

CHAPTER 2

Soil Minerals

- 2.1. Describe the four bonding mechanisms that are important in soil mineralogy. Indicate which mechanisms impart stability to soil minerals in a weathering environment.

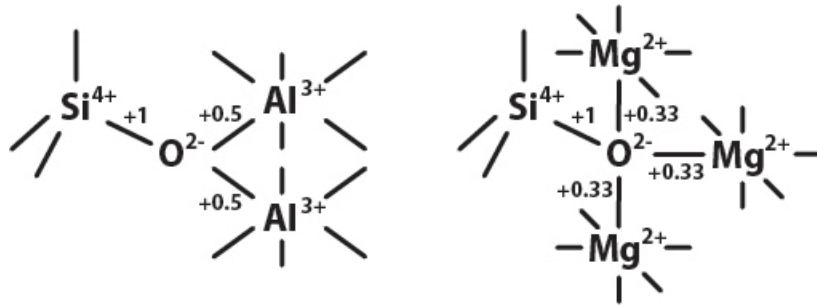
See Section 2.1.

- 2.2. Pauling's Fifth Rule, the Principle of Parsimony, is implied from the first four rules (i.e., it is not an explicitly stated rule in Pauling, 1960). Using the first four Pauling rules, discuss why the Principle of Parsimony must be valid.

See Section 2.2.

- 2.3. Employ Pauling's electrostatic valence principle and show that the residual charge on O^{2-} bound to Si^{4+} in tetrahedral coordination can be satisfied by two Al^{3+} atoms in octahedral coordination or by three Mg^{2+} atoms in octahedral coordination.

The electrostatic valence principle (Pauling's second rule) for the two configurations is illustrated in the figure below.



For Al^{3+} octahedra, each bond radiating from Al^{3+} has a bond strength of $z/CN = +3/6 = +1/2$. Each bond radiating from Si^{4+} has a bond strength of $+4/4 = +1$. A single Si^{4+} bond (+1 strength) plus two Al^{3+} bonds ($2 \times +0.5 = +1$) exactly balance the -2 valence of oxygen; thus, Pauling's second rule is satisfied.

For Mg^{2+} octahedra, each bond radiating from Mg^{2+} has a bond strength of $z/CN = +2/6 = +1/3$. A single Si^{4+} bond (+1 strength) plus three Mg^{2+} bonds ($3 \times +0.33 = +1$) exactly balance the -2 valence of oxygen; thus, Pauling's second rule is satisfied.

- 2.4. The Pauling rules treat ions as hard spheres with fixed ionic radii (termed the Pauling radii). In reality, the ionic radius of a coordinated metal cation is a function of the coordination number. Verify that Al^{3+} satisfies Pauling Rule 1 in both CN 4 and CN 6 configurations, assuming the radius of O^{2-} is 0.140 nm, the radius of Al^{3+} in CN 4 is 0.053 nm, and the radius of Al^{3+} in CN 6 is 0.0675 nm.

In tetrahedral coordination (CN 4), the radius ratio is:

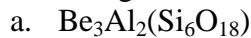
$$r_{\text{Al}^{3+}} = \frac{0.053}{0.140} = 0.379$$

which is between the limiting radius ratios of 0.225 and 0.414 for CN 4 coordination. In octahedral coordination (CN 6), the radius ratio is:

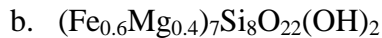
$$r_{\text{Al}^{3+}} = \frac{0.0675}{0.140} = 0.482$$

which is between the limiting radius ratios of 0.414 and 0.732 for CN 6 coordination.

- 2.5. Complexity in the Si tetrahedral arrangement is the criteria used in silicate classification at the class level. On the basis of this criterion, determine the class to which each of the following minerals belongs.



Si:O = 6:18; cyclosilicates



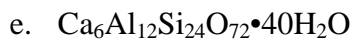
Si:O = 4:11; inosilicates (amphiboles)



Si:O = 2:5; phyllosilicates



Si:O = 1:4; nesosilicates



Si:O = 36:72 (1:2); tectosilicates (Al^{3+} isomorphically substitutes for Si^{4+})



Si:O = 1:3; inosilicates (pyroxenes)



Si:O = 2:7; sorosilicates

- 2.6. Answer the following:

- a. What factors affect the isomorphic substitution of one element for another in a crystal structure?

Size, as dictated by Pauling's first rule.

- b. Why is it more difficult to remove potassium from the interlayer spaces of beidellite than from montmorillonite?

The principle location of the layer charge deficit in beidellite is in the tetrahedral layer; whereas in montmorillonite it is in the octahedral layer. The layer-charge-satisfying K^+ is located closer to the seat of negative charge in beidellite, relative to montmorillonite. Thus, the force of electrostatic attraction (see Equation 5.1) between K^+ and a beidellite surface is greater than that between K^+ and the montmorillonite surface.

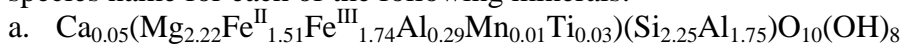
- c. How do chlorite and hydroxyinterlayered vermiculite differ?

Chlorite contains a continuous interlayer metal hydroxide sheet; HIV contains a discontinuous sheet; islands of metal hydroxide polymers.

- d. How do illite and trioctahedral vermiculite differ?

Illite is dioctahedral.

- 2.7. The Association Internationale pour l'Etude des Argiles and the International Mineralogical Association Committee on New Minerals and Mineral Names employ a hierarchical system of mineral Divisions (or Types), Groups, Subgroups, and Species to classify the phyllosilicate minerals (Table 2.7). Use the classification scheme to provide a species name for each of the following minerals:

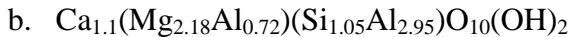


Division: 2:1

Group: Chlorite (x is variable, anion composition $O_{10}(OH)_8$)

Subgroup: Trioctahedral chlorites

Species: Ripidolite



Division: 2:1

Group: Brittle Mica ($x \sim 1.8-2.0$)

Subgroup: Trioctahedral brittle micas

Species: Clintonite

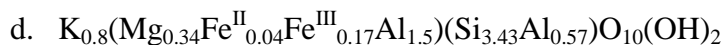


Division: 2:1

Group: Smectite ($0.2 < x < 0.6$)

Subgroup: Dioctahedral smectites

Species: Beidellite

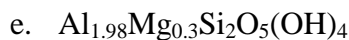


Division: 2:1

Group: Vermiculites ($0.6 < x < 0.9$)

Subgroup: Dioctahedral vermiculites

Species: Dioctahedral vermiculite



Division: 1:1

Group: Serpentine-kaolin ($x \sim 0$)

Subgroup: Dioctahedral

Species: Kaolinite

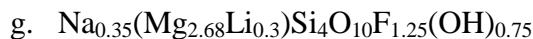


Division: 2:1

Group: Brittle Mica ($x \sim 1.8-2.0$)

Subgroup: Dioctahedral brittle micas

Species: Margarite



Division: 2:1

Group: Smectite ($0.2 < x < 0.6$)

Subgroup: Trioctahedral smectites

Species: Hectorite

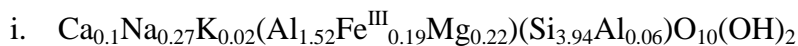


Division: 2:1

Group: Vermiculites ($0.6 < x < 0.9$)

Subgroup: Trioctahedral vermiculites

Species: Trioctahedral vermiculite

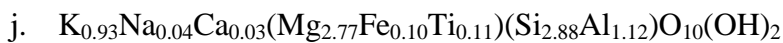


Division: 2:1

Group: Smectite ($0.2 < x < 0.6$)

Subgroup: Dioctahedral smectites

Species: Montmorillonite

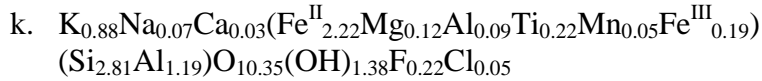


Division: 2:1

Group: True mica ($x \sim 0.85-1.0$)

Subgroup: Trioctahedral micas

Species: Phlogopite

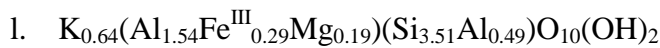


Division: 2:1

Group: True mica ($x \sim 0.85-1.0$)

Subgroup: Trioctahedral micas

Species: Annite

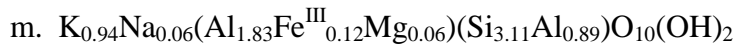


Division: 2:1

Group: Vermiculites ($0.6 < x < 0.9$)

Subgroup: Dioctahedral vermiculites

Species: Dioctahedral vermiculite

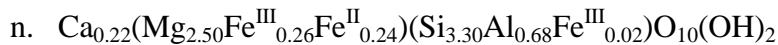


Division: 2:1

Group: True mica ($x \sim 0.85-1.0$)

Subgroup: Dioctahedral micas

Species: Muscovite



Division: 2:1

Group: Smectite ($0.2 < x < 0.6$)

Subgroup: Trioctahedral smectites

Species: Saponite

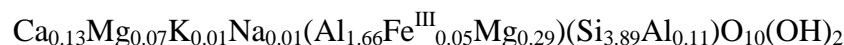
- 2.8. The chemical composition of a clay mineral from the Montmorillone region of France is given in the table below.
- Calculate the unit cell structural formula for this clay mineral.
 - Compute a value for the cation exchange capacity of the mineral.
 - Given that the unit cell parameters are $a = 0.517$ nm and $b = 0.894$ nm, compute a value for the internal specific surface area of the mineral.
 - Estimate a value for the total surface area of the mineral (state any assumptions).

Component	%	Component	%
SiO ₂	51.14	CaO	1.62
Al ₂ O ₃	19.76	K ₂ O	0.11
Fe ₂ O ₃	0.83	Na ₂ O	0.04
MgO	3.22		

The structural formula is determined using the method described in Table 2.10 (chemical composition excludes H₂O). The results are presented in the table below.

Oxide	g kg ⁻¹	Normalized g kg ⁻¹	MW g mol ⁻¹	Mole Cation Charge kg ⁻¹	Normalized Cation Charge	½-Unit Cell Formula
SiO ₂	511.4	666.58	60.08	44.38	15.54	3.89
Al ₂ O ₃	197.6	257.56	101.96	15.16	5.31	1.77
Fe ₂ O ₃	8.3	10.82	159.69	0.41	0.144	0.048
MgO	32.2	41.97	40.30	2.08	0.728	0.364
CaO	16.2	21.12	56.08	0.75	0.263	0.132
K ₂ O	1.1	1.43	94.20	0.030	0.011	0.011
Na ₂ O	0.4	0.52	61.98	0.017	0.006	0.006

The structural (½-unit cell) formula for the layer silicate is:



The mineral is montmorillonite.

The cation exchange capacity is computed using Equation 2.4 with a unit cell layer charge of 0.8 and a molecular mass of 736.78 g mol⁻¹.

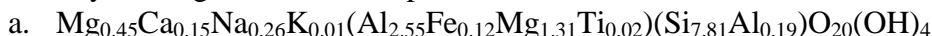
$$\text{CEC} = 0.8 \frac{\text{charge}}{\text{unit cell}} \times \frac{\text{mol}_c}{736.78 \text{ g}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{100 \text{ cmol}_c}{\text{mol}_c} = 108.58 \frac{\text{cmol}_c}{\text{kg}}$$

The internal surface area of the mineral is $2ab = 2 \times 0.517 \text{ nm} \times 0.894 \text{ nm} = 0.9244 \text{ nm}^2$ per unit cell. The specific surface in units of m² g⁻¹ is:

$$S = 0.9244 \frac{\text{nm}^2}{\text{unit cell}} \times 6.022 \times 10^{23} \frac{\text{unit cells}}{\text{mol}} \times \frac{\text{mol}}{736.78 \text{ g}} \times \frac{10^{-18} \text{ m}^2}{\text{nm}^2} = 755.5 \frac{\text{m}^2}{\text{g}}$$

If it is assumed that the internal surface of a 2:1 expansive layer silicate is 80 % of the total, then the total specific surface is $755.5/0.8 = 944.4 \text{ m}^2 \text{ g}^{-1}$.

- 2.9. The unit cell formulas for three phyllosilicates are indicated below. For each mineral, determine (a) the octahedral layer charge, (b) the tetrahedral layer charge, and (c) the interlayer charge. Provide the species name for each mineral.



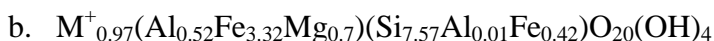
The octahedral occupation is $2.55 + 0.12 + 1.31 + 0.02 = 4$ per unit cell; the mineral is dioctahedral. The positive charge in this layer is $2.55(3) + 0.12(3) + 1.31(2) + 0.02(4) = 10.71$, which satisfies a -12 charge from the surrounding anions; the layer charge is 1.29 per unit cell, or 0.645 per $\frac{1}{2}$ unit cell.

The tetrahedral occupation is $7.81 + 0.19 = 8$, which a layer charge equal to the Al content, or 0.19 per unit cell and 0.095 per $\frac{1}{2}$ unit cell.

The charge deficit from the octahedral and tetrahedral layers is $0.645 + 0.095 = 0.74$ per $\frac{1}{2}$ unit cell, which places this mineral in the Vermiculite Group.

The interlayer charge is $0.45(2) + 0.15(2) + 0.26(1) + 0.01(1) = 1.47$ per unit cell, or 0.74 per $\frac{1}{2}$ unit cell.

The mineral is dioctahedral, and is therefore classified as dioctahedral vermiculite. This mineral is actually Otay montmorillonite, the source clay mineral SCa-3. Although the layer charge is greater than 0.6, the primary location of the layer charge is in the octahedral layer (in vermiculites the layer charge is primarily in the tetrahedral layer), and it is likely that this specimen expands beyond 14.5 \AA upon glycolation.



The octahedral occupation is $0.52 + 3.32 + 0.7 = 4.45$ per unit cell; the mineral is dioctahedral and there is over-occupation in the layer. The positive charge in this layer is $0.55(3) + 3.32(3) + 0.7(2) = 13.01$, which satisfies a -12 charge from the surrounding anions; the excess layer charge is $+1.01$ per unit cell, or $+0.51$ per $\frac{1}{2}$ unit cell.

The tetrahedral occupation is $7.57 + 0.01 + 0.19 = 7.77$. The positive charge in this layer is $7.57(4) + 0.01(3) + 0.19(3) = 30.88$, which satisfies a -32 charge from the surrounding anions; the layer charge is 1.12 per unit cell, or 0.56 per $\frac{1}{2}$ unit cell per $\frac{1}{2}$ unit cell.

The charge deficit from the octahedral and tetrahedral layers is $0.51 - 0.56 = -0.05$.

The interlayer charge is 0.97 per unit cell, or 0.49 per $\frac{1}{2}$ unit cell.

The mineral is dioctahedral, but there is discontinuity between the layer charge (0.05 per $\frac{1}{2}$ unit cell) and interlayer cation charge (0.49 per $\frac{1}{2}$ unit cell).

The mineral is in the Smectite Group (low layer charge, $x < 0.6$) and it is dioctahedral with the layer charge principally arising in the tetrahedral layer. The mineral is also high in Fe, and classifies as a nontronite (this mineral is nontronite, the source clay mineral N Au-2).



The octahedral occupation is $0.61 + 3.08 + 0.24 + 0.07 = 4$ per unit cell; the mineral is dioctahedral. The positive charge in this layer is $0.61(3) + 3.08(3) + 0.24(2) + 0.07(4) = 11.83$, which satisfies a -12 charge from the surrounding anions; the layer charge is 0.17 per unit cell, or 0.085 per $\frac{1}{2}$ unit cell.

The tetrahedral occupation is $7.09 + 0.91 = 8$, which a layer charge equal to the Al content, or 0.91 per unit cell and 0.455 per $\frac{1}{2}$ unit cell.

The charge deficit from the octahedral and tetrahedral layers is $0.085 + 0.455 = 0.54$ per $\frac{1}{2}$ unit cell, which places this mineral in the Smectite Group.

The interlayer charge is $0.18(2) + 0.36(2) + 0.01(1) = 1.09$ per unit cell, or 0.55 per $\frac{1}{2}$ unit cell.

The mineral is dioctahedral, and is therefore classified as dioctahedral smectite. The layer charge arises principally in the tetrahedral layer and the octahedral layer is dominated by Fe. The mineral is nontronite (this mineral is a ferruginous smectite, the source clay mineral S Wa-1).

- 2.10. A 200-mg mass of a clay mineral with a structural formula of $\text{Mg}_{0.06}\text{Ca}_{0.19}\text{Na}_{0.03}\text{K}_{0.05}(\text{Al}_{1.43}\text{Fe}^{\text{III}}_{0.08}\text{Fe}^{\text{II}}_{0.02}\text{Mg}_{0.47})(\text{Si}_{3.93}\text{Al}_{0.07})\text{O}_{10}(\text{OH})_2$ is dissolved using the $\text{HNO}_3\text{-HCl-HF}$ method of Bernas. After neutralizing excess HF with boric acid the solution is placed in a 50-mL volumetric flask and brought to volume with metal-free (Type-I) water. Chemical analysis is then performed using inductively coupled argon plasma. What are the concentrations of K, Na, Ca, Al, Fe, Mg, and Si in this solution?

The molecular mass of the mineral is $747.16 \text{ g mol}^{-1}$ (unit cell basis). Using Si as an example, the concentration of Si in the solution is:

$$\frac{\text{mg}}{\text{L}} = \frac{7.86 \text{ mol Si}}{\text{mol clay}} \times \frac{28.0855 \text{ g Si}}{\text{mol Si}} = \frac{220.752 \text{ g Si}}{\text{mol clay}}$$

$$\frac{220.752 \text{ g Si}}{\text{mol clay}} \times \frac{\text{mol clay}}{747.16 \text{ g}} \times \frac{0.2 \text{ g clay}}{0.05 \text{ L}} \times \frac{1000 \text{ mg}}{\text{g}} = 1181.8 \frac{\text{mg}}{\text{L}}$$

The results are shown in the table below.

Element	mol mol ⁻¹ clay	g mol ⁻¹	g mol ⁻¹ clay	mg L ⁻¹
Si	7.86	28.0855	220.75	1182
Al	3.00	26.98154	80.94	433
Fe	0.20	55.847	11.17	59.8
Mg	1.06	24.305	25.76	138
Ca	0.38	40.08	15.23	81.5
Na	0.06	22.98977	1.38	7.39
K	0.10	39.0983	3.91	20.9

2.11. The compositional data for a 2:1 phyllosilicate is provided in the table below.

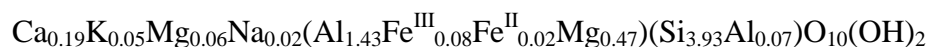
Oxide	%
SiO ₂	50.95
Al ₂ O ₃	16.54
Fe ₂ O ₃	1.36
FeO	0.26
MgO	4.65
CaO	2.26
Na ₂ O	0.17
K ₂ O	0.47

- Determine the ½-unit cell structural formula for the mineral.
- Name the mineral
- Compute the cation exchange capacity of the mineral.
- Compute the surface area of the mineral given that $a = 0.52$ nm and $b = 0.9$ nm.

The structural formula is determined using the method described in Table 2.10 (chemical composition excludes H₂O). The results are presented in the table below.

Oxide	g kg ⁻¹	Normalized g kg ⁻¹	MW g mol ⁻¹	Mole Cation Charge kg ⁻¹	Normalized Cation Charge	½-Unit Cell Formula
SiO ₂	509.5	664.62	60.08	44.25	15.71	3.928
Al ₂ O ₃	165.4	215.76	101.96	12.70	4.51	1.503
Fe ₂ O ₃	13.6	17.74	159.69	0.67	0.24	0.080
FeO	2.6	3.39	71.85	0.09	0.03	0.015
MgO	46.5	60.66	40.30	3.01	1.07	0.534
CaO	22.6	29.48	56.08	1.05	0.37	0.185
K ₂ O	4.7	6.13	94.20	0.13	0.05	0.05
Na ₂ O	1.7	2.22	61.98	0.07	0.02	0.02

The structural (½-unit cell) formula for the layer silicate is:



The mineral is montmorillonite.

The cation exchange capacity is computed using Equation 2.4 with a unit cell layer charge of 0.56 and a molecular mass of $747.16 \text{ g mol}^{-1}$.

$$\text{CEC} = 0.56 \frac{\text{charge}}{\text{unit cell}} \times \frac{\text{mol}_c}{747.16 \text{ g}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{100 \text{ cmol}_c}{\text{mol}_c} = 74.95 \frac{\text{cmol}_c}{\text{kg}}$$

The internal surface area of the mineral is $2ab = 2 \times 0.52 \text{ nm} \times 0.9 \text{ nm} = 0.936 \text{ nm}^2$ per unit cell. The specific surface in units of $\text{m}^2 \text{ g}^{-1}$ is:

$$S = 0.936 \frac{\text{nm}^2}{\text{unit cell}} \times 6.022 \times 10^{23} \frac{\text{unit cells}}{\text{mol}} \times \frac{\text{mol}}{747.16 \text{ g}} \times \frac{10^{-18} \text{ m}^2}{\text{nm}^2} = 754.4 \frac{\text{m}^2}{\text{g}}$$

If it is assumed that the internal surface of a 2:1 expansive layer silicate is 80 % of the total, then the total specific surface is $754.4/0.8 = 943.0 \text{ m}^2 \text{ g}^{-1}$.

2.12. The compositional data for a 2:1 phyllosilicate is provided in the table below.

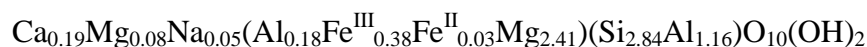
Oxide	%
SiO ₂	34.92
Al ₂ O ₃	13.97
Fe ₂ O ₃	6.25
FeO	0.52
MgO	20.37
CaO	2.15
Na ₂ O	0.32

- Determine the 1/2-unit cell structural formula for the mineral.
- Name the mineral
- Compute the cation exchange capacity of the mineral.
- Compute the surface area of the mineral given that $a = 0.524 \text{ nm}$ and $b = 0.917 \text{ nm}$.

The structural formula is determined using the method described in Table 2.10 (chemical composition excludes H₂O). The results are presented in the table below.

Oxide	g kg ⁻¹	Normalized g kg ⁻¹	MW g mol ⁻¹	Mole Cation Charge kg ⁻¹	Normalized Cation Charge	½-Unit Cell Formula
SiO ₂	349.2	444.84	60.08	29.62	11.37	2.84
Al ₂ O ₃	139.7	177.96	101.96	10.47	4.02	1.34
Fe ₂ O ₃	62.5	79.62	159.69	2.99	1.15	0.38
FeO	5.2	6.62	71.85	0.18	0.07	0.03
MgO	203.7	259.49	40.30	12.96	4.97	2.49
CaO	21.5	27.39	56.08	0.98	0.38	0.19
Na ₂ O	3.2	4.08	61.98	0.13	0.05	0.05

The structural (½-unit cell) formula for the layer silicate is:



The mineral is trioctahedral vermiculite.

The cation exchange capacity is computed using Equation 2.4 with a unit cell layer charge of 0.6 and a molecular mass of 804.21 g mol⁻¹.

$$\text{CEC} = 0.6 \frac{\text{charge}}{\text{unit cell}} \times \frac{\text{mol}_c}{804.21 \text{ g}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{100 \text{ cmol}_c}{\text{mol}_c} = 74.61 \frac{\text{cmol}_c}{\text{kg}}$$

The internal surface area of the mineral is $2ab = 2 \times 0.524 \text{ nm} \times 0.917 \text{ nm} = 0.961 \text{ nm}^2$ per unit cell. The specific surface in units of m² g⁻¹ is:

$$S = 0.961 \frac{\text{nm}^2}{\text{unit cell}} \times 6.022 \times 10^{23} \frac{\text{unit cells}}{\text{mol}} \times \frac{\text{mol}}{804.21 \text{ g}} \times \frac{10^{-18} \text{ m}^2}{\text{nm}^2} = 719.62 \frac{\text{m}^2}{\text{g}}$$

If it is assumed that the internal surface of a 2:1 expansive layer silicate is 80 % of the total, then the total specific surface is $719.62/0.8 = 899.52 \text{ m}^2 \text{ g}^{-1}$.

- 2.13. X-ray diffraction is one of the principal techniques used in mineralogical studies. The Bragg equation is used to explain how x-ray diffraction works.

a. Derive the Bragg equation.

The Bragg equation (Equation 2.6) is developed in Section 2.7.1.

- b. Compute the smallest d -value that can be measured by x-ray diffraction using CuK α radiation ($\lambda = 0.1540598 \text{ nm}$).

The sin function is at its maximum value (1) when $\theta = 90^\circ$, or when

$^{\circ}2\theta = 180^{\circ}$. Thus, $d = \lambda/2 = 0.1540598/2 = 0.0773$ nm is the theoretical lower limit to the d -value that may be measured using CuK α x-radiation.

- c. Using CuK α radiation, calculate the incidence angles ($^{\circ}2\theta$) for diffractions that would indicate d -values of 0.426 nm and 0.334 nm.

Rearranging the Bragg equation:

$$\frac{\lambda}{2d} = \sin \theta$$

or

$$\arcsin\left(\frac{\lambda}{2d}\right) = \theta$$

For $d = 0.426$ nm,

$$\theta = \arcsin\left(\frac{0.1540598}{0.852}\right) = \arcsin(0.180821) = 10.42^{\circ}$$

and $^{\circ}2\theta = 20.84^{\circ}$. Similarly, when $d = 0.334$ nm, $^{\circ}2\theta = 26.67^{\circ}$.

- d. Using CuK α radiation, create a table similar to Table 2.13, displaying the characteristic $^{\circ}2\theta$ values, instead of the characteristic d -values, for the phyllosilicates.

Treatment	Kaolinite	Mica	Vermiculite	Smectite	Chlorite
K ⁺ at 25°C	12.6	8.84	8.84	7.36	6.31
K ⁺ at 300°C	12.6	8.84	8.84	8.84	6.31
K ⁺ at 550°C	—	8.84	8.84	8.84	6.31
Mg ²⁺	12.6	8.84	6.31	6.31	6.31
Mg ²⁺ -glycol	12.6	8.84	6.31	4.91	6.31

- 2.14. A 200-mg mass of a clay mineral with a structural formula of $K_{0.94}Na_{0.06}(Al_{1.83}Fe^{III}_{0.12}Mg_{0.06})(Si_{3.11}Al_{0.89})O_{10}(OH)_2$ is dissolved using the HNO₃-HCl-HF method of Bernas. After neutralizing excess HF with boric acid the solution is placed in a 50-mL volumetric flask and brought to volume with metal-free (Type I) water. Chemical analysis is then performed using inductively coupled argon plasma. What are the concentrations of K, Na, Al, Fe, Mg, and Si in this solution?

The molecular mass of the mineral is 802.07 g mol⁻¹ (unit cell basis). Using Si as an example, the concentration of Si in the solution is:

$$\frac{\text{mg}}{\text{L}} = \frac{6.22 \text{ mol Si}}{\text{mol clay}} \times \frac{28.0855 \text{ g Si}}{\text{mol Si}} = \frac{174.69 \text{ g Si}}{\text{mol clay}}$$

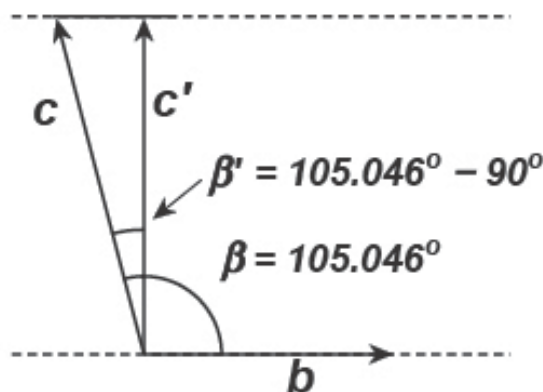
$$\frac{174.69 \text{ g Si}}{\text{mol clay}} \times \frac{\text{mol clay}}{802.07 \text{ g}} \times \frac{0.2 \text{ g clay}}{0.05 \text{ L}} \times \frac{1000 \text{ mg}}{\text{g}} = 871.2 \frac{\text{mg}}{\text{L}}$$

The results are shown in the table below.

Element	mol mol ⁻¹ clay	g mol ⁻¹	g mol ⁻¹ clay	mg L ⁻¹
Si	6.22	28.0855	174.69	871.2
Al	5.44	26.98154	146.78	732.0
Fe	0.24	55.847	13.40	66.8
Mg	0.12	24.305	2.92	14.5
Na	0.12	22.98977	2.76	13.8
K	1.88	39.0983	73.50	366.6

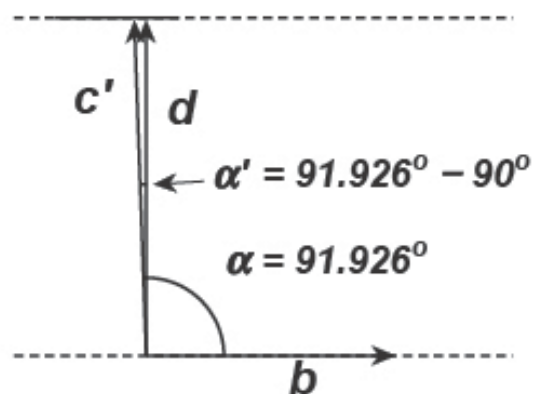
- 2.15. The unit cell parameters for triclinic kaolinite (kaolinite-1*Tc*) are: $a = 5.1536 \text{ \AA}$, $b = 8.9419 \text{ \AA}$, $c = 7.3906 \text{ \AA}$, and $\alpha = 91.926^\circ$, $\beta = 105.046^\circ$, and $\gamma = 89.797^\circ$. Compute the d -value for the 001 plane.

Because kaolinite unit cell is triclinic, the height of the unit cell (d -value) and the c -axis dimension are not equal. The d -value will be affected by α , β , and c . First, a right triangle is isolated (looking down the b -axis):



The distance $c' = c \times \cos(\beta - 90^\circ) = 7.3906 \times \cos(15.046) = 7.137 \text{ \AA}$.

Rotating the structure and looking down the a -axis:

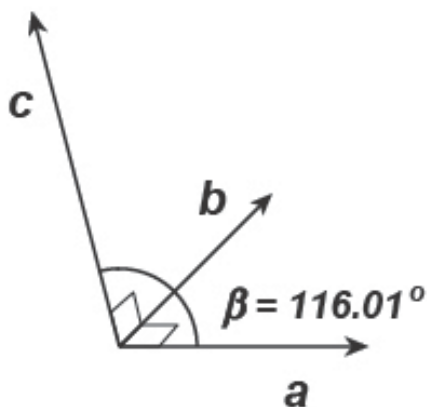


Then, $d_{001} = c' \times \cos(\alpha - 90^\circ) = 7.137 \times \cos(1.926) = 7.133 \text{ \AA}$.

- 2.16. In the table below are a subset of the Miller indices and associated d -values for a mineral with $\beta = 116.01^\circ$. Using these data, determine the remaining unit cell parameters.

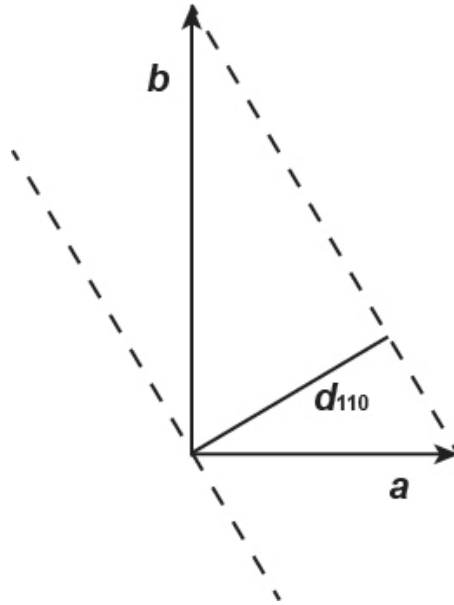
Miller Indices (hkl)	d -Value (\AA)
(110)	6.62
(001)	6.48
($\bar{1}$ 11)	5.86
(021)	4.58
($\bar{2}$ 01)	4.22
(040)	3.25

The unit cell parameters are $\beta = 116.01^\circ$, and $\alpha = \gamma = 90^\circ$:



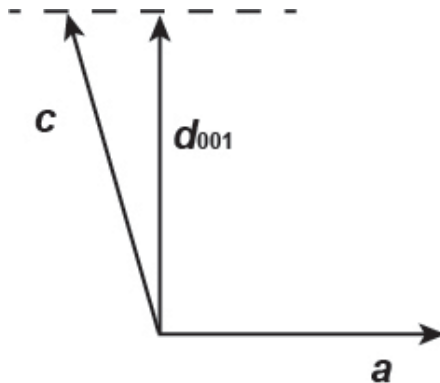
The d -value for the (040) plane is a direct measure of the b -axis length: $b = 4 \times d_{040} = 4 \times 3.25 = 13 \text{ \AA}$.

Looking down the c -axis:



The angle between the b -axis and d_{110} is, $\cos(\angle bd_{110}) = d_{110}/b = 6.62/13 = 0.50923$, or $\angle bd_{110} = 59.387^\circ$. The angle between the a -axis and d_{110} is $\angle ad_{110} = 90^\circ - 59.387^\circ = 30.613^\circ$. The a -axis length is computed using, $\cos(\angle ad_{110}) = d_{110}/a$. Rearranging, $a = 6.62/\cos(30.613) = 6.62/0.8602 = 7.692 \text{ \AA}$.

The c -axis dimension is computed from the d_{001} value and the angle between the c -axis and d_{001} :



The angle between the c -axis and d_{001} is, $116.01^\circ - 90^\circ = 26.01^\circ$. Then, $c = d_{001}/\cos(26.01) = 6.48/0.89872 = 7.21 \text{ \AA}$. The unit cell parameters are: $\alpha = \gamma = 90^\circ$, $\beta = 116.01^\circ$, $a = 7.69 \text{ \AA}$, $b = 13 \text{ \AA}$, and $c = 7.21 \text{ \AA}$, and the unit cell is monoclinic.

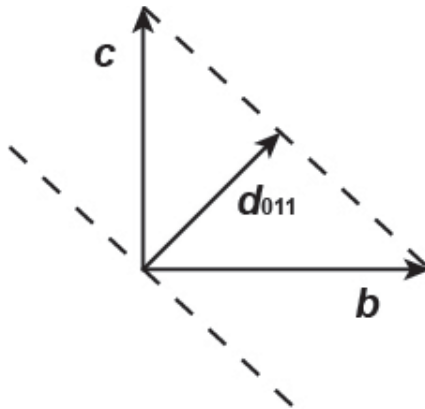
- 2.17. The following x-ray diffraction data were obtained for a phosphate mineral using $\text{CuK}\alpha$ radiation (1.5418 \AA). Compute the unit cell dimensions of this mineral.

Miller Indices (<i>hkl</i>)	$^{\circ}2\theta$
(010)	16.953
(110)	22.337
(101)	23.409
(011)	25.084
(111), (200)	29.183
(210)	33.956
(020)	34.224

Using the Bragg equation (Equation 2.6) with $\lambda = 1.5418 \text{ \AA}$, the $^{\circ}2\theta$ values are converted to d -values:

Miller Indices (<i>hkl</i>)	$^{\circ}2\theta$	d -Value, \AA
(010)	16.953	5.23
(110)	22.337	3.98
(101)	23.409	3.80
(011)	25.084	3.55
(111), (200)	29.183	3.06
(210)	33.956	2.64
(020)	34.224	2.62

Because the angles in the unit cell parameters are not given, it is assumed that $\alpha = \gamma = \beta = 90^{\circ}$. Therefore, the a - and c -axes dimensions may be obtained directly from the d_{200} and d_{010} (or d_{020}) values: $a = 2 \times d_{200} = 2 \times 3.06 = 6.12 \text{ \AA}$; $b = d_{010} = 5.23 \text{ \AA}$. The c -axis dimension may be obtained from the d_{101} or d_{011} values:



$$\cos(\angle bd_{011}) = \frac{d_{011}}{b} = \frac{3.55}{5.23}; \angle bd_{011} = 47.25^{\circ}$$

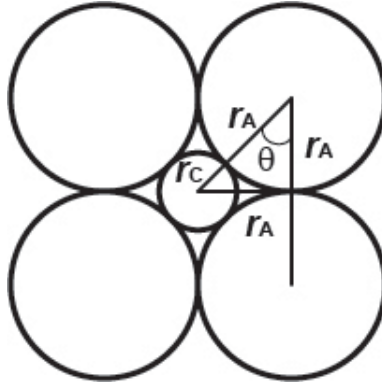
$$\text{Then, } \angle cd_{011} = 90^{\circ} - 47.25 = 42.75^{\circ}$$

$$\cos(\angle cd_{011}) = \frac{d_{011}}{c}; c = \frac{3.55}{\cos(42.75)} = 4.83 \text{ \AA}$$

The unit cell parameters are, $\alpha = \gamma = \beta = 90^\circ$, $a = 6.12 \text{ \AA}$; $b = 5.23 \text{ \AA}$, and $c = 4.83 \text{ \AA}$ and the unit cell is orthorhombic.

- 2.18. The smallest sphere that can be placed in CN = 6 configuration (octahedron) has a radius ratio of 0.414. Prove this to be the case, irrespective of anion size, by computing the minimum radius ratio, using geometric principles, for an octahedron using both O^{2-} ($r = 0.140 \text{ nm}$) and F^- ($r = 0.133 \text{ nm}$) as coordinating anions.

The limiting radius ratio is attained when all atoms in the coordinated polyhedron touch:



Angle θ is computed from the expression $\tan \theta = r_C/r_A$; $\theta = 45^\circ$. Then,

$$\sin \theta = \frac{r_A}{r_A + r_C} = 0.707$$

or

$$1.414 = \frac{r_A + r_C}{r_A} = \frac{r_A}{r_A} + \frac{r_C}{r_A} = 1 + \frac{r_C}{r_A}$$

Therefore, $r_C/r_A = 0.414$, which is the limiting radius ratio for CN 6, irrespective of anion size.

- 2.19. You are given a soil sample and asked to determine the clay mineralogy. Beginning with the bulk soil sample, describe a methodology that could be employed to determine the clay mineralogy of the soil by x-ray diffraction. Include a discussion of any pretreatments, clay isolation techniques, and clay saturation treatments. Also, indicate how the various clay minerals respond to the imposed saturation treatments (it will be necessary to consult a reference that describes Stoke's Law sedimentation).

See Section 2.7.3.

- 2.20. Determine the clay mineralogy of the clay-sized fraction of an Alfisol using the x-ray diffraction data presented below.

Treatment	Peak Location, °2θ
K ⁺ -saturated:	
Room	6.90, 8.73, 12.28, 17.72, 20.81, 24.85, 26.58
400°C	8.77, 12.30, 17.74, 20.80, 24.80, 26.60
550°C	8.70, 17.63, 20.69, 26.50
Mg ²⁺ -glycol saturated	6.08, 8.75, 12.27, 17.75, 20.82, 24.82, 26.57

Using the Bragg equation (Equation 2.6) with $\lambda = 1.5418 \text{ Å}$, the °2θ values are converted to *d*-values:

Treatment	<i>d</i> -Value, Å
K ⁺ -saturated:	
Room	12.8, 10.1, 7.21, 5.00, 4.27, 3.58, 3.35
400°C	10.1, 7.20, 5.00, 4.27, 3.59, 3.35
550°C	10.2, 5.03, 4.29, 3.36
Mg ²⁺ -glycol saturated	14.5, 10.1, 7.21, 5.00, 4.27, 3.59, 3.35

The clay mineralogy is:

Vermiculite-HIV: 14.5 Å in Mg²⁺-glycol that collapses to 12.8 Å (HIV) in K⁺-saturated at room *T*, and to 10 Å at higher *T*

Mica: 10 Å and 5 Å throughout

Kaolinite: 7 Å peak disappears in K⁺-sat, 550°C treatment

- 2.21. Describe how the surface charge characteristics of phyllosilicates and hydrous metal oxides differ.

The phyllosilicates bear both permanent structural charge (the ditrigonal siloxane cavity) and ionizable surface functional groups (e.g., ≡SiOH and ≡AlOH). The reactivity of these functional groups varies depending on the phyllosilicate species (as described in the relevant sections). The hydrous metal oxides bear only ionizable functional groups (described in Section 2.6).

- 2.22. For each of the following minerals: (1) describe (diagram) the structure and provide a structural formula; (2) indicate the locations on the mineral surface where ions may be adsorbed; and (3) identify the characteristic of the mineral that results in surface charge (how is surface charge developed and where is it located).

a. Vermiculite

The structure is illustrated in Figures 2.34 and 2.35. Representative structural formulas are indicated in Table 2.7 and in Section 2.5.2.2.3. Ions may be retained in the interlayer and on the external surfaces. Surface charge is primarily generated by the isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral layer. The ionization of $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ surface functional groups may also generate surface charge.

b. Montmorillonite

The structure is illustrated in Figures 2.34 and 2.35. Representative structural formulas are indicated in Table 2.7 and in Section 2.5.2.2.2. Ions may be retained in the interlayer and on the external surfaces. Surface charge is primarily generated by the isomorphic substitution of Mg^{2+} for Al^{3+} in the octahedral layer. The ionization of $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ surface functional groups may also generate surface charge.

c. Gibbsite

The structure is illustrated in Figures 2.41a. The structural formula is $\text{Al}(\text{OH})_3$. Ions may be retained by the external surface. Surface charge is generated by the ionization of $\equiv\text{AlOH}$ surface functional groups.

d. Goethite

The structure is illustrated in Figures 2.42a. The structural formula is FeOOH . Ions may be retained by the external surface. Surface charge is generated by the ionization of $\equiv\text{FeOH}$ surface functional groups.

e. Clinoptilolite

The structure is illustrated in Figures 2.24. Representative structural formula is indicated in Table 2.5. Ions may be retained in structural vacuoles and channels. Surface charge is primarily generated by the isomorphic substitution of Al^{3+} for Si^{4+} in tetrahedral coordination. The ionization of $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ surface functional groups may also generate surface charge.

f. Kaolinite

The structure is illustrated in Figures 2.28. The structural formula is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Ions may be retained by the external surface. Surface charge is generated by the ionization of $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ surface functional groups.

g. Sepiolite

The structure is illustrated in Figures 2.38. Representative structural formula is indicated in Section 2.5.2.2.6. Ions may be retained in structural channels. Surface

charge is primarily generated by the isomorphic substitution of Al^{3+} for Si^{4+} in tetrahedral coordination. The ionization of $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ surface functional groups may also generate surface charge.

h. Birnessite

The structure is illustrated in Figures 2.43a. Representative structural formulas are indicated in Table 2.12 and in Section 2.6.3. Ions may be retained in the interlayer and on the external surfaces. Surface charge is generated by vacancies in the cation octahedral sheet, by the isomorphic substitution of Mn^{2+} and Mn^{3+} for Mn^{4+} in the octahedral layer, and by the ionization of $\equiv\text{MnOH}$ surface functional groups.

i. Todokorite

The structure is illustrated in Figures 2.43c. Representative structural formulas are indicated in Table 2.12 and in Section 2.6.3. Ions may be retained in the tunnels and on the external surfaces. Surface charge is generated by vacancies in the cation octahedral sheet, by the isomorphic substitution of Mn^{2+} and Mn^{3+} for Mn^{4+} in the octahedral layer, and by the ionization of $\equiv\text{MnOH}$ surface functional groups.

j. Allophane

The structure is illustrated in Figures 2.44. Representative structural formulas are indicated in Section 2.6.4. Ions may be retained in the tubes and on the external surfaces. Surface charge is generated by the ionization of $\equiv\text{SiOH}$ and $\equiv\text{AlOH}$ surface functional groups.