and unpublished sources). The diagram shows the evolution of waters through the cycle as it becomes less oxic and more buffered with respect to pH


affect the chemical quality of ground water contributing to the generation of byproducts such as Fe^{2+}, H_2S, CH_4, and to the preservation or degradation of anthropogenic contaminants (e.g., McMahon and Chapelle 2008) (Fig. 4.8).

4.2.6 Exchangeable Ions

The fine-grained mineral particles that result from the weathering of minerals and rocks are particularly important in supplying a reservoir of exchangeable cations and anions, which may be involved in supplementary weathering processes. These clays (particle size <2 μm) and colloids (particle size <0.2 μm) may be mineral matter or humus and carry many negative charges on their surface, and individual positive exchangeable ions attached to the surface. **Cation exchange** (e.g., H^+, Na^+, Ca^{2+}, Al^{3+}, etc.) is more common than anion exchange (Fig. 4.9).

Applying the mass law to exchange reactions:

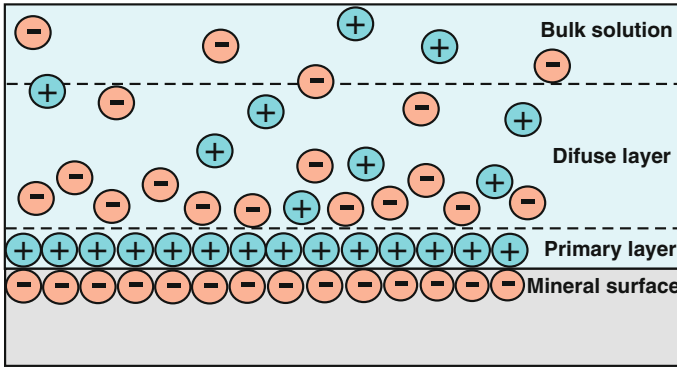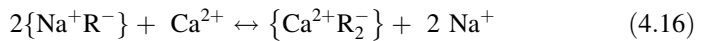$$\{Na^+R^-\} + \ K^+ \leftrightarrow \{K^+R^-\} + \ Na^+ \tag{4.15}$$
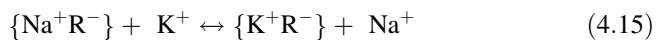
Fig. 4.9 Schematic representation of a diffuse-layer adsorption model showing the association of ions to an exchange surface such as a clay particle

$$2\{Na^+R^-\} + Ca^{2+} \leftrightarrow \{Ca^{2+}R_2^-\} + 2\,Na^+ \tag{4.16}$$

In the previous equations, R^- symbolizes the negatively charged network of the cation exchanger; for most clays the general order of ion affinity (known as the Hofmeister series) is $Cs^+>K^+>Na^+>Li^+$, and $Ba^{2+}>Sr^{2+}>Ca^{2+}>Mg^{2+}$ (Stumm and Morgan 1996).

Different particles (or different soils) have different *cation exchange capacity* (or CEC), which is the concentration of cations in milliequivalents per 100 g of soil or sediment. These adsorbed cations may have an effect on the chemical composition of the soil solution, which in turn may modify weathering processes in the regolith.

Adsorption and desorption processes may be important controlling isotope fractionation in soil profiles, as was shown for Mg isotopes in an extreme weathering scenario, in the basaltic island of Hainan, China (Huang et al. 2012).

Glossary

Cation exchange capacity: Is the maximum quantity of total cations that a soil or sediment is capable of holding, and is available for exchange with the soil solution at a given pH value.

Cenote: Is a deep natural pit, or sinkhole, characteristic of Yucatán (Mexico) that results from the collapse of limestone, exposing the groundwater underneath.

Congruent dissolution: Weathering reaction between a mineral and water that results in its complete dissolution.

Diagenetic processes: Are changes that occur in sediment or sedimentary rocks during and after rock formation (lithification), at temperatures and pressures less than that required for the formation of metamorphic rocks or melting.

Hydrate: A substance that contains water of crystallization or water of hydration, in a definite ratio as an integral part of the crystal.

Incongruent dissolution: Weathering reaction between a mineral and water that results in its partial dissolution and a solid residue.

Karst: Is a geological formation shaped by the dissolution of soluble bedrock, usually carbonate rock but also in gypsum. Given the right conditions it can also occur in weathering-resistant rocks, such as quartzite.

Monomer: Is a molecule that may bind chemically to other molecules to form a polymer.

Playa: Is an ephemeral lakebed, or a remnant of an endorheic lake, consisting of fine-grained sediments infused with alkali salts. Alternative names include dry lake or alkali flat.

Regolith: I Layer of loose, heterogeneous material covering solid rock. It includes dust, soil, broken rock, and other related materials and is present on Earth, the Moon, Mars, some asteroids, and other terrestrial planets and moons

Solubility product: Is a constant (K_{sp}) for a solid substance dissolving in an aqueous solution; represents the level at which a solute dissolves in solution.

References

Alkattan M, Oelkers EH, Dandurand JL et al (1997) Experimental studies of halite dissolution kinetics, 1 the effect of saturation state and the presence of trace metals. Chem Geol 137(3–4):201–219

Anderson SP, von Blackenburg F, White AF (2007) Physical and chemical control on the critical zone. Elements 3:315–319

Banks D, Frengstad B (2006) Evolution of groundwater chemical composition by plagioclase hydrolysis in Norwegian anorthosites. Geochim Cosmochim Acta 70:1337–1355

Benedetti MF, Dia A, Riotte J et al (2003) Chemical weathering of basaltic lava flows undergoing extreme climatic conditions: the water geochemistry record. Chem Geol 201:1–17

Depetris PJ, Pasquini AI (2007) The geochemistry of the Paraná River: an overview. In: Iriondo MH, Paggi JC, Parma MJ (eds) The middle Paraná River: limnology of a subtropical wetland. Springer-Verlag, Berlin

Drever JI (1997) The geochemistry of natural waters. Surface and groundwater environments, 3rd edn. Prentice Hall, Upper Saddle River

Drever JI (2005) (ed) Surface and ground water, weathering, and soils. Elsevier, Amsterdam

Elderfield H, Upstill-Goddard R, Sholkovitz ER (1990) The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. Geochim. Comsmochim Acta 54:971–991

Faure G (1998) Principles and applications of geochemistry, 2nd edn. Prentice Hall, Upper Saddle river

Forti Adolpho MC, Astolfo JMR, Fostier AH (2012) Rainfall chemistry composition in two ecosystems in the northeastern Brazilian Amazon (Amapá State), doi: 10.1029/2000JD900235

Gaillardet J, Dupré B, Allègre CJ (1999) Geochemistry of large river suspended sediments: Silicate weathering or recycling tracer? Geochim Cosmochim Acta 63(23/24):4037–4051

Gaillardet J, Viers J, Dupré B (2005) Trace elements in river waters. In: Drever JI (ed) Surface and ground water, weathering, and soils. Elsevier, Amsterdam

Gavrieli I, Starinsky A, Bein A (1989) The solubility of halite as a function of temperature in the highly saline Dead Sea brine system. Limnol Oceanogr 34(7):1224–1234

Harmon RS, Wicks CM (2006) Perspectives on karst geomorphology, hydrology, and geochemistry: a tribute volume to Derek C. Ford and William B. White. Geological society of America, Boulder

Huang KJ, Teng FZ, Wei GJ et al (2012) Adsorption- and desorption-controlled magnesium isotope fractionation during extreme weathering of basalt in Hainan Island. China. Earth Planet Sc Let. 359–360:73–83

Krauskopf KB (1956) Dissolution and precipitation of silica at low temperatures. Geochim Cosmochim Acta 10:1–26

Krauskopf KB, Bird DK (1995) Introduction to geochemistry, 3rd edn. McGraw-Hill, New York

Langmuir D (1997) Aqueous environmental chemistry. Prentice Hall, Upper Saddle River

Meybeck M (2005) Global occurrence of major elements in rivers. In: Drever JI (ed) Surface and ground water, weathering, and soils. Elsevier, Amsterdam

McMahon PB, Chapelle FH (2008) Redox processes and water quality of selected principal aquifer systems. Ground Water 46(2):259–271

Norstrom DK, Alpers CN, Ptacek CJ, et al. (2000) Negative pH and extremely acidic mine waters from Iron Mountain, California. Environ Sci Technol 34:254–258

Pasquini AI, Depetris PJ (2012) Hydrochemical considerations and heavy metal variability in the middle paraná' river. Environ Earth Sci 65:525–534

Piccini L, Mecchia M (2009) Solution weathering rate and origin of karst landforms and caves in the quartzite of Auyan-tepui (Gran Sabana, Venezuela). Geomorphology 106:15–25

Potter PE, Maynard JB, Depetris PJ (2005) Mud and mudstones. Introduction and overview. Springer, Berlin

Rajamani V, Tripathi JK, Malviya VP (2009) Weathering of lower crustal rocks in the kaveri river catchment, southern India: Implications to sediment geochemistry. Chem Geol 265:410–419

Sholkovitz ER (1995) The aquatic geochemistry of rare earth elements in rivers and estuaries. Aquat Chem 1:1–34

Stallard RF, Edmond JM (1987) Geochemistry of the amazon: 3. Weathering chemistry and limits to dissolved inputs. J Geophys Res 92:8293–8302

Stumm W, Morgan JJ (1996) Aquatic chemistry. Chemical equilibria and rates in natural waters, 3rd ed. Wiley-Interscience, New York

Taylor SR, McLennan SM (1985) The continental crust: its composition and evolution. Blackwell, Oxford

White AF (2005) Natural weathering rates of silicate minerals In: Drever JI (ed) Surface and ground water, weathering, and soils, Elsevier, Amsterdam

White AF, Brantley SL (ed) (1995) Chemical weathering rates of silicate minerals. Reviews in Mineralogy, Vol. 31. Mineralogical Soc. of America, Washington DC

Wray RAL (1997) A global review of solutional weathering forms on quartz sandstones. Earth-Science Rev. 42:137–160

Zakharova EA, Pokrovsky OS, Dupré B et al (2007) Chemical weathering of silicate rocks in Karelia region and Kola Peninsula, NW Russia: Assessing the effect of rock composition, wetlands and vegetation. Chem Geol 242:255–277

Zakharova EA, Pokrovsky OS, Dupré B et al (2005) Chemical weathering of silicate rocks in aldan shield and baikal uplift: insights from long-term seasonal measurements of solute fluxes in rivers. Chem Geol 214:223–248

Zanor GA, Piovano EL, Ariztegui D et al (2013) El registro sedimentario Pleistoceno Tardío-Holoceno de la Salina de Ambargasta (Argentina central): una aproximación paleolimnológica. Revista Mexicana de Ciencias Geológicas 30(2):336–354