A material look at the Universe and the Earth

A BRIEF GEOLOGICAL JOURNEY
What is the Universe made of?

1.1 From universe to us

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic #</th>
<th>Symbol</th>
<th>Universe</th>
<th>Sun</th>
<th>Earth bulk</th>
<th>Earth crust</th>
<th>Earth's Basalt</th>
<th>Earth's Granite</th>
<th>Moon Bulk</th>
<th>Human body</th>
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<tbody>
<tr>
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<td>Ni</td>
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</table>

Top 1 element in each system (%)

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%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Universe</th>
<th>Sun</th>
<th>Earth bulk</th>
<th>Earth crust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.0700</td>
<td>0.0780</td>
<td>31.27</td>
<td>4.78</td>
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<td>O</td>
<td>73.9000</td>
<td>91.2000</td>
<td>30.37</td>
<td>46.60</td>
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<tr>
<td>Si</td>
<td>24.0000</td>
<td>8.7000</td>
<td>15.77</td>
<td>27.70</td>
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<tr>
<td>Mg</td>
<td>1.5</td>
<td>1.27</td>
<td>14.80</td>
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<tr>
<td>Ca</td>
<td>1.5</td>
<td>1.27</td>
<td>1.5</td>
<td>3.97</td>
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<tr>
<td>Al</td>
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<td>0.6</td>
<td>0.6</td>
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<td>K</td>
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<tr>
<td>H</td>
<td>24.0000</td>
<td>8.7000</td>
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</tbody>
</table>

**Major elements**

- **Fe**
- **O**
- **Si**
- **Mg**
- **Ca**
- **Al**
- **Na**
- **K**
- **H**
- **He**
Nucleosynthesis — the first steps

<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:

\[
\begin{align*}
p + n & \rightarrow D \text{ (deuterium)} \quad \text{or} \quad ^2\text{H (heavy hydrogen)} \\
D + n & \rightarrow ^3\text{H (tritium, very heavy hydrogen)} \\
D + p & \rightarrow ^3\text{He (helium, light variety...)} \\
^3\text{He} + ^3\text{He} & \rightarrow ^4\text{He} + 2p \text{ ('normal' helium, helium 4)} \\
^3\text{He} + ^4\text{He} & \rightarrow ^7\text{Li ('normal' lithium)}
\end{align*}
\]

This is highly reactive (doesn’t last long...):

\[
\begin{align*}
\text{Element 1 (one p)} & \quad \text{(unstable):} \\
\text{Element 2} & \quad \text{(quickly...)}
\end{align*}
\]
Nucleosynthesis – the journey continues (2)

State of the matter so far:

**Hydrogen (H)**  \( \rightarrow 1 \text{ proton} \)  
(Deuterium \(^2\text{H}\) or D)  \( \rightarrow 1 \text{ proton} \)  
**Helium (He)**  \( \rightarrow 2 \text{ protons} \)  
**Lithium (Li)**  \( \rightarrow 3 \text{ protons} \)

0 neutron (albeit strictly not part of nucleosynthesis)  
1 neutron  
2 neutrons (or 1, isotope \(^3\text{He}\))  
3 neutrons (or 4, isotope \(^7\text{Li}\))
‘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 %

\[ ^1\text{H} \]
\[ ^1\text{H} + ^1\text{H} \rightarrow ^2\text{He} \]
proton – proton reaction (hydrogen burning) ~74

\[ ^4\text{He} + ^4\text{He} \rightarrow ^8\text{Be} \]
Triple \( \alpha \) reaction ~24

\[ ^6\text{C} + ^4\text{He} \rightarrow ^8\text{Be} \]
This process is promoted by resonances ~0.0046

\[ ^6\text{C} + ^6\text{C} \rightarrow ^8\text{Be} + ^2\text{He} \]
This process is promoted by resonances ~1.070

Examples of element formation:

\[ ^{12}\text{C} + ^{12}\text{C} \rightarrow ^{20}\text{Ne} + ^4\text{He} \]
carbon burning processes ~0.0013

\[ ^{12}\text{C} + ^{12}\text{C} \rightarrow ^{22}\text{Na} + ^4\text{He} \]
“ “ ~0.0006

\[ ^{12}\text{C} + ^{12}\text{C} \rightarrow ^{24}\text{Mg} + ^4\text{He} \]
“ “ ~0.0006

\[ ^{12}\text{C} + ^{12}\text{C} \rightarrow ^{26}\text{Fe} + 2^4\text{He} \]
“ “ ~0.0004

\[ ^{16}\text{O} + ^4\text{He} \rightarrow ^{20}\text{Ne} \]
neon burning process (>8M\text{sun}) ~0.0007

\[ ^{16}\text{O} + ^{16}\text{O} \rightarrow ^{30}\text{Si} + ^4\text{He} \]
on oxygen burning process ~0.0007

\[ ^{22}\text{Ne} \rightarrow ^{14}\text{Si} + ^4\text{He} \]
pure \( \alpha \) process ~0.0004

\[ ^{16}\text{O} + ^{16}\text{O} \rightarrow ^{32}\text{S} + ^4\text{He} \]
pure \( \alpha \) process - also oxygen burning turns Si into Fe ~0.0004

\[ ^{24}\text{Mg} + ^4\text{He} \rightarrow ^{28}\text{Si} \]
“ “ ~0.0007

\[ ^{26}\text{Fe} \rightarrow ^{28}\text{Si} + ^4\text{He} \]
“ “ ~0.0007

All other elements

iron peak ~0.0011

~0.0070
Nearly there, only the small matter of a few more elements...

WHY DOES THIS PROCESS END WITH Fe?

No known nuclei are more stable than $^{56}_{\text{Fe}}$.

This stability also means that the element is unable to fuse with other nuclei to produce more energy (an exothermic process).
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 $^{209}\text{Bi}$ (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**
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.

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.

Would it surprise you to know that most of the relative abundances of elements on the Sun match those of a modelled bulk Earth?
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.
The Formation of the Solar System

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**

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).

<table>
<thead>
<tr>
<th>NAME</th>
<th>FORMULA</th>
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<tbody>
<tr>
<td>DIAMOND, GRAPHITE</td>
<td>C</td>
</tr>
<tr>
<td>MOISSANITE</td>
<td>SiC</td>
</tr>
<tr>
<td>NANO-PARTICLES</td>
<td>TiC, ZrC, MoC, FeC, and Fe-Ni metals</td>
</tr>
<tr>
<td>OSBORNITE</td>
<td>TiN</td>
</tr>
<tr>
<td>RUTILE</td>
<td>TiO₂</td>
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<tr>
<td>CORONDUM</td>
<td>Al₂O₃</td>
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<td>MgAl₂O₄</td>
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<tr>
<td>FORSTERITE</td>
<td>Mg₂SiO₄</td>
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<tr>
<td>HIBONITE</td>
<td>CaAl₁₂O₁₉</td>
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<tr>
<td>PEROVSKITE STRUCTURE</td>
<td>MgSiO₃</td>
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<tr>
<td>GEMS (silicate glass with embedded metal and sulphides)</td>
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</table>
As the building process continued, these planetesimals would have accreted into \textit{planetary embryos}, and, eventually, fully formed \textit{planets}. 

It would have taken around 100,000 years for these rocky bodies to grow to about 10 km in diameter, becoming \textit{‘Planetesimals’}. 

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

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.
The condensation sequence of the solar nebula at pressures of about 10 N m$^{-2}$
The dotted arrow indicate that below 400 K the last compounds to condense were ammonia ($\text{NH}_3$), methane ($\text{CH}_4$), and water.

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

Then, slightly less refractory $\text{Al}_2\text{O}_3$ (aluminium oxide), the platinum-group metals, the REEs, uranium and thorium.

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

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).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>Aluminium oxide (‘alumina’) → major source of Al from Corundum (also rubies, sapphires, etc.)</td>
</tr>
<tr>
<td>$\text{CaTiO}_3$</td>
<td>Calcium titanite (major polymorph of Perovskite, probably the most abundance mineral in the mantle)</td>
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<tr>
<td>$\text{Ca}_2\text{Al}_2\text{Si}_7$</td>
<td>Gehlenite (from the Melilite gehlenite-akermanite solid solution)</td>
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<tr>
<td>$\text{MgAl}_2\text{O}_4$</td>
<td>Spinel – principal mineral in the ‘spinel’ group.</td>
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<tr>
<td>$\text{Mg}_2\text{Si}_4$</td>
<td>Olivine – Forsterite. $\text{Fe}^{+2}$ forms a solid solution in the olivine system Forsterite-Fayalite.</td>
</tr>
<tr>
<td>$\text{MgSiO}_3$</td>
<td>Perovskite (magnesium silicate), or mineralogically Enstatite (opx).</td>
</tr>
<tr>
<td>(Na, K)$\text{AlSi}_3\text{O}_8$</td>
<td>Albite – (Na) Plagioclase Feldspar and Orthoclase - (K) Alkali Feldspar</td>
</tr>
</tbody>
</table>
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’

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.
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.

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

<table>
<thead>
<tr>
<th>Meteorite Type</th>
<th>Overall Sample Representation (%)</th>
<th>Principal Sub-types</th>
<th>Description</th>
<th>Composition</th>
<th>Sub-groups</th>
<th>Composition</th>
<th>Representative of planets’</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>STONY</strong></td>
<td>95</td>
<td>CHONDrites</td>
<td>Contain small, once molten globules, or chondrules, of silicate.</td>
<td>Fe-Mg silicates, Grains of Fe-Ni alloy Troilite (FeS) – iron sulphide</td>
<td><strong>ORDINARY CHONDrites</strong></td>
<td>Most abundant and typical Most depleted in volatiles – highest T of formation</td>
<td></td>
</tr>
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<td></td>
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</tr>
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<td>85</td>
<td></td>
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</tr>
<tr>
<td><strong>ACHONDrites</strong></td>
<td>10</td>
<td></td>
<td>Lack chondrules, Small fraction of Fe-Ni grains</td>
<td>Mainly Fe-Mg silicates</td>
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<tr>
<td><strong>STONY-IRON</strong></td>
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<tr>
<td><strong>IRON</strong></td>
<td>3.5</td>
<td></td>
<td>Hybrids</td>
<td>~50:50 mixture of Fe-Ni alloys and silicate phases</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>BULK COMPOSITION</strong></td>
<td></td>
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<tr>
<td><strong>MANTLE</strong></td>
<td></td>
<td></td>
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<tr>
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<tr>
<td><strong>MANTLE-CORE BOUNDARY REGION</strong></td>
<td></td>
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<tr>
<td><strong>CORE</strong></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
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 to the Sun:

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...
3.5 Are we on a chondritic Earth?

... but, we DON’T.

Have a look at the table below:

<table>
<thead>
<tr>
<th>Element</th>
<th>Lowest value (ppm)</th>
<th>Highest value (ppm)</th>
<th>Ratio of highest to lowest value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>200</td>
<td>4902</td>
<td>24.5</td>
</tr>
<tr>
<td>O</td>
<td>452,341</td>
<td>495,200</td>
<td>1.09</td>
</tr>
<tr>
<td>Na</td>
<td>15,208</td>
<td>28,500</td>
<td>1.87</td>
</tr>
<tr>
<td>Mg</td>
<td>10,191</td>
<td>33,770</td>
<td>3.31</td>
</tr>
<tr>
<td>Al</td>
<td>74,500</td>
<td>88,649</td>
<td>1.19</td>
</tr>
<tr>
<td>Si</td>
<td>257,500</td>
<td>315,896</td>
<td>1.23</td>
</tr>
<tr>
<td>Ar</td>
<td>0.04</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>K</td>
<td>15,773</td>
<td>32,625</td>
<td>2.07</td>
</tr>
<tr>
<td>Ca</td>
<td>16,438</td>
<td>62,894</td>
<td>3.83</td>
</tr>
<tr>
<td>Mn</td>
<td>155</td>
<td>1,549</td>
<td>10.0</td>
</tr>
<tr>
<td>Fe</td>
<td>30,888</td>
<td>64,668</td>
<td>2.09</td>
</tr>
<tr>
<td>Co</td>
<td>12</td>
<td>100</td>
<td>8.33</td>
</tr>
<tr>
<td>Ni</td>
<td>23</td>
<td>200</td>
<td>8.70</td>
</tr>
<tr>
<td>Cu</td>
<td>14</td>
<td>100</td>
<td>7.14</td>
</tr>
<tr>
<td>Ru</td>
<td>0.0001</td>
<td>0.05</td>
<td>500</td>
</tr>
<tr>
<td>Ag</td>
<td>0.02</td>
<td>0.1</td>
<td>5.00</td>
</tr>
<tr>
<td>Cd</td>
<td>0.1</td>
<td>5</td>
<td>50.0</td>
</tr>
<tr>
<td>Ba</td>
<td>179</td>
<td>1,070</td>
<td>5.98</td>
</tr>
<tr>
<td>W</td>
<td>0.4</td>
<td>70</td>
<td>350</td>
</tr>
<tr>
<td>Au</td>
<td>0.001</td>
<td>0.005</td>
<td>5.00</td>
</tr>
</tbody>
</table>

The ‘consensus’ relative abundances of the elements in the Earth’s crust plotted against those in the Sun.
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...

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’.
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.
Iron, for instance, is basically \textit{chalcopehile}, but there is too little \textit{sulphur} in the Earth to utilise all the Fe available.

Some is therefore \textit{siderophile} (Fe in core) and some \textit{lithophile} (in silicates in the crust and mantle).

\textbf{Lithophile} | \textbf{Siderophile} | \textbf{Chalcophile} | \textbf{Atmophile} | very rare
---|---|---|---|---
1 H | | | | | 2 He
3 Li | 4 Be | | | |
11 Na | 12 Mg | | | |
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

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

Obviously, this can’t be, and \textit{it is not}, the whole story!

the Periodic Table subdivision in elemental affinities
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 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 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):

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Earth</td>
<td>~ 27.0</td>
</tr>
<tr>
<td>Mantle</td>
<td>~ 22.4</td>
</tr>
<tr>
<td>Core</td>
<td>~ 47.0</td>
</tr>
</tbody>
</table>

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:

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!
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
The Composition of the Earth’s layers

4.4 The Crust – composition

<table>
<thead>
<tr>
<th>Oxide/element</th>
<th>Estimate 1</th>
<th>Estimate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>60.2</td>
<td>63.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>15.2</td>
<td>16.0</td>
</tr>
<tr>
<td>CaO</td>
<td>5.5</td>
<td>4.1</td>
</tr>
<tr>
<td>FeO</td>
<td>3.8</td>
<td>3.5</td>
</tr>
<tr>
<td>MgO</td>
<td>3.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>3.0</td>
<td>3.7</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Ba</td>
<td>670</td>
<td>1150</td>
</tr>
<tr>
<td>Sr</td>
<td>340</td>
<td>350</td>
</tr>
<tr>
<td>Th</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>Rb</td>
<td>95</td>
<td>85</td>
</tr>
<tr>
<td>Ni</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>U</td>
<td>3</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The table shows that $\frac{3}{4}$ 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$_2$O$_8$], potassium feldspar [KAl(Si,Al)$_3$O$_8$], biotite, and hornblende.

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.

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

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.

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)₂SiO₄]

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.
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:

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45.1</td>
</tr>
<tr>
<td>MgO</td>
<td>38.1</td>
</tr>
<tr>
<td>FeO</td>
<td>8.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.3</td>
</tr>
<tr>
<td>CaO</td>
<td>3.1</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.4</td>
</tr>
</tbody>
</table>

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.
The Composition of the Earth’s layers

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 its 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.
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 K₂S and taken along to the core with it. There is also the possibility that one of the isotopes of potassium (⁴₀K) 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.
The Composition of the Earth's layers

Depth (km)

- Earth's centre: 0 km
- Fe+Ni? Solid, 1210 km
- Fe+? Liquid, 2260 km
- Perovskite, 2220 km
- Spinel, 270 km
- Peridotite, 330 km
- Granodiorite, 70 km

Thickness of compositional layers (in km)

- Fe+Ni? Solid: 1%
- Granodiorite: 3%
- Fe+? Liquid: 16%
- Peridotite: 14%
- Spinel: 11%
- Perovskite: 55%

Relative Volumes
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...

<table>
<thead>
<tr>
<th>Compound (mostly oxides)</th>
<th>Garnet Peridotite (mass%)</th>
<th>Carbonaceous Chondrite (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45.10</td>
<td>33.25</td>
</tr>
<tr>
<td>MgO</td>
<td>38.10</td>
<td>22.04</td>
</tr>
<tr>
<td>FeO</td>
<td>8.00</td>
<td>14.39</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.30</td>
<td>2.27</td>
</tr>
<tr>
<td>CaO</td>
<td>3.10</td>
<td>2.16</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.40</td>
<td>1.02</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.40</td>
<td>0.47</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.20</td>
<td>0.09</td>
</tr>
<tr>
<td>MnO</td>
<td>0.14</td>
<td>0.30</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.03</td>
<td>0.09</td>
</tr>
<tr>
<td>FeS</td>
<td>-</td>
<td>23.20</td>
</tr>
</tbody>
</table>

Let’s readress this by converting mantle abundances to bulk-Earth and plot the results...
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.
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.
The first chart shows our *estimated* percentage distribution of major elements in our planet.

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.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>45.1</td>
</tr>
<tr>
<td>MgO</td>
<td>38.1</td>
</tr>
<tr>
<td>FeO</td>
<td>8.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.3</td>
</tr>
<tr>
<td>CaO</td>
<td>3.1</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.4</td>
</tr>
</tbody>
</table>

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 $\text{O}_2$

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: $\text{Au}_2\text{O}_3$).
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:

\[ ^8\text{O} + ^8\text{O} \rightarrow ^{14}\text{Si} + ^2\text{He} \quad \text{oxygen burning process} \]

\[ ^{12}\text{Mg} + ^2\text{He} \rightarrow ^{14}\text{Si} \quad \text{pure } \alpha \text{ process} \]

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.
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:**

<table>
<thead>
<tr>
<th>Elements distribution</th>
<th>Bulk chemistry</th>
<th>Idealised composition</th>
<th>Composition (formula)</th>
<th>Mineral (Phase - Component)</th>
<th>MOD</th>
<th>Family</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 45</td>
<td>49 SiO₂</td>
<td>CaO₂.Al₂O₃.6SiO₂</td>
<td>CaAl₂(SiO₄)₂</td>
<td>Anorthite (An)</td>
<td>P</td>
<td>Tecto- silicates</td>
<td>25</td>
</tr>
<tr>
<td>Si 23</td>
<td>13 Al₂O₃</td>
<td>CaO₂.(Mg,Fe)O₂SiO₂</td>
<td>Ca(Mg,Fe)(SiO₃)₂</td>
<td>Diopside (Di)</td>
<td>M</td>
<td>Ino- silicates</td>
<td>23</td>
</tr>
<tr>
<td>Al 8</td>
<td>11 CaO</td>
<td>Na₂O₂.Al₂O₃.6SiO₂</td>
<td>NaAl₂Si₂O₆</td>
<td>Albite (Ab)</td>
<td>A</td>
<td>Tecto- silicates</td>
<td>18</td>
</tr>
<tr>
<td>Fe 8</td>
<td>10 MgO</td>
<td>(Mg,Fe)O₂SiO₂</td>
<td>(Mg,Fe)SiO₃</td>
<td>Hypersthene (Hy)</td>
<td>M</td>
<td>Ino- silicates</td>
<td>15</td>
</tr>
<tr>
<td>Ca 7</td>
<td>10 FeO</td>
<td>2(Mg,Fe)O₂SiO₂</td>
<td>(Mg,Fe)₂SiO₄</td>
<td>Olivine (Ol)</td>
<td>M</td>
<td>Neso-silicates</td>
<td>9</td>
</tr>
<tr>
<td>Mg 4</td>
<td>10 Na₂O</td>
<td>FeO.TiO₂</td>
<td>FeTiO₃</td>
<td>Ilmenite (Il)</td>
<td>M</td>
<td>Iron-titanium Oxides</td>
<td>4</td>
</tr>
<tr>
<td>Na 2</td>
<td>2 TiO₂</td>
<td>K₂O.Al₂O₃.6SiO₂</td>
<td>KAl₂Si₃O₈</td>
<td>Orthoclase (Or)</td>
<td>A</td>
<td>Tecto- silicates</td>
<td>3</td>
</tr>
<tr>
<td>Ti 1</td>
<td>1 Fe₂O₃</td>
<td>FeO.Fe₂O₃</td>
<td>Fe₃O₄</td>
<td>Magnetite (Mt)</td>
<td>M</td>
<td>Iron-titanium Oxides</td>
<td>2</td>
</tr>
</tbody>
</table>

**Idealised composition - Composition (formula) - Mineral (Phase - Component) - Modal (observed) - CIPW Norm (idealised) - mineral abundance**

- **Oxide**
  - SiO₂: 49%
  - Al₂O₃: 13%
  - CaO: 11%
  - MgO: 10%
  - FeO: 10%
  - Na₂O: 2%
  - TiO₂: 2%
  - Fe₂O₃: 1%
  - K₂O: 0.5%

- **Idealised composition**
  - CaO₂.Al₂O₃.6SiO₂
  - CaO₂.(Mg,Fe)O₂SiO₂
  - Na₂O₂.Al₂O₃.6SiO₂
  - (Mg,Fe)O₂SiO₂
  - 2(Mg,Fe)O₂SiO₂
  - FeO.TiO₂
  - K₂O.Al₂O₃.6SiO₂
  - FeO.Fe₂O₃

- **Composition (formula)**
  - CaAl₂(SiO₄)₂
  - Ca(Mg,Fe)(SiO₃)₂
  - NaAl₂Si₂O₆
  - (Mg,Fe)SiO₃
  - (Mg,Fe)₂SiO₄
  - FeTiO₃
  - KAl₂Si₃O₈
  - Fe₃O₄

- **Mineral (Phase - Component)**
  - Anorthite (An)
  - Diopside (Di)
  - Albite (Ab)
  - Hypersthene (Hy)
  - Olivine (Ol)
  - Ilmenite (Il)
  - Orthoclase (Or)
  - Magnetite (Mt)

- **Modal (observed) - CIPW Norm (idealised) - mineral abundance**
  - Tecto- silicates
  - Ino- silicates
  - Tecto- silicates
  - Ino- silicates
  - Neso-silicates
  - Iron-titanium Oxides
  - Tecto- silicates
  - Iron-titanium Oxides
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)
### Periodic Table

<table>
<thead>
<tr>
<th>Period</th>
<th>Elements</th>
<th>Cations</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H, He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Li, Be</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>B, C, N, O</td>
<td>Li⁺, Be²⁺, B³⁺, C³⁻, O₂⁻</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>F, Ne</td>
<td>Na⁺, Mg²⁺, Al³⁺, Si⁴⁺</td>
<td>P³⁻, S²⁻, Cl⁻</td>
</tr>
<tr>
<td>5</td>
<td>Na, Mg, Al, Si, P, S, Cl, Ar</td>
<td>K⁺, Ca²⁺, Sc³⁺, Ti⁴⁺, V⁵⁺, Cr⁶⁺, Mn⁷⁺, Fe⁸⁺, Co⁹⁺, Ni¹⁰⁺, Cu¹¹⁺, Zn¹²⁺</td>
<td></td>
</tr>
</tbody>
</table>

**CATIONS valences:**
- Fe²⁺ Ferrous = Iron(II)
- Fe³⁺ Ferric = Iron(III)
- lower v.: ‘-ous’, high ‘-ic’

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

**Legend for element groups:**
- Alkali (metals)
- Noble (Gas)
- Alkali (Earth metals)
- Halogens
- Transition (elements)

### Electronic Configuration

**Example:** C → 1s² 2s² 2pₓ¹ 2pᵧ¹ 2p₂⁰

### Valence Bond Theory

*Determined by quantum mechanical behaviour of electrons – orbital hybridisation*

- Only considers the outermost s and p valency electrons.
- Favours 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).
Metal + nonMetal = IONIC BOND (typical of elements with very different electronegativity). Example: 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 + 3Cl → 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\(^2-\).

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

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

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.
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 ‘\( \# \text{ electrons} = 2n^2 \)’ 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 \( +\frac{1}{2} \) or \( -\frac{1}{2} \) (Pauli Exclusion Principle).

These probability regions are described by the *Azimuthal quantum number* \( \ell \), 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 *remove* an electron

---

**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^2\(^+\).)

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 (from most –ve to most +ve):

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

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
### Periodic Table

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.

**Alkali (metals)**

- H
- Li
- Na
- K
- Rb
- Cs
- Fr

**Halogens**

- F
- Cl
- Br
- I
- At

**Alkali (Earth metals)**

- Be
- Mg
- Ca
- Sr
- Ba
- Ra

**Noble (Gas)**

- Ne
- Ar
- Kr
- Xe
- Rn

**Transition**

- Sc
- Ti
- V
- Cr
- Mn
- Fe
- Co
- Ni
- Cu
- Zn

**Anions**

- O
- S
- Se
- Te
- Po

**Cations**

- H⁺
- Li⁺
- Be⁺²
- B⁺³
- C⁺⁴
- N⁺⁵
- O⁻²; O₂⁻²

### 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
### Radii in a crystal lattice

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.
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”.

Pauling’s Rules:

Please do not confuse electronic structure/geometry with higher-order crystal systems!

SiO₂ valence electron pair geometry is Tetrahedral in space, but as Quartz, it belongs to the Trigonal Crystal System.
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 \( \frac{1}{2} \) the charge on the anion. Here, the e.v. reaching the Si is \( \frac{4}{4} = 1 \).

This leaves the oxygen with a -1 charge that it is not shared. Since this -1 is exactly \( \frac{1}{2} \) 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. Even 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.

**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.

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

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\(^{+}\).

<table>
<thead>
<tr>
<th>Element ion</th>
<th>Ionic radius (in crystal lattice)</th>
<th>C.N. (relative to O)</th>
<th>Coordination Polyhedron</th>
<th>SITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(^{-2})</td>
<td>1.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(^{+})</td>
<td>1.51 (8)</td>
<td>8 - 12</td>
<td>cubic to closest - Hexagon (eightfold)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.64 (12)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>1.18 (8)</td>
<td>8 - 6</td>
<td>cubic to octahedral</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.02 (6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>1.12 (8)</td>
<td>8 - 6</td>
<td>cubic to octahedral</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.00 (6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>0.83</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>0.72</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.72</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>0.65</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti(^{4+})</td>
<td>0.61</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>0.54</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>0.39</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(^{4+})</td>
<td>0.26</td>
<td>4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Silicates examples:**

| \(Ca\)\(Al\)\(_2\)(Si\(_4\)O\(_8\)) \(_2\) | Anorthite (An) | Plagioclase Felds |
| Ca(Mg,Fe)(SiO\(_3\)) \(_2\) | Diopside (Di) | ClinoPyroxene |
| NaAlSi\(_3\)O\(_8\) | Albite (Ab) | Plagioclase Felds |
| (Mg,Fe)\(_2\)SiO\(_3\) | Hypersthene (Hy) | OrthoPyroxene |
| (Mg,Fe)\(_2\)SiO\(_4\) | Forsterite/Fayalite (Ol) | Olivine |
| KAlSi\(_3\)O\(_8\) | Orthoclase (Or) | Alkali Felds |
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)

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).

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

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

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic Salt</td>
<td><img src="image" alt="Cubic Salt" /></td>
</tr>
<tr>
<td>Tetragonal Wulfenite</td>
<td><img src="image" alt="Tetragonal Wulfenite" /></td>
</tr>
<tr>
<td>Hexagonal Beryl</td>
<td><img src="image" alt="Hexagonal Beryl" /></td>
</tr>
<tr>
<td>Trigonal Quartz</td>
<td><img src="image" alt="Trigonal Quartz" /></td>
</tr>
<tr>
<td>Orthorhombic Opx, olivine</td>
<td><img src="image" alt="Orthorhombic Opx, olivine" /></td>
</tr>
<tr>
<td>Monoclinic Clinopyroxene</td>
<td><img src="image" alt="Monoclinic Clinopyroxene" /></td>
</tr>
<tr>
<td>Triclinic Plagioclase</td>
<td><img src="image" alt="Triclinic Plagioclase" /></td>
</tr>
</tbody>
</table>

**Silicates**

**Lattice parameters:**
- Lengths (relative): $a - b - c$
- Angles: $\alpha - \beta - \gamma$

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).
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.SiO₂
(Mg,Fe)₂SiO₄

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

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 \([\text{SiO}_4]^4-\) tetrahedra are linked together to form chains of composition \([\text{SiO}_3]^2-\).

These are bonded together by cations such as \(\text{Mg}^{2+}\), \(\text{Fe}^{2+}\), \(\text{Ca}^{2+}\), and \(\text{Na}^{+}\). There is complete solid-solution between Mg and Fe members. There is also some \(\text{Ca}^{2+}\) 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: \([\text{Si}_3\text{O}_{11}(\text{OH})]^6-\), 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.

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).
The feldspathoids group of minerals are SiO$_2$ poor, alkali rich minerals that occur in low SiO$_2$, high Na$_2$O - K$_2$O igneous rocks. The main feldspathoids are Nepheline (Na,K)AlSiO$_4$, and Leucite KAl(SiO$_3$)$_2$.

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.

Orthoclase

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.

Orthoclase

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$_2$O - K$_2$O igneous rocks.

The main feldspathoids are Nepheline (Na,K)AlSiO$_4$, and Leucite KAl(SiO$_3$)$_2$. 

CaAl$_4$(SiO$_4$)$_2$

KAISi$_3$O$_8$

NaAlSi$_3$O$_8$
TECTOSILICATES or framework silicates have a structure wherein all of the 4 oxygens of SiO$_4$ 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$^{+3}$.

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

The [AlO$_4$] tetrahedron is slightly larger than an [SiO$_4$].
Furthermore the potential energy of Al-O-Al is greater than that of an Al-O-Si linkage, suggesting that [AlO$_4$] are energetically unfavourable, with consequences for aluminosilicate minerals.
As most silicates in igneous and metamorphic rocks consist essentially of silica+metal oxides, free oxides can be considered to form if 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 stricto: MgAl$_2$O$_4$
# Stage | Age (Ga) | Example of minerals | ~Cumulative # species
--- | --- | --- | ---
1. Primary chondrite minerals | >4.56 | Mg-olivine/pyroxene, Fe-Ni metal, FeS, CAIs | 60

2. Planesimal alteration/differentiation | >4.56 to 4.55 | Phyllosilicates, hydroxydes, sulfates, carbonates, halite | 250
   a. Aqueous alteration
   b. Thermal alteration
   c. Shock phases
   d. Achondrites
   e. Iron meteorites

3. Igneous rock evolution | 4.55 to 4.0 | Feldspathoids, biopyroboles (volatile-poor planets) | 500
   a. Fractionation
   b. Volcanism, outgassing, surface hydration

4. Granite formation | 4.0 to 3.5 | Quartz, K-feldspar (perthite), hornblende, micas, zircon | 1000
   a. Granitoids
   b. Pegmatites

5. Plate tectonics | >>3.0 | Sulphides, selenides, arsenides, antimonides, tellurides, sulphosalts | 1500
   a. Hydrothermal ores
   b. Metamorphic

6. Anoxic biological world | 3.9 to 2.5 | Banded iron formations (Fe and Mn) | 4000
   a. Metal precipitates
   b. Carbonates
   c. Sulphates
   d. Evaporites
   e. Carbonate skarns

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 | Extensive ice deposition, but few minerals | >4000
   a. Glaciation
   b. Post-glacial oxidation

10. Phanerozoic Era | 0.542 to present | Extensive skeletal biomineralisation of calcite, aragonite, dolomite, hydroxylapatite, and opal | 4300+
   a. Biominalisation
   b. Bio-weathering

## THE ERA OF PLANETARY ACCRETION (>4.55 Ga)

## THE ERA OF CRUST AND MANTLE REWORKING (4.55 TO 2.5 Ga)

## THE ERA OF BIO-MEDIATED MINERALOGY (>2.5 Ga TO PRESENT)
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** = $2.5 \times 10^{32}$ 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) $= h/i$ 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 $\sim 10^{17}$ W or $\sim 200.00$ Wm$^{-2}$

**Heat flow from the Earth’s interior** is $\sim 0.08$ Wm$^{-2}$

Rocks are poor conductors of heat, e.g., they possess ‘low thermal conductivity’

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

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

### General Formula

- **K**
- **Na**
- **Ca**
- **Mn**
- **Fe**
- **Mg**
- **Ti**
- **Al**
- **Si**

<table>
<thead>
<tr>
<th></th>
<th>K⁺</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mn²⁺</th>
<th>Fe²⁺</th>
<th>Mg²⁺</th>
<th>Fe³⁺</th>
<th>Ti⁴⁺</th>
<th>Al³⁺</th>
<th>Al³⁺</th>
<th>Si⁴⁺</th>
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<tr>
<td>X</td>
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</tbody>
</table>

### General Formula – Phase – Group – Crystal Chemistry and System

<table>
<thead>
<tr>
<th></th>
<th>KAlSi₃O₈</th>
<th>NaAlSi₃O₈</th>
<th>CaAl₂(SiO₄)₂</th>
<th>Ca(Mg,Fe)(SiO₃)₂</th>
<th>(Mg,Fe)SiO₃</th>
<th>(Mg,Fe)₂SiO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthoclase (Or)</td>
<td>Albit (Ab)</td>
<td>Anorthite (An)</td>
<td>Diopside (Di)</td>
<td>Hypersthene (Hy)</td>
<td>Forsterite/Fayalite (Ol)</td>
<td></td>
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<tr>
<td>Alkali Feldspar</td>
<td>Plagioclase Feldspar</td>
<td></td>
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<tr>
<td>TECTOSILICATES</td>
<td></td>
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<tr>
<td>Triclinic</td>
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<tr>
<td>SiO₂</td>
<td></td>
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<tr>
<td>In alkali feldspars</td>
<td>1/4 of the Si⁴⁺ ions are replaced by Al³⁺</td>
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<td>In plagioclase feldspars</td>
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</tbody>
</table>

- **Monoclinic**
  - α ≠ 90°
  - β, γ = 90°

- **Orthorhombic**
  - a ≠ b ≠ c

- M₂ = X
- M₂ = Y

### Cations

- K⁺, Na⁺, and Ca²⁺ to be substituted into void spaces to maintain charge balance.
Example: a hedenbergite, a ferrous clinopyroxene with generic formula $\text{CaFeSiO}_3$ or $\text{Di}_{10} - \text{Di}_0$ might have an actual composition of:

$$\text{Ca}_{0.95}\text{Fe}^{2+}_{0.77}\text{Fe}^{3+}_{0.08}\text{Mg}_{0.20}\text{Si}_{1.92}\text{Al}_{0.08}\text{O}_6$$
One phase: i.e. a quartz crystal $\rightarrow$ **solid** SiO$_2$; molten quartzite $\rightarrow$ **liquid** SiO$_2$

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

**Binary Systems** (two components)

**Complete Solid Solution:**

i.e. *Plagioclase Feldspars* 'albite-anorthite series'

![Diagram](image)

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

8.5
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
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 Fo₉ and the solid is Fo₅₀.

4. At higher temperatures, the proportion of liquid increases at the expense of solid.

5. At T=1500 liquid Fo₂₀ coexists with solid Fo₇₂.

6. At T=1670 liquid Fo₅₀ coexists with an infinitesimal amount of solid Fo₉₀.

7. At T>1670 liquid Fo₅₀ 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 there 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) SYSTEM**

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.

Another ‘text-book’ example of another binary eutectic system is forsterite (Fo, olivine) and diopside (Di, cpx).
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 $T=1274 \, ^\circ\text{C}$, 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 \, ^\circ\text{C}, only crystals of An and Di are present.
Composition: $\text{Di}_{60}\text{An}_{30}\text{Ab}_{20}$
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
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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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

\[ P = 1 \text{ atm} \]
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.

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. SiO₂ (Quartz)

**Minerals**
i.e. silicate oxyanions [SiO₄]⁻⁴  
\[ \text{Olivine} = (\text{Mg, Fe})₂ \text{SiO}_₄ \]

**Rocks**
i.e. gabbro (Ca-plagioclase + pyroxene + olivine)
Let’s get native (rocks)
Igneous Rocks

Volcanic Rocks
- Pumice
- Obsidian
- Scoria
  - Volcanic (glassy)
  - Vesicular Basalt
  - Porphiritic texture

Plutonic Rocks
- Rhyolite
- Andesite
- Basalt
  - Volcanic (fine-grained)
  - Plutonic (course-grained)

Granite
- Diorite
- Gabbro
  - FELSIC
  - INTERMEDIATE
  - MAFIC

Textures
Igneous rocks production settings
From IGNEOUS (and metamorphic) to SEDIMENTARY
Primary ‘P’ waves travel through liquids and solids and they are the first to arrive from an earthquake focus. P-waves 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.
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<sub>K</sub>P) and reflected (PcP) by several zones of sudden density changes, as the core-mantle boundary.
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

- **Crust**
- **Upper Mantle**
  - **Transition Zone**
- **Lower Mantle**
  - **D'' Layer**
- **Outer Core**
  - **(liquid)**
- **Inner Core**
  - **(solid)**

**Depth in Km**
- 410
- 660
- 2600
- 2900
- 5100
- 6378

**Minerals**
- **Peridotite** (olivine + pyroxene + garnet)
- **Spinel** + (majorite)
- **Perovskite** + ferropericlase
- **Fe + (?) alloy**
- **Fe+Ni?**
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%
TOP 100
Km:
Lherzolite makes

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.

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

Typical geotherm boundary for typical crust. Path CD relates to the upwelling of mantle caused by crustal stretching and mantle divergence.
**DEPENDING ON DEGREE (%) OF MELTING (RELATED TO T AND P), DIFFERENT BASALTS ARE PRODUCED:**

- **15% Alkali olivine basalts (1500°) Si-undersaturated**
  - CIPW norm:
    - Cpx: 33.0
    - Oi: 27.0
    - An: 27.0
    - Or: 2.0
  - Olivine Tholeiitic (1600°) Si-saturated
    - CIPW norm:
      - Oi: 48.0
      - Op: 24.0
      - Cpx: 13.0
      - An: 9.0
      - Ab: 4.0
      - Or: 1.0

- **40-60% komatiitic (1700°) Si-oversaturated**
- **20-30% Olivine Tholeiitic (1600°) Si-saturated**
The major division of volcanic rocks is based on the alkali \((\text{Na}_2\text{O} + \text{K}_2\text{O})\) and silica \((\text{SiO}_2)\) content.

<table>
<thead>
<tr>
<th></th>
<th>SUBALKALINE</th>
<th>ALKALINE</th>
</tr>
</thead>
<tbody>
<tr>
<td>% per annum</td>
<td>88</td>
<td>12</td>
</tr>
<tr>
<td>Common representative minerals</td>
<td>Pyroxenes: Augite (cpx) + Hypersthene (opx) ((\text{Mg,Fe})\text{Si}_2\text{O}_6) + small free quartz + plagioclase phenocrysts, some in matrix</td>
<td>Pyroxene: Augite (cpx) + olivine (forsterite) + nepheline/leucite</td>
</tr>
<tr>
<td>THOLEIITIC</td>
<td></td>
<td>CALC-ALKALINE</td>
</tr>
<tr>
<td>% per annum</td>
<td>73</td>
<td>15</td>
</tr>
<tr>
<td>Specific Representative minerals</td>
<td>Hornblende (inosilicate - dark amphibole) Biotite (phylosilicate - mica) Phenocrysts</td>
<td></td>
</tr>
<tr>
<td>Main (mode) parameters</td>
<td>Fe-rich 45-63% (\text{SiO}_2) Very low contents of K, Ba, P, Sr, U, Th and Zr Low (\text{Fe}_2\text{O}_3/\text{FeO}) and (\text{K}_2\text{O}/\text{Na}_2\text{O}) Low initial (\text{Sr}^{87}/\text{Sr}^{86}) ratios</td>
<td>Fe-poor Hydrous Higher almina content (16-20 %) 48-75% (\text{SiO}_2) Higher oxygen fugacity</td>
</tr>
<tr>
<td>Petro-Settings</td>
<td>Low-p / high degree of melting</td>
<td>High-p / low degree of melting</td>
</tr>
<tr>
<td>Where they are found</td>
<td>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</td>
<td>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.</td>
</tr>
</tbody>
</table>

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...

QAPF diagram of coarse-grained igneous rocks

Plag

Opx

Cpx

Anorthosite

Plagioclase Orthopyroxenite

Orthopyroxene Gabbro

QAPF = 100

ANORTHOSITES

(LEUCO-)

GABBROIDS

(MELA-)

ULTRAMAFIC ROCKS

FeO*

Tholeiitic

Calc-Alkaline

Plagioclase Orthopyroxenite

Na₂O + K₂O

MgO

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

### Chemical and modal classification of subalkaline igneous rocks.

### Bowen's Reaction Series

![Bowen's Reaction Series](image)

### Volcanic Plutonic Oxides (%)

<table>
<thead>
<tr>
<th></th>
<th>Peridotite</th>
<th>Basalt</th>
<th>Andesite</th>
<th>Dacite</th>
<th>Rhyolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>43.5</td>
<td>48.4</td>
<td>53.9</td>
<td>66.9</td>
<td>72.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.0</td>
<td>16.8</td>
<td>15.9</td>
<td>17.5</td>
<td>13.9</td>
</tr>
<tr>
<td>CaO</td>
<td>3.5</td>
<td>11.1</td>
<td>7.9</td>
<td>3.6</td>
<td>1.3</td>
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<tr>
<td>MgO</td>
<td>34.0</td>
<td>8.1</td>
<td>5.7</td>
<td>1.6</td>
<td>0.5</td>
</tr>
<tr>
<td>FeO</td>
<td>9.8</td>
<td>7.9</td>
<td>6.5</td>
<td>2.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.5</td>
<td>2.6</td>
<td>2.7</td>
<td>1.3</td>
<td>0.9</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.8</td>
<td>1.3</td>
<td>1.5</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.6</td>
<td>2.3</td>
<td>3.4</td>
<td>3.8</td>
<td>3.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.3</td>
<td>0.6</td>
<td>1.3</td>
<td>3.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>

### Classification (according to SiO₂)

- Ultrabasic
- Basic
- Intermediate
- Acidic

### Top 5 share

<table>
<thead>
<tr>
<th></th>
<th>Ultrabasic</th>
<th>Basic</th>
<th>Intermediate</th>
<th>Acidic</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>95</td>
<td>92</td>
<td>90</td>
<td>95</td>
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</table>

### Minerals (%)

<table>
<thead>
<tr>
<th></th>
<th>Ultrabasic</th>
<th>Basic</th>
<th>Intermediate</th>
<th>Acidic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroxene</td>
<td>45</td>
<td>55</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Plag. feldspar</td>
<td>10</td>
<td>35</td>
<td>55</td>
<td>40</td>
</tr>
<tr>
<td>Olivine</td>
<td>45</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amphibole</td>
<td>15</td>
<td>10</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Alkali feldspar</td>
<td>5</td>
<td>15</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>5</td>
<td>20</td>
<td>35</td>
<td></td>
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<tr>
<td>Mica</td>
<td>5</td>
<td>15</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>
CIPW DIAGRAM — ‘Norm’ conversion from chemical composition to an ideal mineral composition

**Norm Calculation Program**

<table>
<thead>
<tr>
<th>Sample Number:</th>
<th>06/05/2009</th>
</tr>
</thead>
</table>

**Correction Factors**

- SiO$_2$: 56.06 %
- TiO$_2$: 0.07 %
- Al$_2$O$_3$: 15.55 %
- Fe$_2$O$_3$: 2.61 %
- FeO: 0.67 %
- MgO: 0.32 %
- CaO: 2.06 %
- Na$_2$O: 0.42 %
- K$_2$O: 0.01 %
- P$_2$O$_5$: 19.00 %
- CO$_2$: 13.35 %
- SO$_3$: 0.02 %
- F: 0.02 %
- Cl: 0.02 %
- Sr: 0.02 ppm
- Ba: 0.02 ppm
- K$_2$O: 0.02 ppm
- Total: 98.40 %

**Corrected Analysis**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weight %</th>
<th>Norm %</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garnet</td>
<td>55.09</td>
<td>40.39</td>
<td></td>
</tr>
<tr>
<td>Plagioclase</td>
<td>2.65</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Othoclase</td>
<td>1.24</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Leucite</td>
<td>1.15</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Kalsilite</td>
<td>1.35</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Cordierite</td>
<td>1.35</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Pyroxene</td>
<td>1.35</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Hypersthene</td>
<td>1.63</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>Wollastonite</td>
<td>1.63</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>Ulvite</td>
<td>19.31</td>
<td>13.60</td>
<td></td>
</tr>
<tr>
<td>Larnite</td>
<td>13.60</td>
<td>13.60</td>
<td></td>
</tr>
<tr>
<td>Acanthite</td>
<td>1.35</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>K2O3:03</td>
<td>1.35</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>Na2O:03</td>
<td>1.35</td>
<td>0.94</td>
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</tr>
<tr>
<td>Zircon</td>
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<td>0.03</td>
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<tr>
<td>Perovskite</td>
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<tr>
<td>Chromite</td>
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<td>0.94</td>
<td></td>
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<tr>
<td>Sphene</td>
<td>0.42</td>
<td>0.16</td>
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<tr>
<td>Pyrite</td>
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<td>0.16</td>
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<tr>
<td>Halite</td>
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<td>0.03</td>
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<tr>
<td>Anhydrite</td>
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<td>0.03</td>
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<tr>
<td>Calcite</td>
<td>0.20</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>0.20</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>144.33</td>
<td>100.00</td>
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</tr>
</tbody>
</table>

**Norm calculation checks:**

- Warning! May be a problem!

**Density calculations**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Vol %</th>
<th>Cat %</th>
<th>Dv Prop</th>
<th>Cat/cr Cat/cr</th>
<th>0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>56.91</td>
<td>71.73</td>
<td>0.5467</td>
<td>1.4837</td>
<td>Z1 20.46</td>
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<tr>
<td>TiO$_2$</td>
<td>0.07</td>
<td>0.11</td>
<td>0.0004</td>
<td>1.0000</td>
<td>Z2 0.08</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>1.58</td>
<td>2.42</td>
<td>0.0229</td>
<td>0.0047</td>
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</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.65</td>
<td>4.06</td>
<td>0.0266</td>
<td>0.0051</td>
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<tr>
<td>FeO</td>
<td>0.33</td>
<td>0.51</td>
<td>0.0072</td>
<td>0.0072</td>
<td>Z5 0.09</td>
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<tr>
<td>MnO</td>
<td>0.68</td>
<td>1.05</td>
<td>0.0060</td>
<td>0.0060</td>
<td>Z6 0.29</td>
</tr>
<tr>
<td>MgO</td>
<td>2.03</td>
<td>3.13</td>
<td>0.0059</td>
<td>0.0059</td>
<td>Z7 0.80</td>
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<tr>
<td>CaO</td>
<td>0.43</td>
<td>0.65</td>
<td>0.0017</td>
<td>0.0017</td>
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</tr>
<tr>
<td>Na$_2$O</td>
<td>0.43</td>
<td>0.65</td>
<td>0.0017</td>
<td>0.0017</td>
<td>Z9 0.29</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.43</td>
<td>0.65</td>
<td>0.0017</td>
<td>0.0017</td>
<td>Z10 0.15</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
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<td>13.60</td>
<td>1.4573</td>
<td>1.4573</td>
<td>Z11 3.33</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This program was written by Kurt Hollocher, Geology Department, Union College, Schenectady, NY 12308, hollocher@union.edu
Amphibole - hornblende
\[ \text{Ca}_2(\text{Mg},\text{Fe},\text{Al})_5(\text{Al},\text{Si})_8\text{O}_{22}(\text{OH})_2 \]

**Inosilicates**

**Biotite**
\[ \text{K}(\text{Mg},\text{Fe})_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2 \]

**Muscovite**
\[ \text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2 \]

**Phyllosilicates**

**Micas**

**Serpentine** – Mg$_3$Si$_2$O$_5$(OH)$_4$

**Clays** - Al$_2$Si$_2$O$_5$(OH)$_4$ - (Kaolinite)
“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 (>150-200°C) 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.

\[ \text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{MgO} \]
VOLCANOES
THE END

ROBERTO BUGIOLACCHI