

Soil and Environmental Chemistry: Exercises

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Note to Instructors

This manual contains conventional solutions to all chapter exercises. Follow the permalink below to access Excel spreadsheets for each quantitative chapter exercise.

Instructor's Manual Permalink

<http://soilenvirochem.net/6ZQu8S>

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1. Elemental Abundance

A. Calculate the binding energy per nucleon E_b/A in MeV for the carbon isotope $^{12}_6\text{C}$. The proton, neutron and electron rest mass values are: $m_p = 1.00727646688 \text{ Da}$, $m_n = 1.00866491588 \text{ Da}$, $m_e = 0.00054857995 \text{ Da}$.

The mass-energy equivalent is: $1 \text{ Da} = 931.4940954 \text{ MeV}$. You can obtain a complete list of isotope rest masses from the National Institute of Standards and Technology (www.physics.nist.gov/).

Solution

Carbon isotope $^{12}_6\text{C}$ rest mass is, by definition: $m_0 \equiv 12.0000000 \text{ Da}$. Given the relative abundance of the two stable carbon isotopes $^{12}_6\text{C}$ and $^{13}_6\text{C}$, the (relative) atomic mass for carbon is: $A_r(\text{C}) = 12.0107 \text{ g} \cdot \text{mol}^{-1}$.

$$m_u \equiv \frac{m_a(^{12}_6\text{C})}{12} = 1.660539040 \cdot 10^{-27} \text{ kg} \quad (1.1)$$

$$A_r(\text{C}) = \frac{\overline{m}_a(\text{C})}{m_u} \quad (1.2)$$

$$A_r(\text{C}) = \left(\left(\frac{m_a(^{12}_6\text{C})}{m_u} \cdot (0.9893) \right) + \left(\frac{m_a(^{13}_6\text{C})}{m_u} \cdot (0.0107) \right) \right) \quad (1.3)$$

$$A_r(\text{C}) = ((12.0000 \cdot (0.9893)) + (13.0034 \cdot (0.0107))) = 12.0107 \quad (1.4)$$

Each subatomic particle in $^{12}_6\text{C}$ has a rest mass—proton, neutron and electron—which allows us to compute a mass that does not count the binding energy.

$$m(^A_Z\text{E}) = Z \cdot (m_p + m_e) + N \cdot m_n \quad (1.5)$$

$$m(^{12}_6\text{C}) = 6 \cdot (m_p + m_e) + 6 \cdot m_n \quad (1.6)$$

$$m({}^{12}_6\text{C}) = 6 \cdot ((1.00727646688) + (0.00054857995)) + \quad (1.7)$$

$$6 \cdot (1.00866491588) = 12.0989398 \text{ Da} \quad (1.8)$$

The ${}^{12}_6\text{C}$ nuclear mass defect $\Delta m({}^{12}_6\text{C})$ is the difference between $m({}^{12}_6\text{C})$ and $m_a({}^{12}_6\text{C})$.

$$\Delta m({}^{12}_6\text{C}) = m({}^{12}_6\text{C}) - m_a({}^{12}_6\text{C}) \quad (1.9)$$

$$\Delta m({}^{12}_6\text{C}) = 12.0989398 - 12.0000000 = 0.0989398 \text{ Da} \quad (1.10)$$

The nuclear binding energy per nucleon E_b/A for carbon isotope ${}^{12}_6\text{C}$ is computed by dividing the nuclear mass defect $\Delta m({}^{12}_6\text{C})$ by the mass number A and applying the mass-energy equivalent¹ to convert mass units to energy units: $1 \text{ Da} = 931.4940953 \text{ MeV}$.

$$E_b({}^A_Z\text{E})/A = \frac{(\Delta m({}^A_Z\text{E}) \text{ Da}) \cdot (931.4940953 \text{ MeV} \cdot \text{Da}^{-1})}{A} \quad (1.11)$$

$$E_b({}^{12}_6\text{C})/A = \frac{0.0989398 \text{ Da} \cdot (931.4940953 \text{ MeV} \cdot \text{Da}^{-1})}{12} = 7.680151 \text{ MeV} \quad (1.12)$$

¹ $E = m_u \cdot c^2 = 931.4940953 \text{ MeV}$

B. List the stable isotopes for all Period 3 elements (Na through Ar) and explain why some elements have more stable isotopes than others. Stable isotopes and their relative abundances are compiled by the *National Institute of Standards and Technology*: www.physics.nist.gov.

Answer

Table 1.1: Isotopes and their relative abundance for all Period 3 elements.

Z	E	A	N	Abundance
				%
11	Na	23	<u>12</u>	100.00
<u>12</u>	Mg	24	<u>12</u>	78.99
<u>12</u>	Mg	25	13	10.00
<u>12</u>	Mg	26	<u>14</u>	11.01
13	Al	27	<u>14</u>	100.00
<u>14</u>	Si	28	<u>14</u>	92.22
<u>14</u>	Si	29	15	4.69
<u>14</u>	Si	30	<u>16</u>	3.09
15	P	31	<u>16</u>	100.00
<u>16</u>	S	32	<u>16</u>	94.99
<u>16</u>	S	33	17	0.75
<u>16</u>	S	34	<u>18</u>	4.25
<u>16</u>	S	36	20	0.01
17	Cl	35	<u>18</u>	75.76
17	Cl	37	20	24.24
<u>18</u>	Ar	36	<u>18</u>	0.33
<u>18</u>	Ar	38	20	0.06
<u>18</u>	Ar	40	<u>22</u>	99.60

Spin-paired protons (even atomic numbers Z) and spin-paired neutrons (even neutron numbers N) are underlined in Table 1.1. Elements with spin-paired protons have more stable isotopes than elements with unpaired protons (odd Z). Elements with unpaired protons generally have only one stable isotope with spin-paired neutrons. The exception among Period 3 elements is chlorine with two isotopes. Isotope $^{37}_{17}\text{Cl}$ owes its existence to a *magic number* (**20**) of neutrons.

C. Figure 2 (*cf.* Chapter 1, Elemental Abundance) plots the relative abundance of several elements in the solar system, Earth's crust and Earth's soil. Explain the factors that determine the relative abundance of the following elements: cobalt $_{27}\text{Co}$, nickel $_{28}\text{Ni}$ and copper $_{29}\text{Cu}$.

Answer

The silicon-normalized relative molar abundance of cobalt $_{27}\text{Co}$, nickel $_{28}\text{Ni}$ and copper $_{29}\text{Cu}$ in the Earth's outer crust are: $n(_{27}\text{Co})/n(_{14}\text{Si}) = 4.22 \cdot 10^{-5}$, $n(_{28}\text{Ni})/n(_{14}\text{Si}) = 1.43 \cdot 10^{-4}$ and $n(_{29}\text{Cu})/n(_{14}\text{Si}) = 9.40 \cdot 10^{-5}$. Of the three elements, nickel is the most abundant. A similar pattern applies to solar abundances.

Cobalt $_{27}\text{Co}$, which has an uneven atomic number, has one stable isotope $^{59}_{27}\text{Co}$ with an even number of 32 neutrons. Copper $_{29}\text{Cu}$, which also has an uneven atomic number, has two stable isotopes, both with an even number of neutrons (34 and 36, respectively): $^{63}_{29}\text{Cu}$ and $^{65}_{29}\text{Cu}$.

Not only does nickel $_{28}\text{Ni}$ has an even atomic number it has a *magic* atomic number **28**. As a consequence of spin-paired protons and a completely-filled proton nuclear shell, nickel has five stable isotopes: $^{58}_{28}\text{Ni}$, $^{60}_{28}\text{Ni}$, $^{61}_{28}\text{Ni}$, $^{62}_{28}\text{Ni}$, $^{64}_{28}\text{Ni}$. Four of the nickel isotopes have an even number of neutrons.

The even-odd principle accounts for the higher abundance of nickel relative to cobalt and copper. The existence of $^{61}_{28}\text{Ni}$ is probably the result of the magic atomic number.

D. List the half-life of the longest-lived isotope for each element from Po to Th ($84 < Z < 90$). A complete *Table of the Isotopes* is available on the *Abundances of the Elements* (Kaye and Laby Tables of Physical and Chemical Constants, National Physics Laboratory; www.kayelaby.npl.co.uk).

Answer

Table 1.2: The longest-lived unstable isotope and the half-life for its radioactive decay for elements from ${}_{84}\text{Po}$ to ${}_{90}\text{Th}$.

Element	Atomic Symbol	Isotope	Half-life
Polonium	Po	${}^{209}_{84}\text{Po}$	102 years
Astatine	At	${}^{210}_{85}\text{At}$	8.1 hours
Radon	Rn	${}^{222}_{86}\text{Rn}$	3.824 days
Francium	Fr	${}^{223}_{87}\text{Fr}$	21.8 minutes
Radium	Ra	${}^{226}_{88}\text{Ra}$	1600 years
Actinium	Ac	${}^{227}_{89}\text{Ac}$	21.77 years
Thorium	Th	${}^{232}_{90}\text{Th}$	$1.405 \cdot 10^{10}$ years

The half-life of the longest-lived isotope for each element from Po to Th ($84 < Z < 90$) appear in [Table 1.2](#). Bismuth, which has a single isotope ${}^{209}_{83}\text{Bi}$, is the final stable element in the Periodic Table. All remaining elements exist solely as radioactive nuclides.

The time-scale for neutron capture under low neutron-flux (*i.e.*, *s-process*) conditions in the stellar core is on the order of 100–1000 years. The rate of *s-process* neutron capture relative to the half-life of short-lived isotopes listed above means nucleosynthesis is unable to bridge the gap between bismuth and thorium.

E. A reactor accident occurred in Chernobyl, Ukraine in 1986 that deposited $^{137}_{55}\text{Cs}$ and other fission products in a large region of Ukraine, Belarus, and Russia. A significant fraction of the area was contaminated by Cs-137 at levels of $37\text{-}555 \text{ GBq} \cdot \text{km}^{-2}$, equivalent to a radioactivity of $0.055\text{-}0.833 \text{ Bq} \cdot \text{g}^{-1}$ in the top 1 meter of soil.

Cs-137 is a radioactive nuclide with a half-life of $t_{1/2} \approx 30 \text{ years}$. Estimate the length of time necessary for soil Cs-137 levels in this zone to reach $0.018 \text{ Bq} \cdot \text{g}^{-1}$, a level of radioactivity associated with a lifetime cancer risk of 3 per 100,000 persons living in the area.

Solution

The number of half-lives is calculated using this formula.

$$c(n) = c_0 \cdot (1/2)^n \quad (1.1)$$

$$n = \frac{\log_{10}(c(n)/c_0)}{\log_{10}(1/2)} \approx \frac{\log_{10}(c(n)/c_0)}{\log_{10}(-0.3010)} \quad (1.2)$$

Using the highest Cs-137 concentration at the soil surface and the target Cs-137 soil concentration, the number of half lives is: $n = 5.5$.

$$n \approx \frac{\log_{10}(0.018/8.33)}{\log_{10}(-0.3010)} = \frac{\log_{10}(0.0222)}{\log_{10}(-0.3010)} = 5.5 \quad (1.3)$$

The length of time necessary for soil Cs-137 levels in this zone to reach $0.018 \text{ Bq} \cdot \text{g}^{-1}$ is 160 years.

$$t = n \cdot t_{1/2} \approx 5.5 \cdot (30 \text{ years}) = 160 \text{ years} \quad (1.4)$$

F. The Earth's crust contains thorium and uranium although no stable isotope exists for either element. Explain why these unstable elements are present in the Earth's crust.

Answer

Although both all thorium ${}_{90}\text{Th}$ and uranium ${}_{92}\text{U}$ are unstable, the radioactive-decay half-lives are very long compared to the lifetime of the solar system.

For example, the half-life for the unstable uranium isotope ${}^{235}_{92}\text{U}$ is: $t_{1/2} = 7.04 \cdot 10^8 \text{ years}$. During the entire 4.6 billion-year lifetime of the solar system ${}^{235}_{92}\text{U}$ has decayed to 1% of its original amount in the primordial gas cloud.

Isotope ${}^{232}_{90}\text{Th}$ accounts for 100% of the solar system thorium content despite being an unstable nuclide. The half-life for thorium isotope ${}^{232}_{90}\text{Th}$ is: $t_{1/2} = 1.405 \cdot 10^{10} \text{ years}$, 30 times the estimated lifetime of the solar system.

Isotope ${}^{238}_{92}\text{U}$ accounts for 99.2742% of the solar system uranium content despite being an unstable nuclide. The half-life for uranium isotope ${}^{238}_{92}\text{U}$ is: $t_{1/2} = 4.468 \cdot 10^9 \text{ years}$, about 10 times the estimated lifetime of the solar system.

Finally, uranium isotope ${}^{234}_{92}\text{U}$ has a significantly shorter half-life than the two most abundant uranium isotopes ${}^{238}_{92}\text{U}$ and ${}^{235}_{92}\text{U}$, yet ${}^{234}_{92}\text{U}$ accounts for 0.0054% of the solar system uranium content. Uranium ${}^{234}_{92}\text{U}$ is a product in the ${}^{238}_{92}\text{U}$ decay chain. Radioactive decay of ${}^{238}_{92}\text{U}$ sustains the solar system ${}^{234}_{92}\text{U}$ content.

G. The Earth's crust is depleted of certain elements relative to the overall composition of the Solar System. Explain why the following elements (helium, neon, argon, krypton, xenon, silver, gold, platinum) are depleted in the crust.

Answer

Elements He, Ne, Ar, Kr, Xe are noble gases with little tendency to react with other elements to form compounds and exist as gases under the temperature and pressure conditions on planet Earth. These gaseous elements are lost not only from the solid Earth but also from the atmosphere of all terrestrial planets. Elements Ag, Au, and Pt are noble metals with little tendency to react with other elements to form compounds but exist in solid form under the temperature and pressure conditions on planet Earth. These dense solid elements were depleted from the crust and drawn by gravity into the solid metallic core.

H. Explain the significance of the following geochemical terms: atmophilic, lithophilic, siderophilic, and chalcophilic.

Answer

Goldschmidt (1937) used the term *atmophilic* to identify elements that tend to exist as gaseous compounds on the conditions that existed when the Earth's crust formed. These elements were distilled from the basic silicate Earth to form the atmosphere.

The term *siderophilic* to applies to magnetic Group 8 through Group 10 elements in Periods 4, 5 and 6 that form the bulk of the Earth's solid magnetic core.

The term *chalcophilic* to applies Group 16 elements in Periods 3, 4 and 5 that form sulfide, selenide and telluride minerals. The chalcophilic minerals have a higher specific gravity than silicate oxide minerals. Flotation depletes the Earth's solid inner and outer crust and enriches these minerals deep within the molten mantle.

The term *lithophilic* to applies the elements that form silicate and oxide compounds with a relatively high melting temperature. Flotation enriches these compounds in the solid Earth's inner and outer crust.

I. The following data are the vanadium content of samples of Canadian granite (Ahrens, 1954). Determine the geometric mean and geometric standard deviation from this data set.

Table 1.3: The vanadium content in 27 Canadian granite specimens (Source: Ahrens, 1954).

Sample	$w(V)$	Sample	$w(V)$
	$mg \cdot kg^{-1}$		$mg \cdot kg^{-1}$
G-1	21	KB-1	75
KB-2	43	KB-3	200
KB-4	50	KB-5	7.5
KB-6	30	KB-7	33
KB-8	27	KB-9	34
KB-10	42	KB-11	10
KB-12	52	KB-13	51
KB-14	182	KB-15	630
KB-16	144	KB-17	94
KB-18	94	KB-19	29
48-63	8	48-115	11
48-158	5.5	48-118	23
48-485	19	48-489	7
48-490	5.6		

Solution

The following table lists the base-10 logarithmic transform vanadium contents in 27 Canadian granite specimens. Arithmetic statistics are computed from the logarithmic-transformed data while the geometric statistics are computed from the anti-logarithm of the arithmetic statistics. As a consequence, the logarithmic base used has no effect on the final geometric statistics.

Logarithmic-Transform

$$y(V)_i \equiv \log_{10}(w(V)_i) \quad (1.5)$$

Central Tendency Estimate : Arithmetic Mean

$$\bar{y}(V)_A = \frac{1}{27} \cdot \sum_{i=1}^{27} (y(V)_i) = 1.53 \quad (1.6)$$

Arithmetic Standard Error

$$SE(\bar{y}(V)_A) = \sqrt{\frac{1}{27} \cdot \sum_{i=1}^{27} (\bar{y}(V)_A - y(V)_i)^2} = 0.520 \quad (1.7)$$

Table 1.4: Base-10 logarithmic transform of vanadium content (original data units: $mg \cdot kg^{-1}$) in 27 Canadian granite specimens (Source: Ahrens, 1954).

Sample	$\log_{10} w(V)$	Sample	$\log_{10} w(V)$
G-1	21	KB-1	75
G-1	1.32	KB-1	1.88
KB-2	1.63	KB-3	2.30
KB-4	1.70	KB-5	0.88
KB-6	1.48	KB-7	1.52
KB-8	1.43	KB-9	1.53
KB-10	1.62	KB-11	1.00
KB-12	1.72	KB-13	1.71
KB-14	2.26	KB-15	2.80
KB-16	2.16	KB-17	1.97
KB-18	1.97	KB-19	1.46
48-63	0.90	48-115	1.04
48-158	0.74	48-118	1.36
48-485	1.28	48-489	0.85
48-490	0.75		

Central Tendency Estimate : Geometric Mean

$$\bar{w}(V)_G = 10^{\bar{y}(V)_A} = 10^{+1.53} = 33.7 \, mg \cdot kg^{-1} \quad (1.8)$$

Geometric Standard Error

$$SE(\bar{w}(V)_G) = 10^{SE(\bar{y}(V)_A)} = 10^{+0.52} = 3.29 \, mg \cdot kg^{-1} \quad (1.9)$$

J. The data below is the nitrogen content of soil specimens collected in Black Hawk County, Iowa (Professor M. E. Thompson, Iowa State University). Determine the arithmetic mean and geometric mean soil nitrogen content of this data set.

Table 1.5: The organic nitrogen content of soil specimens from Black Hawk, County, Iowa.

Bulk Density	Organic Nitrogen	Bulk Density	Organic Nitrogen
$Mg \cdot m^{-3}$	$mg_N \cdot g^{-1}$	$Mg \cdot m^{-3}$	$mg_N \cdot g^{-1}$
1.37	1.010	1.36	1.988
1.39	1.495	1.34	2.091
1.30	1.496	1.32	2.272
1.39	1.510	1.30	2.445
1.20	1.555	1.21	2.882
1.31	1.679	1.31	2.898
1.31	1.723	1.31	3.054
1.32	1.774	1.37	3.655
1.37	1.786	1.31	3.763
1.31	1.936	1.28	5.289
1.28	1.955		

Solution

The following table lists the base-10 logarithmic transform organic nitrogen contents in 21 soil specimens (Black Hawk County, Iowa). Arithmetic statistics are computed from the logarithmic-transformed data while the geometric statistics are computed from the anti-logarithm of the arithmetic statistics. As a consequence, the logarithmic base used has no effect on the final geometric statistics.

Logarithmic-Transform

$$y(N)_i \equiv \log_{10}(w(N)_i) \quad (1.10)$$

Central Tendency Estimate : Arithmetic Mean

$$\bar{y}(N)_A = \frac{1}{21} \cdot \sum_{i=1}^{21} (y(N)_i) = 0.328 \quad (1.11)$$

Arithmetic Standard Error

$$SE(\bar{y}(N)_A) = \sqrt{\frac{1}{21} \cdot \sum_{i=1}^{21} (\bar{y}(N)_A - y(N)_i)^2} = 0.168 \quad (1.12)$$

Table 1.6: Base-10 logarithmic transform of organic nitrogen content (original data units: $mg \cdot g^{-1}$) in soil specimens from Black Hawk County, Iowa.

$\log_{10} w(N)$	$\log_{10} w(N)$
0.004	0.298
0.175	0.320
0.175	0.356
0.179	0.388
0.192	0.460
0.225	0.462
0.236	0.485
0.249	0.563
0.252	0.576
0.287	0.723
0.291	

Central Tendency Estimate : Geometric Mean

$$\bar{w}(N)_G = 10^{\bar{y}(N)_A} = 10^{+0.328} = 2.13 \, mg \cdot g^{-1} \quad (1.13)$$

Geometric Standard Error

$$SE(\bar{w}(N)_G) = 10^{SE(\bar{y}(N)_A)} = 10^{+0.168} = 1.47 \, mg \cdot g^{-1} \quad (1.14)$$

2. Chemical Hydrology

A. A cylindrical soil core ($L = 20 \text{ cm}$, $r = 3 \text{ cm}$) was collected from a field site in Madison County, Iowa. The weight of the empty metal cylinder is: $m_1 = 225 \text{ g}$. The metal cylinder containing field-moist soil is weighed ($m_2 = 1217.8 \text{ g}$) then dried in a 100°C oven until it ceases to lose weight. The weight of the cylinder containing oven-dried soil is: $m_3 = 977.1 \text{ g}$.

Calculate: 1) the mass water content $w_{fm} [Mg \cdot Mg^{-1}]$ of the field moist soil and 2) the *moist* soil bulk density $\rho_t [Mg \cdot m^{-3}]$.

Solution

Part 1. Compute the mass water content of field moist soil w_{fm} .

The mass water content of the field moist soil w_{fm} is the water loss on drying m_w divided by the dry soil mass m_s . The dry mass must account for the mass of the container.

$$m_w = m_2 - m_3 = 1217.8 \text{ g} - 977.1 \text{ g} = 240.7 \text{ g} \quad (2.1)$$

$$m_s = m_3 - m_1 = 977.1 \text{ g} - 225.0 \text{ g} = 752.1 \text{ g} \quad (2.2)$$

$$w_{fm} = \frac{m_w}{m_s} = \frac{240.7 \text{ g}}{752.1 \text{ g}} = 0.320 \quad (2.3)$$

Part 2. Compute the moist soil bulk density ρ_t .

The field-moist bulk density ρ_t is field-moist soil mass m_{fm} divided by the container volume V_{fm} .

$$V_{fm} = \pi \cdot r^2 \cdot L = \pi \cdot 9 \text{ cm}^2 \cdot 20 = 565.5 \text{ cm}^3 \quad (2.4)$$

$$\rho_t = \frac{m_2 - m_1}{V_{fm}} \quad (2.5)$$

$$\rho_t = \frac{1217.8 \text{ g} - 225.0 \text{ g}}{565.5 \text{ cm}^3} = 1.76 \text{ g} \cdot \text{cm}^3 \quad (2.6)$$

The units $[g \cdot \text{cm}^3]$ are not SI Units however field-moist bulk density ρ_t in SI units is numerically equal to the value quoted above.

$$\rho_t = 1.76 \text{ g} \cdot \text{cm}^3 = 1.76 \text{ Mg} \cdot \text{m}^3 \quad (2.7)$$

B. A cylindrical soil core ($L = 20 \text{ cm}$, $r = 3 \text{ cm}$) was collected from a field site in Madison County, Iowa. The weight of the empty metal cylinder is: $m_1 = 225 \text{ g}$. The metal cylinder containing field-moist soil is weighed ($m_2 = 1217.8 \text{ g}$) then dried in a 100°C oven until it ceases to lose weight. The weight of the cylinder containing oven-dried soil is: $m_3 = 977.1 \text{ g}$.

Calculate: 1) the *moist* porosity ϕ and 2) the *volumetric* water content θ_{fm} [$\text{m}^3 \cdot \text{m}^{-3}$].

Solution

Part 1. Compute the porosity of field moist soil ϕ_{fm} .

Drying alters the volume of many soils with relatively high clay contents. This volume change is quantified as the *coefficient of linear extensibility C.O.L.E.* by the soil science community and the *shrinkage limit* by the geotechnical community.

The field-moist soil volume is V_{fm} simply the container volume.

$$V_{fm} = \pi \cdot r^2 \cdot L = \pi \cdot 9 \text{ cm}^2 \cdot 20 = 565.5 \text{ cm}^3 \quad (2.8)$$

The solids volume V_s , regardless of water content, is dry solids mass m_s divided by the solids density ρ_s . The soil science community uses the density of the mineral quartz $\text{SiO}_2(\text{s})$ as the default density for all soil minerals: $\rho_s \equiv \rho_{\text{SiO}_2(\text{s})} = 2.65 \text{ Mg} \cdot \text{m}^{-3}$.

$$m_s = m_3 - m_1 = 977.1 \text{ g} - 225.0 \text{ g} = 752.1 \text{ g} \quad (2.9)$$

$$V_s = \frac{m_s}{\rho_s} = \frac{752.1 \text{ g}}{2.65 \text{ g} \cdot \text{cm}^{-3}} = 283.8 \text{ cm}^3 \quad (2.10)$$

The field-moist porosity ϕ_{fm} is simply void volume under field-moist conditions divided by the field-moist volume V_{fm} .

$$\phi_{fm} = \frac{V_{fm} - V_s}{V_{fm}} = \frac{565.5 \text{ cm}^3 - 283.8 \text{ cm}^3}{565.5 \text{ cm}^3} = 0.498 \text{ cm}^3 \cdot \text{cm}^{-3} \quad (2.11)$$

Part 2. Compute the field-moist *volumetric* water content $\theta_{fm} [m^3 \cdot m^{-3}]$.

The *volumetric* water content $\theta_{fm} [m^3 \cdot m^{-3}]$ is computed in much the same way as the solids volume V_s . The field-moist water volume V_w is the water mass m_w divided by water density ρ_w .

$$m_w = m_2 - m_3 = 1217.8 \text{ g} - 977.1 \text{ g} = 240.7 \text{ g} \quad (2.12)$$

$$V_w = \frac{m_w}{\rho_w} = \frac{240.7 \text{ g}}{0.997 \text{ cm}^3} = 241.4 \text{ cm}^3 \quad (2.13)$$

$$\theta_{fm} = \frac{V_w}{V_{fm}} = \frac{241.4 \text{ cm}^3}{565.5 \text{ cm}^3} = 0.427 \text{ cm}^3 \quad (2.14)$$

NOTE: Chapter 2 (*Chemical Hydrology*) expression (13) offers an alternative method for computing field-moist volumetric water content θ_{fm} using the mass water content w_{fm} and *dry bulk density* ρ_b . In the present case the dry bulk density ρ_b is not quoted and, therefore, expression (13) would not be an appropriate method.

C. [Table 2.1](#) lists the physical and water retention data for the Macksburg soil series from Madison County Iowa. The Macksburg soil is located on nearly level (0-2% slopes) upland sites, has moderately high permeability and is considered well drained.

Table 2.1: Moist bulk density ρ_t and mass water contents w of the Macksburg soil from Madison County, Iowa. Mass water content at $p_{tension} = -33 \text{ kPa}$ is w_{33} and mass water content at $p_{tension} = -1500 \text{ kPa}$ is w_{1500} .

	ρ_t	w_{33}	w_{1500}
Horizon	$Mg \cdot m^{-3}$	$Mg \cdot Mg^{-1}$	$Mg \cdot Mg^{-1}$
0-15 cm	1.55	0.273	0.153
15-30 cm	1.40	0.278	0.160
30-61 cm	1.50	0.297	0.168
61-91 cm	1.52	0.292	0.180
91-107 cm	1.53	0.297	0.169

Determine the volumetric plant-available water-holding capacity θ_{AWC} of the Macksburg soil profile, reporting the water-holding capacity as centimeters of water for the 107 cm soil depth.

Solution

[Table 2.1](#) quotes the *moist* bulk density ρ_t of each soil horizon, allowing the use of expression (13) to compute the volumetric plant-available water-holding capacity θ_{AWC} of each horizon and the entire profile.

$$\rho_b = \frac{\rho_t}{1 + w_{33}} \quad (2.15)$$

$$\theta_{AWC} = (w_{33} - w_{1500}) \cdot \left(\frac{\rho_b}{\rho_w} \right) \quad (2.16)$$

$$d_{AWC} = \theta_{AWC} \cdot d_t \quad (2.17)$$

The method is illustrated for the Ap horizon (0-15 cm depth).

Horizon A1

$$\rho_b^{\text{Ap}} = \frac{1.55}{1 + 0.273} = 1.22 \text{ Mg} \cdot \text{m}^{-3} \quad (2.18)$$

Horizon A1

$$\theta_{AWC}^{\text{Ap}} \approx (0.273 - 0.153) \cdot \left(\frac{1.22}{1.00} \right) = 0.146 \text{ m}^3 \cdot \text{m}^{-3} \quad (2.19)$$

$$d_{AWC}^{\text{Ap}} = (0.146 \text{ cm}_{\text{water}} \cdot \text{cm}_{\text{soil}}^{-1}) \cdot 15 \text{ cm}_{\text{soil}} = 2.19 \text{ cm}_{\text{water}} \quad (2.20)$$

Table 2.2: Moist bulk density ρ_t , mass water contents w and volumetric *plant-available water-holding capacity* of the Macksburg soil from Madison County, Iowa. Mass water content at $p_{\text{tension}} = -33 \text{ kPa}$ is w_{10} and mass water content at $p_{\text{tension}} = -1500 \text{ kPa}$ is w_{1500} .

d_t cm	ρ_t $\text{Mg} \cdot \text{m}^{-3}$	w_{AWC} $\text{Mg} \cdot \text{Mg}^{-1}$	θ_{AWC} $\text{cm}_{\text{water}} \cdot \text{cm}_{\text{soil}}^{-1}$	d_{AWC} cm_{water}
15	1.22	0.120	0.147	2.20
15	1.10	0.118	0.130	1.94
31	1.16	0.129	0.150	4.64
30	1.18	0.112	0.132	3.96
16	1.18	0.128	0.151	2.42

Table 2.2 lists the volumetric plant-available water-holding capacity θ_{AWC} of each horizon in column 5. The plant-available water-holding capacity as an equivalent water depth of 15.17 cm for the entire horizon is the sum of horizon equivalent-depths d_t appearing in column 6.

Macksburg Soil Profile

$$d_{AWC}^{\text{profile}} = (2.19 + 1.94 + 4.64 + 3.96 + 2.42) \text{ cm}_{\text{water}} = 15.17 \text{ cm}_{\text{water}} \quad (2.21)$$

D. The Robbs soil from Johnson County, Illinois has a moist bulk density of $\rho_t = 1.34 \text{ Mg} \cdot \text{m}^{-3}$ and a field-capacity volumetric water content of $\theta_{fc} =$

$0.38 \text{ cm} \cdot \text{cm}^{-1}$. The solids-water partition coefficient for the herbicide Cyanazine (CAS Registry Number 21725-46-2) in the Robbs soil is: $K_{s/w}^{\oplus} = 2.2 \text{ m}^3 \cdot \text{Mg}^{-1}$.

Calculate the Cyanazine retardation coefficient R_f for the Robbs soil at field capacity.

Solution

Chapter 2 (*Chemical Hydrology*) gives the retardation coefficient as expression (33).

$$R_f = \left(1 + \left(\frac{K_{s/w}^{\oplus} \cdot \rho_t}{\theta_{fc}} \right) \right) \quad (2.22)$$

$$R_f = \left(1 + \left(\frac{2.2 \cdot 1.30}{0.38} \right) \right) = 8.74 \quad (2.23)$$

E. The Macksburg soil (Madison County, Iowa) has a retardation coefficient of $R_f = 42.2$ for the herbicide Atrazine (CAS Registry Number 1912-24-9). In early spring the Macksburg soil is at field capacity and the depth to water table is 45 cm.

Estimate how deep Atrazine applied at the surface of Macksburg soil will migrate after a 7.6 cm rainfall under prevailing conditions.

Solution

When the soil content is at field capacity it has no water storage capacity. The wetting depth, therefore, for the 7.6 cm rainfall is the depth to water table: $L_w = 45 \text{ cm}$.

$$R_f \equiv \frac{L_w}{L_A} \quad (2.24)$$

$$L_A = \frac{L_w}{R_f} = \frac{45 \text{ cm}}{42.2} = 1.07 \text{ cm} \quad (2.25)$$

Percolating water will transport Atrazine to a depth of 1.07 cm in the Mackesburg as the wetting front travels to the water table at a depth of 45 cm.

F. The Antigo soil (Langlade County, Wisconsin) has a retardation coefficient of $R_f = 3.90$ for the organophosphate insecticide Phosmet (CAS Registry Number 732-11-6). The Antigo soil has a field capacity water content of $\theta_{fc} = 0.37 \text{ cm} \cdot \text{cm}^{-1}$.

Estimate how deep Phosmet applied at the surface of Antigo soil will migrate after a 3.27 cm rainfall. The soil water content as rain begins to fall is: $\theta_{fm} = 0.20 \text{ cm} \cdot \text{cm}^{-1}$.

Solution

The water storage capacity ΔS of the Antigo soil is the difference between the water content at field capacity θ_{fc} and the water content θ_{fm} on the date rain begins to fall.

$$\Delta S = \theta_{fc} - \theta_{fm} \quad (2.26)$$

$$\Delta S = (0.37 - 0.20) \text{ cm} \cdot \text{cm}^{-1} = 0.17 \text{ cm}_{\text{water}} \cdot \text{cm}_{\text{soil}}^{-1} \quad (2.27)$$

The wetting depth L_w following a 3.27 cm rainfall is found by dividing the rainfall depth by soil water storage capacity.

$$L_A = \frac{d_w}{\Delta S} = \frac{3.27 \text{ cm}_{\text{water}}}{0.17 \text{ cm}_{\text{water}} \cdot \text{cm}_{\text{soil}}^{-1}} = 19.2 \text{ cm}_{\text{soil}} \quad (2.28)$$

The Phosmet leaching depth $L_A = 4.92 \text{ cm}$ following a 3.27 cm rainfall is found using the retardation coefficient expression.

$$R_f \equiv \frac{L_w}{L_A} \quad (2.29)$$

$$L_A = \frac{L_w}{R_f} = \frac{19.2 \text{ cm}_{soil}}{3.90} = 4.92 \text{ cm}_{soil} \quad (2.30)$$

G. The volumetric moisture content of a fine-sand soil is $\theta = 0.12 \text{ m}^3 \cdot \text{m}^{-3}$.

Use the empirical Clapp-Hornberger water retention function in Appendix D to estimate the tension head $h_{tension}$ at this water content.

Solution

Clapp and Hornberger (1978) published parameters for eleven (11) different soil texture classes required by their empirical water-retention function.

Table 2.3: Clapp-Hornberger water-retention parameters for the sand texture class.

ϕ	h_s	b
<i>cm</i>		
0.395	12.10	4.05

One of these eleven parameters is porosity ϕ . The independent variable for the empirical water-retention function is the *degree of saturation* s .

$$s_{fm} = \frac{\theta_{fm}}{\phi} = \frac{0.12}{0.395} = 0.304 \quad (2.31)$$

The tension head is, by definition, less than zero: $h_{tension} < 0$. The Clapp-Hornberger water-retention function yields the absolute value of the tension head: $|h_{tension}|$.

$$|h_{tension}| = h_s \cdot \left(\frac{\theta_{fm}}{\phi} \right)^{-b} = h_s \cdot s^{-b} \quad (2.32)$$

$$|h_{tension}| = 12.10 \text{ cm} \cdot (0.304)^{-4.05} = 1510 \text{ cm} \quad (2.33)$$

The tension head at field capacity is: $h_{tension} \approx -100 \text{ cm}$. The tension head at the wilting point is: $h_{tension} \approx -15300 \text{ cm}$.

H. Use the empirical Clapp-Hornberger unsaturated hydraulic conductivity function in Appendix D to estimate the hydraulic conductivity k_D of a loam-texture soil at field capacity.

Solution

Clapp and Hornberger (1978) published parameters for eleven (11) different soil texture classes required by their empirical unsaturated hydraulic-conductivity function.

Table 2.4: Clapp-Hornberger hydraulic conductivity parameters for the loam texture class.

ϕ	h_s	K	b
	cm	$mm \cdot hour^{-1}$	
0.451	12.10	25.02	5.39

One of these eleven parameters is porosity ϕ . The independent variable for the empirical water-retention function is the *degree of saturation* s .

$$\theta_{fc} = \phi \cdot \left(\frac{h_s}{|h_{tension}|} \right)^{1/b} \quad (2.34)$$

$$\theta_{fc} = 0.451 \cdot \left(\frac{5.39}{|-100 \text{ cm}|} \right)^{1/5.39} = 0.392 \quad (2.35)$$

$$s_{fc} = \frac{0.392}{0.451} = 0.869 \quad (2.36)$$

The *degree of saturation* s is the independent variable for the empirical unsaturated hydraulic-conductivity function.

$$K_D = K_s \cdot s^{2 \cdot b + 3} \quad (2.37)$$

$$K_D = (25.02 \text{ mm} \cdot \text{hour}^{-1}) \cdot (0.869)^{2 \cdot (5.39) + 3} = 3.61 \text{ mm} \cdot \text{hour}^{-1} \quad (2.38)$$

I. Use the Thornthwaite potential evapotranspiration model to estimate the mean evapotranspiration water loss during May 2016 in Dane County, Wisconsin. Identify the weather station you use to make your estimate.

Solution

The Thornthwaite model (below) relies on a two site-specific parameters and the immediate mean monthly temperature to estimate potential evapotranspiration on a monthly time scale. Mean monthly day length $\bar{L}_m$ is determined by site longitude.

$$PET [cm \cdot month^{-1}] = 1.6 \cdot \left(\frac{\bar{L}_m}{12} \right) \cdot \left(\frac{N_m}{30} \right) \cdot \left(\frac{10 \cdot \bar{T}_m}{I} \right)^{a(I)} \quad (2.39)$$

The heat index I is a function of long-term mean monthly temperatures for the entire year. A reliable estimate of site heat index I requires 10, 20 or more years of data to compute long-term mean monthly temperatures.

The National Climate Data Center (U.S. National Oceanic and Atmospheric Administration) *Climate Data Online* is the source of 20 years of monthly mean temperatures ([Table 2.5](#)) recorded at the Dane County Regional Airport MSN (NCDC Station USW00014837), Madison, WI.

$$I = \sum_{m=1}^{12} \left(\frac{\bar{T}_m}{5} \right)^{1.514} \quad (2.40)$$

Table 2.5: Monthly mean temperatures for Dane County Regional Airport MSN, Madison, Wisconsin (NCDC Station USW00014837). The period was from January 1996 through December 2015. Source: NCDC Climate Data Online

Month	$\bar{T}_m$	Month	$\bar{T}_m$
	$^{\circ}\text{C}$		$^{\circ}\text{C}$
JAN	-6.78	JUL	21.41
FEB	-5.02	AUG	20.33
MAR	0.88	SEP	16.22
APR	8.04	OCT	9.63
MAY	13.86	NOV	2.99
JUN	19.27	DEC	-3.75

The heat index for Dane County Regional Airport MSN, Madison, Wisconsin (NCDC Station USW00014837), computed using data listed in Table 2.5 and expression (2.40), is: $I = 40.99$. Exponent $a(I)$, a function of the site heat index I , is computed using the coefficients listed in Table 2.6 and the following expression.

Table 2.6: Coefficients for exponent $a(I)$ appearing in expressions (2.37) and (2.38).

Coefficient	Value
a_0	0.49239
a_1	$1.7921 \cdot 10^{-2}$
a_2	$7.711 \cdot 10^{-5}$
a_3	$6.751 \cdot 10^{-7}$

$$a(I) = a_0 \cdot I^0 + a_1 \cdot I^1 + a_2 \cdot I^2 + a_3 \cdot I^3 \quad (2.41)$$

The mean monthly temperature for May 2016 in Dane County, Wisconsin was: $\bar{T}_m = 15.0 \text{ }^{\circ}\text{C}$. The mean day length for May at Dane County Regional Airport is $\bar{L}_m = 14.12 \text{ hours}$. The mean monthly potential evapotranspiration is $PET = 8.6 \text{ cm} \cdot \text{month}^{-1}$ or $PET = 0.28 \text{ cm} \cdot \text{day}^{-1}$.

$$PET = 1.6 \cdot \left(\frac{14.12}{12} \right) \cdot \left(\frac{31}{30} \right) \cdot \left(\frac{10 \cdot 15.0}{40.99} \right)^{1.14} = 8.6 \text{ cm} \cdot \text{month}^{-1} \quad (2.42)$$

J. The estimated evapotranspiration water loss during June 2008 in a Dane County, Wisconsin watershed averaged 4.9 mm of water per day. The average soil depth in the watershed is 100 cm and has a total water storage capacity of: $\theta = 0.400 \text{ cm} \cdot \text{cm}^{-1}$. At the beginning of June 2008 the soil moisture content in the watershed averaged $\theta_{initial} = 0.370 \text{ cm} \cdot \text{cm}^{-1}$.

Predict stream discharge from this watershed at the end of June 2008 during which 167.6 mm of precipitation fell.

Solution

Table 2.7 lists the soil water balance parameters for Gordon Creek catchment during June 2008.

Table 2.7: Water balance parameters for the Gordon Creek catchment (Dane County, Wisconsin) during June 2008.

Parameter	Symbol	Value	Units
Precipitation	P	167.6	mm
Daily Evapotranspiration	ET	4.9	$mm \cdot day^{-1}$
Field-Capacity Water Content	θ_{fc}	0.400	$mm \cdot mm^{-1}$
Initial Water Content	θ_i	0.370	$mm \cdot mm^{-1}$
Soil Profile Depth	d_{soil}	100	cm

The soil profile water storage capacity at the end of May 2008 is $\Delta S_i = 30.48 \text{ mm}$.

$$\Delta S_i = (\theta_{fc} - \theta_i) \cdot d_{soil} \quad (2.43)$$

$$\Delta S_i = (0.400 - 0.370 \text{ mm} \cdot \text{mm}^{-1}) \cdot 1000 \text{ mm} = 30.48 \text{ mm} \quad (2.44)$$

The water *surplus* (or *deficit*) at the end of June 2008 is the difference between precipitation minus the evapotranspiration water loss for the entire month.

$$ET = (4.9 \text{ mm} \cdot \text{day}^{-1}) \cdot 30 \text{ day} = 146.0 \text{ mm} \quad (2.45)$$

$$P - ET = 167.6 \text{ mm} - 146.0 \text{ mm} = 21.6 \text{ mm} \quad (2.46)$$

The June 2008 water surplus is less than the soil profile water storage capacity at the beginning of month: $(P - ET) < \Delta S_i$. Stream discharge D that can be attributed to precipitation minus evapotranspiration water loss is zero.

3. Clay Mineralogy and Chemistry

A. Identify the Jackson Weathering Stage where smectite minerals first appear.

Answer

Transmission electron microscopy has revealed the formation of phyllosilicates through the solid-state transformation of all pyribole minerals. The mechanism involves the cross-linking of I-beam silicate chains. The earliest appearance of phyllosilicates through the chemical weathering of igneous minerals would be Jackson stage 3. This assignment recognizes Jackson stage 1 and 2 minerals are indicative of soils and surficial materials in arid climate zones and not the product of igneous mineral weathering.

B. Identify any crystallographic feature that would permit the solid-state transformation of feldspar minerals into layer silicate minerals.

Answer

Unlike pyribole minerals, whose I-beam framework structures cross-link to form phyllosilicate layers without dissolution, feldspar minerals do not have a crystallographic framework structure that allows a direct solid-state transformation into layer silicates.

The transformation of feldspar minerals into clay minerals appears to follow a surface-site controlled process. Clay minerals appear to develop at etch pits on the surface of naturally weathered feldspar minerals. Etch pits are the surface manifestation of cleavage planes, crystal dislocations, twin planes and other unidentified defects within the bulk feldspar crystal.

C. Describe the importance of plasticity in the field identification of clay content and identify the minerals typically found in the clay-size fraction that exhibit plasticity.

Answer

Field identification of soil, residuum or sediment texture—the particular blend of sand, silt and clay particle-size classes—relies on evidence of plasticity and grittiness. The presence of sand gives rise to grittiness while the presence of clay gives rise to plasticity.

Plasticity, the capacity of a material to hold its shape after being molded, is an expression of the adhesive effect of water films on particles with a very high surface-to-volume ratio. That being said, not all mineral particles in the clay particle-size clay exhibit plasticity. Some clay chemists believe plasticity is conferred solely by smectite clay minerals; the plasticity of clay specimens composed predominantly of oxide minerals or layer silicates other than smectites may ultimately be due to trace amounts of smectite minerals in the specimen.

Regardless, oxide minerals are not plastic and clay minerals such as kaolinite, halloysite, clay-sized micas, sepiolite and palygorskite are much lower plasticity than smectite clay minerals.

D. Apply Pauling’s *Radius Ratio rule* to determine the preferred coordination of the cation listed in [Table 3.1](#). The ionic radius of oxygen is: $r_{\text{O}^{2-}} = 0.140 \text{ nm}$.

Table 3.1: Ionic radii r_c of the eight most abundant cations in the Earth’s outer crust.

Abundance Rank	Cation	Ionic Radius r_c nm
2	Si^{4+}	0.034
3	Al^{3+}	0.053
4	Fe^{2+}	0.077
4	Fe^{3+}	0.065
5	Ca^{2+}	0.100
6	K^{+}	0.138
7	Na^{+}	0.102
8	Mg^{2+}	0.072
9	Ti^{4+}	0.069

Solution

Pauling’s first rule *The Nature of the Coordinated Polyhedra* (Pauling, 1929) relies the geometry of coordination polyhedra—specifically, the radius of a hypothetical sphere occupying the void at the center of polyhedron made from close-packed spheres with unit radii—to predict cation coordination number. [Table 3.2](#) lists the coordination number and *minimum* radius ratio for 5 regular coordination polyhedra.

Table 3.2: Regular coordination polyhedra: coordination number and minimum radius ratio r_c/r_a .

Polyhedron	Coordination Number	Minimum Radius Ratio r_c/r_a
triangular	3	$2/\sqrt{3} - 1 = 0.155$
tetrahedron	4	$\sqrt{3/2} - 1 = 0.225$
octahedron	6	$\sqrt{2} - 1 = 0.414$
cube	8	$\sqrt{3} - 1 = 0.732$
cubeoctahedron	12	1.000

The radius ratios listed in [Table 3.3](#) were computed using the radii listed in [Table 3.1](#) and $r_{\text{O}^{2-}} = 0.140 \text{ nm}$. The computed radius ratio ([Table 3.3](#), column 3) will lie between two minimum radius ratios. The predicted coordination number ([Table 3.3](#), column 4) is the larger of the two minimum radius ratios.

Table 3.3: Radius ratio r_c/r_a for O^{2-} anion and coordination number of the eight most abundant cations in the Earth's outer crust.

Abundance Rank	Cation	Radius Ratio r_c/r_O	Predicted Coordination Number
2	Si^{4+}	0.39	4
3	Al^{3+}	0.49	6
4	Fe^{2+}	0.66	6
4	Fe^{3+}	0.49	6
5	Ca^{2+}	0.81	8
6	K^+	1.09	12
7	Na^+	0.83	8
8	Mg^{2+}	0.61	6
9	Ti^{4+}	0.54	6

Coordination polyhedra in minerals are generally distorted (flattened, elongated, twisted, etc.). Furthermore, Pauling's rules were published in the early days of X-ray diffraction crystallography and should not be considered "hard and fast" rules. They were published in an era when chemists and mineralogists had refined relatively few crystal structures.

For example, Pauling (1929) predicted 4-fold oxygen coordination for Al^{3+} .

"So far as I know, Al^{3+} has the coordination number 6 in all of its compounds with oxygen the structures of which have been determined. The coordination number 4 would also be expected for it, however; it is probable that it forms tetrahedra in some of its compounds, as, for example, γ -alumina, the cubic form of Al_2O_3 , and the feldspars, in which there occurs replacement of Na^+ and Si^{4+} by Ca^{2+} and Al^{3+} ." (Pauling, 1929)

E. The structure of four layer silicate minerals appear in [Figure 3.1](#).

Associate the following with each structure: 1) a specific mineral name, 2) the Jackson chemical weathering stage dominated by each mineral, and 3) whether the mineral is capable of *crystalline* swelling when hydrated.

Answer

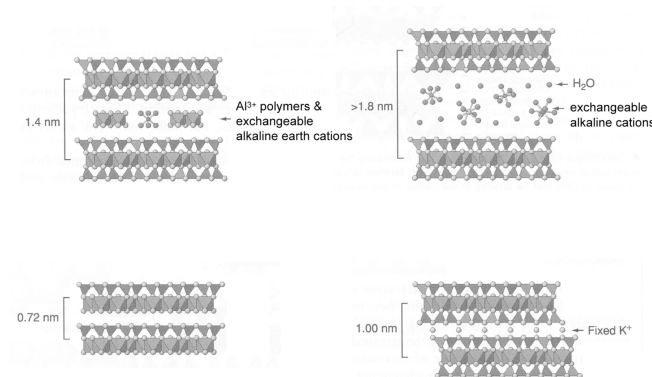


Figure 3.1: Layer silicate structures showing tetrahedral sheets, octahedral sheets and, where appropriate, interlayer components.

The 1.4 *nm* clay mineral with aluminum polymers occupying the interlayer is related to the non-swelling 2:1:1 clay mineral chlorite: hydroxy-interlayered smectite representative of moderately acid soils and residuum. The mineral chlorite has a magnesium hydroxide (or brucite) interlayer and is a dominant mineral in the fine silt to clay particle-size fraction at Jackson stage 4. Hydroxy-interlayered smectite is associated with Jackson stage 9.

The clay mineral with layer spacings exceeding 1.8 *nm* is a smectite clay mineral. Smectite clay minerals are capable of both crystalline and free swelling and associated with Jackson stage 9.

The 0.72 *nm* clay mineral is kaolinite, a non-swelling clay mineral associated with Jackson stage 10.

The 1.00 *nm* clay mineral with interlayer K^+ cations is a mica, a non-swelling clay mineral associated with Jackson stage 4 (biotite) or 7 (muscovite).

F. The specific surface area of kaolinite specimens from the clay ($< 0.2 \mu m$) fraction is: $a_s \approx 10 m^2 \cdot g^{-1}$. The specific surface area of smectite specimens from the clay ($< 0.2 \mu m$) fraction is: $a_s \approx 700 m^2 \cdot g^{-1}$.

Explain the dramatic difference in surface area despite the fact that both specimens have the same particle radius.

Answer

Kaolinite is a non-swelling clay mineral. Specimens with a particle radius less than $2\ \mu\text{m}$ owe their specific surface area solely to the particle diameter.

Smectite are clay minerals that occur solely in the less than $2\ \mu\text{m}$ particle-size fraction. Smectite clays are capable of free swelling if the interlayer cation is Na^+ and the electrolyte concentration is very low. Free-swelling smectite delaminates into particles whose lateral dimensions are less than $2\ \mu\text{m}$ but whose thickness is on the order of $1\ \text{nm}$.

If the interlayer is counted in the crystalline-swelling state, which is justified for swelling clay minerals smectite and vermiculite, the specific surface area will exceed $700\ \text{m}^2 \cdot \text{g}^{-1}$.

G. Consider a landscape underlain by granite that weathers *in situ* to residuum. The x-ray diffraction pattern from the silt-size fraction of the residuum collected near the contact with the underlying granite bedrock clearly shows the presence of fine-grained muscovite. The x-ray diffraction pattern from the clay-size fraction of the residuum collected from the soil profile at the land surface lacks the characteristic diffraction lines of muscovite; instead, the dominant mineral is kaolinite.

Explain the significance of these findings.

Answer

Detection of muscovite at the contact between residuum and granite indicates Jackson weathering stage 4. The clay fraction of a soil specimen from the land surface is dominated by the clay mineral kaolinite, indicating Jackson stage 10. The residuum remnant at the land surface has progressed from stage 4 to stage 10, which is considered a very advanced stage. The land surface could reach Jackson stage 10 only if erosion or deposition are negligible.

H. Clay mineral layer charge influences a variety of chemical and physical properties: swelling behavior, surface area, and the exchangeability of interlayer ions.

Explain the relationship between layer charge and the chemical and physical

properties listed above.

Answer

Swelling results from the entry of water molecules into the phyllosilicate interlayer, hydrating interlayer cations. This is the general rule for layer silicates. Three notable exceptions—involving chlorite, halloysite, sepiolite and palygorskite minerals—are given at the close.

Cation substitution is found in all mica group minerals (including the micaceous clay *illite*) and vermiculite-smectite group minerals. The distinction separating mica group minerals from vermiculite-smectite group minerals is the magnitude of layer charge and, consequently, swelling behavior. Mica group minerals do not have water hydrating interlayer K^+ (or, in the case of brittle mica: Ca^{2+}) cations because the electrostatic energy binding interlayer cations to negatively-charged 2:1 aluminosilicate layers exceeds the hydration energy of the interlayer cations.

The significantly lower layer charge density in vermiculite results in an electrostatic binding energy that is less than the interlayer cation hydration energy, allowing limited crystalline swelling. Smectite minerals, by definition, have a still lower layer-charge density, allowing free swelling provided the interlayer cation (i.e., Na^+ and Li^+) has a very strong hydration energy.

EXCEPTIONS: *Tschermak* cation substitution in chlorite group minerals couples $Al^{3+} \rightarrow Si^{4+}$ substitution in the tetrahedral sheets of the 2:1 aluminosilicate layer to $Al^{3+} \rightarrow Mg^{2+}$ substitution in the interlayer $Mg(OH)_2$ octahedral sheet.

The neutral-layer mineral halloysite has interlayer water and, therefore, a larger layer spacing than kaolinite, the interlayer water was replaced as halloysite formed. Halloysite dehydration is irreversible.

So-called *zeolitic* water in sepiolite and palygorskite hydrate hydroxyl OH^- ions lining the channels between cross-linked I-beams. I-beam cross-linking in sepiolite and palygorskite prevent swelling.

I. Describe the special characteristics of *Tschermak* cation substitution and its significance for cation substitution in layer silicates.

Answer

The incorporation of aluminum into amphibole minerals results from a special type of coupled cation substitution: *Tschermak* cation substitution. Classical *Tschermak* cation substitution couples $\text{Al}^{3+} \longrightarrow \text{Si}^{4+}$ substitution in I-beam tetrahedral sites to $\text{Al}^{3+} \longrightarrow \text{Mg}^{2+}$ substitution in I-beam octahedral sites.

Tschermak cation substitution in chlorite group minerals couples $\text{Al}^{3+} \longrightarrow \text{Si}^{4+}$ substitution in the tetrahedral sheets of the 2:1 aluminosilicate layer with $\text{Al}^{3+} \longrightarrow \text{Mg}^{2+}$ substitution in the interlayer $\text{Mg}(\text{OH})_2$ octahedral sheet.

If *Tschermak* cation substitution is seen as the deposition of negative charge on an aluminosilicate framework by coupling $\text{Al}^{3+} \longrightarrow \text{Si}^{4+}$ substitution to the deposition of a corresponding positive charge in the vicinity, then the deposition of negative layer charge in phyllosilicates coupled to the emplacement of positively-charged interlayer cations can be considered *Tschermak*-like cation substitution.

J. Estimate the unit cell composition of a Wyoming montmorillonite specimen *Volclay* (American Colloid Company) using the *oxide* mass-fraction $w(\text{E}_x\text{O}_y)$ data listed in [Table 3.4](#).

Table 3.4: The chemical composition of a Na^+ -saturated *Volclay* montmorillonite specimen, expressed in oxide mass-fraction units. Source: Brindley and Ertem (1971)

Oxide	$w(\text{E}_x\text{O}_y)$	Oxide	$w(\text{E}_x\text{O}_y)$
	$g \cdot g^{-1}$		$g \cdot g^{-1}$
$\text{SiO}_2(\text{s})$	0.613	$\text{TiO}_2(\text{s})$	0.0011
$\text{Al}_2\text{O}_3(\text{s})$	0.224	$\text{MgO}(\text{s})$	0.0281
$\text{Fe}_2\text{O}_3(\text{s})$	0.0355	$\text{Na}_2\text{O}(\text{s})$	0.0271
$\text{FeO}(\text{s})$	0.0039	$\text{K}_2\text{O}(\text{s})$	0.0004

Solution

The unit cell formula cannot be computed without an essential parameter determined by X-ray diffraction: the number of oxygen atoms in the unit cell. The unit cell oxygen count is used to normalize the number of cation per unit cell. The unit cell formulas for many silicate minerals group cations according to coordination: tetrahedral, octahedral and interlayer coordination for layer silicate minerals.

Step 1. Convert the oxide mass-per-mass composition to oxide mole-

per-mass composition. Table 3.5 lists the *oxide* mole-per-mass $b(E_xO_y)$ composition of a Wyoming montmorillonite specimen *Volclay* (American Colloid Company)².

Table 3.5: The chemical composition of a *Volclay* montmorillonite specimen listing oxide mass-fraction units, formula mass of each oxide and oxide mole-per-mass units.

Oxide	$m_f(E_xO_y)$	$w(E_xO_y)$	$b(E_xO_y)$
	$g \cdot mol^{-1}$	$g \cdot g^{-1}$	$mol \cdot g^{-1}$
SiO ₂ (s)	60.0844	0.613	$1.02 \cdot 10^{-2}$
Al ₂ O ₃ (s)	101.9614	0.224	$2.20 \cdot 10^{-3}$
Fe ₂ O ₃ (s)	159.6887	0.0355	$2.22 \cdot 10^{-4}$
FeO(s)	71.8446	0.0039	$5.43 \cdot 10^{-5}$
TiO ₂ (s)	79.8656	0.0011	$1.38 \cdot 10^{-5}$
MgO(s)	40.3045	0.0281	$6.97 \cdot 10^{-4}$
Na ₂ O(s)	61.9790	0.0271	$4.42 \cdot 10^{-4}$
K ₂ O(s)	94.1961	0.0004	$4.67 \cdot 10^{-6}$

The *oxide* mole-per-mass concentration $b(E_xO_y)$ (Table 3.5, column 4) is calculated by dividing the oxide mass fraction $w(E_xO_y)$ (Table 3.5, column 3) by the oxide formula mass $m_f(E_xO_y)$ (Table 3.5, column 2).

Step 2. Normalize the oxide mole-per-mass content by the oxygen content of the unit cell. Although there are 24 oxygen atoms in the O₂₀(OH)₄ unit cell, the unit cell anion charge is equivalent to 22 divalent oxygen anions. Multiplying the $b(E_xO_y)$ values in column 4 of Table 3.5 by the oxygen stoichiometry of each oxide yields the values listed in column 2 of Table 3.6.

For example, the oxygen stoichiometry of SiO₂ requires multiplying $b(SiO_2) = 1.02 \cdot 10^{-2}$ from in row 1, column 4 (table above) by 2 to yield $2.04 \cdot 10^{-2}$ which appears in row 1, column 2 of the normalized composition table (following). The sum over all $b(O)$ values for each oxide (expression 3.1) yields $b(O) = 2.89 \cdot 10^{-2} mol \cdot g^{-1}$. The normalizing factor $f_N [cell \cdot g^{-1}]$ is the summed moles of oxygen per gram divided by the number of oxygen atoms in the unit cell.

$$f_N = \frac{2.89 \cdot 10^{-2}}{22} = 1.31 \cdot 10^{-3} cell \cdot g^{-1} \quad (3.1)$$

²The American Colloid Company mine is near Colloid Spur, Wyoming, along the CB & Q Railroad, two miles northeast of Upton, in Weston County, Wyoming. The actual deposit covers part of Section 27, Township 48 north, Range 65 west of the 6th Principal Meridian.

Table 3.6: The normalized elemental composition of the *Volclay* montmorillonite unit cell.

Oxide	$b(\text{O})$	$n(\text{O})$	Cation	$n(\text{E})$
	$\text{mol}_{\text{O}} \cdot \text{g}^{-1}$	$\text{mol}_{\text{O}} \cdot \text{cell}^{-1}$		$\text{mol} \cdot \text{cell}^{-1}$
SiO ₂ (s)	$2.04 \cdot 10^{-2}$	15.54	Si ⁴⁺	7.77
Al ₂ O ₃ (s)	$6.59 \cdot 10^{-3}$	5.02	Al ³⁺	3.35
Fe ₂ O ₃ (s)	$6.67 \cdot 10^{-4}$	0.51	Fe ³⁺	0.25
FeO(s)	$5.43 \cdot 10^{-5}$	0.04	Fe ³⁺	0.04
TiO ₂ (s)	$2.75 \cdot 10^{-5}$	0.02	Ti ⁴⁺	0.01
MgO(s)	$6.97 \cdot 10^{-4}$	0.53	Mg ²⁺	0.53
Na ₂ O(s)	$4.47 \cdot 10^{-4}$	0.34	Na ⁺	0.68

The unit-cell oxygen stoichiometry values $n(\text{O})$ column 3 (Table 3.6) are computed by dividing the $b(\text{O})$ values in column 2 (Table 3.6) by the normalizing factor $f_{\text{N}} = 1.31 \cdot 10^{-3}$ (expression (3.1)). A sum over the normalized values $n(\text{O})$ in column 3 (Table 3.6) should equal 22 if the normalization is correct. Unit-cell cation stoichiometry $n(\text{E})$ appears in column 5 (Table 3.6). These values are computed by multiplying the moles of oxygen per unit cell for each oxide $n(\text{O})$ by the moles of cation per oxide. For example, there is $\frac{1}{2}$ moles of Si⁴⁺ in each mole of the oxide SiO₂(s).

Silicon Dioxide SiO₂(s)

$$n(\text{Si}^{4+}) = \frac{1}{2} \cdot n(\text{O}) = \frac{1}{2} \cdot 15.54 = 7.77 \quad (3.2)$$

Table 3.6 does not list K₂O(s) or K⁺. To simplify the method we can assume Na⁺ and K⁺ both occupy the same interlayer coordination sites. The Na₂O(s) and Na⁺ content listed in row 7, Table 3.6 includes the molar potassium content computed in Table 3.5.

Step 3. Assign the unit-cell cations to each coordination site to determine the final unit cell formula. In this case, as with all layer silicates, the rules for assigning cations is very simple. First, all Si⁴⁺ cations are assigned to unit cell tetrahedral coordination sites. Since there are a total of eight (8) tetrahedral sites in each unit cell, another cation must occupy the remaining 0.23 tetrahedral sites. Extensive research has revealed that of the remaining cations only Al³⁺ cations will occupy those remaining sites. The stoichiometry coefficient for tetrahedral Al³⁺ is 0.23.

All of the remaining cations except Na⁺ can occupy octahedral sites; assign all 0.68 moles of Na⁺ to the interlayer.

Each $\text{O}_{20}(\text{OH})_4$ unit cell contains a total of 6 octahedral sites. Dioctahedral 2:1 layer silicates will have approximately 4 octahedral sites occupied by a combination of trivalent cations (e.g., Al^{3+} and Fe^{3+}) and divalent cations (e.g., Mg^{2+}). The total number of cations that can occupy octahedral sites are 4.02.

$$(n(\text{Al}^{3+}) - 0.23) + n(\text{Fe}^{3+}) + n(\text{Ti}^{4+}) + n(\text{Mg}^{2+}) = 4.02 \quad (3.3)$$

Cations substitutions ($\text{Al}^{3+} \longrightarrow \text{Si}^{4+}$)^{iv} and ($\text{Mg}^{2+} \longrightarrow \text{Al}^{3+}$)^{vi} add negative layer charge while cation substitution ($\text{Ti}^{4+} \longrightarrow \text{Al}^{3+}$)^{vi} adds positive layer charge. Net negative layer charge equals $0.80 \text{ mol}_c \cdot \text{cell}^{-1}$, which is larger than the $0.68 \text{ mol}_c \cdot \text{cell}^{-1}$ assigned to the interlayer based on the Na^+ and K^+ analysis.

The unit cell formula, based on the normalized molar composition listed in the preceding table and the assignments just discussed, appears below.



K. Compute the osmotic head $h_{osmotic}$ of a $\text{CaSO}_4(\text{aq})$ solution: $c_{\text{CaSO}_4} = 1.600 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$.

Solution

When using the *van't Hoff-Morse* equation the solute concentration is expressed in *molal* units. The molar-to-molal conversion requires the density of the $c_{\text{CaSO}_4} = 1.600 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ solution. In this case we will assume the $\text{CaSO}_4(\text{aq})$ solution has the same density as pure water at 25°C .

$$\rho_{\text{CaSO}_4(\text{aq})} \approx 997.41 \text{ g} \cdot \text{dm}^{-3} \quad (3.4)$$

The water mass-concentration m_w/V [$\text{g} \cdot \text{dm}^{-3}$] of the solution is computed by subtracting the CaSO_4 mass in the solution from the total solution mass.

$$m_w/V = \rho_{\text{CaSO}_4(\text{aq})} - (c_{\text{CaSO}_4} \cdot m_f(\text{CaSO}_4)) \quad (3.5)$$

$$m_w/V = (997.41 \text{ g} \cdot \text{dm}^3) - (1.600 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3} \cdot 136.14 \text{ g} \cdot \text{mol}^{-1}) \quad (3.6)$$

$$m_w/V = 997.82 \text{ g} \cdot \text{dm}^3 \quad (3.7)$$

The molal concentration $b_{\text{CaSO}_4} [\text{mol} \cdot \text{kg}^{-1}]$ is simply the molar concentration $c_{\text{CaSO}_4} [\text{mol} \cdot \text{kg}^{-1}]$ divided by the solution water mass $w(\text{H}_2\text{O}(\text{l}))$.

$$b_{\text{CaSO}_4(\text{aq})} = \frac{c_{\text{CaSO}_4} [\text{mol} \cdot \text{dm}^3]}{m_w/V [\text{kg} \cdot \text{dm}^3]} \quad (3.8)$$

$$b_{\text{CaSO}_4(\text{aq})} = \frac{1.600 \cdot 10^{-2} \text{ mol} \cdot \text{dm}^{-3}}{0.99782 \text{ kg} \cdot \text{dm}^3} = 1.602 \cdot 10^{-2} \text{ mol} \cdot \text{kg}^{-1} \quad (3.9)$$

The osmotic head h_{osmotic} of a $b_{\text{CaSO}_4(\text{aq})} = 1.602 \cdot 10^{-2} \text{ mol} \cdot \text{kg}^{-1}$ solution is computed using the *van't Hoff-Morse* equation, rearranged to replace pressure units with head units. This requires the following parameters and constants: solute stoichiometry factor $\nu_{\text{CaSO}_4(\text{aq})} = 2$, $R = 8.314 \cdot 10^{+3} \text{ dm}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $T = 298.15 \text{ K}$, and standard gravity $g_0 = 9.80655 \text{ m} \cdot \text{s}^{-2}$.

$$h_{\text{osmotic}} = \frac{\nu_{\text{CaSO}_4(\text{aq})} \cdot b_{\text{CaSO}_4(\text{aq})} \cdot R \cdot T}{\rho_{\text{CaSO}_4(\text{aq})} \cdot g_0} \quad (3.10)$$

$$h_{\text{osmotic}} = \frac{2 \cdot (1.602 \cdot 10^{-2}) \cdot (8.314 \cdot 10^{+3}) \cdot 298.15}{(997.41) \cdot (9.80655)} \quad (3.11)$$

$$h_{\text{osmotic}} = 8.11 \text{ m} \quad (3.12)$$

NOTE: A more accurate calculation replaces the solute stoichiometry factor $\nu_{\text{CaSO}_4(\text{aq})}$ with the more accurate *van't Hoff factor* $i_{\text{CaSO}_4(\text{aq})}$, which is the product of the *osmotic coefficient* ϕ and the solute stoichiometry factor $\nu_{\text{CaSO}_4(\text{aq})}$.

$$i_{\text{CaSO}_4(\text{aq})} = \phi \cdot \nu_{\text{CaSO}_4(\text{aq})} \quad (3.13)$$

The *osmotic coefficient* ϕ is a function of the solute activity coefficient, $\gamma_{2\pm}$ in the case of a $\text{CaSO}_4(\text{aq})$ solution.

$$\phi = 1 + \ln(\gamma_{2\pm}/3) = 1 + \ln(0.801/3) = 0.926 \quad (3.14)$$

$$i_{\text{CaSO}_4(\text{aq})} = 0.926 \cdot 2 = 1.85 \quad (3.15)$$

$$h_{\text{osmotic}} = \frac{1.85 \cdot (1.602 \cdot 10^{-2}) \cdot (8.314 \cdot 10^3) \cdot 298.15}{(997.41) \cdot (9.80655)} \quad (3.16)$$

$$h_{\text{osmotic}} = 7.51 \text{ m} \quad (3.17)$$

L. Figure 15 (*cf.* Chapter 3, Clay Mineralogy and Chemistry) plots the crystalline swelling of a Na^+ -saturate smectite specimen.

Estimate the number of water layers in the interlayer of this smectite at each crystalline swelling state.

Solution

Table 3.7 lists the layer spacing of a K^+ -saturated montmorillonite specimen undergoing crystalline swelling. The data (Foster, 1954) are for a montmorillonite specimen described as "of the Belle Fourche variety," supplied by the Hancock Mud Sales and Service Company, Houston, Texas. American Petroleum Institute specimen API-27 is identified as the Belle Fourche bentonite³ from Belle Fourche, South Dakota.

Table 3.7: The crystalline swelling of a K^+ -saturated montmorillonite specimen from the Belle Fourche, South Dakota formation (Foster, 1954).

Layer Spacing d_{001}	Gallery Spacing τ	Pauling	Brown-Shannon
<i>nm</i>	<i>nm</i>	Water Layers	Water Layers
0.98	0.00	0.0	0.0
1.26	0.28	1.0	1.0
1.55	0.57	2.0	2.1
1.90	0.92	3.3	3.4

The diameter of interlayer water molecules can be estimated from the ionic radius of the O^{2-} ion: Pauling radius, $r_{\text{O}^{2-}} = 0.140 \text{ nm}$ or Brown and Shannon radius, $r_{\text{O}^{2-}} = 0.135 \text{ nm}$. The diameter of a water molecule, ignoring the effect of hydrogen-bonding, is about $0.27 \text{ nm} \leq d_{\text{H}_2\text{O}} \leq 0.28 \text{ nm}$.

Table 3.7, column 2 above lists the height of the interlayer gallery, found by subtracting the layer thickness $\tau = 0.98 \text{ nm}$ from the experimental layer spacing d_{001} . Columns 3 and 4 above list the estimated number of water layers based on the Pauling radius $r_{\text{O}^{2-}}$ and the Brown and Shannon radius $r_{\text{O}^{2-}}$, respectively.

The first two crystalline swelling states correspond to 1-layer and 2-layer hydrates. The third swelling state shows signs of disorder, expressed as a greater than integral increase water layers.

³Clay mineralogists do not recognize the term *bentonite*, recommending either montmorillonite or a specimen from the vermiculite-smectite group. Bentonite refers to vermiculite-smectite group specimens that are naturally Na^+ -saturated.

M. Figure 24 (*cf.* Chapter 3, Clay Mineralogy and Chemistry) shows the tension head $h_{tension}$ of a 13.5% suspension of Cheto montmorillonite.

Compute the actual height of the clay gel above pure water in an osmotic cell equivalent to the osmotic head: $h_{osmotic} = 13.4 \text{ cm}$.

Solution

Leonard and Low (1963) measured the clay-suspension tension head $h_{tension}$ in Figure 24 (*cf.* Chapter 3, Clay Mineralogy and Chemistry) using a null-point tensiometer. Since tensiometers are typically used to measure $h_{tension}$ in porous media the reference fluid is pure water.

A null-point tensiometer operates by adjusting the pressure imposed on the soil-water system until it matches the target tension head $h_{tension}$. Since the fluid of interest is water the density that relates the imposed tension (i.e., vacuum or suction) $p_{tension} < 0$ to the experimental $h_{tension}$ is the density of pure water ρ_w .

The clay-suspension tension head $h_{tension} = -13.4 \text{ cm}$ corresponds to an equivalent tension $p_{tension} = -1.310 \cdot 10^3 \text{ kPa}$ expressed in pressure units. Where g_0 represents standard gravity.

$$p_{tension} \equiv \rho_w \cdot g_0 \cdot h_{tension} \quad (3.18)$$

$$p_{tension} = 997.0 \text{ kg} \cdot \text{m}^{-3} \cdot 9.807 \text{ m} \cdot \text{s}^{-2} \cdot -0.0134 \text{ m} = -1.310 \cdot 10^3 \text{ kPa} \quad (3.19)$$

The actual osmotic head $h_{osmotic}$ of the 13.5% Cheto montmorillonite clay suspension, separated by a dialysis membrane from pure water, must take into account the density of the clay suspension. Assume the Cheto montmorillonite has the density generally assigned to soil minerals: $\rho_{quartz} = 2.65 \text{ Mg} \cdot \text{m}^{-3}$.

$$V_c \approx \frac{m_c/V}{\rho_{quartz}} = \frac{0.135 \text{ Mg} \cdot \text{m}^{-3}}{2.65 \text{ Mg} \cdot \text{m}^{-3}} = 0.050 \text{ m}^3 \cdot \text{Mg}^{-1} \quad (3.20)$$

$$V_w \approx \frac{1 - m_w/V}{\rho_w} = \frac{0.865 \text{ Mg} \cdot \text{m}^{-3}}{0.997 \text{ Mg} \cdot \text{m}^{-3}} = 0.868 \text{ m}^3 \cdot \text{Mg}^{-1} \quad (3.21)$$

$$\rho_{suspension} = \frac{1}{(V_c + V_w)} \quad (3.22)$$

$$\rho_{suspension} = \frac{1}{(0.050 \text{ m}^3 \cdot Mg^{-1} + 0.868 \text{ m}^3 \cdot Mg^{-1})} = 1.089 \text{ Mg} \cdot m^{-3} \quad (3.23)$$

NOTE: Using the unit cell dimensions and chemical formula for montmorillonite specimens the density montmorillonite is somewhat higher than the density of quartz: $\rho_{mont} \approx 2.72 \text{ Mg} \cdot m^{-3}$. The impact is minimal, amounting to one-part in ten thousand for the clay suspension density.

The osmotic head of a 13.5% Cheto montmorillonite suspension with a $p_{tension} = +1.310 \cdot 10^3 \text{ kPa}$ is found rearranging the relationship between head and pressure while using the clay suspension density for the fluid.

$$h_{osmotic} = \frac{-p_{tension}}{\rho_{suspension} \cdot g_0} \quad (3.24)$$

$$h_{osmotic} = \frac{+1.310 \cdot 10^3 \text{ kPa}}{1.089 \text{ Mg} \cdot m^{-3} \cdot 9.807 \text{ m} \cdot s^{-2}} = 0.123 \text{ m} \quad (3.25)$$

Since the clay suspension is more dense then pure water, the clay suspension head rises only 12.3 *cm* above the pure water level in the osmotic cell.

4. Ion Exchange

A. The clay fraction of the Twotop soil series (Crook County, Wyoming) is predominantly smectite with a reported cation exchange capacity *CEC* of $n_+^\sigma/m = 76.4 \text{ cmol}_c \cdot \text{kg}^{-1}$. An asymmetric ($\text{Ca}^{2+}, \text{K}^+$) cation exchange experiment reports the following results: $c_{\text{K}^+} = 10.17 \text{ mmol} \cdot \text{dm}^{-3}$, $c_{\text{Ca}^{2+}} = 0.565 \text{ mmol} \cdot \text{dm}^{-3}$, $n_{\text{K}^+}^\sigma/m = 38.2 \text{ cmol}_c \cdot \text{kg}^{-1}$, and $n_{\text{Ca}^{2+}}^\sigma/m = 38.2 \text{ cmol}_c \cdot \text{kg}^{-1}$

Compute the selectivity coefficient $K_{\text{Ca/K}}^c$ for ($\text{Ca}^{2+}, \text{K}^+$) exchange in this soil clay specimen.

Solution

The Gaines-Thomas convention uses equivalent fractions to quantify exchanger-bound ions.

$$E_{\text{K}^+} = \frac{n_{\text{K}^+}^\sigma/m}{n_{\text{K}^+}^\sigma/m + 2 \cdot n_{\text{Ca}^{2+}}^\sigma/m} = \frac{n_{\text{K}^+}^\sigma/m}{n_+^\sigma/m} \quad (4.1)$$

$$E_{\text{K}^+} = \frac{38.2 \text{ cmol}_c \cdot \text{kg}^{-1}}{76.4 \text{ cmol}_c \cdot \text{kg}^{-1}} = 0.500 \quad (4.2)$$

The equilibrium cation exchange quotient (Gaines-Thomas convention) appears below. The single-point selectivity coefficient $K_{\text{Ca/K}}^c = 0.366$ for ($\text{Ca}^{2+}, \text{K}^+$) exchange in the Twotop soil clay specimen.

$$K_{\text{Ca/K}}^c = \frac{E_{\text{Ca}^{2+}} \cdot c_{\text{K}^+}^2}{c_{\text{Ca}^{2+}} \cdot E_{\text{K}^+}^2} \quad (4.3)$$

$$K_{\text{Ca/K}}^c = \frac{0.500 \cdot (1.017 \cdot 10^{-2})^2}{(5.650 \cdot 10^{-4}) \cdot 0.500} = 0.366 \quad (4.4)$$

B. The Ness soil series (Hodgeman County, Kansas) has a cation exchange capacity CEC of $n_+^\sigma/m = 38.0 \text{ cmol}_c \cdot \text{kg}^{-1}$ balanced by $n_{\text{Ca}^{2+}}^\sigma/m = 33.1 \text{ mol} \cdot \text{kg}^{-1}$ of exchangeable Ca^{2+} and $n_{\text{Na}^+}^\sigma/m = 4.9 \text{ mol} \cdot \text{kg}^{-1}$ exchangeable Na^+ . The concentrations of Ca^{2+} and Na^+ in the soil saturated paste extract are $c_{\text{Ca}^{2+}} = 10 \text{ mmol} \cdot \text{dm}^{-3}$ and $c_{\text{Na}^+} = 81 \text{ mmol} \cdot \text{dm}^{-3}$, respectively.

Determine which cation— Na^+ or Ca^{2+} —is selectively enriched during this ion exchange reaction.

Solution

Selectivity in an asymmetric exchange reaction can be determined only by comparing the experimental the equivalent fraction on the exchanger with the equivalent fraction of that with the selectivity coefficient set equal to unit.

$$K_{\text{Ca}/\text{Na}}^c \equiv 1 = \frac{E_{\overline{\text{Ca}^{2+}}} \cdot c_{\text{Na}^+}^2}{c_{\text{Ca}^{2+}} \cdot E_{\overline{\text{Na}^+}}^2} \quad (4.5)$$

Substitute the equilibrium solution concentrations, leaving the the exchanger equivalent fraction $E_{\overline{\text{Ca}^{2+}}}$ as the dependent variable, into the equilibrium cation exchange quotient.

$$\frac{E_{\overline{\text{Ca}^{2+}}} \cdot (8.10 \cdot 10^{-2})^2}{1.00 \cdot 10^{-2} \cdot (1 - E_{\overline{\text{Ca}^{2+}}})^2} \equiv 1 \quad (4.6)$$

$$E_{\overline{\text{Ca}^{2+}}} \cdot (8.10 \cdot 10^{-2})^2 = 1.00 \cdot 10^{-2} \cdot (1 - E_{\overline{\text{Ca}^{2+}}})^2 \quad (4.7)$$

The resulting quadratic equation appears below with $E_{\overline{\text{Ca}^{2+}}}$ as the dependent variable.

$$x \equiv E_{\overline{\text{Ca}^{2+}}} \quad (4.8)$$

$$(0.0100) \cdot x^2 + (-2 \cdot (0.0100) - (6.50 \cdot 10^{-4})) \cdot x + (0.0100) = 0 \quad (4.9)$$

The physically reasonable root of this quadratic equation is a positive value between zero and unity.

$$a = c \equiv 0.0100 \quad (4.10)$$

$$b \equiv -2.656 \cdot 10^{-2} \quad (4.11)$$

$$x_- = \frac{-b - \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a} = 0.454 \quad (4.12)$$

The exchanger-bound Ca^{2+} equivalent fraction for *non-selective* exchange would be 0.454 while the experimental equivalent fraction is: $E_{\overline{\text{Ca}^{2+}}} = 0.87$. The soil clay favors Ca^{2+} over Na^+ .

C. The Maxfield soil series (Olmsted County, MN) has a cation exchange capacity CEC of $n_+^\sigma/m = 41.0 \text{ cmol}_c \cdot \text{kg}^{-1}$ balanced by $n_{\text{Ca}^{2+}}^\sigma/m = 39.5 \text{ cmol}_c \cdot \text{kg}^{-1}$ of exchangeable Ca^{2+} and $n_{\text{Na}^+}^\sigma/m = 1.5 \text{ cmol}_c \cdot \text{kg}^{-1}$ exchangeable Na^+ . The concentrations of Ca^{2+} and Na^+ in the soil saturated paste extract are $c_{\text{Ca}^{2+}} = 4.49 \text{ mmol} \cdot \text{dm}^{-3}$ and $c_{\text{Na}^+} = 4.58 \text{ mmol} \cdot \text{dm}^{-3}$, respectively.

Calculate the equilibrium concentrations Ca^{2+} and Na^+ in soil pore water concentrated through water loss by evaporation to the wilting point (concentration factor $F_c = 3.31$). The following are soil physical properties of the Maxfield soil: moist ($p_{\text{tension}} = -33 \text{ kPa}$) bulk density $\rho_t = 1.30 \text{ Mg} \cdot \text{m}^{-3}$, volumetric water content at field capacity $\theta_{fc} = 0.255 \text{ m}^3 \cdot \text{m}^{-3}$ and wilting point $\theta_{wp} = 0.176 \text{ m}^3 \cdot \text{m}^{-3}$.

Solution

The exchanger-bound equivalent fraction only one cation is sufficient.

$$E_{\overline{\text{Ca}^{2+}}} = \frac{39.5}{41.0} = 0.963 \quad (4.13)$$

The selectivity coefficient for (Ca^{2+} , Na^+) exchange is: $K_{\text{Ca}/\text{Na}}^c = 3.36$.

$$K_{\text{Ca}/\text{Na}}^c = \frac{E_{\text{Ca}^{2+}} \cdot c_{\text{Na}^+}^2}{c_{\text{Ca}^{2+}} \cdot E_{\text{Na}^+}^2} \quad (4.14)$$

$$K_{\text{Ca}/\text{Na}}^c = \frac{0.963 \cdot (4.58 \cdot 10^{-3})^2}{4.49 \cdot 10^{-3} \cdot (1 - 0.963)^2} = 3.36 \quad (4.15)$$

Multiply the saturated-paste solution ion concentrations by the concentration factor F_c to compute ion concentrations at the wilting point. The exchanger-bound equivalent fraction $E_{\text{Ca}^{2+}}$ becomes the dependent variable.

The equilibrium ion exchange quotient for the soil at the wilting point appears below.

$$K_{\text{Ca}/\text{Na}}^c = \frac{E_{\text{Ca}^{2+}} \cdot (F_c \cdot c_{\text{Na}^+})^2}{(F_c \cdot c_{\text{Ca}^{2+}}) \cdot (1 - E_{\text{Ca}^{2+}})^2} = 3.36 \quad (4.16)$$

$$3.36 = \frac{E_{\text{Ca}^{2+}} \cdot (1.517 \cdot 10^{-2})^2}{(1.487 \cdot 10^{-2}) \cdot (1 - E_{\text{Ca}^{2+}})^2} \quad (4.17)$$

$$E_{\text{Ca}^{2+}} \cdot (2.302 \cdot 10^{-4}) = 3.36 \cdot 1.487 \cdot 10^{-2} \cdot (1 - E_{\text{Ca}^{2+}})^2 \quad (4.18)$$

The resulting quadratic equation appears below with $E_{\text{Ca}^{2+}}$ as the dependent variable.

$$x \equiv E_{\text{Ca}^{2+}} \quad (4.19)$$

$$(4.927 \cdot 10^{-2}) \cdot x^2 + (-9.877 \cdot 10^{-2}) \cdot x + (4.927 \cdot 10^{-2}) = 0 \quad (4.20)$$

The physically reasonable root of this quadratic equation is a positive value between zero and unity.

$$a = c \equiv 4.927 \cdot 10^{-2} \quad (4.21)$$

$$b \equiv -9.877 \cdot 10^{-2} \quad (4.22)$$

$$x_- = \frac{-b - \sqrt{b^2 - 4 \cdot a \cdot c}}{2 \cdot a} = 0.934 \quad (4.23)$$

Evapotranspiration resulting in the loss of 69.8% of the water present at saturation increases the exchangeable Na^+ content from $n_{\text{Na}^+}^\sigma/m = 1.5 \text{ cmol}_c \cdot \text{kg}^{-1}$ to $n_{\text{Na}^+}^\sigma/m = 2.7 \text{ cmol}_c \cdot \text{kg}^{-1}$.

D. The Bssyz2 horizon of the Duke soil series (Fine, mixed, active, thermic Sodic Haplusterts; Harmon County, OK) is 64.7% clay, has the following chemical properties (NCSS Pedon ID: S2003OK-057-006): $\text{pH} = 7.7$, $\text{CEC7} = 24.2 \text{ cmol}_c \cdot \text{kg}^{-1}$, and a saturated-paste $\text{SAR} = 19.4$.

Determine the conditional selectivity coefficient $K_{\text{Na/K}}^c$ for $(\text{Na}^+, \text{K}^+)$ exchange using the ammonium-acetate and saturated-paste extract data from the National Cooperative Soil Survey for the Duke soil series (Hamon County, OK; NCSS Pedon ID: S2003OK-057-006).

The ion exchange reaction between each pair of cations is independent of the exchange reactions between all other cation pairs.

Solution

Table 4.1 lists the exchangeable spectator cations from the Duke soil series (Hamon County, OK; NCSS Pedon ID: S2003OK-057-006). The sum of exchangeable spectator cations in columns 1-4 equals 64.0, however, does not equal the cation exchange capacity CEC7 listed in column 5. The National Cooperative Soil Survey report for Pedon S2003OK-057-006 lists the following warning.

"Extractable Ca may contain Ca from calcium carbonate or gypsum."

Table 4.1: Spectator cations extracted from the Duke soil (Hamon County, OK; NCSS Pedon ID: S2003OK-057-006): 1 molar ammonium acetate solution buffered to pH 7 (upper) and aqueous saturated-paste extract (lower).

Ammonium Acetate Extract				
Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC7
$\text{cmol}_c \cdot \text{kg}^{-1}$	$\text{cmol}_c \cdot \text{kg}^{-1}$	$\text{cmol}_c \cdot \text{kg}^{-1}$	$\text{cmol}_c \cdot \text{kg}^{-1}$	$\text{cmol}_c \cdot \text{kg}^{-1}$
41.0	9.9	12.0	1.1	24.2
Aqueous Saturated-Paste Extract				
Ca^{2+}	Mg^{2+}	Na^+	K^+	SAR
$\text{mmol}_c \cdot \text{dm}^{-3}$	$\text{mmol}_c \cdot \text{dm}^{-3}$	$\text{mmol}_c \cdot \text{dm}^{-3}$	$\text{mmol}_c \cdot \text{dm}^{-3}$	
32.0	15.8	94.9	0.3	19.41

The true cation exchange capacity CEC7 listed in Table 4.1 is found by first extracting the soil extracted by 1 molar ammonium acetate followed by a second extraction using 2 molar KCl(aq). The values listed in columns 1-4 are based on analysis of the first extract while the CEC7 listed in column 5 is based on a NH_4^+ analysis of the second extract.

The presence of calcite $\text{CaCO}_3(\text{s})$ and gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ in the soil means the exchangeable Ca^{2+} content listed in Table 4.1 is suspect. Absent a reliable value for exchangeable Ca^{2+} it is unwise to attempt to estimate selectivity coefficients involving this cation.

The conditional selectivity coefficient $K_{\text{Na/K}}^c$ for $(\text{Na}^+, \text{K}^+)$ is independent of all other cation pairs. This independence determines how exchanger equivalent fractions are defined.

$$E_{\text{Na}^+} \equiv \frac{n_{\text{Na}^+}^\sigma / m}{n_{\text{Na}^+}^\sigma / m + n_{\text{K}^+}^\sigma / m} \quad (4.24)$$

$$E_{\text{Na}^+} = \frac{12.0}{12.0 + 1.1} = 0.916 \quad (4.25)$$

A single-point estimate of the conditional selectivity coefficient for $(\text{Na}^+, \text{K}^+)$ exchange based on the 1 molar ammonium acetate extract and saturated-paste

data for the Duke soil series (Hamon County, OK; NCSS Pedon ID: S2003OK-057-006) is: $K_{\text{Na/Ca}}^c = 3.45 \cdot 10^{-2}$.

$$K_{\text{Na/K}}^c = \frac{E_{\text{Na}^+} \cdot c_{\text{K}^+}}{c_{\text{Na}^+} \cdot E_{\text{K}^+}} \quad (4.26)$$

$$K_{\text{Na/K}}^c = \frac{(0.916) \cdot 0.3 \cdot 10^{-3}}{(94.9 \cdot 10^{-3})^2 \cdot (1 - 0.916)} = 3.45 \cdot 10^{-2} \quad (4.27)$$

The exchanger equivalent fraction E_{K^+} is significantly *greater than* the solution equivalent fraction E_{Na^+} , which is consistent with the anticipated selectivity for $(\text{Na}^+, \text{K}^+)$ exchange.

$$E_{\text{K}^+} = 1 - 0.916 = 0.084 \quad (4.28)$$

$$E_{\text{K}^+} = \frac{3 \cdot 10^{-4}}{(3 \cdot 10^{-4} + 9.49 \cdot 10^{-2})} = 0.003 \quad (4.29)$$

A similar analysis of asymmetric $(\text{Na}^+, \text{Mg}^{2+})$ exchange yields $K_{\text{Na/Mg}}^c = 0.583$. The exchanger equivalent fraction E_{Na^+} is significantly *less than* the solution equivalent fraction E_{Na^+} , which is consistent with the anticipated selectivity for $(\text{Na}^+, \text{Mg}^{2+})$ exchange.
