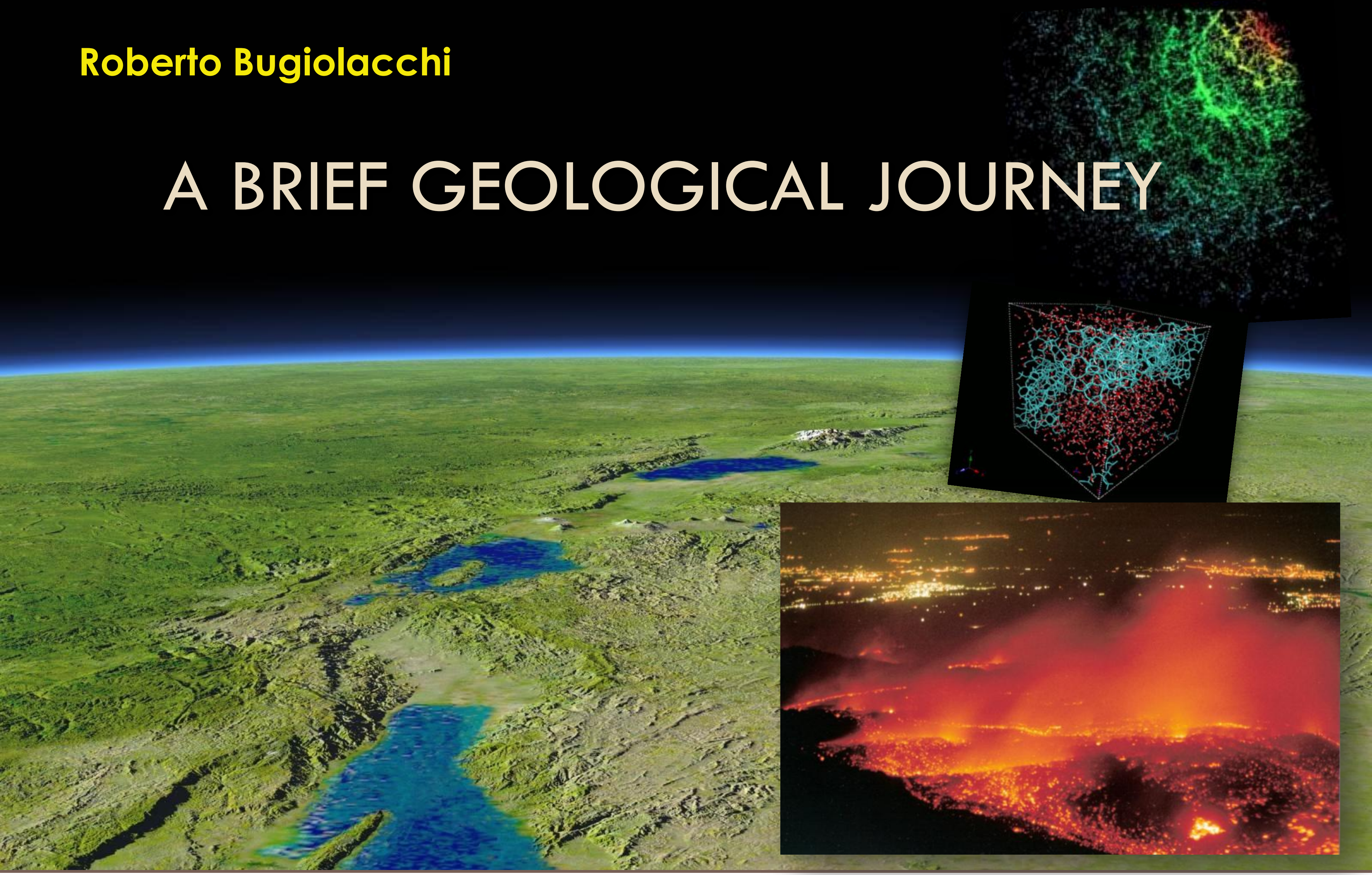


Roberto Bugiolacchi

A BRIEF GEOLOGICAL JOURNEY

A material look at the Universe and the Earth

What is the Universe made of?

1.1 From universe to us

Element	Atomic #	Symbol	Universe	Sun	Earth bulk	Earth crust	Earth's Basalt	Earth's Granite	Moon Bulk	Human body
hydrogen	1	H	**73.9000**	**91.2000**		0.22	0.11	0.07		**63.00**
helium	2	He	**24.0000**	**8.7000**						
carbon	6	C	0.0046	0.0430		0.41	0.03	0.01		**9.50**
nitrogen	7	N	0.0010	0.0088						1.40
oxygen	8	O	**1.0700**	**0.0780**	**30.37**	**47.37**	**44.70**	**49.10**	**42.00**	**25.50**
neon	10	Ne	0.0013	0.0035						
sodium	11	Na			0.60	4.37	2.16	2.73	0.07	0.03
magnesium	12	Mg	0.0006	0.0038	14.80	2.10	4.06	0.43	**18.70**	0.01
aluminium	13	Al			1.27	**8.16**	**8.33**	**7.58**	4.20	
silicon	14	Si	0.0007	0.0045	**15.77**	**28.67**	**23.00**	**33.30**	**19.60**	
phosphorus	15	P					0.15	0.05		0.22
sulphur	16	S	0.0004	0.0015	3.30				0.30	0.05
potassium	19	K				2.42	0.91	3.38		0.06
calcium	20	Ca			1.50	3.97	6.77	1.32	4.30	0.31
titanium	22	Ti				0.46	1.10	0.19		
iron	26	Fe	0.0011	0.0030	**31.27**	4.78	8.19	2.12	9.30	
nickel	28	Ni			1.93				0.60	

Top 1 element in each system (%)

2nd, 3re, and 4th, top elements (%)

Refractory element

Volatile 1300-600 K

Volatile <600

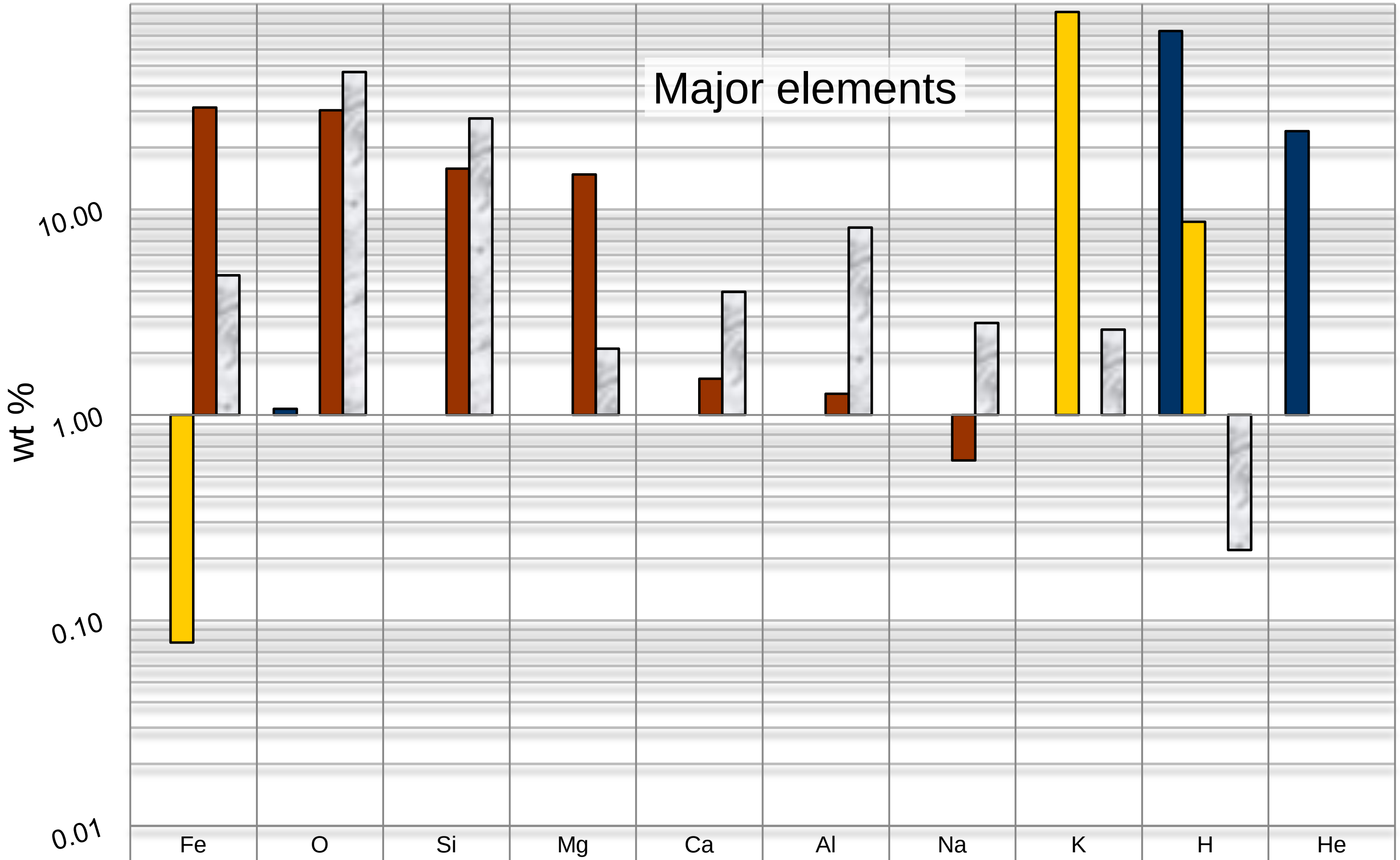
Average and estimates compositional abundances.

Weight percent – wt%

Percentage distribution of major elements

1.2 Major elements

Comparison of the ten principal elements (weight percent - wt%)



	Fe	O	Si	Mg	Ca	Al	Na	K	H	He
Universe		1.0700							73.9000	24.0000
Sun	0.0780							91.2000	8.7000	
Earth bulk	31.27	30.37	15.77	14.80	1.5	1.27	0.6			
Earth crust	4.78	46.60	27.70	2.10	3.97	8.16	2.8	2.6	0.22	

Nucleosynthesis – the first steps

1.3 Time begins…

<1 second: temperatures are so high that energy/matter is organised and freely distributed in fundamental quanta called quarks.

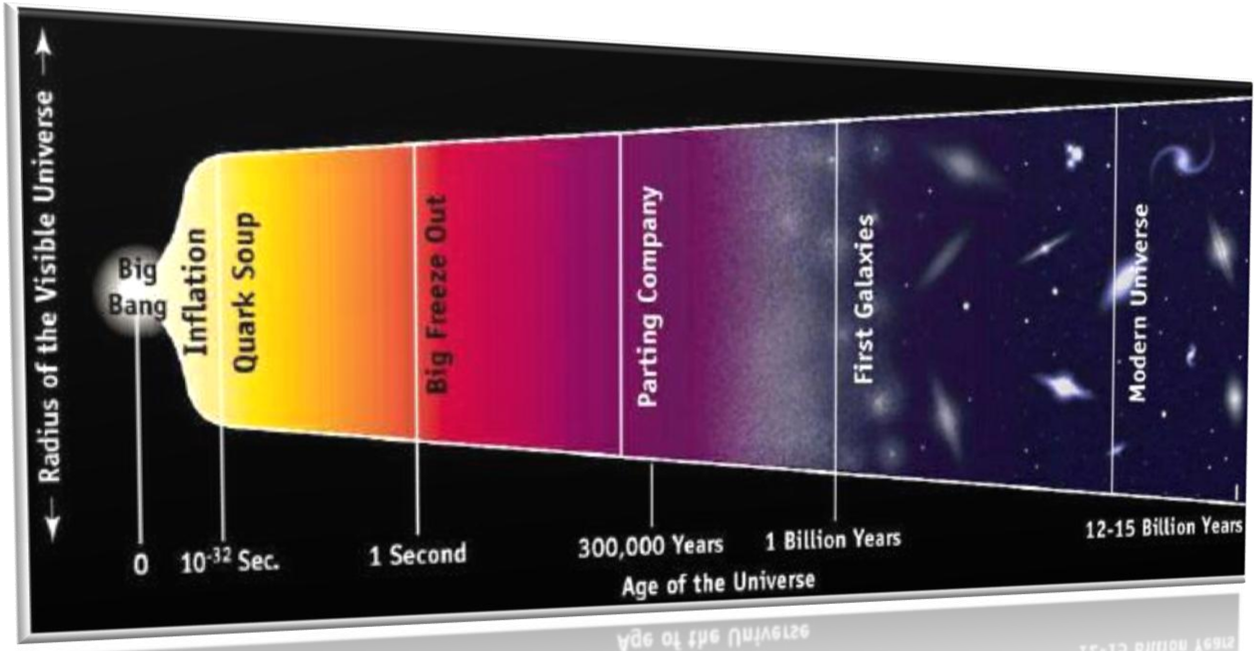
After this 'crucial' first, possibly 'inflationary' second, space has expanded enough for quarks to overcome fundamental repulsion forces and 'bunch' together (in triplets of at least two different quark types, or 'colour') to form baryons, i.e. protons and neutrons.

For the next three minutes or so nucleons also come together into the first nuclei of 'ordinary' matter:

p + n → D (deuterium)	or	**^{2}H** (heavy hydrogen)	This is highly reactive (doesn't last long…):	
D + n	→	**^{3}H** (*tritium*, very heavy hydrogen)	Element 1 (one p)	(unstable):
D + p	→	**^{3}He** (*helium*, light variety…)	Element 2	(quickly…)
^{3}He + ^{3}He	→	**^{4}He** + 2p ('**normal**' *helium*, helium 4)	Element 2	
^{3}He + ^{4}He	→	**^{7}Li** ('normal' *lithium*)	Element 3	

Nucleosynthesis – the journey continues (2)

1.4 Time has begun…



State of the matter so far:

Hydrogen (H)	→ *1 proton*	*0 neutron* (albeit strictly not part of nucleosynthesis)
(Deuterium ^{2}H or D)	→ 1 proton	1 neutron
Helium (He)	→ 2 protons	2 neutrons *(or 1, isotope* ^{3}He)
Lithium (Li)	→ 3 protons	3 neutrons *(or 4, isotope* ^{7}Li)

Nucleosynthesis – the journey continues (3)

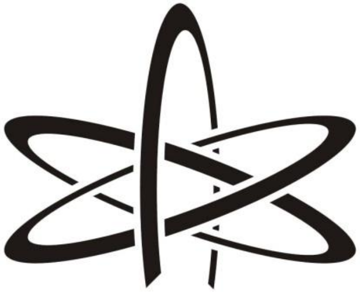
1.5 Time expands…

‘Normal’ helium (2 p + 2 n) is the most stable of these elements because it is ‘energetically favourable’, i.e. its energy is smaller than the combined energy of its nucleons.

Consequently,

nearly all neutrons should end up in/as helium, with some ‘’free’ residual protons, but… observations show that the Universe’s composition is:

75%	hydrogen
24%	**helium**
1%	heavier elements (‘metals’)

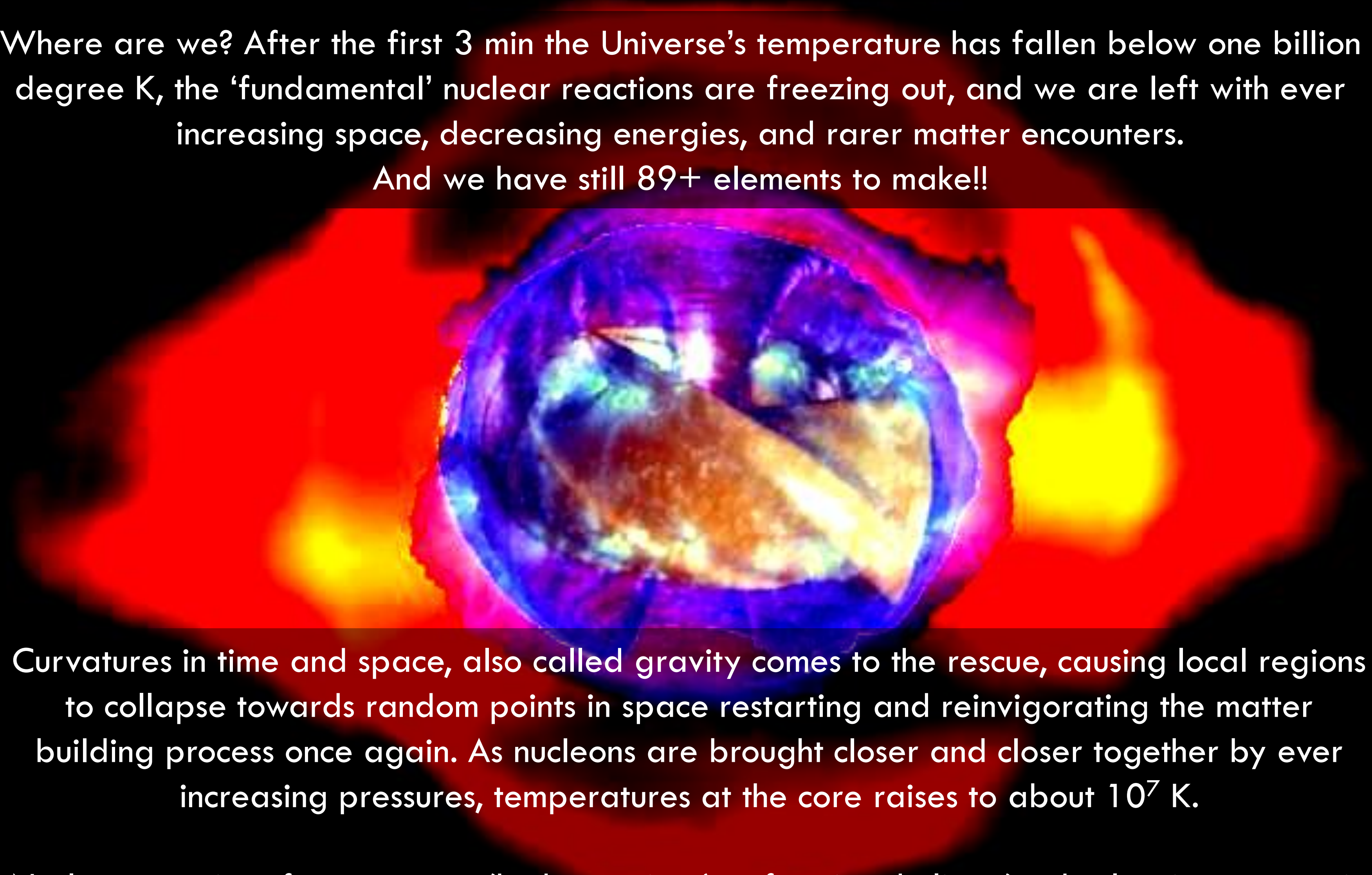


Why?

This is because the availability of free neutrons gets smaller and smaller as nuclear reactions proceed due to the decay of (unbound) neutrons into protons, electrons, and neutrinos, hence **stalling** the nucleosynthesis **$p + n = D$ process.**

Nucleosynthesis – the journey gets interesting...

Where are we? After the first 3 min the Universe's temperature has fallen below one billion degree K, the 'fundamental' nuclear reactions are freezing out, and we are left with ever increasing space, decreasing energies, and rarer matter encounters.
And we have still 89+ elements to make!!



Curvatures in time and space, also called gravity comes to the rescue, causing local regions to collapse towards random points in space restarting and reinvigorating the matter building process once again. As nucleons are brought closer and closer together by ever increasing pressures, temperatures at the core raises to about 10^7 K.

Nuclear reactions force protons (hydrogen ions) to fuse into helium (and releasing energy in the process), in a process called proton-proton reaction (hydrogen burning).

We are still synthesising...

- Now, it’s all down to size! (i.e. mass, T, P,)
- small stars <4*Sun: end up as white dwarfs, ‘dead’ compact objects mainly comprising of He.
- stars ≥4*Sun <8*Sun: ($T>10^8$ K) heavier elements are synthesised, such as carbon (C, 6 protons) and oxygen (O, 8), in a process called ‘helium burning’.
- stars >8*Sun: produce elements such as silicon (Si, 14) up to, but not heavier than, iron (Fe, 26) in various processes such as α reaction, carbon, neon, and oxygen burning processes.

…and we are still synthesising…

		Universe’s estimated abundance %
${}_{1}\mathrm{H}$		~74
$\mathrm{H + H \rightarrow {}_{2}He}$	proton – proton reaction (hydrogen burning)	~24
$\mathrm{He + He \rightarrow {}_{4}Be}$	Triple α reaction	
$\mathrm{Be + He \rightarrow {}_{6}C}$	This process is promoted by resonances	~0.0046
$\mathrm{C + He \rightarrow {}_{8}O}$		~1.070
Examples of element formation:		
$\mathrm{C + C \rightarrow {}_{10}Ne + He}$	carbon burning processes	~0.0013
$\mathrm{C + C \rightarrow {}_{11}Na + H}$	“ “	
$\mathrm{C + C \rightarrow {}_{12}Mg}$	“ “	~0.0006
$\mathrm{C + C \rightarrow {}_{8}O + 2He}$	“ “	
$\mathrm{O + He \rightarrow {}_{10}Ne}$		
$\mathrm{Ne + He \rightarrow Mg}$	neon burning process (>8M_{sun})	
$\mathrm{Na + He \rightarrow {}_{12}Mg}$		
$\mathrm{O + O \rightarrow {}_{14}Si + He}$	oxygen burning process	~0.0007
$\mathrm{Mg + He \rightarrow Si}$	pure α process	
${}_{14}\mathrm{Si}$	pure α process - also oxygen burning turns Si into Fe	
${}_{16}\mathrm{S}$		~0.0004
${}_{18}\mathrm{Ar}$		
${}_{20}\mathrm{Ca}$	pure α process	
${}_{22}\mathrm{Ti}$		
${}_{23}\mathrm{V}$		
${}_{24}\mathrm{Cr}$		
${}_{25}\mathrm{Mn}$		
${}_{26}\mathrm{Fe}$	iron peak	~0.0011
All other elements		~0.0070

Nearly there, only the small matter of a few more elements...

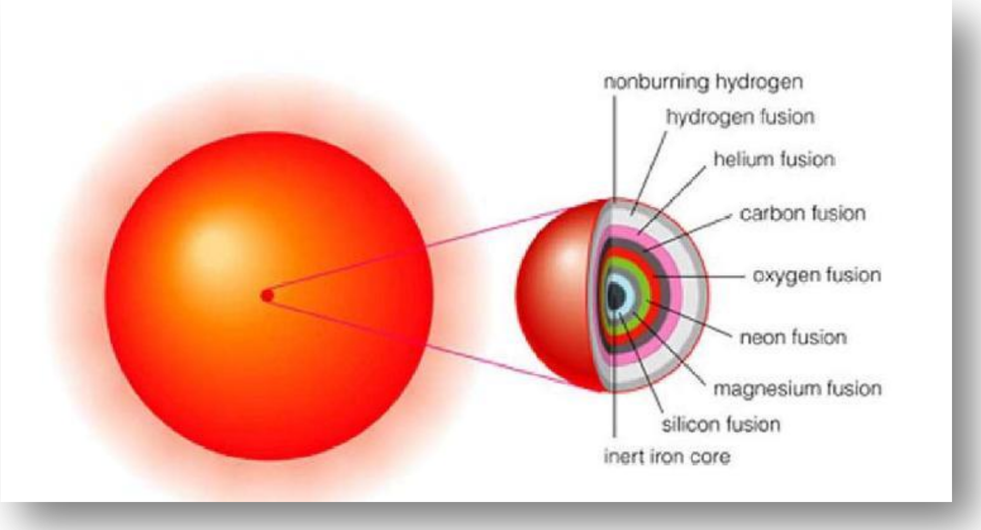
1.9 Iron gate

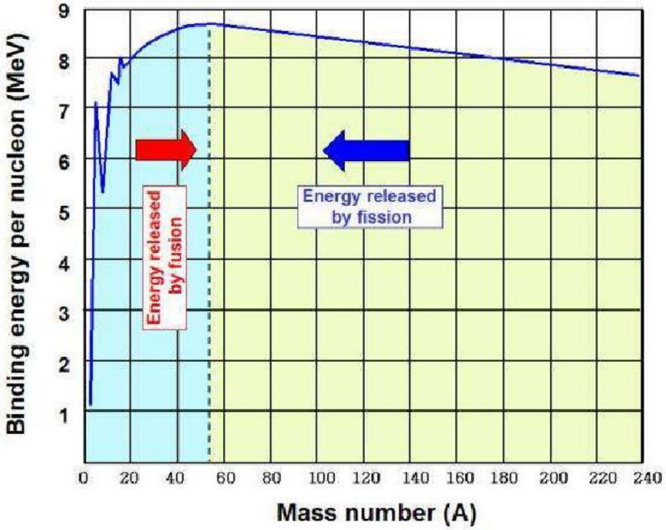
WHY DOES THIS PROCESS END WITH FE?

No known nuclei are more stable than ^{56}Fe

This stability also means that the element is unable to fuse with other nuclei to produce more energy (an exothermic process).

Onion shell structure of (massive) stars





Nucleosynthesis goes supernova!

Deep in the hearts of massive, highly evolved and collapsing stars, nuclei are subject to enormous heat and pressures

Nuclei that are not destroyed in this process interact with neutrons (neutron-capture process 's', as per 'slow'), to produce elements all the way up to ^{209}bismuth (element 83)

By the time a massive star has acquired a metallic core, fusion in the core cannot progress any longer

Gravity leads to ever increasing pressures and temperatures (>one billion degrees K) causing the disintegration of certain elements and the collapse of the centre of the star

Nucleosynthesis goes supernova!

Outer layers collapse inwards at first, and then they are thrown out again in a 'supernova' explosion, scattering the newly formed elements into space.

This explosion also generates a flood of neutrons that are quickly captured by the heavier elements in the environment.

The remaining 'natural' elements (up to ^{238}U) are thus produced by another neutron-capture process, this time called 'r', as per 'rapid'.

OUR TABLE OF ELEMENTS IS NOW COMPLETE

The Solar System

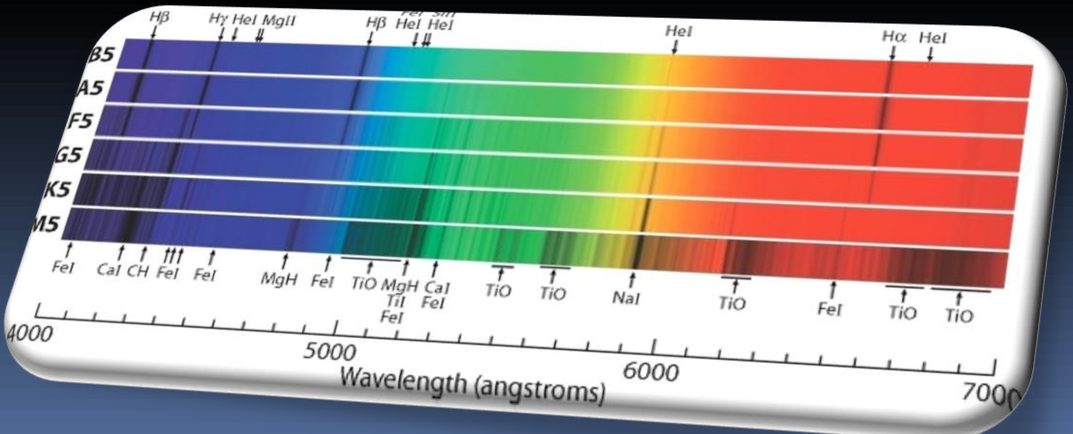
At this point of our journey we need to take a step back and remind ourselves of the distribution of elements throughout the universe, with hydrogen and helium together representing 99% of its mass.

These two elements are under 'normal' circumstances in a gaseous state. The Earth is clearly both solid and molten, with just an extremely tenuous (in comparison to its diameter) gaseous shell.

Would it surprise you to know that most of the relative abundances of elements on the Sun *match* those of a modelled bulk Earth?

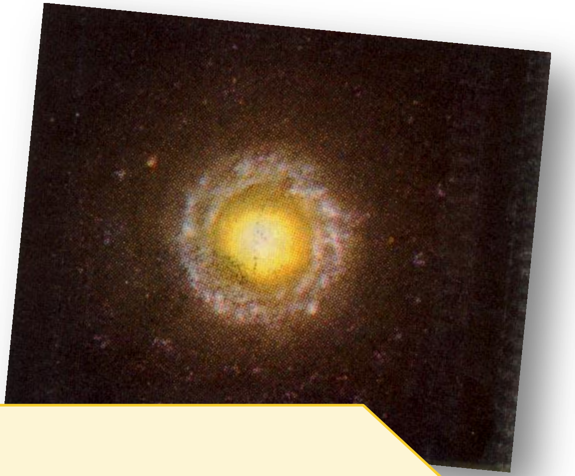
How do we know this? The Sun's photosphere (~500 km thick, T~6000 K) radiates a continuous spectrum of light, but before it reaches us it crosses a cooler layer where T drops by 2000 K in ~500 km.
Atoms of elements in this layer absorb some of this radiation in a particular frequency or range of frequencies.

When studied in detail, the solar spectrum appears crossed by dark lines, called Fraunhofer lines: they are the 'fingerprint' evidence of elements, revealing both their presence and relative abundances.

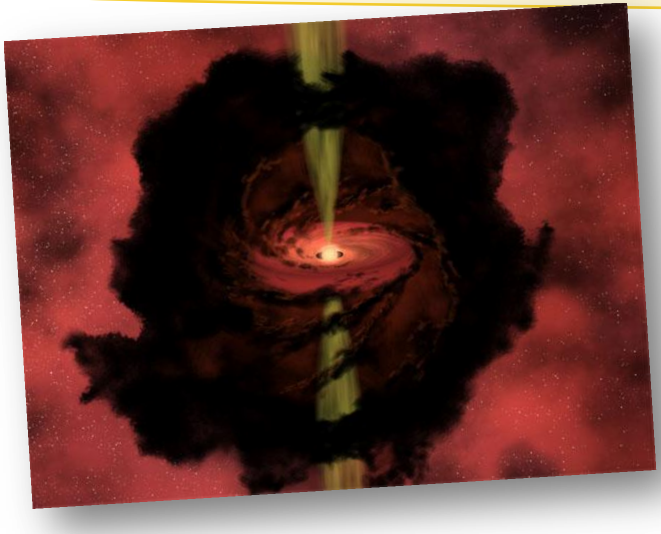


2. THE FORMATION OF THE SOLAR SYSTEM

Some 15 billion years after the Big Bang, space was (sparsely) populated with solid matter, mostly as multi-generational recycled gaseous materials more or less bound by gravitational force fields.



In a corner of the Milky Way, a 'pulse' of gravitational instability, maybe triggered by a local supernova explosion, encountered a dense, rotating interstellar molecular cloud causing it to progressively collapse towards its centre of gravity.



The process of compressing gases, principally hydrogen and helium, would have caused temperatures to raise dramatically, eventually initiating nuclear fusion in its core, producing energy and, well, **SHINE**.

The **Sun** **was born**.

NAME	FORMULA
Diamond, Graphite	C
Moissanite	SiC
Nano-particles	TiC, ZcC, MoC, FeC, and Fe-Ni metals
Osbornite	TiN
Rutile	TiO_2
Corondum	Al_2O_3
Spinel	$MgAl_2O_4$
Forsterite	Mg_2SiO_4
Hibonite	$CaAl_{12}O_{19}$
Perovskite structure	$MgSiO_3$
GEMS (silicate glass with embedded metal and sulphides)	

The Formation of the Solar System

BUT, at this age of the Universe, interstellar nebulae were populated also by a rich (albeit modest in proportion) range of heavier elements, collectively described as 'metals' by physicists (interstellar dust).

The centrifugal forces generated by the rotating star and nebula would have allowed a small proportion of the gases and dust (1-2%) to escape the gravitational pull of the proto-Sun, organising itself in an flattened, orbiting disc:

The **SOLAR NEBULA**

THE FORMATION OF THE SOLAR SYSTEM

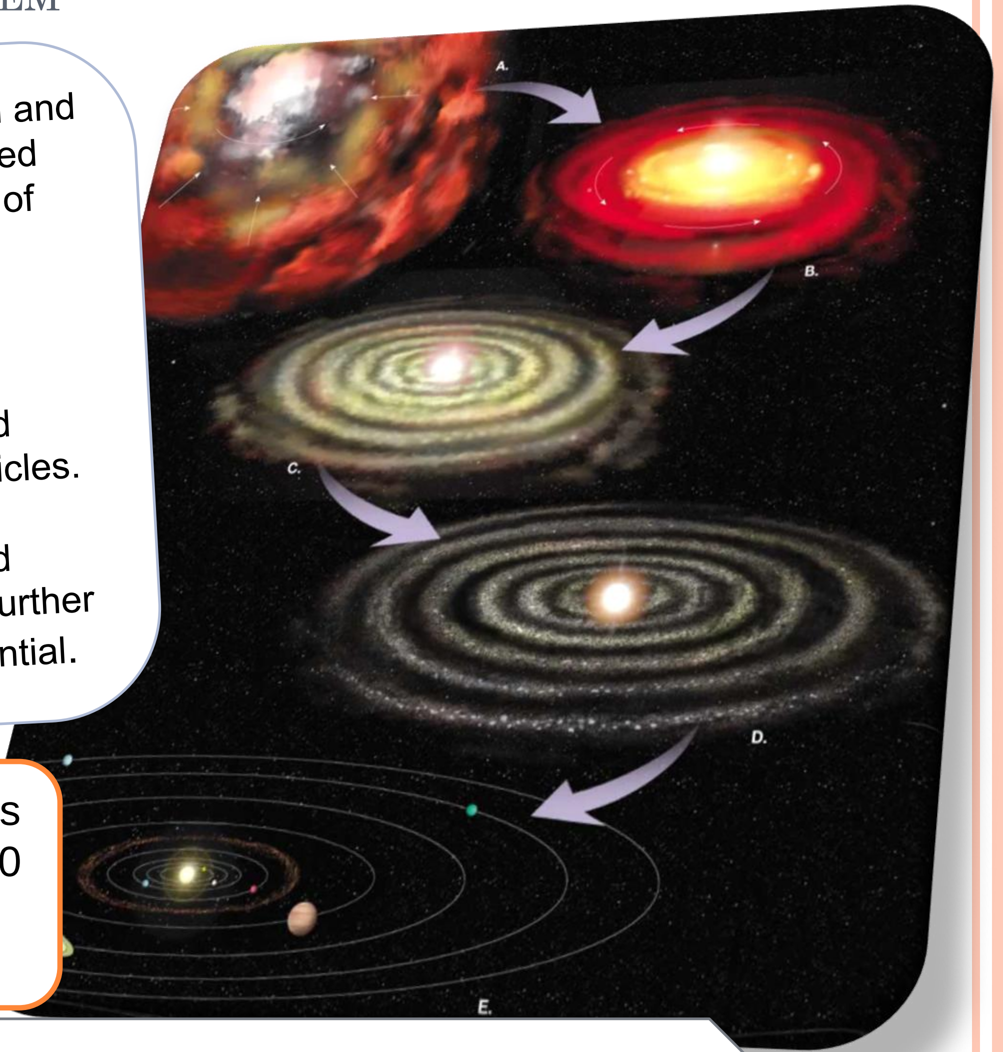
4.65 - 4.55 Ga

Elements heavier than H and He would have condensed soon after the formation of the disc.

4.56 - 4.40 Ga

T<1800 K, magnesium and iron silicates also started to condense and aggregate into tiny particles.

As the materials condensed and clumped together, their increasing gravity would have further accelerated their growth and 'scooping' potential.

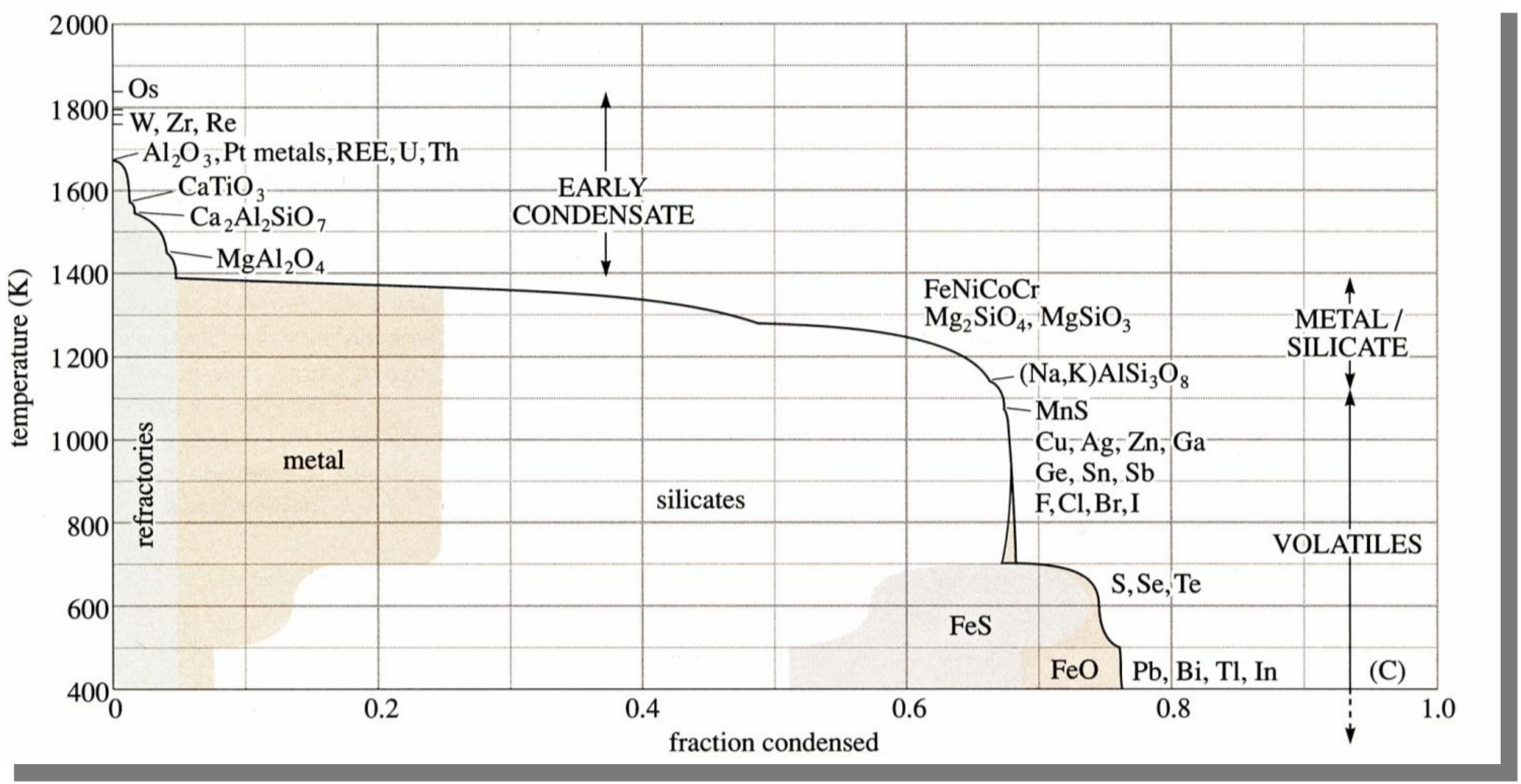


It would have taken around 100,000 years for these rocky bodies to grow to about 10 km in diameter, becoming '***Planetesimals***'.

As the building process continued, these planetesimals would have accreted into ***planetary embryos***, and, eventually, fully formed **planets.**

The Making and Composition of the Earth

2.5 The order of condensation



The condensation sequence of the solar nebula at pressures of about 10 N m^{-2}

The Making and Composition of the Earth

2.6 Compounds condense…

Al_2O_3	**Aluminium oxide** (‘alumina’) → major source of Al from Corundum (also rubies, sapphires, etc.)
$CaTiO_3$	**Calcium titanite** (major polymorph of ***Perovskite***, probably the most abundance mineral in the mantle)
$Ca_2Al_2SiO_7$	**Gehlenite** (from the Melilite gehlenite-akermanite solid solution)
$MgAl_2O_4$	**Spinel** – principal mineral in the ‘spinel’ group.
Mg_2SiO_4	**Olivine** – *Forsterite*. Fe^{+2} forms a solid solution in the olivine system Forsterite-Fayalite.
$MgSiO_3$	**Perovskite** (magnesium silicate), or mineralogically Enstatite (opx).
$(Na, K)AlSi_3O_8$	**Albite** – (Na) *Plagioclase Feldspar* and *Orthoclase* - (K) *Alkali Feldspar*

- As T drops, the first materials to condense out would be the highly refractory (i.e. high melting point) such as Os (Osmium, 76), Re (Rhenium, 75), W (Tungsten, 74), and Zr (Zirconium, 40).

- Then, slightly less refractory Al_2O_3 (aluminium oxide), the platinum-group metals, the REEs, uranium and thorium.

- ‘Third stage’: silicates and titanates of calcium, aluminium, and magnesium

- At ~1400 K, iron would have condensed, closely followed by the bulk of the silicates, and later, elements such as copper, silver, and zinc.

- The dotted arrow indicate that below 400 K the last compounds to condense were ammonia (NH_3), methane (CH_4), and water.

SO, ARE ALL PLANETS THE SAME?

Obviously not, there are ‘terrestrial’ or inner planets (Mercury, Venus, Earth and Mars) and the ‘Jovian’ or outer planets (Jupiter, Saturn, Uranus, Neptune). Interestingly, Jupiter and Saturn are sometimes described as ‘failed stars’ (brown stars).

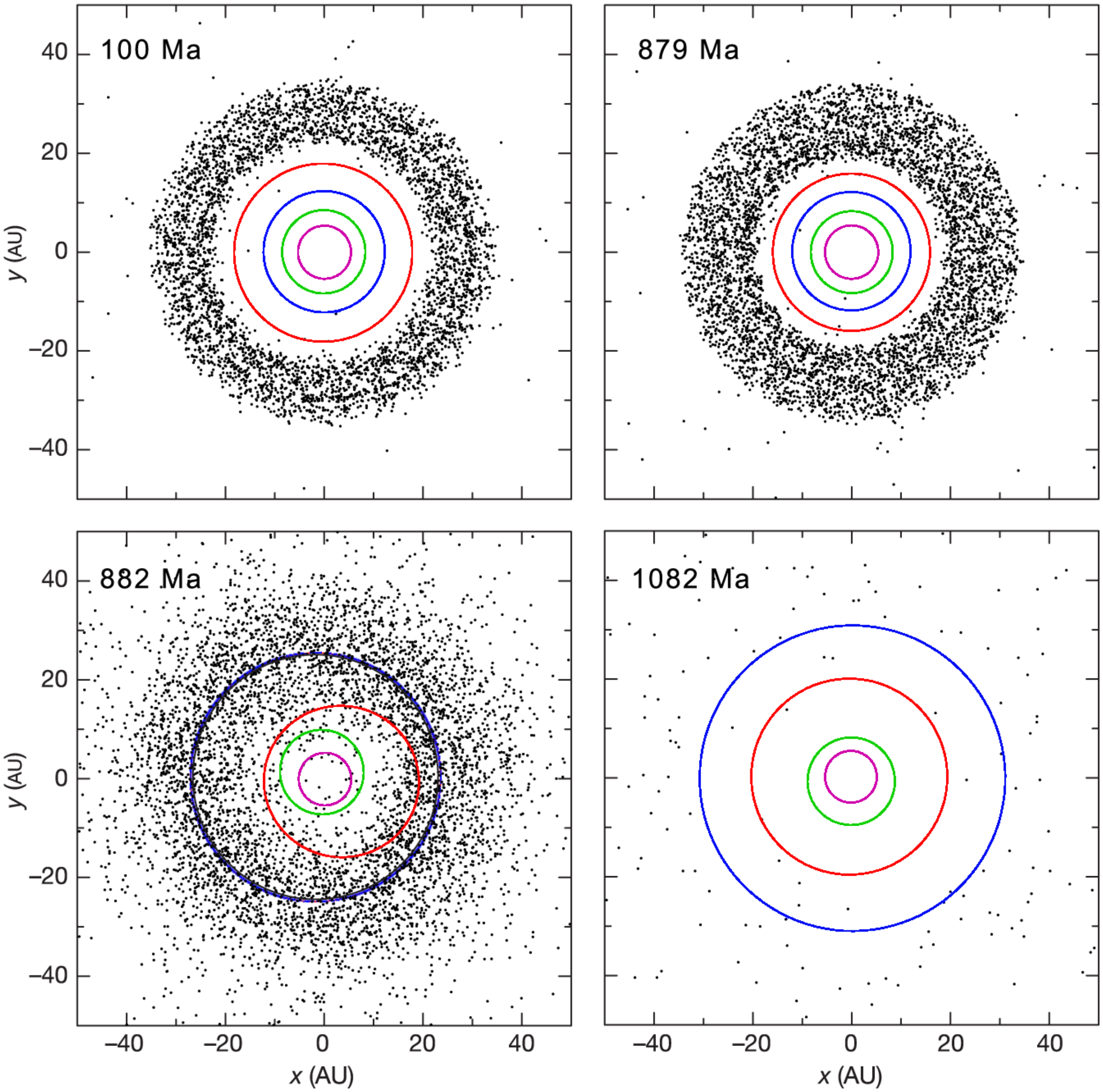
In fact, Jupiter has an estimated rocky core the size of 10-17 Earths mass!

Saturn probably has a proportionally similar core component and both Uranus and Neptune are mainly consisting of undifferentiated rock materials and ice.

--- Why the dichotomy? ---

- In the **Right Place** (distance from the Sun), at the **Right Time...**
  - our star output would have kept ice and vapour at distances somewhere between the orbits of Mars and Jupiter, allowing the outer planets to ‘collect’ more volatile materials
  - one million years following the proto-Sun formation, a phase of strong solar winds would have dispersed all the gases outwards, allowing the planetary giants to capture a large proportions of these.

The ‘NICE MODEL’



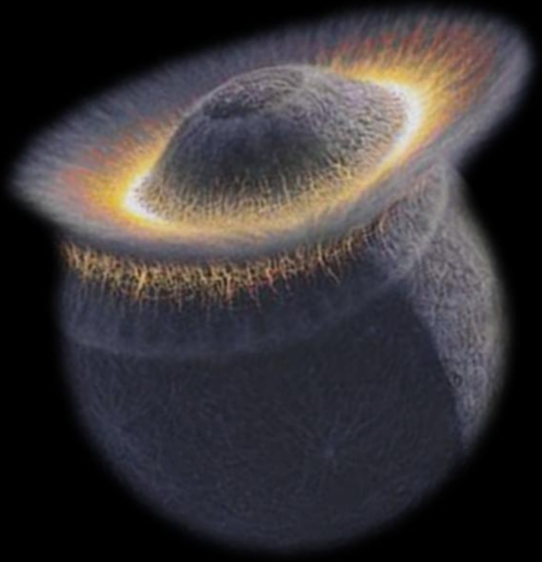
○ Jupiter
○ Saturn
○ Uranus
○ Neptune
○ Planetesimal disk

‘Planetary migration’ started around 880 Ma after the formation of the Solar System.

Jupiter and Saturn crossed their mutual 1:2 Mean Motion Resonance, destabilising the giant planets and the planetary disk.

GIANT IMPACTS

A major key player in planetary evolution



Mercury’s anomalous small silicate mantle

vaporised by a catastrophic collision?

All planetary equators are tilted away from their orbital planes at different angles.

Violent interplanetary encounters?

Inner planets could have had a substantial hydrogen/helium atmosphere, *before* the endosphere could develop.

Did giant impacts strip away these gaseous envelops?

The lunar giant-impact hypothesis where a Mars-like body smashed into a young Earth ejecting into space enough material to coalesce into a large orbiting body.

Do we owe terrestrial (complex) life to this hypothetical cataclysm?

The Making and Composition of the Earth

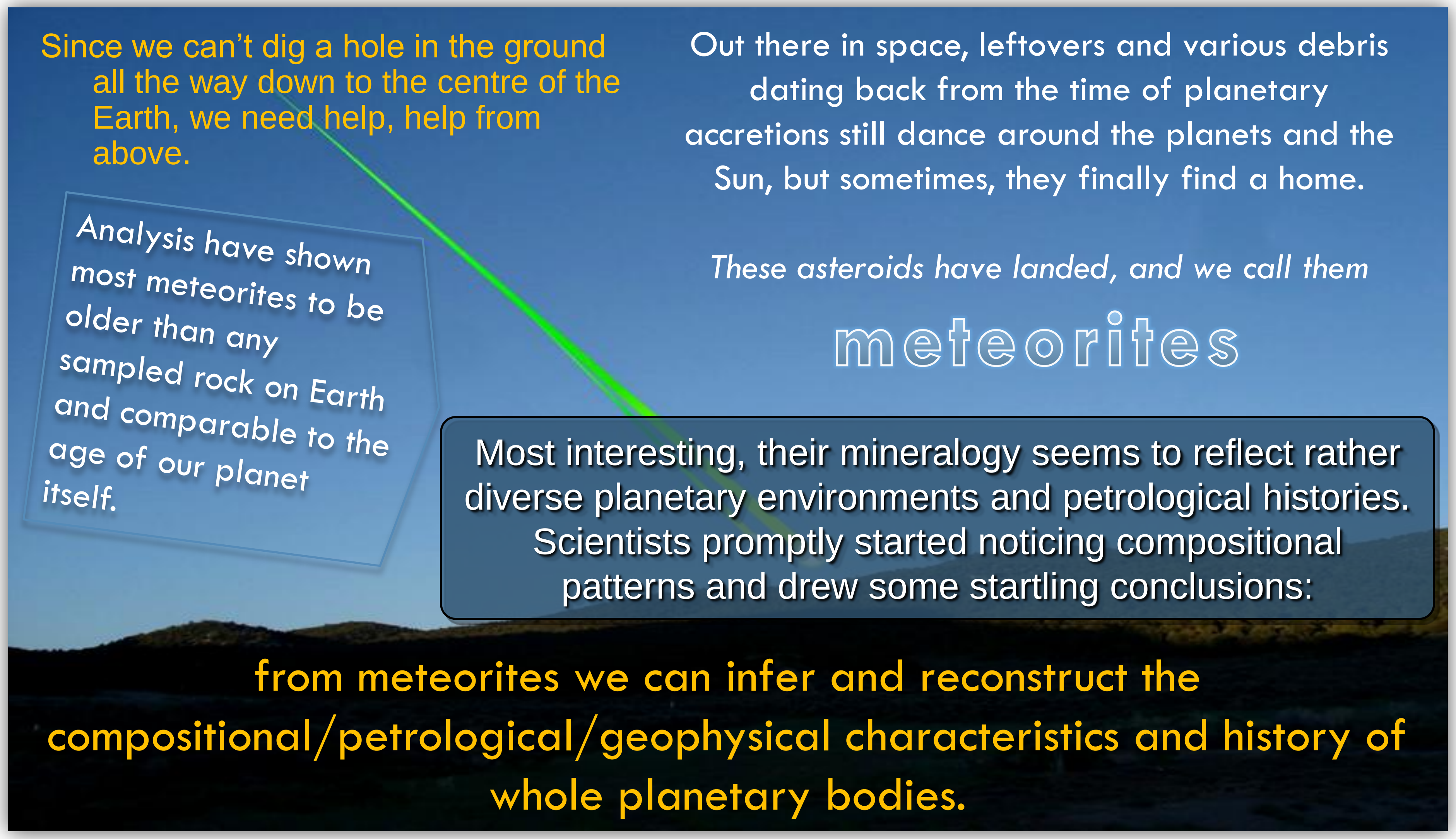
3.1 What is the Earth made of? Well....

- ☺ *We landed probes on Mercury, Venus, the Moon, Mars and asteroids, travelling thousands of kilometres into space. Various instruments are presently sampling surfaces and a wide range of physical planetary characteristics.*
- ☺ *Ordinary people nowadays can climb Mt. Everest, 9000 meters high.*
- ☺ *There are, at any one time, around 1000 active satellites orbiting the Earth.*
- ☹ How deep have we directly sampled the ground below our feet? 10 km. This is out of an average Earth's radius of 6360 km.

OUR QUEST TO FIND OUT WHAT 'BLEND' OF COSMIC MATERIALS ENDED UP MAKING UP OUR PLANETS IS GOING TO GET, WELL, A BIT COMPLICATED...

The Making and Composition of the Earth

3.2 What is the Earth made of?



Since we can't dig a hole in the ground all the way down to the centre of the Earth, we need help, help from above.

Analysis have shown most meteorites to be older than any sampled rock on Earth and comparable to the age of our planet itself.

Out there in space, leftovers and various debris dating back from the time of planetary accretions still dance around the planets and the Sun, but sometimes, they finally find a home.

These asteroids have landed, and we call them

meteorites

Most interesting, their mineralogy seems to reflect rather diverse planetary environments and petrological histories. Scientists promptly started noticing compositional patterns and drew some startling conclusions:

from meteorites we can infer and reconstruct the compositional/petrological/geophysical characteristics and history of whole planetary bodies.

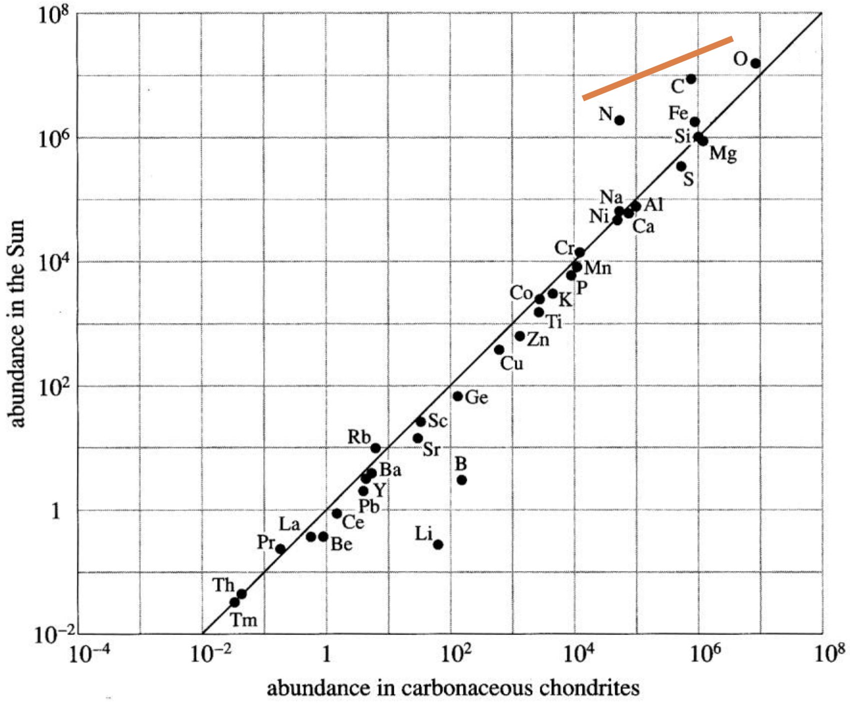
Meteorite types - a simplified classification

Meteorite Type	Overall Sample Representation (%)		Principal Sub-types	Description	Composition	Sub-groups	Composition	Representative of planets'
Stony	95	85	**Chondrites**	Contain small, once molten globules, or ***chondrules***, of silicate.	Fe-Mg silicates Grains of Fe-Ni alloy Troilite (FeS) – iron sulphide	**Ordinary Chondrites**	Most abundant and typical *Most depleted in volatiles – highest T of formation*	
						Enstatite Chondrites	High abundance of Enstatite ($MgSiO_3$) *Depleted in volatiles – high T of formation*	
						Carbonaceous Chondrites	Silicate mineral Abiogenic organic compounds *Least depleted in volatiles – low T of formation*	**Bulk composition**
		10	**Achondrites**	Lack chondrules Small fraction of Fe-Ni grains	Mainly Fe-Mg silicates			**Mantle**
Stony-Iron	1.5			Hybrids	~50:50 mixture of Fe-Ni alloys and silicate phases			**Mantle-Core boundary region**
Iron	3.5			>90% metallic Commonly found because they contrast with most terrestrial rocks.	Fe-Ni alloys (4-20% Ni) Some Troilite			**Core**

The Making and Composition of the Earth

3.4 Carbonaceous Chondrites?

Chemical analysis has shown that Carbonaceous Chondrites (CC) meteorites to be the closest in composition <u>to the Sun:</u>



A few exceptions to a 'perfect' match: *lithium* (Li) and *boron* (B) (for particular chemical reasons) and, significantly, *nitrogen* and *carbon*. The latter are *volatile* elements that were presumably been depleted either during formation or subsequently.

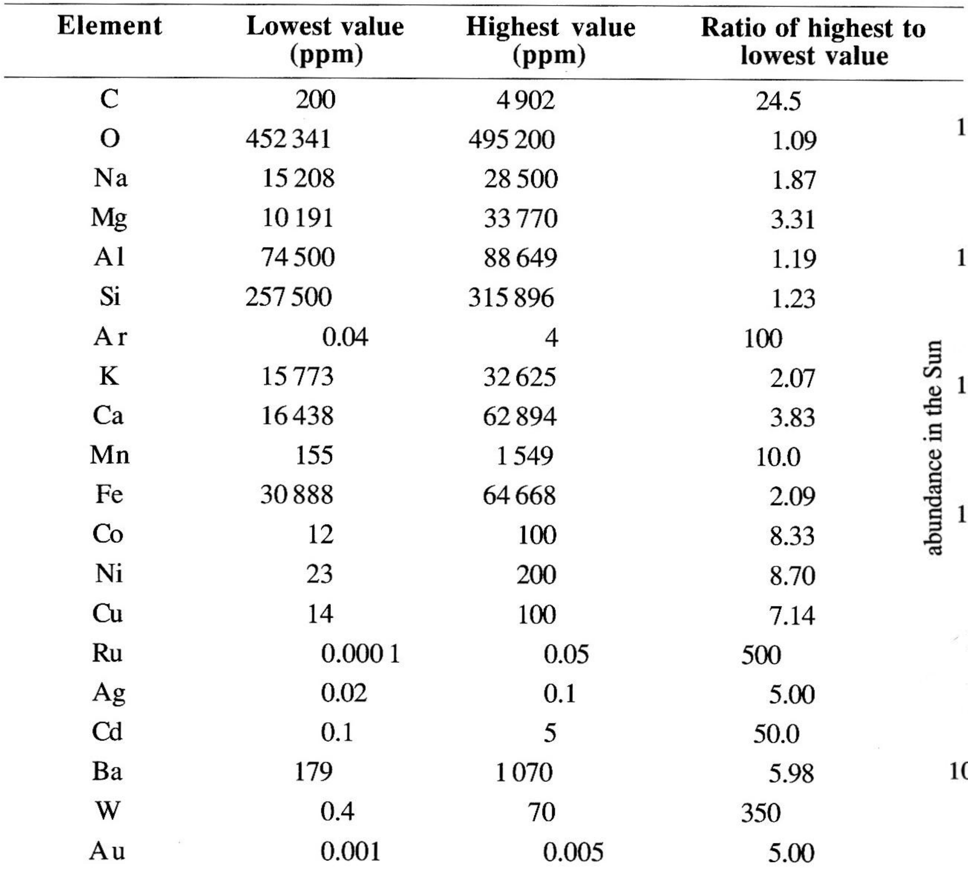
OK, the Sun and CC are comparable in composition. Could we use this relationship to estimate the overall element abundances in the Earth?

We can start from the planet's crust. We can sample it directly, we must have a good idea of what it is made of...

The Making and Composition of the Earth

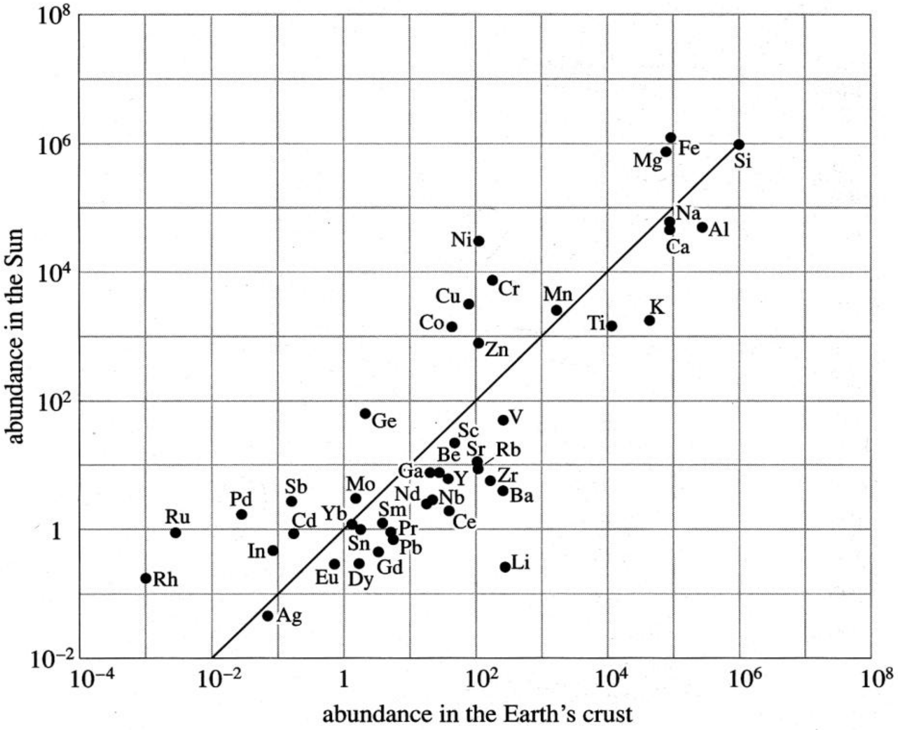
3.5 Are we on a chondritic Earth?

... but, we DON'T.
Have a look a the table below:



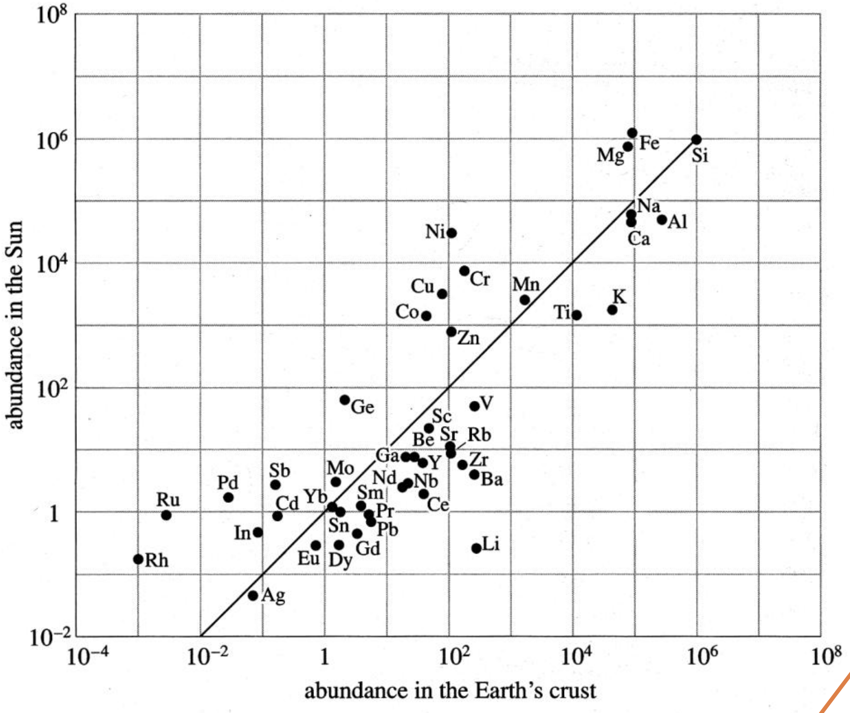
Element	Lowest value (ppm)	Highest value (ppm)	Ratio of highest to lowest value
C	200	4 902	24.5
O	452 341	495 200	1.09
Na	15 208	28 500	1.87
Mg	10 191	33 770	3.31
Al	74 500	88 649	1.19
Si	257 500	315 896	1.23
Ar	0.04	4	100
K	15 773	32 625	2.07
Ca	16 438	62 894	3.83
Mn	155	1 549	10.0
Fe	30 888	64 668	2.09
Co	12	100	8.33
Ni	23	200	8.70
Cu	14	100	7.14
Ru	0.000 1	0.05	500
Ag	0.02	0.1	5.00
Cd	0.1	5	50.0
Ba	179	1 070	5.98
W	0.4	70	350
Au	0.001	0.005	5.00

The 'consensus' relative abundances of the elements in the Earth's crust plotted against those in the Sun



The Making and Composition of the Earth

3.6 Is it a matter of compatibility?



The relative abundances of the elements in the Earth's crust plotted against those in the Sun

Back to the figure we saw earlier. Elements to the left of the line are depleted in the crust *relative* to the Sun/CC.
Why?

Each element naturally possess a degree of 'affinity' with certain other elements, they can enter a particular chemical combination, and in these instances, they are said to be 'compatible'.

THIS COULD EXPLAIN SOME OF THE 'SHORTAGES' OF ELEMENTS IN THE CRUST, IF WE SUPPOSE THAT THEY WERE SEGREGATED BY 'HEAVIER' ELEMENTS, WHICH, AT SOME POINT HAD SUNK TO THE DEPTHS OF THE EARTH…

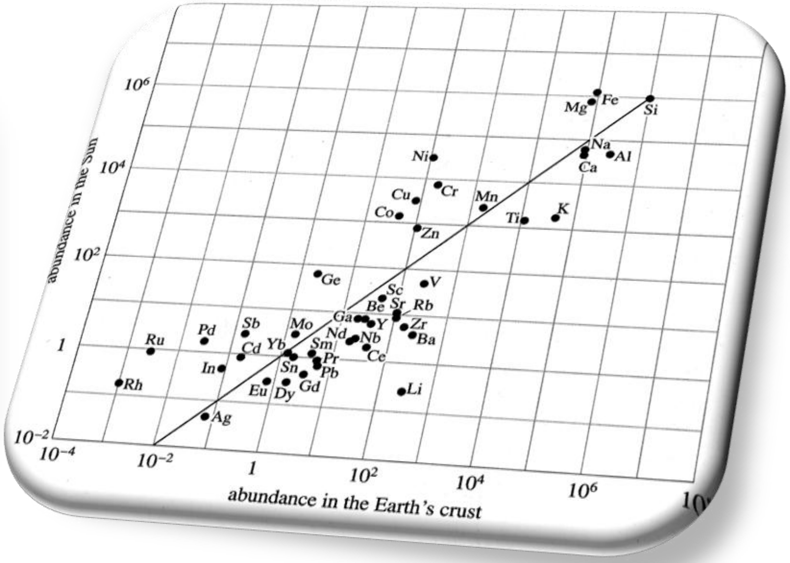
The Making and Composition of the Earth

3.7 Who likes whom then?

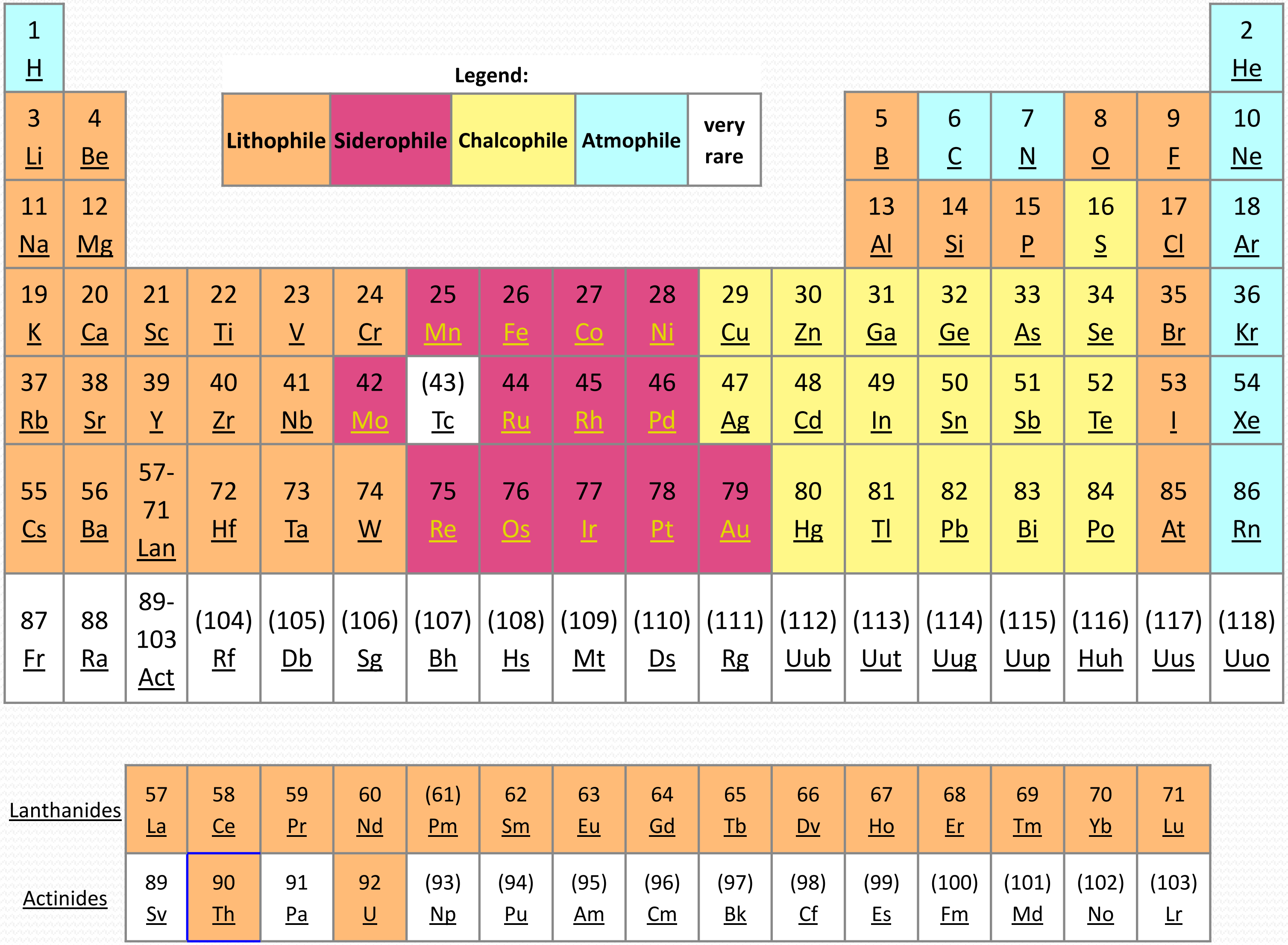
Lithophile elements:	preferentially enter into combination with oxygen and/or silicon (as silicates)
Chalcophile elements:	they have a preferential tendency to form sulphides, e.g. Zn, Pb, Cd, and Ag.
Siderophile elements:	they prefer to exist as metals and tend to be concentrated in the core, e.g. Ni, Pd, and Rh.

we previously noticed that elements on the *left* of the graph are estimated [in the crust] in smaller abundances than predicted by the CEM.

Clearly, all elements to the *right* are *enriched* in the crust relative to chondritic abundances



A table for... 92+



Legend:

Lithophile	Siderophile	Chalcophile	Atmophile	very rare

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	(43) Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 Lan	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Act	(104) Rf	(105) Db	(106) Sg	(107) Bh	(108) Hs	(109) Mt	(110) Ds	(111) Rg	(112) Uub	(113) Uut	(114) Uug	(115) Uup	(116) Huh	(117) Uus	(118) Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	(61) Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dv	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Sv	90 Th	91 Pa	92 U	(93) Np	(94) Pu	(95) Am	(96) Cm	(97) Bk	(98) Cf	(99) Es	(100) Fm	(101) Md	(102) No	(103) Lr

the Periodic Table subdivision in elemental affinities

Obviously, this can't be, and *it is not*, the whole story!

Iron, for instance, is basically *chalcophile*, but there is too little *sulphur* in the Earth to utilise all the Fe available.

Some is therefore *siderophile* (Fe in core) and some *lithophile* (in silicates in the crust and mantle).

The Making and Composition of the Earth

3.9 Let's assemble a planet...

Back to the first 100 Ma of the Solar system. We have now solid materials colliding and accreting (and disassembling too...) across the solar system. Let's briefly look into the accretion mechanisms.

There are two main schools of thought:

the **HETEROGENEOUS** model advocating the accretion of the Earth as a progressive process, i.e. differentiation into a crust, mantle, and core would have been concurrent with accretion.

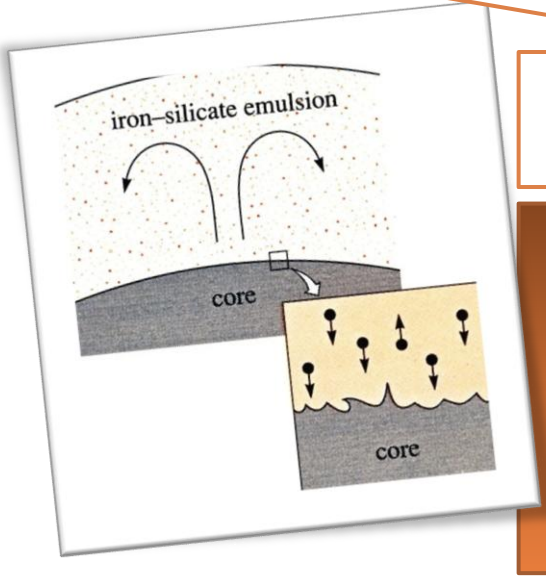
Many issues with this model: for instance, the first materials to condense would have been the refractory fractions, not Fe and Ni, so these fractions would have had to 'swap places' to end up where they are now...

The Making and Composition of the Earth

3.10 Let's assemble a planet…

the **HOMOGENEOUS** model assumes that the condensation phase occurred *before* planetary accretion began: the solar nebula would have been populated by discreet mineral fragments as condensation progressed. *Subsequently*, these particles would have coalesced into bodies containing the full complement of refractory and volatiles.

The implication is that the Earth would have been fully assembled in a chemically uniform globe. - *What mechanism(s) would have then led the planet to segregate its components?*



The necessary energy would have been available in the form of **HEAT**

The Earth would have comprised of an emulsion of liquid iron and liquid silicates. Iron would have accumulated into clouds of droplets, which gradually would have sunk towards the centre of the Earth.

Computing modelling shows this 'rainout' process to have been accomplished within a short geological time of a few thousand years.

The Composition of Earth's layers

As we were exploring the formation of the Earth and its composition, comparing it to that of meteorites and other evidential sources, we have assumed all along three layer subdivision of our planet, with a Crust, a Mantle, and a Core. We will be looking at evidence (seismic, gravitational, momentum etc.) for this structure further on. But for now, let's give a final look at compositional abundances of the bulk Earth.

We have to understand that until now we have been dealing with abundance estimates in terms of percentage share of atoms and *not* atomic masses:

for instance, on Earth the relative abundance of iron and silicon is 1.2 (1.2 Fe atoms for every Si atom). Because of their different atomic masses (55.85 and 28.09 respectively), the relative abundance of Fe compared to Si (as mass) is ~2.4, which means that

the total amount of iron on Earth 'weighs' more than 2.4 times that of silicon.

We have good estimates of the Earth's Mean Atomic Mass (MAM):

Bulk Earth	~ 27.0
Mantle	~ 22.4
Core	~ 47.0

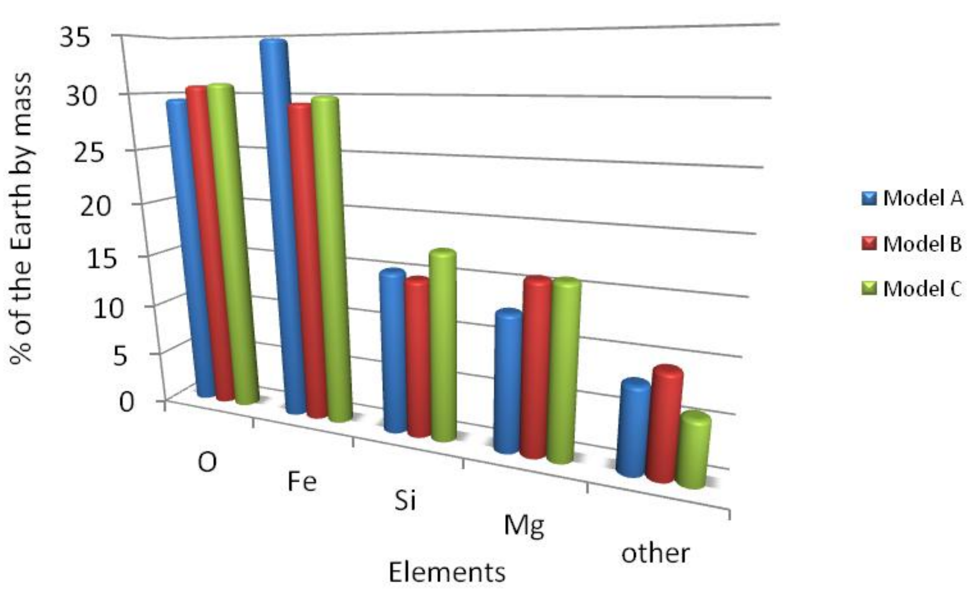
How do we know? There is a relationship between the seismic wave velocity in a material and its MAM. Instruments like those above have allowed us to build up experimental data bases to use in comparison with seismic data.

The Composition of Earth's layers

Now, all we need to do is to match these figures with materials from various meteorites, and compare their compositions: there we would have proof of CEM and its differentiation history.

Sadly, it is not so straightforward: for instance carbonaceous chondrites have MAM of 23.4-24.0 and iron meteorites of 55, hence, a nearly infinite number of mixing permutation would gives us the right 'numbers'. After much research and experimentation, estimates have 'settled' around the most plausible geochemical scenarios.

Here's a sample of three:


Three models of the bulk composition of the Earth

These figures were obtained by mixing possible meteorite compositions according to their presumed representation of origin (mantle, core) and the known volume ratios (mantle:core mass ratio of 8:17).

Despite their uncertainties in absolute values, all models predict that OVER 90% OF THE MASS OF THE PLANET IS REPRESENTED BY ONLY FOUR ELEMENTS: O, Fe, Si, and Mg!

The Composition of the Earth’s layers

4.3 THE CRUST – rocks (5–70 km)

Obtaining seismic/density readings of crustal rocks is a relatively straightforward process and masses of data can be sourced, for instance, from oil prospecting research.

But, as discussed earlier, extrapolating local and regional petrological records to build a three-dimensional compositional map of the whole Earth’s upper layer, *is a whole different story*!

Average densities of major crustal rocks

ROCK	AVERAGE DENSITY (kg m^{-3})
SEDIMENTARY	
alluvium	1980
sand	2000
clay	2210
sandstone	2350
shale	2400
limestone	2550
IGNEOUS	
rhyolite	2520
andesite	2610
granite	2640
diorite	2850
basalt	2990
gabbro	3030
peridotite	3150
METAMORPHIC	
quartzite	2600
schist	2640
granulite	2650
marble	2750
slate	2790
gneiss	2800

The Composition of the Earth's layers

4.4 THE CRUST – composition

Oxide/element	Estimate 1	Estimate 2
SiO_2	60.2	63.3
Al_2O_3	15.2	16.0
CaO	5.5	4.1
FeO	3.8	3.5
MgO	3.1	2.2
Na_2O	3.0	3.7
K_2O	2.9	2.9
Fe_2O_3	2.5	1.5
H_2O	1.4	0.9
TiO_2	0.7	0.6
Ba	*670*	*1150*
Sr	*340*	*350*
Th	*100*	*6*
Rb	*95*	*85*
Ni	*50*	*20*
U	*3*	*1.8*

Two examples of estimated chemical composition for the whole crust (note: the largest fractions are present as oxides, both in the crust and the mantle. Individual elements are ppm

The table shows that ¾ of the crustal composition is represented by silica and, in much smaller proportion, aluminium oxides.

if these figures were to translate into a rock of comparable composition, it would be represented by the rock ***granodiorite***, a course-grained igneous (plutonic) rock consisting mainly of the minerals quartz [SiO_2], plagioclase [$(Na,Ca)Al(Si,Al)Si_2O_8$], potassium feldspar [$KAl(Al,Si)_3O_8$], biotite, and hornblende.

Grain colours:

white: plagioclase
grey: quartz
pink: K-feldspar
dark: biotite and hornblende

The Composition of the Earth's layers

4.5 THE CRUST – composition

A 'granodioritic' composition is also consistent with upper-crust seismic velocities, but it certainly doesn't mean that all the rocks we walk on are of this composition! Far from it. **But** the bulk composition of the upper crust **is**, so most crustal rocks are either derived from, or related to, rocks of comparable composition to granodiorite.

Feldspar matrix, pyroxene crystals (small/dark), and garnet crystals (red)

Nevertheless, these are estimations for the upper crust of the Earth. The lower crust's seismic velocities are too fast to reflect rocks of granodioritic composition, even if adjusted for higher pressures. Instead, it is now thought that a metamorphic rock called ***granulite*** might be a better match. Granulite is a *metamorphosed basalt* consisting mainly of feldspars, pyroxene, and garnet.

Nevertheless, *xenoliths* (fragments of rocks not belonging to the magma source) suggest a much more complex mineralogy and care should be taken in generalising these compositional assumptions

The Composition of the Earth's layers

4.6 THE MANTLE – composition (35-670 km upper mantle; 670-2890 km lower mantle)

Surprisingly, we enjoy a better knowledge of the overall composition of the upper mantle than we do of the crust. This is because its composition is relatively simple, being dominated by just six oxides (>98% in fact), relatively uniform distribution, and with small spatial variations.

Clues to the composition of the upper mantle come from laboratory studies of high-pressure and temperature materials, seismic velocity/densities, geochemical models based on meteorite compositions, and direct sampling, mostly from xenoliths in *Kimberlite pipes* and *ophiolites*.

Ophiolites are exposed sections of the oceanic crust (thinner than the continental one) that has been uplifted and exposed, notably in places such as Cyprus and Oman.

Below the expected oceanic sediments, followed by distinct types of basalt layers, we find ***peridotite***, a type of rock mainly consisting of the mineral olivine [$(Mg,Fe)_2SiO_4$]

The Composition of the Earth’s layers

4.7 THE MANTLE – composition (35-670 km upper mantle; 670-2890 km lower mantle)

Seismic wave velocities in peridotite (8.1 km/s) also *match* those measured in the upper mantle. In particular, one type of peridotite (garnet peridotite) is thought to represent the bulk of the upper mantle. Based on this model, the *estimated oxide content of the upper mantle is:*

Oxide	**Mass** (%)
SiO_2	45.1
MgO	38.1
FeO	8.0
Al_2O_3	3.3
CaO	3.1
Na_2O	0.4

What happens in the ***lower mantle***? it is believed that the composition and chemistry stays similar to the peridotite model, but, due to increased pressures and temperatures, the minerals assume higher-pressure forms: both seismic data and laboratory experiments show that at depths of around 400 km, olivine transforms into ***spinel***, where the atoms are packed closer together, increasing the rocks’ density by around 10%.

Further down (~670 km), and at even higher pressures, spinel rearranges itself into **perovskite** (and residual MgO).

Therefore, most of the (whole) mantle (78%) comprises minerals with a perovskite structure

So you have it, **more than 90%** of the composition of the upper mantle can be accounted for by the system **SiO_2-MgO-FeO**

The Composition of the Earth’s layers

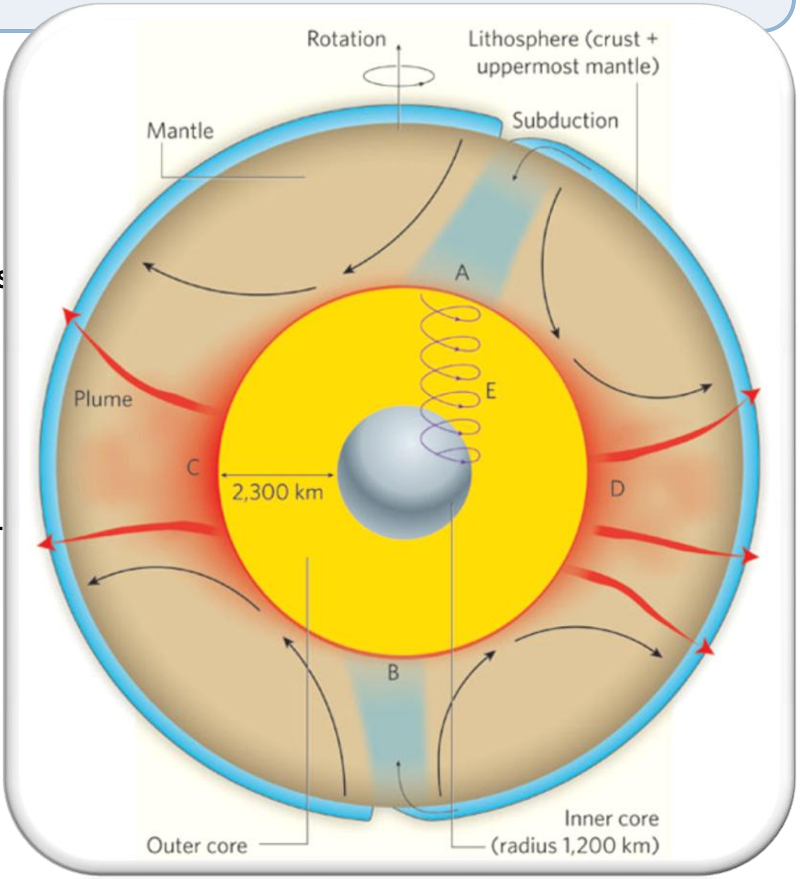
4.8 THE CORE – 2890-5150 km [liquid] outer core; 5150-6360 km [solid] inner core

The existence of a terrestrial metallic core was first suggested by R. D. Oldham in 1908 while analysing seismic data from large earthquakes. Lacking any type of direct evidence, how do we know it is not made of any other material?

1. *Assuming a* chondritic composition of the Earth, and distinct meteorites reflecting differentiated layers, then iron-meteorites would be representative of a planet’s denser layer. This is also suggested by the paucity of Fe in the models of mantle composition, chondritic meteorites and against known cosmic abundances.

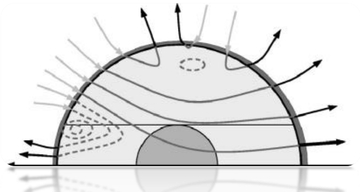
2. *Within a* planetary body, the most likely source of a powerful magnetic field is a dynamic metallic (highly conductive) layer. Iron is the strongest candidate due to it electromagnetic properties and high cosmic abundance.

3. *The only* other metals with similar densities and seismic velocities to iron are titanium (Ti), chromium (Cr), cobalt (Co), and nickel (Ni), none of which available in the necessary quantities within the solar nebula to form a sizable planetary core.



The Composition of the Earth's layers

4.9 The core – just Fe?



Nevertheless, as per the outer, liquid core, high-pressure and –temperature experiments show that a pure (molten) iron layer would display seismic velocities and densities somewhat higher than those deduced from refracted/reflected seismic waves generated by large earthquakes.

Calculations have shown that **iron must be present as an alloy containing 5-15% of a less-dense element.** These are the most likely candidates:

Oxygen → **The contact layer between the silicate lower mantle and the core is now believed to be an extremely turbulent and dynamic environment. It is highly likely that the Earth's core might derive oxygen from it in the quantities suggested by evidence (7-13% by mass).**

Sulphur → **all chondritic meteorites, irrespective of their state of oxidation, contain substantial amounts of sulphur in the form of sulphides (mainly FeS).**

Carbon → **the same arguments used to justify the presence of sulphur can be also applied to carbon, an element which readily alloys with iron.**

Hydrogen → **an iron-hydrogen compound 'iron hydride' (FeH) is stable at core pressures. Hydrogen being the main constituent of the solar nebula makes it a strong contender as the 'necessary' light element.**

Potassium → **this alkali metal is known to *be depleted* in the crust and upper mantle relative to chondritic abundances. It could have been 'captured' by sulphide as K_2S and taken along to the core with it. There is also the possibility that one of the isotopes of potassium (^{40}K) might be the heat source required for generation of the magnetic field (to initiate and sustain rotational convection in the outer core). *Nevertheless, the core's motion could simply be the consequence of the Earth's rotation, and/or latent heat generated by the solidification of the liquid outer core***

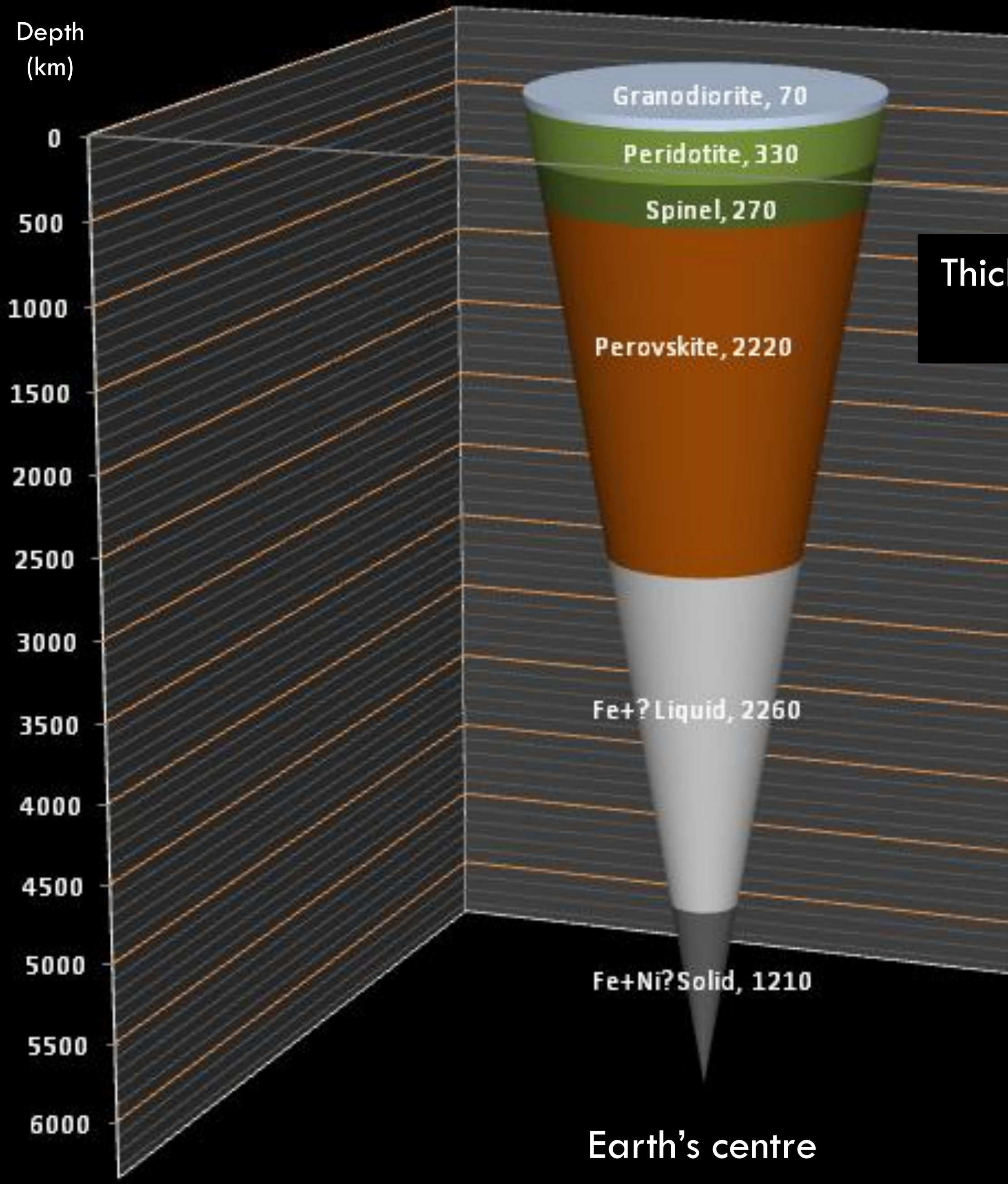
We have not discussed the **INNER CORE** at al until now, and the reason is… we know very little about it!

Papers have been advocating sometimes a denser, an equal, or less dense than iron core, with endless permutations of heavier or lighter elements and compounds.. as required by each model…:

MOSTLY FE WITH A NI PROPORTION OF AROUND 20% SEEMS THE MOST LIKELY SCENARIO.

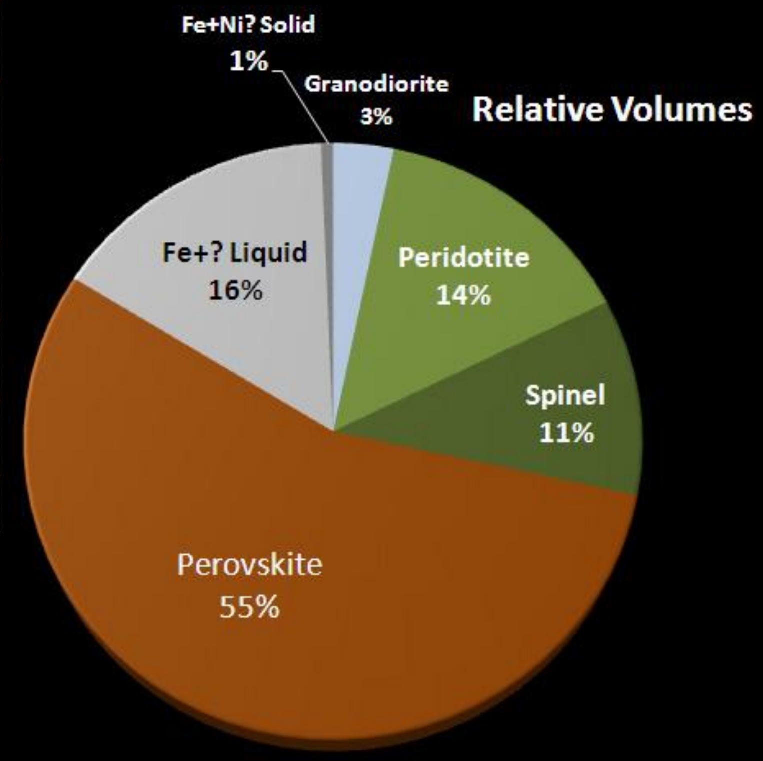
SO FAR.

The Composition of the Earth's layers



Thickness of compositional layers (in km)

Earth's centre



Conclusions and Reflections

The aim of chapter 1 was to offer a highly condensed overview on the current state of knowledge on the composition of the bulk Earth: how and where the fundamental elements were produced and how, and in what proportions, they ultimately ended up as this rocky planet we all call home (*how 'American'*...).

The chondritic model has turn out to fit our compositional models and evidence rather well. If we ignore in our calculations the Earth's crust (<3% the mass of the planet) and its complex geo-petrological make up and evolution, and we simplify our core model as being entirely composed of iron , but not including Fe in our calculations, we end up with...

...a comparison between garnet peridotite and the average carbonaceous chondrite.

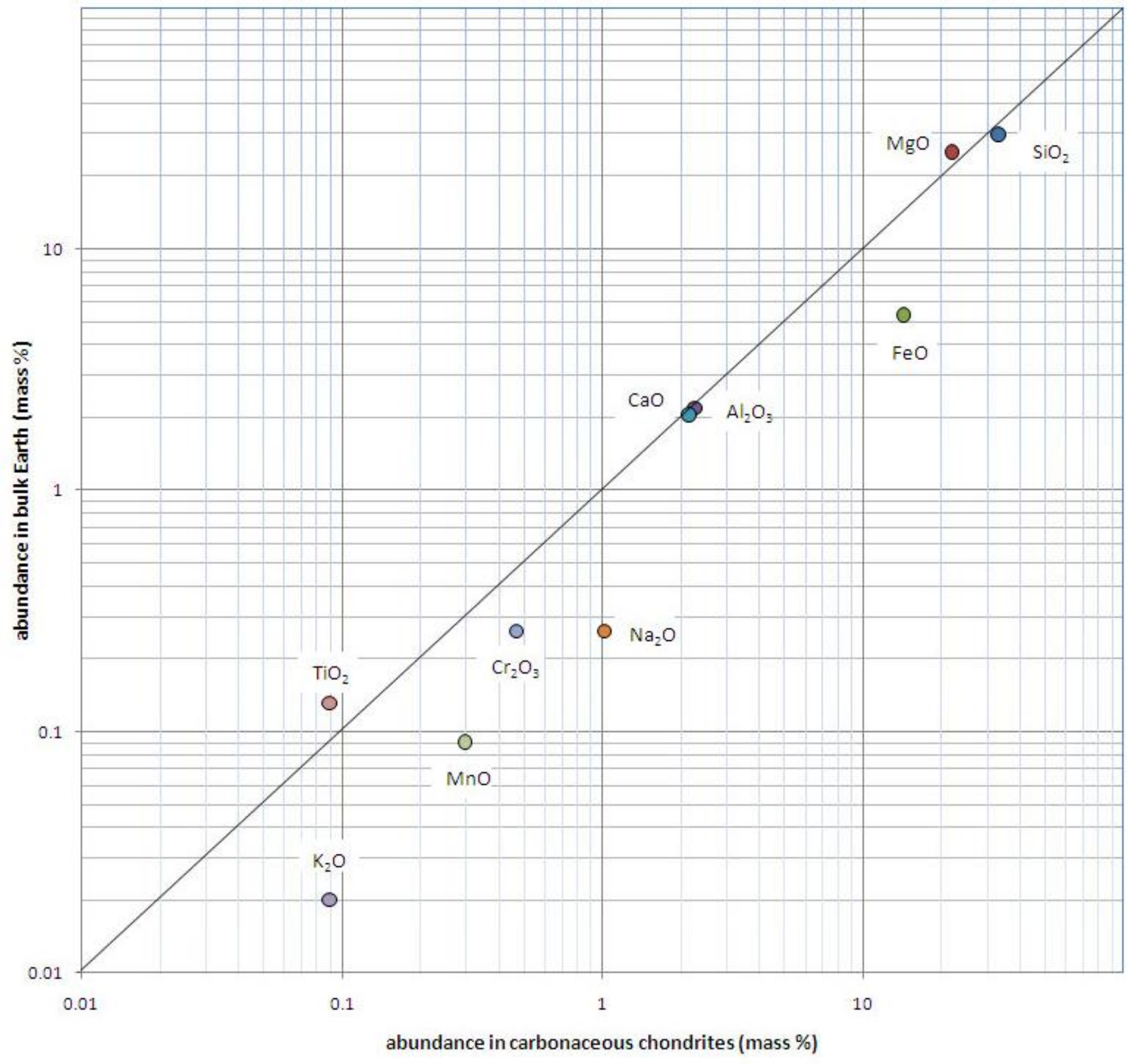
But they don't match! There are large mineralogical differences, **but we have not taken into account the Earth's core yet...**

Compound *(mostly oxides)*	**Garnet Peridotite** (mass%)	**Carbonaceous Chondrite** (mass%)
SiO_2	**45.10**	**33.25**
MgO	**38.10**	**22.04**
FeO	**8.00**	**14.39**
Al_2O_3	**3.30**	**2.27**
CaO	**3.10**	**2.16**
Na_2O	**0.40**	**1.02**
Cr_2O_3	**0.40**	**0.47**
TiO_2	**0.20**	**0.09**
MnO	**0.14**	**0.30**
K_2O	**0.03**	**0.09**
FeS	**-**	**23.20**

Let's readdress this by converting mantle abundances to bulk-Earth and plot the results...

Conclusions and Reflections

4.12 FINDING THE PLOT…



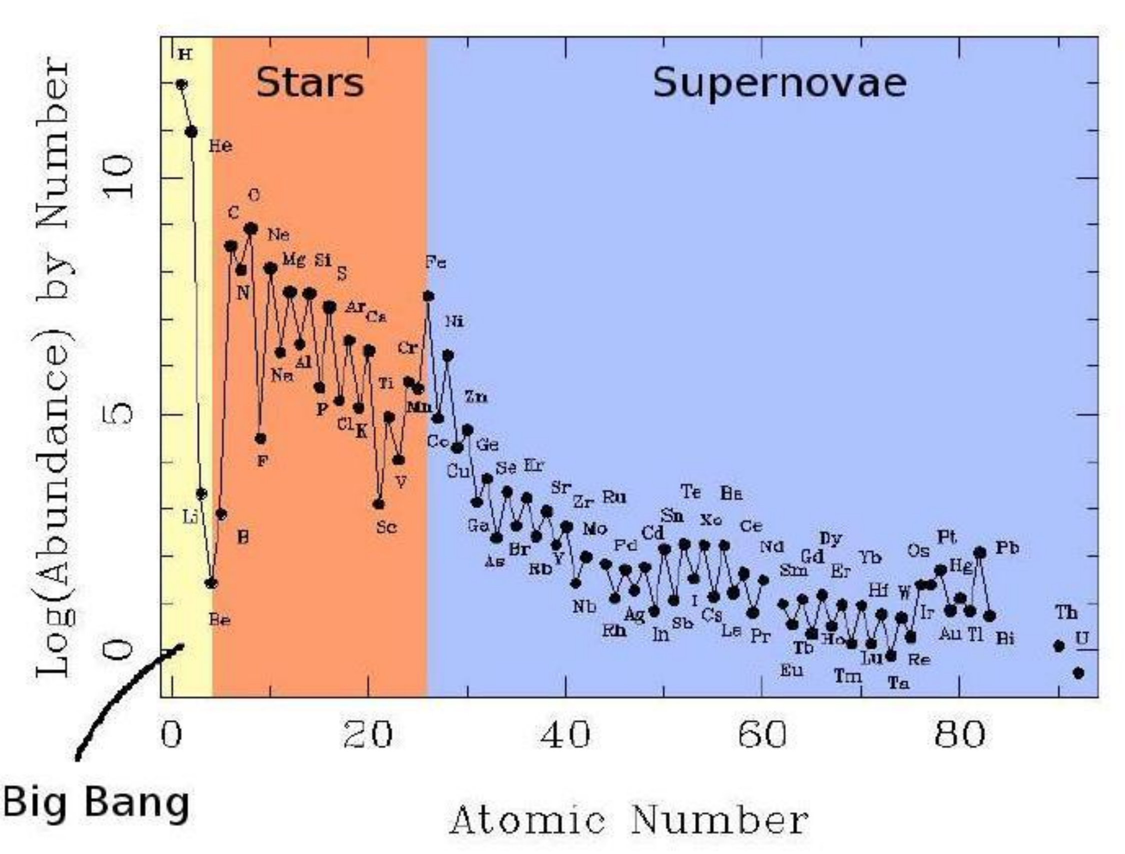
Compound *(mostly oxides)*	**Garnet peridotite** (mass%)	**Carbonaceous Chondrite** (mass%)	**Adjusted bulk-Earth composition** (mass%)
SiO_2	45.1	**33.25**	**29.80**
MgO	38.1	**22.04**	**25.10**
FeO	8.00	**14.39**	**5.30**
Al_2O_3	3.30	**2.27**	**2.18**
CaO	3.10	**2.16**	**2.05**
Na_2O	0.40	**1.02**	**0.26**
Cr_2O_3	0.40	**0.47**	**0.26**
TiO_2	0.20	**0.09**	**0.13**
MnO	0.14	**0.30**	**0.09**
K_2O	0.03	**0.09**	**0.02**

What does the graph tell us? The Si, Mg, Al, and Ca oxides are *present* in the bulk Earth in *chondritic*, or near chondritic proportions. And let's not forget that these four oxides are representative of more than *95% of the Earth's mass…*

Conclusions and Reflections

4.13 END, FINALLY…

So, we have established the bulk composition of the Earth, hence what kind of ‘stuff’ most of its inorganic materials are made of and where they came from.



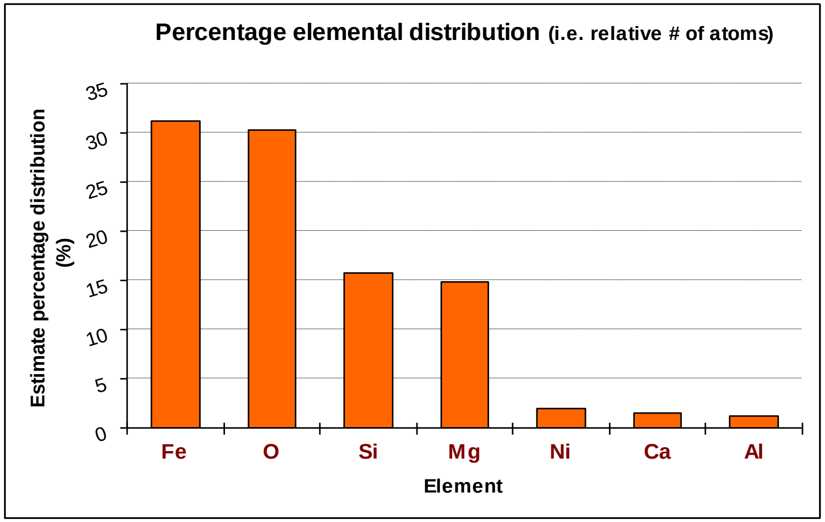
This relationship works the other way round too, namely that now we *may assume* that the composition of the other planets and solar system’s rocky objects, as far as refractory elements and their solid bodies are concerned at least, should all *share similar mineralogical abundances*.

To conclude this journey, much research has gone into establishing a compositional pattern also for minor elements, such as uranium, gold, fluorite, sodium, etc. Without going into much detail, there is strong evidence that the abundance of elements that accreted to form the Earth was strongly influenced by their volatility and that, generally, the more volatile an element (e.g. Bi, Pb, Cd, Se and S), the less likely it is to be found in the Earth at chondritic proportions.

Percentage distribution of major elements

5.1 Bulk Earth compositional estimates - Oxides

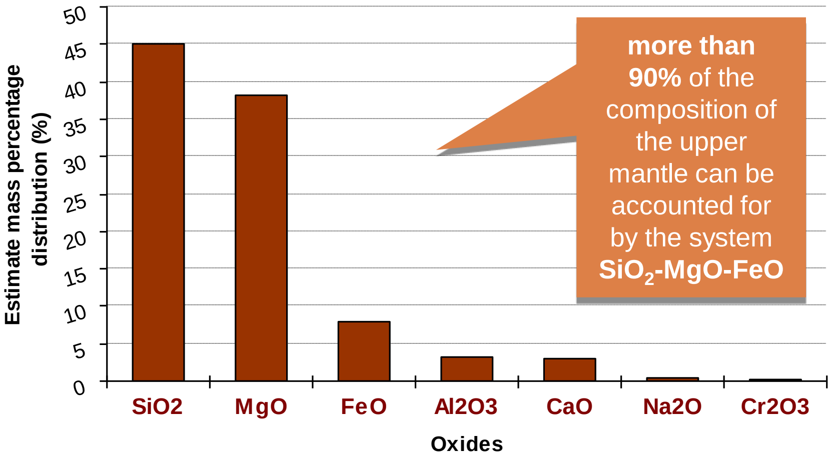
The first chart shows our *estimated* percentage
distribution of major elements in our planet


Percentage elemental distribution (i.e. relative # of atoms)

Obviously, when dealing with real-world compositions, we need to take into account the chemical relationships between elements, and in particular oxygen and cations (metals): the **oxides.**

Oxide	**Mass** (%)
SiO_2	45.1
MgO	38.1
FeO	8.0
Al_2O_3	3.3
CaO	3.1
Na_2O	0.4

Percentage oxides mass distribution



more than 90% of the composition of the upper mantle can be accounted for by the system **SiO_2-MgO-FeO**

Indeed, we can state that most elements in the mantle-crust layers are no longer in their native state: they are oxidised.

An oxidised planet

A few *facts* about OXYGEN…:

- Definition: “*highly reactive non metallic period 2 element*”
- O is the third most abundant element in the universe, after H and He.
- At standard temperature and pressure two atoms of the element bind to form dioxygen, a colourless, odourless, tasteless diatomic gas with the formula O_2

A few *interesting facts* about OXYGEN…:

- 94%, yes 94% of the Earth’s crust volume is represented by oxygen! (~63% by atomic % or ~47% of its mass).
- Together with silicon (Si), they make up ~75% of the crust’s mass.
- Oxygen is the second most reactive element (second only to fluorine) due to its ‘*small size*’ and high *electronegativity*. It has two unpaired electrons on the outermost layer, also making it paramagnetic (it needs two extra e^- to complete its 2p layer).
- Most elements will react (“burn”) with oxygen at appropriate temperature and pressure conditions (*including* gold: Au_2O_3).

Silicon is so abundant in the universe (eighth elements) because it represents a step stone product of fundamental thermonuclear fusion reactions in stars with mass bigger than eight times our own Sun:

${}_{8}\mathrm{O} + {}_{8}\mathrm{O} \rightarrow {}_{14}\mathbf{Si} + {}_{2}\mathrm{He}$ oxygen burning process

${}_{12}\mathrm{Mg} + {}_{2}\mathrm{He} \rightarrow {}_{14}\mathbf{Si}$ pure α process

A pure-Si mirror appears rather dark and opaque in visible, but ‘shiny’ and faithful in the infrared (it is totally transparent in these wavelengths).

It belongs to a family of elements (together with other 6 members) called metalloids, which include Germanium and Arsenic. Their properties are intermediate between all other 86 metal and non-metal elements.

Silicon hardly ever occurs as a pure element in nature, because it promptly reacts with environmental oxygen.

PURE SILICON IS USED TO PRODUCE ULTRA-PURE SILICON WAFERS USED IN THE SEMICONDUCTOR INDUSTRY, IN ELECTRONICS AND IN PHOTOVOLTAIC APPLICATIONS

Outer electron configuration: 3p – 2, hence it needs 4 electrons to fill layer (it has four bonding electrons), similarly to Carbon.

Silicon donates its 4 outer layer e^- to Oxygen, thus forming a very stable compound: SiO_2.

A given rock can be classified and described in several ways, relating to: composition, aspect, origin, evolution, chemistry, fractionation, etc.

To give an example: a common mid-ocean ridge **BASALT** (73% of all annual extrusive output) can be described as:

a silica-saturated extrusive (volcanic) igneous ROCK,
a melanocratic olivine-tholeiitic MORB:

Elements distribution

Element	%
O	45
Si	23
Al	8
Fe	8
Ca	7
Mg	4
Na	2
Ti	1
K	1

✓

Bulk chemistry

Oxide	%
SiO_2	49
Al_2O_3	13
CaO	11
MgO	10
FeO	10
Na_2O	2
TiO_2	2
Fe_2O_3	1
K_2O	0.5

✓

Modal (observed) **- CIPW Norm** (idealised) **- mineral abundance**

Idealised composition	Composition (formula)	Mineral (Phase - Component)	MODAL	Family	Wt %
$CaO.Al_2O_3.6SiO_2$	$CaAl_2(SiO_4)_2$	Anorthite (An)	P	Tecto- **silicates** “alumino-” *Plagioclase feldspar*	**25**
$CaO.(Mg,Fe)O.2SiO_2$	$Ca(Mg,Fe)(SiO_3)_2$	Diopside (Di)	M	Ino- **silicates** ‘ferromagnesian-’ Clino*pyroxene* (cpx)	**23**
$Na_2O.Al_2O_3.6SiO_2$	$NaAlSi_3O_8$	Albite (Ab)	A	Tecto- **silicates** “alumino-” *Plagioclase feldspar*	**18**
$(Mg,Fe)O.SiO_2$	$(Mg,Fe)SiO_3$	Hypersthene (Hy)	M	Ino- **silicates** ‘ferromagnesian-’ Ortho*pyroxene* (opx)	**15**
$2(Mg,Fe)O.SiO_2$	$(Mg,Fe)_2SiO_4$	Olivine (Ol)	M	Neso-**silicates** ‘ferromagnesian-’	**9**
$FeO.TiO_2$	$FeTiO_3$	Ilmenite (Il)	M	***Iron-titanium Oxides***	**4**
$K_2O.Al_2O_3.6SiO_2$	$KAlSi_3O_8$	Orthoclase (Or)	A	Tecto- **silicates** “alumino-” *Alkali feldspar*	**3**
$FeO.Fe_2O_3$	Fe_3O_4	Magnetite (Mt)	M	***Iron-titanium Oxides***	**2**

MEASUREMENT OF BULK COMPOSITION

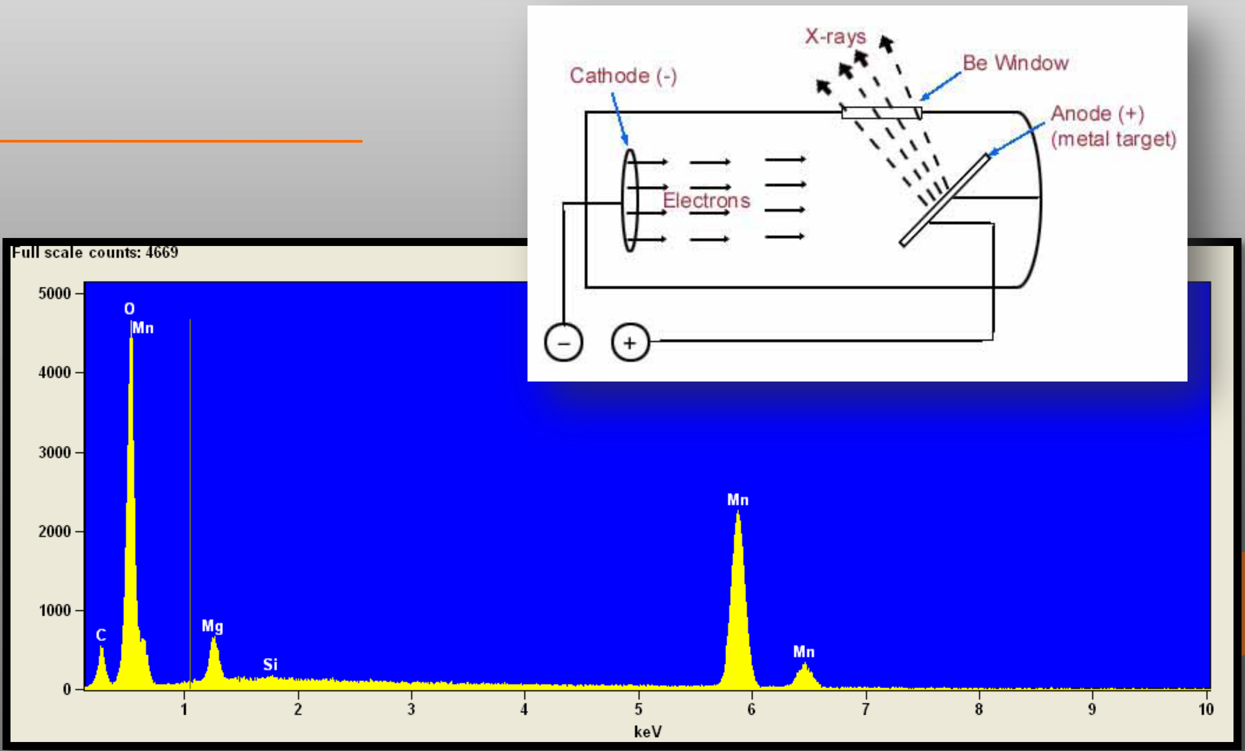
- Point counting of thin sections: modal abundance

Most common analysis until 60's:

- Wet chemistry: dissolve rock in acids
- Precipitate oxides of each cation and weigh material

Nowadays several sophisticated methods of analysis are employed, mostly based on X-ray spectrometry

(e.g. X-Ray Fluorescence, XRF)



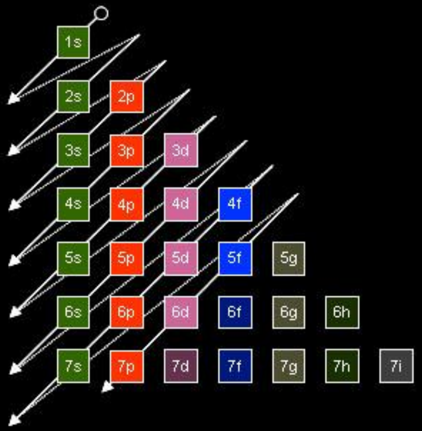
ELECTRONIC CONFIGURATION OF THE ELEMENTS

(n)		K (1)	L (2)		M (3)			N (4)				O (5)				P (6)				Q (7)		CATIONS	ANIONS
1. Period		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p		
1	H	1																					H^-
2	He	2																					
2. Period		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p		
3	Li	2	1																			Li^+	
4	Be	2	2																			Be^{2+}	
5	B	2	2	1																		B^{3+}	
6	C	2	2	2																		Ca^{4+}	
7	N	2	2	3																			N_3^-; N^{3-}
8	O	2	2	4																			O^{2-}; O_2^{2-}
9	F	2	2	5																			F^-
10	Ne	2	2	6																			
3. Period		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p		
11	Na	2	2	6	1																	Na^+	
12	Mg	2	2	6	2																	Mg^{2+}	
13	Al	2	2	6	2	1																Al^{3+}	
14	Si	2	2	6	2	2																Si^{4+}	
15	P	2	2	6	2	3																	P^{3-}
16	S	2	2	6	2	4																	S^{2-}
17	Cl	2	2	6	2	5																	Cl^-
18	Ar	2	2	6	2	6																	
4. Period		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p		
19	K	2	2	6	2	6		1														K^+	
20	Ca	2	2	6	2	6		2														Ca^{2+}	
21	Sc	2	2	6	2	6	1	2														Sc^{3+}	
22	Ti	2	2	6	2	6	2	2														$Ti^{3+;\ 4+}$	
23	V	2	2	6	2	6	3	2														$V^{2+;\ 3+;\ 4+}$	
24	Cr	2	2	6	2	6	5	1														$Cr^{2+;\ 3+;\ 4+}$	
25	Mn	2	2	6	2	6	5	2														$Mn^{2+;\ 3+;\ 4+;\ 7+}$	
26	Fe	2	2	6	2	6	6	2														$Fe^{2+;\ 3+}$	
27	Co	2	2	6	2	6	7	2														$Co^{2+;\ 3+}$	
28	Ni	2	2	6	2	6	8	2														$Ni^{2+;\ 3+}$	
29	Cu	2	2	6	2	6	10	1														$Cu^{+;\ 2+;\ 3+}$	
30	Zn	2	2	6	2	6	10	2														Zn^{2+}	

ORBITALS DESCRIBED BY FOUR QUANTUM NUMBERS:

- Principal (n) - ‘shells’ 1 (L), 2 (M) etc.
- Azimuthal (l) – ‘subshells’ s, p, d, etc.
- Magnetic (m_l) – orientation in space x, y, z.
- Spin (m_r) – Exclusion principle (Pauli), +1/2, -1/2

example : C → $1s^2$ $2s^2$ $2p_x^1$ $2p_y^1$ ($2p_z^0$)



CATIONS valences:
Fe^{2+} Ferrous = Iron(II)
Fe^{3+} Ferric = Iron(III)
lower v.: ‘-ous’, high ‘-ic

(simple) ANIONS:
“**-ide**”, i.e. Ox-ide, Chlor-ide etc.

Legend for element groups:

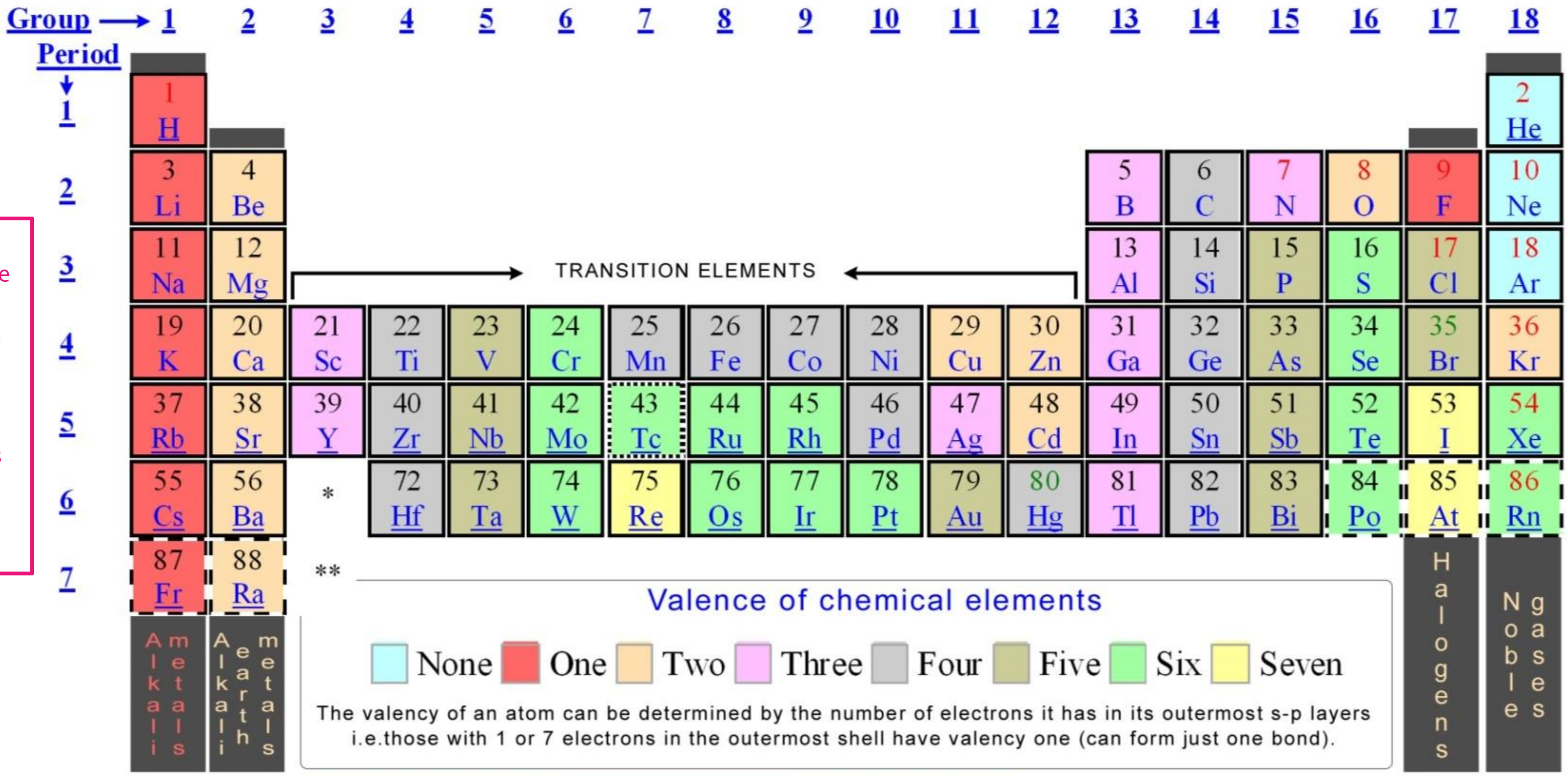
- Alkali (metals)
- Noble (Gas)
- Alkali (Earth metals)
- Halogens
- Transition (elements)

Valence bond theory of the chemical bond

Determined by quantum mechanical behaviour of electrons – orbital hybridisation

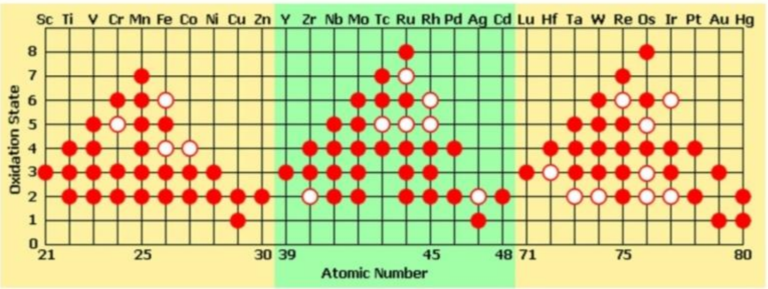
- Only considers the outermost s and p valency electrons .
- Favourable low-energy state: either **full or empty *octet*** (as in noble gases).
- Non-noble gases will tend to completely fill or empty their outermost octet of electrons by: **losing and/or gaining e⁻ (ionic bonds), or sharing** them (**covalent bonds**).

When bonds are formed, energy is released and the system becomes more stable.



The valency of an atom can be determined by the number of electrons it has in its outermost s-p layers i.e.those with 1 or 7 electrons in the outermost shell have valency one (can form just one bond).

Electropositive
1 electron
outermost (s) layer.
They can 'lose' it and
become positive
charged cations
i.e. K^+



Electronegativity
(from most –ve to
most +ve:
F>O>Cl>N>S>C>
H>P>Fe>
Mg>Ca>Na>K>Fr)

Electronegative
5 electrons
outermost (p) layer.
They can gain one and
become negative
charge ions
i.e. Cl^-

Metal + **nonMetal** = **IONIC BOND** (typical of elements with very different electronegativity). Example: $\mathbf{Cl^-}$ + Na^+ → NaCl (sodium chloride, salt, halite, etc.)
Metal + **Metal** = similar to covalent bonds BUT all the valency atoms are shared between all atoms.
nonMetal + **nonMetal** = **COVALENT BOND**. 'Perfect' bonds relate only to same-element bonds, e.g. Cl_2. All the others have slightly ionic character (polarity) and these bonds are said to be polar covalent. Example: **P** + 3**Cl** → $\mathbf{PCl_3}$

Consequence of polarity is the concept of *oxidation* number (state). For instance H in water is slightly positive (valence 1), so the ion equivalent is H^+, while oxygen is slightly negative (valence 2), so O^{2-}.

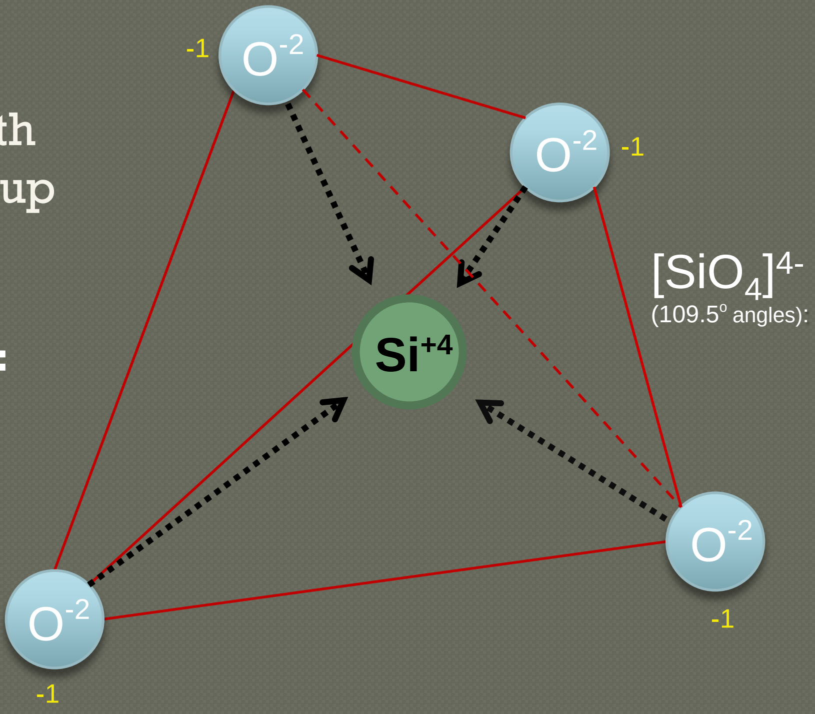
We have seen how two oxygen and a silicon atoms combine to form SiO_2 (silicon dioxide or silica), an extremely stable (and hardwearing) compound very familiar to us, as quartz (most sands), glass, etc.

But silicon and oxygen can also bond and form the most fundamental and ubiquitous building component of most rocks both on Earth and other planets: the ***silicate oxyanion*** $[SiO_4]^{4-}$ **tetrahedron:**

In this arrangement, each oxygen is left with a net charge of -1, resulting in the SiO_4^{4-} group that can be bonded to other cations.

It is this tetrahedron that forms the basis of:

SILICATE MINERALS



In silicate minerals, the system of classification commonly used by mineralogists hinges upon how many oxygens in each tetrahedron are shared with other similar tetrahedral.

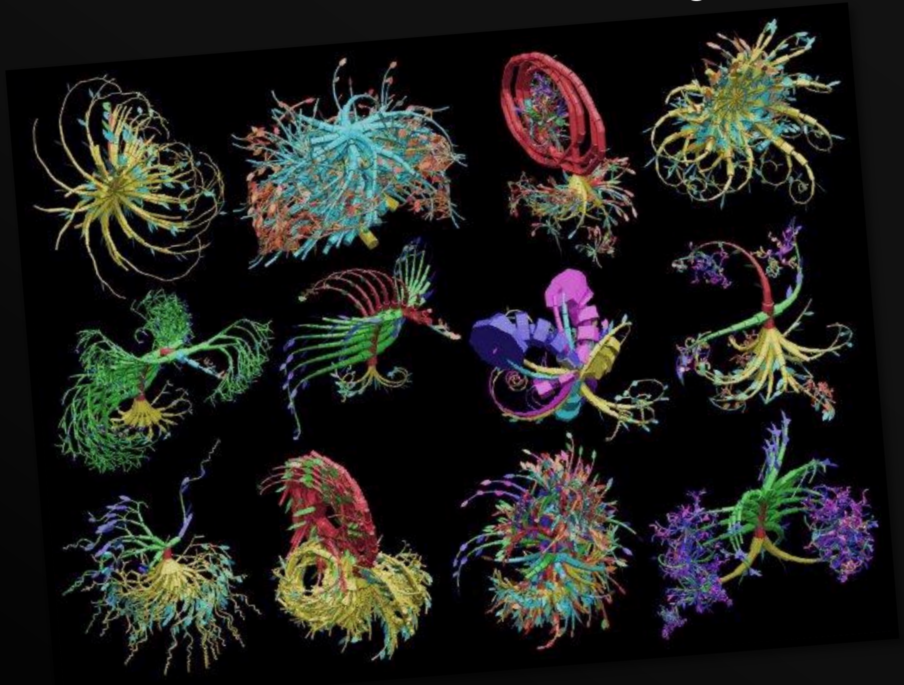
THE CRYSTALLINE STATE – PRINCIPLES OF CRYSTAL STRUCTURE

There are three states of matter ('+plasma'):
gaseous, liquid, and solid,
from complete atomic disorder to complete order (in crystals).

Nevertheless, apart from perfect crystals at 0 K, the Kinetic Energy of the atoms causes them to vibrate about their mean position in the crystal lattice and, if the KE is large enough, the crystal loses its rigidity: **it melts or decomposes**.

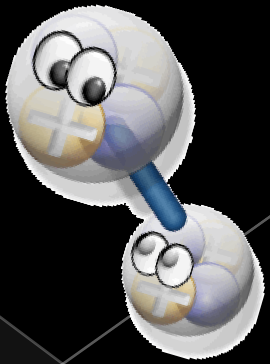
The structure of ionic compounds is determined primarily by the demands of geometrical and electrical stability, where the most stable structure will be that for which the potential energy of the ions is lowest

The chemical and physical properties of crystals depend almost entirely on the forces that bind atoms together in a crystal structure, collectively known as:



CHEMICAL BONDS

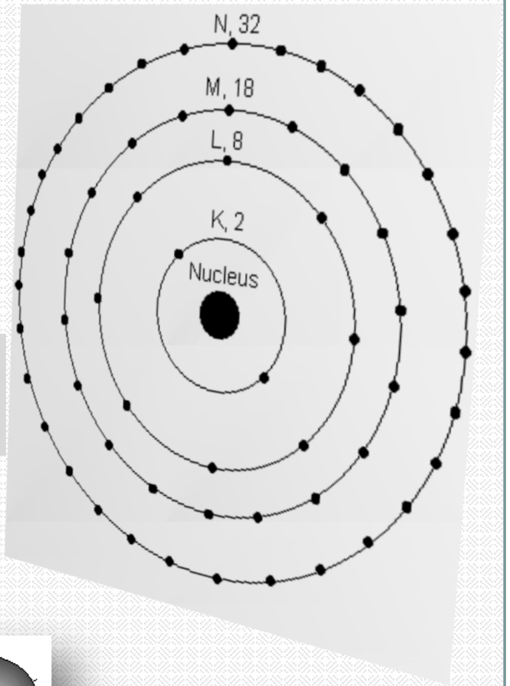
Chemical bonding
depends on the electronic
structure of the atoms
involved, in particular:
the ***valence***
electrons in the
outermost shells, and on
the **size**
of the ion or atom



Bohr atom:

Electrons orbit a nucleus at quantised energy levels **K, L, M, N**, etc. each with associated a progressive ***Principle*** *quantum number n* (as n_K=1, n_L=2, etc.).

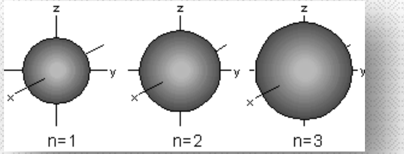
The maximum number of e^- in each shell is '# electrons = $2n^2$' so: K=2, L=8, M=18, etc.



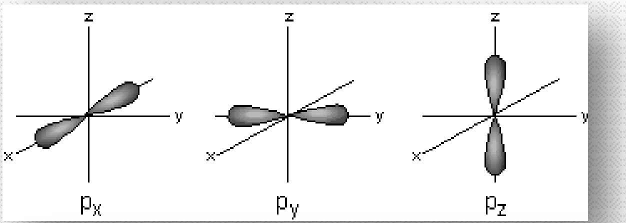
The quantum mechanical view of the atom suggests that the electrons are located within specific regions of probability.

A maximum of 2 electrons can be found in each probability region, each with a spin quantum number with a value of either +½ or -½ (Pauli Exclusion Principle)

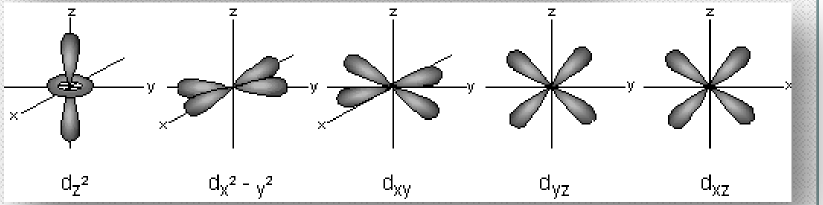
These probability regions are described by the ***Azimuthal*** *quantum number 'l'*, sub-shells *[s, p, d, f]:*



s - orbitals - are spherical shaped probability regions. The radius of these spherical regions increases with increasing principal quantum number, n. Again, each of these orbitals can contain a maximum of **2** electrons.



p - orbitals - these can only be present if the principal quantum number is 2 or greater. There are 3 different types of p orbitals, designated p_x, p_y, and p_z. These are approximately peanut shaped orbitals, with the axis oriented vertically (p_z) and horizontally (p_x & p_y).
Since 2 electrons can occur in each of the different p orbitals, a maximum of **6** electrons are associated with p-orbitals in each principal shell.



d - orbitals - there are 5 different probability regions of d orbitals and are designated d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{yz}, and d_{xz}.
Since 2 electrons can occur in each of the different d orbitals, a maximum of **10** electrons can occur in d-orbitals for each principal shell.

f – orbitals - very difficult to represent graphically, with 7 possible orbits (**14** max. electrons)

IONs

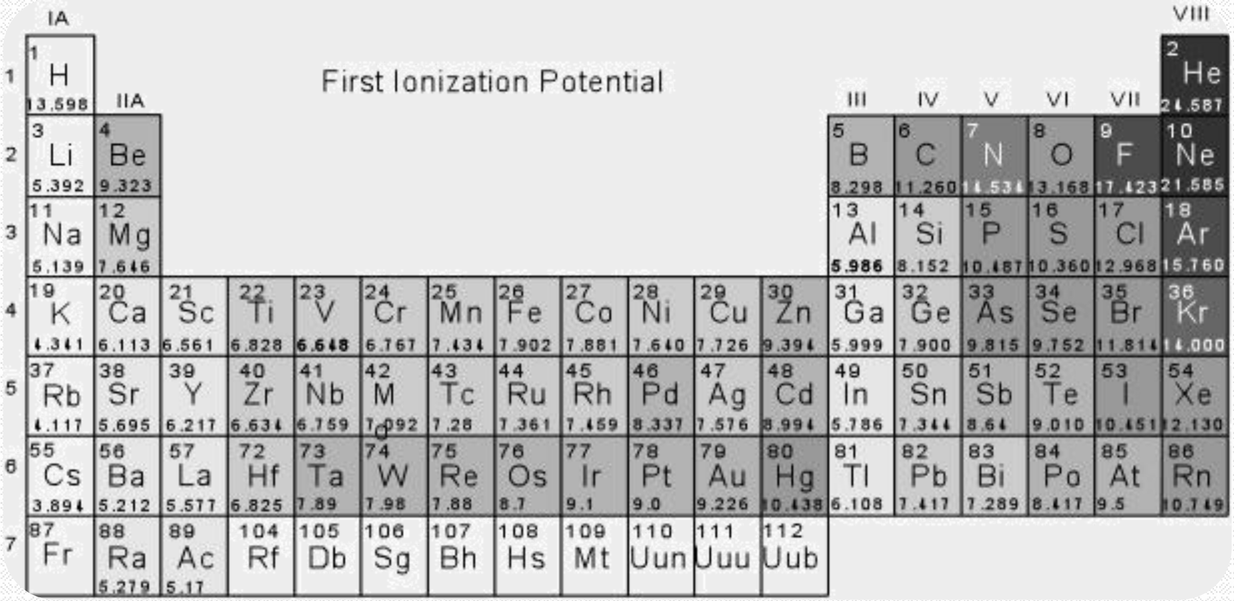
when an element gains electron(s) to become negatively charged (non-metals or **Anions**) or loses electron(s) and become positively charged (metals or **Cations**).

When electrons are either *removed* or *gained* by an atom there is a transfer of energy

---

Ionisation Potential (IP)

The amount of energy required to <u>remove</u> an electron

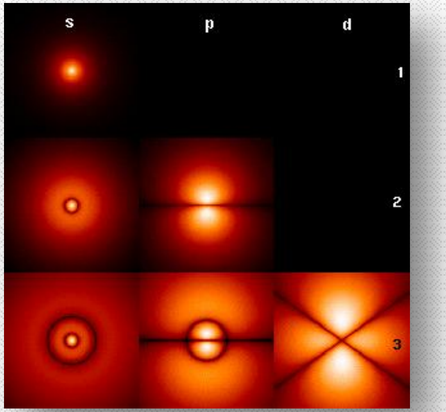


First Ionization Potential

	IA	IIA											III	IV	V	VI	VII	VIII
1	1 H 13.598																	2 He 24.587
2	3 Li 5.392	4 Be 9.323											5 B 8.298	6 C 11.260	7 N 14.534	8 O 13.168	9 F 17.423	10 Ne 21.585
3	11 Na 5.139	12 Mg 7.646											13 Al 5.986	14 Si 8.152	15 P 10.487	16 S 10.360	17 Cl 12.968	18 Ar 15.760
4	19 K 4.341	20 Ca 6.113	21 Sc 6.561	22 Ti 6.828	23 V 6.648	24 Cr 6.767	25 Mn 7.434	26 Fe 7.902	27 Co 7.881	28 Ni 7.640	29 Cu 7.726	30 Zn 9.394	31 Ga 5.999	32 Ge 7.900	33 As 9.815	34 Se 9.752	35 Br 11.814	36 Kr 14.000
5	37 Rb 4.117	38 Sr 5.695	39 Y 6.217	40 Zr 6.634	41 Nb 6.759	42 M 7.092	43 Tc 7.28	44 Ru 7.361	45 Rh 7.459	46 Pd 8.337	47 Ag 7.576	48 Cd 8.994	49 In 5.786	50 Sn 7.344	51 Sb 8.64	52 Te 9.010	53 I 10.451	54 Xe 12.130
6	55 Cs 3.894	56 Ba 5.212	57 La 5.577	72 Hf 6.825	73 Ta 7.89	74 W 7.98	75 Re 7.88	76 Os 8.7	77 Ir 9.1	78 Pt 9.0	79 Au 9.226	80 Hg 10.438	81 Tl 6.108	82 Pb 7.417	83 Bi 7.289	84 Po 8.417	85 At 9.5	86 Rn 10.749
7	87 Fr	88 Ra 5.279	89 Ac 5.17	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub						

TRANSITION ELEMENTS

all have d-orbital electrons in their outermost shells, and because they have low to high IP their behaviour is somewhat variable. Columns 3 to 5 tend to become +3 to +5 ions, but 5 to 11 is more variable.



Group **I** – Alkalis → v.low IP
they have in common an outermost shell containing 1 electron in the s – orbital; they tend to become +1 ions

Group **II** – Alkaline earths → low IP
lose 2 electrons, thus +2 ions.

Group **III** → low IP
lose 3 electrons, thus +3 ions.

Group **IV** → Mid IP
lose 4 electrons, thus +4 ions (apart from Pb, only loses 2, i.e. +2)

Group **V** → Mid-high IP
lose 5 electrons, thus +5 ions

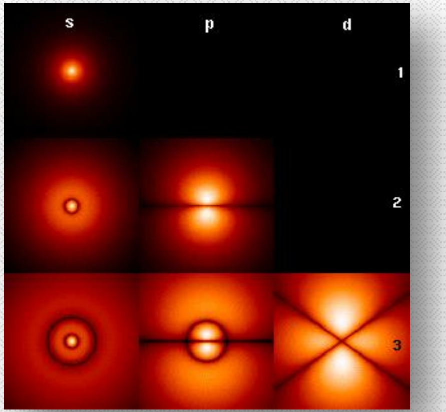
Group **VI** → Mid-high IP
gain 2 electrons, thus -2 ions (apart from S, which sometimes loses 6 e to become S^{+6}.

Group **VII** – Halogens → v. high IP
gain 1 electron, thus -1.

Group **VIII** – Noble gases → v. high IP

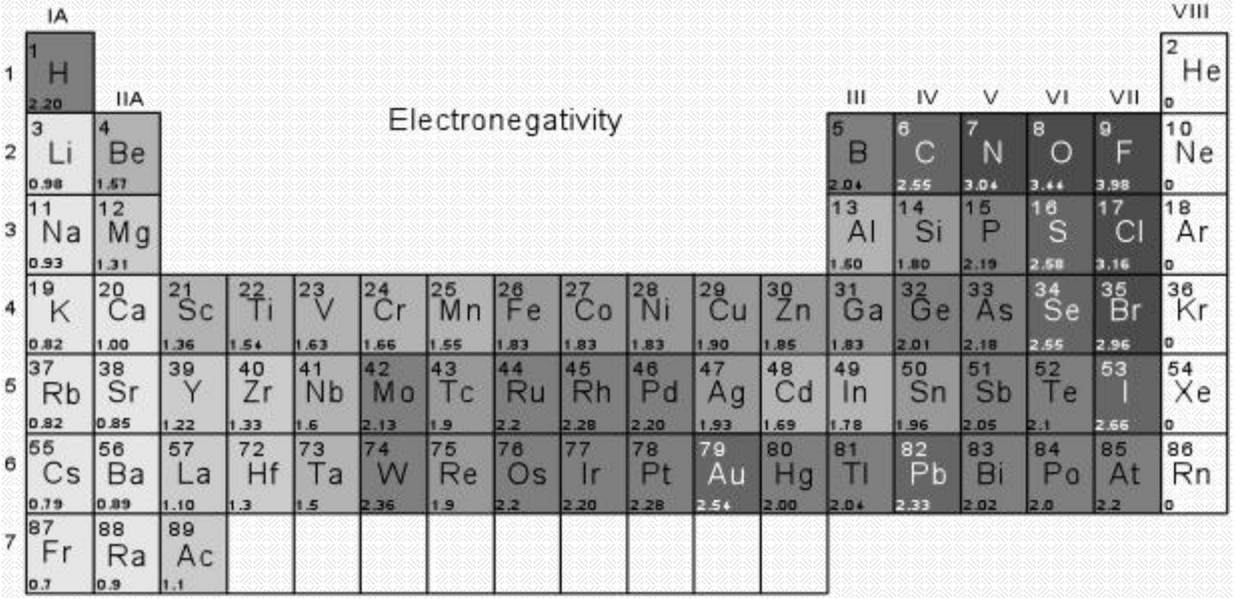
Electronegativity

The ability of an atom in a crystal structure or molecule to ***attract*** *electrons into its outer layer*



Elements with low values of electronegativity are electron donors, and those with high values are electron acceptors.

Electronegativity difference between atoms plays an important role in determining the type of chemical bond that forms between elements.



Electronegativity

	IA	IIA											III	IV	V	VI	VII	VIII
1	1 H 2.20																	2 He 0
2	3 Li 0.98	4 Be 1.57											5 B 2.04	6 C 2.55	7 N 3.04	8 O 3.44	9 F 3.98	10 Ne 0
3	11 Na 0.93	12 Mg 1.31											13 Al 1.60	14 Si 1.80	15 P 2.19	16 S 2.58	17 Cl 3.16	18 Ar 0
4	19 K 0.82	20 Ca 1.00	21 Sc 1.36	22 Ti 1.54	23 V 1.63	24 Cr 1.66	25 Mn 1.55	26 Fe 1.83	27 Co 1.83	28 Ni 1.83	29 Cu 1.90	30 Zn 1.85	31 Ga 1.83	32 Ge 2.01	33 As 2.18	34 Se 2.55	35 Br 2.96	36 Kr 0
5	37 Rb 0.82	38 Sr 0.85	39 Y 1.22	40 Zr 1.33	41 Nb 1.6	42 Mo 2.13	43 Tc 1.9	44 Ru 2.2	45 Rh 2.28	46 Pd 2.20	47 Ag 1.93	48 Cd 1.69	49 In 1.78	50 Sn 1.96	51 Sb 2.05	52 Te 2.1	53 I 2.66	54 Xe 0
6	55 Cs 0.79	56 Ba 0.89	57 La 1.10	72 Hf 1.3	73 Ta 1.5	74 W 2.36	75 Re 1.9	76 Os 2.2	77 Ir 2.20	78 Pt 2.28	79 Au 2.54	80 Hg 2.00	81 Tl 2.04	82 Pb 2.33	83 Bi 2.02	84 Po 2.0	85 At 2.2	86 Rn 0
7	87 Fr 0.7	88 Ra 0.9	89 Ac 1.1															

Group **I** → 0.7 – 1.0

Group **II** → 0.9 – 1.6

Group **III** → 1.6 – 2.0.

Group **IV** → 2.0 – 2.6

Group **V** → 2.0 – 3.0

Group **VI** → 2.0 – 3.4

Group **VII** → 2.2 – 4.0

Electronegativity
(from most –ve to most +ve):

F>O>Cl>N>S>C>
H>P>Fe>
Mg>Ca>Na>K>Fr

(n)		K (1)	L (2)		M (3)			N (4)				CATIONS	ANIONS
1. Period		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f		
1	H	1										H^-	
2	He	2											
2. Period		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f		
3	Li	2	1									Li^+	
4	Be	2	2									Be^{+2}	
5	B	2	2	1								B^{+3}	
6	C	2	2	2								Ca^{+4}	
7	N	2	2	3								N^{+5}	
8	O	2	2	4									O^{-2}; O_2^{-2}
9	F	2	2	5									F^-
10	Ne	2	2	6									
3. Period		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f		
11	Na	2	2	6	1							Na^+	
12	Mg	2	2	6	2							Mg^{+2}	
13	Al	2	2	6	2	1						Al^{+3}	
14	Si	2	2	6	2	2						Si^{+4}	
15	P	2	2	6	2	3						P^{+5}	
16	S	2	2	6	2	4						S^{+6}	S^{-2}
17	Cl	2	2	6	2	5							Cl^-
18	Ar	2	2	6	2	6							
4. Period		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f		
19	K	2	2	6	2	6		1				K^+	
20	Ca	2	2	6	2	6		2				Ca^{+2}	
21	Sc	2	2	6	2	6	1	2				Sc^{+3}	
22	Ti	2	2	6	2	6	2	2				$Ti^{+3; +4}$	
23	V	2	2	6	2	6	3	2				$V^{+2; +3; +4; +5}$	
24	Cr	2	2	6	2	6	5	1				$Cr^{+2; +3; +4}$	
25	Mn	2	2	6	2	6	5	2				$Mn^{+2; +3; +4; +7}$	
26	Fe	2	2	6	2	6	6	2				$Fe^{+2; +3}$	
27	Co	2	2	6	2	6	7	2				$Co^{+2; +3}$	
28	Ni	2	2	6	2	6	8	2				$Ni^{+2; +3}$	
29	Cu	2	2	6	2	6	10	1				$Cu^{+; +2; +3}$	
30	Zn	2	2	6	2	6	10	2				Zn^{+2}	

- Alkali (metals)
- Alkali (Earth metals)
- Noble (Gas)
- Halogens
- Transition

Valence States

The cohesive forces between atoms are determined by the distribution of the outer, or valency (s and p) electrons.

When atoms participate in bonding these outer electrons interact in ways which determine the symmetry of the atomic structure.

SIZE...

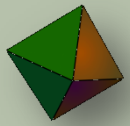
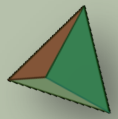
We may consider atoms as being made up of electric charges distributed through a small sphere that has an effective radius of the order of 1 Å (0.1 nm)

Its size depends not only on the nature of the element but also its ***state of ionisation*** and the manner in which it is linked to adjacent atoms.

i.e. Na in *metallic* sodium is 1.86 Å
but in *sodium* salts is 1.02 Å

SIZE

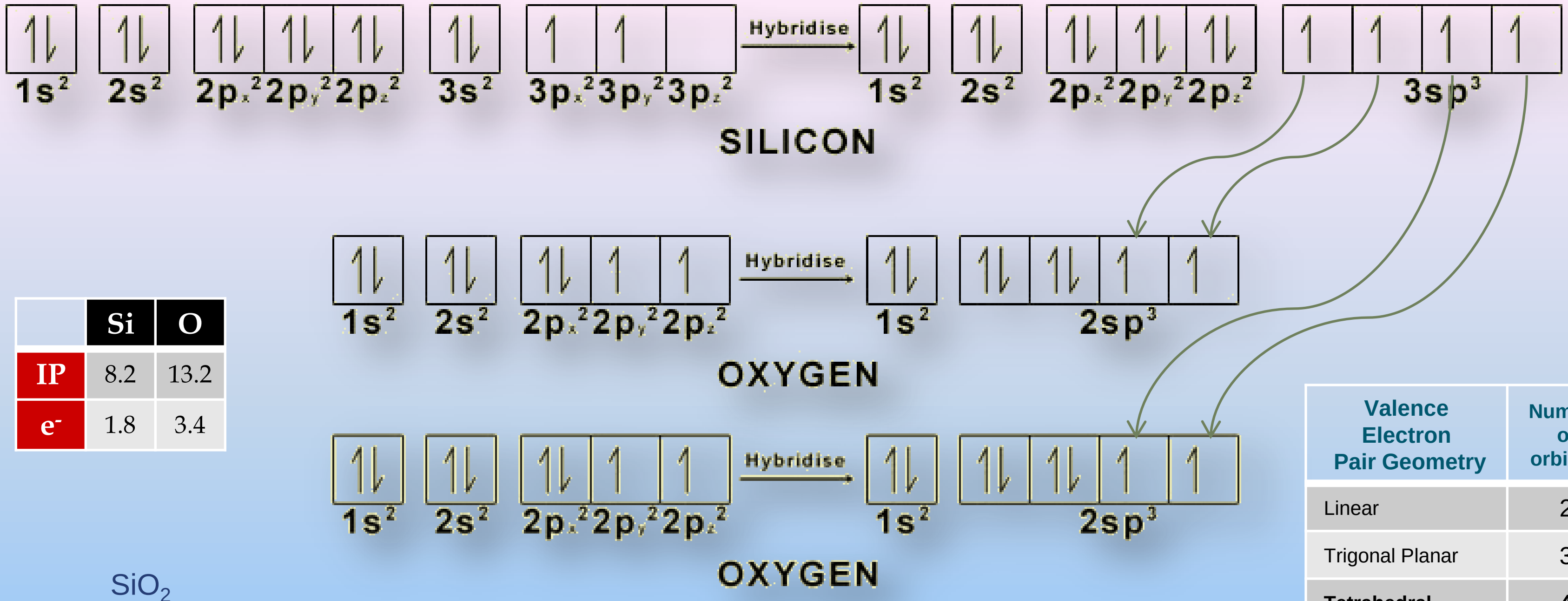
Radii in
a crystal
lattice

Element ion	Ionic radius (in crystal lattice) R (Å)	Radius of element/oxygen R/R_O	Coordination Number (C.N.) (with oxygen)	Coordination Polyhedron Geometrical arrangement of ions
S^{2-}	1.84			
Cl^{-}	1.81			
O^{2-}	**1.40**			
K^{+}	1.51 (8) – 1.64 (12)	1.0+	8 - 12	cubic to closest - Hexagon (eightfold)
Na^{+}	1.18 (8) - 1.02 (6)	0.84 - 0.73	8 - 6	cubic to octahedral 
Ca^{2+}	1.12 (8) – 1.00 (6)	0.80 - 0.71	8 - 6	
Mn^{2+}	0.83	0.59	6	Octahedral (sixfold) 
Fe^{2+}	0.78	0.56	6	
Mg^{2+}	0.72	0.51	6	
Fe^{3+}	0.65	0.46	6	
Ti^{4+}	0.61	0.44	6	
Al^{3+}	0.54	0.39	6	
Al^{3+}	0.39	0.28	4	Tetrahedral (fourfold) 
Si^{4+}	0.26	0.19	4	
P^{5+}	0.17	0.12	4	
S^{6+}	0.12	0.09	4	
C^{4+}	0.08	0.06	3	Triangular

When the radius lies near the theoretical boundary between two types of coordination, both may occur. → In this case the coordination is mainly controlled by the temperature and pressure at which crystallisation took place.

High Temperatures and Low Pressure favour Low(er) coordination

1. All matter strives to reach equilibrium with its environment, i.e. atoms try to arrange themselves in such a way that the free energy of the system is a minimum (ordered crystal structures = minimum potential energy.
2. Each ion surrounds itself with as many ions of the other species as is geometrically possible: the principle of close-packing of essentially spherical atom applies.



$1s^2$ $2s^2$ $2p_x^2 2p_y^2 2p_z^2$ $3s^2$ $3p_x^2 3p_y^2 3p_z^2$ Hybridise $1s^2$ $2s^2$ $2p_x^2 2p_y^2 2p_z^2$ $3sp^3$

SILICON

$1s^2$ $2s^2$ $2p_x^2 2p_y^2 2p_z^2$ Hybridise $1s^2$ $2sp^3$

OXYGEN

$1s^2$ $2s^2$ $2p_x^2 2p_y^2 2p_z^2$ Hybridise $1s^2$ $2sp^3$

OXYGEN

	Si	O
IP	8.2	13.2
e^-	1.8	3.4

Valence Electron Pair Geometry	Number of orbitals	Hybrid orbitals
Linear	2	*sp*
Trigonal Planar	3	*sp*^{2}
Tetrahedral	**4**	***sp*^{3}**
Trigonal Bipyramidal	5	*sp*^{3}*d*
Octahedral	6	*sp*^{3}*d*^{2}

SiO_2

Quartz

Please do not confuse electronic structure/geometry with higher-order crystal systems!
SiO_2 valence electron pair geometry is Tetrahedral in space, but as Quartz, it belongs to the Trigonal Crystal System

In synthesis:

Pauling's Rules:

1. *"around every cations, a coordination **polyhedron** of anions forms, in which the cation-anion distance is determined by the radius sums and the coordination number is determined by the radius ratio".*

2. *"an ionic structure will be stable to the extent that the sum of the strengths of the electrostatic bonds that reach an ion equal the charge on that ion".*

3. *"shared edges, and particularly faces of two anion polyhedra in a crystal structure decreases its stability".*

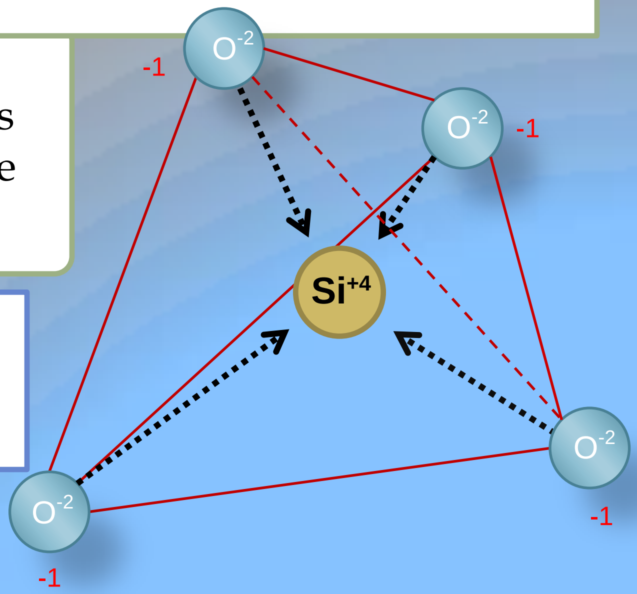
4. *"In a crystal structure containing several cations, those of high valency and small coordination number tend not to share polyhedral elements".*

5. *"The number of different kinds of constituents in a crystal tends to be small".*

From Rule 2. Definition of *electrostatic valency*, e. v. = Charge on the ion/C.N.

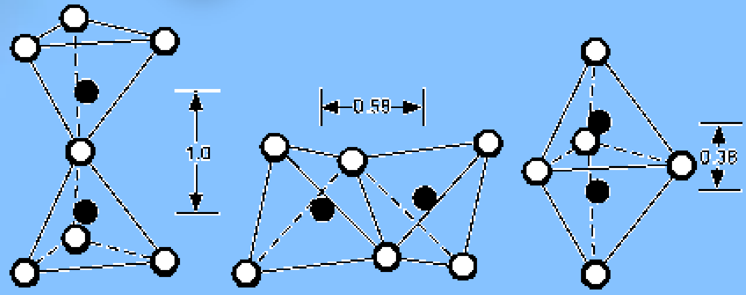
Let's 'stick' to Silica: in SiO_4 each Si^{+4} is surrounded by 4 O^{-2}. The Si is thus in a fourfold coordination and C.N. = 4. The e.v. reaching the cations is exactly ½ the charge on the anion. Here, the e.v. reaching the Si is 4/4=1.

This leaves the oxygen with a -1 charge that it is not shared. Since this -1 is exactly ½ the original charge on O^{-2}, the oxygens in the $[SiO_4]^{-4}$ group can be just as tightly bound to ions outside the group as to the centrally coordinated Si.



From Rule 3. Sharing of only corners of polyhedra places the positively charged cations at the greatest distance from each other.

For tetrahedral coordination, if the distance between the cations in the polyhedrons that share corners is taken as 1, then sharing edges reduces the distance to 0.58, and sharing of faces reduces the distance to 0.38.



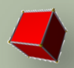
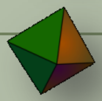
Rules 1-5 maximise the cation-anion attractions and minimise the anion-anion and cation-cation repulsions

Rule 5 tell us that there are only a few different types of cation and anion sites in a crystal. event though a crystal may have tetrahedral, octahedral, and cubic sites, most crystals will be limited to this small number of sites, although different elements may occupy similar sites.

SILICATES, WHO GOES WITH WHOM?

One substitution is crucial in the framework structure of silicates: Al^{3+} with C.N. 4 which substitutes easily with Si^{4+}.

When this takes place, it creates a charge imbalance that must be made up somewhere else in the silicate structure.

Element ion	Ionic radius (in crystal lattice) R (Å)	C.N. (relative to O)	Coordination Polyhedron	SITE
O^{2-}	1.40			
K^+	1.51 (8) 1.64 (12)	8 - 12	cubic to closest - Hexagon (eightfold)	 X
Na^+	1.18 (8) 1.02 (6)	8 - 6	cubic to octahedral	
Ca^{2+}	1.12 (8) 1.00 (6)	8 - 6		
Mn^{2+}	0.83	6	Octahedral (sixfold)	 Y
Fe^{2+}	0.78	6		
Mg^{2+}	0.72	6		
Fe^{3+}	0.65	6		
Ti^{4+}	0.61	6		
Al^{3+}	0.54	6		
Al^{3+}	0.39	4	Tetrahedral (fourfold)	 Z
Si^{4+}	0.26	4		

General formula for SILICATES

$$X_mY_n(Z_pO_q)W_r$$

The subscripts m, n, and r depend on the ratio of p to q and are chosen to maintain charge balance.

W is a hydroxyl (OH^{-1}) site into which can substitute large anions like F^{-1} or Cl^{-1}.

Silicates examples:

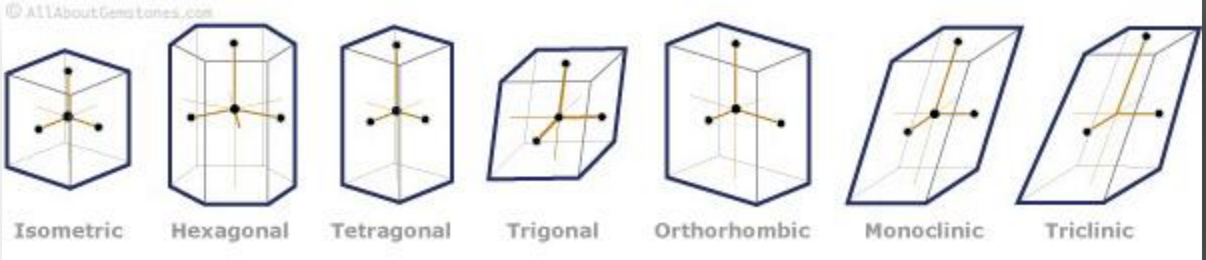
$CaAl_2(SiO_4)_2$	Anorthite (An)	**Plagioclase Felds**
$Ca(Mg,Fe)(SiO_3)_2$	Diopside (Di)	**ClinoPyroxene**
$NaAlSi_3O_8$	Albite (Ab)	**Plagioclase Felds**
$(Mg,Fe)SiO_3$	Hypersthene (Hy)	**OrthoPyroxene**
$(Mg,Fe)_2SiO_4$	Forsterite/Fayalite (Ol)	**Olivine**
$KAlSi_3O_8$	Orthoclase (Or)	**Alkali Felds**

As we can see from the table, there is very little substitution that takes place between ions.
The exceptions are mainly substitution of Al^{3+} for Si^{4+} and whether the X (M2) site is large enough to accept the largest cations like K^+

Crystal – the ‘definition’ → “ *a homogeneous body in which the atoms or molecules are arranged in a regular, repeating pattern that may be outwardly manifested by plane faces*”.
– “*Any solid having an essentially discrete diffraction pattern*” (Int. Union of Crystallography)

When the cooling process is ‘rapid’, the atoms cannot travel to their lattice sites before they lose mobility, resulting in amorphous, vitreous, **or** glassy **materials.**

Inorganic matter, if free to take the physical state it is most stable, always tends to crystallise
(i.e. from an aqueous solution or molten magma).



Quartz
Olivine
Opx
Cpx
Plag

Crystal systems – classification of crystals according to common symmetry characteristics.
Shown are crystallographic axes relating to crystal symmetry

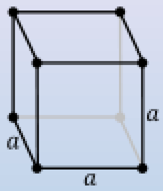
CRYSTAL LATTICE: the 3D arrangement of atoms or ions to form a crystal

Which crystal structure the fluid will form depends principally on its chemistry, the conditions under which it is being solidified, and also the ambient pressure.

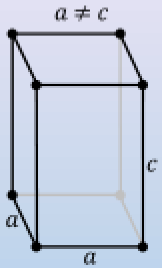
UNIT CELLS: The smallest complete unit of the pattern that can be repeated in all directions

Crystal Systems

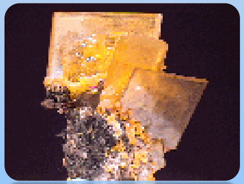
"a category of space groups, which characterize *symmetry of structures* in three dimensions with **translational symmetry** in three directions, having a discrete class of **point groups**"

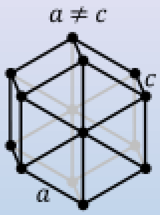


Cubic
Salt

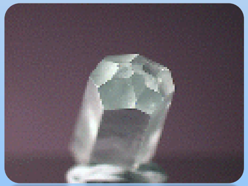


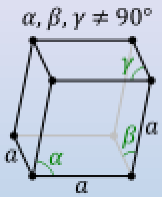
Tetragonal
Wulfenite



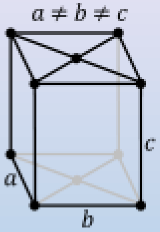


Hexagonal
Beryl

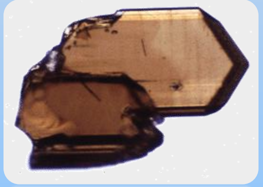


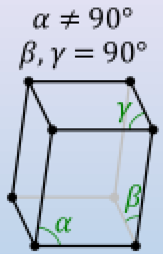


Trigonal
Quartz

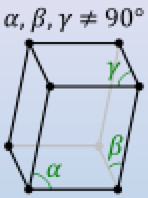


Orthorhombic
Opx, olivine



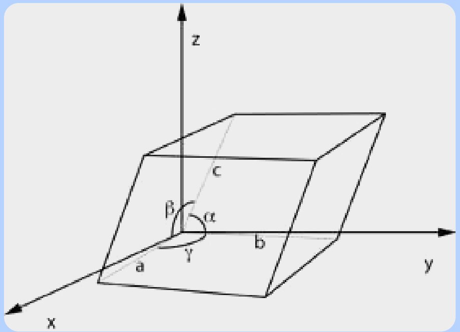


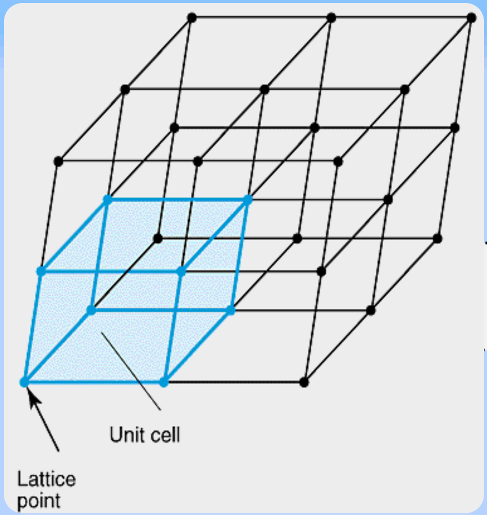
Monoclinic
Clinopyroxene



Triclinic
Plagioclase

Silicates





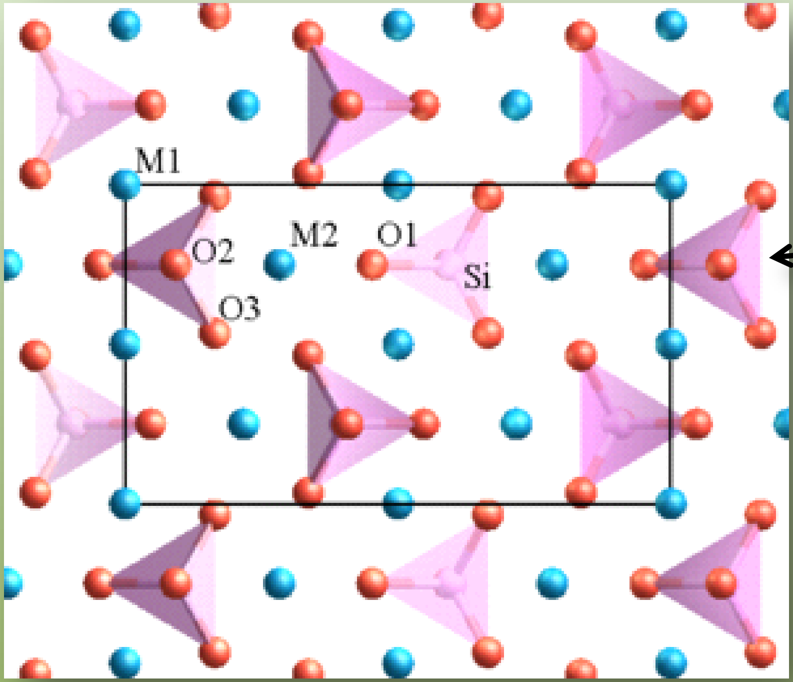
Lattice parameters:

Lengths (relative): a-b-c
Angles: α-β-γ

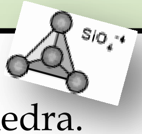
The unit cell of a lattice is the smallest unit which can be repeated in three dimensions in order to construct the lattice

One of the implications of the symmetric lattice of atoms is that it can support resonant *lattice vibration modes*.
On the scale of the lattice spacing, these vibrational modes are quantised (into *phonons*).

OLIVINE

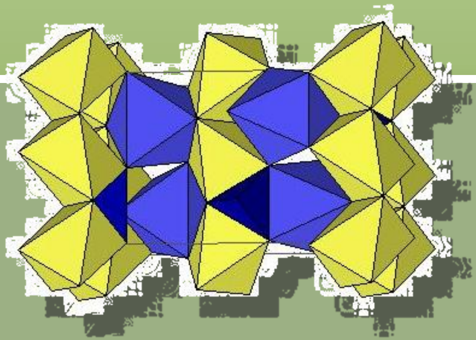


Oxygen = Red
Silicon = Pink
Magnesium/iron = **blue**
Rectangle = projection of unit cell



Minerals in the olivine group crystallize in the orthorhombic system with isolated silicate tetrahedra.

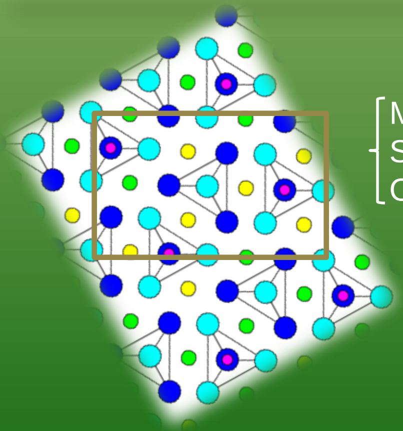
There are three distinct oxygen sites (O1, O2, O3), two distinct metal sites (M1, M2), and only one distinct silicon site (Si). O1, O2, M2, and Si all lie on mirrorplanes, while M1 exists on an inversion center.
M2 site is also larger and more regular than M1 (thus preferred by the larger Ca ion, when present).



2(Mg,Fe)O.SiO_2
$(Mg,Fe)_2SiO_4$

Olivine lattice

In an alternative view, the atomic structure can be described as a hexagonal, close-packed array of oxygen ions with half of the *octahedral sites* occupied with magnesium or iron ions and one-eighth of the *tetrahedral sites* occupied by silicon ions.



Mg or Fe = yellow/green
Si = magenta
O = blue

Perovskite lattice

Silicate tetrahedral(s) can combine with other elements (cations) in many geometrical and compositional permutations.

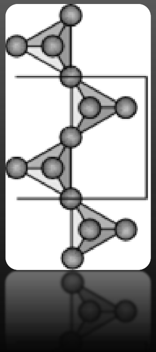
SILICATE MINERALS

INOSILICATES

(CHAIN)-

In inosilicates two or two and a half oxygens are shared by adjacent tetrahedra.

Most minerals in this group are called single chain silicates because the $[SiO_4]^{4-}$ tetrahedra are linked together to form chains of composition $[SiO_3]^{2-}$



These are bonded together by cations such as Mg^{2+}, Fe^{2+}, Ca^{2+}, and Na^{+}.

There is complete solid-solution between Mg and Fe members.

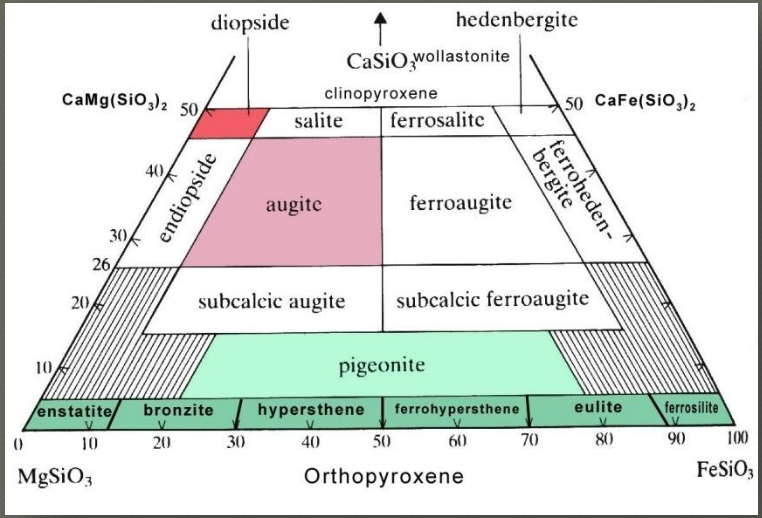
There is also some Ca^{2+} in most pyroxene structures that become distorted by the large calcium ion.

CLINOPYROXENE (cpx)

Augite occurs mainly in igneous rocks and represents an essential mineral constituent of gabbros, dolerites and basalts.

In plutonic gabbros augites frequently occur with opx.

There is complete Mg-Fe solid solution between the pyroxenes Di and Hd, and as with most Mg-Fe solid solutions, the Mg-rich end members crystallize at higher temperatures than the Fe-rich end members.



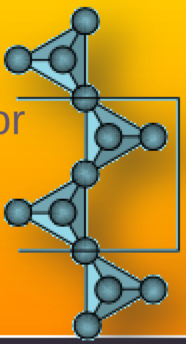
ORTHOPYROXENE (opx)

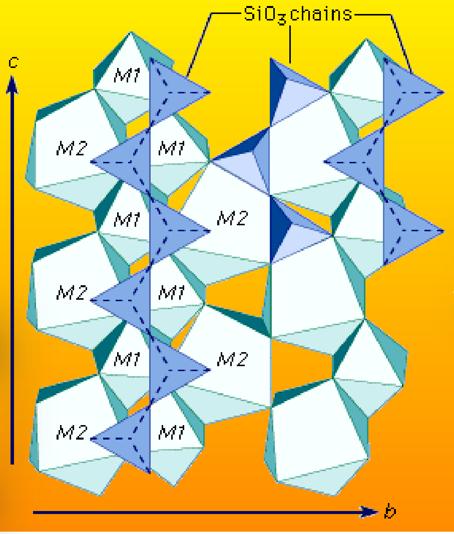
Mg-rich varieties of orthopyroxene are called Hypersthene, whereas Fe-rich varieties are called Ferrosilite. *Pigeonite* occurs only in rapidly chilled rocks. In most igneous rocks that have undergone slow cooling, pigeonite is inverted to opx.

AMPHIBOLES – Double chain inosilicates.

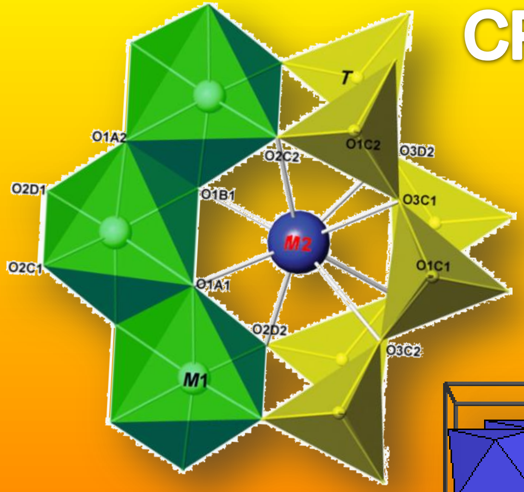
Unlike pyroxenes, amphiboles include some hydroxyl ions ($(OH)^-$). There is one hydroxyl group per repeat unit: $[Si_4O_{11}(OH)]^{7-}$, and this is common to all amphiboles (i.e. Hornblende).

When two of the oxygens are shared in a way to make long single chains of linked SiO_4 tetrahedra we get the single chain silicates or **INOSILICATES**.

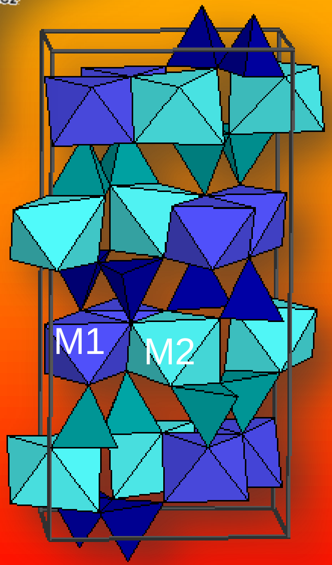




CPX



OPX

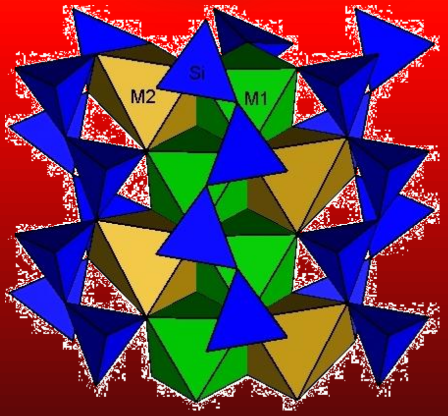


The *pyroxene* group is composed of minerals of the general formula **$XY(SiO_3)_2$**, where X and Y are...:

.. two divalent cations and X is a large-radius cation like Ca^{2+} : the structure is *monoclinic* → clinopyroxene (cpx).
(Ca in M2 position)

..the **same small-radius divalent** cation like Fe^{2+} or Mg^{2+} the resultant structure is commonly *orthorhombic* → orthopyroxene (opx)
(Fe^{2+} prefers the M2 site, being larger than Mg).

..a monovalent and a trivalent cation (i.e. Na^+ and Fe^{3+}) then the structure is *monoclinic* → Na-pyroxene (aegirine).



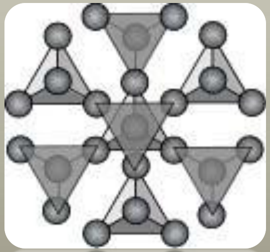
Silicate tetrahedral(s) can combine with other elements (cations) in many geometrical and compositional permutations.

SILICATE MINERALS

TECTOSILICATES

(FRAMEWORK)-

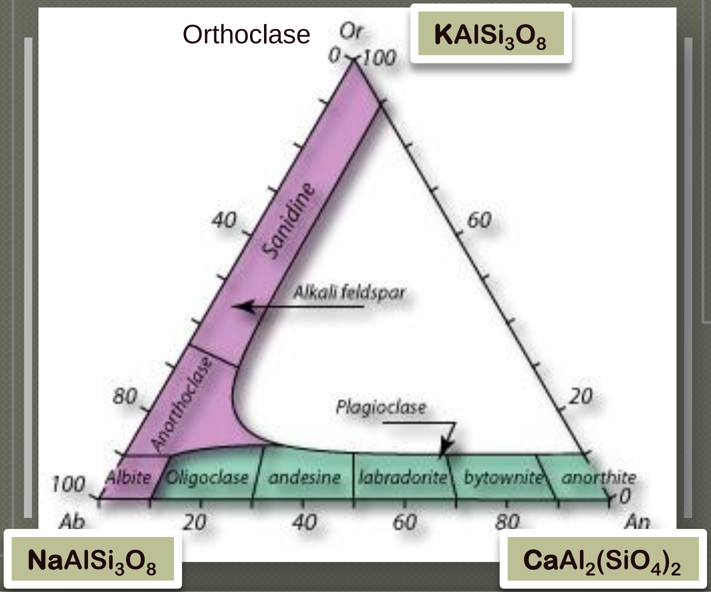
Are those where all four oxygens are shared with other tetrahedra. If composed entirely of silicon and oxygen, such framework will have the composition of SiO_2, as in quartz



These silicates are divided into two main mineral groups: Alkali and Plagioclase Feldspars. Feldspars are the most important constituents of many rocks found at the Earth's surface.

PLAGIOCLASE feldspars end members are characterised by the similarity of ionic radii for Ca^{2+} and Na^{+} allowing complete ionic substitution to occur between albite and anorthite to form a solid-solution series.

In basic lava, Ca-rich plag. felds. occur both as phenocrysts and constituents of the groundmass. In basic plutonic rocks, layering and differentiation can occur.

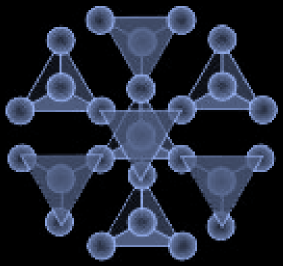


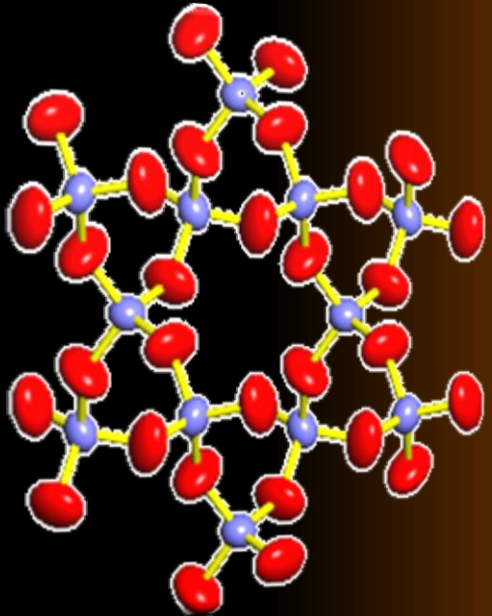
ALKALI feldspars are essential constituents of alkali and acid igneous rocks (such as granites). In K-feldspars the ionic substitution of K^{+} by Na^{+} is limited because of the large difference in size of these cations: i.e. the two minerals form separately.

The FELDSPATHOIDS group of minerals are SiO_2 poor, alkali rich minerals that occur in low SiO_2,
high Na_2O - K_2O igneous rocks.

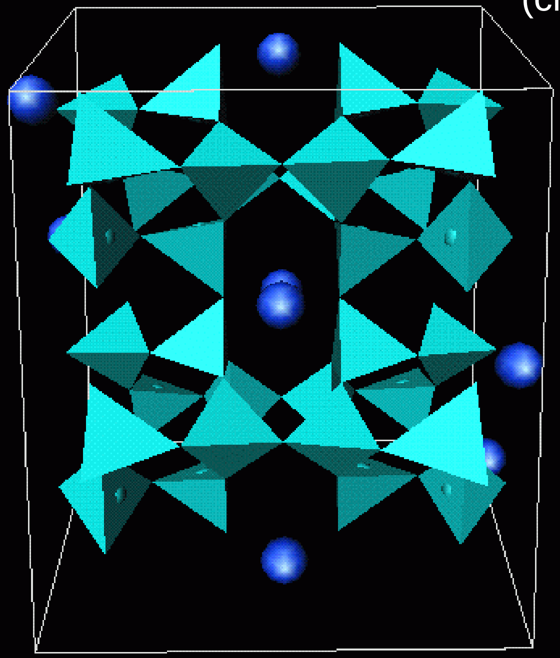
The main feldspathoids are Nepheline $(Na,K)AlSiO_4$, and Leucite $KAl(SiO_3)_2$.

TECTOSILICATES or framework silicates have a structure wherein all of the 4 oxygens of SiO_4^{-4} tetrahedra are shared with other tetrahedra. The ratios of Si to O is thus 1:2.





Hence, the basic structural group becomes SiO_2, i.e. **quartz** or one of its polymorphs (cristobalite, tridymite, etc.)



However:

- in **alkali feldspars** 1/4 of the Si^{+4} ions are replaced by Al^{+3}

- in **plagioclase feldspars** 1/4 to 1/2 of the Si^{+4} ions are replaced by Al^{+3}.

The $[AlO_4]$ tetrahedron is slightly larger than an $[SiO_4]$.

Furthermore the potential energy of Al-O-Al is greater that that of an Al-O-Si linkage, suggesting that $[AlO_4]$ are energetically unfavourable, with consequences for aluminosilicate minerals.

Feldspar group

Alkali Feldspars
$KAlSi_3O_8$ to $NaAlSi_3O_8$

Plagioclase Feldspars
$NaAlSi_3O_8$ to $CaAl_2Si_2O_8$

This allows for the cations **K^+**, **Na^+**, and **Ca^{+2}** to be substituted into void spaces to maintain charge balance.

As most silicates in igneous and metamorphic rocks consist essentially of silica+metal oxides, free oxides can be considered to form ***if***

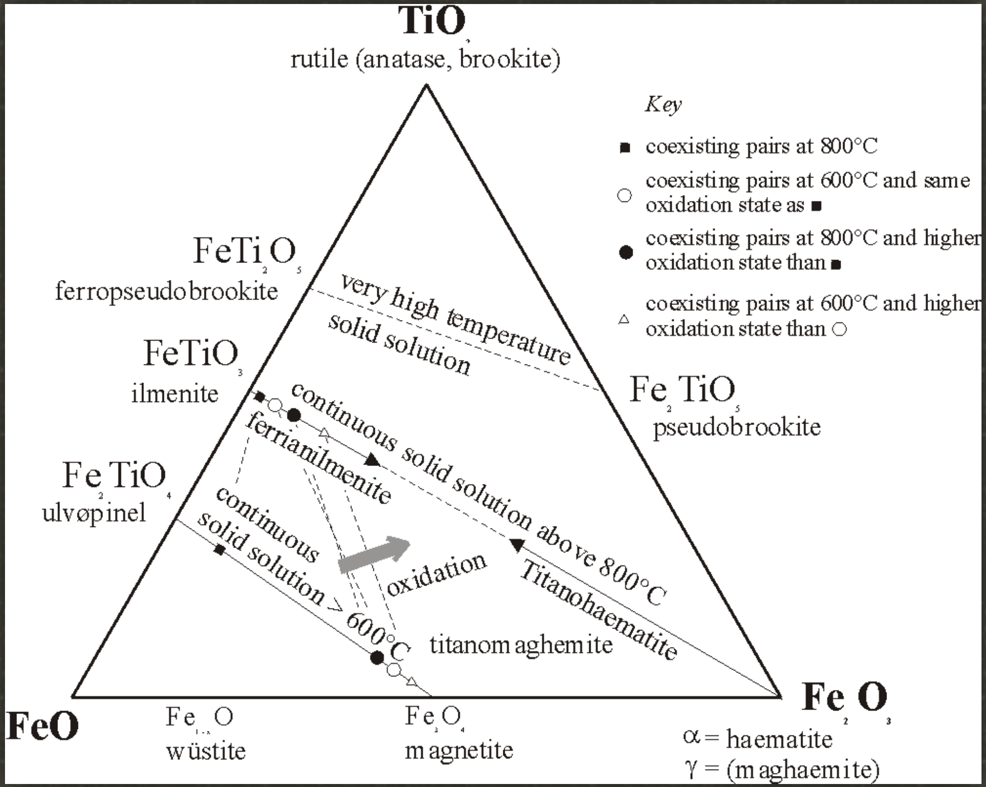
Metal OXIDES

are present surplus to the needs of silicates
(or the rocks are silica-deficient)

Iron-titanium oxides

Their identification and classification is important because diagnostic of the crystallisation history of the host rock.

In *particular* they are key indicators of both the ambient temperature and the chemical potential of oxygen during metamorphism



Spinel group

is represented by the general formula $R^{2+}R^{3+}O_4$ where R^{2+} can be Mg, Fe, Zn, Mn, and Ni, and R^{3+} Al, Fe, and Cr.

All spinels are cubic and there is considerable variation in colours and opacities.

Spinel in *senso strictu:* $MgAl_2O_4$

Stage	*Age (Ga)*	*Example of minerals*	*~Cumulative # species*
THE ERA OF PLANETARY ACCRETION (>4.55 Ga)			
1. Primary chondrite minerals	**>4.56**	Mg-olivine/pyroxene, Fe-Ni metal, FeS, CAIs	60
2. Planetesimal alteration/differentiation	**>4.56** to **4.55**		250
a. Aqueous alteration		Phyllosilicates, hydroxydes, sulfates, carbonates, halite	
b. Thermal alteration		albite, feldspathoids, biopyriboles	
c. Shock phases		ringwoodite, majorite, akimotoite, wadsleyite	
d. Achondrites		quartz, K-feldspar, titanite, zircon	
e. Iron meteorites		Many transition metal sulphides and phosphates	
THE ERA OF CRUST AND MANTLE REWORKING (4.55 TO 2.5 Ga)			
3. Igneous rock evolution	**4.55** to **4.0**		500
a. Fractionation		Feldspathoids, biopyriboles (volatile-poor planets)	350
b. Volcanism, outgassing, surface hydration		Hydroxides, clay minerals (volatile-rich planets)	500
4. Granite formation	**4.0** to **3.5**		1000
a. Granitoids		Quartz, K-feldspar (perthite), hornblende, micas, zircon	
b. Pegmatites		Beryl, tourmaline, spodumene, pollucite, many others	
5. Plate tectonics	**>>3.0**		
a. Hydrothermal ores		sulphides, selenides, arsenides, antimonides, tellurides, sulphosalts	
b. metamorphic		kyanite, sillimanite, cordierite, chloritoid, jadeite, staurolite	
6. Anoxic biological world	**3.9** to **2.5**		1500
a. Metal precipitates		Banded iron formations (Fe and Mn)	
b. Carbonates		Ferroan carbonates, dolostones, limestones	
c. Sulphates		Barite, gypsum	
d. Evaporites		Halides, borates	
e. Carbonate skarns		Diopside, tremolite, grossularite, wollastonite, scapolite	
THE ERA OF BIO-MEDIATED MINERALOGY (>2.5 Ga TO PRESENT)			
7. Paleoproterozoic atmospheric changes surface oxidation	**2.5** to **1.9**	>2000 new oxide/hydroxide species, especially ore minerals	>4000
8. Intermediate ocean	**1.9** to **1.0**	Minimal mineralogical innovation	
9. Neoproterozoic biogeochemical changes	**1.0** to **0.542**		>4000
a. Glaciation		Extensive ice deposition, but few minerals	
b. Post-glacial oxidation		Extensive oxidative weathering of all surface rocks	
10. Phanerozoic Era	**0.542** to **present**		4300+
a. Biomineralisation		Extensive skeletal biomineralisation of calcite, aragonite, dolomite, hydroxylapatite, and opal	
b. Bio-weathering		Increased production of clay minerals, soils	

The Earth can be regarded as a heat 'engine': most geological phenomena on or within the Earth involve the transfer of energy, and most of that energy is eventually discharged into space as **HEAT**.

Estimates of *primordial* (original) heat:

Heat of accretion = 10^{32}J (KE transfer $\Delta T \frac{mv^2}{2MC}$) C = specific heat capacity

Heat of compression = 2.5 x 10^{32}J (self-compression as the planet grows)

Core formation = 10^{31}J (gravitational energy lost by Fe falling towards the centre)

Short-lived radioactive isotopes = 10^{32}J (^{36}Cl, ^{60}Fe, ^{244}Pu, ^{129}I = h/l 0.5 Ma ¦ ^{26}Al = 0.88 Ma)

Long-lived radioactive isotopes = 10^{28}J ($^{235-238}$U, ^{232}Th, ^{40}K, *still* important heat producers)

Tidal dissipation = 10^{25}J/yr (solid + fluid tides, *slow down of Earth's rotation + lunar distance)*

Heat flow from the **Sun** is ~10^{17} W or ~200.00 Wm^{-2}
Heat flow from the **Earth's interior** is ~ 0.08 Wm^{-2}

Minor sources of geo-energy:
Sun → weathering of rocks (water cycle, thermal expansion)
Earth's **rotation** → core's dynamics
Impacts → geomorphology

Rocks are poor conductors of heat, e.g. they posses 'low thermal conductivity'

No seasonal variations below 20m - daily temperature changes are already less than 1°C at depth of 1 meter!

Average geothermal gradient near the Earth's surface is ~30 K Km^{-1}

Upper crustal rocks generate heat at the highest rate due to high radioisotopes concentrations.

Calculations have suggested that the four heat-producing radioactive isotopes $^{235-238}$U, ^{232}Th, ^{40}K, could account for at least 80% of the heat flow currently observed, and possibly all of it.

However, because of the low thermal conductivities of the Earth's rocks, the current heat flow must include a component (possibly up to 50%) of heat generated at the time of formation.

General formula for SILICATES

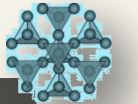
$$X_m Y_n (Z_p O_q) W_r$$

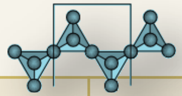
The subscripts m, n, and r depend on the ratio of p to q and are chosen to maintain charge balance.

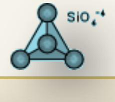
K^+	Na^+	Ca^{2+}	Mn^{2+}	Fe^{2+}	Mg^{2+}	Fe^{3+}	Ti^{4+}	Al^{3+}	Al^{3+}	Si^{4+}
X			Y						Z	

GENERAL FORMULA – PHASE – GROUP – CRYSTAL CHEMISTRY AND SYSTEM

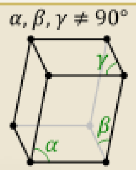
$KAlSi_3O_8$	$NaAlSi_3O_8$	$CaAl_2(SiO_4)_2$	$Ca(Mg,Fe)(SiO_3)_2$	$(Mg,Fe)SiO_3$	$(Mg,Fe)_2SiO_4$
Orthoclase (Or)	Albite (Ab)	Anorthite (An)	Diopside (Di)	Hypersthene (Hy)	Forsterite/ Fayalite (Ol)
Alkali Feldspar	Plagioclase Feldspar		Clinopyroxene	Orthopyroxene	Olivine
TECTOSILICATES			INOSILICATES		NESOSILICATES

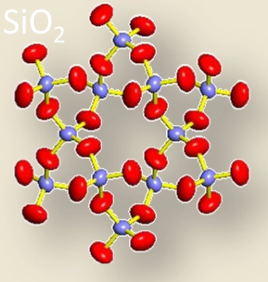






Triclinic

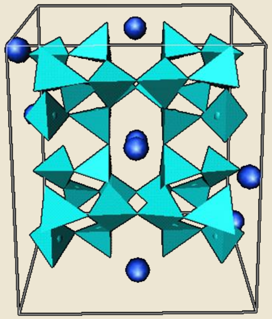




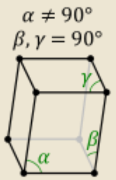
In **alkali feldspars** 1/4 of the Si^{+4} ions are replaced by Al^{+3}

In **plagioclase feldspars** 1/4 to 1/2 of the Si^{+4} ions are replaced by Al^{+3}.

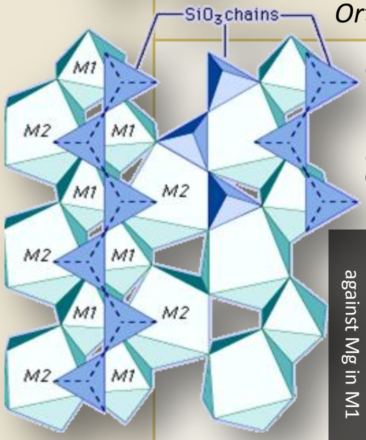
This allows for the cations $\mathbf{K^+}$, $\mathbf{Na^+}$, and Ca^{+2} to be substituted into void spaces to maintain charge balance.



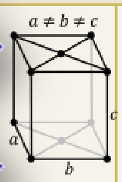
Monoclinic



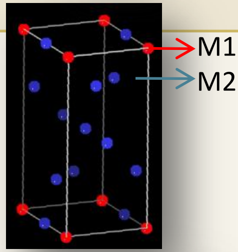
M2 = X

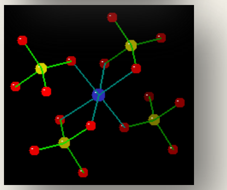


Orthorhombic



M2 = Y and preferred by Fe^{2+} against Mg in M1





A WORD OF WARNING!

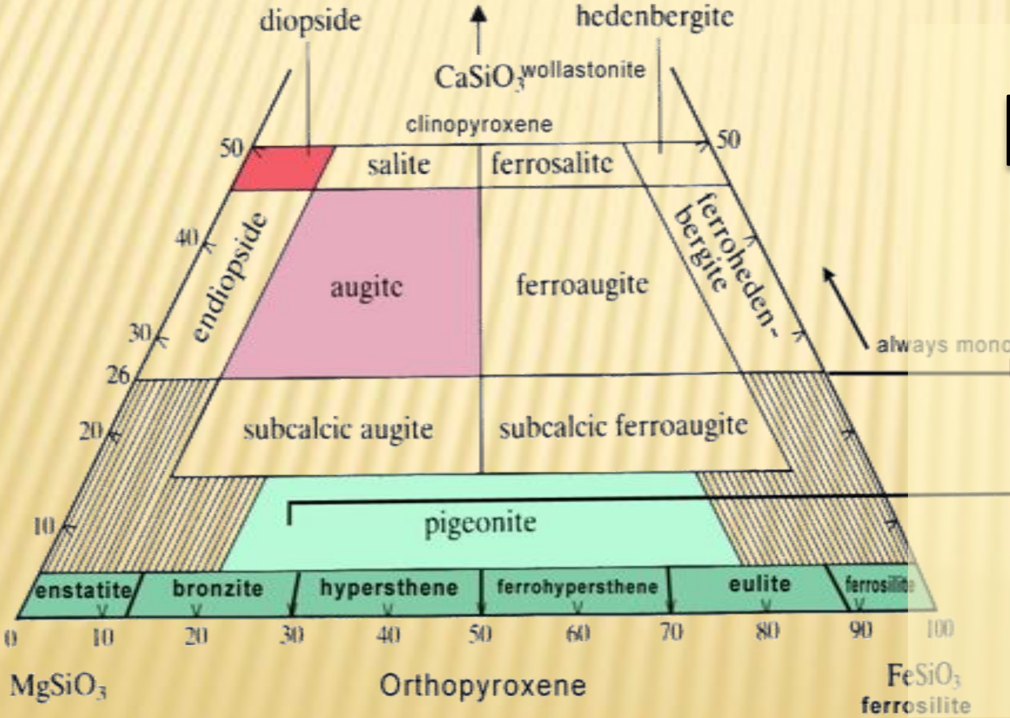
(simplified) Descriptive mineralogy only tells part of the compositional story:

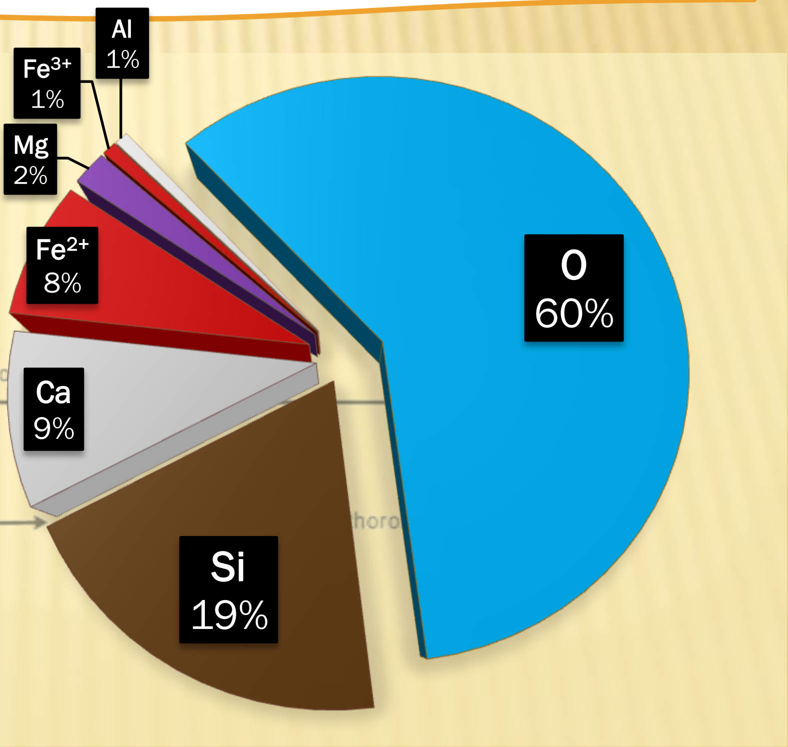
Example: a **hedenbergite**, a ferrous clinopyroxene with generic formula

$\mathbf{CaFeSiO_3}$ or $\mathbf{Di_{10} - Di_0}$

might have an actual composition of:

$Ca_{0.95}Fe^{2+}_{0.77}Fe^{3+}_{0.08}Mg_{0.20}Si_{1.92}Al_{0.08}O_6$





PHASE RELATIONS OF SILICATES AND SILICATE MELTS

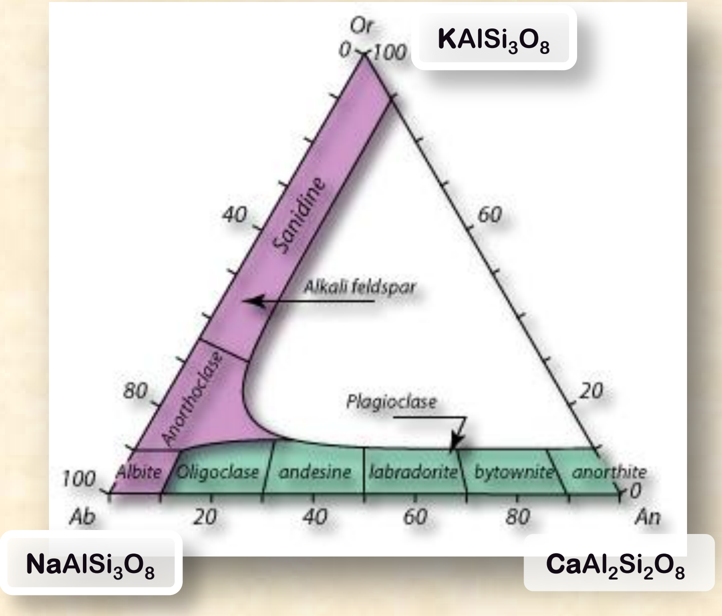
One phase: i.e. a quartz crystal → **solid** SiO_2; molten quartzite → **liquid** SiO_2

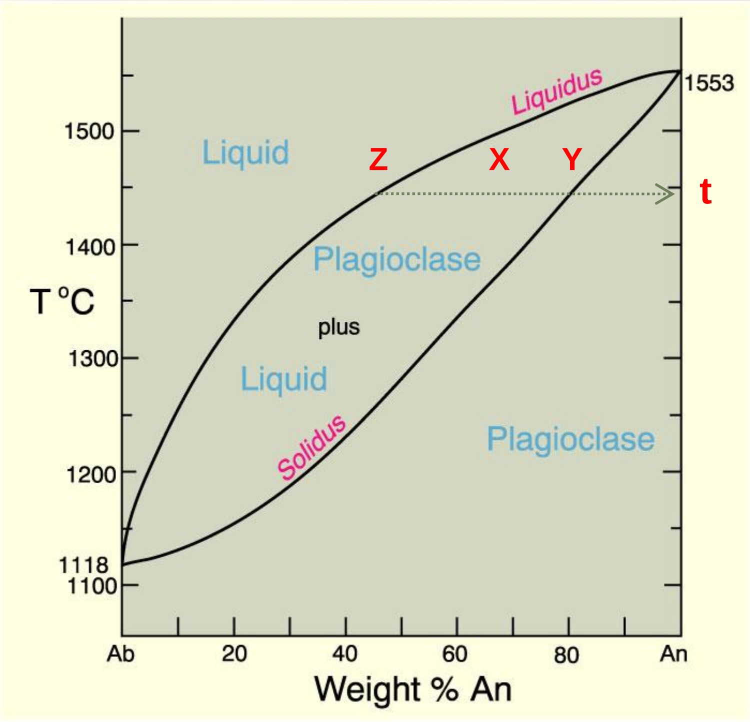
Typical basalt: **solid** phases (feldspar, pyroxene, etc.). When molten ***one phase***: a basalt **liquid** + (possibly) an exsolved **gas** phase

Gases and most liquids are miscible, with exceptions
(i.e. Ab-An and Fo-Fa)

BINARY SYSTEMS (two components)

Complete Solid Solution:
i.e. *Plagioclase Feldspars*
'albite-anorthite series'





X composition between liquidus and solidus at T= t exists as a mixture of crystals of composition Y and liquids with compositions Z

CRYSTALLIZATION THE PLAGIOCLASE FELDSPARS

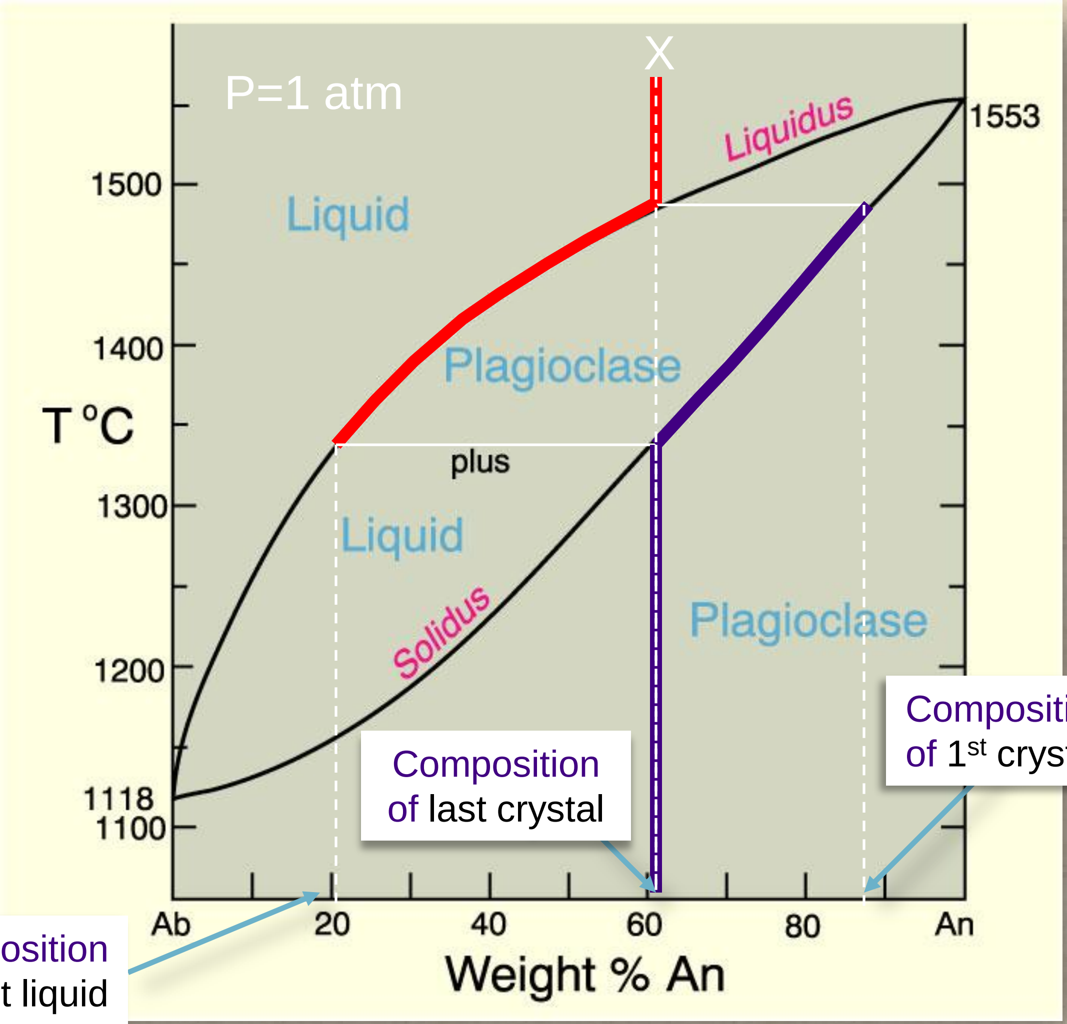
1. Liquid of composition X (An61) cools to the liquidus

2. Crystals of approximately An87 begin to form

3. Crystals have higher Ca/Na than liquid; partition of crystals causes liquidus composition to become more sodic.

4. Ratio of Ca/Na in both crystals and liquid decrease with decreasing temperature; proportion of crystals increases as liquid decreases

5. Crystals of An61 cool without further change in composition



Composition of 1st crystal

Composition of last crystal

Composition of last liquid

$NaAlSi_3O_8$

$CaAl_2Si_2O_8$

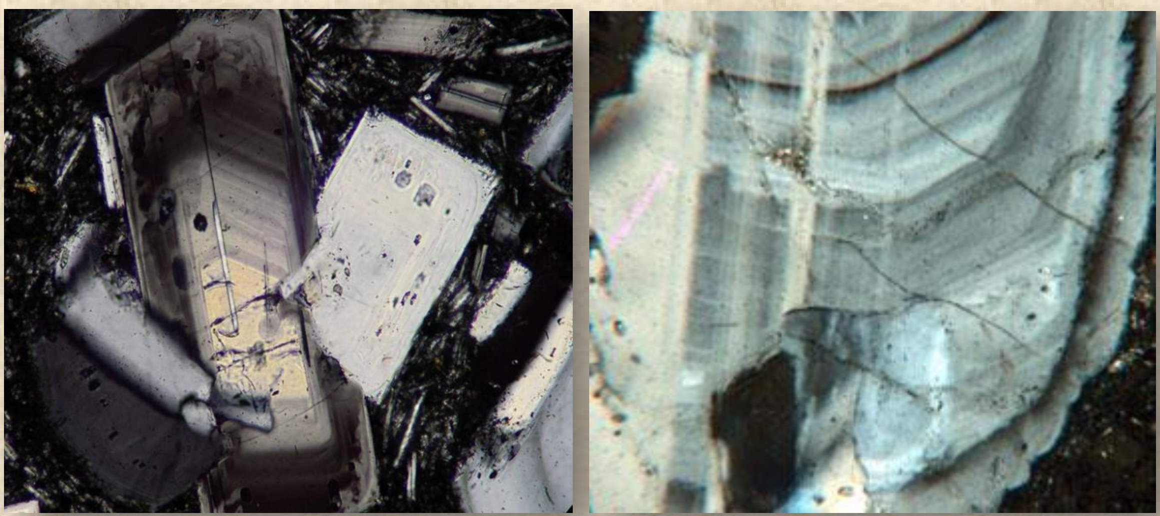
What happened in this case, to the already formed crystals?

Equilibrium Crystallisation:

as the melt changed in composition, becoming more Ab-rich, the crystals that have already separated from the melt reacted with it and also become more albite-rich. Ultimately, the solid plagioclase when **all** the liquid has crystallised must have the same composition as the starting melt.

Fractional Crystallisation (FC):

the melt **does not** react with the early formed crystals to bring them into equilibrium as its composition changes. As the crystals grow, successive layers of crystals are progressively enriched in the albite constituent, i.e. the crystal is ***zoned****.*

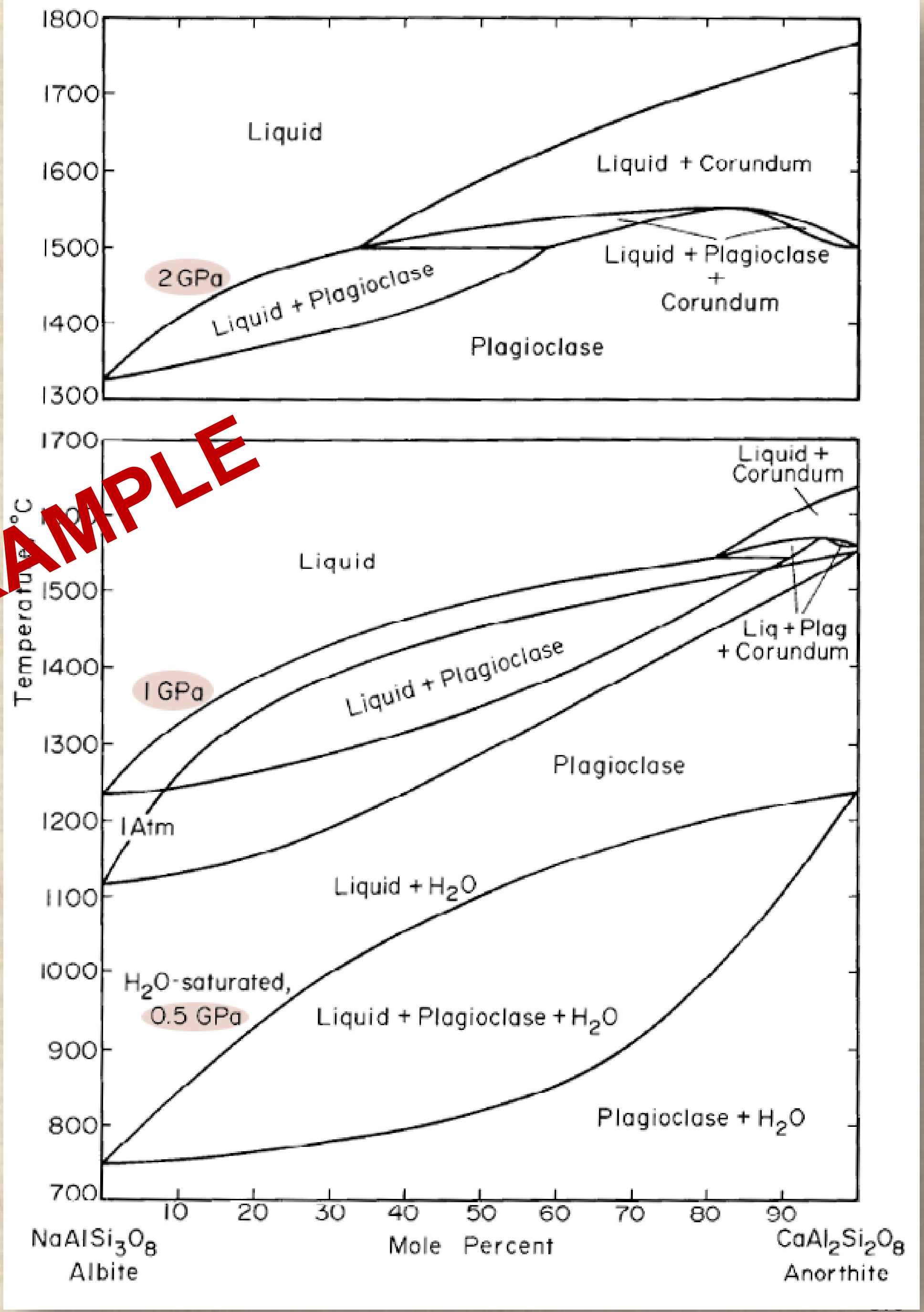


In general, rapid cooling is most conductive to FC, and this is why the plagioclase in volcanic rocks is more strongly zoned than that in plutonic igneous rocks.

EQUILIBRIUM CRYSTALLIZATION

THE PLAGIOCLASE FELDSPARS

A MORE REALISTIC EXAMPLE



(PARTIAL) MELTING IN THE FORSTERITE-FAYALITE SYSTEM

1. SOLID OF COMPOSITION X (FO50) IS PROGRESSIVELY HEATED

2. THE SOLIDUS IS INTERSECTED AT 1320°C: THIS IS THE LOWEST T AT WHICH LIQUID AND SOLID COEXIST.

3. AT THIS POINT THE LIQUID HAS COMPOSITION FO$_9$ AND THE SOLID IS FO$_{50}$

4. AT HIGHER TEMPERATURES, THE PROPORTION OF LIQUID INCREASES AT THE EXPENSE OF SOLID.

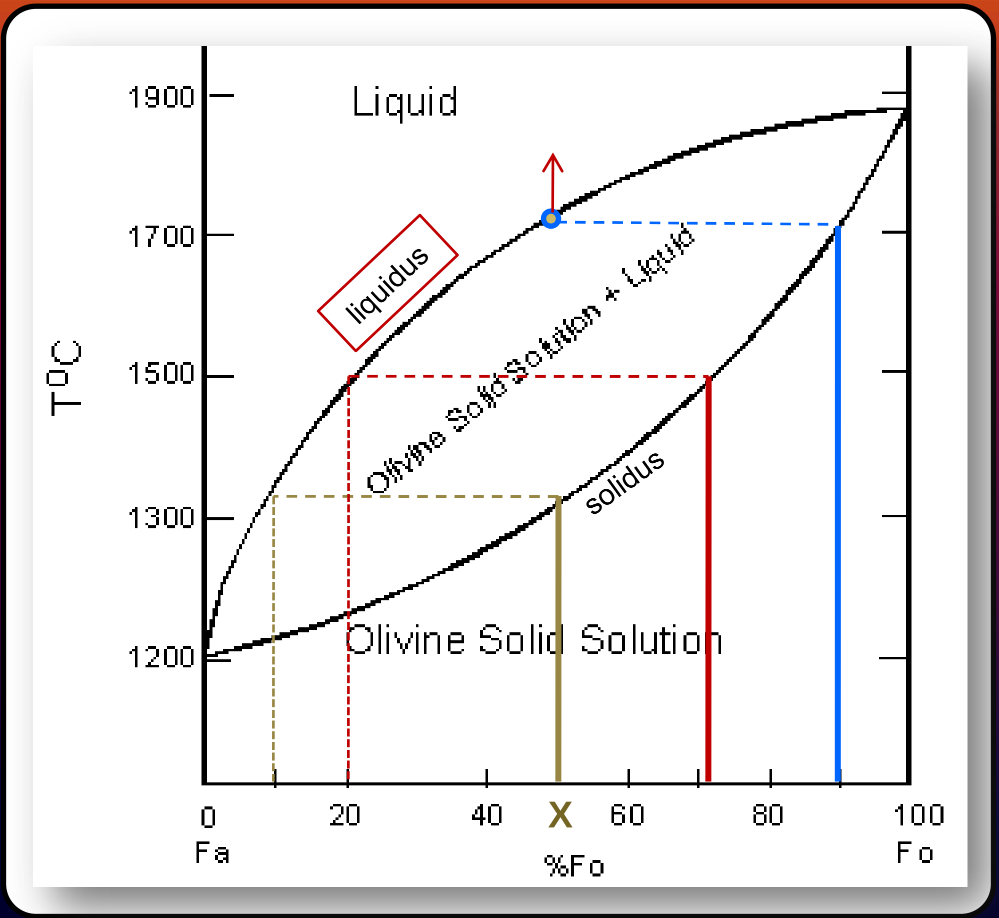
5. AT T=1500 LIQUID FO$_{20}$ COEXISTS WITH SOLID FO$_{72}$.

6. AT T=1670 LIQUID FO$_{50}$ COEXISTS WITH AN INFINITESIMAL AMOUNT OF SOLID FO$_{90}$.

7. AT T>1670 LIQUID FO$_{50}$ IS THE ONLY PHASE PRESENT.

Another example of a Solid Solution in a Binary System - OLIVINE

P=1 atm



We have seen Binary Systems (BS) showing complete Solid Solution (ss), but the are several other types of binary phase diagrams:

- •BS containing a ss series with an intermediate minimum
- •BS with complete ss at the melting temperature but not at lower temperatures
- •BS with limited ss
- •BS containing an incongruently melting compound

etc., but let's look at a BS with a ***eutectic point*** (no ss):

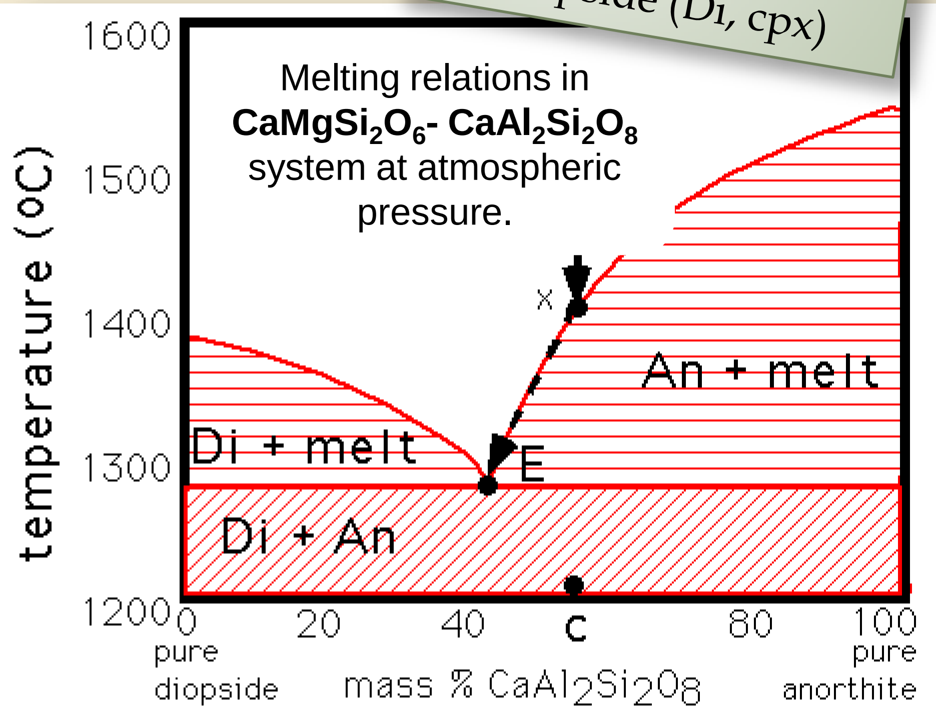
THE DIOPSIDE (CPX) – ANORTHITE (PLAGIOCLASE) BI

Another 'text-book' example of another binary eutectic system is forsterite (Fo, olivine) and diopside (Di, cpx)

In this system there is **no solid solution** between end members: all compositions are completely molten above the liquidus and completely solid below the solidus

This means that unlike in a 'ss' series where at subsolidus Ts only one phase is present, here there is a mixture of separate Di and An crystals

'**E**' is the **eutectic** point, the only location on the phase diagram where the three phases solid Di, solid An, and liquid coexist

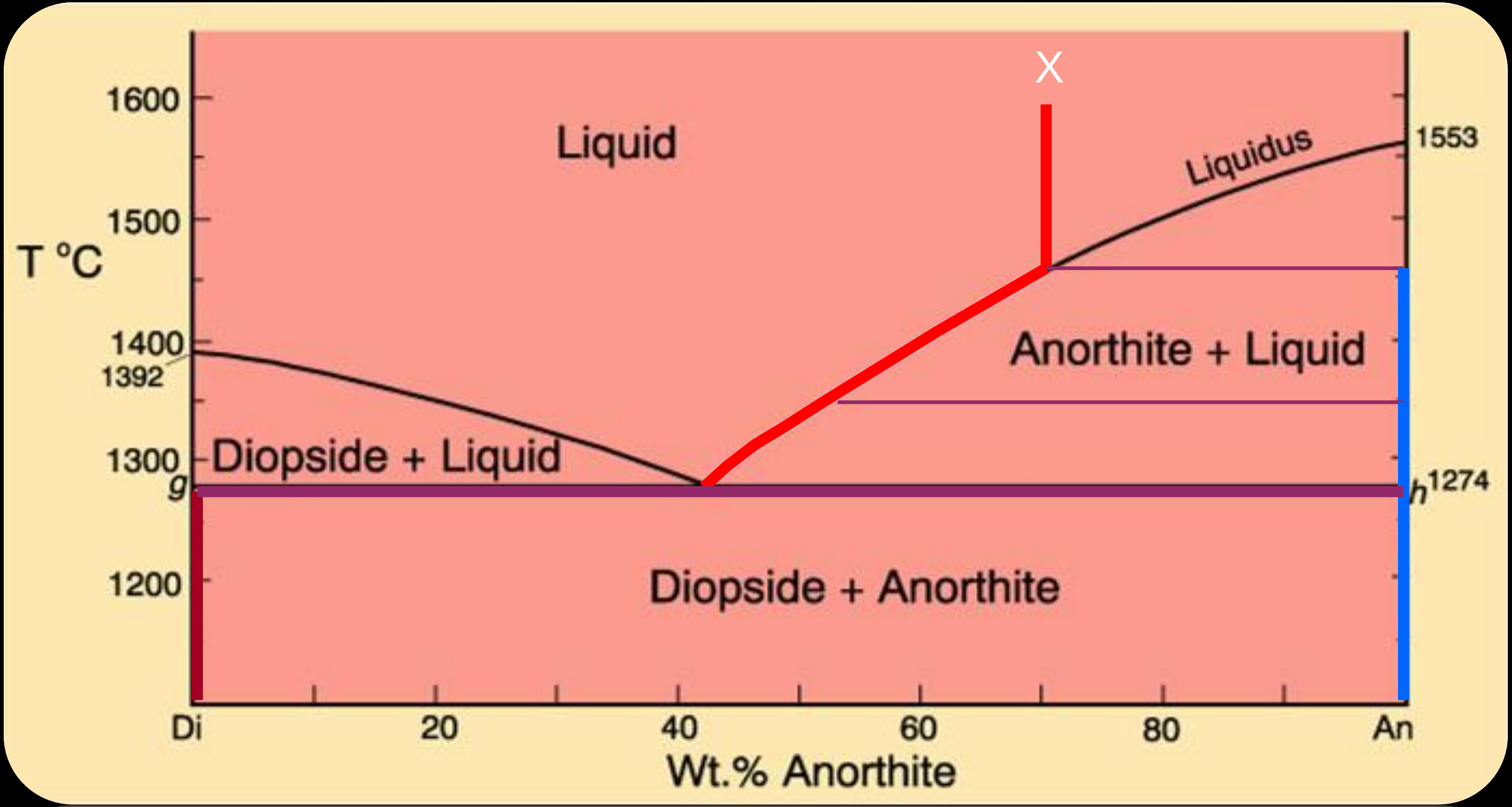

Melting relations in **$CaMgSi_2O_6$- $CaAl_2Si_2O_8$** system at atmospheric pressure.

1. A bulk composition of X cools to the liquidus, at which point An crystallizes.

2. Continued crystallization of An causes liquid composition to move toward Di.

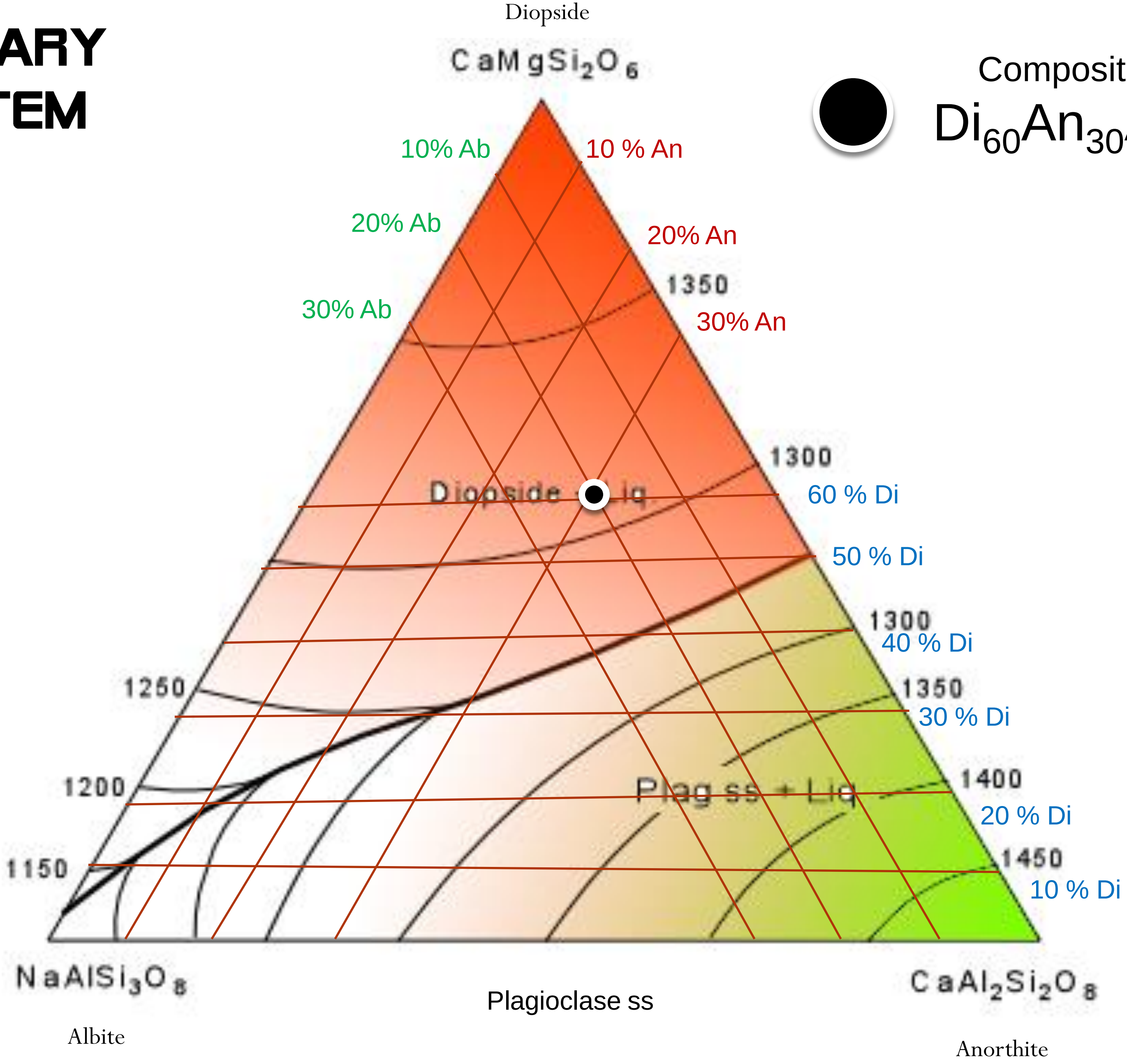
3. When T=1274 C, liquid has moved to eutectic; Di begins to crystallize. No change in temperature or composition of any of the 3 phases is permitted until the liquid has completely crystallized.

4. At temperatures below 1274 C, only crystals of An and Di are present.



TERTIARY SYSTEM

Composition: ● $Di_{60}An_{30}Ab_{20}$



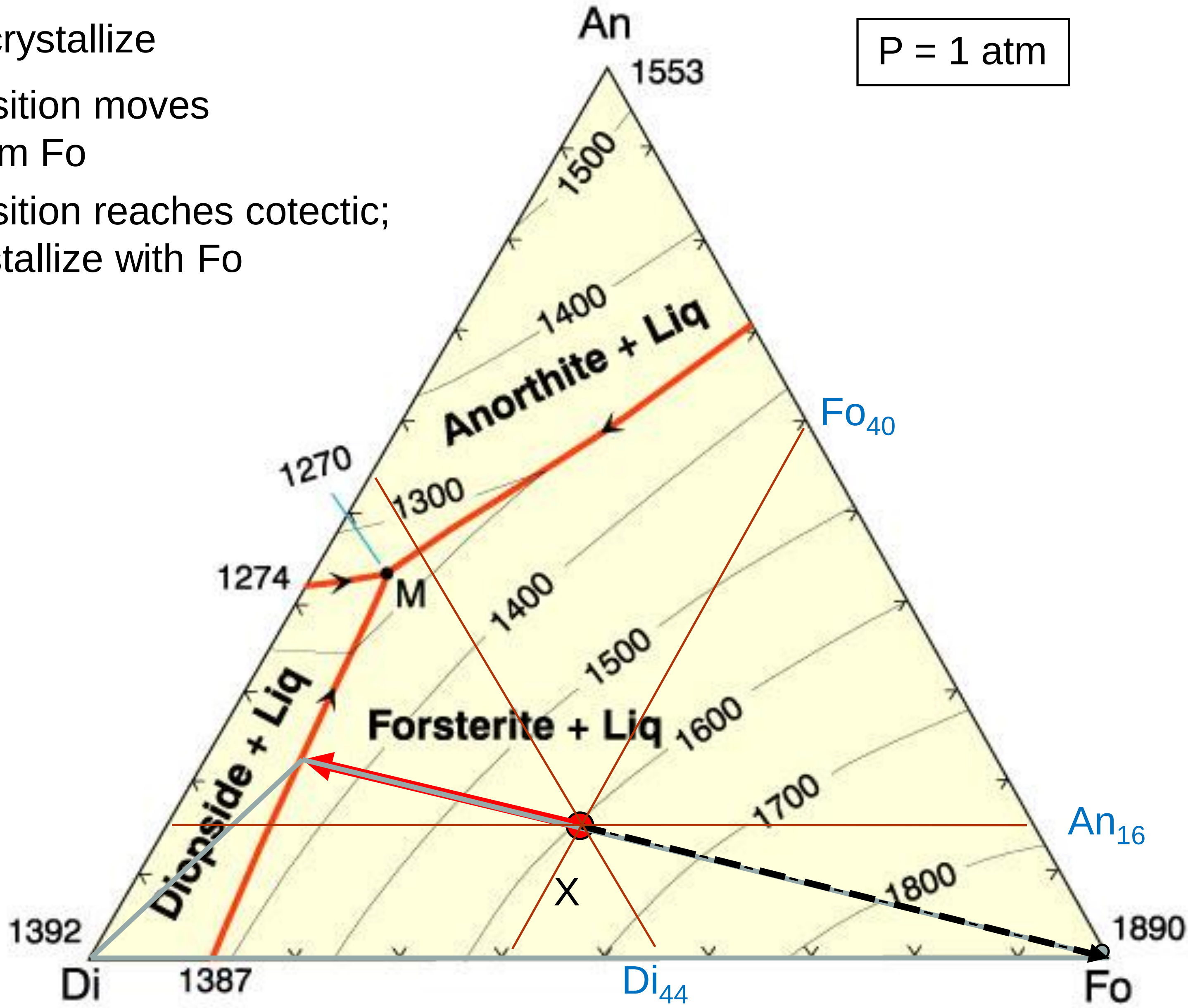
1. For bulk composition X, liquid cools to liquidus at 1600 C

2. Fo begins to crystallize

3. Liquid composition moves directly away from Fo

4. Liquid composition reaches cotectic; Di begins to crystallize with Fo

P = 1 atm



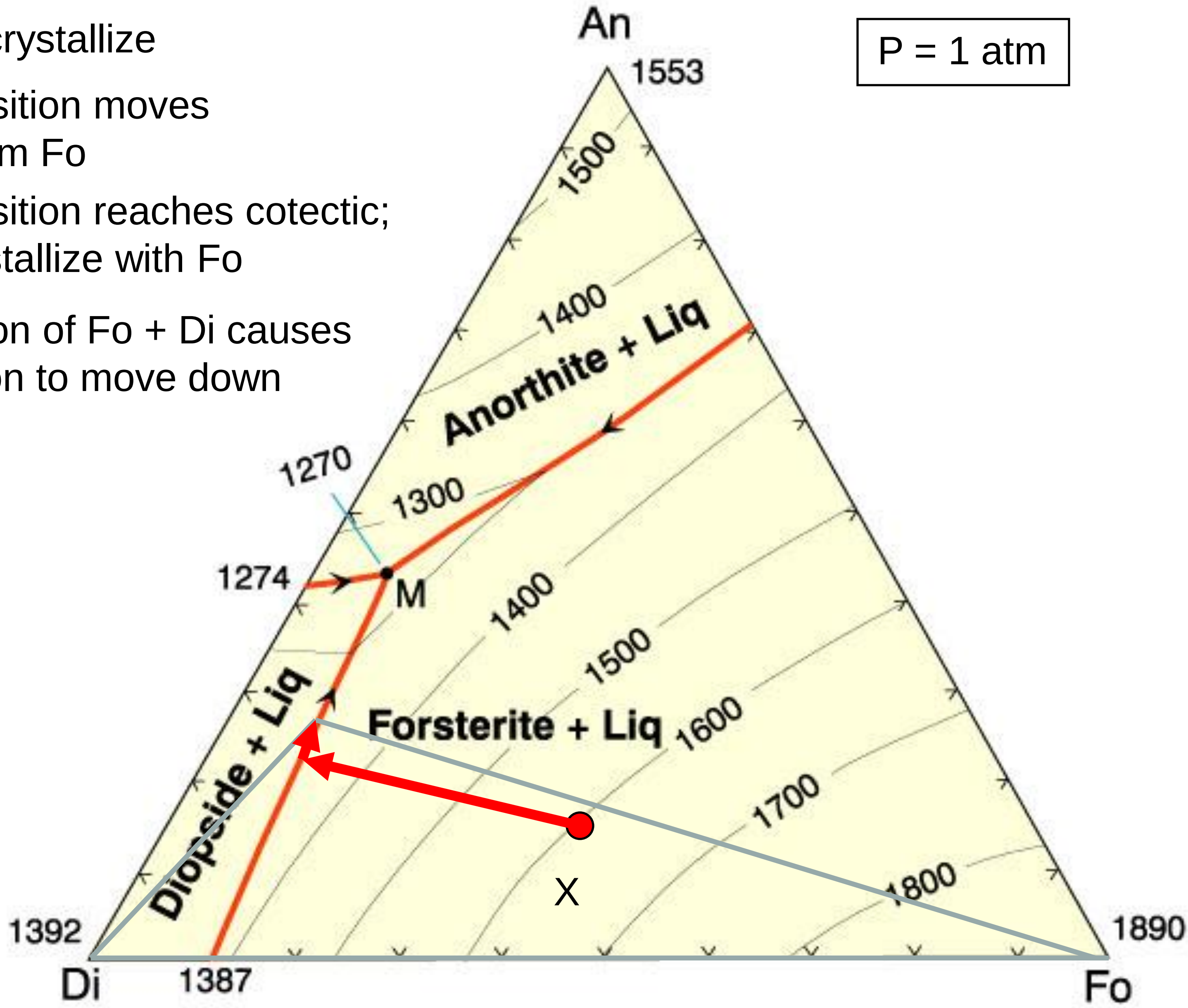
1. For bulk composition X, liquid cools to liquidus at 1600 C

2. Fo begins to crystallize

3. Liquid composition moves directly away from Fo

4. Liquid composition reaches cotectic; Di begins to crystallize with Fo

5. Co-precipitation of Fo + Di causes liquid composition to move down cotectic curve



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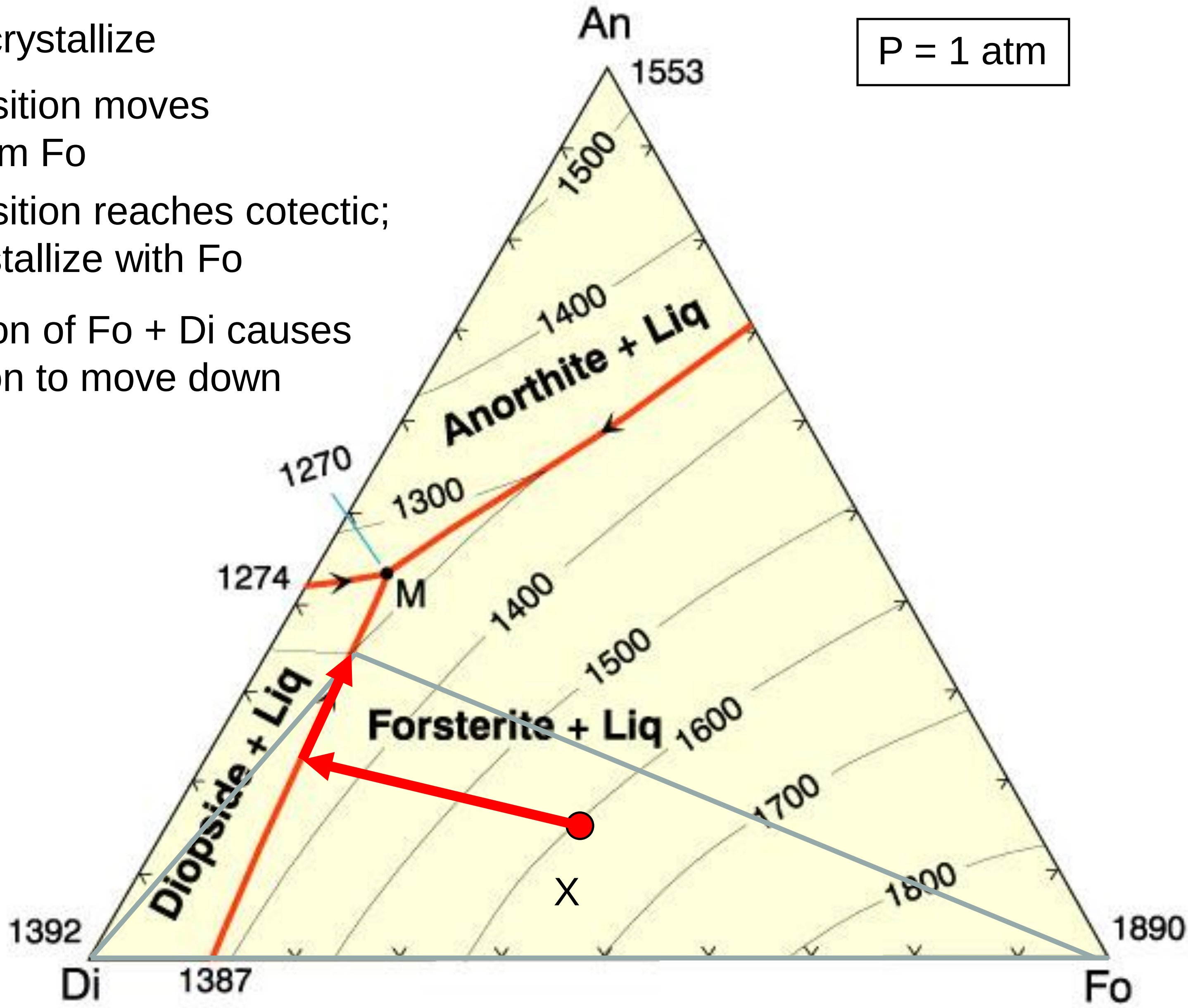

8.13

1. For bulk composition X, liquid cools to liquidus at 1600 C

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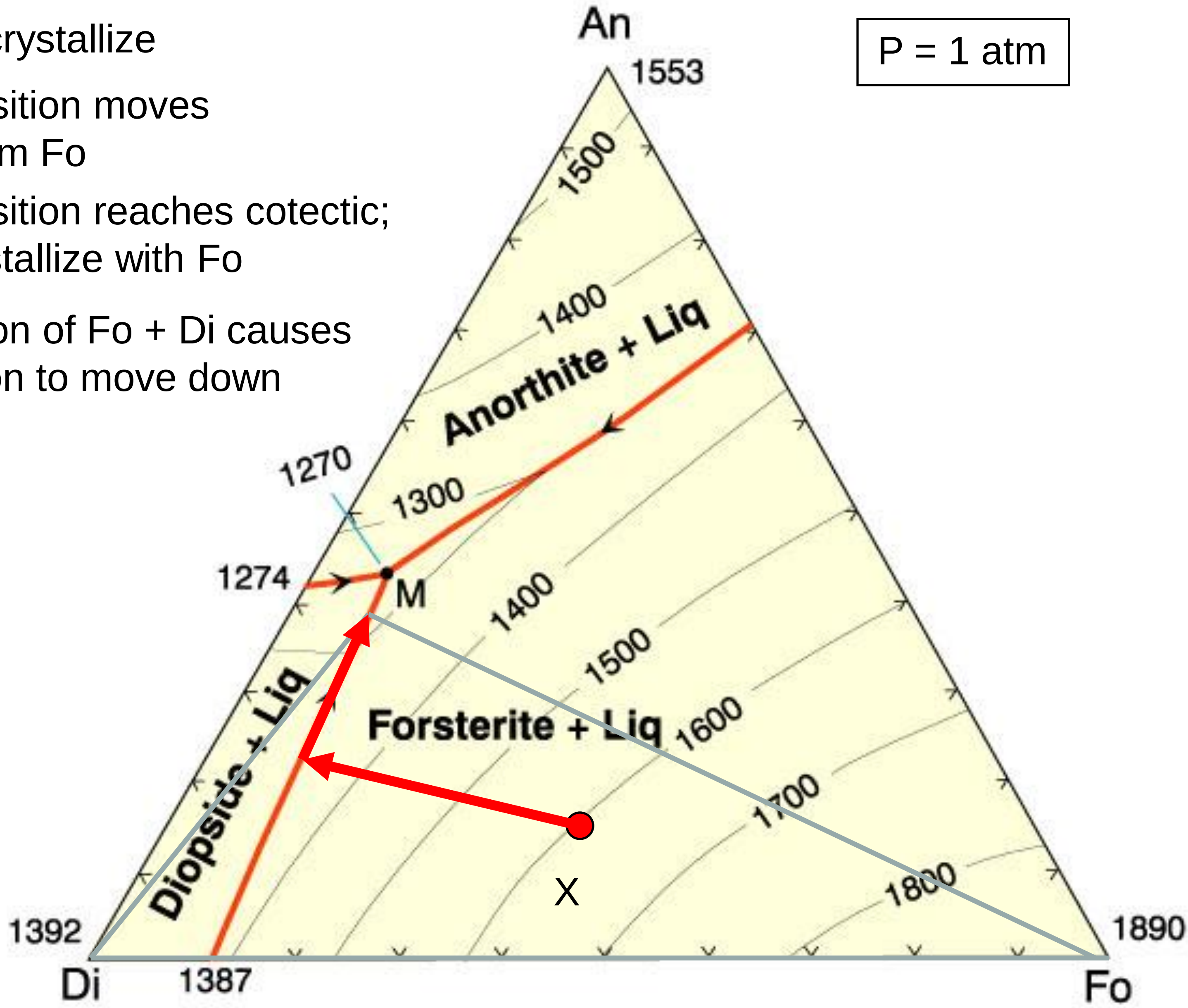
5. Co-precipitation of Fo + Di causes liquid composition to move down cotectic curve

P = 1 atm



8.13

1. For bulk composition X, liquid cools to liquidus at 1600 C

2. Fo begins to crystallize

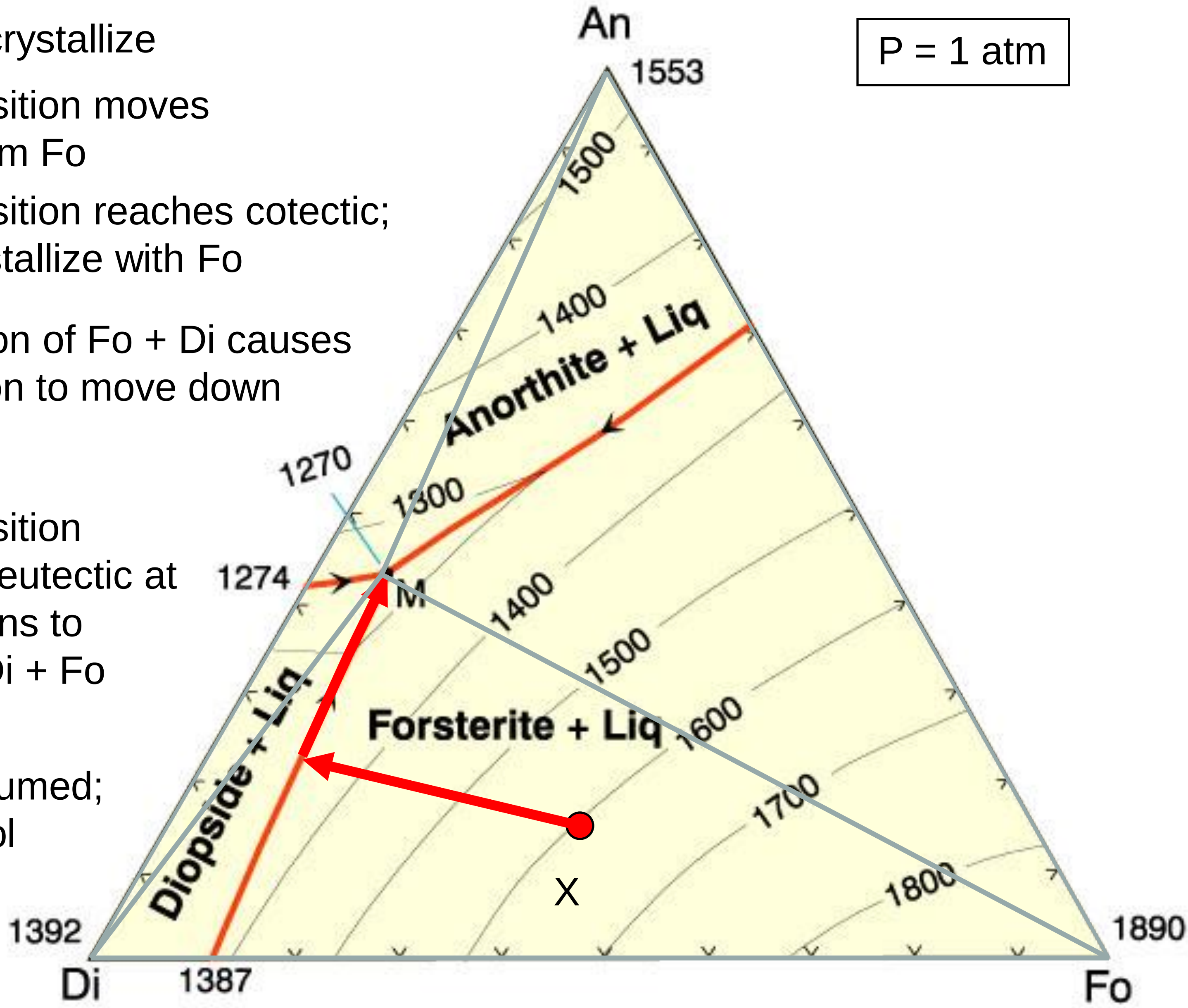
3. Liquid composition moves directly away from Fo

4. Liquid composition reaches cotectic; Di begins to crystallize with Fo

5. Co-precipitation of Fo + Di causes liquid composition to move down cotectic curve

6. Liquid composition reaches ternary eutectic at 1270 C; An begins to crystallise with Di + Fo

7. Liquid is consumed; An + Di + Fo cool below 1270 C



Classification of elements, minerals, and rocks

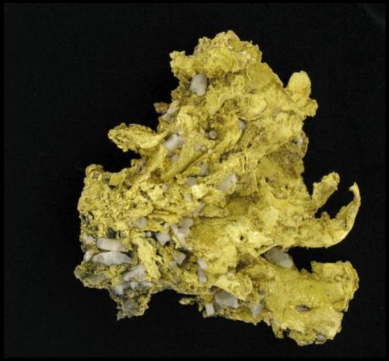
Elements i.e. Si (*silicon*)

Compounds i.e. SiO_2 (*Quartz*)

Minerals i.e. silicate oxyanions $[SiO_4]^{-4}$ *Olivine* $(Mg, Fe)_2 SiO_4$

Rocks i.e. gabbro (*Ca-plagioclase* + *pyroxene* + *olivine*)

Platinum (Pt)



Gold (Au)

Silver (Ag)

Let’s get native (rocks)

Copper (Cu)

Sulphur (S)

Carbon (C)

Igneous Rocks

Pumice

Obsidian

Scoria

Volcanic
(glassy)

Rhyolite

Andesite

Basalt

Volcanic
(fine-grained)

Granite

Diorite

Gabbro

Plutonic
(course-grained)

FELSIC

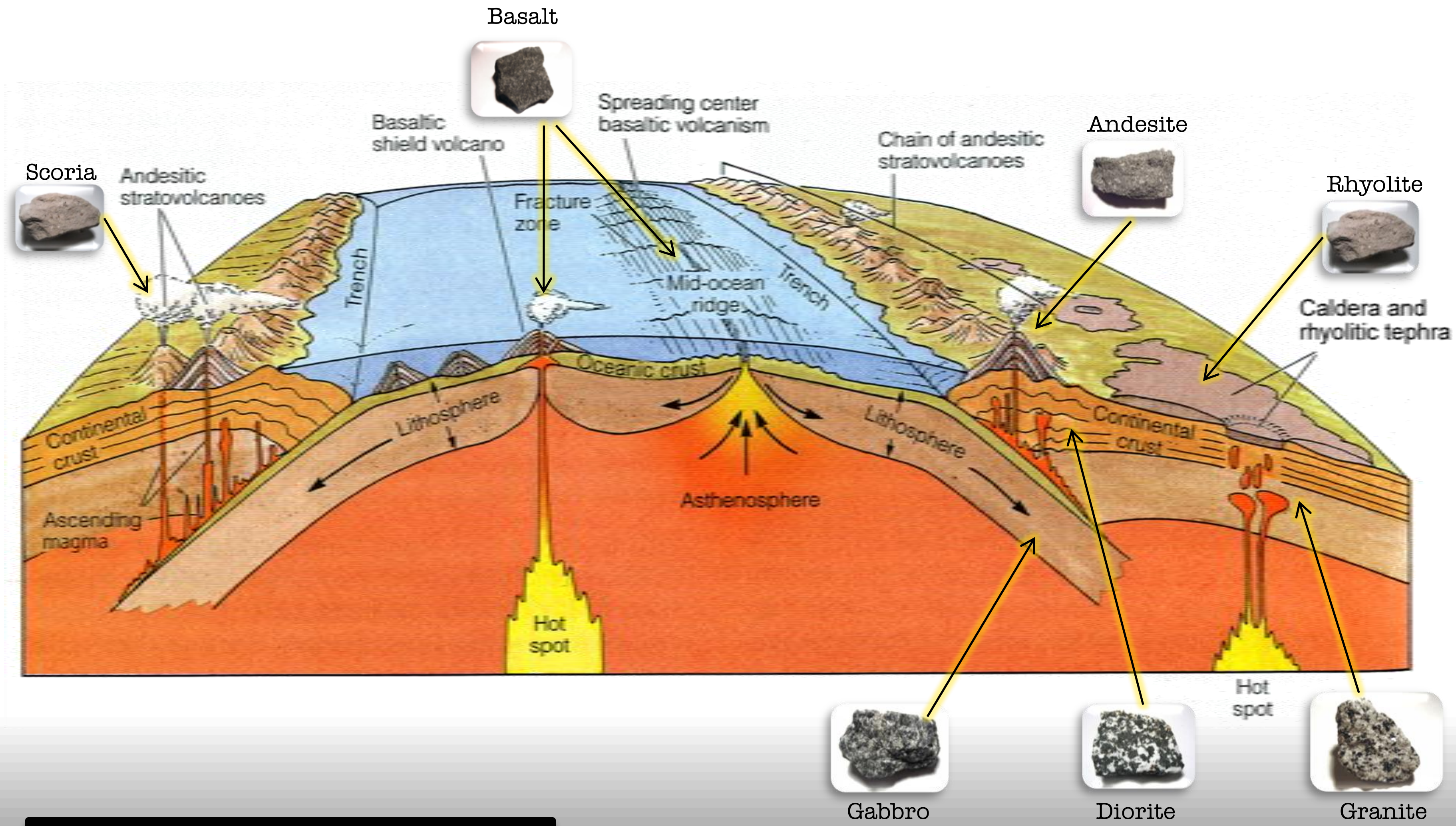
INTERMEDIATE

MAFIC

Vesicular Basalt

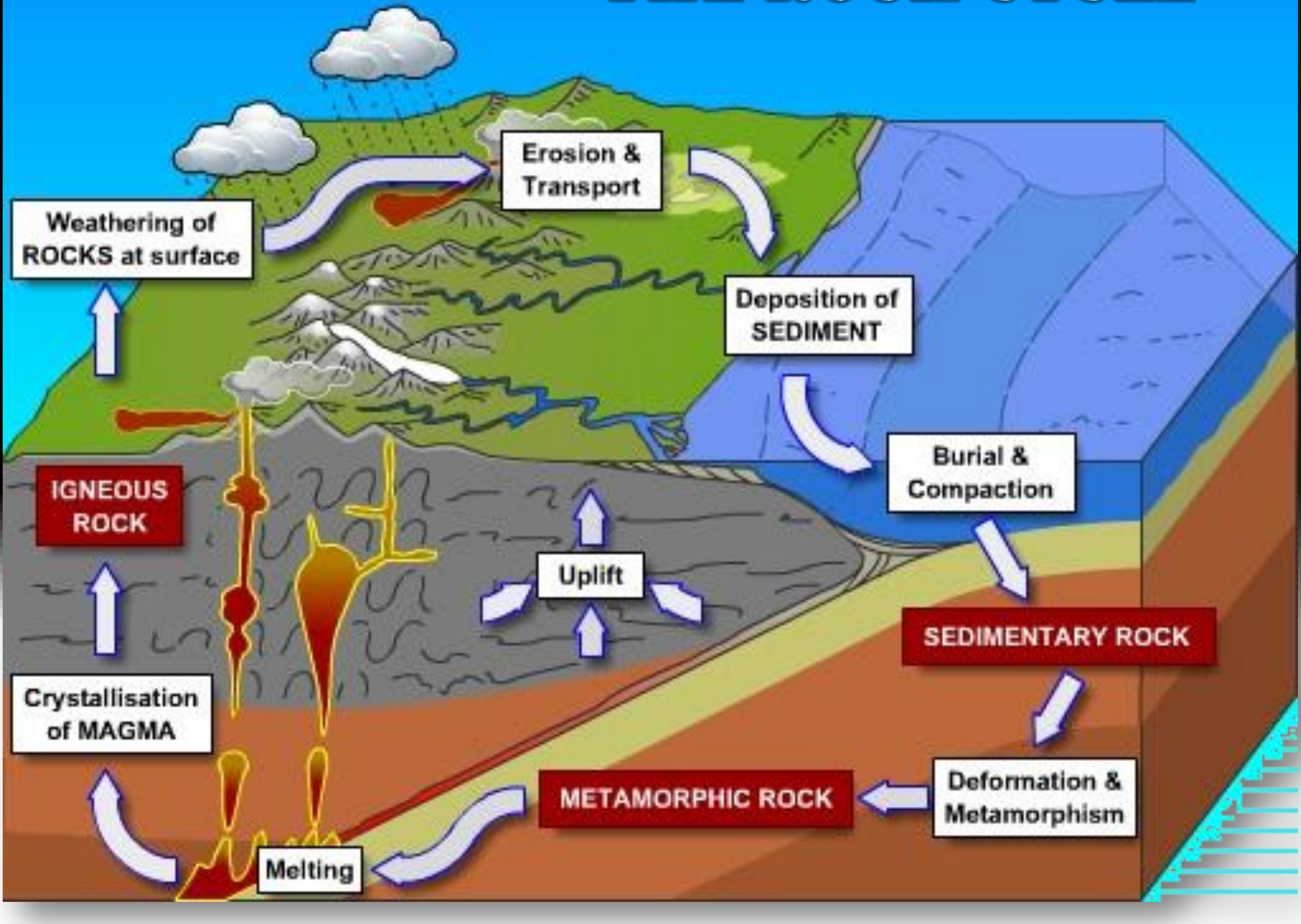
Porphiritic texture

Textures

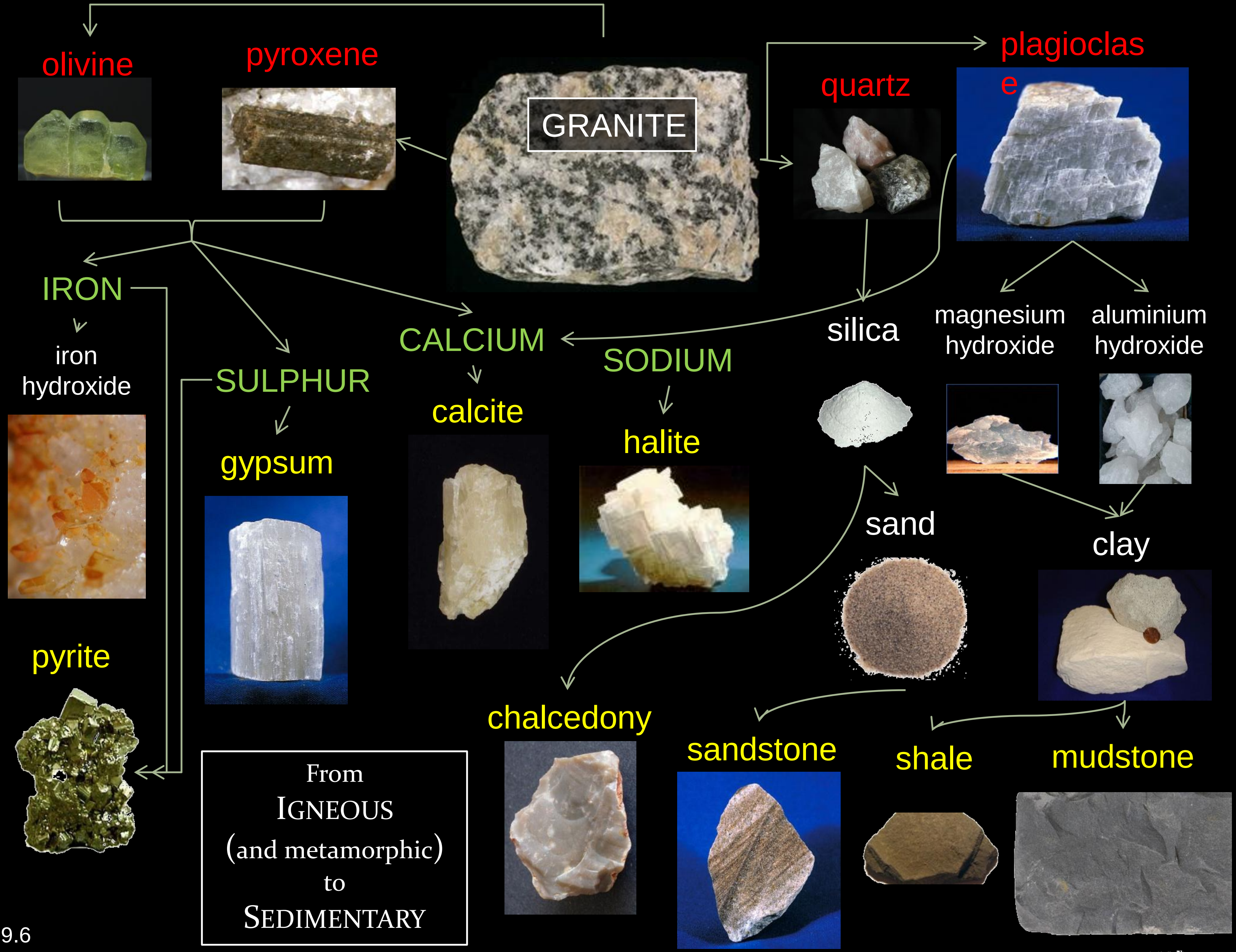


Igneous rocks production settings

THE ROCK CYCLE



From
IGNEOUS
(and metamorphic)
to
SEDIMENTARY



olivine

pyroxene

GRANITE

quartz

plagioclase

IRON

iron hydroxide

pyrite

SULPHUR

gypsum

CALCIUM

calcite

SODIUM

halite

silica

sand

chalcedony

magnesium hydroxide

aluminium hydroxide

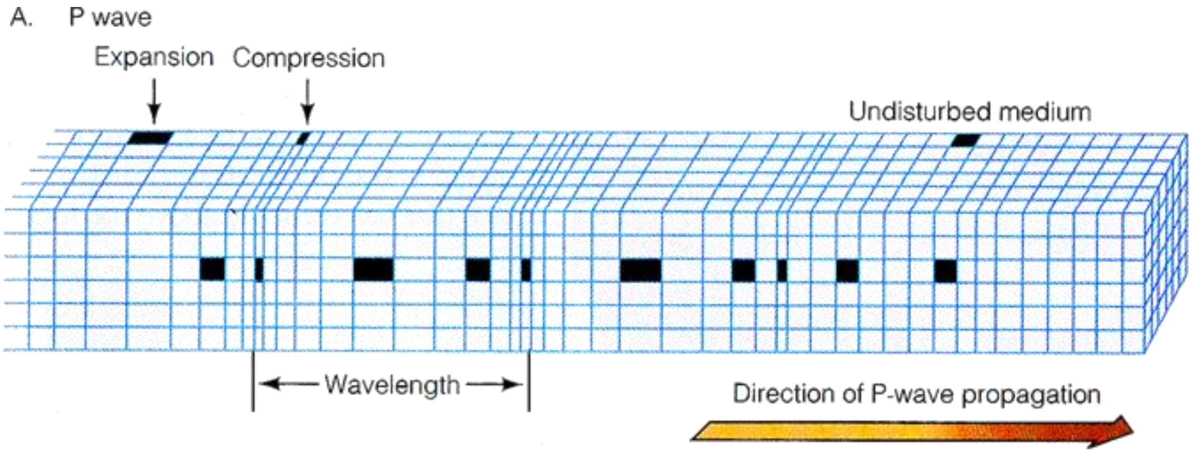
clay

sandstone

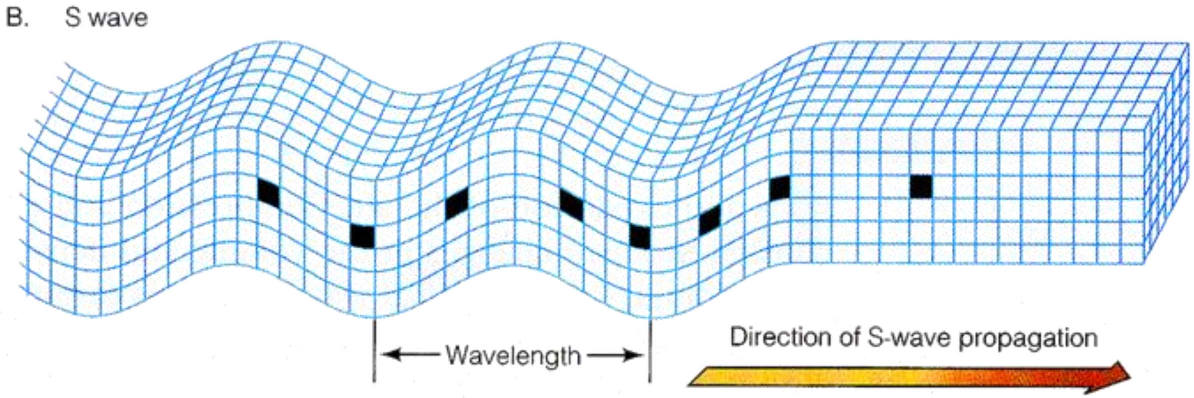
shale

mudstone

Seismic Waves…



Primary 'P' waves travel through liquids and solids and they are the first to arrive from an earthquake focus. P-wave are compressional waves (they effect volume but not shape of the effected materials).

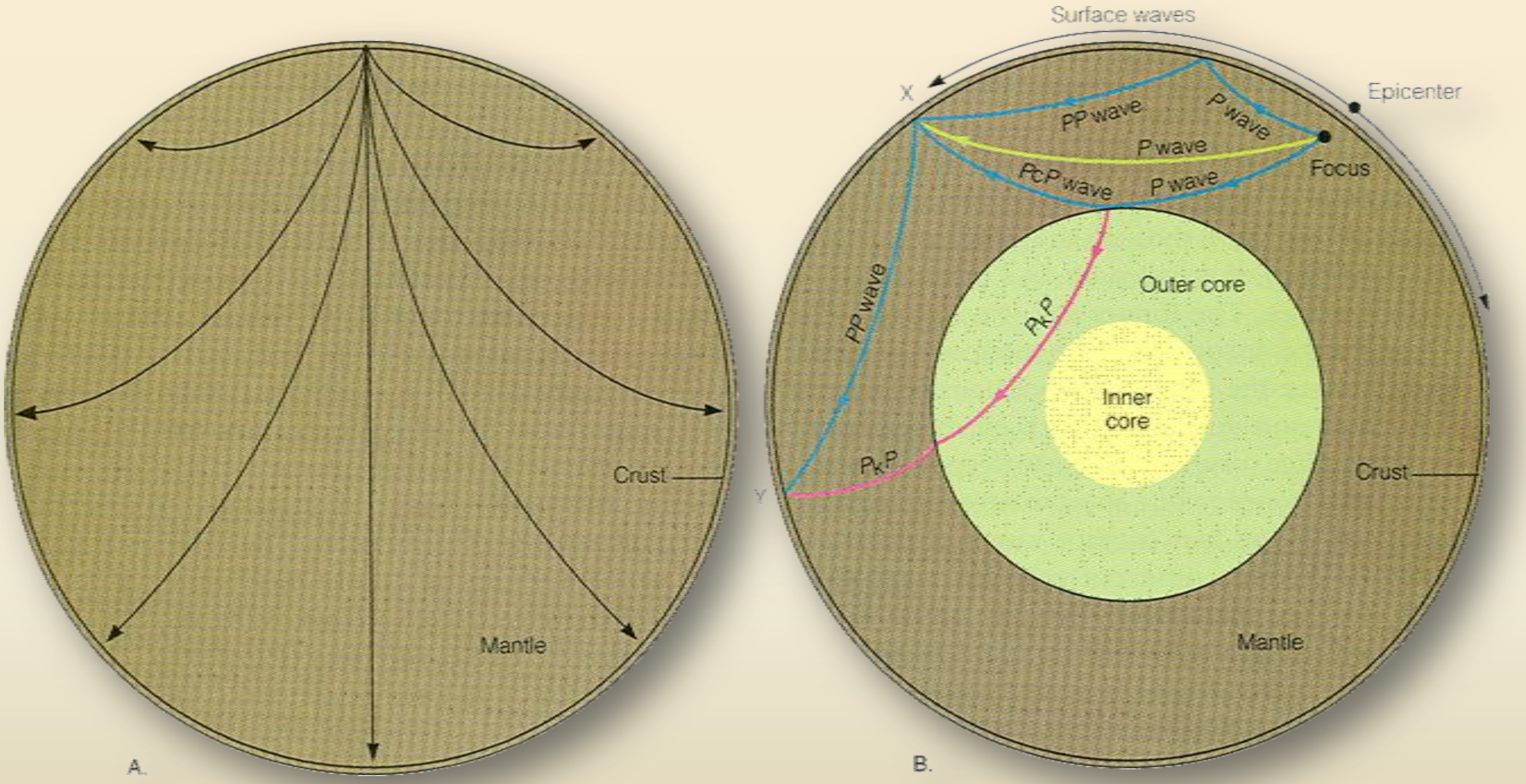


Secondary 'S' waves travel through solids only and they are nearly half as fast as the P-waves. S-waves are shear waves

Surface waves, as the name implies, pass around the Earth rather than through it, thus they are the least useful to probe the inner works of the planet. They are also last waves (i.e. being the slowest) to be detected by a seismograph.

Waves through the Earth…

Seismic body waves behave like **light waves** and **sound waves,** in so much that they can also be **reflected** and refracted through a medium. Refraction is characterised by a change in the speed and direction of the travelling wave.

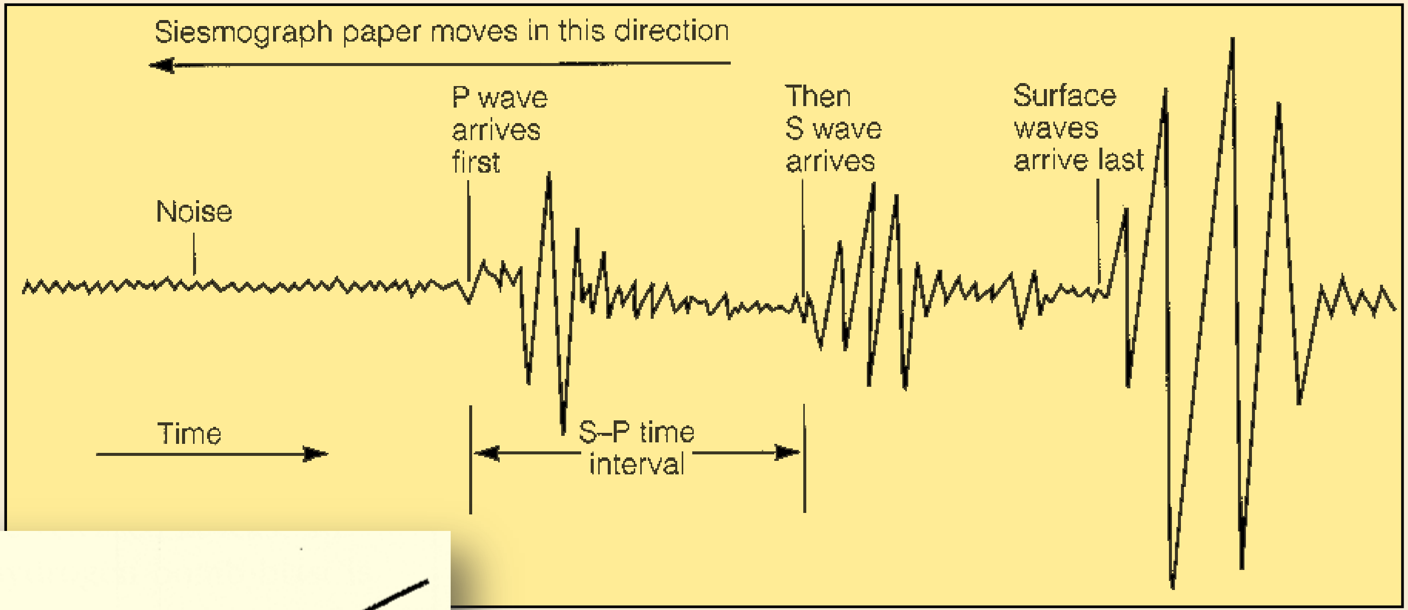


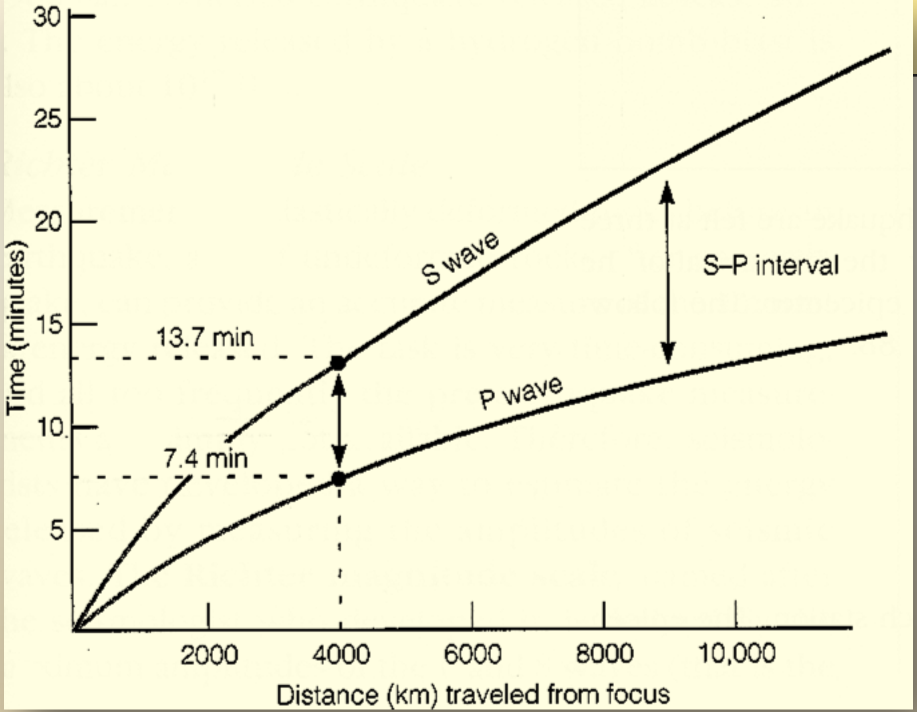
Wave speeds are a function of rock density. In a simple model of homogeneous Earth composition, increase in density due to pressure, would cause seismic waves to curve.

Inside the Earth the wave paths are indeed curved but they are also refracted (P_KP) and reflected (PcP) by several zones of sudden density changes, as the core-mantle boundary.

Reading the waves…

Working out the distance of the seismic epicentre: the delay in arrival times between P and S waves is proportional to the distance travelled by the waves.

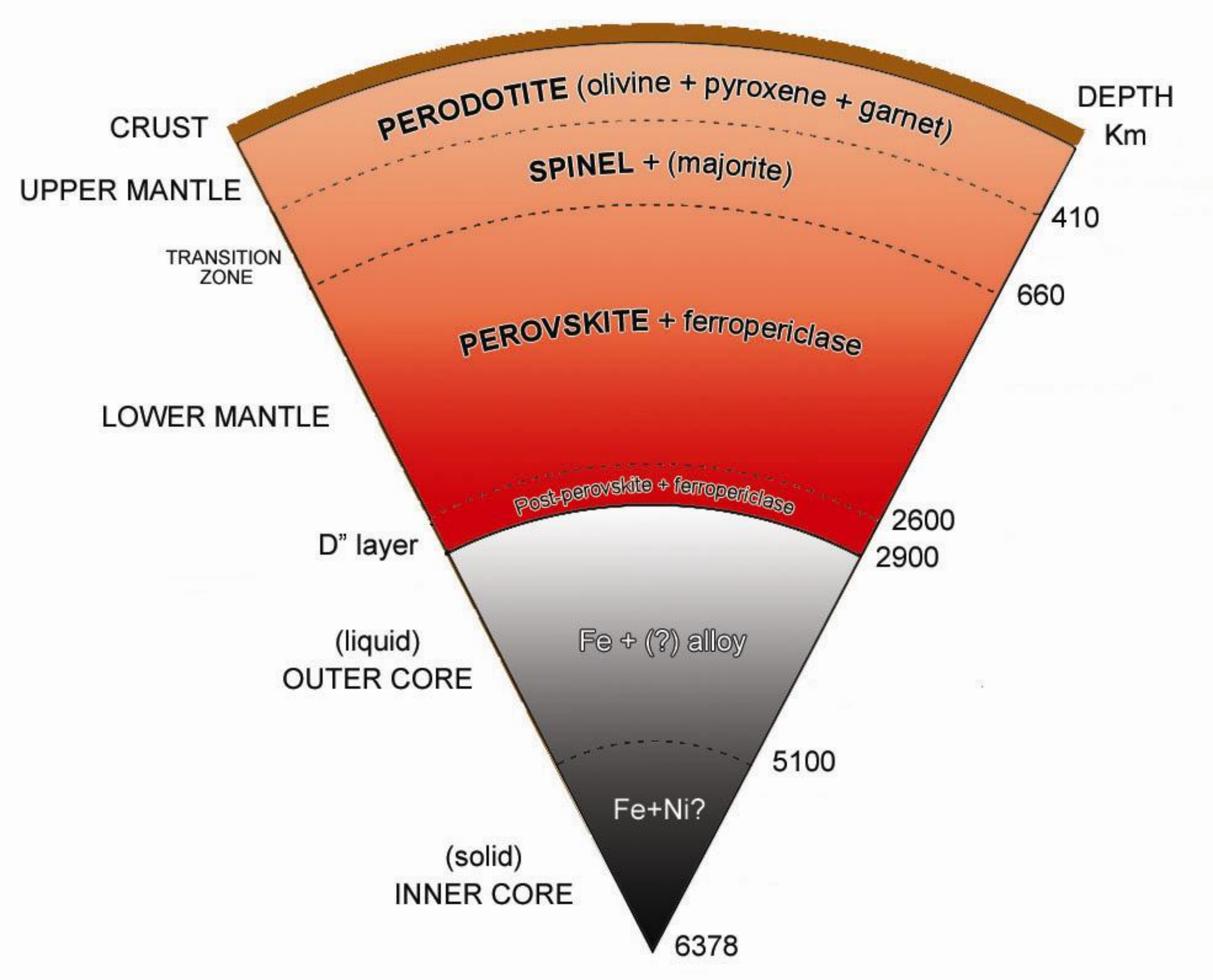




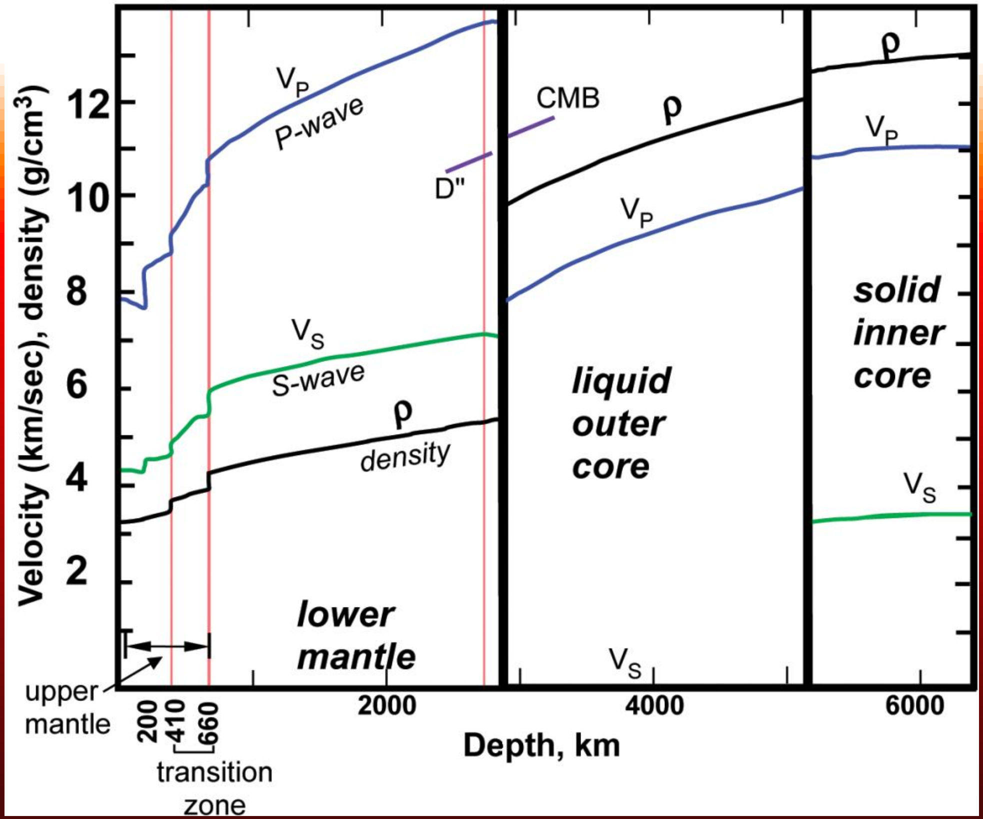
An example:

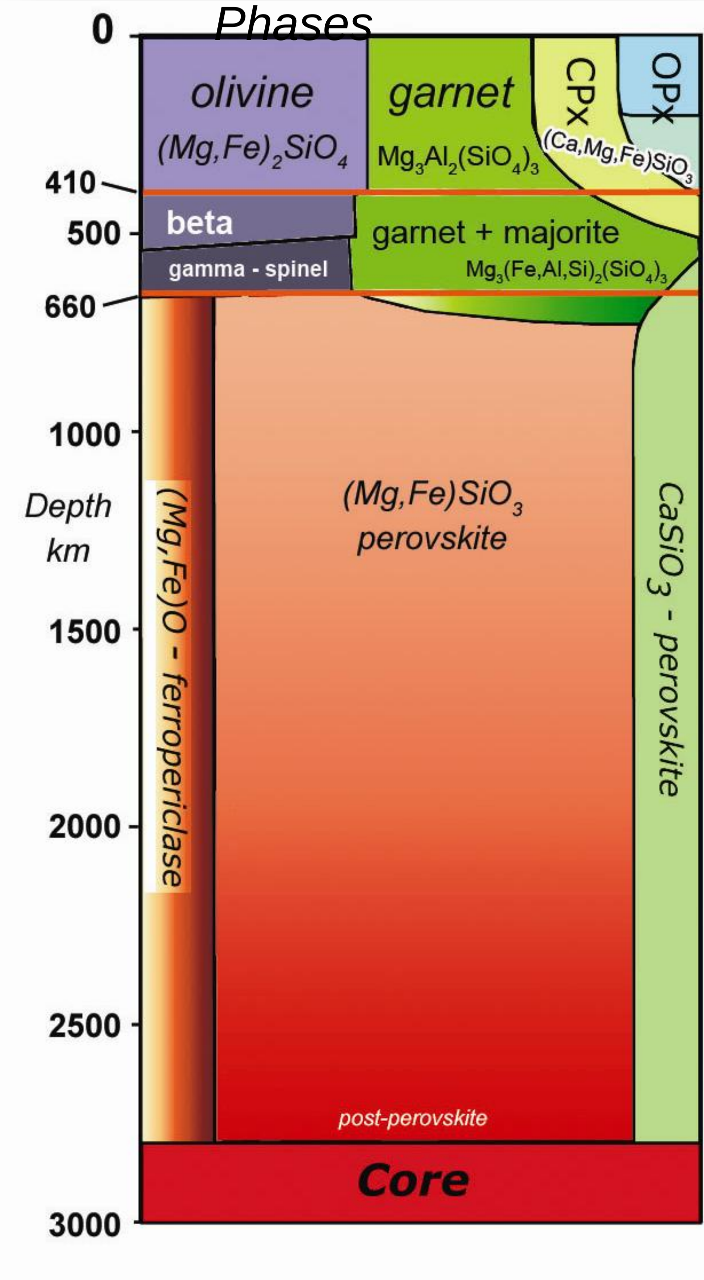
seismologists measure a difference in P and S waves arrival times of 6.3 minutes, which when related to the average speed of seismic waves travelling through crustal materials, give us an estimated distance from the epicentre of 4000 km.

The Composition of the Earth's layers

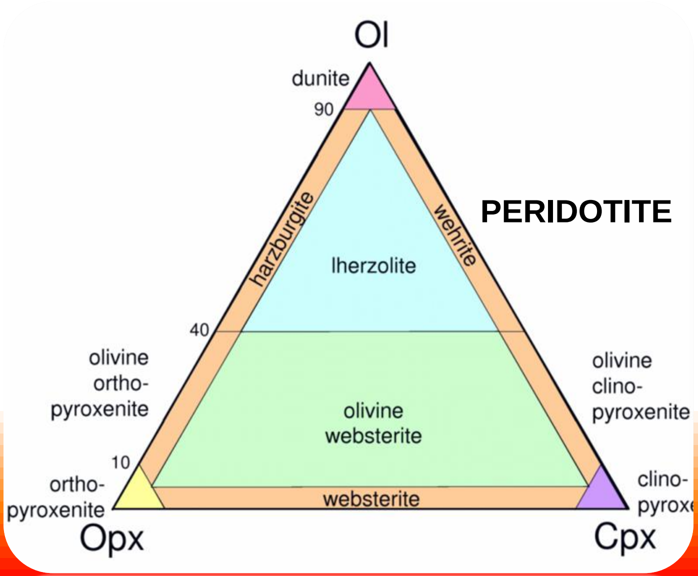


% Minerals / Phases



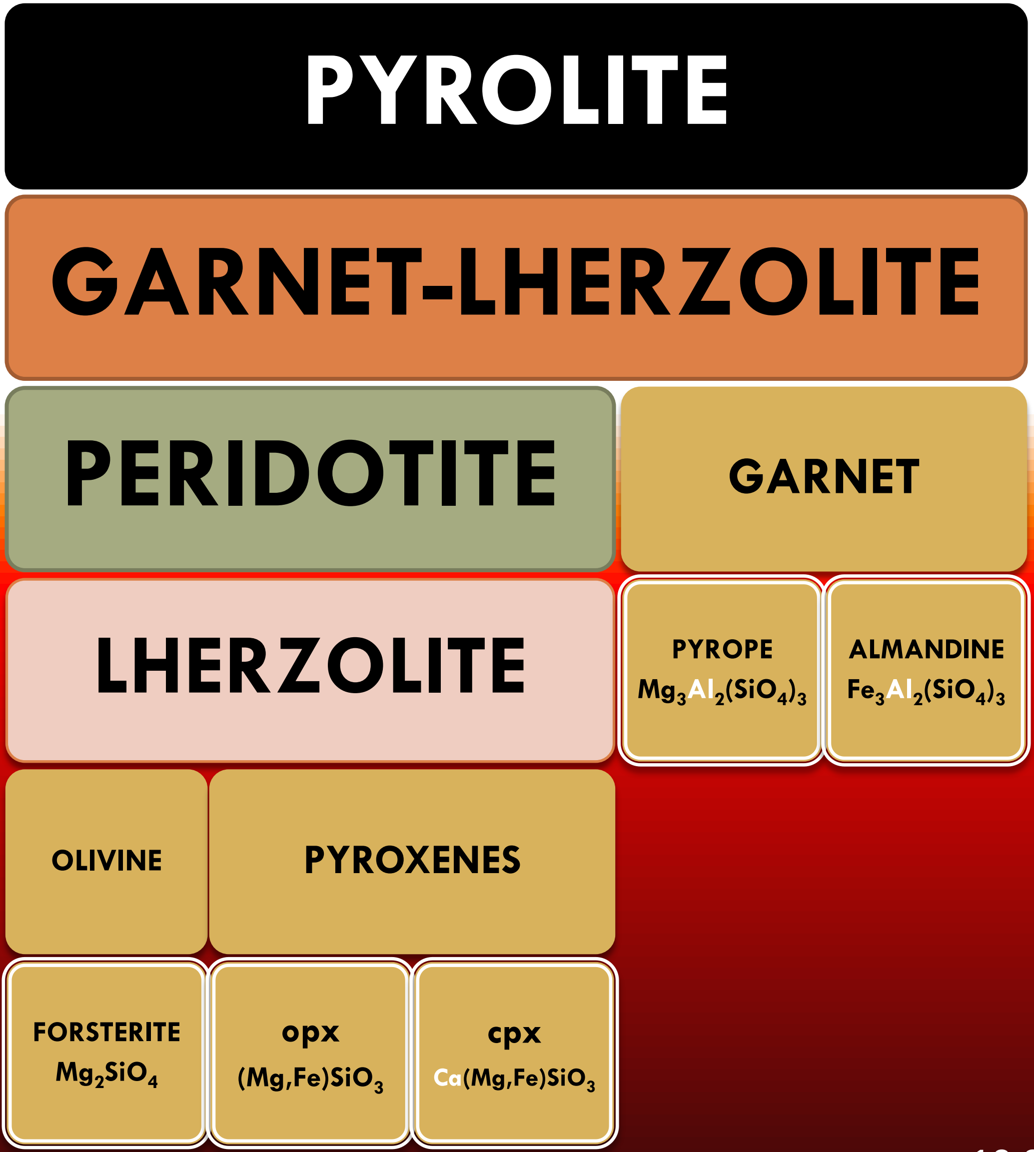


The typical rock type of the ***top 200 km*** upper mantle is described as **PYROLITE** – a source of most erupting magmas; it can be described as the equivalent to:



"Pyrolite is an olivine-rich rock that, upon equilibrium partial melting, yields the great volumes of basalt that underlie the world's ocean basins".

In the pyrolite mantle model, the olivine component in lherzolite is about 55-60%



PYROLITE

GARNET-LHERZOLITE

PERIDOTITE

GARNET

LHERZOLITE

PYROPE
$Mg_3Al_2(SiO_4)_3$

ALMANDINE
$Fe_3Al_2(SiO_4)_3$

OLIVINE

PYROXENES

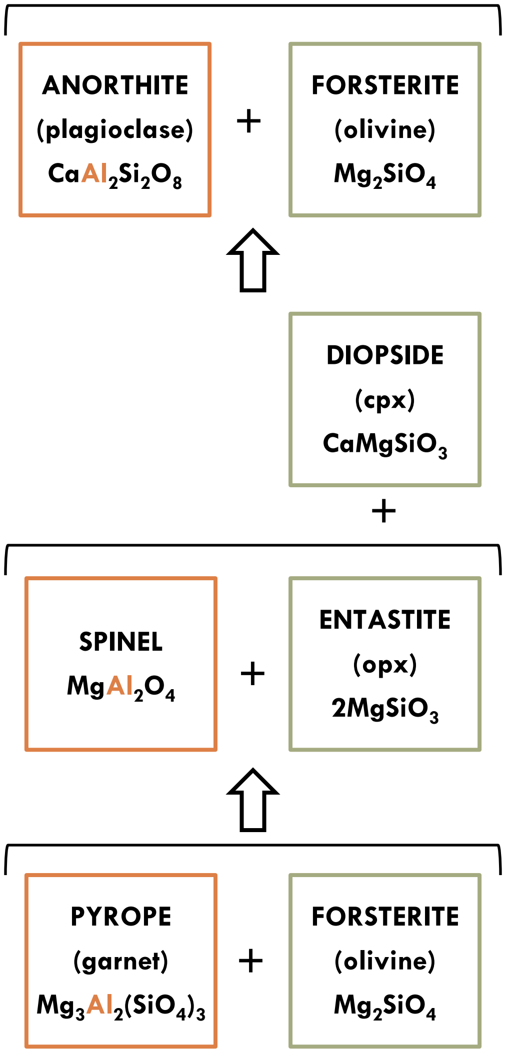
FORSTERITE
Mg_2SiO_4

opx
$(Mg,Fe)SiO_3$

cpx
$Ca(Mg,Fe)SiO_3$

TOP 100 Km: lherzolite

The peridotite phase diagram shows that partial melting, and hence magma generation, is linked to decompression associated with large-scale flow processes within the mantle.



ANORTHITE (plagioclase) $CaAl_2Si_2O_8$ + **FORSTERITE** (olivine) Mg_2SiO_4

⇧

DIOPSIDE (cpx) $CaMgSiO_3$

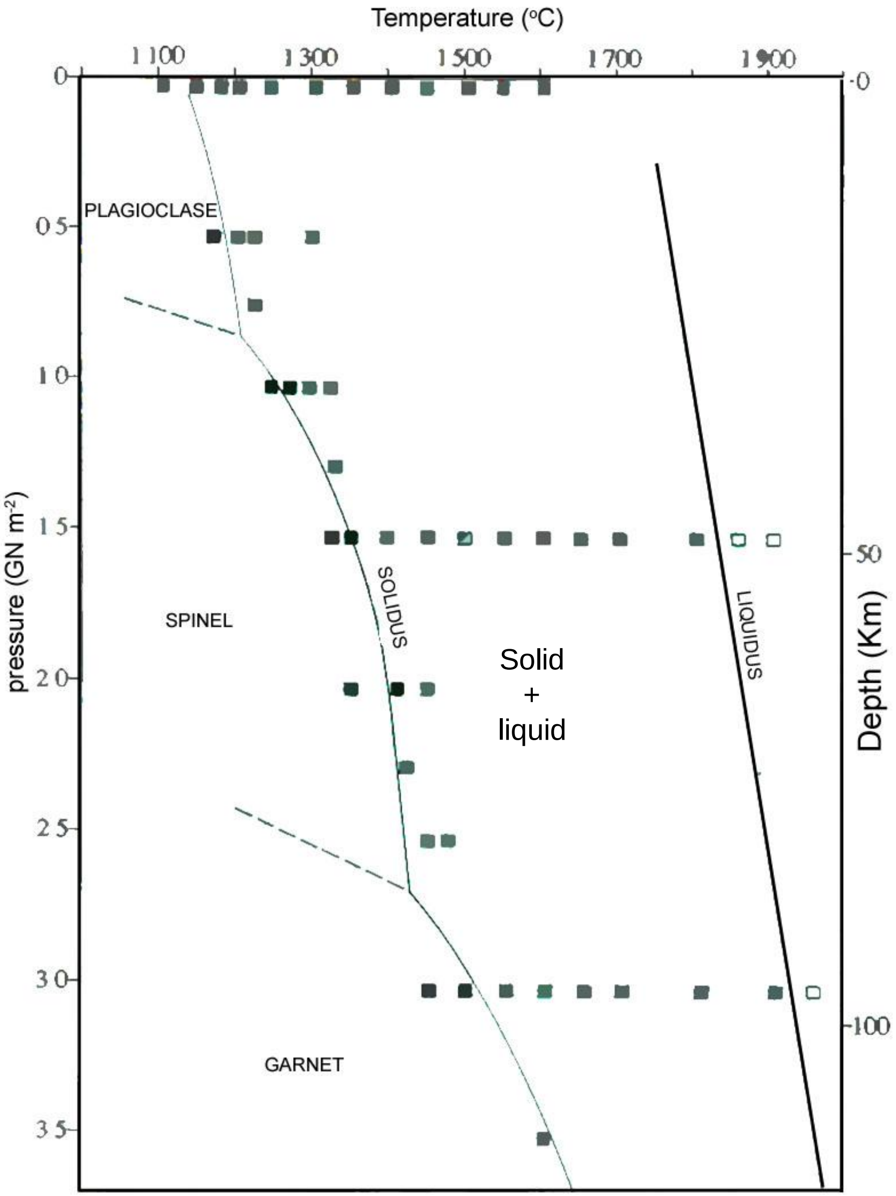
+

SPINEL $MgAl_2O_4$ + **ENTASTITE** (opx) $2MgSiO_3$

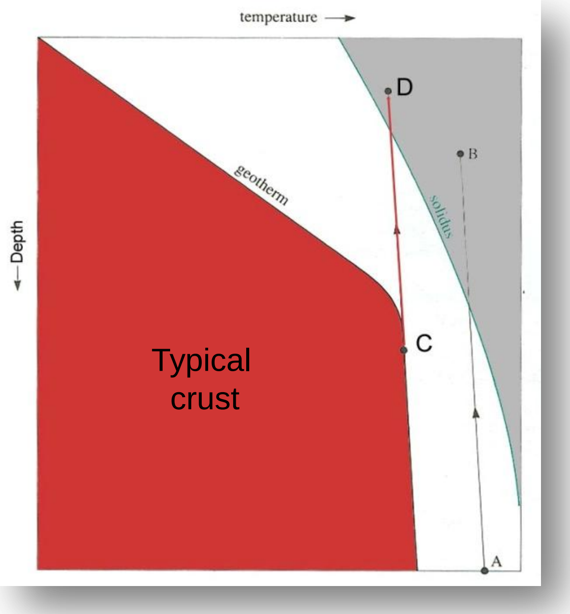
⇧

PYROPE (garnet) $Mg_3Al_2(SiO_4)_3$ + **FORSTERITE** (olivine) Mg_2SiO_4

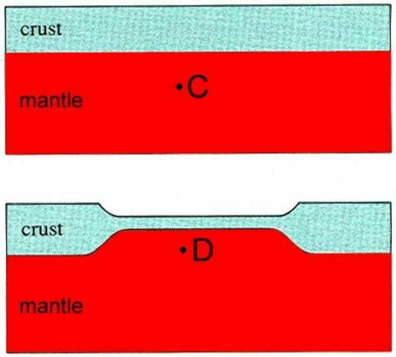
The identity of the **Al**-bearing phase depends on **pressure.** Although the **chemical composition** of the rock remains the same, the **mineralogy** is pressure-dependent

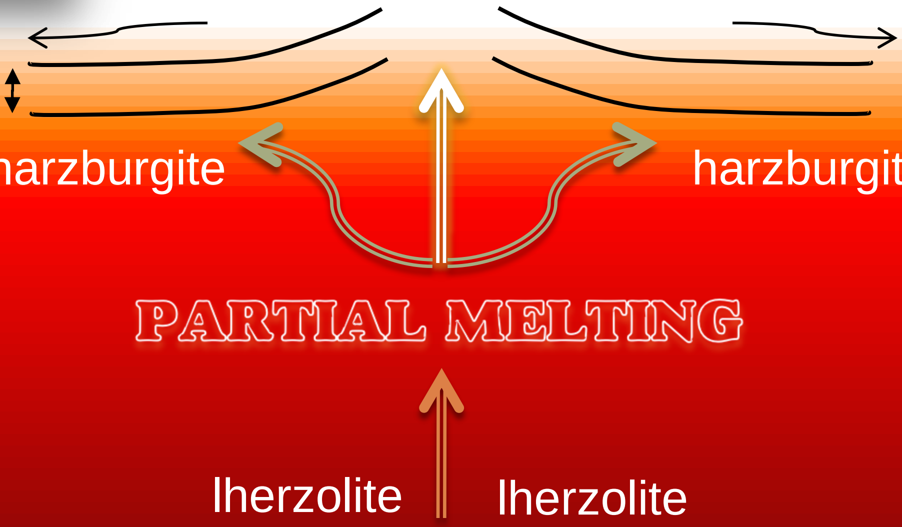


Phase diagram of typical lherzolites:
garnet-lherzolite
spinel-lherzolite
plagioclase-lherzolite



Typical geotherm boundary for typical crust. Path CD relates to the upwelling of mantle caused by crustal stretching and mantle divergence.





basalt

basaltic ocean crust

harzburgite

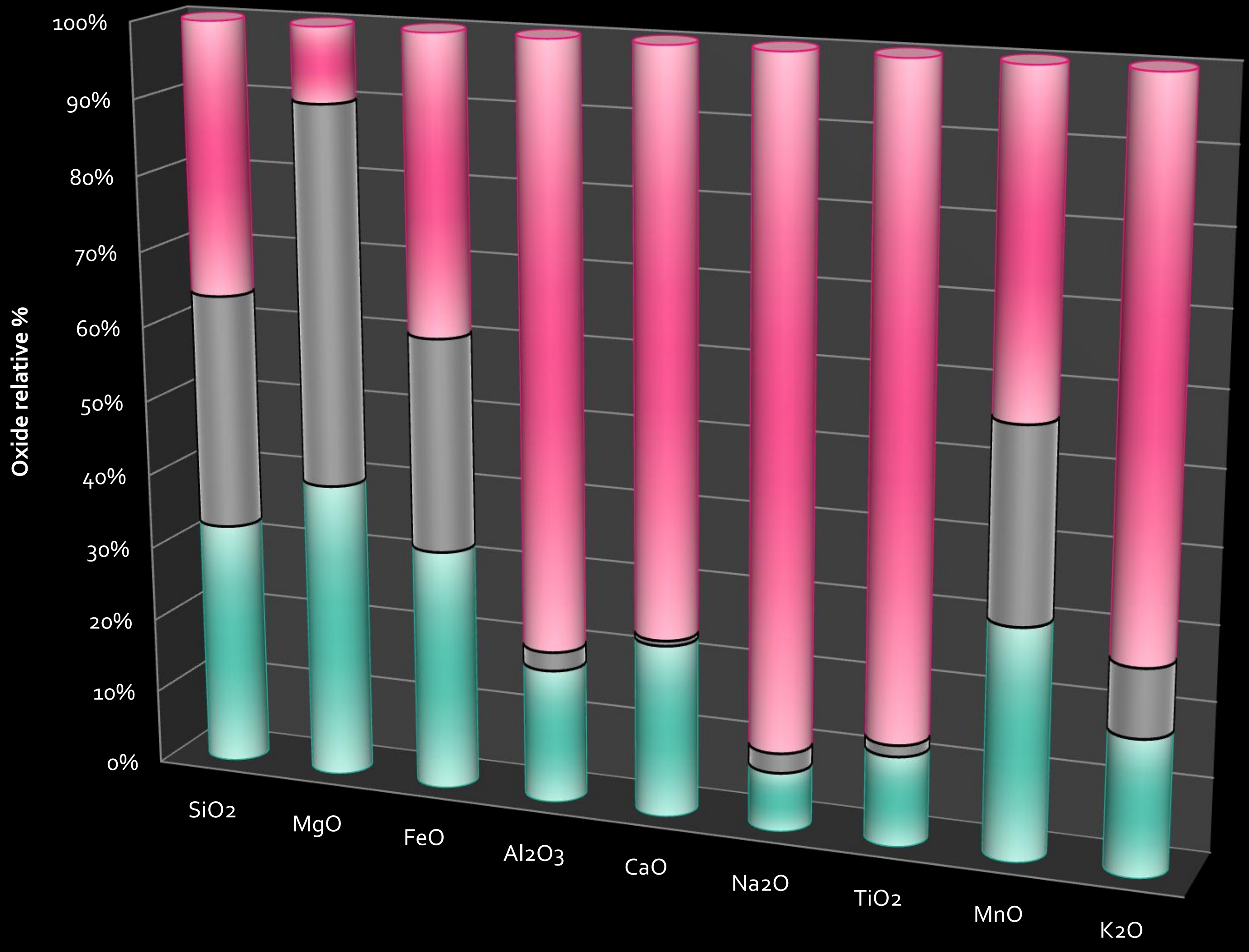
harzburgite

PARTIAL MELTING

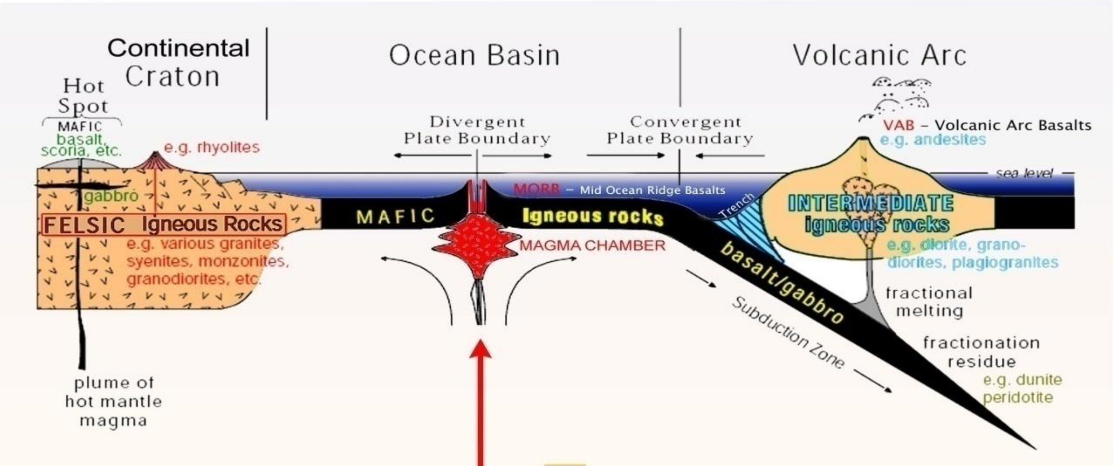
lherzolite

lherzolite

At constructive plate margins **lherzolite-peridotite** from within the upper mantle rises and partially melts to produce basalt magma and complementary residual **harzburgite-peridotite**.

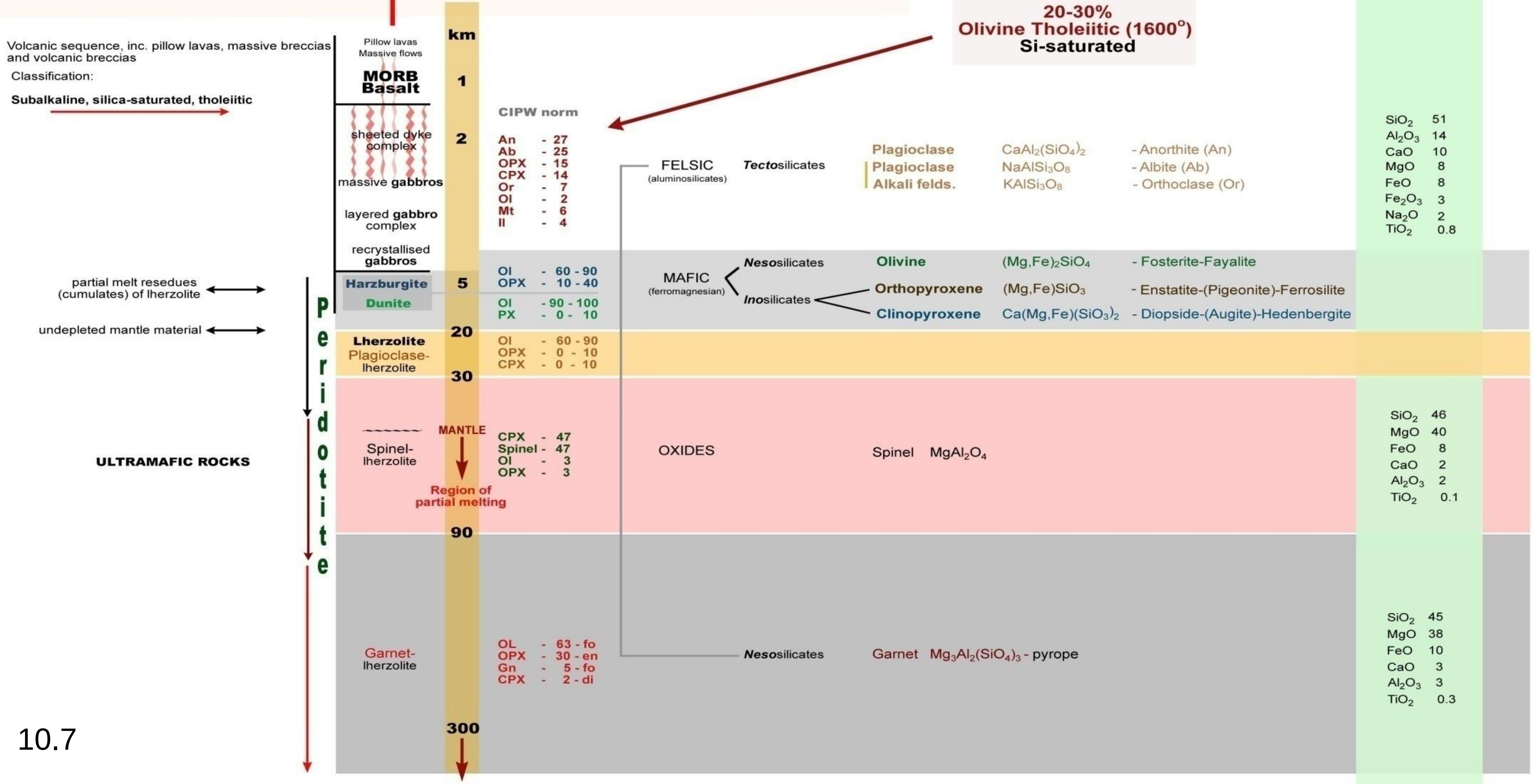


	SiO_2	MgO	FeO	Al_2O_3	CaO	Na_2O	TiO_2	MnO	K_2O
🟥 Basalt	48.80	9.70	9.80	15.90	11.20	3.40	1.15	0.17	0.08
⬛ Harzburgite	42.30	49.60	7.10	0.50	0.10	0.10	0.02	0.10	0.01
🟩 Lherzolite	44.50	39.20	8.10	3.60	3.40	0.30	0.16	0.12	0.02



Depending on degree (%) of melting (related to T and p), different basalts are produced:

	CIPW norm	OXIDES
15% **Alkali olivine basalts (1500°)** **Si-undersaturated**	CPX - 33.0 Ol - 27.0 An - 27.0 Or - 2.0	SiO_2 44 MgO 12 FeO 14 CaO 14 Al_2O_3 13 TiO_2 1.4
40-60% **komatiitic (1700°)** **Si-oversaturated**	Ol - 48.0 OPX - 24.0 CPX - 13.0 An - 9.0 Ab - 4.0 Or - 1.0	SiO_2 46 MgO 27 FeO 15 CaO 5 Al_2O_3 5 TiO_2 0.5
20-30% **Olivine Tholeiitic (1600°)** **Si-saturated**	An - 27 Ab - 25 OPX - 15 CPX - 14 Or - 7 Ol - 2 Mt - 6 Il - 4	SiO_2 51 Al_2O_3 14 CaO 10 MgO 8 FeO 8 Fe_2O_3 3 Na_2O 2 TiO_2 0.8



Volcanic sequence, inc. pillow lavas, massive breccias and volcanic breccias

Classification:

Subalkaline, silica-saturated, tholeiitic

partial melt resedues (cumulates) of lherzolite

undepleted mantle material

ULTRAMAFIC ROCKS

Peridotite

km

Pillow lavas
Massive flows
MORB Basalt
1

sheeted dyke complex
2
massive **gabbros**
layered **gabbro** complex
recrystallised **gabbros**

CIPW norm

An - 27
Ab - 25
OPX - 15
CPX - 14
Or - 7
Ol - 2
Mt - 6
Il - 4

Harzburgite
5
Ol - 60 - 90
OPX - 10 - 40

Dunite
Ol - 90 - 100
PX - 0 - 10

20
Lherzolite
Plagioclase-lherzolite
Ol - 60 - 90
OPX - 0 - 10
CPX - 0 - 10
30

MANTLE
Region of partial melting

Spinel-lherzolite
CPX - 47
Spinel - 47
Ol - 3
OPX - 3

90

Garnet-lherzolite
OL - 63 - fo
OPX - 30 - en
Gn - 5 - fo
CPX - 2 - di

300

FELSIC (aluminosilicates)	***Tecto*silicates**	**Plagioclase**	$CaAl_2(SiO_4)_2$	- Anorthite (An)
		Plagioclase	$NaAlSi_3O_8$	- Albite (Ab)
		Alkali felds.	$KAlSi_3O_8$	- Orthoclase (Or)
MAFIC (ferromagnesian)	***Neso*silicates**	**Olivine**	$(Mg,Fe)_2SiO_4$	- Fosterite-Fayalite
	***Ino*silicates**	**Orthopyroxene**	$(Mg,Fe)SiO_3$	- Enstatite-(Pigeonite)-Ferrosilite
		Clinopyroxene	$Ca(Mg,Fe)(SiO_3)_2$	- Diopside-(Augite)-Hedenbergite
OXIDES		Spinel	$MgAl_2O_4$	
	***Neso*silicates**	Garnet	$Mg_3Al_2(SiO_4)_3$	- pyrope

OXIDES

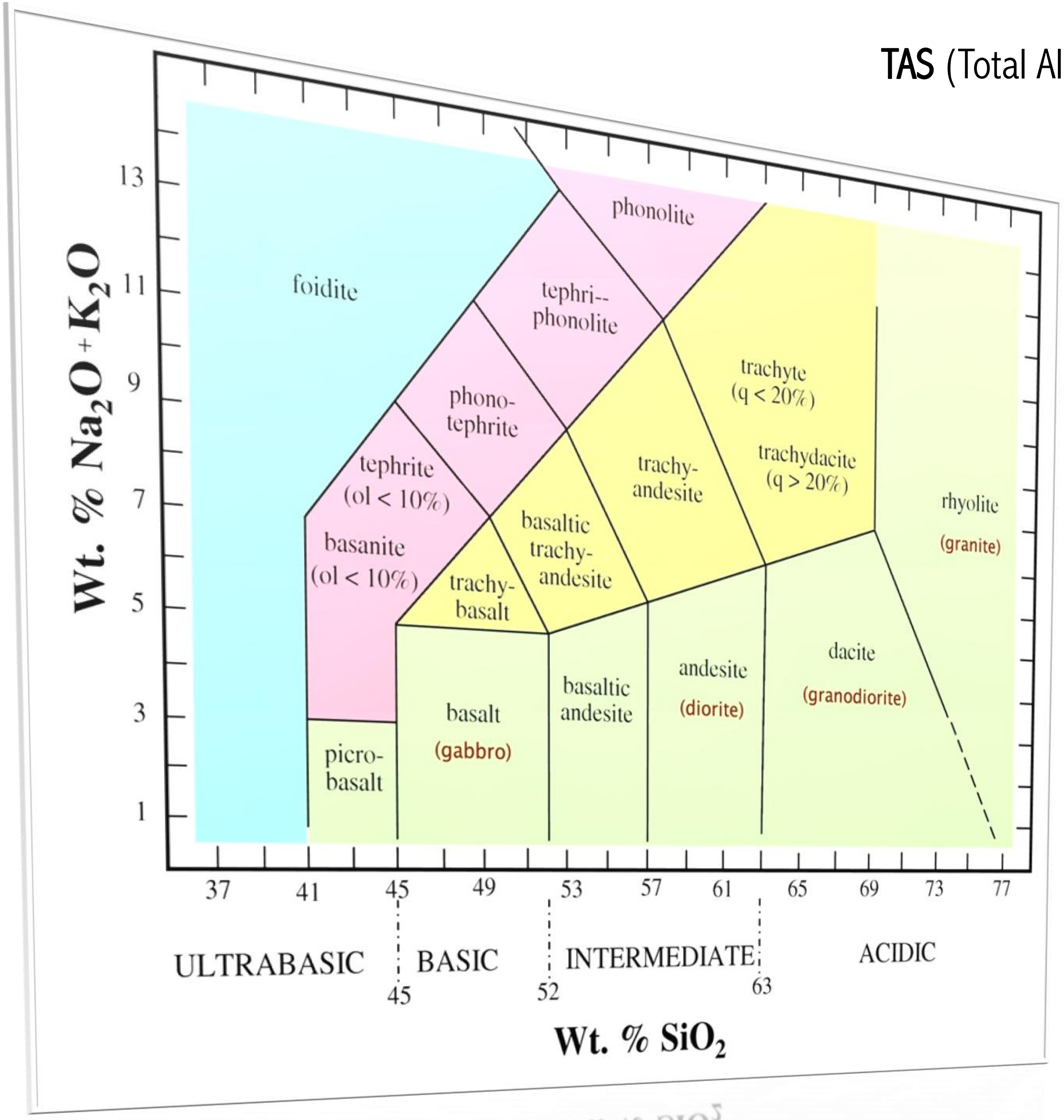
Spinel-lherzolite:
SiO_2 46
MgO 40
FeO 8
CaO 2
Al_2O_3 2
TiO_2 0.1

Garnet-lherzolite:
SiO_2 45
MgO 38
FeO 10
CaO 3
Al_2O_3 3
TiO_2 0.3

The major division of *volcanic rocks* is based on the **alkali** (Na_2O + K_2O) and **silica** (SiO_2) content.

	SUBALKALINE		**ALKALINE**
Silica-	**saturated**		**under-saturated**
% per annum	88		12
*Common representative **minerals***	*Pyroxenes:* Augite (cpx) + Hypersthene (opx) [$(Mg,Fe)Si_2O_6$] + small free *quartz* + *plagioclase* phenocrysts, some in matrix		*Pyroxene*: Augite (cpx) + *olivine* (forsterite) + *nepheline/leucite*
	THOLEIITIC	**CALC-ALKALINE**	
% per annum	73	15	12
*Specific Representative **minerals***		*Hornblende* (inosilicate - dark amphibole *Biotite* (phyllosilicate - mica) Phenocrysts	
*Main (**mode**) parameters*	*Fe*-rich 45-63% *SiO_2* *Very low* contents of K, Ba, P, Sr, U, Th and Zr *Low* Fe_2O_3/FeO and K_2O/Na_2O, *Low* initial Sr^{87}/Sr^{86} ratios	*Fe*-poor *Hydrous* Higher *alumina* content (16-20 %) 48-75% *SiO_2* Higher *oxygen* fugacity	
Petro-Settings	Low-ρ / high degree of melting	High-ρ / low degree of melting	
Where they are found	Submarine volcanism at mid-ocean ridges. Middle Oceanic Ridge Basalts (**MORB**) are the most common volcanic rocks. MORBs are a low incompatible-element variety of tholeiites	Above subduction zones, commonly on volcanic arcs, and particular on those arcs on continental crust (**VAB**) Andean type volcanism. Lavas are dominantly andesite with sub-ordinate calc-alkaline basalts. Lavas show a characteristically increasing alkalinity continent inwards.	Oceanic Islands (**OIB**), hot spots. Intra-continental volcanoes.
	In mature island arcs there is a progression from tholeiitic to calc-alkali to alkaline series from the oceanic to the continental side.		

TAS (Total Alkali Silica) diagram



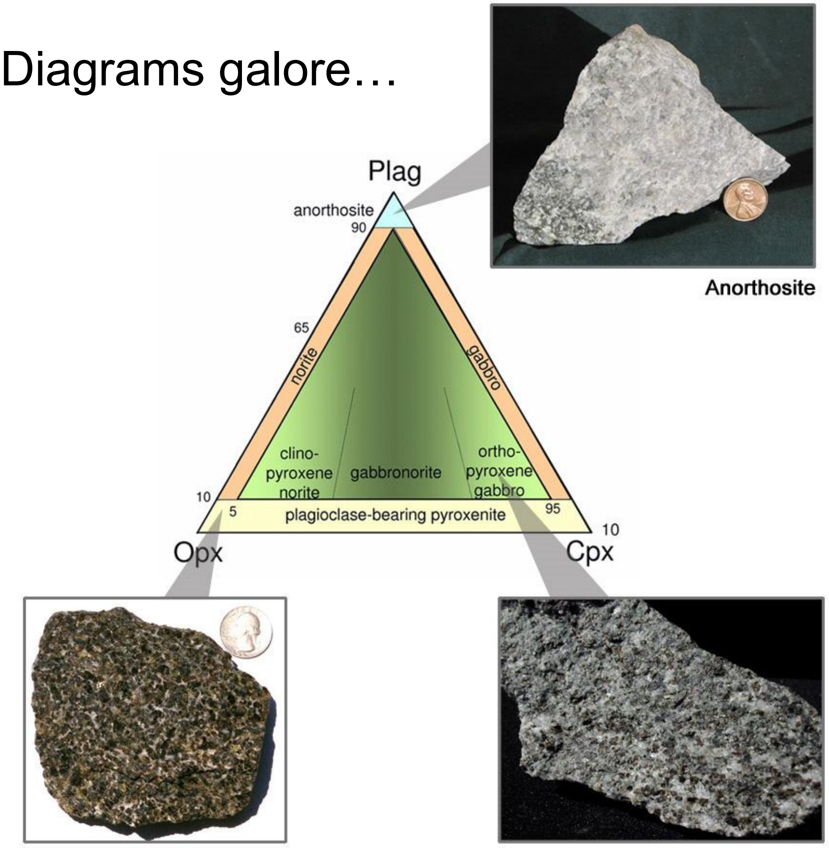
RED = Intrusive
BLACK = Extrusive

Rock series

🟩 Tholeiitic/ Calc-alkaline

🟨
🟥 Alkaline

Diagrams galore…

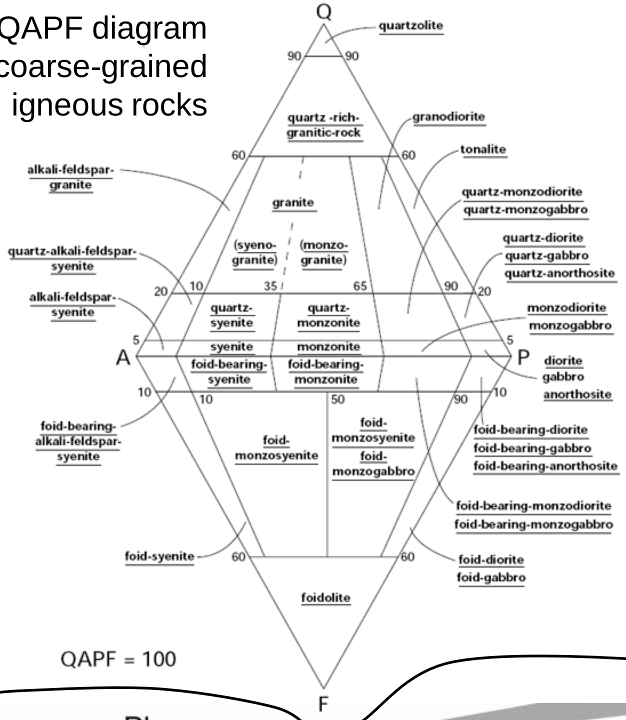


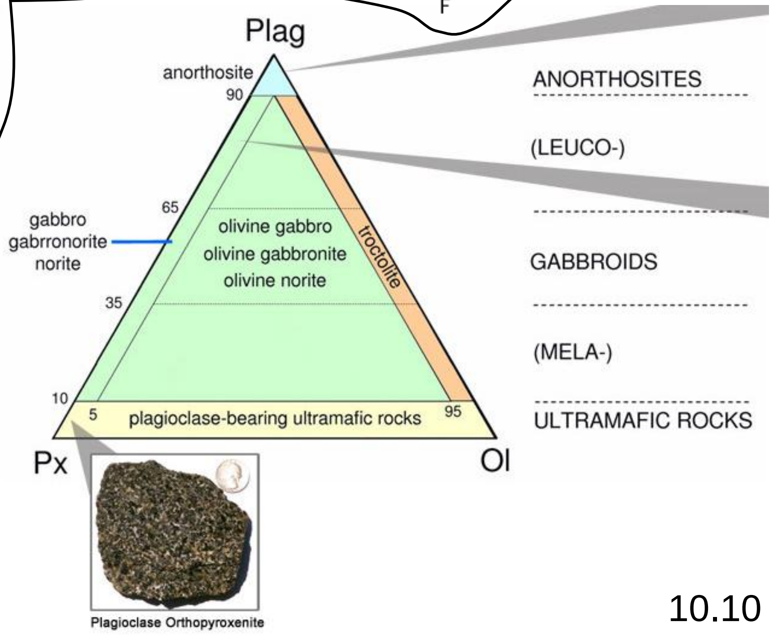
Anorthosite

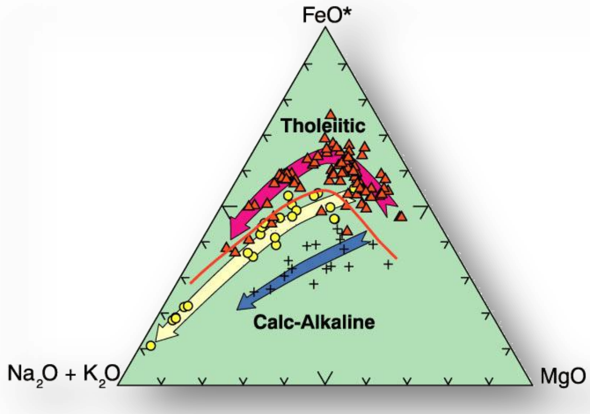
Plagioclase Orthopyroxenite

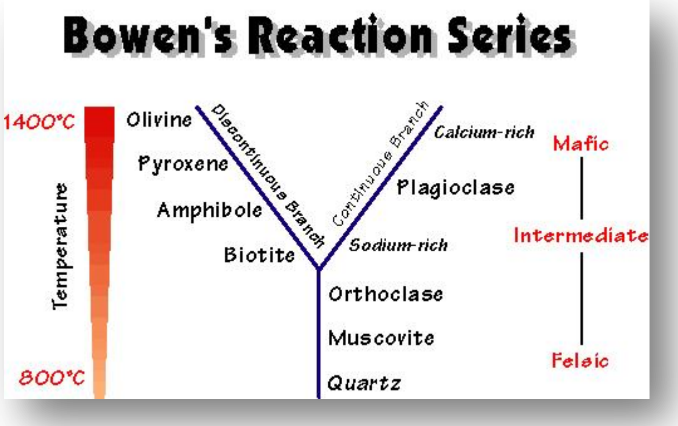
Orthopyroxene Gabbro

QAPF diagram of coarse-grained igneous rocks





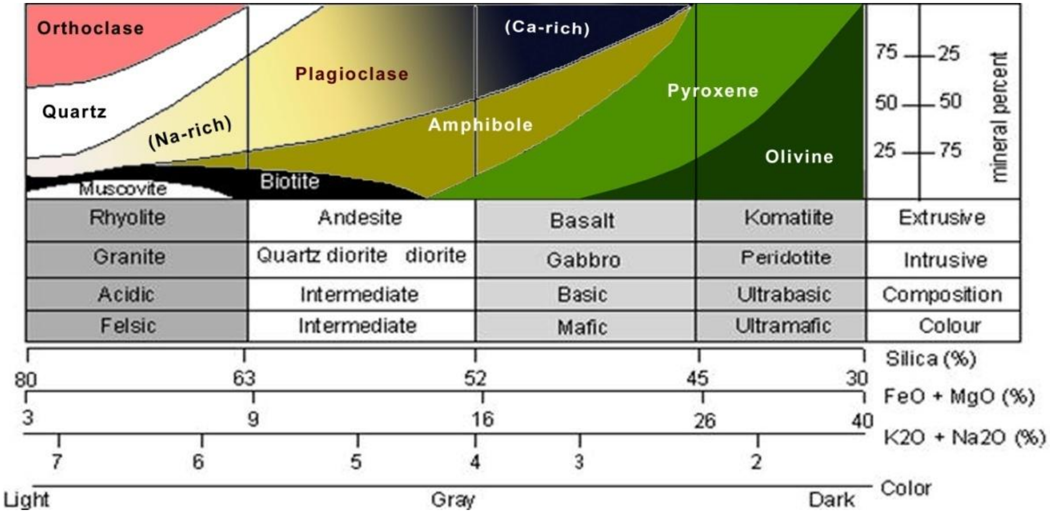




Crystallisation sequence: Discontinuous branch and continuous branch join around 1100 degrees C.

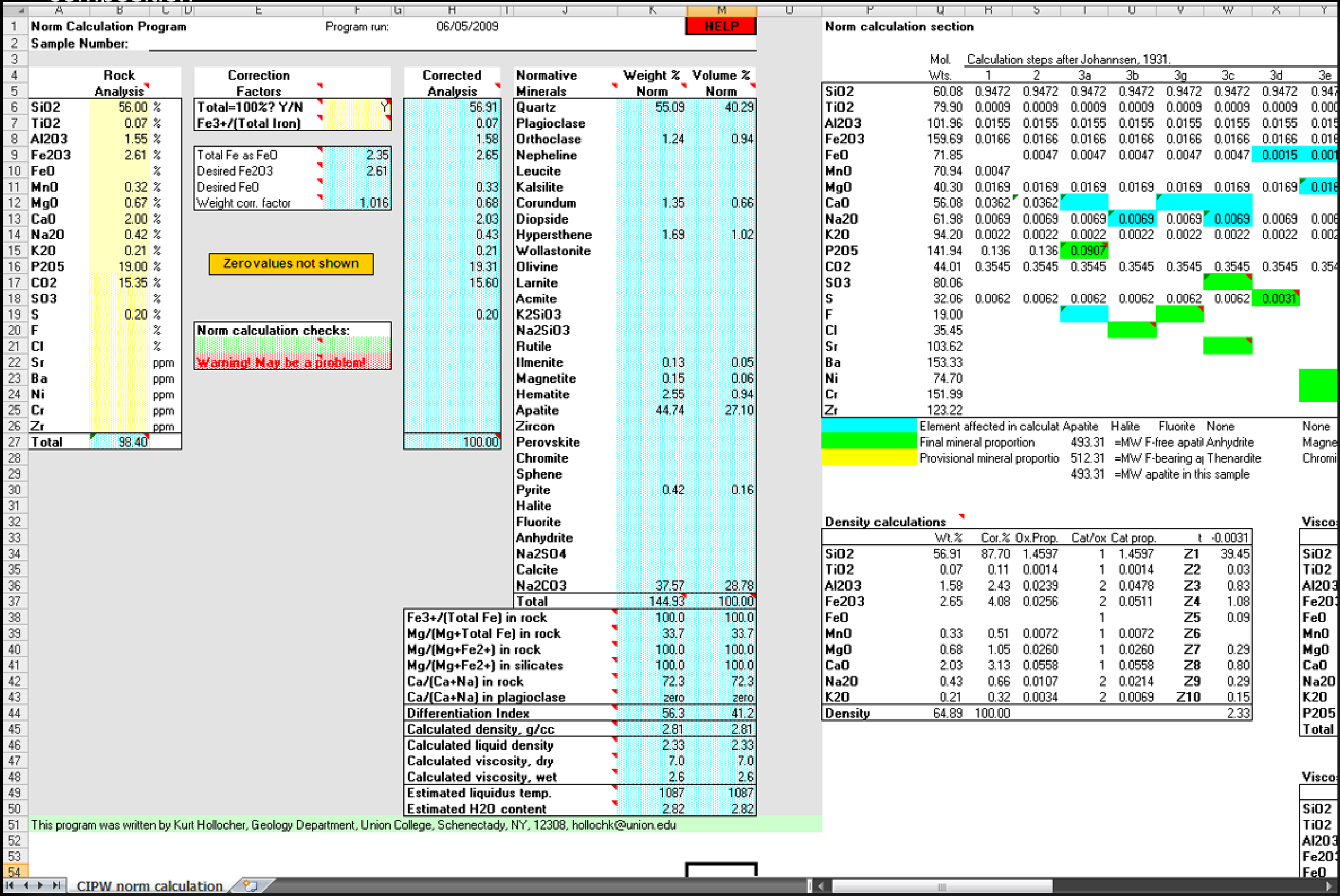
Chemical and modal classification of subalkaline igneous rocks.

Volcanic Plutonic **Oxides** (%)	- PERIDOTITE	BASALT GABBRO	ANDESITE DIORITE	DACITE GRANODIORITE	RHYOLITE GRANITE
SiO_2	43.5	48.4	53.9	66.9	72.1
Al_2O_3	4.0	16.8	15.9	17.5	13.9
CaO	3.5	11.1	7.9	3.6	1.3
MgO	34.0	8.1	5.7	1.6	0.5
FeO	9.8	7.9	6.5	2.6	1.7
Fe_2O_3	2.5	2.6	2.7	1.3	0.9
TiO_2	0.8	1.3	1.5	0.6	0.4
Na_2O	0.6	2.3	3.4	3.8	3.1
K_2O	0.3	0.6	1.3	3.1	5.5
Classification (according to SiO_2)	ultrabasic	basic	intermediate		acidic
Top 5 share	95	92	90	95	95
Minerals (%) (modal)					
Pyroxene	45	55	15		
Plag. feldspar	10	35	55	40	18
Olivine	45	10			
Amphibole			15	10	2
Alkali feldspar			5	15	27
Quartz			5	20	35
Mica			5	15	18



Rhyolite	Andesite	Basalt	Komatiite	Extrusive
Granite	Quartz diorite diorite	Gabbro	Peridotite	Intrusive
Acidic	Intermediate	Basic	Ultrabasic	Composition
Felsic	Intermediate	Mafic	Ultramafic	Colour

CIPW DIAGRAM – ‘Norm’ conversion ***from chemical*** composition to an ***ideal mineral*** composition



Norm Calculation Program Program run: 06/05/2009 HELP

Sample Number:

	Rock Analysis	
SiO2	56.00	%
TiO2	0.07	%
Al2O3	1.55	%
Fe2O3	2.61	%
FeO		%
MnO	0.32	%
MgO	0.67	%
CaO	2.00	%
Na2O	0.42	%
K2O	0.21	%
P2O5	19.00	%
CO2	15.35	%
SO3		%
S	0.20	%
F		%
Cl		%
Sr		ppm
Ba		ppm
Ni		ppm
Cr		ppm
Zr		ppm
Total	98.40	

Correction Factors	
Total=100%? Y/N	Y
Fe3+/(Total Iron)	

Total Fe as FeO	2.35
Desired Fe2O3	2.61
Desired FeO	
Weight corr. factor	1.016

Zero values not shown

Norm calculation checks:

Warning! May be a problem!

Corrected Analysis
56.91
0.07
1.58
2.65
0.33
0.68
2.03
0.43
0.21
19.31
15.60
0.20
100.00

Normative Minerals	Weight % Norm	Volume % Norm
Quartz	55.09	40.29
Plagioclase		
Orthoclase	1.24	0.94
Nepheline		
Leucite		
Kalsilite		
Corundum	1.35	0.66
Diopside		
Hypersthene	1.69	1.02
Wollastonite		
Olivine		
Larnite		
Acmite		
K2SiO3		
Na2SiO3		
Rutile		
Ilmenite	0.13	0.05
Magnetite	0.15	0.06
Hematite	2.55	0.94
Apatite	44.74	27.10
Zircon		
Perovskite		
Chromite		
Sphene		
Pyrite	0.42	0.16
Halite		
Fluorite		
Anhydrite		
Na2SO4		
Calcite		
Na2CO3	37.57	28.78
Total	144.93	100.00

Fe3+/(Total Fe) in rock	100.0	100.0
Mg/(Mg+Total Fe) in rock	33.7	33.7
Mg/(Mg+Fe2+) in rock	100.0	100.0
Mg/(Mg+Fe2+) in silicates	100.0	100.0
Ca/(Ca+Na) in rock	72.3	72.3
Ca/(Ca+Na) in plagioclase	zero	zero
Differentiation Index	56.3	41.2
Calculated density, g/cc	2.81	2.81
Calculated liquid density	2.33	2.33
Calculated viscosity, dry	7.0	7.0
Calculated viscosity, wet	2.6	2.6
Estimated liquidus temp.	1087	1087
Estimated H2O content	2.82	2.82

This program was written by Kurt Hollocher, Geology Department, Union College, Schenectady, NY, 12308, hollochk@union.edu

Norm calculation section

Calculation steps after Johannsen, 1931.

	Mol. Wts.	1	2	3a	3b	3g	3c	3d	3e
SiO2	60.08	0.9472	0.9472	0.9472	0.9472	0.9472	0.9472	0.9472	0.947
TiO2	79.90	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.000
Al2O3	101.96	0.0155	0.0155	0.0155	0.0155	0.0155	0.0155	0.0155	0.015
Fe2O3	159.69	0.0166	0.0166	0.0166	0.0166	0.0166	0.0166	0.0166	0.016
FeO	71.85		0.0047	0.0047	0.0047	0.0047	0.0047	0.0015	0.001
MnO	70.94	0.0047							
MgO	40.30	0.0169	0.0169	0.0169	0.0169	0.0169	0.0169	0.0169	0.016
CaO	56.08	0.0362	0.0362						
Na2O	61.98	0.0069	0.0069	0.0069	0.0069	0.0069	0.0069	0.0069	0.006
K2O	94.20	0.0022	0.0022	0.0022	0.0022	0.0022	0.0022	0.0022	0.002
P2O5	141.94	0.136	0.136	0.0907					
CO2	44.01	0.3545	0.3545	0.3545	0.3545	0.3545	0.3545	0.3545	0.354
SO3	80.06								
S	32.06	0.0062	0.0062	0.0062	0.0062	0.0062	0.0062	0.0031	
F	19.00								
Cl	35.45								
Sr	103.62								
Ba	153.33								
Ni	74.70								
Cr	151.99								
Zr	123.22								
		Apatite		Halite	Fluorite	None			None
			Anhydrite						Magne
			Thenardite						Chromi

🟦 Element affected in calculat

🟩 Final mineral proportion 493.31 =MW F-free apatit

🟨 Provisional mineral proportio 512.31 =MW F-bearing ap

493.31 =MW apatite in this sample

Density calculations

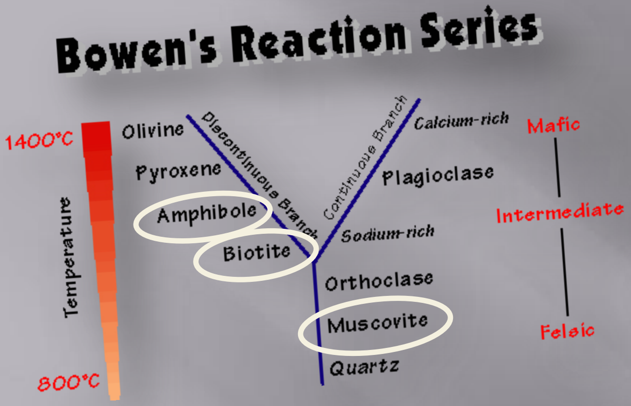
	Wt.%	Cor.%	Ox.Prop.	Cat/ox	Cat prop.	t	-0.0031
SiO2	56.91	87.70	1.4597	1	1.4597	Z1	39.45
TiO2	0.07	0.11	0.0014	1	0.0014	Z2	0.03
Al2O3	1.58	2.43	0.0239	2	0.0478	Z3	0.83
Fe2O3	2.65	4.08	0.0256	2	0.0511	Z4	1.08
FeO				1		Z5	0.09
MnO	0.33	0.51	0.0072	1	0.0072	Z6	
MgO	0.68	1.05	0.0260	1	0.0260	Z7	0.29
CaO	2.03	3.13	0.0558	1	0.0558	Z8	0.80
Na2O	0.43	0.66	0.0107	2	0.0214	Z9	0.29
K2O	0.21	0.32	0.0034	2	0.0069	Z10	0.15
Density	64.89	100.00					2.33

Visco

SiO2
TiO2
Al203
Fe20
FeO
MnO
MgO
CaO
Na2O
K2O
P2O5
Total

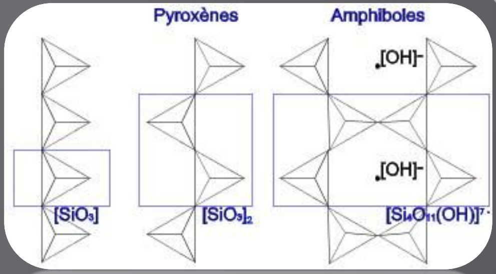
Visco

SiO2
TiO2
Al203
Fe20
FeO



Amphibole - hornblende

$Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$



Inosilicates

Biotite

$K(Mg,Fe)_2(AlSi_3O_{10})(F,OH)_2$

Muscovite

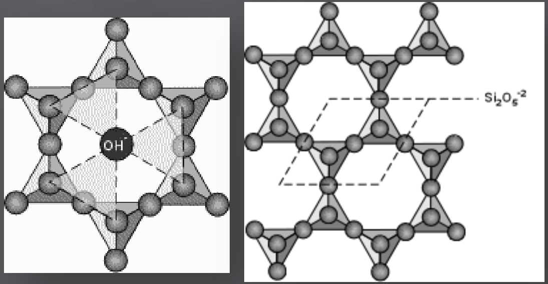
$KAl_2(AlSi_3O_{10})(F,OH)_2$

Phyllosilicates

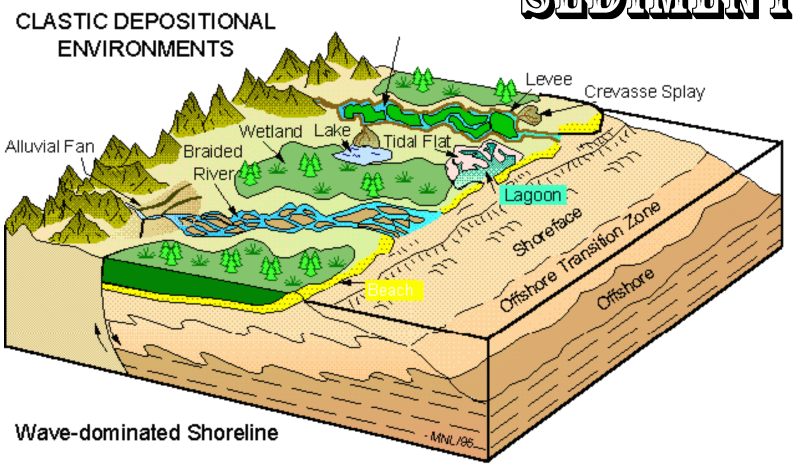
← Micas

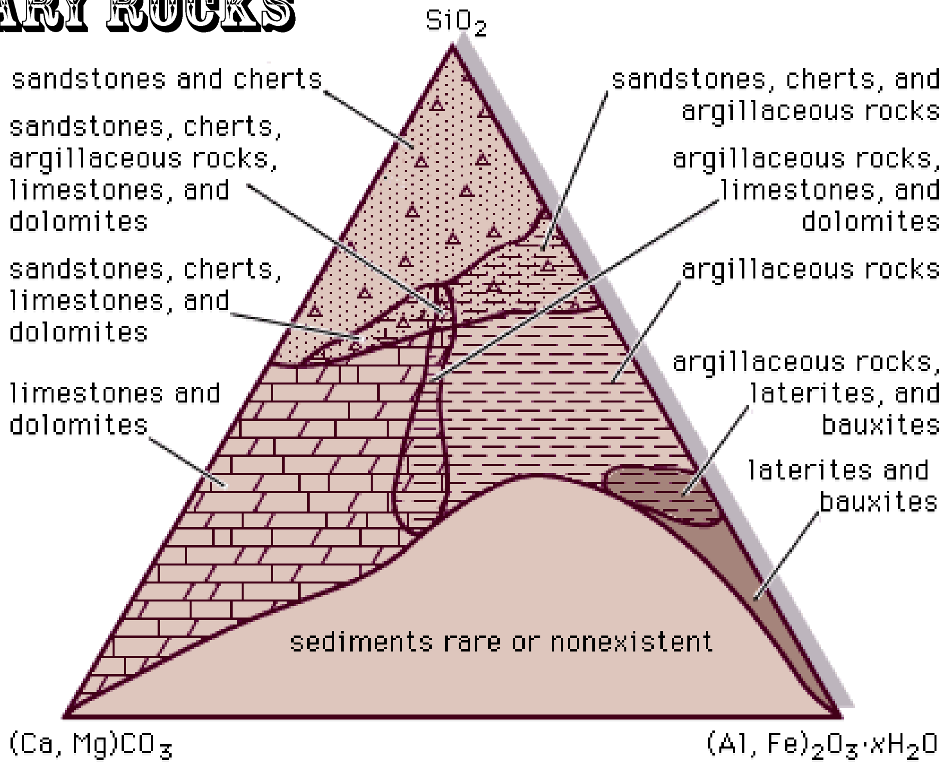
Serpentine – $Mg_3Si_2O_5(OH)_4$

Clays - $Al_2Si_2O_5(OH)_4$ - (Kaolinite)



SEDIMENTARY ROCKS





“Sedimentary rock is formed by deposition and consolidation of mineral and organic material and from precipitation of minerals from solution”.
Wikipedia, yesterday.

Classification by origin:

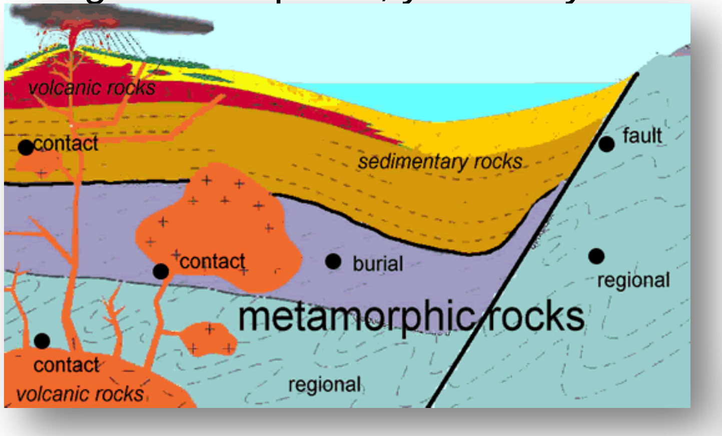
CLASTIC ROCK **- made up of fragments of broken rock either by weathering (mechanical or chemical) or erosion.** ***Components***: quartz + feldspar, amphibole, clay minerals, or other fragments. ***Typical rocks***: sandstone, conglomerates, breccias.

BIOGENETIC (organic) - **materials from (ex)-living forms.**
Components: carbonate minerals from corals, molluscs and foraminifera + calcite. **Typical rocks:** limestone, flint, chalk, coal, etc.

CHEMICAL (precipitation from solution) - **precipitation from oversaturated water.**
Components: *minerals in solution precipitate, including calcium carbonate and salts.* **Typical rocks***:* *limestones, halite, gypsum.*

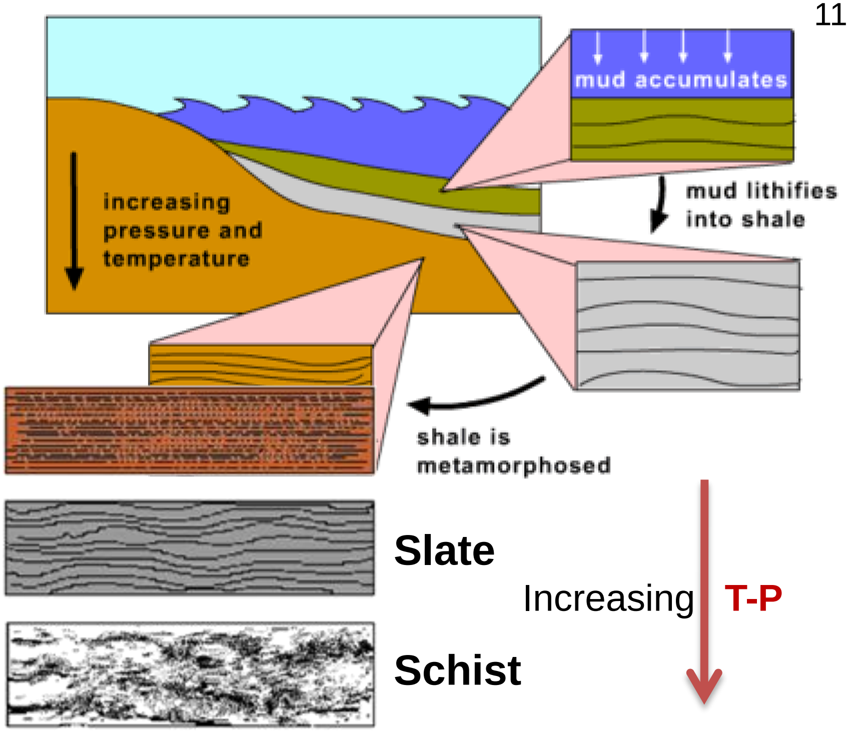
METAMORPHIC ROCKS

“the result of the transformation of an *__existing__* *rock type due to high temperatures (>150-200ºC) and/or pressures of 1.5 Kbars, causing profound physical and/or chemical changes*”. Wikipedia, yesterday.



Olivine reacts with water at High-P and Low-T to form *serpentine* plus magnesium oxide. Typical rock of faulting zones.

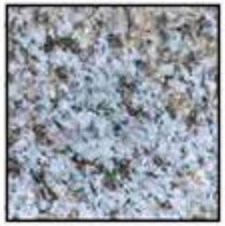
$Mg_2SiO_4+H_2O \rightarrow Mg_3Si_2O_5(OH)_4+MgO$



Slate

Increasing **T-P**

Schist

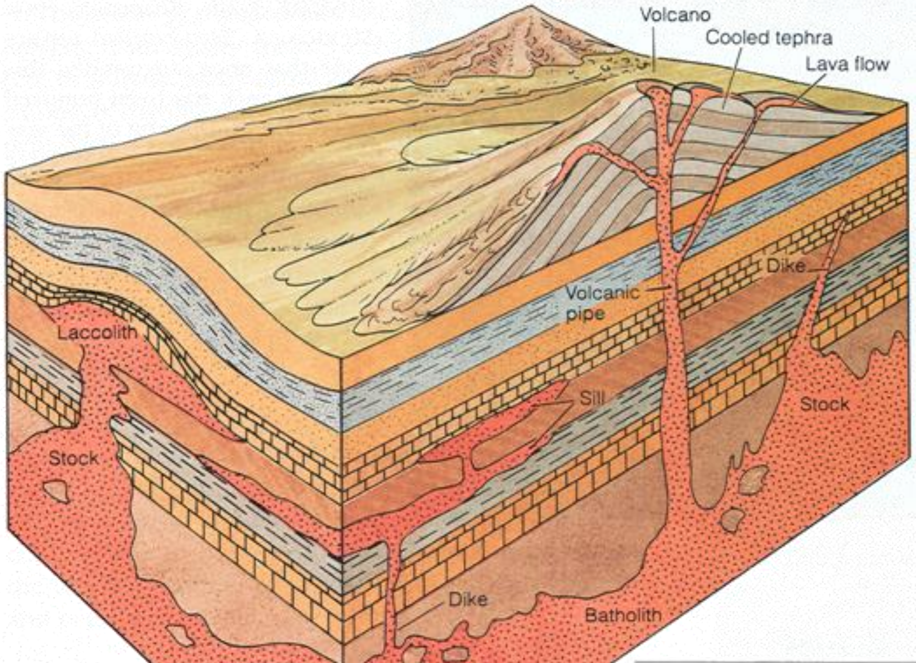


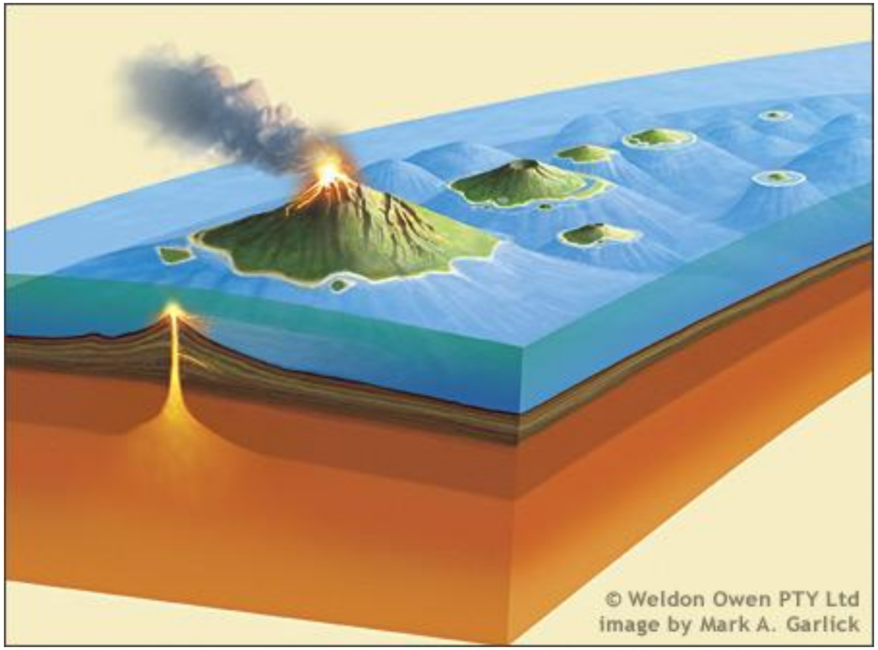
GRANITE

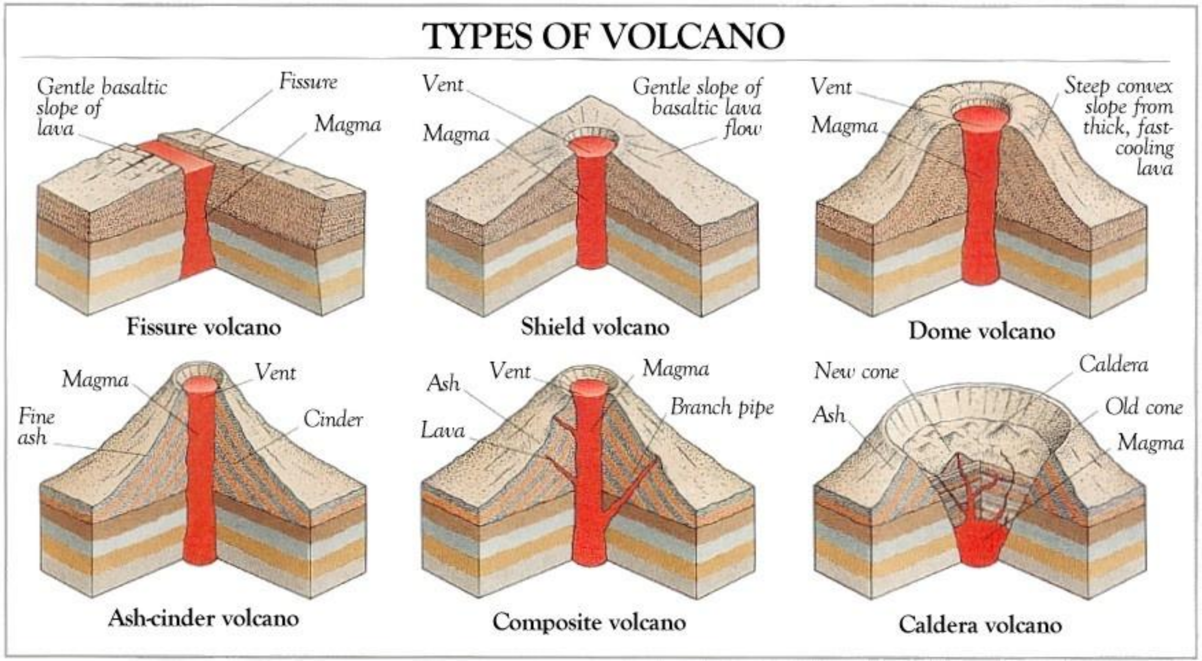
GNEISS

LIMESTONE

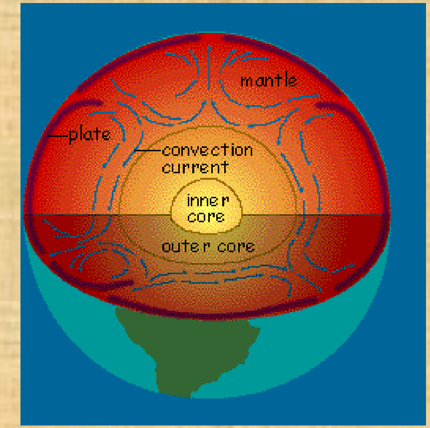
MARBLE

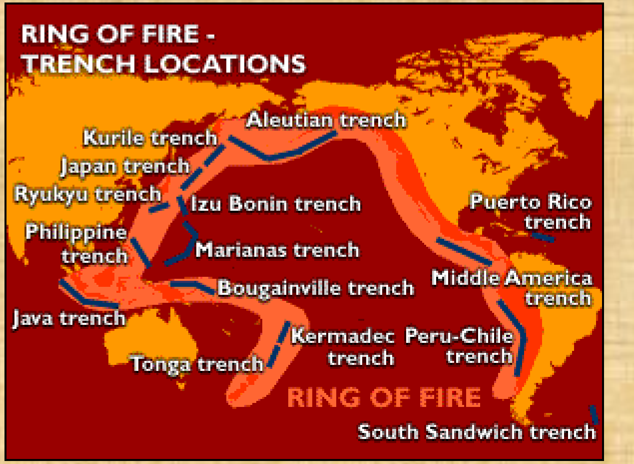


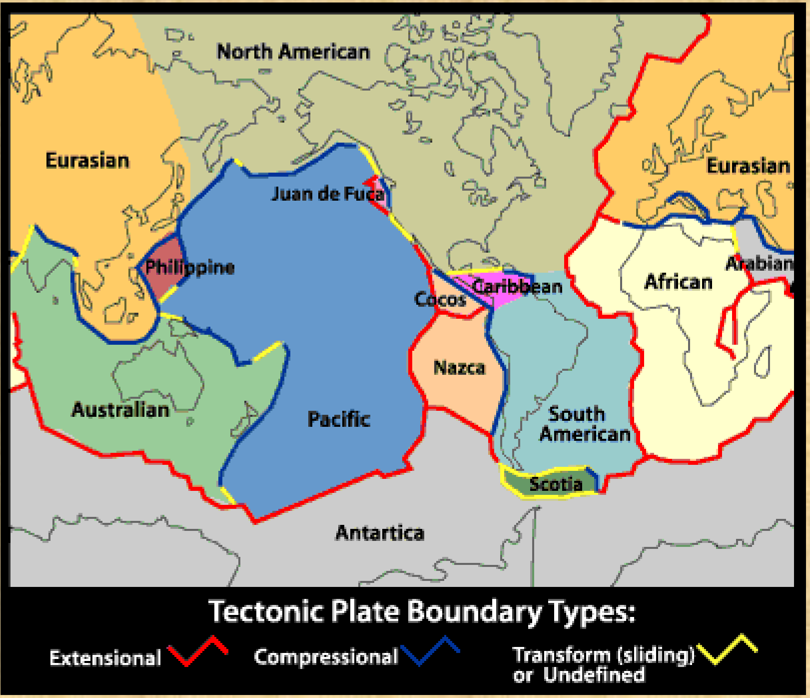

© Weldon Owen PTY Ltd
image by Mark A. Garlick


TYPES OF VOLCANO

VOLCANOES


mantle
plate
convection current
inner core
outer core


RING OF FIRE - TRENCH LOCATIONS
Aleutian trench
Kurile trench
Japan trench
Ryukyu trench
Izu Bonin trench
Puerto Rico trench
Philippine trench
Marianas trench
Middle America trench
Bougainville trench
Java trench
Kermadec trench
Peru-Chile trench
Tonga trench
RING OF FIRE
South Sandwich trench


North American
Eurasian
Juan de Fuca
Eurasian
Philippine
Arabian
Caribbean
African
Cocos
Nazca
Australian
Pacific
South American
Scotia
Antartica
Tectonic Plate Boundary Types:
Extensional
Compressional
Transform (sliding) or Undefined

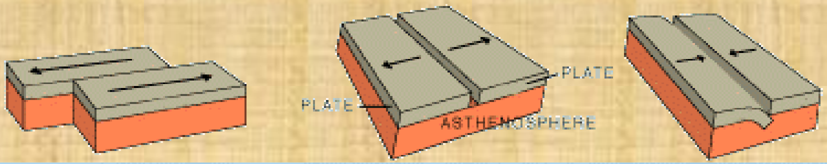
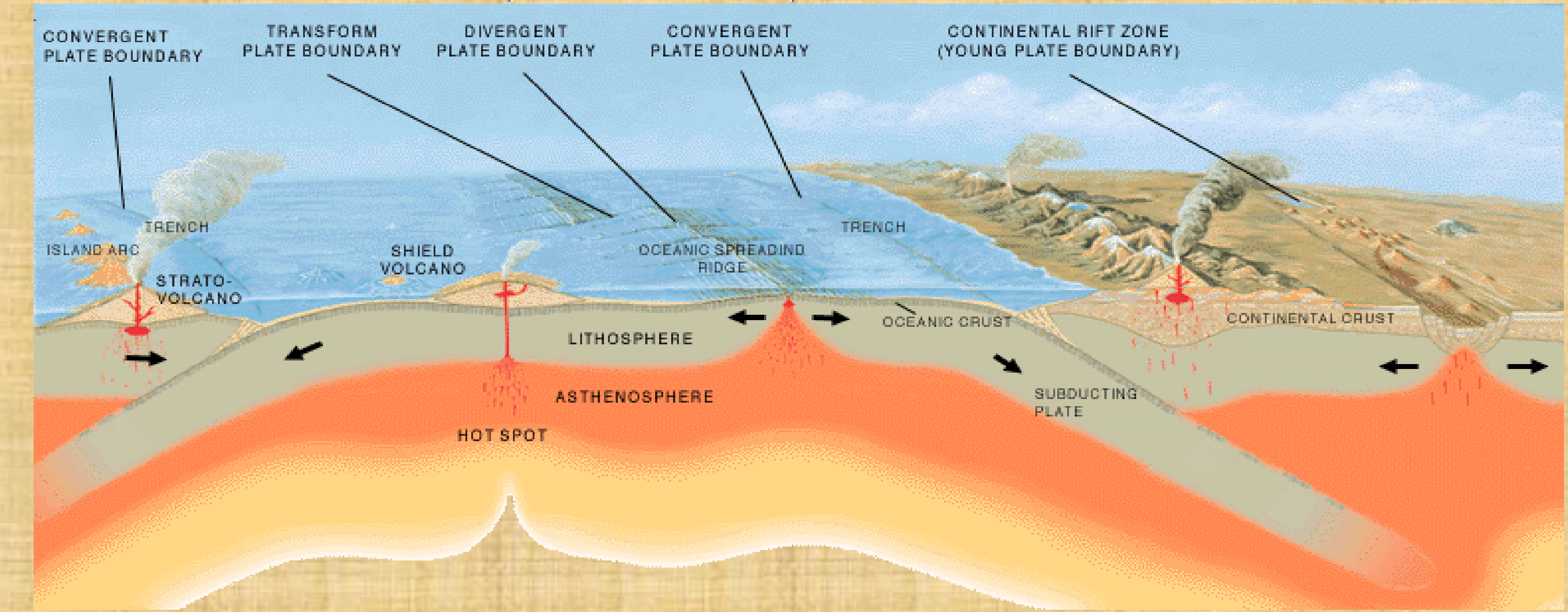


PLATE
PLATE
ASTHENOSPHERE


CONVERGENT PLATE BOUNDARY
TRANSFORM PLATE BOUNDARY
DIVERGENT PLATE BOUNDARY
CONVERGENT PLATE BOUNDARY
CONTINENTAL RIFT ZONE (YOUNG PLATE BOUNDARY)
TRENCH
ISLAND ARC
STRATO-VOLCANO
SHIELD VOLCANO
OCEANIC SPREADING RIDGE
TRENCH
OCEANIC CRUST
CONTINENTAL CRUST
LITHOSPHERE
ASTHENOSPHERE
HOT SPOT
SUBDUCTING PLATE

THE END

ROBERTO BUGIOLACCHI