

Chapter 1: The Nature of Water

Water, H_2O , is a molecule of most unusual characteristics. Its stability as a liquid over a wide temperature range permits it a vital role in a host of processes from the formation of ore deposits to the basis of life on Earth. The high heat capacity of water, coupled with its enthalpy of vaporization, drives the global redistribution of heat that in turn drives climate. Crystallized, it has a remarkable open-tetrahedral framework that is less dense than liquid water, such that ice floats — playing a key seasonal role in aquatic habitat and albedo. In geochemistry and biology, it is its capacity to dissolve solids and transport solutes that makes H_2O so remarkable.

Water's asymmetrical charge distribution is central to its unique properties. The two hydrogen atoms and single oxygen atom share four tetrahedrally oriented electron orbitals, which give rise to a dipolar configuration (Fig. 1-1).

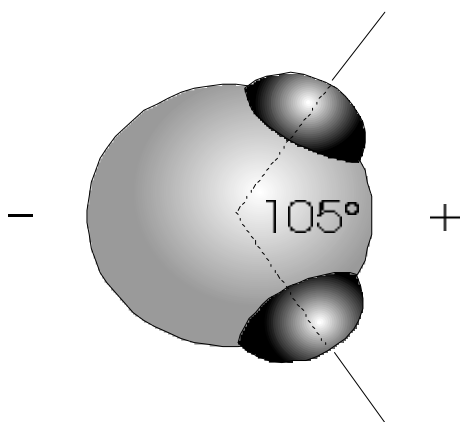


Fig. 1-1 The dipolar molecule of H_2O with two hydrogen atoms configured within the oxygen atom at an angle of 105° .

The importance of this attribute cannot be overstated, and has three principal effects. This dipolar nature allows H_2O molecules to attract and condense to a loosely structured liquid at Earth surface temperatures (Fig. 1-2). Secondly, these dipolar molecules can also orient themselves around ions of other elements, thus holding them in solution. This makes liquid water a solvent, and so an effective weathering agent. A third effect is how the bonding between water molecules varies between the different isotopes of water. As we will see below, these differences allow a disproportionate and measurable distribution of these isotopes throughout the hydrological cycle, which can be used to trace the origin and evolution of water.

The positive and negative poles of neighboring water molecules attract to form a weak hydrogen bond that is easily broken and reformed. The result is loose clusters of molecules that are continually breaking apart and reforming. At 25° , about 80% of the water molecules are so structured. At the boiling point, this is slightly less, and as water freezes, it becomes fully structured.

Because hydrogen bonds are weak, they easily break as water molecules evaporate to water vapor. When humidity exceeds the dew point of the air, hydrogen bonds reform and water vapor condenses — key steps in the hydrological cycle.

SOLUTES IN WATER

The brines of the Dead Sea in the Jordan Rift Valley are a remarkable example of water as a solvent. Held within each kilogram of this clear liquid are more than 350 grams of magnesium and sodium chloride salts. How can so much salt be dissolved in this water? Positively charged ions, Mg^{2+} for example, are

surrounded by a cloud of water molecules, oriented with their negative pole towards the ion. Negative Cl^- ions are surrounded by water molecules with their positive pole oriented inward. This electrostatic interaction with water reduces the interaction between cations and anions that would otherwise allow them to bond and form minerals – an important aspect of aqueous geochemistry that begins with a look at what constitutes matter dissolved in water.

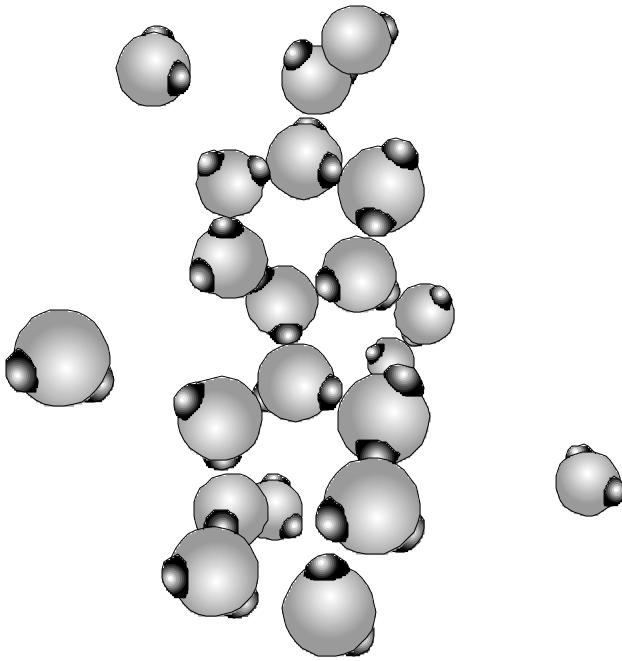


Fig. 1-2 Hydrogen bonding and the tetrahedral structure of water

Dissolved solids

The old primary school experiment of leaving a glass of tap water to dry demonstrated not only the principle of evaporation, it also showed us that the clear water contained solids. The weight of residue left at the bottom of the glass is a measure of the total dissolved solids (TDS), usually expressed in mg/L. Just what these solids contain requires additional analyses, but in large part they include inorganic salts formed from the major cations found in water — Ca^{2+} , Mg^{2+} , Na^+ and K^+ and complementary anions, HCO_3^- , SO_4^{2-} and Cl^- . The typical range of TDS found in rain, surface runoff and in groundwaters is shown in Fig. 1-3.

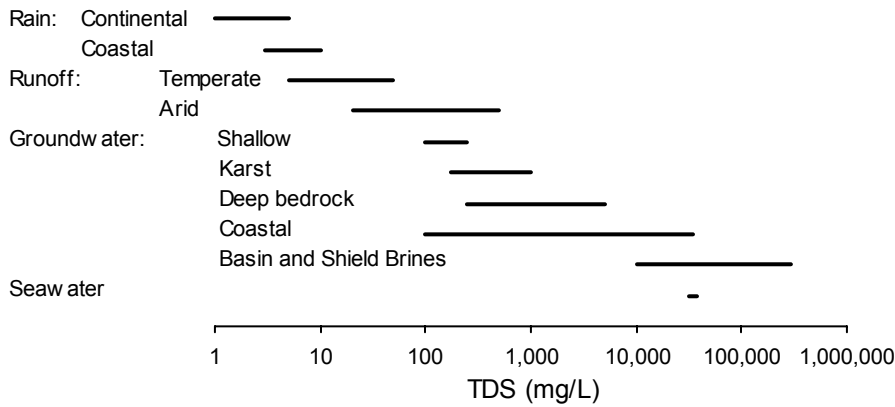


Fig. 1-3 Typical range for total dissolved solids in various waters through the hydrological cycle

3 Chapter 1 The Nature of Water

TDS is a formal analytical measurement of the solids left by drying a filtered sample, although it is often expressed by summing the weight of all major analytes found in solution. The latter is often acceptable as TDS is not generally used in quantitative geochemical calculations. The salinity of water is a measure of its dissolved ion load, and so is essentially the same as TDS. Salinity can be expressed as mg/L, like TDS. For more saline waters, it is often expressed as parts per thousand (ppt) or permil (‰) although this latter can lead to confusion with stable isotope data, discussed below.

fresh	→ 0 to 1000 mg/L	(0 to 1 ppt)
brackish	→ 1000 to 10,000 mg/L	(1 to 10 ppt)
saline	→ 10,000 to 100,000 mg/L	(10 to 100 ppt)
seawater	→ 35,000 mg/L	(35 ppt)
brine	→ greater than 100,000 mg/L	(>100 ppt)

So what makes up most of the dissolved solids in natural waters? In addition to the major ions, the load of dissolved solids includes minor and trace metals, colloids (charged complexes of mineral and/or organic molecules of high molecular weight), viruses and bacteria. The size of some of these species requires that *dissolved* solids be distinguished from *suspended* solids. As membrane filtration can remove most solids from water, including most ions (by reverse osmosis) a practical definition of dissolved solids is that which will pass through 0.45 μm pore diameter filter paper. This size is widely available and has become the industry standard for field filtration in routine geochemical investigations. Table 1-1 gives the size ranges for most of the species that are found in natural waters.

Table 1-1 Size range of solutes and compounds in water

Species	diameter (Å) (10,000 angstrom units (Å) = 1 μm)	
Inorganic ions	1-10	
Dissolved Gases	1-10	
Organic molecules	10-1000	← 0.45 μm (4,500 Å)
Colloids	10-10,000	
Viruses	~100	
Bacteria	~10,000	

Of the species in Table 1-1, it is inorganic ions that contribute most to the load of total dissolved solids (TDS) in waters. Organic molecules are important, but usually represent far less of the TDS in natural waters. The amount of mass carried in water will depend mainly on the setting and exposure to sources of solutes. Through the hydrological cycle from condensation to infiltration and deep circulation in the crust, the mass carried by water can increase exponentially.

The chemistry of rainwater in non-polluted environments is dominated by dissolved atmospheric gases including N₂, O₂ and CO₂, plus minor contributions from soluble atmospheric compounds such as sulfuric and nitrous oxides and some Na-Cl aerosols from sea spray. Concentrations are very low (TDS less than about 10 mg/L) although this can increase 10-fold as precipitation passes through the vegetation canopy before hitting the ground.

Surface waters typically have low salinity (less than 500 mg/L TDS) comprising mainly dissolved inorganic ions and humic compounds (humic and fulvic acids) derived from soils, and organic molecules from in-situ biochemical processes (algae growth and decay). Groundwaters generally have higher concentrations of dissolved inorganic species as a result of interaction with aquifer minerals.

Units of solute concentration

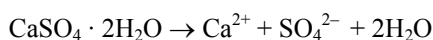
Before getting into the treatment of geochemical data, we need to first look at the units of measure that are commonly used. Geochemical analyses are generally made using spectrometric or chromatographic

instruments, which are calibrated with laboratory standards. These standards are most accurately prepared by weighing soluble salts and adding to weighed or measured volumes of distilled water. This allows us to express solute concentrations as either:

mass solute per mass water: milligrams per kilogram H₂O or parts per million — ppm. Trace elements can be expressed as parts per billion — ppb.

mass solute per volume water: milligrams per liter – mg/L or for trace concentrations, as micrograms per litre – µg/L.

Geochemical reactions are expressed stoichiometrically, that is according to the number, not mass, of ions and compounds that react and are produced. To do so, concentrations are expressed as the number of moles of ions or compounds per volume or mass of water. One mole of a given element contains $6.023 \cdot 10^{23}$ atoms of that element and is equivalent to its atomic weight expressed in grams. One mole of a compound such as H₂O is equivalent to its gram formula weight — gfw, which is the sum of atomic weights of all constituent atoms (i.e. a mole of carbon weighs 12 grams and a mole of water weighs 18 grams). For example, dissolving one mole (172.2 g) of gypsum:



gives one mole of dissolved calcium (40.1 g), one mole of dissolved sulphate (96.1 g), and two moles of water (18 g).

We convert from the mass concentration to the mole concentration of a solute by dividing by the gram formula weight (gfw) of the ion, and dividing again by 1000 (for the difference between ppm (10⁶) and the kg (10³) of H₂O). For concentrations per mass of water (ppm or ppb), the result is the molal concentration (m). For this and subsequent conversions in this section, the example of Ca²⁺ with an analytical concentration of 46 mg/L is used. At this low concentration, this can also be expressed as 46 ppm.

$$\text{molality, } m = \text{moles / kg H}_2\text{O} = \frac{\text{ppm}}{\text{gfw} \cdot 1000} \quad m_{\text{Ca}^{2+}} = \frac{46}{40.1 \cdot 1000} = 0.00115 \text{ mol/kg}$$

Converting from concentrations per volume solution (mg/L or µg/L), the result is the molar concentration (M):

$$\text{molarity, } M = \text{moles / L of solution} = \frac{\text{mg / L}}{\text{gfw} \cdot 1000} \quad M_{\text{Ca}^{2+}} = \frac{46}{40.1 \cdot 1000} = 0.00115 \text{ mol/L}$$

In charge balance calculations is necessary to take into account the valence (z) of the ion in solution. For example, it takes twice the concentration of Na⁺ (z = 1) to balance with Ca²⁺ (z = 2) in exchange reactions. In this case, we can use the units of equivalents per million (epm):

$$\begin{aligned} \text{epm} &= \frac{\text{ppm}}{\text{gfw}} \times z & \text{Ca}^{2+} &= \frac{46}{40.1} \times 2 = 2.3 \text{ epm} \\ &= m \cdot z \cdot 1000 & &= 0.00115 \cdot 2 \cdot 1000 = 2.3 \text{ epm} \end{aligned}$$

For volume-based concentrations in molarity and equivalents (eq) or milli-equivalents (meq):

$$\begin{aligned} \text{meq/L} &= \frac{\text{mg/L}}{\text{gfw}} \times z & \text{Ca}^{2+} &= \frac{46}{40.1} \times 2 = 2.3 \text{ meq/L} \\ &= M \times z \times 1000 & &= 0.00115 \cdot 2 \cdot 1000 = 2.3 \text{ meq/L} \end{aligned}$$

With low salinity solutions (TDS less than about 10,000 mg/L), there is little difference between concentrations expressed as mg/L or ppm. Thus, ppm \cong mg/L and $m \cong M$. At higher concentrations the values diverge due to changes in density, the error in this simplification will exceed the error in the laboratory measurement. Converting between weight and volume-based units is made by taking into account the solution density (g/ml) and the weight of solutes (from TDS as mg/L, converted to g/ml):

mg/L = ppm (density – weight solutes)

$$M = m \left(\frac{\text{weight solution} - \text{weight solutes}}{\text{weight solution}} \right) \times \text{density}$$

Example 1-1 Conversion of concentration units

Given a measurement of 85 ppm Ca^{2+} (gfw 40.1) in a solution with a density of 1.0004 at 25°C and TDS of 400 mg/L:

$$\begin{aligned} m_{\text{Ca}} &= 85 / (40.1 \times 1000) = 0.00212 \text{ mol/kg} \\ \text{epm Ca}^{2+} &= 0.00212 \times 2 \times 1000 = 4.14 \\ M_{\text{Ca}} &= 0.00212 \times [(1000 - 0.400) / 1000] \times 1.0004 \\ &= 0.00212 \text{ mol/L} \\ \text{meq/L Ca}^{2+} &= 0.00212 \times 2 \times 1000 = 4.14 \text{ meq/L} \\ \text{mg/L Ca}^{2+} &= 0.00212 \times 40.1 \times 1000 = 85 \\ \therefore \text{ppm Ca}^{2+} &\cong \text{mg/L Ca}^{2+} \end{aligned}$$

For a high salinity solution with 15,000 ppm Ca^{2+} , a measured density of 1.070 and TDS of 100 g/L:

$$\begin{aligned} m_{\text{Ca}} &= 15,000 / (40.1 \times 1000) = 0.374 \text{ mol/kg} \\ \text{epm Ca}^{2+} &= 0.374 \times 2 \times 1000 = 748 \text{ epm} \\ M_{\text{Ca}} &= 0.374 \left(\frac{1070 - 100}{1070} \right) \times 1.07 \\ &= 0.363 \text{ mol/L} \\ \text{meq/L Ca}^{2+} &= 0.363 \times 2 \times 1000 = 726 \text{ meq/L} \\ \text{mg/L Ca}^{2+} &= 0.363 \times 40.1 \times 1000 = 15,600 \text{ mg/L} \\ \therefore \text{ppm Ca}^{2+} &\neq \text{mg/L Ca}^{2+} \end{aligned}$$

STABLE ISOTOPES IN WATER

The chemical nature of an element is defined by its atomic number and electron configurations, leading to a host of geochemical reactions and processes. By contrast, variations in the number of neutrons has lead to a host of isotopes and isotopic processes, which complement geochemistry. Take oxygen, for example. This element has 8 protons in its nucleus. The repulsive forces of these protons are stabilized by 8 neutrons (Fig. 1–4). This gives oxygen a weight of 16 atomic mass units (amu). However, the process of nucleosynthesis during the formation of our early solar system allowed that about 0.2% of all oxygen atoms had a complement of 10 neutrons. Oxygen–18, or ^{18}O , is an isotope of common oxygen–16, and behaves chemically like all oxygen. However, it's additional weight affects the rate at which it reacts, as compared with ^{16}O . Accordingly, the concentration or abundance of ^{18}O can vary between different compounds and reservoirs of O–bearing compounds. This makes isotopes very useful tracers.

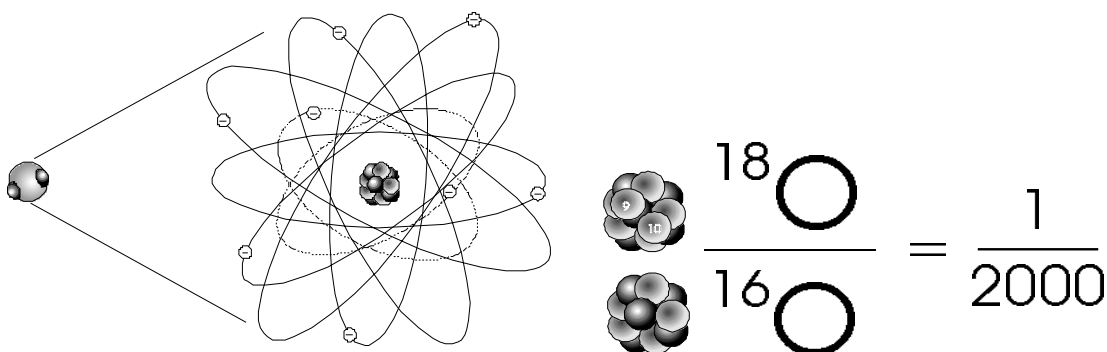


Fig. 1-4 The atomic structure of oxygen-16 and oxygen-18 and their average natural abundance ratio.

Although oxygen can exist with more than 10 or fewer than 8 neutrons, these radionuclides are not stable and decay to other elements. Similarly, other elements can have a greater or lesser complement of neutrons, creating a host of stable and radioactive nuclides. In water, two principal isotopes exist: oxygen with mass 18 and hydrogen with mass 2. The following terms and notations are used in isotope geochemistry:

Element: Atoms defined by a fixed number of protons (atomic number, z) in the nucleus.

Nuclide: An atom with specific number of neutrons and protons.

Isotope: Nuclide with more or fewer neutrons, n , than other atoms (usually the common or most abundant nuclide) of a given element.

Table 1-2 Isotope notation

<i>Element</i>	<i>Oxygen</i>	<i>Hydrogen</i>
Element symbol	O	H
Common nuclide	$^{16}_8\text{O}_8$	$^1_1\text{H}_0$
Common isotope	$^{18}_8\text{O}_{10}$	$^2_1\text{H}_1$
Standard notation for isotope	^{18}O	^2H or D

Following the discovery of stable isotopes of the elements in the early part of the last century, Earth scientists began systematically measuring their concentrations in various natural materials. Remarkably, it was found that isotope abundances were highly variable, and that their concentrations behaved in predictable fashions. So began the study of environmental isotope geochemistry.

The environmental isotopes

What are the “environmental” isotopes? These are naturally occurring isotopes of the major elements that participate in Earth surface processes. Of the stable environmental isotopes, only a few are currently of practical importance. In hydrology, the principal isotopes of interest are oxygen-18 and deuterium. Others, including carbon-13, nitrogen-15 and sulphur-34 are used to trace biogeochemical processes and the contamination of water resources. The routinely measured stable environmental isotopes are given in Table 1-3 along with their average natural abundance and the typical samples in which they are measured.

The list of isotopes used in hydrology is expanding as new methods and advances in mass spectrometry are developed. Helium isotopes ($^3\text{He}/^4\text{He}$) are often used in studies of water residence time. Others, including ^9Li , ^{11}B , ^{37}Cl and ^{87}Sr are used to study weathering, sources of salinity and contaminants.

Table 1-3 The routinely measured stable environmental isotopes

<i>Isotope</i>	<i>Ratio</i>	<i>% natural abundance</i>	<i>Reference (abundance ratio)</i>	<i>Commonly analysed samples</i>
Routine				
² H	² H/ ¹ H	0.015	VSMOW (1.5575 · 10 ⁻⁴)	H ₂ O, clay minerals
¹³ C	¹³ C/ ¹² C	1.11	VPDB (1.1237 · 10 ⁻²)	DIC, calcite, organics, CO ₂
¹⁵ N	¹⁵ N/ ¹⁴ N	0.366	AIR N ₂ (3.677 · 10 ⁻³)	N ₂ , NO ₃ ⁻ , organics
¹⁸ O	¹⁸ O/ ¹⁶ O	0.204	VSMOW (2.0052 · 10 ⁻³)	H ₂ O, calcite, SO ₄ ²⁻ , NO ₃ ⁻
³⁴ S	³⁴ S/ ³² S	4.21	CDT (4.5005 · 10 ⁻²)	Sulfates, sulfides, H ₂ S, S-organics

Isotope concentrations and measurement

Isotope concentrations or abundances are measured as a ratio of the isotope to the common nuclide, eg. ¹⁸O/¹⁶O. However, accurate measurement of an abundance ratio is a complicated affair. Gas-source mass spectrometry simplifies the analysis by precisely measuring the difference in abundance ratio between the sample and a reference gas of known absolute isotopic abundance. The reference gas is calibrated with an internationally recognized reference, providing consistency between stable isotope data produced in different laboratories. Stable isotope data are then expressed as the difference between the sample and the reference, according to the equation (for the example of ¹⁸O):

$$\delta^{18}\text{O}_{\text{sample}} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{reference}}}{(^{18}\text{O}/^{16}\text{O})_{\text{reference}}}$$

Simplified and expressed as a permil (‰) value, this becomes:

$$\delta^{18}\text{O}_{\text{sample}} = \left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{reference}}} - 1 \right) \cdot 1000 \text{‰ VSMOW}$$

where: δ is the standard symbol for an isotopic measurement
VSMOW is the standard used in this example (Vienna Standard Mean Ocean Water)
‰ is the permil notation

The reference is selected according to the type of sample. Waters are routinely analyzed against the Vienna Standard Mean Ocean Water reference, and so $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data are expressed as ‰ difference from VSMOW. Carbon isotope ratios are always expressed against the Vienna Pee Dee Belemnite reference, and so we use $\delta^{13}\text{C}$ ‰ VPDB. Other reference materials are given in Table 1-3.

A δ -‰ value that is positive, say +10‰, signifies that the sample has more of the measured isotope than the reference. For example, a sample of water with $\delta^{18}\text{O} = 10\text{‰ VSMOW}$ has 10 permil or 1% more ¹⁸O than the reference. Similarly, a sample that has 10‰ less ¹⁸O than VSMOW would be expressed as $\delta^{18}\text{O}_{\text{sample}} = -10\text{‰ VSMOW}$.

The isotopic difference between two samples can also be directly calculated. A water sample A with $\delta^{18}\text{O}_A = -5\text{‰}$, compared with a second sample B with $\delta^{18}\text{O}_B = -8\text{‰}$ has 3‰ or 0.3% more ¹⁸O than sample B. We can say that sample A is *enriched* in ¹⁸O by 3‰ over sample B, or that sample B is 3‰ *depleted* in ¹⁸O compared to sample A. The manner by which isotopes become enriched or depleted in different waters, minerals and solutes, is the subject of another chapter.

Example 1-2 Abundance ratio from isotope data

A rain water sample and snow sample have $\delta^{18}\text{O}$ values of -4.5% and -15.0% respectively. Compare their actual isotope abundance ratios.

$$\begin{aligned}\delta^{18}\text{O}_{\text{rain}} &= -4.5\% \text{ VSMOW} \\ \delta^{18}\text{O}_{\text{snow}} &= -15.0\% \text{ VSMOW}\end{aligned}$$

^{18}O abundance ratio for VSMOW = $2.0052 \cdot 10^{-3}$ (from Table 1-3)

$$\delta^{18}\text{O}_{\text{sample}} = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{reference}}} - 1 \right) \cdot 1000$$

$$-4.5 = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{rain}}}{2.0052 \cdot 10^{-3}} - 1 \right) \cdot 1000$$

$$-15.0 = \left(\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{snow}}}{2.0052 \cdot 10^{-3}} - 1 \right) \cdot 1000$$

$$\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{rain}} = 1.9962 \cdot 10^{-3}$$

$$\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{snow}} = 1.9751 \cdot 10^{-3}$$

Thus, the rain has a greater abundance of ^{18}O than does the snow.

FROM ELEMENTS TO AQUIFERS

The geochemistry of water is to a very large degree controlled by the geosphere — the mineral and rock envelope that hosts the hydrological and biological processes of environmental geochemistry. The following is a brief introduction to the elements, minerals and rocks that dominate in the geosphere.

Elements, atoms and ions

Each of the 92 natural elements from hydrogen to uranium (plus the transuranic elements) is defined by its atomic number representing the number of the positively charged protons — p in the nucleus. The reactivity of the elements arises from the configuration of the electrons — e^- , which orbit the nucleus in pairs within discrete shells. Atoms in their elemental state have the same number of electrons as protons, and so carry a net charge of 0. The Periodic Table (Table 1-4) arranges the elements in rows (periods) for each electron shell, and the sequential filling of the outer shell occurs from left to right along a row. Only with all of the electron orbitals filled, is this outer shell is stable, making the element inert or unreactive. This is the case for the six noble gases (He — $2e^-$, Ne — $10e^-$, Ar — $18e^-$, Kr — $36e^-$, Xe — $54e^-$, Rn — $86e^-$), which are found on the right-hand end of their respective rows (Table 1-4). However, the rest of the elements have an unfilled outer shell, and will shed or acquire electrons to stabilize it. These are the valence electrons, which affect much of the geochemical behavior of an element.

The valence of an element is given by the number of electrons lost or gained to stabilize the outer shell at a given electron configuration. Elemental hydrogen, for example, has only one electron in its (only) electron shell, which it shares with another H to complete this shell at 2 electrons, making H_2 . Alone, H sheds its sole electron to become a hydrogen ion H^+ . Elemental oxygen will acquire two additional electrons to complete its outer shell at 8, making a total of 10 (2 inner and 8 outer shell electrons), with a charge of $2-$. In its elemental state, two oxygen atoms share two electrons to make elemental oxygen or O_2 . The affinity for O_2 to acquire additional electrons makes elemental oxygen a strong oxidant or electron acceptor in redox reactions (below).

9 Chapter 1 The Nature of Water

While most elements can have a variety of stable or quasi-stable oxidation states, most have only one or two common states in the environment. Oxidation states are shown for each element in Table 1-6. Major groups of elements in the periodic table can be characterized by their ionization potential and common oxidation state:

The noble gases (Group VIII B): He, Ne, Ar, Kr, Xe and Rn, noted for their fully filled outer shell, making them geochemically inert. Unwilling to bond, they remain as gases.

Alkali metals (Group IA): Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ and Fr⁺, always carry a charge of 1+, whether in solution or mineral phase.

The alkaline-earth metals (Group IIA): Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺ and Ra²⁺, will always be 2+, as solutes and in minerals, with Mg²⁺ and Ca²⁺ as dominant cations in most waters and rocks.

The halides (Group VIII B): F⁻, Cl⁻, Br⁻, I⁻ and At⁻ are anions, occurring only rarely in elemental state (e.g. Cl₂ gas in some volcanic situations)

Transition metals (Groups III A to IIB): including the more common members — Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn, share the characteristic of being cations with higher and usually several redox states. Iron, for example, is found as either Fe²⁺ or Fe³⁺. In their elemental state, transition metals possess high electrical conductivity and metallic bonding (electron sharing).

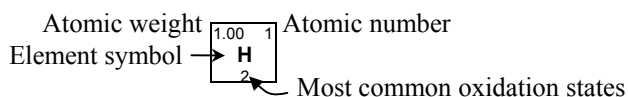
Non-metals: B, C, N, O, Si, P, S, As, Se and Te. Elements of this group of form crystalline solids in their elemental state. The most common, in aqueous and biological systems, C, N, O, P and S, are important for their electron exchange properties. Carbon, for example, has four common states, 4-, 2-, 0, and 4+, which makes it such a key element in biological reactions.

The rare earth elements (REE): Lanthanum — La, plus cerium — Ce to lutetium — Lu. The REEs, a continuation of La's position in the periodic table, have such uniform geochemical characteristics (e.g. valence of 3+) that they behave as a group in high temperature geochemical processes. They are of traditional interest in magmatic and metamorphic studies. The high sensitivity of ICP-MS instruments now allows the REEs to be used in low temperature aqueous geochemistry to study weathering and transport phenomena.

The actinides: Actinium — Ac, thorium — Th, protactinium — Pa and uranium — U are the only naturally occurring elements of the actinide series of "super-heavies". Transuranic elements, including neptunium — Np to lawrencium — Lr, have been discovered over the past several decades. Of the naturally occurring actinides, only U is found in significant aqueous concentrations, due to its elevated solubility in the 6+ state. Thorium, by contrast, has an exceedingly low solubility in natural waters. Isotopes of Ac and Pa are generated within the ²³⁵U and ²³⁸U decay chains.

Table 1-4 Periodic Table of the elements.

IA										VIII B																	
1.00 1 H 1	IIA																										4.00 2 He 0
6.94 3 Li 1	9.01 4 Be 2											10.8 5 B 6	12.0 6 C -4 -2 0	14.0 7 N -3 0 3 5	16.0 8 O -2 0	19.0 9 F -1	20.2 10 Ne 0										
23.0 11 Na 1	24.3 12 Mg 2	IIIA IVA VA VIA VIIA ← VIII A →										IB	IIB	27.0 13 Al 3	28.1 14 Si 4	30.1 15 P -3 5	32.1 16 S -2 0 4 6	35.5 17 Cl -1	40.0 18 Ar 0								
39.1 19 K 1	40.1 20 Ca 2	45.0 21 Sc 3	47.9 22 Ti 4	50.9 23 V 5	52.0 24 Cr 3	54.9 25 Mn 4 3 2	55.8 26 Fe 2 3	58.9 27 Co 2 3	58.7 28 Ni 2	63.5 29 Cu 1 2	65.4 30 Zn 2	69.7 31 Ga 3	72.6 32 Ge 4	74.9 33 As 3 5	79.0 34 Se -2 0 4 6	79.9 35 Br -1	83.8 36 Kr 0										
85.5 37 Rb 1	87.6 38 Sr 2	88.9 39 Y 3	91.2 40 Zr 4	92.9 41 Nb 3 5	95.9 42 Mo 4 6	98 43 Tc 7	101 44 Ru 3 4	103 45 Rh 2 3 4	106 46 Pd 2 4	108 47 Ag 1	112 48 Cd 2	115 49 In 3	119 50 Sn 4 2	122 51 Sb 3 5	128 52 Te -2 0 4 6	127 53 I -1	131 54 Xe 0										
133 55 Cs 1	137 56 Ba 2	139 57 La 3	178 72 Hf 4	181 73 Ta 5	184 74 W 4 6	186 75 Re 7	190 76 Os 3 4	192 77 Ir 2 4 6	195 78 Pt 2 4	197 79 Au 1 3	200 80 Hg 2	204 81 Tl 1 3	207 82 Pb 2	209 83 Bi 3 5	209 84 Po 2 4	210 85 At -1	222 86 Rn 0										
223 87 Fr 1	226 88 Ra 2	227 89 Ac 3																									
140 58 Ce 3	141 59 Pr 3	141 59 Nd 3	145 61 Pm 3	150 62 Sm 3	152 63 Eu 3	157 64 Gd 3	159 65 Tb 3	163 66 Dy 3	165 67 Ho 3	167 68 Er 3	169 69 Tm 3	173 70 Yb 3	175 71 Lu 3														
232 90 Th 4	231 91 Pa 5	238 92 U 4 6	237 93 Np 4 5	244 94 Pu 4	243 95 Am 3	247 96 Cm 3	247 97 Bk 3	251 98 Cf 3	252 99 Es 3	257 100 Fm 3	258 101 Md 3	259 102 No 3	260 103 Lr 3														



Note: the double line separates metals (metallic luster and electrical conductivity in elemental state at low temperature) from non-metals (crystalline form in elemental state).

Distribution of elements in the Earth's crust

The order of abundance by weight of elements in the Earth's crust is given in Table 1-7. After oxygen, silica and aluminum, which are the principal components of silicate minerals, we see that iron is the fourth most abundant, followed by the alkali and alkaline-earth elements (Na, K, Ca, Mg). With the exception of iron, all are familiar components of major cation composition of water. The low solubility of Si, Al and Fe oxides limits their concentration in most natural waters. The lower crustal abundance of the elements found as anions (Cl^- , SO_4^{2-} , HCO_3^-) is compensated by the high solubility of these species.

Table 1-7 Principal elements of the Earth's crust, by weight

Element	Atomic Number	Crustal Abundance %	Element	Atomic Number	Crustal Abundance ppm
O	8	46.6	P	15	1050
Si	14	27.7	Mn	25	950
Al	13	8.13	F	9	625
Fe	26	5.00	Ba	56	425
Ca	20	3.63	Sr	38	375
Na	11	2.83	S	16	260
K	19	2.59	C	6	200
Mg	12	2.09	Zr	40	165
Ti	22	0.43	V	23	135
H	1	0.14	Cl	17	130

Source: Mason, 1966

The distribution of elements was addressed by the pioneer of modern geochemistry, V.M. Goldschmidt, who classified the elements by their affinities to different geological environments and processes, as an extension of Mendeleev's periodic table. Based on Goldschmidt's classification, naturally occurring elements can be divided according to their affinity to native iron of the core (siderophile), silicate phases of the Earth's crust (lithophile) and sulfides of base metal deposits (chalcophile). A final group includes those elements with a tendency to volatilize (atmophile). His divisions were based on observations of meteorites and of metallurgical processes. Some of the common and more notable elements of each division are:

Siderophile elements: Fe, Co, Ni, Pt, Au, C and P

Lithophile elements: alkalis and alkaline-earths, the halides, Mn, O, Cr, and U

Chalcophile elements: transition metals including Cu, Zn, Ag, Cd, Hg and Pb, plus S, As and Se

Atmophile elements: hydrogen (H_2), nitrogen (N_2) and the noble gases

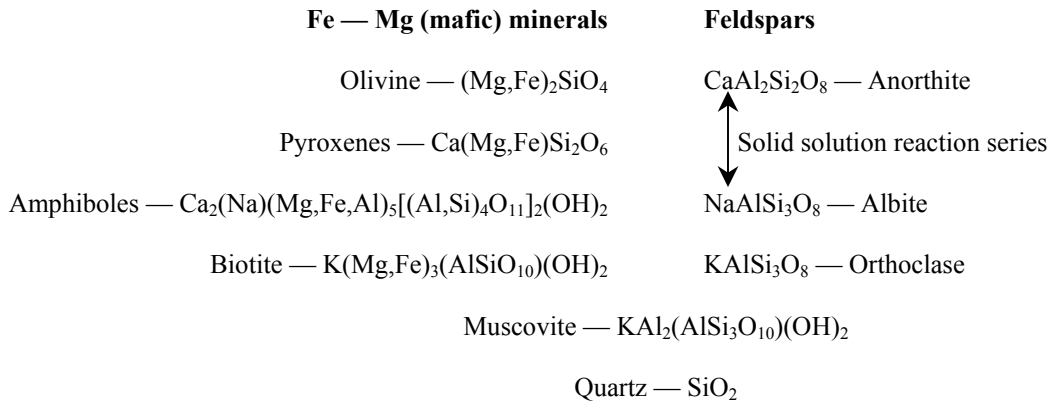
While elements have preferences of membership in one of Goldschmidt's four groups many share characteristics with more than one. For example, Fe is the principal element of the siderophile group, yet is also chalcophylic, as pyrite [FeS_2]. It is also found as an element in lithophilic, ferromagnesian-silicate minerals. Nonetheless, the classification provides general categories of elemental characteristics in geochemistry. The Earth is differentiated according to Goldschmidt's classification, with a siderophilic core, a lithophilic crust and the volatile phases of the hydrosphere and atmosphere. Chalcophile phases as sulfides are underrepresented, however, and so do not form a discrete sphere.

The rock forming minerals

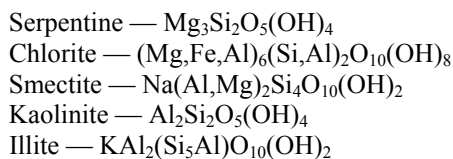
The principal rock forming minerals can be classified according to a variety of subdivisions. The following is a classification from the perspective of aqueous geochemistry. Note that these minerals are ideal end-members and normally occur with minor concentrations of other elements. Calcium carbonate, for example, will always have a minor component of Mg^{2+} which substitutes for Ca^{2+} in CaCO_3 .

Silicates

The process of magma differentiation and crystallization produces a series of mineral types ranging from high temperature, including Ca-plagioclase feldspar and silica-depleted minerals rich in Fe and Mg (mafic), to lower temperature ($>300^\circ\text{C}$) minerals that are silica and aluminum rich (sialic). Plutonic rocks and cratons — the metamorphic shields of most continents, are comprised principally of sialic rocks. While oceanic crust is composed of mafic and ultramafic (olivine rich) rocks, continental terrains often include obducted oceanic crust, mafic intrusions and mafic (basaltic) volcanics. Silicates are hard, durable minerals with low solubilities and weather slowly to clay minerals, silt and sand. In order of decreasing temperature of formation, and increasing stability in low temperature settings, the principal groups of silicate minerals are as follows. Elements within parentheses can be substituted for each other in the lattice, providing charge balance is respected.

*Clay minerals*

Clay minerals form the class of minerals known for their “leaf” structure as the phyllosilicates. They are the weathering product of primary silicate minerals. This can be confused with the geotechnical definition, where mineral particles that are $< 2 \mu\text{m}$ in diameter are clay-size. While most clay minerals are also of clay size, many clay-size particles may be of quartz or other materials. The common feature of clay minerals is their sheet structure, which has negatively charged boundaries and faces onto which cations can be fixed and exchanged. They are of considerable importance given this affinity for cation exchange, which can affect the geochemistry of the groundwater. Clay minerals embrace a range of chemical compositions and structures, which are discussed in a later chapter. Note that all carry hydroxyl groups (OH^-), from their origin by aqueous alteration of silicate minerals. Serpentine and chlorite are commonly produced by hydrothermal alteration of mafic minerals (olivine and pyroxene). Meteoric alteration of mafic minerals produces smectite clay, while kaolinite and illite commonly form by meteoric weathering of feldspar-rich rocks. Substitutions of the major cations are common, giving a range of compositions for these principal clay groups. Typically, Na and K are interchangeable. Mg, Fe and Al substitute in the divalent sites (although Al produces a charge imbalance that must be accommodated), and Al commonly substitutes for Si in the tetrahedral sites. The principal clay mineral groups and general formulae are:



Carbonates

Carbonate rocks are the greatest reservoir of carbon on Earth, comprising over 100,000 times the living biomass equivalent of C. Marine limestone and dolomites can host significant aquifers, and so have an impact on the geochemistry of drainage from such regions. Carbonate minerals are also common fracture filling minerals in crystalline (silicate) or sedimentary rocks. As the carbonate minerals can be formed at low temperature, they are fundamental controls on the geochemistry of natural waters. There are two principal minerals, calcite and dolomite, with higher temperature polymorphs, as well as less common carbonates. Carbonates are more soluble than silicate minerals, particularly under acidic conditions, and so will dissolve under near-surface conditions, thus increasing fissure permeability and groundwater circulation.

Calcite — CaCO_3
 Dolomite — $\text{CaMg}(\text{CO}_3)_2$
 Siderite — FeCO_3
 Magnesite — MgCO_3

Evaporites

Evaporite minerals are the highly soluble salts formed by the evaporation of seawater or formation waters. These are most commonly found in certain sedimentary rocks packaged with limestone, dolomite or shale, formed in Paleozoic seas, although modern evaporites are still forming. An example is the precipitation of some 40m of halite at the bottom of the Dead Sea over the past 5000 years. However, evaporite minerals may also precipitate from hydrothermal or formation fluids circulating in fractures. While a vast array of evaporite minerals exists, the following are the most common:

Sulfates: Gypsum — $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
 Anhydrite — CaSO_4
 Mirabilite — $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
 Epsomite — $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Chlorides: Halite — NaCl
 Sylvite — KCl

Carbonates: Trona — $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$

Phosphates

Phosphorus is a minor element in aqueous systems, yet is often the rate-limiting nutrient for photosynthetic activity. The largest reservoir of phosphorus in the form of phosphate is in apatite, an accessory mineral in many igneous rocks. Four varieties occur, depending on the exchangeable anion. Phosphorite formations, marine precipitates of complex calcium phosphates, occur in sedimentary rocks throughout the world.

Fluorapatite — $\text{Ca}_5(\text{PO}_4)_3\text{F}$
 Chlorapatite — $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$
 Hydroxylapatite — $\text{Ca}_5(\text{PO}_4)_3\text{OH}$
 Carbonate-apatite — $\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)\text{H}_2\text{O}$

Sulfides

The most common sulfide, although not an economic mineral, is pyrite, or iron sulfide. As an uneconomical accessory mineral in many mining camps, it is concentrated in mine tailings and waste rock. Pyrite is ubiquitous in organic rich sediments such as shales and some limestones. Glacial till often contains a small percentage of pyrite exposed by erosion of bedrock. Mackinawite, a more amorphous iron sulfide mineral, can form in low temperature aqueous settings. With their capacity for oxidation, iron sulfides are important controls on redox, sulfur and iron geochemistry in natural waters.

Pyrite — FeS_2

Mackinawite — FeS

Other sulfide minerals are the source of most base metals (Cu, Zn, Pb, Ni), which can occur in association with iron sulfide. The most abundant arsenic mineral is an iron sulfide.

Chalcopyrite — CuFeS₂

Sphalerite — (Zn,Fe)S

Galena — PbS

Pentlandite — (Fe,Ni)₉S₈

Cinnabar — HgS

Arsenopyrite — FeAsS₂

Oxy-hydroxides

Oxides and hydroxides of iron and manganese form during weathering of pyrite and mafic minerals. These are the oxidized form of these two common transition metals — Fe³⁺ and Mn⁴⁺. They can form hydrated amorphous deposits on mineral or organic surfaces in soils and fractures, or can crystallize to a distinct mineral phase. They can also be found as rock forming minerals, particularly in metamorphic rocks. In soils they are particularly important as redox buffers, and as a negatively charged substrate for adsorption of other metals and contaminants.

Magnetite — Fe₃O₄

Hematite — Fe₂O₃

Goethite — FeOOH

Ferrihydrite — Fe(OH)₃

Pyrolusite — MnO₂

Manganite — MnOOH

Pyrochroite — Mn(OH)₂

Sediments, rocks and aquifers

Aquifers come in many sizes and materials. Formally defined as a water-saturated geological medium capable of storing and transmitting groundwater, aquifer types include porous, fractured and fissured (karst) media, and can be confined or unconfined. Unconfined or phreatic aquifers are the shallowest hydrostratigraphic unit, bounded above by the water table where the groundwater pressure is equal to 1 atmosphere. Unconfined aquifers are generally recharged by infiltration of meteoric waters through the overlying soil and unsaturated zone, or by seepage from adjacent surface water bodies. Atmospheric gases and soil CO₂ also exchange with groundwaters through the unsaturated zone. Confined or artesian aquifers are overlain by lower permeability materials such as clays or silts, and so have no upper unsaturated zone. Recharge occurs either by flow from a region where the aquifer “outcrops” and has unconfined conditions, or by leakage of groundwater from the adjacent confining beds. A hypothetical “piezometric” surface replaces the water table, defined as the elevation to which water rises in piezometers (monitoring wells) drilled into the aquifer.

Porous aquifers are generally deposits of unconsolidated clastic material of sand and gravel size, but also include sandstone and other lithified strata with intergranular porosity. Porous media can have effective porosities of 15 to 25 percent. Sand and sandstone aquifers are almost always dominated by quartz, which is the most stable of the common clastic minerals, with minor feldspar. Most other major minerals have been dissolved or altered to clays by weathering of parent materials and transport of the clastic sediments. Heavy minerals such as magnetite, zircon and garnet can also be present in trace amounts. Limestone is seldom present in sandy aquifers due to its low durability and high solubility, although it can be the dominant component of gravel aquifers.

The clastic material of which most sandy aquifers are generally composed is derived from weathering and transport of silicate parent rocks. As a result, such aquifers generally provide little in the way of solutes to

groundwater. However, secondary cements are present, such as calcite or ferrihydrite, can be a source of dissolved solids.

Fractured rock aquifers most often occur in crystalline silicate rocks including plutonic, volcanic and metamorphic materials. Sedimentary formations such as shales and sandstones can also be fractured, the later often with a secondary intergranular porosity, giving such aquifers a dual porosity. Seemingly intact granites and metamorphic rocks can also have a secondary porosity as microfractures and intergranular discontinuities, although these serve more often as a source of solutes rather than significant storage of water. Movement of water and solutes through this porosity is strictly by diffusion, but can be a source of salinity to groundwater moving through the open fractures. As silicate minerals have low solubility, fracture development is essentially by tectonic activity.

Although fracture density and aperture vary widely, fractured aquifers invariably have low bulk porosity (volume of fractures per volume of rock), on the order of one percent. The dominant mineralogy of fractured silicate aquifers is quartz and feldspar. Granites are composed of potassium and sodium feldspars (alkali feldspars), which are sources of low but significant concentrations Na and K in groundwaters through weathering. Rocks of intermediate to mafic composition are dominated by calcium feldspars and by increasing amounts of Mg-Fe minerals. Basalts make excellent aquifers due to the dense fracturing from cooling joints and along flow beds, and are principally plagioclase feldspar (Ca and Na) with additional pyroxene and amphibole.

Karst aquifers are among the most exploited freshwater resources in the world. The principal mineral — calcite, is soluble under acidic conditions. This leads to a continual opening of porosity through fissure dissolution. While dolomite is less soluble, it too provides good aquifer conditions. As groundwater recharging through soils gains carbonic acid through the dissolution of CO₂ in the soil, it is the upper limestone and dolostone surface that is most intensely fissured. Consequently, fissured limestone and dolostone aquifers are often phreatic. Karst groundwaters are typically dominated by Ca²⁺, Mg²⁺ and HCO₃⁻. As carbonate aquifers are most often found within sedimentary basins, additional solutes including Na⁺, Cl⁻ and SO₄²⁻ may be derived from saline pore waters and minor gypsum in the carbonates and/or shaley units.

GEOCHEMICAL ANALYSES

The laboratory analysis of a water sample (a water quality analysis) can vary in terms of completeness, from a basic analysis of major species, to a more complete analysis including isotopes, minor and trace metals, dissolved gases, organic carbon, solvents and pesticides, and radioactivity. The level of analysis required depends on the application. Studies on watershed dynamics and water resource management may require only a basic geochemical analysis to determine the principal factors controlling salinity and groundwater flow. Monitoring for drinking water quality and detailed studies such as geochemical exploration or contaminated sites characterization would require a more comprehensive list of analytes including organo-contaminants and trace metals.

More complex analyses can also be undertaken to determine the speciation or form of the dissolved component, involving filtration at different pore size and selective preservation methods. Radiological parameters may often be measured, usually as gross alpha and gross beta activity, or as the activities of specific radionuclides. Radioactivity is now measured in becquerels per liter (Bq/L), where one becquerel is one disintegration or decay event per second. Fuels (diesel and BTX — the benzene-toluene-xylene mixture which constitutes gasoline) and halogenated carbon compounds (pesticides, herbicides and solvents) can be analyzed on a selective basis for water contamination studies.

Field parameters

The analysis of water quality begins in the field with in-situ measurement of unstable parameters such as temperature, pH and redox potential (Eh). These measurements, together with sampling and preservation

methods are covered in more detail in subsequent chapters. Examples of basic water quality analyses are given in Table 1-5.

Accurate measurements of water temperature and pH are essential to any thermodynamic calculation of mineral solubility and solute speciation, and should be measured in the field. pH is the negative log of the hydrogen ion activity ($a_{\text{H}^+} = 10^{-\text{pH}}$), which is involved in most geochemical reactions. While pH can also be measured in the lab, it is often found to change due to changes in temperature, or due to degassing of CO_2 .

Electrical conductivity (EC) is an assessment of water salinity, by measuring the resistance to current flow between two electrodes with a given voltage. The value, in milli- or micro-Siemens (formerly mhos) per centimeter, is a measure of ions in solution and so is used as a field proxy for TDS, where:

$$\begin{aligned} \text{TDS} &\cong 0.55 \text{ EC } (\mu\text{S}/\text{cm}) \text{ for low salinity bicarbonate waters} \\ &\cong 0.75 \text{ EC } (\mu\text{S}/\text{cm}) \text{ for high } \text{SO}_4^{2-} \text{ waters} \\ &\cong 0.9 \text{ EC } (\mu\text{S}/\text{cm}) \text{ for high } \text{Cl}^- \text{ waters} \end{aligned}$$

Redox potential or Eh is a bulk measurement of electron activity or availability for oxidation and reduction reactions. Elements such as C, S, N, Fe, Mn, and As have two or more common redox states, which control their form and solubility (e.g. iron occurs as either soluble ferrous iron — Fe^{2+} or insoluble ferric iron — Fe^{3+}). Thus, measurement of Eh is important biogeochemical reactions involving trace metals, nutrient cycling, and degradation of organic compounds, as they involve redox transformations.

Major ions and isotopes

With the exception of very detailed studies, no water quality analysis is complete without measurement of the major cations and anions. In most meteoric waters, the major cations include the alkaline-earths — Ca^{2+} and Mg^{2+} , and the alkali metals — Na^+ and K^+ . These four elements are the principal cations of the primary rock-forming minerals including the silicates (feldspars, micas, amphiboles and pyroxenes), and the carbonates (calcite and dolomite). The major anions include the carbonate species — HCO_3^- (bicarbonate) and CO_3^{2-} (dissolved carbonate) commonly derived from weathering by soil CO_2 . Sulfate — SO_4^{2-} , is a product of weathering of sulfide minerals and evaporite beds, or from marine sources, and chloride Cl^- , is a highly soluble ion found in crustal fluids, salt formations and seawater.

The positive valences of the major cations follows from their positions in the Periodic Table (Table 1-4). The major anions carry charges that relate to the valence of their constituent elements and covalently bound oxygen, which carries a 2- valence. For SO_4^{2-} , oxygen contributes 8 negative charges ($4 \times 2-$) and so sulfur is in the 6+ oxidation state. For HCO_3^- , oxygen contributes $3 \times 2- = 6-$ and H has a charge of 1+, therefore carbon is in the 4+ state. This is mineralized carbon (including CO_2 , CaCO_3 , etc.) as opposed to fixed carbon in the “fixed” or 0 valence state (as C, or CH_2O) or reduced carbon with valence 4- (e.g. CH_4). HCO_3^- , CO_3^{2-} and dissolved CO_2 are collectively referred to as dissolved inorganic carbon, or DIC.

In natural waters, these seven major geochemical species generally contribute over 95% of the TDS. They also have anthropogenic sources in industrial, municipal and agricultural activities. Thus, these major ions provide insights to not only the weathering and mixing history of natural waters, but also to anthropogenic impacts in polluted landscapes.

While the major ions reflect the biogeochemical history of water, the principal isotopes of water — ^{18}O and D provide complementary perspective on the origin of the water itself. Their routine analysis now makes these isotopes a component of many geochemical analyses. Similarly, the isotopic content of dissolved inorganic carbon — $\delta^{13}\text{C}_{\text{DIC}}$ provides a constraint on the origin of DIC, telling us then about the biogeochemical history of the water. Finally, in many studies, the isotopic composition of sulfate — $\delta^{34}\text{S}_{\text{SO}_4}$ allows us to determine the source of sulfate and the biogeochemical reactions that affect water quality.

Table 1-5 Examples of geochemical analyses of water

<i>Parameter</i>	<i>Rain</i> ¹	<i>River</i> ²	<i>Ground-water</i> ³	<i>Seawater</i>	<i>Brine</i> ⁴	<i>Water Quality Standards</i> ⁵
<i>Field Measurements</i>						
T °C	22	9.8	21.8	—	25	15
pH	5.7	7.58	6.3	~7.0	6.50	6.5 – 8.5
Eh (mV)	380	314	-44	~400	90	—
alkalinity (meq/L)	0.005	1.02	6.31	2.3	0.24	—
EC (µS)	38	125	950	39 mS	484 mS	—
density (g/cc)	0.997	0.997	0.999	1.0	1.32	—
<i>Major Ions (ppm)</i>						
calcium — Ca ²⁺	0.62	17.4	92.8	410	73500	—
magnesium — Mg ²⁺	0.11	3.39	31.6	1290	287	—
sodium — Na ⁺	0.20	3.06	40.5	10,760	29800	200
potassium — K ⁺	0.01	0.72	3.9	400	272	—
bicarbonate — HCO ₃ ⁻	0.29	62.0	378	142	14.6	—
sulfate — SO ₄ ²⁻	1.4	8.47	53.7	2700	130	250
chloride — Cl ⁻	0.31	2.4	58.6	19,350	185,000	250
TDS	2.9	66.4	530	35,100	292,000	1000
<i>Isotopes</i>						
δ ¹⁸ O _{H₂O} ‰ VSMOW	-8.2‰	-12.6‰	-5.8‰	0.0‰	-13.6	—
δD _{H₂O} ‰ VSMOW	-55‰	-96‰	-27‰	0‰	-62	—
δ ¹³ C _{DIC} ‰ VPDB	—	-4.5‰	-12.9‰	+1.5‰	-8.0	—
δ ³⁴ S _{SO₄} ‰ CTD	+5.6‰	+6.9‰	-4.8‰	+21‰	+24.6‰	—
<i>Minor Species and Nutrients (ppm)</i>						
aluminum — Al ³⁺	—	0.08	0.11	0.001	0.08	0.2
iron — Fe _{total}	—	2.72	0.025	0.002	2.66	0.3
manganese — Mn _{total}	—	0.062	0.015	0.0002	14.1	0.05
silica — SiO ₂	—	3.47	15.1	0.5–10	1.05	—
strontium — Sr ²⁺	—	0.10	4.55	8.1	1230	—
nitrate — NO ₃ ⁻	0.31	0.09	<0.01	0.005–2	<0.5	45
nitrite — NO ₂ ⁻	—	0.01	<0.01	—	<0.5	3.3
ammonium — NH ₄ ⁺	0.05	0.08	0.15	<0.1	<0.5	—
phosphate — PO ₄ ³⁻ (P)	—	0.29	0.02	<0.05	nd	—
sulfide — H ₂ S and HS ⁻	—	<0.01	0.8	<0.01	<0.01	0.05
fluoride — F ⁻	—	0.02	1.02	1.3	<1	2
bromide — Br ⁻	—	0.08	3.2	67	1336	—
DOC (mg-C/L)	0.05	3.6	7.8	0.3 – 2	nd	—

¹ Ottawa, Canada² Fraser River, British Columbia, Canada³ Amman water supply well, Carbonate bedrock, Mukhebeh, Jordan⁴ Canadian Shield Brine, Con mine, 5300' level, Yellowknife, NWT, Canada⁵ US Environmental Protection Agency

Minor and trace constituents

Minor metals in solution include iron and manganese, which are important redox parameters in many settings. Strontium is minor component in most waters, derived from the same geochemical environments as Ca²⁺. Silica, expressed analytically as SiO₂, and aluminum — Al³⁺, are contributed from the weathering of silicate minerals. Below about pH 9, Si occurs as the neutral species — H₄SiO₄⁰ and so contributes to TDS but not to salinity.

Nutrients, including nitrogen species (NO₃⁻ and NH₄⁺), phosphate (HPO₄²⁻) and DOC are minor constituents that are the basis of biogeochemical reactions in groundwaters and surface waters. Halides

including fluoride and bromide often correlate with chloride, and so are useful supporting tracers of salinity.

The transition metals and heavy metals have low crustal abundance and so are typically found at only trace concentrations in waters. Many are commonly derived from human activities and so have specified water quality objectives (Table 1-5). Redox is an important solubility control that can enhance transport, as in the case of U under oxidizing conditions or Fe under reducing conditions. The analysis of trace metals depends on the objectives of the study, and can vary from a select few analytes to a full scan of metals.

Table 1-6 Additional compounds and parameters typically analysed in water quality studies, and their Maximum Contaminant Level in drinking water, US Environmental Protection Agency (¹ www.epa.gov) and Environment Canada (² www.ec.gc.ca)

<i>Inorganic elements (mg/L)</i>					
Antimony — Sb	0.006 ^{1,2}	Chromium — Cr	0.1 ^{1,2}	Selenium — Se	0.01 ²
Arsenic — As	0.005 ¹	Copper — Cu	1.3 ^{1,2}	Thallium — Tl	0.002 ¹
Barium — Ba	1 ²	Cyanide — CN ⁻	0.2 ^{1,2}	Silver — Ag	0.05 ²
Boron — B	5.0 ²	Lead — Pb	0.015 ¹	Uranium — U	0.02 ²
Beryllium — Be	0.004 ¹	Mercury — Hg	0.001 ²	Zinc — Zn	5 ^{1,2}
Cadmium — Cd	0.005 ^{1,2}				

<i>Selected organic parameters (µg/L)^{source}</i>					
Atrazine ^p	3	Dioxin ¹	0.00003	Pentachlorophenol ⁱⁿ	1
Benzene ^{hc}	5	Ethylbenzene ^{hc}	700	Trichloroethylene ^s	5
Carbon tetrachloride	5	Hexachlorobenzene ⁱⁿ		Toluene ^{hc}	1000
2,4-D ^h	70	Lindane ^h	0.2	THMs ^{wc}	100
1,2-Dichloroethane ^s	5	PCBs ⁱⁿ	0.5	Vinyl chloride ⁱⁿ	2

Source: ^p pesticide, ^{hc} hydrocarbon, ^h herbicide, ^s solvent, ¹ incineration, ⁱⁿ industrial, ^{wc} water chlorination

<i>Radiological parameters (Bq/L)</i>					
¹³⁷ Cs	50	²²⁶ Ra	1	³ H	7000
¹³¹ I	10	⁹⁰ Sr	10	Gross alpha	0.55

<i>Microorganisms (colonies per 100mL)</i>			
Total coliform	10	Fecal coliform	0
<i>E. coli</i>	0	<i>Giardian lamblia</i>	0

Charge balance and the analysis error

The accuracy of a geochemical analysis can be tested by comparing the total of the negative charges in solution with the total of positive charges. The laboratory analyses are converted to equivalents (meq = ppm×valence/gfw) for the major and minor species. The difference between the sum of all major cations (Σcat) and anions (Σan) is then compared with the sum of all major ions according to give the error on the geochemical analysis:

$$\text{Analytical error (\%)} = \frac{\Sigma\text{cat} - \Sigma\text{an}}{\Sigma\text{cat} + \Sigma\text{an}} \times 100$$

The measured alkalinity (in meq/L) should be used in the charge balance rather than the derived concentrations of carbonate species. Further, in solutions with a very low or high pH, the activities of H⁺ or OH⁻ should be use in the calculation. A charge balance error of less than 5% is acceptable. When errors are greater than 5%, a major contributing species may have been overlooked, or a parameter such as pH or alkalinity not correctly calculated. An excess of cations may have been analyzed if samples were acidified but not filtered. Low salinity waters, including surface waters, achieving a good charge balance due to the

inherently larger percent error on individual analyses, and in particular for alkalinity titrations (discussed below).

Example 1-3 Determination of analysis error for geochemical analyses

Determine the analysis error for these two geochemical analyses of spring waters, (values in mg/L):

	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	Cl ⁻
Spring A	7.55	72.5	32.2	132	10.6	177	0.27	126	213
Spring B	10.40	1.91	0.12	42.5	0.20	19.2	21.1	11.7	10.1

Converting data to meq/L

(e.g. Ca²⁺ in Spring A = 72.5/40.1x2 = 3.62 meq/L)

Spring A	7.55	3.62	2.65	5.74	0.27	2.90	0.01	2.62	6.00
Spring B	10.40	0.10	0.01	1.85	0.01	0.31	0.70	0.24	0.28

Calculation of the analysis error is then:

$$\text{Spring A analysis error} = \frac{12.28 - 11.53}{12.28 + 11.53} \times 100 = 3.1\%$$

$$\text{Spring B analysis error} = \frac{1.96 - 1.54}{1.96 + 1.54} \times 100 = 11.8\%$$

The error for Spring A is quite acceptable although for Spring B there is an excess of cations over anions. However, considering the high pH, it is possible that the hydroxide concentration (OH⁻) might make a considerable contribution to the anion total.

At neutral pH, both H⁺ and OH⁻ have concentrations (activities) of 10⁻⁷ mol/L and do not contribute significantly to the dissolved ion load of most waters. At pH 10.4, H⁺ has an activity of 10^{-10.4}. As the dissociation of water, H₂O ↔ H⁺ + OH⁻, has a dissociation constant of 10⁻¹⁴, the OH⁻ activity increases at this pH to 10^{-3.6} (14 - 10.4), or 0.25 meq/L. When this contribution is added to the 1.53 meq/L of HCO₃⁻, SO₄²⁻ and Cl⁻ anions, the charge balance error reduces to an acceptable 4.0%.

Further reading:

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Kendall, C. and Caldwell, E.A., 1998. Fundamentals of Isotope Geochemistry. Chapter 2 in: *Isotope Tracers in Catchment Hydrology* (C. Kendall and J.J. McDonnell, editors), Elsevier, pp. 51-86.

Moses, C.O., 1999. Water. *In: Encyclopedia of Geochemistry* (C. Marshall and R.W. Fairbridge, editors), Encyclopedia of Earth Sciences Series, Kluwer Academic, pp. 661-666.

Faure, G., 1998. *Principles and Applications of Geochemistry* Second Edition. Prentice Hall, New Jersey, 600 pp.

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Problems

1. Calculate the TDS for each of the water quality analyses in Table 1-4 and classify them according to their salinity.
2. For each of the water samples in Table 1-4, determine the concentration for Cl^- in the following units: mg/L, ppm, meq/L, M and *m*. Given an acceptable error on the analysis of Cl^- to be $\pm 5\%$ of the measurement, can ppm and mg/L be used interchangeably for these data?
3. Runoff water from a sulfur extraction plant has the following basic geochemical composition:
pH = 2.3; $\text{Ca}^{2+} = 25 \text{ mg/L}$; $\text{SO}_4^{2-} = 300 \text{ mg/L}$
Does this analysis conform to the law of electro-neutrality?
4. A sample of river water has measured stable isotope values of $\delta^{18}\text{O} = -6.8\text{‰}$ VSMOW and $\delta\text{D} = -44\text{‰}$ VSMOW. What are the isotope abundance ratios ($^{18}\text{O}/^{16}\text{O}$ and $\text{D}/^1\text{H}$) for this water?
5. Two samples of precipitation taken in summer and winter had the following $\delta^{18}\text{O}$ values:
 $\delta^{18}\text{O}_{\text{summer}} = -3.0\text{‰}$ and $\delta^{18}\text{O}_{\text{winter}} = -10.0\text{‰}$ VSMOW. Which has the greater concentration of ^{18}O and by how much?
6. What are some potential sources of SO_4^{2-} and Cl^- in groundwaters? What about HCO_3^- ?