

Silicate Chemistry



Teacher Notes and Student Activities

Gary B. Lewis 1994

Further Information: (06) 249 9570

Record No. 1995/19

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DEPARTMENT OF PRIMARY INDUSTRIES AND ENERGY

Minister for Resources: Hon. David Beddall, MP

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AUSTRALIAN GEOLOGICAL SURVEY ORGANISATION

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AGSO Record No. 1995/19

ISSN: 1039 - 0073 ISBN: 0 642 22332 7

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Activities

CRUSTAL ELEMENTS

CHEMICAL WEATHERING OF FELDSPAR

READING TERNARY DIAGRAMS

CHEMICAL ZONES

MINERAL PHASES

Silicate Chemistry

While students are taught about chemistry using simple examples of inorganic and organic substances, very few are exposed to the chemistry of the most abundant group of chemicals on Earth - the silicate group of minerals.

Silicates can be used to study bonding, crystal structure, differentiation of chemistry due to temperature, physical properties and more.

1. Elements in the Earth's Crust

The average composition of the Earth's crust, calculated in grams per tonne, gives the following elements in order of abundance:

Oxygen	46.6%
Silicon	27.7%
Aluminium	8.1%
Iron	5.0%
Calcium	3.6%
Sodium	2.8%
Potassium	2.6%
Magnesium	2.1%

98.5%

This means that the majority of the minerals must be made up of a combination of oxygen and silicon with the other elements acting as bonding cations.

2. Silicon

- Silicon is a non-metallic element
- It has four electrons in its outer shell i.e. valence 4
- It is a semi-conductor.
- It does not occur free in nature.
- It is a small atom compared to oxygen

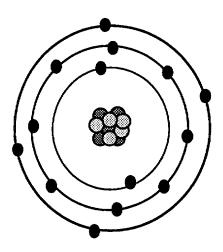


Figure 1. Silicon electron configuration

3. Silicon Building Blocks

The basic silicon-oxygen structure is known as the silicon tetrahedron. This structure involves four oxygen atoms bonded to one silicon atom. The bonding is 50% covalent and 50% ionic.

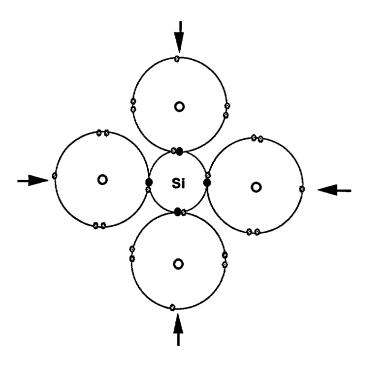


Figure 2. The silicate building block electron configuration. The arrows point to sites where the unit can bond either to another unit or to a cation.

The powerful bond between the silicon and oxygen ions is literally the "cement" that bonds the crust of our planet together.

Ionic radii

For simplicity, ions can be thought of as spheres, each ionic element having a given size. This size is known as the ionic radius of the element. Anions have large ionic radii while cations have small ionic radii.

The size of the silicon ion (radius = 0.39 Å) to the oxygen ion (radius = 1.40 Å) is such that the silicon atom sits surrounded by the oxygen atoms in a triangular pyramid form (Figure 3).

In structural diagrams of the silicates, the tetrahedron is represented by the plan view of a triangular pyramid (Figure 4).

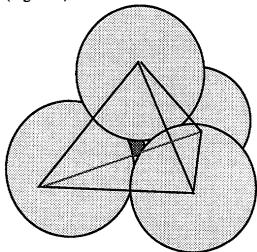


Figure 3. The small dark sphere represents the silicon atom surrounded by the four larger oxygen atoms. The centre of each oxygen atom forms the points of a triangular pyramid or tetrahedron.

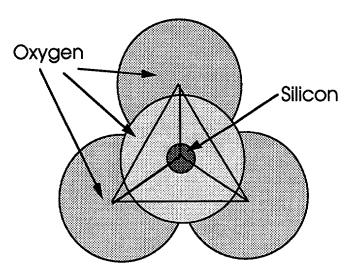


Figure 4. Plan view of tetrahedron showing structural symbol.

As each oxygen in the tetrahedron has a free bonding site, a tetrahedron can either bond to another tetrahedron or to a metallic ion. It is this ability that allows the multitude of silicate minerals to be formed.

The variety of minerals is due to the arrangement of the tetrahedra as well as the type and availability of metallic cations to bond the tetrahedrons together. The most common metallic cations in the Earth's crust are Fe^{2+} (radius = 0.74Å), Mg^{2+} (radius = 0.66Å), Na^+ (radius = 0.97Å), K^+ (radius = 1.33Å), Ca^{2+} (radius = 0.99Å) and Al^{3+} (radius = 0.51Å). The size of the cations affects which bonding sites they can occupy. Fe^{2+} and Mg^{2+} for example, are similar in size and can therefore be interchanged with each other if they are available at the time of formation.

4. The Basic Silicate Structures

Like carbon chemistry, silicate chemistry is based around a number of common structures. These structures are formed around the linking of the tetrahedra.

Nesosilicates (Isolated tetrahedron)

These are minerals in which single tetrahedrons are isolated from each other by metallic cations. An example is the mineral Olivine (Mg, Fe)SiO₄. In Olivine each of the oxygen atoms in the tetrahedron is ionically bonded to either an iron or a magnesium cation. As the oxygen atoms only bond with one of the available sites on the cation, the remaining free bonding site on the cation can bond ionically to another tetrahedron. This allows a crystal structure to develop.

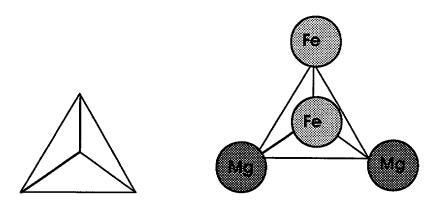


Figure 5. The single tetrahedron and a tetrahedron surrounded by bonded cations.

The ratio of iron to magnesium can change from 100% Fe through to 100% Mg. This means that Olivine represents a group of minerals (the Olivine Group) with Forsterite (Mg₂SiO₄) and Fayalite (Fe₂SiO₄) being end members.

Sorosilicates (Double tetrahedrons)

These are minerals in which two tetrahedrons are bonded together through the sharing of a oxygen atom. The structural formula unit is Si₂O₇. Like the nesosilicates, the remaining oxygen bonding sites can ionically bond with metallic cations to form a crystal structure. Epidote is an example of a sorosilicate mineral.

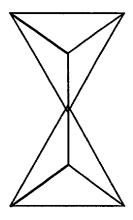


Figure 6. The Sorosilicate structure.

Cyclosilicates (Rings)

These minerals consist of rings of tetrahedrons linked through shared oxygen atoms with each ring joined to other rings via metallic cations. The number of tetrahedra in each ring can vary. Benitoite (BaTiSi₃O₉), a rare mineral, has only three tetrahedron in its rings. Tourmaline and emerald have six (Figure 7).

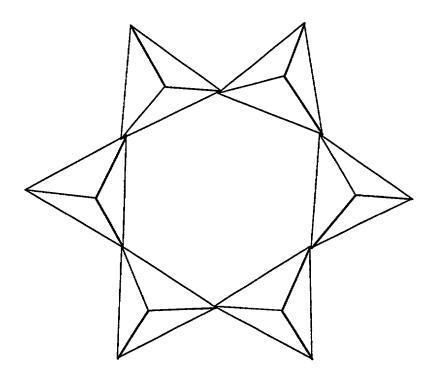


Figure 7. Cyclosilicate structure of minerals such as emerald and tourmaline

Inosilicates (Chains)

These minerals consist of chains of tetrahedrons linked through metallic cations to other chains.

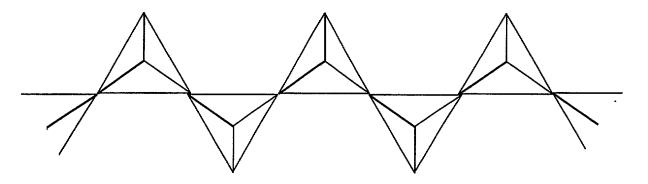


Figure 8. Inosilicate structure

Single Chains

An example of a single chain inosilicate minerals belonging to the Pyroxene group such as Enstatite (MgSiO₃), Diopside (CaMgSi₂O₆), Wollastonite (CaSiO₃) and Rhodonite (MnSiO₃). Notice that the only difference between these minerals is the cation which binds the single chains of tetrahedrons together (Figure 8 & 9a).

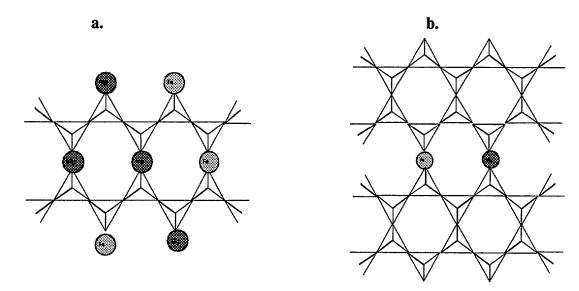


Figure 9. a. Two single chains joined together by metallic cations
b. Double Chain Inosilicate structure

Double Chains

An example of double chain inosilicate minerals are those belonging to the Amphibole Group, such as Tremolite (Ca₂Mg₅Si₈O₂₂(OH)₂). (Figure 9b.).

Phyllosilicates (Sheets)

These minerals are made up of two dimensional sheets of tetrahedra. Within the large spaces in the sheet sit hydroxyl (OH) groups. These hydroxyl bearing sheets are bounded together by metallic cations to form a sandwich of silica sheets and cation sheets. Examples of Phyllosilicates are Talc (Mg₃Si₄O₁₀(OH)₂), Kaolinite - a clay mineral (Al₂Si₂O₅(OH)₄) and the Mica Group of minerals.

Tectosilicates (Framework)

These minerals, which make up 75% of crustal rocks, are built up from a three dimensional framework of linked tetrahedrons. In its most pure form, each oxygen is shared by two tetrahedra resulting in a highly stable, strongly bonded mineral called Quartz (SiO₂). Other tectosilicates include the Feldspar group of minerals.

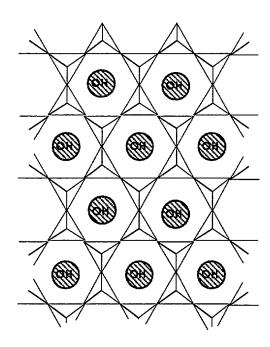


Figure 11. Phyllosilicate Structure

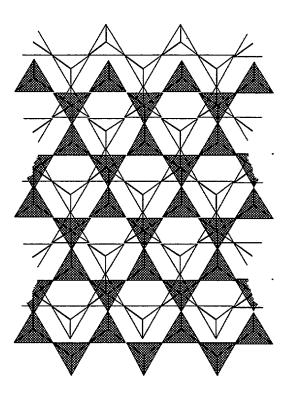


Figure 12. Tectosilicate structure. Grey tetrahedron represent a layer above the white layer but connected through oxygen atoms.

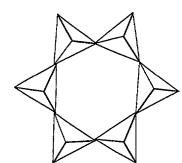
Silicate Structures Summary Table

Nesosilicate



SiO₄

Example: Olivine



Cyclosilicate

Si₆O₁₈

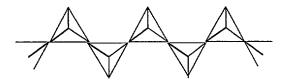
Example: Tourmaline



Sorosilicate

Si₂O₇

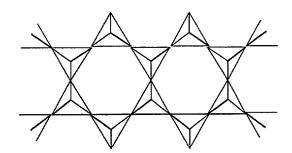
Example: Epidote



Inosilicate - Single Chain

SiO₃

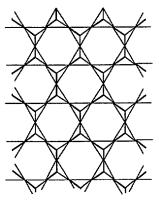
Example: Pyroxenes, Augite



Inosilicate - Double Chain

Si4O11

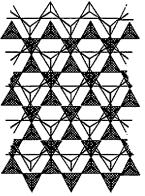
Example: Amphibole, Hornblende



Phyllosilicate

Si₂O₅

Example: Micas, muscovite, biotite



Tectosilicate

SiO2

Examples: Quartz, feldspars

5. The Aluminium Factor

This simple classification of silicates is further complicated by the substitution of some of the silicon atoms by aluminium atoms. This can occur because of the similarity in size of the two - Si^{4+} ionic radius = 0.39Å, Al^{3+} ionic radius = 0.51Å. Aluminium is able to squeeze between the oxygen to replace silicon but causes two changes to the mineral structure :

- 1. The slight difference in size changes the alignment of atoms in the structure
- 2. The lower valence of Al^{3+} to Si^{4+} leaves an overall negative charge on the tetrahedron

The first change is manifested in the zones of weakness in the mineral, called cleavage, along which a mineral will split. The second allows future cations to be introduced into the structure.

Case Studies

Feldspar Group

The pure formula for the tectosilicates (the mineral Quartz) is SiO_2 . In the case of the Feldspar group one in four Si are replaced by aluminium to form the basic building block $AlSi_3O_8$. The negative charge allows a metallic cation to be bonded into the structure and, in the case of the feldspars, the cations are either K^+ (radius = 1.33Å), Na^+ (radius = 0.97Å) or Ca^{2+} (radius = 0.99Å) or a combination of these cations. The end members of the group are Orthoclase (KAlSi $_3O_8$), Albite (NaAlSi $_3O_8$) and Anorthite (CaAl $_2Si_2O_8$).

Feldspar Composition Ternary Diagram

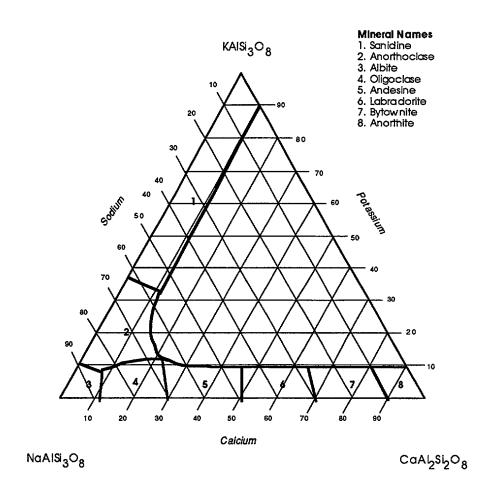


Figure 13. Nomenclature of the Feldspar mineral group. Adapted from Hurlbut & Klein (1977).

Mica Group

The non-aluminium phyllosilicates, such as talc, are very soft due the weak electrostatic bonds holding the sheets together. If some of the silicon is replaced aluminium, large cations, such as potassium, can be ionically linked to the sheets forming a stronger sheet to sheet bond making the minerals, such as the micas, much harder.

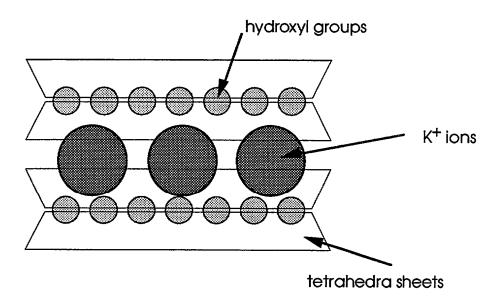


Figure 14. Mica structure

6. Structure and Silicate mineral characteristics

One of the most important features of a mineral which can be used to aid in the minerals identification is its cleavage (the tendency to split along flat planes). All minerals will exhibit a crystal shape, which is an expression of the internal arrangement of the atoms, when the environment for crystallisation is ideal. Unfortunately these environments are rare. However, cleavage, or a lack of it, can be found on broken faces of even the most minute mineral fragments.

The internal structure of the silicates directly influences the cleavage of the mineral.

Case Studies

Mica

Muscovite mica $(KAl_2(AlSi_3O_{10})(OH)_4)$ belongs to the phyllosilicate group. The sheet structures of muscovite have an overall negative charge due to the substitution of some of the Si^{4+} with Al^{3+} ions. This allows K^+ ions to sit in the structure. Because of their size, the K^+ ions sit between the sheets forming a zone of weakness along which the mineral cleaves. This cleavage is so pronounced that Muscovite mica appears to peel off like sheets.

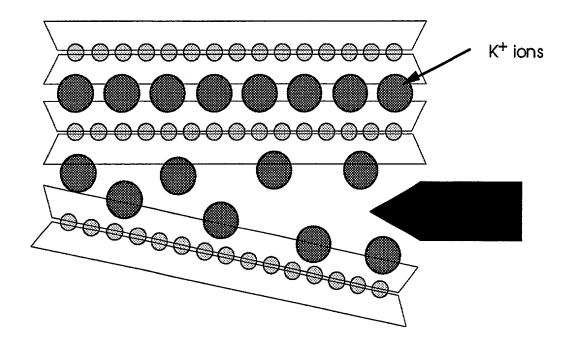


Figure 15. The cleaving of Mica sheets

Pyroxenes and Amphiboles

Different inosilicate structures display different cleavage angles. This is due to the width of the chains i.e. single of double chains. In a single chain mineral, such as the pyroxene group mineral Diopside (CaMgSi₂O₆), the zones of weakness occur between the tetrahedra chains causing the mineral to cleave along zones which are almost at right angles to each other (Figure 16).

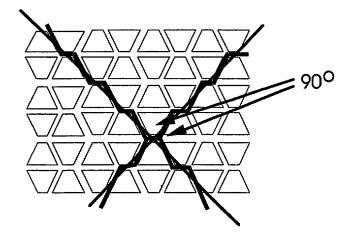


Figure 16. Single Chain inosilicate. The zones of weakness between the chains (dark lines) manifest themselves as a cleavage in two directions at approximately 90° to each other

In double chain minerals, such as the amphibole group mineral Hornblende, the zones of weakness also occur between the tetrahedra chains but because these are wider, the mineral cleavage angles are close to 1240 and 560 (Figure 17).

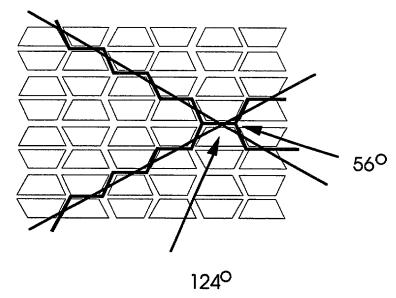


Figure 17. Double Chain inosilicate. The zones of weakness (dark lines) are approximately 1240 to each other due to the width of the tetrahedra chains.

Quartz and Feldspars

Quartz, a pure SiO2 framework structure has no zones of weakness as each Si⁴⁺ ion is bonded to oxygens in a 3D framework. If Quartz is split the mineral tend to form rounded (conchoidal) faces rather than cleavage planes (Figure 18).

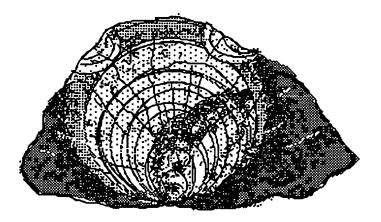


Figure 18. Conchoidal fracture of volcanic glass. Glass is an atomically unordered form of quartz.

The feldspar group, while also having a framework structure, possess zones of weakness caused by the replacement of some Si⁴⁺ by Al³⁺. Cleavage occurs along these zones of weakness.

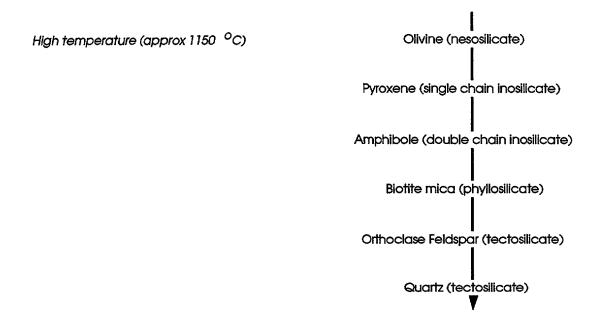
7. Structure and silicate mineral formation

If a mass of molten rock, called magma, starts to cool, a distinctive order of silicate mineral precipitation (crystallisation) occurs. This was first discovered in the 1930's by an American geoscientist called Bowen and the order is known as the Bowen's Reaction Series (Figure 19.)

The most obvious feature of the series is that as the magma cools more and more complex silicate structures crystallise, starting from single tetrahedra (nesosilicate minerals) and finishing with the most complex frameworks (tectosilicates). Two factors influence this:

- 1. Atom movement due to heat atoms move in the melt more quickly at high temperatures making complex framework structures difficult to crystallise.
- 2. Removal of cations as minerals crystallise they remove cations from the melt. The remaining material at the end of crystallisation may contain almost no cations and therefore only a framework structure of pure tetrahedrons can crystallise

i.e.. Quartz.



Low temperature (approx 700 °C)

Figure 19. Simplified Bowen's Reaction Series

In nature the process is complicated by the amounts of cations and silica in the original melt.

Mineral Colour

The colour of a mineral is not a good physical property to use in the minerals identification. In many cases colour is caused by impurities contained in a minerals structure. Quartz, for example, can appear in a number of colours. Small amounts of Ti⁴⁺ can make the mineral a rose pink colour (rose quartz); Fe³⁺ can make quartz a deep violet (amethyst).

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Geoscience Education

Activities

Gary Lewis 1994

Further Information (06) 249 9570

Crustal Elements

	Periodic Table blank satisfies the following st	sheet, summarise the information in the "Elements in the Earth's Crust eps.
Ø wi	th a black pen, write	the element symbol and ionic radii in the correct square.
	ng the following colo arth's crust.	urs, lightly colour the squares to show the abundance of the elements
]	Red	greater than 25.0%
,	Yellow	less than 25.0% but greater than 1.0%
]	Blue	less than 1.0% but greater (or equal to) than 0.01%
1	Leave blank (white) a	all those elements which are less than 0.01%
? Hov	w many elements are	red
? Hov	w many elements are	yellow
? Hov	w many elements are	blue
? Ho	w many elements are	white

Elements in the Earths Crust

(Percent by weight/Ionic Radii of most common ion)

Atomic Number		g/t	%	Ionic Radii Angstrom units
1	Н	1400	0.140000%	0.46
3	Li	20	0.002000%	0.68
<i>A</i>	Be	2.8	0.000280%	0.35
5	B	10	0.000200%	0.23
6	Č	200	0.020000%	0.16
7	Ň	200	0.002000%	0.16
3 4 5 6 7 8	Ö	466000	46.600000%	1.40
9	F	625	0.062500%	1.33
11	Na	28300	2.830000%	0.97
12	Mg	20900	2.090000%	0.66
13	Al	81300	8.130000%	0.51
14	Si	277200	27.720000%	0.39
15	P	1050	0.105000%	0.44
16	S	260	0.026000%	1.74
$\overline{17}$	Cl	130	0.013000%	1.81
19	K	25900	2.590000%	1.33
20	Ca	36300	3.630000%	0.99
21	Sc	22	0.002200%	0.81
22	Ti	4400	0.440000%	0.76
23	V	135	0.013500%	0.88
24	Cr	100	0.010000%	0.63
25	Mn	950	0.095000%	0.80
26	Fe	50000	5.000000%	++ 0.74
				+++ 0.64
27	Co	25	0.002500%	0.72
28	Ni	75	0.007500%	0.69
29	Cu	55	0.005500%	0.96
30	Zn	70 1.5	0.007000%	0.74
31	Ga	15	0.001500%	0.62
32	Ge	1.5	0.000150%	0.73
33	As	1.8	0.000180%	0.58
34	Se	0.05	0.000005%	1.93
35	Br	2.5	0.000250%	1.96
37	Rb	90 375	0.009000%	1.47
38 39	Sr Y	375 33	0.037500% 0.003300%	1.12 0.92
40	Zr	165	0.003300%	0.79
41	Nb	20	0.002000%	0.74
42	Mo	1.5	0.002000%	0.74
44	Ru	0.01	0.000130%	0.67
	270	0.01	0.00000170	0.0,

4.00	Atomic Number		%	Ionic Radii
45	Rh	0.005	0.000001%	Angstrom units 0.68
46	Pd	0.005	0.000001%	0.80
47	Ag	0.07	0.000001%	1.26
48	Cd	0.07	0.000007%	0.97
49	In	0.2	0.000020%	0.81
50	Sn	2	0.000200%	0.93
50 51	Sb	0.2		
51 52			0.000020%	0.76
	Te	0.01	0.000001%	2.11
53 55	I	0.5	0.000050%	2.20
55 56	Cs	3	0.000300%	1.67
56	Ba	425	0.042500%	1.34
57 50	La	30	0.003000%	1.14
58	Ce	60	0.006000%	1.07
59	Pr	8.2	0.000820%	1.06
60	Nd	28	0.002800%	1.04
62	Sm	6	0.000600%	1.00
63	Eu	1.2	0.000120%	0.98
64	<u>G</u> d	5.4	0.000540%	0.97
65	Tb	0.9	0.000090%	0.93
66	Dy	3	0.000300%	0.92
67	Ho	1.2	0.000120%	0.91
68	Er	2.8	0.000280%	0.89
69	Tm	0.5	0.000050%	0.87
70	Yb	3.4	0.000340%	0.86
71	Lu	0.5	0.000050%	0.85
72	Hf	3 2	0.000300%	0.78
73	Ta		0.000200%	0.68
74	W	1.5	0.000150%	0.70
75	Re	0.001	0.000000%	0.72
76	Os	0.005	0.000001%	0.69
77	Ir	0.001	0.000000%	0.68
78	Pt	0.01	0.000001%	0.80
79	Au	0.004	0.000000%	1.37
80	Hg	0.08	0.000008%	1.10
81	Tl	0.5	0.000050%	1.47
82	Pb	13	0.001300%	1.20
83	<u>B</u> i	0.2	0.000020%	0.96
90	Th	7.2	0.000720%	1.02
92	U	1.8	0.000180%	0.97

la	lla	_]	Period	dic Tal	ole of	the E	lemer	nts	Ke Atomic No.	У		IIIa	IVa	Va	Vla	VIIa	VIIIa 2
	4											5	6	7	8	9	10
1	12	ШЬ	IVb	Vb	VIb	VIIb				lb	ПЬ	13	14	15	16	17	18
19	20	21	22	23	24		26	VIIIb 27	28	29	30	31	32	33	34	35	36
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
87	88	89	58	58	60	61	62	63	64	65	66	67	68		69 7	0 71	
	<u> </u>		30	91	92	93	94	95	96	97	98	99	100	101	102	103	

Chemical Weathering of Feldspar

Orthoclase Feldspar, a potassium- aluminium tectosilicate, chemically alters to form clay minerals. This is due to the reaction of the mineral with carbonic acid disolved in rainwater.

The inputs are:

Orthoclase feldspar

KAlSi₃O₈

Carbonic acid

 H_2CO_3

Water

H₂O

The outputs are:

Clay mineral

Al₂Si₂O₅(OH)₄

Potassium carbonate

 K_2CO_3

Silica

SiO₂

Write a balanced equation for the reaction:

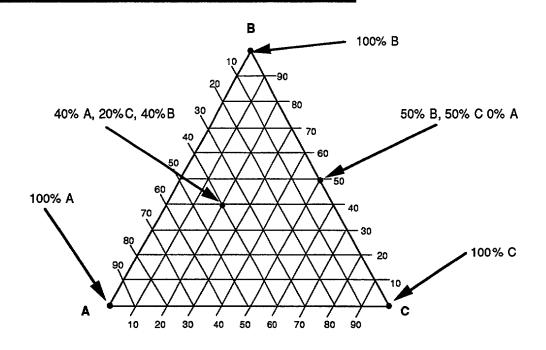
Other members of the feldspar group include Albite (NaAlSi₃O₈) and Anorthite (CaAl₂Si₂O₈). Write chemical equations for the chemical weathering of these minerals.

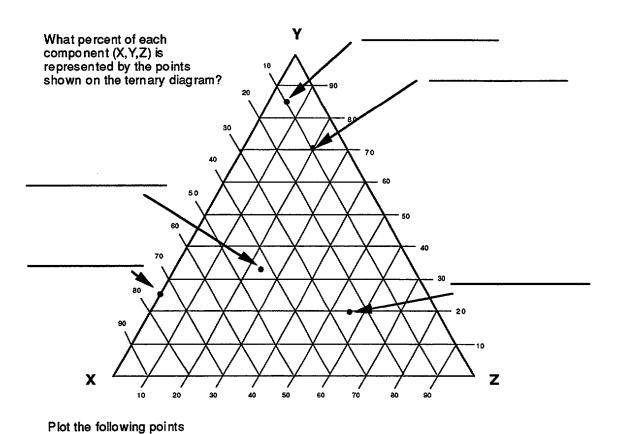
NaAlSi₃O₈

CaAl₂Si₂O₈

Note: Silica is not formed in this reaction.

Reading Ternary Diagrams





33%X, 33%Y, 33%Z

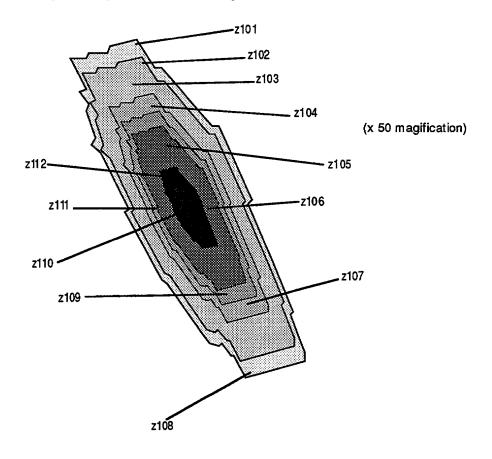
28%X, 24%Y, 48%Z

Chemical Zones

A geologist collected a sample of a rock containing the mineral feldspar (a tectosilicate) and noticed that the feldspars were zoned. Zonation occurs when a mineral crystallises from a solution, in this case molten rock, which changes composition over time.

The geologist gave a piece of the rock to a geochemist who used an electron probe to obtain chemical data about each of the zones on one feldspar crystal. The sites on the crystal sampled, and the results, are shown below.

Feldspar crystal electron probe sites



Sample site	CaO	NaO	K2O
z101	12	67	21
z102	18	73	9
z103	27	71	2
z104	28	67	5
z105	63	29	8
z106	66	31	3
z107	32	65	3
z108	12	70	18
z109	69	29	2
z110	96	2	2
z111	68	_26	6
z112	85	11	4

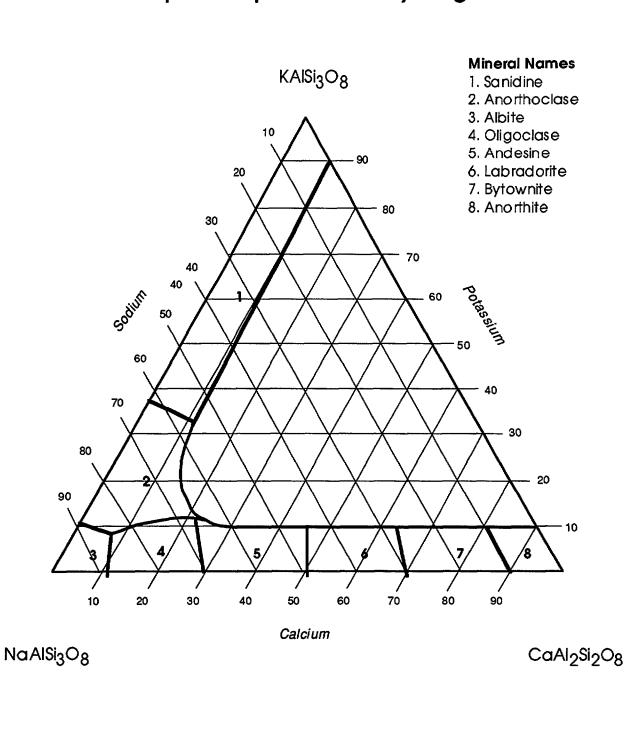
Note: Electron probe results are given as the percent of metallic oxide found in the sample. In this case, the probe only calculated the relative amounts of calcium, potassium and sodium. Any other metal oxides, such as aluminium oxide, were disregarded.

The Feldspar group of minerals differ in composition due to the type of metallic ions in their structure. As calcium, sodium and potassium can fit into the crystal structure there is a continuum of compositions with the end members being Orthoclase (100% potassium), Albite (100% sodium) and Anorthite (100% calcium).

What to Do

- 1. Using the Feldspar Composition Ternary diagram, plot the composition of each of the sites.
- 2. As a crystal adds layers to the outside, write the feldspar mineral sequence from the core to the outside of the crystal.
- 3. What happens to the composition of the solution that this crystal formed in over time and what may have caused the changes?

Feldspar Composition Ternary Diagram



Mineral Phases

The existence of a chemical in more than one structural form is known as *polymorphism*, with each of the different structures being *allotropes* of the chemical. Diamond and graphite, for example, are naturally occurring allotropes of carbon.

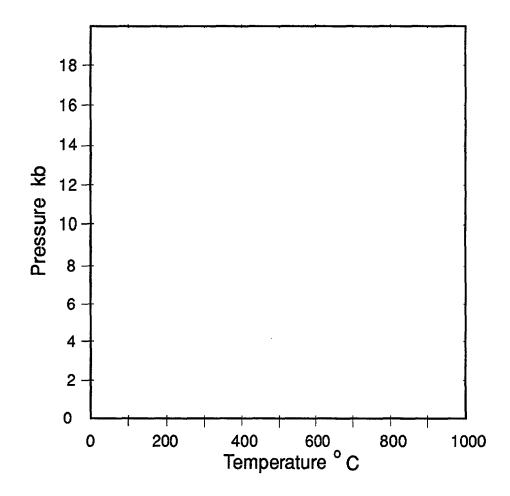
The chemical Al₂SiO₅ is found in nature as three allotropes. These are the minerals Andalusite, Kyanite and Sillimanite. Experiments have shown that the formation of these minerals is somehow dependant on the temperature and pressure of the environment in which they form. In mineralogy, these minerals are referred to as *phases*, and a diagram which represents the relationship between their "environment-of-formation" conditions and mineral phase is call a *Phase Diagram*.

What to do

A number of experiments have been undertaken in which Al_2SiO_5 was placed under different temperature and pressure conditions and the resultant mineral phase recorded. The table of results is below:

Pressure kb	Temperature C	Mineral
7	300	Andalusite
4	50	Andalusite
6	400	Andalusite
3	550	Andalusite
1	100	Andalusite
2	600	Andalusite
6	50	Kyanite
10	400	Kyanite
14	800	Kyanite
8	200	Kyanite
12	300	Kyanite
10	300	Kyanite
16	200	Kyanite
14	700	Kyanite
4	700	Sillimanite
6	500	Sillimanite
8	400	Sillimanite
10	700	Sillimanite
2	800	Sillimanite
12	800	Sillimanite
4	800	Sillimanite
15	900	Sillimanite
5	150	Andalusite
3	300	Andalusite
5	350	Andalusite
7	150	Kyanite
11	550	Kyanite
11	50	Kyanite
13	200	Kyanite
15	450	Kyanite
12	650	Kyanite
9	550	Sillmanite
5	600	Sillmanite
7	650	Sillmanite
7	850	Sillmanite

1. On the graph, plot each of the experiments results, using (a) for Andalusite, (k) Kyanite and (s) Sillimanite.



2. Draw lines on the graph which separate the mineral phases.

3. What mineral phase would you expect to form under the following temperature and pressure environments.

4. A rock containing the mineral Andalusite was close to a volcanic vent where the temperatures reached 500°C and the mineral phase did not change. What conclusion can you draw from the pressure environment for this location?

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