

Problems

1. Calculate the TDS for each of the water quality analyses in Table 1-7, and if there are differences from the measured TDS values, suggest reasons why.

The TDS is calculated by adding the ppm (or mg/L) values for all major ions. Some minor ions will also contribute, particularly in low salinity solutions (e.g. nitrate in rain) and so must be included.

	Rain	River	Groundwater	Seawater	Brine
total dissolved solids — TDS, measured	2.90	66.4	469	34,900	289,000
total dissolved solids — TDS, calculated	2.94	104	675	35,052	289,000

The principal difference between measured and calculated TDS is the loss of CO₂ from the bicarbonate (alkalinity) by drying as roughly half only will remain to form calcium and magnesium carbonate. This is mostly observed in the river and groundwater. The seawater and brine are mostly chloride salts and the carbonate component is minor.

2. For each of the water samples in Table 1-7, determine the concentration for Cl⁻ in the following units: molality, *m*, molarity, *M*, mg/L and meq/L. Given an acceptable error on the analysis of Cl⁻ to be ±5% of the measurement, could the units of mg/L and ppm be used interchangeably?

chloride — Cl ⁻ ppm	0.31	2.4	58.6	19,350	185,000
<i>m</i>	8.73E-06	6.76E-05	1.65E-03	5.45E-01	5.22
<i>M</i>	8.71E-06	6.74E-05	1.65E-03	5.26E-01	5.02
mg/L	0.31	2.4	58.6	19,062	177,785
meq/L	0.009	0.068	1.65	537	5008
error, %	0.0	0.0	0.0	0.9	3.9

3. Runoff water from a sulfur extraction plant has the following geochemical composition: pH = 2.3; Ca²⁺ = 25 mg/L; SO₄²⁻ = 300 mg/L

Does this analysis conform to the law of electro-neutrality?

sum cations:	Ca ²⁺ – 25/40.1*2 = 1.25	sum anions:	SO ₄ ²⁻ – 300/96x2 = 6.25
	H ⁺ – 10 ^{-2.3} x1000 = 5.01		OH ⁻ – 10 ^{-11.7} x 1000 = 0.00
	6.25 meq/L		6.25 meq/L

Yes it does. Note that the contribution of H⁺ at this low pH is included in the sum of the cations. In neutral pH waters it is not significant in the charge balance.

4. What are the ion concentrations in mg/L and the TDS (mg/L) of a solution with 0.01 mmol/L NaCl, 0.005 mmol/L CaSO₄ and 0.05 mmol/L CaCO₃?

These salts in solution give the following concentrations, calculated by multiplying the amount of each compound (in mmol/L) by the gfw of each solute and again by the number of atoms of the element per unit of the compound (1 for all these salts in this question):

		Na ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	CO ₃ ²⁻	
mmol/L	gfw	23	40.1	35.5	96.1	60	
0.1	NaCl	2.3		3.55			
0.05	CaSO ₄		2.01		4.81		
1	CaCO ₃		40.1			60	
	mg/L	2.3	42.1	3.55	4.81	60	TDS = 112.8

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The solution then has 2.3 mg/L Na⁺, 42.1 mg/L Ca²⁺, 3.55 mg/L Cl⁻, 4.81 mg/L SO₄²⁻ and 60 mg/L CO₃²⁻. Note that while CO₃²⁻ is a dissociation product of CaCO₃, in most waters it is generally converted to bicarbonate, HCO₃⁻.

5. What are the mg/L concentrations of Ca²⁺, SO₄²⁻, CO₃²⁻ and Cl⁻, and TDS, in groundwater which has dissolved 1 g gypsum, 0.5 g calcite and 0.05 g calcium chloride?

g		gfw	moles	Ca ²⁺ mg/L	Cl ⁻ mg/L	SO ₄ ²⁻ mg/L	CO ₃ ²⁻ mg/L	TDS mg/L
1	CaSO ₄ ·2H ₂ O	172.2	0.005807	233		558		
0.5	CaCO ₃	100.1	0.004995	200			300	
0.05	CaCl ₂	110.7	0.000452	18	32			
Total	mg/L			451	32	558	300	1341

First, calculate the moles of each mineral dissolved in the groundwater. The moles of each solute is equal to the mineral molalities multiplied by the stoichiometric representation of that element in the mineral (for example, 1 mole of CaCl₂ yields 2 moles of Cl⁻).

6. Which of these two groundwaters has the higher meq/L concentration of cations?
 A – groundwater with 1 g/L gypsum
 B – groundwater with 1 g/L dolomite

g	mineral	gfw	moles	Ca(meq/L)
1	CaSO ₄ ·2H ₂ O	172.2	0.005807	11.6
1	CaMg(CO ₃) ₂	184.4	0.005423	10.8

Find the moles of each mineral in solution by dividing grams by gfw. This gives the number of moles of Ca²⁺ in solution, or meq/L Ca²⁺ (moles x 1000 x charge, z). Gypsum yields more Ca²⁺ in solution.

7. Stable isotope data are always expressed relative to an internationally recognized standards or reference materials which have a known isotope ratio. What is the reference material for isotopes of water (¹⁸O and D), what are its ¹⁸O/¹⁶O and D/H ratios, and how are isotope ratios measured by stable isotope mass spectrometry (IRMS) normalized to the reference standard.

The international standard for water isotopes is VSMOW – the Vienna Standard Mean Ocean Water, with ¹⁸O/¹⁶O = 2.0052 · 10⁻³ and D/H = 1.5575 · 10⁻⁴. The ratio measured by IRMS, while being very precise, is not accurate. Referencing to a known standard provides this accuracy, and is expressed as:

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

8. 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 (¹⁸O/¹⁶O and D/¹H) for this water?

$$\begin{aligned} \delta^{18}\text{O}_{\text{river}} &= -6.8\text{‰ VSMOW} \\ \delta\text{D}_{\text{river}} &= -44\text{‰ VSMOW} \\ ^{18}\text{O abundance ratio for VSMOW} &= 2.0052 \cdot 10^{-3} \text{ (from Table 1-3)} \\ \text{D abundance ratio for VSMOW} &= 1.5575 \cdot 10^{-4} \text{ (from Table 1-3)} \\ \delta^{18}\text{O}_{\text{sample}} &= \left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{reference}}} - 1 \right) \cdot 1000 \end{aligned}$$

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$$-6.8 = \left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{river}}}{2.0052 \cdot 10^{-3}} - 1 \right) \cdot 1000$$

$$(^{18}\text{O}/^{16}\text{O})_{\text{river}} = 1.9916 \cdot 10^{-3}$$

$$(\text{D}/^1\text{H})_{\text{river}} = 1.4890 \cdot 10^{-4}$$

9. 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?

$$\delta^{18}\text{O}_{\text{summer}} = -3.0\text{‰} \quad \delta^{18}\text{O}_{\text{winter}} = -10.0\text{‰}$$

$$(^{18}\text{O}/^{16}\text{O})_{\text{summer}} = 1.9992 \cdot 10^{-3} \quad (^{18}\text{O}/^{16}\text{O})_{\text{winter}} = 1.9851 \cdot 10^{-3}$$

$$\text{permil difference} = \left(\frac{(^{18}\text{O}/^{16}\text{O})_{\text{summer}}}{(^{18}\text{O}/^{16}\text{O})_{\text{winter}}} - 1 \right) \cdot 1000$$

$$= \left(\frac{1.9992 \cdot 10^{-3}}{1.9851 \cdot 10^{-3}} - 1 \right) \cdot 1000$$

$$= 7.10\text{‰}$$

The summer rain is enriched by 7.1‰ in ^{18}O . Note that a common shortcut is to simply subtract one from the other, i.e. $(-3.0) - (-10.0) = 7.0\text{‰}$, which gives an error within the analytical precision.

10. What are the four most abundant elements by mass in the Earth's crust, and in what mineral groups do they dominate?

O — 46.6%	Most minerals contain oxygen
Si — 27.7%	Silicate minerals include the feldspars, ferromagnesian minerals (olivines, pyroxenes and amphiboles), micas, clay minerals and quartz.
Al — 8.13%	Feldspars, micas and clay minerals
Fe — 5.00%	Ferromagnesian silicates, sulfides, iron oxides and hydroxides.

11. List the four major cations in natural waters and give two common minerals that represent a major weathering source for each.

Ca^{2+} :	calcite — CaCO_3 , anorthosite — $\text{CaAl}_2\text{Si}_2\text{O}_8$
Mg^{2+} :	dolomite — $\text{CaMg}(\text{CO}_3)_2$, Pyroxene — $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$
Na^+ :	halite — NaCl , albite — $\text{NaAlSi}_3\text{O}_8$
K^+ :	sylvite — KCl , orthoclase — KAlSi_3O_8

Note that K^+ and Mg^{2+} have lower crustal abundances than their adjacent group elements N^+ and Ca^{2+} and so are commonly found substituting for them in impure mineral phases.

12. What are some potential sources of SO_4^{2-} and Cl^- in groundwaters? What about HCO_3^- ?



- dissolution of gypsum and anhydrite
- oxidation of pyrite and other sulfide minerals
- mixing with seawater or other high salinity brines
- sour-gas plants
- atmospheric sources – seaspray aerosols, coal-fired power plants



- road salt
- evaporites with halite
- leaching from crustal rocks
- mixing with seawater or brines



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- soils – uptake of CO₂ and dissociation of carbonic acid
- dissolution of carbonate rocks (esp. limestone and dolomite)
- deep sources of CO₂ from mantle and metamorphism (in tectonic settings)
- oxidation of organics in the aquifer (e.g. buried peat)

13. Name as many gases as you can that are commonly found in groundwater that are: (i) essentially of an atmospheric origin, (ii) produced in the soil or groundwater by geochemical processes, and (iii) geogenic gases produced by reactions in bedrock. Note that some gases can originate from more than one of these sources.

(i) Atmospheric — N₂, O₂, Ar, Ne, Kr, Xe, CO₂ (minor)

(ii) Soil and groundwater — CO₂ (aerobic and anaerobic biodegradation)
— CH₄ (bacterial methanogenesis in saturated soils)
— N₂ (from NO₃⁻ and NH₄⁺)

(iii) Geogenic — He (from α decay of U and Th series nuclides),
— Ar (from β decay of ⁴⁰K)
— CH₄ (from high temperature modification of organic-rich rocks)
— CO₂ (from metamorphic zones, volcanism, and mantle degassing)