#### INTERNAL GEODYNAMICS (ENDOGENOUS PROCESSES OF THE EARTH)

#### İÇ JEODİNAMİK (DÜNYANIN ENDOJEN OLAYLARI)

A. M. C. Şengör İTÜ Avrasya Yerbilimleri Enstitüsü 2005 Kış yarıyılı



AB R<sup>45</sup> THÉOPHILE WERNER (Gélogiste et minéralogiste), Associé étranger de l'Académic royale des Sciences, Professeur de minéralogie à Freyberg et Ceanciller des mines de Saxe. Né Warm das labute lasace en 156. Mer à Desde m hy.

#### To the memory of Abraham Gottlob Werner

### Lesson 3:

# The Composition of the Earth

## Part IIa: The minerals- basic concepts

In the first part of this lesson, we familiarised ourselves with the atomic structure of matter with a view to understanding how substances that make up our planet (and other rocky bodies out in space and those bodies that somehow affect our earth, such as the Sun) are formed and structured. It is the purpose of this second part to become familiar with the minerals themselves, the most basic "building blocks" of the geologist, because they constitute most of the rocks (but not all! Can you say why not?).

To that end, let us remember the definition of a mineral:

A mineral is a naturally occurring inorganic crystalline solid of a definite (variable within fixed limits) chemical composition.

Because a mineral is a crystalline solid, we must find out how atoms come together to form solids. The answer to this query is the *nature of the chemical bond*.

#### Definition of chemical bond:

A *chemical bond* is the electrical interaction between atoms that holds them together.

All chemical bonds are formed as the result of the simultaneous attraction of two or more atomic nuclei for electrons. Now we are in a position to consider how the atomic structure affects the structure of matter, including the minerals. To study this, we need to take a look at the periodic table and discuss certain characteristics of the elements in it with respect to the materials they may form.

First of all let us remember that the periodic table is called periodic, because there is a periodicity (*i.e. regular recurrence*) in the physical and chemical properties of the elements in the universe. But fundamentally *the periodic table is based on the periodic recurrence of an outer shell electronic configuration*.

For example let us take the Group IIA (the rare earth metals):

Be  $1s^{2}2s^{2}$ Mg  $1s^{2}2s^{2}2p^{6}3s^{2}$ Ca  $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}$ Sr  $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{16}$ Ba  $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}4p^{6}4$  Notice the last orbitals, all of which are s orbitals and all have 2 electrons

#### Percent Ionic Character of a Single Chemical Bond

	Difference in electronegativity 0.1 0.2 0.3	0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2	1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2	2.1 2.2 2.3 2.4 2.5 2.6 2.7 2	.8 2.9 3.0 3.1 3.2			
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							H	<b>e</b>
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The Periodic Table

- 1. The groups IA-VIIA are called the *representative elements*. These have an outer orbital configuration of ns or and ns and np combination. The outer shell is called the *valence shell*, in other words, *the shell that does the chemical bonding*.
- The *rare* or the *noble gases* form the group VIIIA. All of them have a completely filled outer orbital, such as He (1s<sup>2</sup>) or Ne (1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>). This called the *octet condition* (octet:eight-membered). *A filled valence shell represents a stable configuration for an atom, a condition that is not conducive to bonding.*
- 3. The groups IB to VIIIB are the *transition elements*. In these the d subshell is partially filled, as, for example, in iron:

Fe (Z=26)  $1s^22s^22p^63s^23p^63d^64s^2$ here the d subshell is missing 4 electrons.

4. The *lanthanides* and *actinides* contain partially-filled f orbitals. *NOTE THAT APART FROM THE NOBLE GASES ALL OTHER ELEMENTS HAVE PARTIALLY FILLED VALENCE SHELLS*  Elments with partially-filled valence shells readily form chemical bonds. Let us remember the definition of a chemical bond:

A chemical bond is the electrical interaction between atoms that holds them together.

All chemical bonds are formed as the result of the simultaneous attraction of two or more nuclei for electrons. There are five kinds of chemical bonds:

- 1. The ionic bond, in which electron exchange occurs between atoms that thus become ionised.
- 2. The covalent bond, in which atoms share electrons
- 3. The van der Waals bond forms between covalent molecules and is held by the weak *van der Waals forces*.
- 4. The hydrogen bond is one that forms in such compounds as  $H_20$ ,  $NH_3$  and HF and binds their molecules.
- 5. The metallic bond, in which electrons wander through the substance.

Ionic bonds form between elements that can readily give up and accept electrons from their outermost shells. So we can use the periodic table to predict those elements that are most likely to form ionic compounds. Three periodic properties are of the greatest importance to form ions: (1) *ionisation energy*, (2) *electron affinity* and (3) *electronegativity*. *Substances with low ionisation energies and low electronegativities should readily form ionic compounds with substances with high electron affinities and high electronegativities*. In general, if the absolute difference between the electronegativities of two atoms A and B,  $|X_A - X_B|$ , is greater than 2, the bond between them will be ionic in character.

Thus all Group IA metallic elements react readily with Group VIIA nonmetallic elements to form stable ionic compounds (for example halite: NaCl). To a lesser extent this is also true of the Group II and Group VIA elements (for example barite: BaSO<sub>4</sub>).

BARITE





#### HALITE

#### Characteristics of ionic crystals:

1. Ionic crystals tend to be hard and brittle because of the nature of the packing. When the ions are moved with respect to one another, the crystal shatters because of strong repulsions which appear when ions of like charge approach one another.

2. Solid ionic crystals do not conduct an appreciable electric current because the electrons are held very firmly in ionic bonds.

3. Ionic crystals have relatively high melting and boiling points, low volatilities and low vapour pressures.

4. Ionic crystals are transparent and do not reflect light.

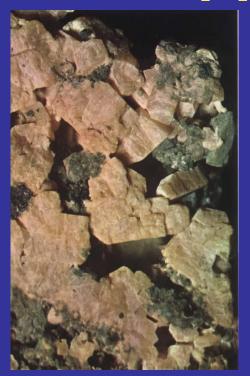
Feldspars, for example, form mostly ionic crystals (in the silicate part however there is considerable covalent bonding). The reason why they are not usually transparent is because they contain many tiny meteoric liquid inclusions (Prof. George R. Rossman, pers. comm., 2005)

Orthoclase

KalSi<sub>3</sub>O<sub>5</sub>



Anorthite  $CaAl_2Si_2O_3$ 



Albite

NaAlSi<sub>2</sub>O<sub>3</sub>

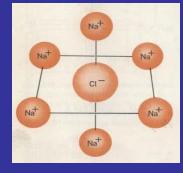


The architecture of ionic crystals is largely determined by the relative sizes of its constituent ions. In most crystals the ions cannot be packed so as to form a compact entity, because usually the negative ions are large and are in contact with one another, and the positive ions find a place for themselves amongst them.

The number of the nearest ions in a crystal is known as the *coordination number* of that ion in that crystal.

In general, the ratio of the radius of the cation to that of the anion can be used as a guide to the number of anions that can be fitted around a cation. When the radius ratio is between 0.41 and 0.73, six anions can pack around one anion forming an octahedral (i.e. eightfaced) arrangement with six corners at wihch the anions are

located.

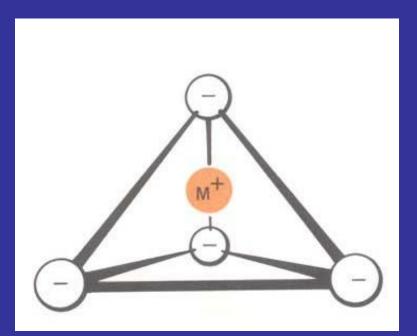




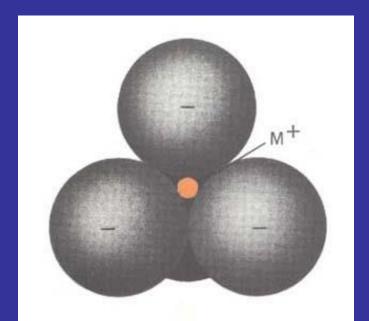
The octahedral arrangement of Cl<sup>-</sup> ions around the NA<sup>+</sup> ion.

From Toon et al. (1968)

When the ionic radius ratio goes below 0.41, the anions can no longer touch the cation without their negatively charged electon clouds overlapping. This creates a stong repulsive force making an octahedral arrangement impossible. Then, instead of six anions gathering around one cation, only four anions form a tetraheedral (i.e. four-faced, with only four corners) arrangement.



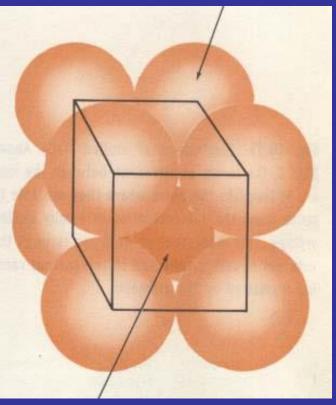
The principle of the tetragonal arrangement



This is how many tetragonal arrangements really look like

When the ionic radius ratio reaches and exceeds 0.73, the coordination becomes cubic and the coordination number goes up to 8 to 12!

Anions



Cation

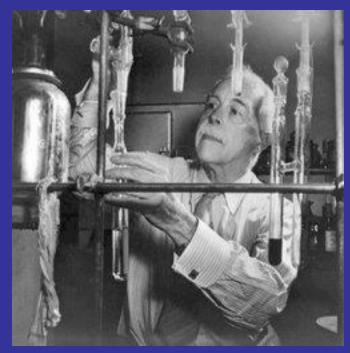
Hyd Min	ne Common lons (Exclusive of lrogen) that Occur in Rock-Forming lerals, Arranged in Decreasing ic Size
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lon		ordination er with Oxygen	Ionic Radius Å		
0 <sup>2-</sup>			1.36 [3]		
$K^+$	8-12		1.51 [8]-1.64 [12]		
Na <sup>+</sup> Ca <sup>2+</sup>	8–6 8–6 }	*2	1.18 [8]–1.02 [6] 1.12 [8]–1.00 [6]		
$Mn^{2+}$ $Fe^{2+}$ $Mg^{2+}$ $Fe^{3+}$ $Ti^{4+}$ $Al^{3+}$	6 6 6 6 6	- octahedral	0.83 [6] 0.78 [6] 0.72 [6] 0.65 [6] 0.61 [6] 0.54 [6]		
Al <sup>3+</sup> Si <sup>4+</sup> P <sup>5+</sup> S <sup>6+</sup>	$ \left.\begin{array}{c} 4 \\ 4 \\ 4 \\ 4 \\ 4 \end{array}\right\} $	tetrahedral	0.39 [4] 0.26 [4] 0.17 [4] 0.12 [4]		
C <sup>4+</sup>	3	triangular	-0.08 [3]		

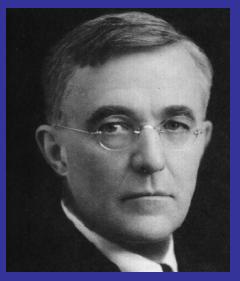
\*The first column lists the most common ionic (valency) states of the elements. The second column lists their most common coordination with respect to oxygen, and the third column lists ionic sizes for specific coordinations (the number in square brackets is **C.N.**). A complete listing of elemental abundances is given in Table 3.1.

From Klein, 2002, p. 74

When two atoms with similar electronegativities are bonded together by not exchanging but actually sharing electrons in their outermost shells the resulting bond is called *covalent*, emphasising that both atoms are "valents," i.e. donors. This type of bond was first recognised in 1916 by the remarkably versatile American physical chemist Gilbert N. Lewis, but the term "covalent" was

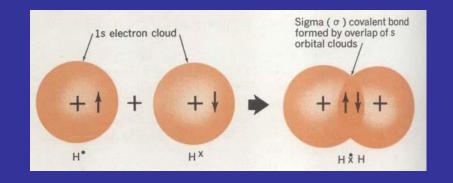


Gilbert Newton Lewis (1875-1946) in his Berkeley laboratory introduced in 1919 by another American chemist Irving Langmuir (1881-1957).



Langmuir

## Let us look at the simple molecule of $H_2$ to study some properties of the covalent bonds:



Each H atom has a sinlge electron in the 1s orbital. To attain the noble He configuration, it needs just another electron. This can be supplied by another H atom. Because their electronegativities are the same they cannot "steal" each other's electrons. As the atoms approach each other the pull of the nuclei on the electron clouds first decrease the potential energy and when they are so close that the electron clouds begin to repulse each other the internuclear distance stabilises over a minimum energy interval.

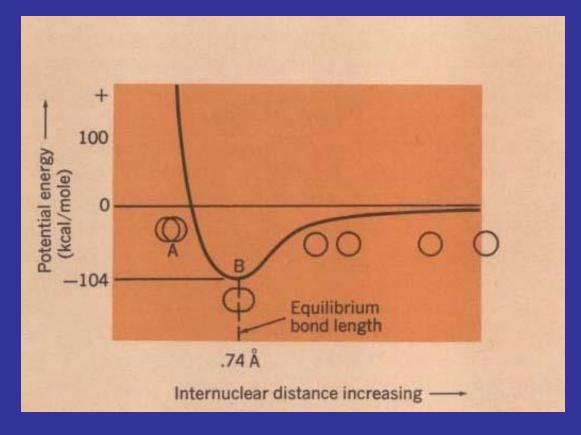
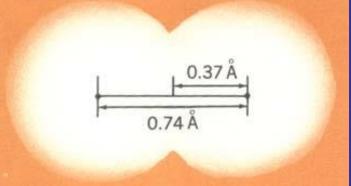
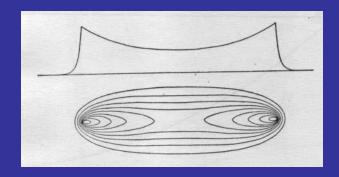


Diagram showing the potential energy as the two H atoms approach each other. The lowest energy value corresponds to the *equilibrium bond length*.

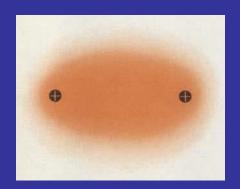
The *covalent radius* of an H atom is 1/2 the bond length (0.37Å).



When the two H atoms form a covalent bond, the shared electrons are mostly found between the two nuclei. Their probability contours and the probability graph are shown below

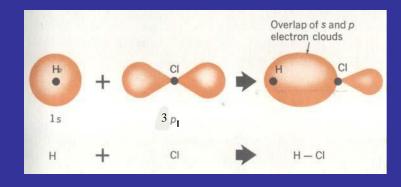


Such a molecule is said to have a *non-polar bond*, because the electron density has no preference for either end of the elongate molecule.

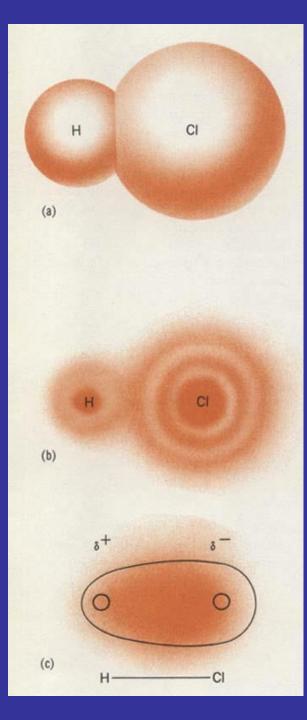


The electrically symmetrical molecules are called *non-polar molecules*. The  $H_2$  molecule is an example of such a non-polar molecule.

When the two atoms forming a covalent molecule are dissimilar, the resulting covalent bonds are always polar, i.e. directional. If the resulting molecule is also polar, it is called a *dipole*. The HCl (hydrochloric acid) molecule is, for example, one such molecule.



HCl forms by the H atoms 1s orbital sharing an electron with the Cl atom's  $3p_i$  orbital which also has a single electron (where i could be any of the x, y or z orbitals). H needs one electron to be like He, and Cl needs an electron to be like Ar. However, as the Cl has a greater electronegativity than H, the electrons would be much more strongly pulled towards it. Thus the Cl en of the molecule will acquire a greater — charge than the H end. The molecule will be a *dipole*.



Various representations of the dipolar HCl molecule. The (b) is somewhat misleading because it gives the impression as if the electrons of the s orbitas are being shared. As you know this is not true. In the case of Hcl, the 1s orbital of the H and the 3p orbital of the Cl share electrons.

The great American chemist and pacifist Linus Pauling 1901-1994 pointed out in 1939 that in such strongly dipolar molecules the covalent bond also has a partial ionic bond character.

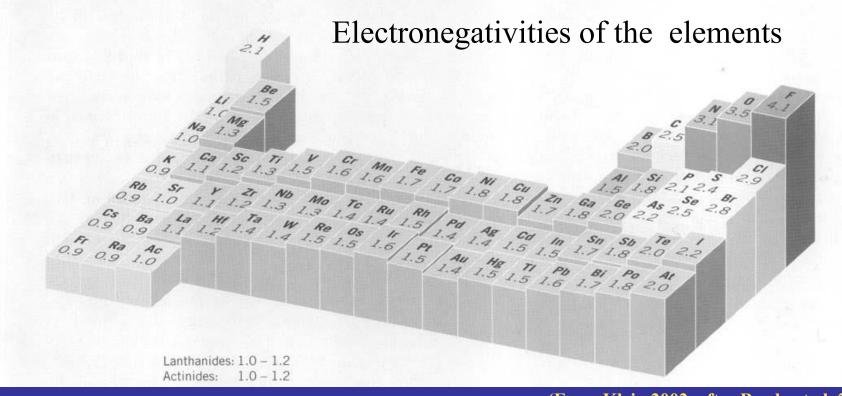


Pauling

Pauling provided a formula to estimate the percent (%) ionic character of a chemical bond:

Percent ionic character =  $1 - e^{-1/4(X_A - X_B)}$ 

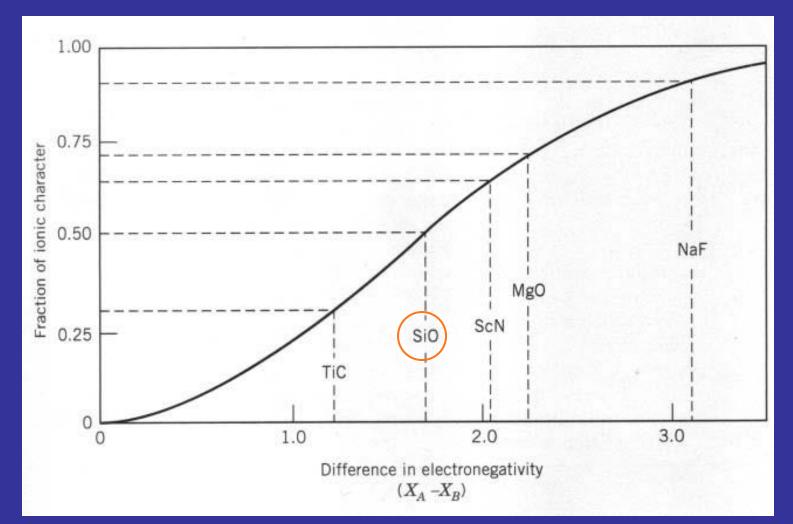
Here X is the electronegativity of the elements A and B being bonded.



(From Klein 2002, after Brady et al. 2000)

## An application of Pauling's formula for the degree of ionic bonding in chemical bonds:

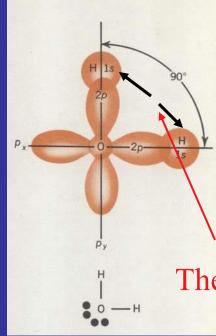
Percent ionic character =  $1 - e^{-1/4(X_A - X_B)}$ 



(From Klein, 2002, as modified from Pauling, 1944; emphasis on SiO bonding is mine)

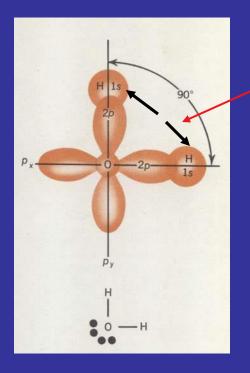
Covalent bonds can thus be polar or non-polar. The polarity of a covalent molecule is the geometrical sum of the covalent bonds holding it together. If the two atoms forming a molecule are identical, the molecule would be non-polar, if different, it will be polar. If more than two atoms are involved in a molecule, the covalent bonds forming it may lie on a line (*linear molecules*) or the molecule may be *angular* or *bent*.

The bending is explained as a result of the repulsion of the various electron orbitals in a molecule. Let us the water molecule, for example, which consits of  $H_20$ :

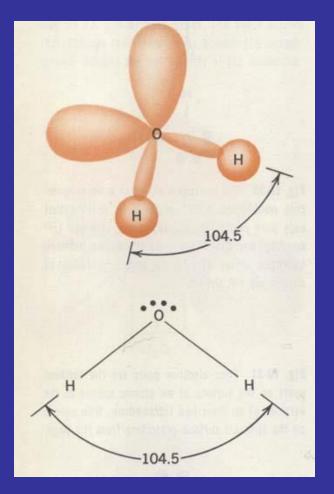


The two H atoms are bonded to the one O atom using their single 1s electrons and pairing them with the single electrons of the  $2p_x$  and the  $2p_y$  orbitals of the O. If there were no contribution from the mutual repulsion of the negatively charged electron cloud of the H 1s orbitals, the H<sub>2</sub>0 molecular angle would have been simply that between the  $p_x$  and the  $p_y$  orbitals, namely 90°

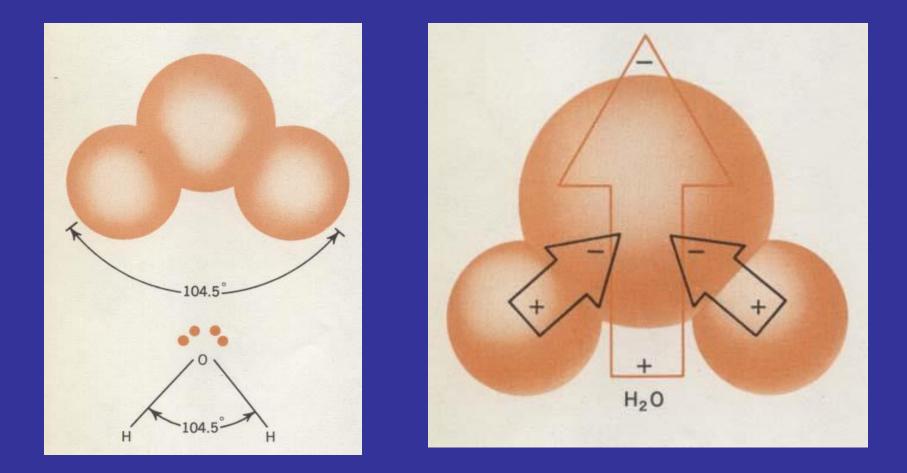
The mutual repulsion of the 1s clouds of the H atoms



Because of this repulsion, the two p orbitals are pushed farther apart and the intramolecular angle of  $H_2O$  grows to 104°30' as seen below.

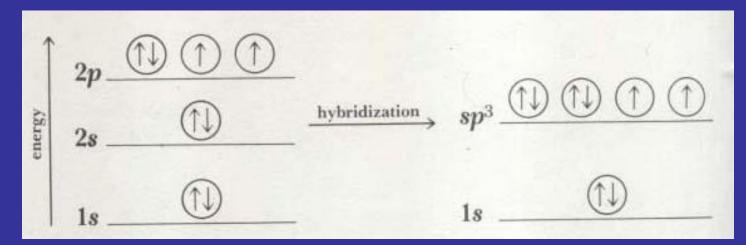


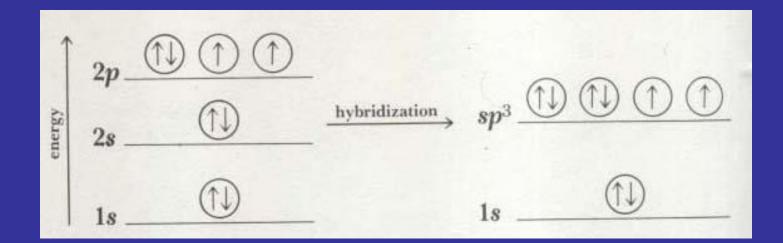
This is a characteristic shape of the triatomic molecules formed by the Group VIA elements.

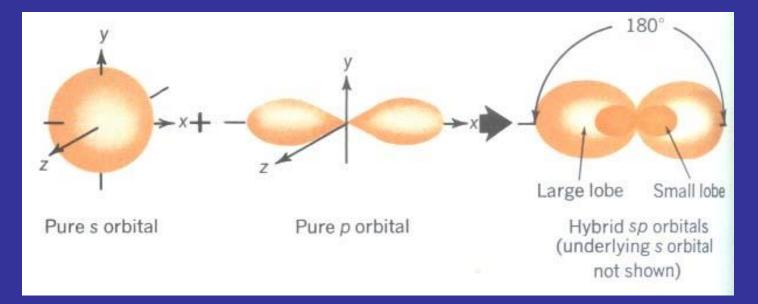


Since O has a greater electronegativity (3.5) than H (2.1) and that the H nuclei form the + "side" of the H<sub>2</sub>O molecule and the O the — "side", the water molecules are said to be polarised. These "aberrant" angles clearly violate the characters of the orbitals, because for some, such as the p, d and f orbitals, their directional attributes are parts of their definitions. To make the spectroscopic data, that yield the intramolecluar angles, and the quantum mechanics, the chemists and physicists mustresort to models of "hybrid orbitals" that are neither the one nor the other, but a mixture.

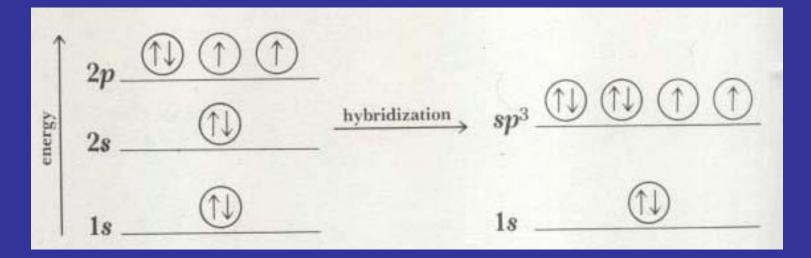
For instance, in the water molecule, what really bonds with the 1s of the h atom is not the two 2p orbitals of the O, but two sp<sup>3</sup> orbitals (the superscript 3 shows that 3 p orbitals are involved in the hybridisation as shown below).

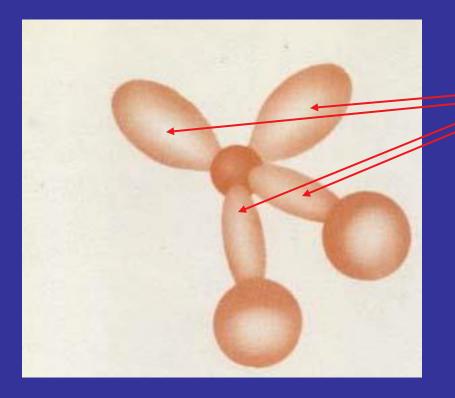






A highly schematic "visualisation" of hybridisation of orbitals





The four sp<sup>3</sup> orbitals of the O atom. They form upon the approach of the two H atoms that change the "electrical environment" of the O atom. The shapes and polarities of molecules are very important in determining the physical properties of crystalline solids and, therefore, minerals.

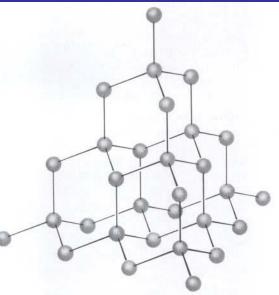
*Covalent bonds are the strongest chemical bonds in existence.* Therefore, the crystalline substances they form have the following properties:

1. They are hard and not workable (in fact the hardest substance known, diamond, is a covalent crystal)



*Koh-i Noor* (105 carat=21.6 g), the world's largest diamond

> The diamond structure (the grey balls correspond to C atoms)



(From Klein, 2002)

Carbon (C) atom has the following electronic configuration:  $1s^22s^22p^2$ 

Silicon (Si) has a very similar outer shell configuration:

 $1s^22s^22p^63s^23p^2$ 

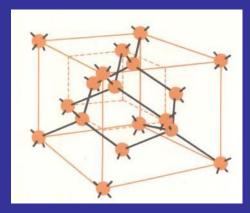
Therefore both C and Si can form complex, rigid crystal structures. They also form numerous compounds. For that reason, C is the basic element of life on earth and <u>Si</u> is the basic element of the <u>inorganic world</u> (i.e. rocks and minerals). 2. The electrical conductivity of the covalent crystals is poor, because the electrons are strongly localised by the bonds and cannot move about in the crystal structure.

3. Their heat conductivity is poor, because the atoms are tightly held by the bonds.

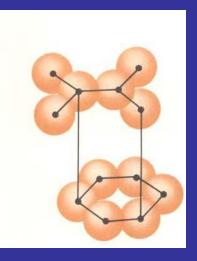
4. They are transparent, because the electrons and the nuclei are tightly fixed and thus localised and cannot form a barrier to light (remember that atoms are mostly empty space).

5. They have very high melting points, because it is difficult to break the bonds forming the crystalline solid held by strong covalent bonds.

6. Covalent crystals consist of a one-, two-, or three- dimensional network of atoms joind by covalent bonds. Let us investigate further the effect of the network of molecules on mineral properties:



In *diamond* every C atom is bonded to others by strong covalent bonds between sp<sup>3</sup> hybridised orbitals. (Why?)



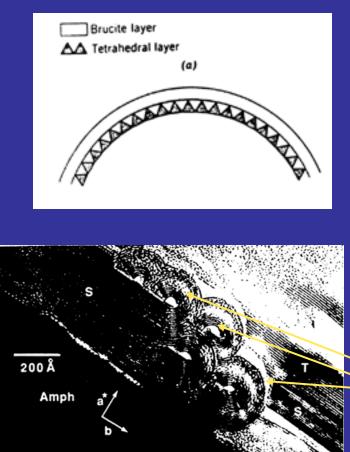
In *graphite*, the covalent bonds in each layer is between sp<sup>2</sup> hybridised orbitals. The remaining p orbital electrons are delocalised in the entire 2dimensional molecule. The C sheets are held together by van der Waals forces, which are weak. This accounts for the softness of graphite (it is so soft that we can use it to write on paper!). In the minerals classified as "asbestos" the individual crystals have neither a framework nor a sheet structure, but a one-dimensional structure.

The term "asbestos" does not signify any one mineral, but a group of minerals that display *fibrous habit* because of their thin and long crystals\*. For a mineral to classify as asbestos its crystals must have lengths more than 5 micrometres ( $\mu$ ), maximum diameter less than 5 $\mu$  and length to diameter ration of 3 or greater.

The most common asbestos minerals are amphiboles:

Tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$ Anthophyllite $Mg_2Mg_5Si_8O_{22}(OH)_2$ Actinolite $(Ca,Fe)_2Mg_5Si_8O_{22}(OH)_2$ Crocidolite $Na_2Fe_2+3Fe^{3+}_2Si_8O_{22}(OH)_2$ Amosite $Fe_2Fe_5Si_8O_{22}(OH)_2$ 

\*For the history of the asbestos concept and the term asbestos, see **Ross**, **M. and Nolan**, **R.P.**, 2003, History of asbestos discovery and asbestos-related disease in context with the occurrence of asbestos within ophiolite complexes: *Geological Society of America Special Paper 373*, pp. 447-470 However, the serpentine mineral chrysotile  $Mg_3Si_2O_5(OH)_4$  is also an asbestos mineral, although it has a sheet-like structure similar to graphite. Then, how is it that it is an asbestos mineral?



It turns out that the individual crystals of chrysotile are oftern so small and thin that surface tension causes them to "curl up" as indicated in the diagram to the left. If the curling is sufficiently extreme, the sheets can curl up into hollow tubes that are long and very thin, thereby meeting the definition of asbestos. Chrysotile is often found in "cross fiber veins" in which the tubes or fibers line up perpendicular to the walls of fractures, especialy in ultramafic rocks.

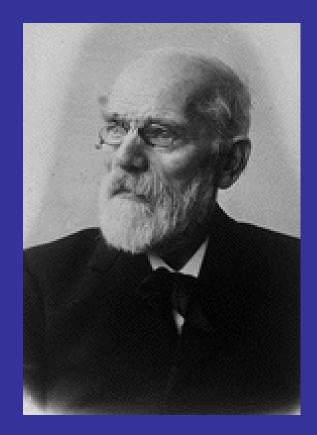
Chrysotile "fibers", in reality curled up sheets

From <u>http://darkwing.uoregon.edu/~jrice/geol\_311/Asbestos.html</u> "mineralogy of asbestos" Thomas Andrews [1813-1885] discovered that for a pure gas, the distinction between the liquid and gas phases vanishes at the "critical temperature". This is formally called the "continuity of the gas and liquid phases". In 1873, the Dutch physicist Johannes van der Waals made some first-order corrections to the ideal gas law, accounting for molecular volume and the small attractive forces responsible for the gasliquid phase distinction at low temperatures.

He deduced the empirical equation:

- [P+(an<sup>2</sup>/V)][V-nb]=nRT
- In a "perfect gas", nRT=VP, where

n is moles of gas molecules,
R is molar gas constant
T is absolute temperature
V is volume P is pressure

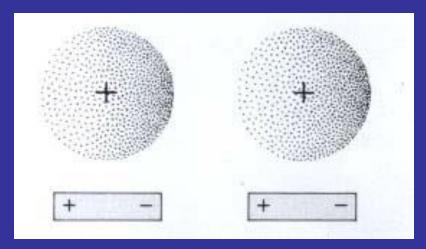


Johannes Diderik van der Waals (1837-1923)

In the van der Waals equation, **a** is a proportionality constant measuring the weak electromagnetic attractive forces between the gas molecules and **b** is the molar volume of gas molecules.

It is this a term in the van der Waals equation that shows us the existence of weak electrical forces that exist between molecules and hold them together. For instance water molecules are held together by van der Waals forces. Since it is water that makes life possible on earth, it is safe to say that we owe life to the van der Waals forces.

The van der Waals forces arise from electrical polarities in atoms and molecules. These polarities are caused because in atoms, the electrons tend to synchronise their motions so as to avoid each other as much as possible, thus creating instantaneous polarities.



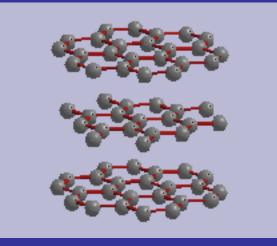
The dipoles thus created cause attraction and this attraction is the van der Waals force. As there is neither electron exchange, as in ionic bonds, nor sharing, as in covalent bonds, van der Waals bonds are much weaker than either.

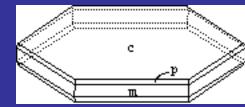
From Kline, 2002

Van der Waals bonds

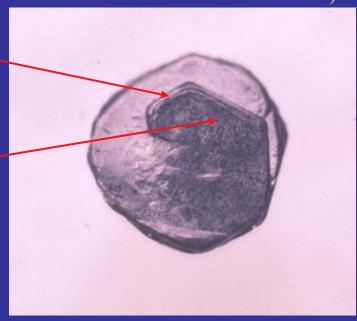
#### Covalent bonds

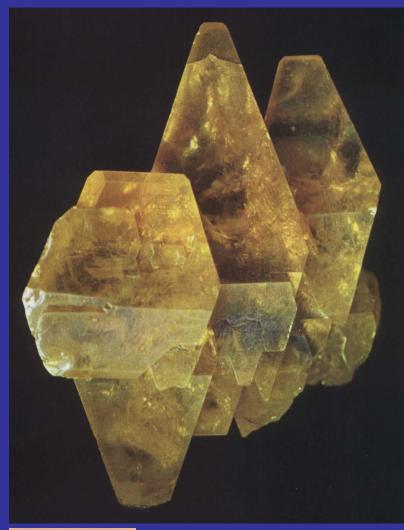
Graphite structure explained as a combination of covalent and van der Waals bonding

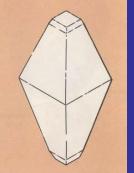




(from http://www.phy. mtu.edu/~jaszcz ak/limegraph.ht ml)



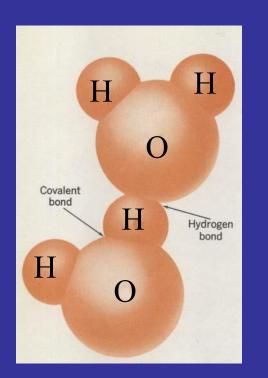




Rhombic sulfur crystals from Sicily

Crystalline sulfur (S) consists of molecules with the formula  $S_8$ . Sulfur crystals consist of such ring-shaped molecules packed into rhombohedral crystals. The S atoms in the rings are held together by strong covalent bonds, but weak van der Waals bonds ties the rings to each other. That is why sulfur is brittle and does not flow easily.

Not only atoms can be bipolar, but also entire molecules may be bipolar and when so they are called *dipoles*. When H atoms take part in such molecules, they behave like exposed protons, i.e. positively charged protrusions, and exert strong attractive forces on nearby highly electronegative atoms such as O. Water molecules are held together by such *hydrogen bonds* that are much stronger than the van der Waals bonds.



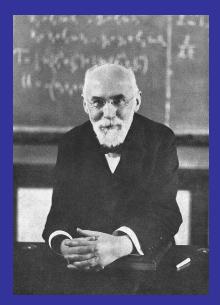
Tetrahedron

Ice molecule showing H bonds (dotted lines)

From Klein 2002

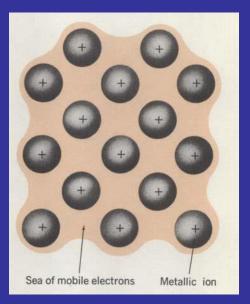
Modified from Toon et al 1968

Metals have characteristics that set them sharply apart from other crystalline substances. They have higher ductilities and are malleable (i.e. "workable"), conduct heat and electricity very efficiently and have shiny lusters of a kind known as metallic ("mirror-like"). These properties are difficult to account for in terms of the chemical bonds wehave so far considered.



Hendrik Antoon Lorentz (1853-1928)

In 1916 the great Dutch physicist Hendrik Lorentz, better known for the Lorentz transformations that made Einstein's theory of relativity possible, developed the idea that metals consist of a crystalline arrangement of hard spheres (atoms) held together by freely wandering electrons in the interstices. This free-electron theory provides a simple explanation of metallic luster, high electrical and heat conductivity, high values of heat capacity and entropy (Pauling, 1940, p. 401).



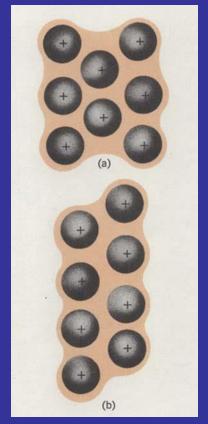
Lorentz's theory of the metallic bond. When light strikes the outer surface of a metal, it makes the electrons of the outer surface oscillate with the same frequency as the incoming light. This oscillation creates electromagnetic energy that gets radiated back and is perceived as the reflection of the incident light. This gives the metallic crystals

their typical metallic luster.

Galena crystals from Freiberg, Saxony (From Michele, 1972)



In metallic bonds, because the elctrons are not fixed, but are free to move about within the crystal, they easily transmit electricity. The same mobility also accounts for the high ductility and malleability of the metallic crystals, because the atoms "swim freely" in a sea of electorns and are thus not hindered from moving about under applied stresses.



Applied stress makes a sheet out of a lumpy metal by shifting its constituent atoms within the metallic crystals Elments with partially-filled valence shells readily form chemical bonds. Let us remember the definition of a chemical bond:

A chemical bond is the electrical interaction between atoms that holds them together.

All chemical bonds are formed as the result of the simultaneous attraction of two or more nuclei for electrons. There are five kinds of chemical bonds:

- 1. The ionic bond, in which electron exchange occurs between atoms that thus become ionised.
- 2. The covalent bond, in which atoms share electrons
- 3. The van der Waals bond forms between covalent molecules and is held by the weak *van der Waals forces*.
- 4. The hydrogen bond is one that forms in such compounds as  $H_20$ ,  $NH_3$  and HF and binds their molecules.
- 5. The metallic bond, in which electrons wander through the substance.

Minimum Radius Ratio R <sub>A</sub> : R <sub>X</sub>	Coordination Number C. N.		Packing Geometry
< 0.155	2	Linear	0.0 0.0
0.155	3	Corners of an equilateral triangle (triangular coordination)	00 ~3
0.225	4,	Corners of a tetrahedron (tetrahedral coordination)	
0.414	6	Corners of an octahedron (octahedral coordination)	
0.732	8	Corners of a cube (cubic coordination)	
1.0	12	Corners of a cuboctahedron (close packing)	

Coordination or packing geometries (from Klein, 2002)

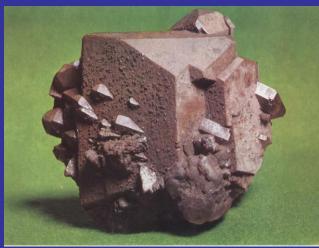
Now the question is how these various coordination geometries are packed into ordered structures that repeat the same patterns at long ranges to form the actual mineral crystals.

#### Let us remember what a crystal is:

#### A crystal is a homogeneous solid with long-range, threedimensional order.



#### Beryl crystals (milky-green)



Orthoclase crystals



A topaz crystal



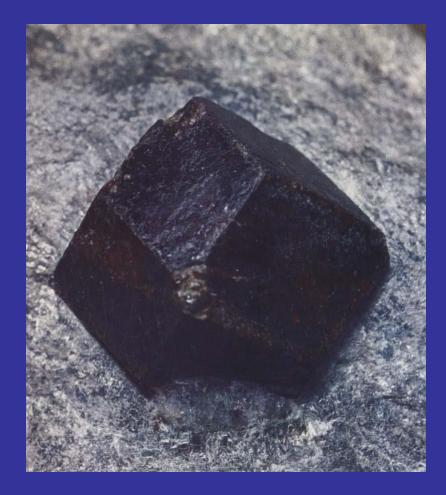
#### An halite crystal

diopside

crystal



If a crystal has well-formed faces it is said to be *euhedral* (from a combination of the Classical Greek words  $\varepsilon v$  {eu}=good,well and  $\varepsilon \delta \rho \alpha$  {edra}=seat, fundament).



A euhedral **almandine**   $(Fe_3Al_2Si_3O_{12})$ crystal, a kind of garnet If a crystal has imperfectly developed faces, it is said to be *subhedral*, from a combination of the Latin prefix *sub*-meaning "to be ranked under something," and  $\epsilon\delta\rho\alpha$ .



A subhedral **albite** (NaAlSi<sub>3</sub>O<sub>8</sub>) crystal, a kind of plagioclase feldspar

If a crystal has no faces at all, it is said to be *anhedral* (from the Classical Greek  $\alpha v$ - {an}or  $\alpha v \alpha$ - {ana}, the negative prefix, and  $\epsilon \delta \rho \alpha$ .)



Anhedral **goethite** (αFeO(OH)), a hydroxide mineral In a crystalline substance, if the crystals are so small as to be seen only under the microscope, it is said to be microcrystalline.

If the crystals of a solid are smaller than can be resolved by a microscope and be established only by X-ray diffraction techniques, that solid is said to be cryptocrystalline.

If a solid lacks an ordered internal structure, it is said to be amorphous (from the Classical Greek,  $\alpha$ - (a), the negative prefix and  $\mu \rho \rho \phi \eta$  (morphe) meaning form, shape. Thus, amorphous literally means shapeless, but this "shapelessness" in modern terminology simply refers to a lack of internal order. The ordered internal structure of a cystal is expressed by its *lattice* i.e., *a periodic array of points*.

A lattice is an imaginary pattern of points (or nodes) in which every point (node) has an environment that is identical to any other point (node) in the pattern.

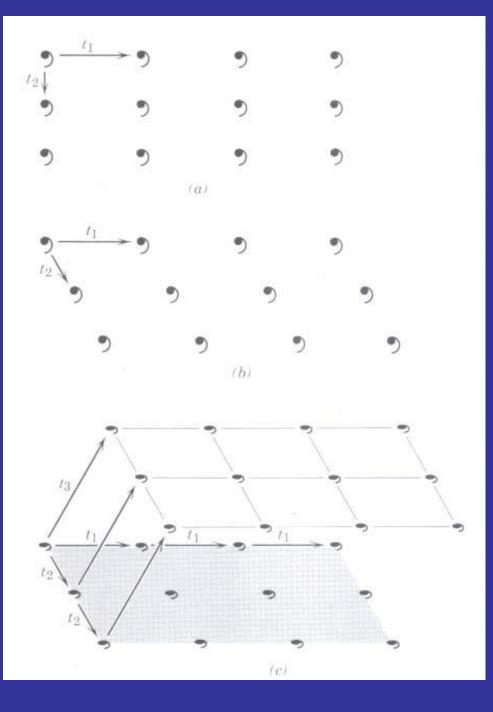
A lattice has no specific origin point and can be shifted parallel with itself.

Any motion that brings a motif coincident with a point or node in the lattice into coincidence with an identical motif elsewhere in the lattice is known as an *operation*.

Shifting the entire lattice in such a way as to repeat it is known as a *translation*.



t here is the translation of a one-dimensional array of stars.

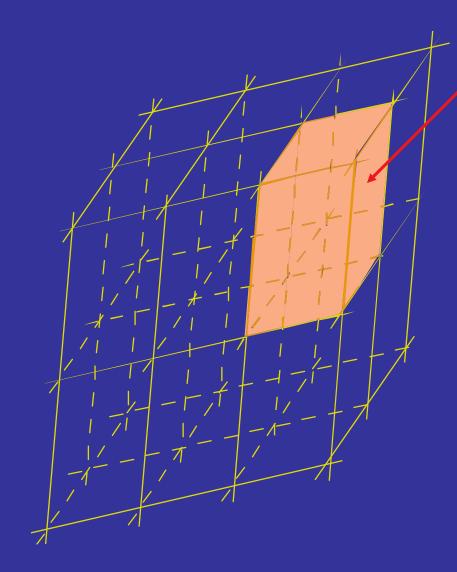


 (a) A two dimensional translation of a comma motif, in which translation angles are both 90° to one another

(b) A two dimensional translation, in which  $t_1$  is as in (a), but  $t_2$  direction is <90°

(c) A three-dimensional translation, in which the  $t_2$ and the  $t_3$  translation directions are <90° to the  $t_1$ direction.

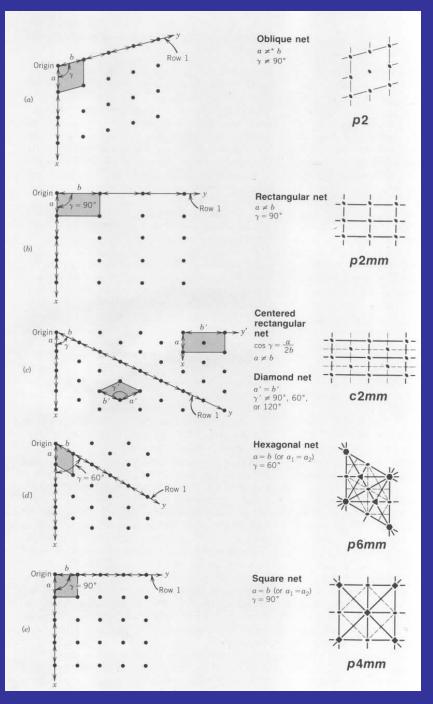
From Klein 2002



## Unit cell

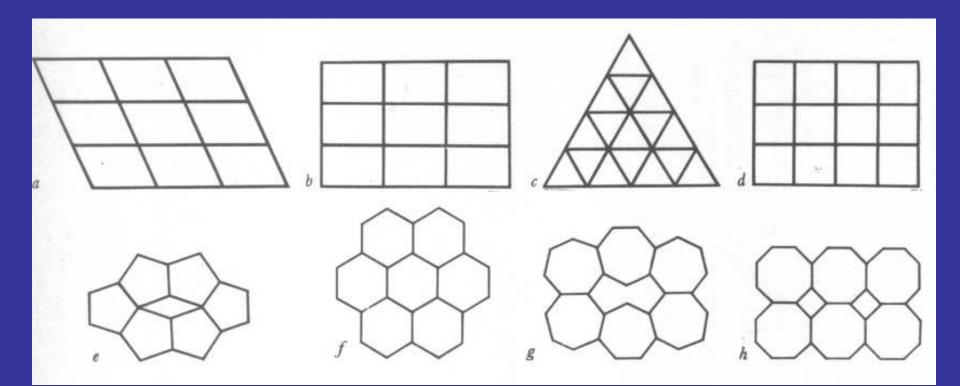
In a three dimensional lattice, the smallest repeating threedimensional volume is known as the *unit cell*.

A three-dimensional lattice with one unit cell shaded.



There are only a finite number of ways an infinitely repeatable pattern my be created by lattices. In two dimensional lattices there are only five ways a laterally infinite lattice may be created.

Here p stands for "primitive", c for "centred" and m represents a mirror line of symmetry. The numbers refer to the maximum folds of axes of symmetry. In the figure, the diamonds are 2-fold (diad) symmetry axes, triangles, 3-fold (triad), squares, 4-fold (tetrad), and hexagons (hexad), 6-fold. Solid lines are mirror-planes and dashed lines are glide planes. From Klein (2002)



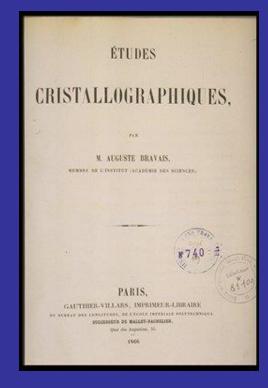
A complete tessalation is only possible by individual objects with 2-, 3-, 4-, and 6-fold symmetries. Objects with symmetries that are 5fold (petagonal) or higher than a hexad, cannot cover a surface completely.

(From Vincenzo de Michele, 1972, Crystals, London)



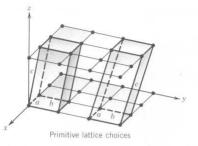
## Auguste Bravais (1811-1863)

It was the great French polymath (physicist, mineralogist, botanist, astronomer) Auguste Bravais, who showed in his posthumous 1866 book that there are only 14 different ways a threedimensional lattice may be generated that can extend in three

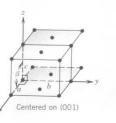


## Bravais (1866)

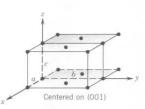
dimensons infinitely. That is why they are called the *Bravais lattices*. The Bravais lattices represent the only ways that constituent units of minerals (atoms, ions and molecules) may be arranged within a mineral crystal. Once you understand them you know how all mineral structures form. These 14 different lattices give the six (or seven, depending on definition) crystal classes!



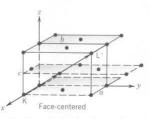
 Stacking of an oblique net (or plane lattice) at an arbitrary angle results in *primitive triclinic lattices*.



(3) Stacking of a centered rectangular net in a vertical direction (z), with x ∧ z angle (β) ≠ 90°, results in a centered monoclinic lattice.



(5) Stacking of a centered rectangular net in a vertical direction (z), with the x \lapha z angle = 90°, leads to a centered orthorhombic lattice.



(7) Stacking of a centered rectangular net along the direction between nodes K and L' (on the front face) leads to centering on all faces of the three-dimensional lattice. This is a face-centered orthorhombic lattice.



Stacking of a primitive rectangular net in a vertical direction (z), with  $x \wedge z$  angle ( $\beta$ )  $\neq$  90°, leads to a primitive monoclinic lattice.

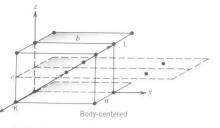
(2)

(6)

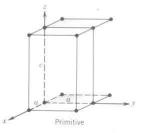
(8)



(4) Stacking of a primitive rectangular net in a vertical direction (z), with the x ∧ z angle = 90°, leads to a primitive orthorhombic lattice.

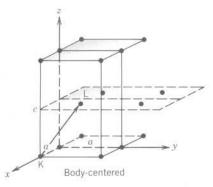


Stacking of a primitive rectangular net along the direction between nodes K and L results in an orthorhombic lattice with a central node. This is an *orthorhombic body-centered lattice*.

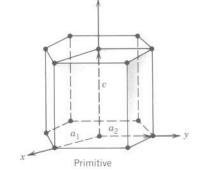


Stacking of a square net along the z direction, with angle  $x \wedge z = 90^{\circ}$ , and with the c translation  $\neq a_1$  or  $a_2$ , results in a primitive tetragonal lattice.

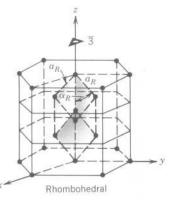
# Eight of the 14 Bravais lattices (From Klein 2002)



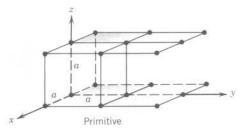
(9) Stacking of the same net as in (8) but now in a direction between nodes K and L results in a body-centered tetragonal lattice.



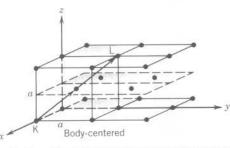
(10) Stacking of a hexagonal net in a z direction such that angle x ∧ z = 90° leads to a primitive hexagonal lattice. If this lattice choice is rotated 3 times about z, it results in a c-centered hexagonal lattice.



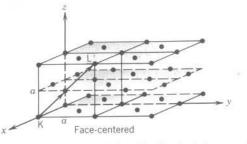
1) A hexagonal net can also be stacked along the edge directions of a rhombohedron  $(a_R)$ . This results in a *rhombohedral lattice*, the edge directions of which are symmetrical with respect to the  $\overline{3}$  axis along the *z* direction.



(12) Stacking of a square net along the *z* direction, with *x* ∧ *z* angle = 90° and with *c* translation = *a*<sub>1</sub>, and *a*<sub>2</sub>, results in a *primitive isometric lattice*.

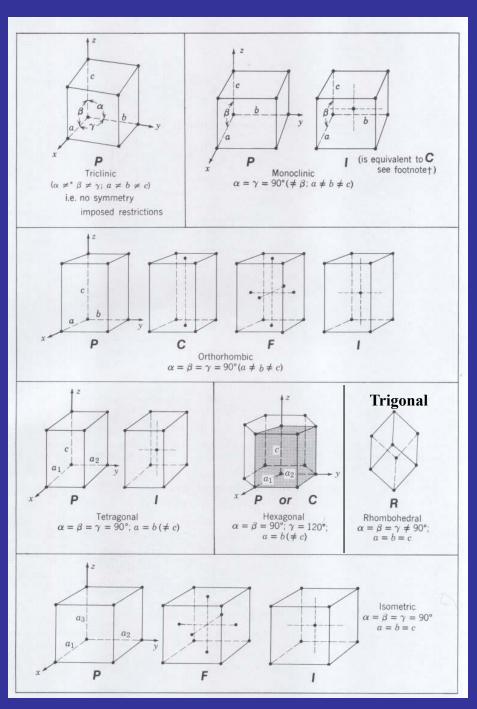


(13) Stacking of a square net along the direction between nodes K and L (a body diagonal) results in a *body-centered isometric lattice*.



(14) Stacking of a square net along the direction between nodes K and L' (along the front face), results in a face-centered isometric lattice.

# The remaining six Bravais lattices (from Klein 2002).



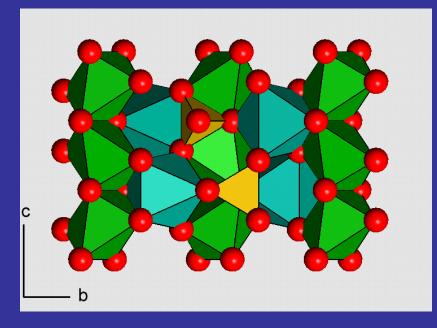
The six (or seven) crystal classes as derived from the Bravais lattices. Here again P is primitive, C is Ccentred (can be A-or B-centred), F is face-centred (if centring occurs on all faces) and I is simply internally cenred (from the German *innenzentriert*.)

Now the question is how do the various atoms, ions, or molecules choose this or that system to crystallise in to form the various mineral species.

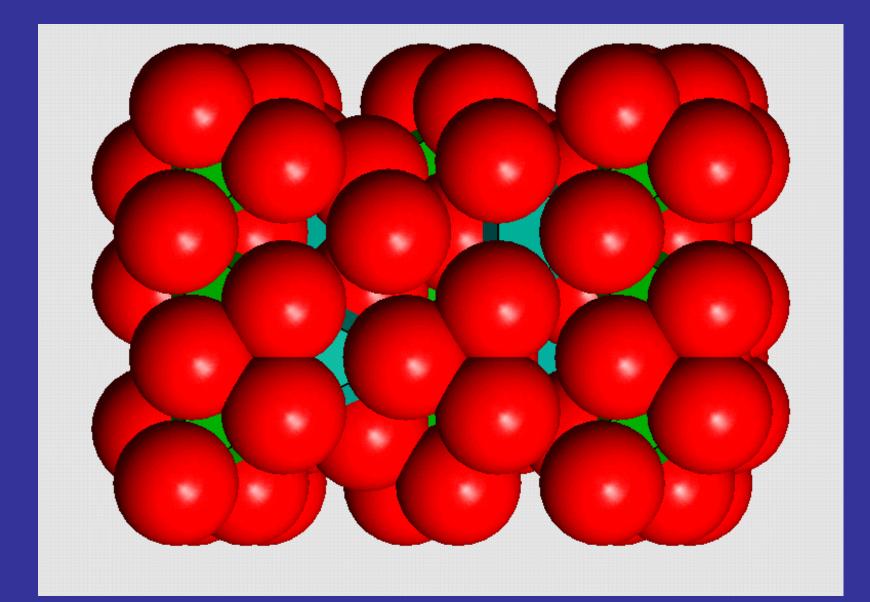
But, before we answer that question let us do some practicals to see some real examples of the different crystal classes. The simple answer to the question we had just posed as to how the various atoms, ions or molecules know in which system of crystals they will crystallise or which particular crystal form they will adopt, is that we really do not know and it is one of the most important and promising areas of mineralogy to do research in (this is one possible way you might get a Nobel Prize as a geologist!)

Research in recent years has shown that this question has in part to do with *surface energies*. If you somehow "poison" a surface by adhering to it certain types of atoms or ions or molecules, cystal growth will simply continue in a different direction.

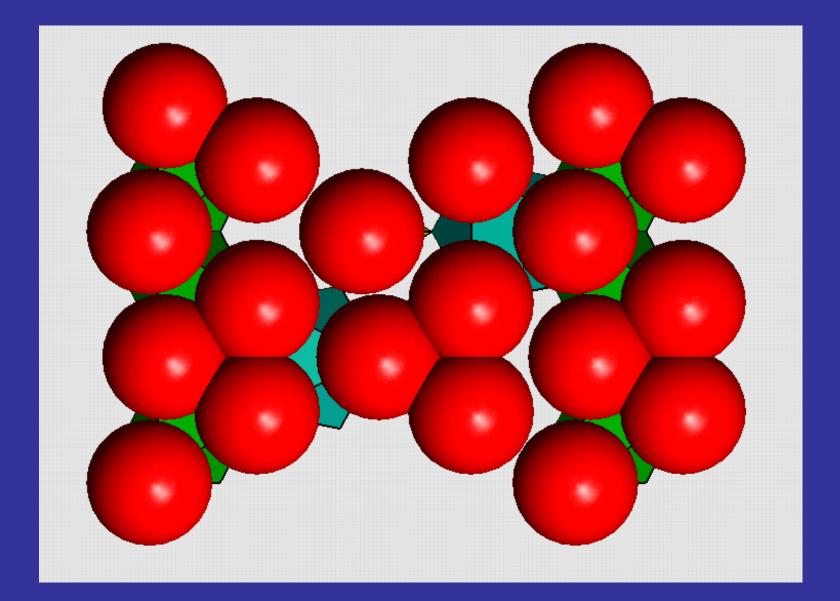
But how do the atoms, ions or molecules know which *crystal system* they will choose to grow in? In other words, how do they choose their axes and why (almost) always a particular composition always chooses the same crystal system? The question we have just posed is one of the most fundamental questions in mineralogy and has not yet been completely answered. However, enough is understood to know that it is first the *composition* and then the *conditions of crystallisation* that determine the crystal system in which a mineral will crystallise. Let us illustrate this after Prof. George Rossman of Caltech, by using olivine and olivine-composition minerals, the most abundant group of minerals in our earth.



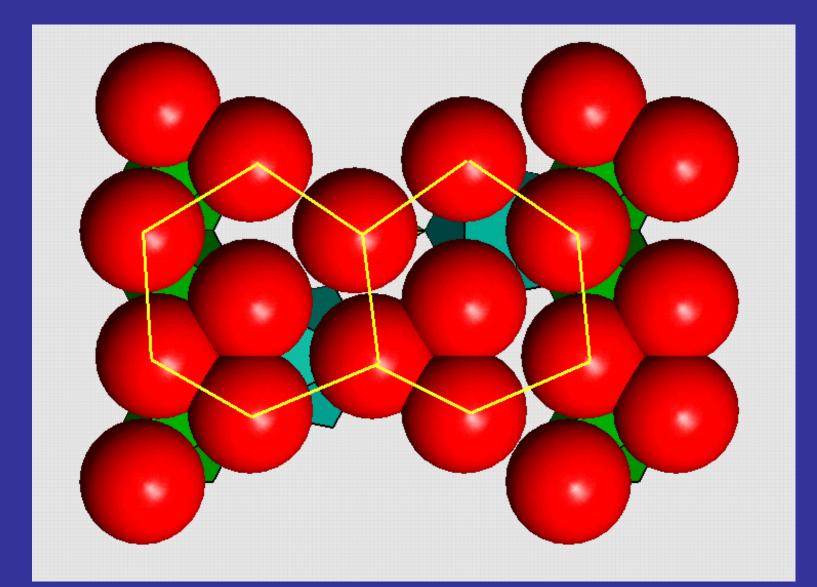
Olivine structure consisting of individual  $SiO_4$  tetrahedra. The red balls are the O atoms.



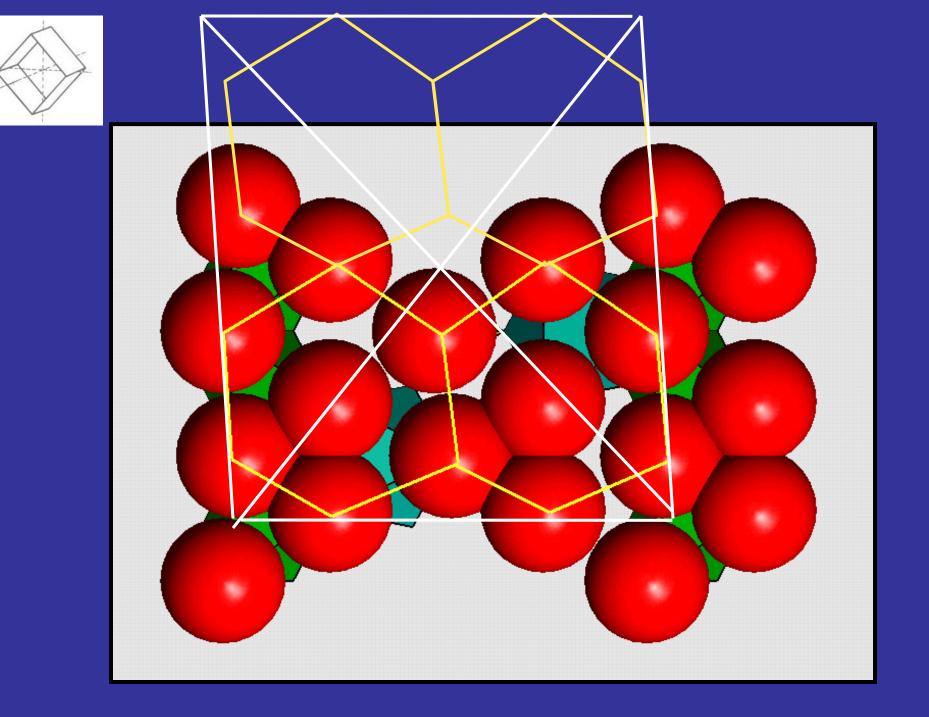
This is what the olivine structure looks like because of the fat O atoms and ...



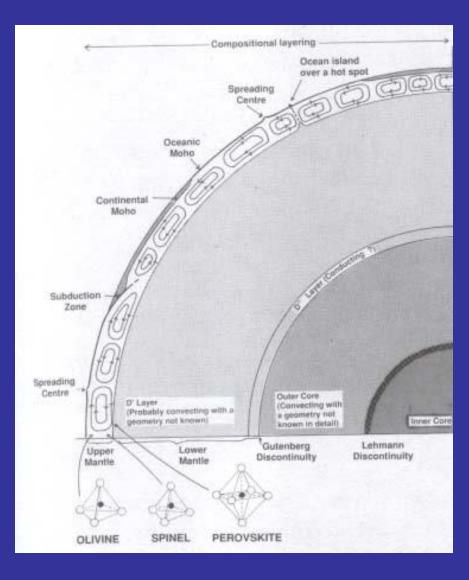
# Let us take the top layer of the O to see the structure better ...



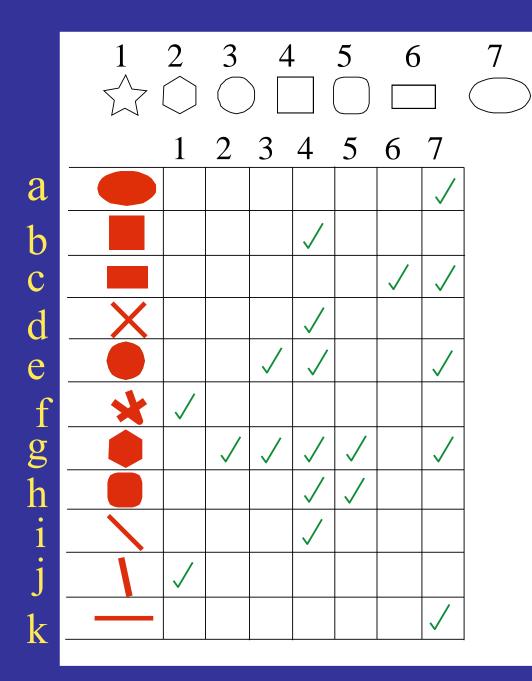
Almost hexagonal close-packing. But not quite, because of the cations that hold the  $SiO_4$  tetrahedra together! So the structure becomes orthorhombic!



Olivine has a four-fold coordination of the Si atom in a tetrahedral arrangement. When the pressure increases, at some 300 to 400 km, olivine converts to spinel (in Mars this is expected to occur at some 1200 km), which also has a tetrahedral coordination of the Si atom, but in a more compact tetrahedron in which the chemical bonds are shorter. This results in the fact that the olivine composition with such a small tetrahedron crystallises in a the cubic system and no longer in the orthorhombic system. With further increase in pressure, beyond the 650-km discontinuity, the four-fold Si coordination switches to 6-fold coordination. The olivine composition now crystallises again in the orthorhombic system and becomes the mineral perovskite.



Mineral compositions and associated interatomic structures fit in wherever they can into the 14 possible Bravais lattices that form the seven crystal systems. This is like having seven openings into which a multitude of forms must fit in order to pass through. The following diagram illustrates what I mean:



In this matrix, only certain interatomic structures (represented by the red figures, a, b, c, ...) can pass through certain crystal systems (represented by the empty figures, 1, 2, 3, 4, ...). Some of the red figures fit perfectly, others more loosely, into certain crystal systems. The perfect fitters create the monomorphic minerals, whereas the more loosely fitting ones the polymorphs (rows) and a kind of isomorphs (columns).

Now that we have learnt how to "make" minerals, we are ready to investigate their various kindsand how they combine to form rocks. That is the subject of Lesson 4.