



Peter Ryan

# ENVIRONMENTAL AND LOW TEMPERATURE GEOCHEMISTRY



WILEY Blackwell

# CONTENTS

[Cover](#)

[Title page](#)

[Copyright page](#)

[Acknowledgements](#)

[1 Background and Basic Chemical Principles](#)

[1.1 An Overview of Environmental Geochemistry – History, Scope, Questions, Approaches, Challenges for the Future](#)

[1.2 The Naturally Occurring Elements – Origins and Abundances](#)

[1.3 Atoms and Isotopes: A Brief Review](#)

[1.4 Measuring Concentrations](#)

[1.5 Periodic Table](#)

[1.6 Ions, Molecules, Valence, Bonding, Chemical Reactions](#)

[1.7 Acid-Base Equilibria, PH,  \$K\$  Values](#)

[1.8 Fundamentals of Redox Chemistry and Chemical Reactions](#)

[1.9 Chemical Reactions](#)

[1.10 Equilibrium, Thermodynamics and Driving Forces for Reactions: Systems, Gibbs Energies, Enthalpy And Heat Capacity, Entropy, Volume](#)

[1.11 Kinetics and Reaction Rates: Distance from Equilibrium, Activation Energy, Metastability](#)

[Review Questions](#)

[References](#)

[2 Surficial and Environmental Mineralogy](#)



[2.1 Introduction to Minerals and Unit Cells](#)

[2.2 Ion Coordination, Pauling's Rules and Ionic Substitution](#)

[2.3 Silicates](#)

[2.4 Clay Minerals \(T-O Minerals, T-O-T Minerals, Interstratified Clays\)](#)

[2.5 Crystal Chemistry of adsorption and Cation Exchange](#)

[2.6 Low-Temperature Non-Silicate Minerals: Carbonates, Oxides and Hydroxides, Sulfides, Sulfates, Salts](#)

[2.7 Mineral Growth and Dissolution](#)

[2.8 Biomineralization](#)

[Review Questions](#)

[References](#)

### [3 Organic Compounds in the Environment](#)

[3.1 Introduction to Organic Chemistry: Chains and Rings, Single, Double, and Triple Bonds, Functional Groups, Classes of Organic Compounds, Organic Nomenclature](#)

[3.2 Natural Organic Compounds at the Earth Surface](#)

[3.3 Fate and Transport of Organic Pollutants, Controls on Bioavailability, Behavior of Dnaps and Lnaps, Biodegradation, Remediation Schemes](#)

[3.4 Summary](#)

[Questions](#)

[References](#)

### [4 Aqueous Systems – Controls on Water Chemistry](#)

[4.1 Introduction to the Geochemistry of Natural Waters](#)

[4.2 The Structure of Water – Geometry, Polarity and Consequences](#)

[4.3 Dissolved Versus Particulate: Examples of Solutions and Suspensions](#)

[4.4 Speciation: Simple Ions, Polyatomic Ions and Aqueous Complexes](#)

[4.5 Controls on the Solubility of Inorganic Elements and Ions](#)

[4.6 Ion Activities, Ionic Strength, TDS](#)

[4.7 Solubility Products, Saturation](#)

[4.8 Co-Precipitation](#)

[4.9 Behavior of Selected Elements in Aqueous Systems](#)

[4.10 Effect of Adsorption and Ion Exchange on Water Chemistry](#)

[4.11 Other Graphical Representations of Aqueous Systems: Piper and Stiff Diagrams](#)

[4.12 Summary](#)

[Questions](#)

[References](#)

## [5 Carbonate Geochemistry and the Carbon Cycle](#)

[5.1 Carbonate Geochemistry: Inorganic Carbon in the Atmosphere and Hydrosphere](#)

[5.2 The Carbon Cycle](#)

[Questions](#)

[References](#)

## [6 Biogeochemical Cycles – N, P, S](#)

[6.1 The Nitrogen Cycle](#)

[6.2 The Phosphorus Cycle](#)

[6.3 Comparison of N and P](#)



[6.4 The Sulfur Cycle](#)

[6.5 Integrating The C, N, P and S Cycles](#)

[Questions](#)

[References](#)

## [7 The Global Atmosphere](#)

[7.1 Atmospheric Structure, Circulation and Composition](#)

[7.2 Evaporation, Distillation, CO<sub>2</sub> Dissolution and the Composition of Natural Precipitation](#)

[7.3 The Electromagnetic Spectrum, Greenhouse Gases and Climate](#)

[7.4 Greenhouse Gases: Structures, Sources, Sinks and Effects on Climate](#)

[Questions](#)

[References](#)

## [8 Urban and Regional Air Pollution](#)

[8.1 Oxygen and its Impact on Atmospheric Chemistry](#)

[8.2 Free Radicals](#)

[8.3 Sulfur Dioxide](#)

[8.4 Nitrogen Oxides](#)

[8.5 Carbon Monoxide](#)

[8.6 Particulate Matter](#)

[8.7 Lead \(Pb\)](#)

[8.8 Hydrocarbons and Air Quality: Tropospheric Ozone and Photochemical Smog](#)

[8.9 Stratospheric Ozone Chemistry](#)

[8.10 Sulfur and Nitrogen Gases and Acid Deposition](#)

[8.11 Trace Elements In Atmospheric Deposition: Organochlorine Pesticides, Mercury And Other Trace Elements](#)

[Questions](#)

[References](#)

## [9 Chemical Weathering and Soils](#)

[9.1 Primary Minerals, Mineral Instability, Chemical Weathering Mechanisms and Reactions, Soil-Forming Factors, and Products of Chemical Weathering](#)

[9.2 Secondary Minerals, Controls on Their Formation, and Mineral Stability Diagrams](#)

[9.3 Soils and the Geochemistry of Paleoclimate Analysis](#)

[9.4 Effects of Acid Deposition on Soils and Aquatic Ecosystems](#)

[9.5 Soils and Plant Nutrients](#)

[9.6 Saline and Sodic Soils](#)

[9.7 Toxic Metals and Metalloids](#)

[9.8 Organic Soil Pollutants and Remediation \(Fuels, Insecticides, Solvents\)](#)

[Questions](#)

[References](#)

## [10 Stable Isotope Geochemistry](#)

[10.1 Stable Isotopes – Mass Differences and the Concept of Fractionation](#)

[10.2 Delta \( \$\delta\$ \) Notation](#)

[10.3 Fractionation: Vibrational Frequencies, Temperature Dependence](#)

[10.4  \$\delta^{18}\text{O}\$  and  \$\delta\text{D}\$](#)

[10.5  \$\delta^{15}\text{N}\$](#)

[10.6  \$\delta^{13}\text{C}\$](#)

[10.7  \$\delta^{34}\text{S}\$](#)

[10.8 Non-Traditional Stable Isotopes](#)



[10.9 Summary](#)

[Questions](#)

[References](#)

[11 Radioactive and Radiogenic Isotope Geochemistry](#)

[11.1 Radioactive Decay](#)

[11.2 Radionuclides as Tracers in Environmental Geochemistry](#)

[11.3 Radionuclides as Environmental Contaminants](#)

[11.4 Geochronology](#)

[Questions](#)

[References](#)

[Appendix I: Case Study on the Relationship of Volatile Organic Compounds \(VOCs\), Microbial Activity, Redox Reactions, Remediation and Arsenic Mobility in Groundwater](#)

[I.1 Site Information, Contaminant Delineation](#)

[I.2 Remediation Efforts](#)

[I.3 Sources Of Pce And As](#)

[I.4 Mobilization Of Arsenic](#)

[References](#)

[Appendix II: Instrumental Analysis](#)

[II.1 Analysis of Minerals and Crystal Chemistry](#)

[References](#)

[Appendix III: Table of Thermodynamic Data of Selected Species at 1 atm and 25 °C](#)

[Supplemental Images](#)

[Index](#)

[Access the Companion Website](#)

[End User License Agreement](#)

# List of Tables

## Chapter 01

Table 1.1 Chemical differentiation of Earth with major elements and selected trace elements. Major elements ( $\text{SiO}_2$  through  $\text{P}_2\text{O}_5$ ) are presented in units of wt% oxides and the trace elements are presented in concentrations of parts per million (ppm, or mg/kg). Data sources are as follows: granite is the United States Geological Survey granite standard "G-2"; basalt and ultramafic data are averages from Turekian and Wedepohl (1961) and Vinogradov (1962); sandstone and carbonate rock data are unpublished analyses of early Paleozoic sedimentary rocks from northwestern Vermont performed by the author; and shale is the North American Shale Composite (Gromet et al., 1984). Trace element values with asterisks are averages from Turekian and Wedepohl (1961) and Vinogradov (1962). Additional resource include the text *The Continental Crust: Its Composition and Evolution* by Taylor and McLennan (1985) and the chapter by Rudnick and Gao (2003) in *Treatise on Geochemistry*.

Table 1.2 Conversion factors for wt% element to wt% oxide.

Table 1.3 Selected acids and their  $K_a$  values,  $\text{p}K_a$  values and conjugate bases.

## Chapter 02

Table 2.1 Radii of selected major and trace element ions in minerals. For some elements with multiple oxidation states (e.g. Cr, Mn), selected oxidation states that commonly occur in minerals are given. Ions are arranged from lowest charge ( $\text{O}^{-2}$ ) to highest



charge, first for common rock-forming minerals (O through Si), followed by heavy metals plus As, then other useful ions (S through U). Note that coordination number (CN) corresponds to geometry, i.e. CN of 4 produces tetrahedral geometry, CN of 6 produces octahedral geometry, CN of 8 produces cubic or dodecahedral geometry, and CN = 12 results in close-packed (CP) geometry, as explained in the text. Source: (Shannon 1976.)

Table 2.2 Composition of the Earth's crust presented as both wt% element (left) and wt% oxide (right). The difference between the sums listed and 100% reflects the abundance of all other elements.

Table 2.3 Classification of smectites based on octahedral occupancy and origin of 2:1 layers charge (i.e. octahedral vs. tetrahedral sheets).

Table 2.4 Isoelectric points and points of zero charge (PZC) of selected minerals (values = pH) and non-minerals. Note that isoelectric points and PZC values are very similar, but unlike isoelectric points, which are only a function of protonation and deprotonation, PZCs are also controlled by solution chemistry (e.g. adsorption-desorption of metals and other ions). At pH values below the isoelectric point, the mineral is an anion exchanger; above this value, the mineral sorbs cations.

Table 2.5 Cation-exchange capacities of selected minerals (note that oxyhydroxides are anion exchangers at pH values approximately < 7). These values were determined at pH = 7; values vary as a function of pH and aqueous composition. (Sparks 1995; Drever 1997; Langmuir 1997.)

Table 2.6 Hydraulic conductivity ( $K$ ) of selected rocks and sediments (from Heath, 1983). Values are in units of meters per day (m/d).

## Chapter 03

Table 3.1 Prefixes used in IUPAC nomenclature applied to common alkanes.

Table 3.2 Examples of some relatively common functional groups.

Table 3.3 Compositional ranges of some natural organic compounds (by wt%).

Table 3.4 Data on various properties of organic compounds.

## Chapter 04

Table 4.1 Representative values for natural waters (in mg/L) from various reservoirs within the hydrologic cycle. Data are from Livingstone (1963), Holland (1978), Meybeck (1979), Mayo and Loucks (1995), Berner and Berner (1997) and other sources cited therein.

Table 4.2 Half-cell reactions and standard electrode potentials (25 °C, 1 atm) presented from strongest oxidizing agents (top) to weakest oxidizing agents (strongest reducers, bottom).

Table 4.3 Computation of ionic strength from dataset with concentrations in mg/L.

Table 4.4 Ranges of total dissolved solids for different classifications of waters (after Gorrell 1953).

Table 4.5 Examples of solubility products for three lead (Pb) minerals (25 °C, 1 atm).



Table 4.6 Hydration radii relative to ionic radii and charges of selected cations (Volkov et al., 1997).  $R_{\text{ionic}}$  is ionic radius and  $R_{\text{hydr}}$  is hydration radius. Lower ratios of  $R_{\text{hydr}} : \text{chg}$  ( $\text{chg}$  = ionic charge) correspond to stronger adsorption to cation exchange sites.  $\text{H}_3\text{O}^+$  is the hydronium ion form of  $\text{H}^+$ .

Table 4.7 Determination of values plotted on a Stiff diagram (Fig. 4.22).

## Chapter 05

Table 5.1 Equilibrium reactions and constants for the carbonate system in fresh water at 10 °C ( $K_{10}$ ) and 25 °C ( $K_{25}$ ). Note that (cc) refers to calcite (rather than  $\text{CaCO}_3$  polymorphs aragonite or vaterite).

Table 5.2 Equilibrium constants of common carbonate minerals at 20 °C and 1 atm. (Morse et al. 2007 and sources cited therein).

Table 5.3 The abundance of carbon in major reservoirs globally.

Table 5.4 Changing fluxes of carbon among the main reservoirs for 3 time periods. In Table 5.4, negative values indicate that combustion of fossil fuel, production of cement and land-use practices (e.g. deforestation) are causing loss of C from those three reservoirs; reforestation and other changes to land are also a sink for C, and the net change in C in the terrestrial reservoir (mainly biota and soil) is the “terrestrial mass balance” - from 1980-2010, the terrestrial reservoir has experienced a net gain in C. So too has the ocean reservoir and the atmosphere. Table 5.4b depicts gross transfer of C from the lithosphere (FF/cem = fossil fuels and cement) and land-use change (LUC) to the atmosphere. Total C

removed from the atmosphere is “Net sinks”. Also shown are percentages of fossil fuel and cement-derived C that remains in the atmosphere (increasing from 1960–2010), the amount of C sourced from fossils fuels and cement sequestered in the ocean (decreasing from 1960–2010), and total fossils fuels and cement sequestered (oceans + land; also decreasing with time).Table 5.4a Fluxes of carbon (Pg/yr). Negative values indicate reservoirs that are losing C.

## Chapter 06

Table 6.1 Some common nitrogen species and the oxidation state of nitrogen in the compounds.

Table 6.2 Examples of sulfur species and the oxidation states of sulfur in these compounds, presented from most-reduced,  $S^{-2}$ -bearing species to the most-oxidized, sulfate-bearing species.

## Chapter 07

Table 7.1 Concentrations of selected fixed gases in the atmosphere (sea level). Data are from Spiro and Stigliani (2006) and the Global Monitoring Division of the National Oceanic and Atmospheric Administration (USA) data on greenhouse gases. Data from Earth System Research Laboratory of US National Oceanic and Atmospheric Administration (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>).

Table 7.2 Selected properties of greenhouse gases. Data are from Oak Ridge National lab ([http://cdiac.ornl.gov/pns/current\\_ghg.html](http://cdiac.ornl.gov/pns/current_ghg.html)) and Forster et al. (2007).

## Chapter 08

Table 8.1 Ambient Air Quality Standards According to the US Environmental Protection Agency (EPA) and the EU European Commission (EC).

## Chapter 09

Table 9.1 Weathering rates of common rock-forming minerals assuming hypothetical 1-mm sphere of each mineral in a dilute solution of pH = 5. Data compiled from Chou et al. (1989), Lasaga et al. (1994), Drever (1997), Brantley (2005), Buss et al. (2008) and numerous sources cited therein. Variation in rates between time (yr) versus dissolution rate and log dissolution rate reflects different approaches to measuring rates. See Brantley (2005) for details. The composition of hornblende is  $(\text{K}, \text{Na})_{0-1}(\text{Ca}, \text{Na}, \text{Fe}, \text{Mg})_2(\text{Mg}, \text{Fe}, \text{Al})_5(\text{Si}, \text{Al})_8\text{O}_{22}(\text{OH})_2$ .

Table 9.2 Geochemical changes in a soil sequence where 10 ka and 125 ka terrace soils are derived from parent material (PM) comprised of river sediments dominated by basaltic and andesitic volcanic detritus intermixed with soil minerals derived from erosion further upstream. Data are obtained from B horizons of soils along the central Pacific coast of Costa Rica (Fisher and Ryan, 2006; Ryan and Huertas, 2009). All values for PM, 10 ka and 125 ka (except for Zr [ppm]) are presented as wt.% element or mineral. The two columns on the right are explained in the text. The mass-transfer coefficient does not apply to minerals.

Table 9.3 Thermodynamic data used in development of the mineral stability diagram in Fig. 9.9. Data are from Dean (1979) and Robie et al. (1979). Given uncertainty in Gibbs free energy values, precision is shown to only 1 decimal place. See Appendix III for a more-extensive table of thermodynamic data.

Table 9.4 Examples of nutrient concentrations in grasses (e.g. alfalfa, clover, ryegrass), apple leaves, pine needles and tomato leaves. Data obtained from Brady and Weil (2002) and the University of Arkansas Cooperative Extension Service ([http://www.uaex.edu/Other\\_Areas/publications/pdf/FSA-3043.pdf](http://www.uaex.edu/Other_Areas/publications/pdf/FSA-3043.pdf)), and various other sources. Typical values for carbon, hydrogen and oxygen in bulk plant tissue are: C = 40-50%, H = ~5% and O = 40-50%.

Table 9.5 Plant nutrients, their common forms and sources. For each of the macronutrients, decomposing organic matter is also a source.

## Chapter 10

Table 10.1 Examples of stable isotope combinations in water and carbon dioxide.

Table 10.2 Stable isotopes, abundances (relative %), differences in mass (relative %), delta notations and ratios of standard values of a representative (but not complete) list of the stable isotopes applied in environmental geochemistry.

## Chapter 11

Table 11.1 Decay mechanisms, half-lives and energies for numerous radionuclides.

# List of Illustrations

## Chapter 01

Figure 1.1 Abundance of elements in the solar system normalized to Si =  $10^6$  on a logarithmic y-axis – this is a standard means of normalizing and plotting values for this type of data set.

Figure 1.2 Schematic sketches of Bohr models of a carbon atom ( $^{12}\text{C}$ ) showing, on the left, 6 protons and 6 neutrons in the nucleus with 6 electrons in 2 separate orbitals, and on the right, an atom that attempts to show the actual size of the nucleus compared to the electron cloud, yet even here the nucleus is  $\sim 100$  times larger than an actual nucleus. The example on the right also introduces the idea of separate orbitals in the outer electron “shell”.

Figure 1.3 Lewis electron dot diagrams showing valence electrons of sodium and oxygen in their ground states (left) and in the compound  $\text{Na}_2\text{O}$  (right), where each sodium has lost an electron to oxygen, resulting in two  $\text{Na}^+$  and one  $\text{O}^{2-}$ .

Figure 1.4 Road sign in southwestern Ecuador.

Figure 1.5 Solubilities of ions as a function of ionic charge, from Inset 4 of *An Earth Scientist's Periodic Table of the Elements and Their Ions* (Railsback, 2003). Oxides of the elements are used as reference (e.g. lime, periclase, etc.). Note that low-charge base cations/alkali metals and cations of the alkaline Earth metals are relatively soluble, as are high-charge cations such as  $\text{S}^{+6}$  and  $\text{N}^{+5}$ , which form polyatomic anions (,). Cations with +3 and +4 charges (e.g.  $\text{Al}^{+3}$ ,  $\text{Ti}^{+4}$ ,  $\text{Zr}^{+4}$ ) are insoluble in most surficial environments, with activities in  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$  of  $\sim 10^{-8}$  to  $10^{-10}$ . (Railsback 2003.)

Figure 1.6 Schematic representation of formation of an ionic bond by transfer of the Na valence electron to Cl.

Figure 1.7 Lewis electron dot diagram of an oxygen molecule ( $\text{O}_2$ ) shown using two different notations.



Note double bond between oxygen atoms consisting of two electron pairs depicted by the double dashed lines in the lower example.

Figure 1.8 Electronegativity of elements based on Linus Pauling's early 20<sup>th</sup>-century research.

Figure 1.9 Plot of relationship between difference in electronegativity of two atoms in a bond and the percent ionic character of the bond. Note that no bond is 100% ionic; however, diatomic gases (e.g. N<sub>2</sub>, Cl<sub>2</sub>, O<sub>2</sub>) and the C-C bonds in diamond are 100% covalent.. Based on early and middle 20<sup>th</sup>-century work of Linus Pauling and more recent research by Lu et al. (2006).

Figure 1.10 Diagram of three water molecules showing polarity of the water molecule ( $\delta^+$ ,  $\delta^-$ ) as well as hydrogen bonds (dashed lines) between H and O in adjacent molecules.

Figure 1.11 Van der Waals bonds between adjacent atoms. A and B represent nuclei of adjacent atoms and dots are electrons. In the example on the left, electron clouds are shifted to the left, causing attraction of the atoms. In the example on the right, electron clouds are shifted to the right, also enhancing attraction of the atoms. If this type of alternating motion is synchronized, the atoms will be weakly attracted.

Figure 1.12 Typical progression of a geochemical system towards equilibrium. A high degree of disequilibrium in the early stages causes rapid rates of change, but as the system approaches equilibrium, rates decrease logarithmically.

Figure 1.13 Phase diagram for H<sub>2</sub>O depicting one component (H<sub>2</sub>O) and three phases (solid, liquid and gaseous water).

Figure 1.14 Schematic diagram illustrating relative stability conditions, from unstable at points A and C, to metastable at point B and stable at point D. Note that the metastable point B can be reached from points A or C, and that to shift from metastable (B) to stable (D), some energy must be introduced. If not, the metastable condition may persist for a long time.

Figure 1.15 Arrhenius plots showing relationship between equilibrium constant ( $K$ ) and temperature for endothermic and exothermic reactions. For endothermic reactions, increasing temperature increases  $K$ , i.e. adding heat increases reaction rate; for exothermic reactions, the opposite is true.

Figure 1.16 Two graphical representations of zeroth (0<sup>th</sup>)-order chemical reactions, where  $[A]$  represents concentration of a chemical species (e.g. ion, mineral or compound). In the example on the left, decrease in concentration of A is linear, and on the right, the rate of change is constant.

Figure 1.17 Two graphical representations of first (1<sup>st</sup>)-order chemical reactions, where  $[A]$  represents concentration of a chemical species. On the left, change in concentration of A is logarithmic (solid line) or exponential (dashed line); on the right, for both cases (increasing or decreasing concentration), rate of change decreases in a linear fashion with time. Arrows in diagrams indicate direction of forward reaction (emphasizing that, on the right, the solid line represents decreasing  $[A]$  with time).

Figure 1.18 Two graphical representations of second (2<sup>nd</sup>)-order chemical reactions, where [A] represents concentration of a chemical species. In the example on the left, [A] decreases exponentially, and on the right, we see that rate of change decreases exponentially with time.

Figure 1.19 Effect of temperature on chemical weathering rate of rhyolite as a function of temperature. (Yokoyama and Banfield 2002. Reproduced with permission of Elsevier.)

## Chapter 02

Figure 2.1 Sketches of halite (NaCl), with a 2-dimensional example on the left and a 3-dimensional example on the right. Note the relative sizes of cations (Na<sup>+</sup> in this case) compared to anions (Cl<sup>-</sup> in this case) as well as the ordered crystalline lattice structure.

Figure 2.2 Schematic two-dimensional sketch of a unit cell of halite. Small spheres (circles) are Na<sup>+</sup> and large ones are Cl<sup>-</sup>.

Figure 2.3 Sketch of cations in three-fold (trigonal, on left) and six-fold (octahedral, on right) coordination. The cation in each case is represented by the small black circle with a white center representing the nucleus, and the anions (oxygen in most minerals) are the large white circles (not to scale). The dashed circle in the sketch on the right represents one anion above the plane of the four anions, as well as one anion below the plane of the four anions.

Figure 2.4 Examples of geometric arrangement of cations and anions in minerals (or gases, e.g. CO<sub>2</sub>), showing range of radius ratio (ratio of ionic radius of cation : anion) for each configuration.

Figure 2.5 Halite showing coordination of six  $\text{Cl}^-$  ions around a central  $\text{Na}^+$  ion.

Figure 2.6 Trigonal coordination of three oxygen atoms ( $\text{O}^{2-}$ ) around a central carbon ( $\text{C}^{+4}$ ) atom.

Figure 2.7 Two potential arrangements of adjacent tetrahedra with cations (e.g.  $\text{Si}^{+4}$ ) as black spheres and anions (e.g.  $\text{O}^{2-}$ ) as gray spheres. Note that the arrangement on the left produces a greater distance between cations ( $3.2 \text{ \AA}$ ) compared to the arrangement on the right ( $1.2 \text{ \AA}$ ), so Pauling's Rule #3 indicates that the structure on the left is more stable.

Figure 2.8 Representations of the silica tetrahedron (). The three basal oxygen atoms are shaded gray, the apical oxygen is clear, and the silicon atom is black. The view of the example on the right is from above, looking down at the apical oxygen with three basal oxygens below (hidden Si atom is represented by dashed circle).

Figure 2.9 Schematic representation of the silica tetrahedron.

Figure 2.10 Sketch of an olivine crystal showing isolated silica tetrahedra (triangles) as well as atoms of Mg or Fe represented by black and gray circles. Dotted line indicates parameters of an olivine unit cell.

Figure 2.11 Sketch of pyroxene group structure. Note linked silica tetrahedra that form chain structures, and occurrence of cations (e.g.  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Na}^+$ ) in interstices.

Figure 2.12 Sketch of amphibole group structure. Note cross-linked chains of silica tetrahedra and

occurrence of cations (e.g.  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Na}^{+}$ ) in interstices. Larger sites mainly hold  $\text{Na}^{+}$  or  $\text{Ca}^{+2}$  whereas smaller sites hold  $\text{Al}^{+3}$  or  $\text{Mg}^{+2}$ .

Figure 2.13 Morphology of asbestiform amphibole (US Geological Survey Microbeam Lab; <http://usgsprobe.cr.usgs.gov/picts2.html>).

Figure 2.14 Arrangement of silica tetrahedra in phyllosilicates, showing laterally extensive development of sheet-like structures. This diagram shows a top-down view onto a tetrahedral sheet of a phyllosilicate.

Figure 2.15 Sketches of octahedral coordination of anions (typically  $\text{O}^{-2}$  or  $\text{OH}^{-}$ ) around a cation (black). Anions are gray and white to allow the viewer to correlate the basal plane (gray spheres) to the upper plane (white spheres).

Figure 2.16 Two representations of a mica, both showing tetrahedral and octahedral sheets as well as interlayer potassium. (Adapted from Moore and Reynolds 1997.)

Figure 2.17 Schematic of pyrophyllite (left) and talc (right). Note (a) substitution of 3 Mg (talc) for 2 Al (pyrophyllite) in octahedral sheet, and (b) absence of interlayer cations in both.

Figure 2.18 Schematic sketches of mica and pyrophyllite. Note effect of presence/absence of interlayer potassium on the thickness of the unit cells in the  $c$  direction.

Figure 2.19 Chlorite (left) and a 1:1 phyllosilicate (e.g. serpentine or kaolinite). Note that the interlayer in chlorite is an octahedral sheet, and that both chlorite and 1:1 phyllosilicates consist of alternating



octahedral and tetrahedral sheets, the difference being the orientation of every other tetrahedral sheet.

Figure 2.20 The two ways that serpentines deal with the “mismatch problem”. On the left, the slightly larger octahedral sheet in chrysotile is draped over the curved tetrahedral sheet, ultimately forming rolled fibers. In antigorite (on the right), the mismatch is solved by short-period alternations (often of ~17 tetrahedra in length) of tetrahedral and octahedral sheets.

Figure 2.21 Rolled tetrahedral and octahedral sheets viewed down long axis of chrysotile from a transmission electron microscope image(A) (Yada 1971. Reproduced with permission from IUCR.) and fibrous white chrysotile on a serpentine rock surface(B).

Figure 2.22 Sketch of potassium feldspar showing potassium ions and silica tetrahedra. Gray triangles represent silica tetrahedral whose apices point away from the viewer. Note also that  $\frac{1}{4}$  of tetrahedral sites are occupied by Al.

Figure 2.23 Two smectite 2:1 layers with hydrated cations (black spheres) occupying the interlayer site. Layer charge on each of the 2:1 layers (T-O-T) is  $-0.2$  to  $-0.5$  and this negative charge attracts cations to the interlayer. Variability in c-axis spacing is due to ability to intercalate different amounts of interlayer water (where the water is bonded to cations).

Figure 2.24 The transition from smectite to illite via interstratified illite/smectite, including the ordered I/S phase rectorite, a mineral in which illite and

smectite layers alternate in an ordered manner. In sedimentary basins, this transition typically takes place progressively with increasing burial over the temperature range of 50 °C to 200 °C.

Figure 2.25 Schematic representation of the differences in cation exchange between kaolinite and smectite. "LC" indicates layer charge, which is zero in kaolinite but is  $-0.2$  to  $-0.5$  per unit cell in smectite. CEC of smectites is also enhanced by expandable interlayer spaces and smaller crystal size (not shown here).

Figure 2.26 Sketch of a goethite surface in solutions at pH = 5 (left) and pH = 9 (right), demonstrating the effect of IEP or PZC on ion-exchange capabilities of soil solids. Note the occurrence of anionic arsenate as inner sphere complex at pH = 5 (facilitated by  $H^+$ ) compared to the occurrence of  $Ca^{+2}$  as an inner sphere complex at pH = 9. Negative signs near the goethite surface indicate a net negative charge at the mineral surface.

Figure 2.27 Molecule of calcite. Note rhombohedral structure that is also expressed in macroscopic crystals. Lines between oxygen atoms are used to indicate individual molecules within the mineral structure.

Figure 2.28 Schematic diagram of sulfate (left) and sulfide (right) anions, with S ions drawn to scale (the radius of  $S^{-2}$  is approximately six times greater than  $S^{+6}$  in tetrahedral coordination).

Figure 2.29 Salts on dessicated shoreline of Salt Creek, Death Valley, USA. The white crusty coating is halite and other soluble salts precipitated at the surface when evaporation caused solute

concentrations to rise above the saturation point. Dessication polygons are ~ 0.5 m in diameter. Source: (Courtesy of the US Geological Survey.)

Figure 2.30 Schematic representation of diffusion across the semi-permeable boundary between a clay-rich layer (upper) and sandy layer (lower). The pronounced difference in concentration of the two species across the boundary drives diffusion over time, from “Early” to “Later” (this system has not reached dynamic equilibrium). Loss of arsenate from the upper layer could drive further dissolution or desorption of the As-bearing minerals. According to Fick’s Law, as time passes in this example, the rate of diffusion will decrease as the chemical gradient decreases. Also, note the charge balance, where two monovalent arsenate ions exchange for each divalent carbonate ion.

Figure 2.31 Biogenic calcite (left, formed by an echinoderm) and inorganically precipitated calcite (right). (Weiner and Dove 2003. Reproduced with permission of the Mineralogical Society of America.)

## Chapter 03

Fig. 3.1 Hybridization of carbon atoms, with ethane, ethene (ethylene), and ethyne (acetylene) shown as examples of compounds containing the different hybridizations.

Fig. 3.2 Structural formula of octane.

Fig. 3.3 Melting point (MP) and boiling point (BP) both increase with increasing length of alkane chain. LPG = liquid petroleum gas. Methane would plot as “1” on the x-axis, octane would plot as “8”, and so on.

Fig. 3.4 Structural formulas for two common chlorofluorocarbons.

Fig. 3.5 Structural formula for cyclohexane (left) and the hexagon that is the commonly used symbol for cyclohexane.

Fig. 3.6 Common ethenes.

Fig. 3.7 Examples of two functional groups attached to an ethane chain. Ethanol contains a hydroxyl group (OH-) in place of a hydrogen atom. Acetic acid contains a carboxylic acid functional group (COOH-).

Fig. 3.8 Representations of benzene rings. A and B indicate alternation of sigma and pi bonds. At one instant in time, the double bonds are located as is shown in example A; the next instant in time they switch to the configuration in example B. This rapid alternation that characterizes the delocalized single and double bonds in aromatic hydrocarbons. C is the commonly used, pared-down structural formula for benzene, and a more-detailed structural formula is presented in D.

Fig. 3.9 Structural formulas of naphthalene and benzo(a)pyrene.

Fig. 3.10 Structural formulas for toluene, the three isomers of xylene, and ethylbenzene. Composition, abundance and positioning of functional groups distinguish these compounds.

Fig. 3.11 Structural formulas of phenol (C<sub>6</sub>H<sub>5</sub>OH) and pentachlorophenol (C<sub>6</sub>Cl<sub>5</sub>OH).

Fig. 3.12 Structural formula of the compound variably known as dichloro-diphenyl-trichloroethane (DDT) and 4,4'-(2,2,2-trichloroethane-1,1-diyl)bis(chlorobenzene).

Fig. 3.13 Structural formula of the class of compounds known as Polychlorinated biphenyls

(PCBs). The numbered sites on the left correspond to potential bonding sites of functional groups (in PCBs, mainly H or Cl, sometimes OH). The example on the right is 3,3',5,5'-tetrachlorobiphenyl.

Fig. 3.14 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), a member of the dioxins. Sites labelled with 1, 4, 6 and 9 are occupied by H.

Fig. 3.15 Structural formula of 2,4-dichloroethylene. Note the carboxyl (COOH) functional group in the upper right of the diagram and two Cl functional groups.

Fig. 3.16 Structural formula of glyphosate, known as N-(phosphonomethyl) glycine in IUPAC nomenclature. Note carboxyl group (far left), amine group (center), and phosphate (far right).

Fig. 3.17 Structural formula of malathion, which is known as O,O-dimethyl dithiophosphate or diethyl mercaptosuccinate in IUPAC nomenclature. Note the numerous functional groups, including methyl (CH<sub>3</sub>), phosphate with sulfide in place of an O atom (thiophosphate), and esters (region with O double bonded to C-O).

Fig. 3.18 Methyl tert-butyl ether (MTBE), or 2-Methoxy-2-methylpropane according to IUPAC nomenclature.

Fig. 3.19 Top = structural formulas of bisphenol-A (top), known as BPA and also as 4,4'-(propane-2,2-diyl)diphenol in IUPAC nomenclature. Bottom = structural formula of estradiol, also known in IUPAC nomenclature as (17 $\beta$ )-estra-1,3,5(10)-triene-3,17-diol.

Fig. 3.20 Plot of  $\log(K_{OW})$  against  $\log$  (bioconcentration factor, BCF), showing trend for a range of organic compounds in middle trophic level species (BCF generally increases with trophic level). Note the linear relationship for most of the plot (decreasing solubility in water = increased BCF), and the curious dip at high values of  $K_{OW}$ . Created from data in Banerjee and Baughman (1991) and Arnot and Gobas (2006).

Fig. 3.21 Correlation between the solubility in water (presented as  $\log S^w$ , the aqueous solubility) and octanol-water coefficient (presented as  $\log K_{OW}$ ) of organic compounds. Low-solubility compounds such as DDT and PCBs plot in the upper left of the line and relatively soluble compounds such as benzene, PCE and 2,4-D plot in the lower right of the line. (Data from Chiou et al. 1977, 2005.)

Fig. 3.22 Formation of 2,4-D anion by deprotonation. The resulting anion may be sorbed to anion exchange sites.

Fig. 3.23 Isotherms describing chemisorptions (left) and physisorption (right) of organic compounds.

Fig. 3.24 Schematic diagram of behavior of NAPLs in the subsurface. Shown are two leaking underground storage tanks (USTs). Triangles indicate water table. The scale of the diagram does not permit depiction of sorption in the soil (refer to Chapter 9, Section 9.8).

Fig. 3.25 Decomposition of trichloroethylene (TCE) to the metabolite DCE, then to the metabolite vinyl chloride, under (most likely) microbially mediated reducing conditions and. Decomposition of vinyl chloride to the metabolite chloroethylene oxide tends to occur rapidly via microbial mediation in aerobic



(oxidizing) waters but very slowly in anaerobic waters, and thus may persist in groundwater for years or decades.

## Chapter 04

Fig 4.1 Hydrologic cycle with volumes of reservoirs given in units of  $\text{km}^3$  and *fluxes* shown in units of  $\text{km}^3/\text{year}$ . Surface water as shown above refers to fresh water on the continents, and the overwhelming majority of this reservoir is accounted for in a few large lakes. Also, less than one-half of groundwater is accessible for use by humans; some is too deep and salty. (Modified from Winter et al. 1998.)

Fig 4.2 The white deposits surrounding the shallow pond in the foreground are evaporite salts that crystallized because evaporation of spring water raised dissolved ion concentrations to saturation. Evaporite minerals in this area include halite, gypsum, calcite and borax. Death Valley, USA. (Courtesy of the US Geological Survey.)

Fig 4.3 Sketch showing, from top to bottom, the vadose zone (unsaturated zone), which includes soil and any sediment or rock above the water table) and the shallow part of an aquifer (the saturated zone). Connections between groundwater and surface water are also shown by arrows indicating, typical groundwater flow paths. Relative total dissolved solids (TDS) of precipitation, soil water, groundwater and surface water for a temperate region are shown.

Fig 4.4 Changes in the ratio of  $\text{Na}/(\text{Na} + \text{Ca})$ , based on units of mass (e.g.  $\text{mg/L}$ ), plotted against total dissolved solids (TDS, in  $\text{mg/L}$ ), for streams from different climate zones, and also for seas and oceans. Arrows indicate changes in stream composition that

occur progressively downstream; for example, with increasing contributions from chemical weathering, tropical soils increase in TDS and the Na/(Na + Ca) ratio decreases. (Modified from Gibbs 1970 and Andrews et al. 2004.)

Fig 4.5 The structure of the H<sub>2</sub>O molecule. (A) emphasizes the tetrahedral nature of the molecule, and (B) and (C) show the structure and dipolar nature in two dimensions.

Fig 4.6 Schematic sketch of the relationship of polar water molecules to a sodium cation (above) and chloride anion (below) in solution.

Fig 4.7 Hydrogen bonds (dashed lines) between adjacent water molecules.

Fig 4.8 Decreasing rate of dissolution of a mineral (e.g. sodium feldspar) in a closed system as measured by the concentration of a dissolved constituent (e.g. Na<sup>±</sup>) released during dissolution. Note that concentration in solution increases until the solution reaches saturation, at which time the system reaches dynamic equilibrium. In an open system, leaching of Na<sup>±</sup> would likely prevent attainment of dynamic equilibrium. In terms of residence time, the concentrations of dissolved constituents will increase with time in this type of example.

Fig 4.9 Prediction of solubility of aqueous ions based on the ratio of ionic charge ( $z$ ) to ionic radius ( $r$ , in Å), a ratio known as ionic potential. In the case of polyatomic molecules (e.g. H<sub>4</sub>SiO<sub>4</sub>), radius ( $r$ ) is for the elemental ion shown (e.g. Si<sup>+4</sup>), not for the entire molecule. The  $z$  values on both upper and lower  $x$ -axes are absolute values, and the  $y$ -axis data are based on concentrations in river water determined by

Martin and Whitfield (1983); the plot shown is based on a graph in Andrews et al. (2004).

Fig 4.10 Solid curve is sum of all dissolved Al species and dashed lines correspond to Al species indicated. Note low solubility of Al between pH = 6 to 7 and exponential increase in solubility with decreasing or increasing pH.

Fig 4.11 Structural formula of ethylenediaminetetraacetate (EDTA) molecule, a good example of a chelating compound.

Fig 4.12 Approximate locations of selected natural systems as a function of reduction-oxidation potential and pH. Note that redox units are given in terms of Eh (left) and pe. The thin line bounding the natural environments indicates the limits of nearly all natural waters (after Bass Becking et al. 1960).

Fig 4.13 Copper and lead Eh-pH diagrams at 25 °C and 1 atm pressure. Activities of Cu and Pb are  $10^{-6}$  mol/L,  $p\text{CO}_2 = 400$  ppmv ( $10^{-3.4}$  atm) and total S =  $10^{-2}$  mol/L.

Fig 4.14 Arsenic and uranium Eh-pH diagrams for systems at 25 °C and 1 atm pressure. For the arsenic diagram, activity of  $\text{As}_{\text{total}} = 10^{-6}$  and S activity =  $10^{-2}$  mol/L. For the uranium diagram, activity of U =  $10^{-8}$  mol/L and C (as  $\text{CO}_2$ ) is  $10^{-3.4}$  atm.

Fig 4.15 Eh-pH diagram for iron and aluminum. For the iron diagram, activity of Fe =  $10^{-6}$  mol/L, S =  $10^{-2}$  mol/L and  $\text{CO}_2 = 10^{-3.4}$  atm. For aluminum diagram, Al =  $10^{-9}$  mol/L. Note that iron speciation is influenced by both Eh and pH; conversely, aluminum speciation is controlled by pH but not Eh. The arrow from A to B represents oxidation as shown in Plate 5.

Fig 4.16 Solubility of silica as a function of pH in equilibrium with amorphous silica and with quartz. Note that if amorphous silica is the solid phase in equilibrium with silica, dissolved silica concentrations are approximately an order of magnitude greater than when quartz controls silica solubility.

Fig 4.17 Adsorption of metal cations onto ferrihydrite as a function of pH. Data are from Dzombak and Morel (1990) except for uranyl, which is from Hsi and Langmuir (1985). The curvature in the adsorption edges indicate that, at low pH, adsorption is relatively weak; with increasing pH, cations are more-strongly adsorbed. For example, at pH = 4,  $\text{Cu}^{+2}$  is weakly adsorbed (i.e. only a small proportion of  $\text{Cu}^{+2}$  ions in solution will be adsorbed at pH = 4), but at pH = 5.5, nearly all  $\text{Cu}^{+2}$  in solution will be adsorbed onto ferrihydrite. The boundary between pH 4 and 5.5 is the adsorption edge for  $\text{Cu}^{+2}$ .

Fig 4.18 Adsorption of the polyatomic anions selenate, sulfate, chromate, arsenite () and arsenate () onto ferrihydrite as a function of pH. Data are from Dzombak and Morel (1990). Note that for all anions shown but arsenite, the shape of the curve is the inverse of the curves for metal cations shown in Fig. 4.19, reflecting the fact that, as pH decreases, surfaces of ferrihydrite become progressively more occupied by  $\text{H}^+$ , creating positive surface charge needed for adsorption of anions. Thus, adsorption increases to the left of this diagram. Although not shown, decreasing pH causes protonation of the anions (e.g. toto, toto, etc.).

Fig 4.19 Adsorption isotherms. A = linear isotherm, B = Langmuir isotherm and C = Freundlich isotherm. The x-axis is activity of sorbate (e.g. ion) and y-axis is