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PLANETARY GEOLOGY

The aim of two day course is to offer a hopefully clear and logical journey through our 'material world'. The geological domain encompasses, well, a bit of everything. A first understanding of the word implies the study and classification of rocks but this narrow explanation has been gradually modified and expanded throughout the years. A rock cannot be adequately 'explained' without zooming in towards its physical properties, elemental and mineralogical composition, genesis and evolution, and zooming out to its origins and evolution, morphology, tectonics, planetary, and universal placement. Each rock also bears witness of a complex dynamic history linked to the particular physical conditions on our planet, including its evolving biosphere. So, where to start? As they say, the best starting point is the beginning, and this is where we will commence our journey from...



A PLANETARY JOURNEY THROUGH THE MATTER THAT COUNTS...

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LESSON 1- THE JOURNEY BEGINS, WHAT'S THE MATTER?

- 1.1 *From universe to us...*Estimated elemental abundances in key domains, from universe as a whole to human bodies. Key questions: why the differences in composition? What are the key (major) elements? Why do abundances cluster around a few elements in the periodic table? Refractory and Volatile elements (i.e. melting points, differences).
- 1.2 *Major elements*. Comparison between the seven major elements distribution in the universe, sun, bulk, and crustal Earth. Note marked differences between Earth's crust and mantle.
- 1.3 *Time Begins...* Following the Big Bang (or whatever first instance energy expansion mechanism), after around a second, baryons (i.e. protons and neutrons) are assembled from fundamental energy units (quarks). This phase lasts for around three minutes and results in the synthesis of the first nucleons (apart from H⁺ ions).
- 1.4 *Time has begun...* What we have in the universe so far: hydrogen, helium, and lithium.
- 1.5 *Time Expands...* Here we explain why, albeit helium is the most stable of elements so far, it does not dominate the overall composition of the universe.
- 1.6 Helium production starts again... Due to random gravitational irregularities, matter is squashed together and brought to temperatures of about 10⁷ K, hence initiating 'hydrogen burning', which produces helium.
- 1.7 Entropy defiant universe...Medium stars produce heavier elements in a process called 'helium burning', and stars >8*Sun produce the remaining elements up to iron (Fe 26).
- 1.8 Nucleosynthesis processes in more detail... Various processes are here proposed. Please note that these processes are not the only one producing matter. Indeed, nearly all the new elements have even numbers (we will see why later something to do with nuclear stability...).
- 1.9 *Iron gate...* Why does nucleosynthesis in a stellar environment end with iron/nickel? It's a matter of stability and exothermic processes.
- 1.10 Nucleosynthesis goes supernova... In the centre of massive and collapsing stars nuclei interact with neutrons to produce all the remaining elements up to bismuth (83) until fusion in the core cannot progress any longer. The metallic core collapses in extremely high temperature and pressure conditions and the star can only go one way... up!
- 1.11 Supernova!... The outer layers collapse inwards at first to then bounce out again in a supernova explosion, scattering the newly formed elements into space. Free neutrons are also produced and captured by colliding elements to produce all the remaining stable elements, up to ²³⁸U.

LESSON 2 - THE JOURNEY CONTINUES, WHERE IS THE MATTER?

- 2.1 *The Solar System...* The Sun composition of heavier elements than hydrogen and helium closely match those of the modelled bulk Earth, i.e. are they made out of the same stuff?
- 2.2 The formation of the Solar System... A step back; let's look back at the origin of the Solar system itself. It all starts with a rotating interstellar molecular cloud that at some point is 'disturbed' by a nearby gravitational instability, possibly due to a supernova explosion. The materials collapse towards a gravitational centre causing pressure and temperatures to rise dramatically. Nuclear fusion of hydrogen gas molecules commence and the Sun is born.
- 2.3 From interstellar gas and dust to us... Centrifugal forces generated by the rotating star and nebula would have allowed a proportion (1-2 %) of gas and dust to escape the proto-Sun and organising itself in a flattened, orbiting disc: the solar nebula. Here you find a table listing micro- and nano-mineral phases identified from interstellar grains in chondritic meteorites.
- 2.4 Planetary accretion...The era of planetary accretion starts after 4.55 Ga when temperatures within the solar nebula drop to temperatures below 1800 K, allowing the condensation of magnesium and iron silicates. The most primitive meteorites feature small spherical objects (~ 1 mm) that represent molten droplets formed in space, presumably by flash heating and rapid cooling during the T-Tauri phase of the Sun's formation. The clumping of matter would have taken 'only' around 100,000 years to grow to about 10 km in diameter (planetesimals) and eventually larger bodies (planetary embryos) to their present size order.
- 2.5 The order of condensation... This table shows the condensation sequence of the solar nebula at pressures of about 10 Nm⁻². This graph can be read from top to bottom, left to right: with dropping environmental temperatures, elements and molecules condensate sequentially according to their refractory (i.e. volatile) properties.
- 2.6 Interpreting the condensation sequence... First we see the condensation of the most refractory elements (staring from Os), then the ubiquitous aluminium oxide, then the platinum metal group, Rear Earth Elements (REE), Uranium (92) and Thorium (90). This is followed by Perovskite (CaTiO₃), probably the most abundant element on Earth (!), Gehlenite, the most refractory alumino-silicate, not common in evolved planetary settings, and finally Spinel (MgAl₂O₄), a mineral common in the upper part of the Earth's mantle. When temperature drops to less than 1400 K native metals would have condensed (Fe, Ni, Co, Cr) along the most common silicates in the solar system, Olivine and orthopyroxene (Enstatite). Below 1200 K plagioclase would 'appear', together with metals such as copper, silver, zinc, fluorine, chlorine, etc. Below ~ 700 K iron would form molecular compounds with sulphur (FeS, iron sulphide), and oxygen (FeO, iron oxide). The last compounds to condense would have been the highly volatile water, ammonia (NH₃) and methane (CH₄).
- 2.7 The same stuff, the same planets?... With similar elemental and compound building blocks, we would expect the solar system planetary bodies to be very similar in composition and structure. But they are not. For a start we have the inner planets (terrestrial) and the outer planets (Jovian). This was probably due to two main factors, both linked to the

distance of the material from the Sun and its (stellar) evolution, including an early phase of intense strong solar wind production that would have 'blown out' much of the lighter elements outwards (the T-tauri phase). This process would have lasted no more than a few million years.

- 2.8 The Nice model...The 'Nice model' as it has become known, is based on a computational model of gravitational interactions between planetary bodies soon after the major planetary accretion phase. In short, it offers an explanation for the eccentricities of Jupiter, Saturn, and Uranus and their orbital inclinations. The original coplanar orbits would have been disrupted when Jupiter and Saturn crossed their 1:2 orbital resonance, due to their interaction with a disk of planetesimals. Furthermore, the orbital swapping between Uranus and Neptune would have disrupted and scattered the materials in the planetary disk, causing them to leak out of the asteroid belt towards the inner Solar System. This could also explain the so called Late Heavy Bombardment of asteroids and comets at around 3.8 Ga, evidence of which has been found (and dated) on returned lunar materials.
- 2.9 *Giant impacts...* To conclude this section it is important to remember that the Solar System took many million years to gradually settle to its present form. Model simulations (Monte Carlo, e.g. Wetherill 1986) suggest that at least for the inner planets, most of the mass was accreted in the first 10 Ma, but significant accretion continued for up to 100 Ma. But even after this period, gravitational instabilities within the solar system brought into collisions planetary bodies of considerable size with catastrophic consequences for the young planets (as explained in the previous slide).



LESSON 3 - THE JOURNEY CONTINUES, WHERE IS THE MATTER?

- 3.1 What on earth is the Earth made of?... The sad reality (for science that is) is that we have little direct evidence for the overall composition of our planet, i.e. what lies beneath our feet. Indeed, we have directly sampled only about 10 km of the terrestrial crust.
- 3.2 *Meteorites: how can they help us?...* Out in space there are 'leftovers' from the time of the Solar System formation that we believe to be representative of the materials used to build planets and planetary bodies...
- 3.3Meteorite types... Meteorites are divided and subdivided into dozens of types, according to their mineralogical composition, crystallisation characteristics, origin (planetary, asteroids, etc.), representation, etc. Crucially, as per the asteroid family, they exhibit a range of compositions and mineral differentiation that is thought to relate to different pressures and temperatures environments. In particular, some could be representative of discreet compositional layers within differentiated planetary bodies, as per core, mantle, and crust, hence the main classification between Iron, Stony-iron, and Stony meteorites. A special class of meteorites called 'Carbonaceous Chondrites' (CC) are thought to represent the bulk composition of young planetary bodies, samples of potentially undifferentiated building-material formed directly through condensation, melt solidification, and/or solidstate recrystallisation. It is important to recognise that unaltered chondrites contain all the chemical complexity of terrestrial planets. Indeed, their typical composition could be summarised (as per the chondrules minerals) as Mg-rich olivine and pyroxene, Fe-Ni metals, and Troilite (FeS) as the major iron-bearing phase. Finally, most of the 83 stable geochemical elements are present in solid solutions, but they are presumably too widely dispersed to form their own discrete mineral phases.
- 3.4 Carbonaceous Chondrites?... Chemical analysis of CC meteorites have shown a composition close to that of the Sun (and presumably also similar to the overall composition of the early Solar Nebula) minus H and He. The graph plots relative abundances and the line represents 1:1 elemental abundances match. There is a remarkable match between the two bodies: key elements such as silicon, magnesium, aluminium, sodium, and calcium are practically present in the same proportions (remember, one is a glowing ball of gas kept 'alive' by thermonuclear reactions, and the other, a piece of ancient, primordial rock assembled from tiny 'chondrules' of basic minerals!). Notable exceptions of this trend are represented by lithium and boron (for particular chemical reasons) and, crucially, nitrogen and carbon (relatively depleted in the rock in respect to the Sun): these two are highly volatile elements that were presumably depleted either during formation of the rock or subsequently. A similar element, oxygen, succeeded to 'hang on' to the rock by readily combining with metals, i.e. forming oxides.
- 3.5 Are we on a chondritic Earth?... OK, now that we have an idea of the presumed initial composition of the primordial Earth, we could assume that, allowing for billions of years of remelting and mixing of terrestrial rocks, the planet should still retain a comparable composition to the CC meteorites and the Sun. Let's start with the 'stuff' beneath our feet, the Earth's crust. Average compositional estimates are surprisingly difficult to obtain and vary considerably between workers, sometimes in the order of two magnitudes between the lowest and the highest estimates (i.e. Ar, Ru, W). Thankfully, there is better consensus over the main elements such as oxygen, silicon and aluminium. This time, when plotting the 'best' average estimates against the CC-Sun averages, we notice a

peculiar division: most (heavy) metals lie above the straight line (i.e. they are depleted in the crust), including Fe, Mg, Ni, Cu, Zn, etc. (with one notable exception, Ti), with volatile elements instead, including 'light' metals, enriched in the crust (K, Na, Ca, Al).

- 3.6 Is it a matter of compatibility?... One of the reasons for this elemental dichotomy relates to the degree of 'affinity' that certain elements display in relation to others. If they can easily enter a particular chemical composition they are said to be 'compatible'. We can already 'guess' that heavier metals by some gravitational mechanism related to their relatively larger mass would have favoured their segregation toward the depths of the Earth. Compatible elements would have been 'dragged along' hence vacating their crustal/mantle abode.
- 3.7 Who goes with whom, then?... Elements (in a mineralogical context) are classified according to their compatibility characteristics: lithophile, chalcophile, and siderophile elements. The focus of this classification are the lithophile elements, which will 'stay' where silicates (silicon + oxygen compounds) are present, and the siderophile, which tend to concentrate in the depths of the earth (the core).
- 3.8 A table for ...92+... The periodic table, highlighting the classification of elements according to their '-philic' properties. All classification and rules are obviously made to be broken... and offer plenty of 'exceptions'. Notably iron, a chalcophile element in the chemical domain, i.e. readily 'captured' by sulphur in an ideal environment (as in chondrules, Troilite, FeS), but in such larger proportions in the bulk Earth, that there is not enough sulphur to 'go around'; hence the metal behaves as siderophile (Fe in core) and lithophile (in silicates in the crust and mantle).
- 3.9 Let's assemble a planet... A step back to the first 100 Ma of the Solar System. In our brief introduction we have seen that the Earth's crust is not fully representative of what we believe it to be the bulk composition of the planet. Consequently, we can assume that the materials in the depths of the Earth vary with depths. How did they end up where they are now? There are two main schools of thought: one proposes that the planet (and possibly all larger planetary bodies) assembled heterogeneously, i.e. the 'ingredients' would have accreted in the 'right' temporal order to form the observed distinct mineralogical layers. But there are problems with this model: for instance Fe and Ni are in the 'wrong' place according to the condensation model (later for instance than silicates).
- 3.10 The homogeneous model... 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. For instance, heat (energy) would have facilitated the segregation of iron and its compatible elements by gravitational processes, leading to the accumulation and formation of a (mainly) iron core(s). And this process would have been extremely quick by geological standards: just a few thousand years.

LESSON 4 - A LAYERED EARTH

- 4.1 The composition of Earth's layers... Here we have to go back to the basic elements making up our planet. We are now 'switching' between compositional estimates in terms of atomic population statistics to relative mass, to facilitate our journey and discourse on a reliable and plausible bulk Earth composition model. Estimating the mean atomic mass of a planetary body is relatively easy, helped by gravitational and compositional data and assumptions. On Earth, seismic waves (both natural and manmade) have been employed throughout the last century to probe the inward structure of our planet, in terms of rock density and the best estimates are shown here.
- 4.2 *Comparing the world...* If we had reliable estimates on the MAM of the different Earth's layers, all we would need to do is match them with those from various meteorites and see which one are the closest to the CEM. But the MAM of the range of meteorites at our disposal are so diverse that a near infinite number of permutations would supply comparable compositions. Nevertheless, as the figure shows, by mixing various meteorite types within plausible and geo-chemically permitted boundaries, estimates converge towards a more narrow range of possible compositions. One of the remarkable points is that despite uncertainties, over 90% of the mass of the Earth is represented by only four elements: oxygen, iron, silicon, and magnesium!
- 4.3 The Crust... We can start from here. Determining average rock densities (through their density estimated from data of seismic wave velocities) is relatively straightforward and easily comparable to known values. The table lists average densities of major crustal rocks. Densities vary from 'light' alluvium and sands to 'dense' gabbros (the intrusive equivalent of basalt) and peridotite (a typical mantle rock). Given that the average density of the Earth as a whole is 5.5 g/cm³, there is some work to be done here... Nevertheless, we can guess that an heavier element might be involved here than the listed rock types, something like iron, with a density of 7.874 g/cm³ for instance...
- 4.4 The Crust composition... Elements in geology are most often represented in their 'natural' oxidised states, a process that will be explained in some detail later. If we take the given compositional estimates, we see that three quarter of the crustal composition is mostly represented by silica, followed by aluminium oxide. If these figures were to translate into a rock of comparable composition, it would be represented by the rock granodiorite, a coarse-grained igneous (plutonic) rock consisting mainly of the minerals quartz, feldspars, biotite, and hornblende.
- 4.5 The Crust composition 2... A 'granodioritic' composition is also consistent with uppercrust 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. But as we descend deeper, even within the crust, seismic data tell us that the rocks become denser and here increasing pressures and temperature conjure to accommodate a metamorphosed basalt rock called granulite, consisting mainly of feldspars, pyroxene, and garnet. Again, these are assumptions, only corroborated by density estimates, a few exposed examples of lower crust materials and xenoliths, so caution should be used to reach simplistic conclusions about the petrological state of the whole crust.

- 4.6 The Mantle composition... 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 of xenoliths in Kimberlite pipes and ophiolites. Looking at the exposed strata, below the oceanic sediments, followed by distinct types of basalt layers, we find peridotite $[(Mg,Fe)_2SiO_4]$, a dense, coarse-grained igneous rock, consisting mostly of the minerals olivine and pyroxene. The rock contains less than 45% silica and it is high in magnesium. Different types of peridotite exist: Dunite (>90 olivine), Wehrlite (olivine + cpx), Harzburgite (olivine + opx; a low proportion of basaltic ingredients).
- 4.7 The Mantle composition 2... The experimental and actual density models of the upper mantle match those of rocks of composition close to the garnet peridotite rock. The table offers the oxide distribution based on this assumption. The Lower Mantle composition is thought to reflect that of the upper mantle, but the much higher P/T environment causes the minerals in peridotites to change into higher-pressure phases. Between depths of 520 and 670 km olivine 'contracts' into the crystal phase spinel (i.e. Ringwoodite, an olivine polymorph) increasing the rock's density by around 10%. Further down (>670 km), and at even higher pressures, spinel turns into perovskite (MgSiO₃) and residual MgO. As we have seen earlier, most of the whole mantle ('78%) is composed of minerals with a perovskite structure.
- 4.8 The Core... Here again, seismic data supplies us with the only 'direct' evidence of the existence of a deep terrestrial layer with distinct density characteristics. Indirect evidence is offered by the assumptions of a chondritic composition of the Earth and distinct meteorites reflecting differentiated layers: accordingly, iron-meteorites would be representative of a planet's denser layer. This is also indicated by the paucity of Fe in the models of mantle composition, chondritic meteorites, and against known cosmic abundances. Furthermore, 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. 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.
- 4.9 The Core 2... Nevertheless, as per the outer, liquid core, high-pressure and -temperature experiments show that a pure (molten) iron layer would display seismic velocities and densities somewhat higher than those deduced from refracted/reflected seismic waves generated by large earthquakes. Calculations have shown that iron must be present as an alloy containing 5-15% of a less-dense element. The most likely candidates are O, S, C, H, and K. As per the Inner Core all we know is that it is probably solid with a density (i.e. composition) similar, but not identical, to that of iron. There are as many schools of thought as there are permutations of likely elements, but the present consensus appears to cluster around the idea of a core of mostly iron composition with nickel making up nearly 20% of the remnant.

- 4.10 The Earth layers... Here we have a graphical representation of the layers just discussed. The layers are represented proportionally within the Earth's radius; the numerical values next to the typical rock type at the layers' depths indicate the starting boundary depth (taken from the surface). The insect pie chart shows the relative volumes of the same layers for the whole planet. Apart from the siderophile cores, most of the composition and mineralogical structure of the Earth (80%) is represented by the rocks Peridotite, Spinel, and Perovskite, themselves composed mainly the mineral olivine and its polymorphs.
- 4.11 *Conclusions 1...* 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 its iron core, we end up with a comparison between garnet peridotite and the average carbonaceous chondrite. Since this doesn't work, something is out of balance, and we need to include the metallic core in our calculations: obviously CC meteorites do not represent a straight mantle composition.
- 4.12 Conclusions 2... The adjusted bulk Earth composition model is now a better match to the average CC meteorites. The graph tells us that the Si, Mg, Al, and Ca oxides are indeed 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, the CEM could work, with notable difference concerning alkalis (K and Na), Cr, Mn, and, again, Fe. The conclusion is that the Earth appears depleted in volatiles and iron in comparison to idealised pristine samples dating from the early solar system time. There are several chemical models proposed to explain these differences, but again, the most remarkable point is the correspondence between the bulk composition of the Earth (>95%) and CC meteorites.

4.13 And finally... To conclude, much research has gone into establishing a compositional pattern for minor elements too, i.e. 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. A final though brings us back to the elements abundances in the universe and their peculiar zigzag comparative abundances. It's a bit odd (or even), isn't it?

LESSON 5 - FROM ELEMENTS TO MOUNTAINS

- 5.1 A step back... We are now taking a brief step back to our previous quest for the key compositional elements in the Solar System / Earth. When we are dealing with geochemical quantities, we refer mostly to the (major) elements in their oxidised states. We can compare the elemental chart to the left, which includes oxygen in its native state, and the percentage oxides mass distribution for the upper mantle showing silica 'jumping' to the first spot, due to its double oxygen bonding, and the 'relegation' of iron to a third place, due to its physical segregation in the Earth's core.
- 5.2 So, an oxidised planet... Now, let's focus briefly on the process of oxidisation, starting from the key actors in this play: oxygen and silicon. First, let's not forget that oxygen is the third most abundant element in the universe, after the 'primordial' hydrogen and helium. At standard temperature and pressure it exists as a diatomic gas (O_2) . Interestingly, we literarily walk (but also swim...) on oxygen since it represents 94 % of the Earth's crust volume. Oxygen is the second most reactive element (second only to fluorine), due to its relatively small atomic size and high electronegativity (we will look into more detail further on). Because of its 'eager' to combine (or oxidise), oxygen, at the appropriate temperature and pressure conditions, will form compounds with most elements, including precious gold (as Au_2O_3).
- 5.3 Silicon... 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 " $_{8}O + _{8}O \rightarrow _{14}$ Si + $_{2}$ He" oxygen burning process; and " $_{12}$ Mg + $_{2}$ He $\rightarrow _{14}$ Si" pure α process. We are going to look at the properties of the electronic properties of silicon soon.
- Scary box chart... OK, here is the magnum classification of mineral types, from elements to 5.4 mineralogical families, and it is still incomplete... The reason for presenting this slide at this point in the lectures is to offer you an overall feel of the complexity and intricacies of geological classifications and jargon. I have taken the most common terrestrial basalt type (>2/3) that erupts in Mid-Ocean-Ridges as an example, which sutures and fills in the widening oceanic crustal along spreading ridges, thus becoming new (oceanic) crustal material (i.e. see floor). The full name of this rock is 'Silica-saturated (which means the liquid was produced in a relatively silica-rich environment) extrusive (i.e. volcanic, erupted) igneous (volcanic rock-type) rock, a melanocratic (dark) olivine-tholeiitic (olivine is present in the mineralogy) MORB (Mid-Ocean Ridge Basalt)". This rock composition is then broken down into a number of distinct classification ways: so, a rock sample can be described according to its elemental distribution (i.e. oxygen, silicon %), or bulk chemistry (the same elements but in their 'natural' oxidised state); from this point, the classification can be expressed in two different ways: Modal (as in observed, next slide) or CIPW (idealised) which is an ideal and experimentally derived likely minerals assemblages obtained from the given bulk chemistry (for instance with 49% SiO₂ and 13% Al_2O_3 one is likely to get, among other components, 25% anorthite). The first and the second columns in the table express the same compositional formula (i.e. anorthite for the first row) either as oxide contribution $(CaO.Al_2O_3.6SiO_2)$ or 'standard' mineral formula $[CaAl_2(SiO_3)_2]$: they are both equivalent, but emphasising the same chemistry differently. The 'phase component' is the name of mineral phase with in brackets the standard abbreviation. 'Modal' is a first order nomenclature, with P as per Plagioclase, M

for Mafic, and A for Alkali. The family is a two tear level classification: first the silicate family which the mineral belongs to (for instance plagioclase is a Tecto-silicate, more later), but it is also part of the feldspar family, which includes, for instance, the alkali feldspars. The last column shows the (idealised) weighted percentage of each mineral present in the rock sample. Simple.

- 5.5 *Mineral census...* One chooses one or more sampling area and, under the microscope and employing a number of techniques, literally count the discernible mineral phases. Another technique method until the 1960s used 'wet' chemistry to dissolve rock in acids and analyse the oxides concentrations. Nowadays, several and more sophisticated methods of analysis are employed (such as X-Ray Fluorescence).
- 5.6 The Periodic Table... This is the key to most chemical behaviour of elements and, consequently, mineralogical order. This table also remind us that the arrangement and properties of the outside 's' and 'p' electrons (orbitals) dictates much of the electronic interaction behaviour between atoms. As we can see, the nominal electronic vacancies or 'surpluses' of the sp orbitals have a direct consequence on the elements' properties, as to behave as cations (potentially positive ion) or anions (negative ions). This does not mean that an ideally isolated atom, for instance of hydrogen, has a negative charge (being an anion), but if it interacts with another ion will preferentially 'gain' or share an electron into its 1s orbital, thus gaining a negative potential. Conversely, A sodium atom would ideally 'lose' or share its 3s orbital electron, hence 'becoming' positively charged. This behaviour is underpinned by fundamental quantum forces behaviour and the tendency of atoms to reach 'noble gas' electronic equilibrium (status), i.e. 'filling' of the outermost 's or p' layer (2 and 6 electrons respectively). The chemistry, behaviour, and characteristics of each element are thus dictated principally by its mass and electronic configuration (mainly the outermost orbitals). Since the orbital characteristics of certain elements are recurrent and similar, it's no surprise to find that most elements can be grouped according to similar physical characters. Thus we have the group of alkali metals, halogens, transition elements and so on, each with its own individual properties but also sharing bonding and behavioural characteristics. Valence bond theory of the chemical bond tells us that 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).
- 5.7 The Table is set... This is a graphical representation and grouping of the elements. The valence of chemical elements is represented by different colours. The type and strength of molecular bonds are related again to the electronic arrangement of the outermost layers. Electronegativity is a property of the ion and it relates to its electrical potential field strength. As we can see, for instance, clorine (Cl) is strongly electronegative and sodium (Na) electropositive: they form a strong ionic bond and a familiar molecule (salt). Covalent bonds are usually non metals plus non metals or the same element bond, as in Cl₂.

LESSON 6 - THE SILICATE WORLDS

- 6.1 Silicate Minerals... So, we have seen that silicon dioxide represents an estimated 45 wt% of the mass of Earth (the rest is made up of Mg [~40%], Fe [8%] and Al+Ca [~6%] oxides). Let's now focus on silicates, by far the most abundant compound on bulk Earth (and over 60 wt% of the estimate terrestrial crust materials!).
- 6.2 Back to basics?... The key to a better understanding of the properties of rocks, minerals and compounds obviously lies at the deeper level of atomic interactions. This is why we need to go back and dust off some 'college' level basics we might have shelved away all those years ago... the way matter (atoms) stick together is fundamental to our understanding of the universe and dictates the shape and behaviour of everything around us. Here we are talking about atomic potential energy: the structure of ionic compounds (from H_2O to CH_4 to basic O_2) 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: a crystal structure. As we will see, the forces that bind atoms together in a crystal structure are collectively known as chemical bonds and in particular they are expressions of the type and arrangement of electrons in the outermost shells in an atom (valence) and the size of the atom or ion itself. Let's dig in a bit...
- 6.3 Boring you with Bohr again?... Yes, just to refresh our memories: the quantum mechanical view of the atom suggests that the electrons are located within specific regions of probability. Each energy region (orbit) can only accommodate a given number and type of electrons, this o<mark>rbit can have 'gaps' or being partially unfill</mark>ed, but never 'overfilled'. Electrons will have different energy levels according to their 'distance' and orbital geometry in respect to the (positively charged) nucleus. The closer to the nucleus, the smaller the num<mark>ber of cohabiting</mark> electrons: so, each quantised energy level (K, L, M, N, moving progressively further away from the protons) can 'house' a maximum of $2n^2$ electrons, i.e. 2 for K, 8 for L, 18 for M and so on. Each level is subdivided into probability regions, each with a spin quantum number of +1/2 or -1/2 (Pauli Exclusion Principle): what we have then is the K level, with two 'spaces', will have the 's' type orbitals only (which are spherical); the L level, with a 'capacity' for 8 will have the two 's' electrons and 'room' for other six (or three Pauli's pairs), in orbitals called 'p', and arranged in space along the xyz planes. The next orbital, the M (with capacity for 18 e) would now include the two 's' electrons, the six 'p', and ten extra orbitals 'd' with five different probability regions. The next orbital N... you get the drift by now.
- 6.4 Repercussions in the macro world... The interaction of key orbital electronic 'layers' between atoms is the key to the behaviour of all matter. The propensity of atoms to lose (land) or gain (borrow) electrons dictates the fundamental characteristic of each element: the Ionisation Potential (IP) represents the amount of energy required to remove an electron form a give orbit. Some elements, such as those in group IA (alkalis), share a similar electronic orbital configuration (one electron in the 's' orbital); since it takes the least amount of energy to remove this electron, these elements have very low IP values and have the potential of becoming positively charged ions, i.e. cations (charge unbalance between the nucleus charge [+ve] and the electron). On the other end of the scale, Groups VI and VII elements, which include the highly reactive oxygen and fluorine respectively, have very high IP: therefore they tend to gain, instead of loose, an electron; when this happens they become negatively charged (Anions). Group VIII is represented

by the noble gases and they don't 'give up' their electrons easily, since they are tightly bond in filled spherical orbits, so they rarely become ionised and form compounds with other elements. Because of this 'exclusivity', they are named 'noble' and they exist in a gaseous state at 'normal' temperatures and pressures. A case apart are the Transition elements, which have 'd' orbital electrons in their outermost shells; they also have low-tohigh IP and their electronic (or ionic) behaviour is somewhat unpredictable and display a diverse range of valences.

- 6.5 On the other hand... Another fundamental property of atoms is their ability to attract electrons into their outer layer within a crystal structure or molecule: elements with low values of electronegativity are electron donors, and those with high values are electron acceptors. Obviously, this atomic behaviour is linked again to the electron orbital characteristic of each element and it is asymmetrical to its IP. So, here the electronegativity of each elements is somewhat predictable from its outer layer characteristics: for instance, both fluorine and oxygen are the most electronegative elements because they will readily incorporate electron to achieve 'noble status' (hence forming strong compounds such as fluorocarbons polymers, like Teflon, an extremely stable compound); oxygen will scavenge the universe for two electrons for its 'p' layer hence oxidising most elements it encounters, if fluorine has not got there first, that is! These two elements indeed cannot easily be found in a 'native' state at all; they exist mostly as bivalent compounds: O_g or F_g .
- 6.6 A big table and size... A quick glance again at the electron arrangements of the first 30 elements and their somewhat predictable electronic behaviour from the orbital characteristics of native elements. We introduce here the term 'valence' or valency, relating to the distribution of the outer 's' and 'p' electrons (note which elements are potential cations and which ones are anions). Now, ions may exist in isolation (as plasma for instance), and electronic characteristics are fundamental here. But when they come together in compounds, another characteristic of the atom, which somewhat is also related to electronic arrangement as we will see soon, comes into play: its ionic radius, or size. Here the idealised and much simplified model of an atom as a sphere with the surface dictated by the orbit of the outermost electrons can be successfully employed to describe the physical dimension of the ion with good approximation. The size of an atom depends not only on the nature of the element, but also its state of ionisation and the manner in which is linked to adjacent atoms: for instance, Na as metallic sodium has a radius of 1.86 Å (or 18.6 nm) but in sodium salts is 1.02 Å.
- 6.7 Give me room to breathe... Now, 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). If we accept a model of atoms as (plastic) spheres, then we can start arrange them in space against other similar (or indeed different) spheres, each ion surrounded by as many ions of the other species as it is geometrically possible: the principle of close-packing. The table list (average and typical) ionic radii of the main mineral forming elements within a crystal lattice. Since, as we have seen, most of these elements will combine in some fashion with oxygen (will exist in an oxidised state), the radius of element against oxygen becomes a fundamental parameter and will dictate the geometrical arrangement of ions, which in tern, will influence the type and physical characteristic of the minerals formed. Simple close-packing geometric calculations will show that spheres with a given radius

will arrange themselves as polyhedron of different types according to their ionic sizes. For instance, when coordinated with oxygen, six iron or magnesium ions will arrange themselves in an octahedral shape around the oxygen atom (described as sixfold symmetry or having a Coordination Number [C.N.] 6); on the other hand, four silicon ions will form a tetrahedron with 109.5° angles (C.N. 4).

- 6.8 Zooming in back to silica... First, a quick look at the atomic level of the silica compound: to the left we have idealised electronic configurations for the silicon and oxygen atoms. As we saw earlier, silicon as a metal tends to 'lose' or lend its outermost electrons in order to achieve noble status (hence becoming cations, or positive ions). Here we see the 3s pairs, and the $3p_x$ and $3p_y$ electrons in an 'isolated' atom. Oxygen instead, with high IP and low electronegativity will strongly attract electrons to fill its $2p_x$ and $2p_y$ orbitals. The quantum processes here get slightly complicated, but it should suffice to say that the outermost orbits degenerate into hybrid orbits '3sp' and '2sp' for silicon and oxygen respectively, rearranging themselves according to the electronic forces exerted by their neighbouring ions. OK, so we have explored the electronic and physical configuration of the omnipresent silica compound. Pauling's rules govern the way ions behave in a given crystalline physical structure. We are going to concentrate on 'rule 2', which states that "...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". Hummm.
- 6.9 Rules: a few... We introduce the concept of electrostatic valency (e.v.) which is defined as the 'charge on the ion divided by its coordination number (C.N.)'. Here we see that Rule 2 applied to silica molecules tells us that the oxygens in the $[SiO_4]^4$ group can be just as tightly bound to ions outside the group as to the centrally coordinated silicon. Soon we will see how this relates to silicates... Another useful Rule (3): sharing of only corners of polyhedra places the positively charged cations at the greatest distance from each other. The implication for silica is that, in a tetrahedral coordination, the 'shared corners' configuration is the most stable, with consequences for the different behaviour of silica phases. The physical size and electronic behaviour so far mentioned results in a limited number of ways for the atoms to arrange themselves within a crystal structure, although different elements may occupy similar sites, as we will discover...

LESSON 7 - THE SILICATE WORLDS - 2

- 7.1 Silicate minerals, which goes with whom?... Focus on silicates. The general formula for silicates is $X_m Y_n(Z_p O_q) W_r$, where the capital letters stand for elements as listed in the upper table and 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 Al³⁺ for Si⁴⁺ and whether the X (M2) site is large enough to accept the largest cations like K⁺.
- 7.2 Finally: crystals!... The textbook definition of a crystal describes it as "a homogeneous body in which the atoms or molecules are arranged in a regular, repeating pattern that may be outwardly manifested by plane faces". 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). 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. On the other hand plutonic 'gabbro', which magma had time to cool down slowly below the surface, features crystals of varying sizes and 'maturity'; basalts, the extrusive equivalent of gabbro, instead have crystals which are generally much smaller but still might include phenocrysts, or individual sizable crystals formed at depths; finally, obsidian, sharing the same composition again, but quenched quickly in the atmosphere or water, is totally amorphous (like glass) and features no visible crystals. Again, these rather different looking rocks essentially share the same composition, both as in oxides type and elemental ratios. Incidentally, crystals can be 'broken down' to their most basic geometrical unit, retaining a repeating and translatable atomic arrangement (unit cell) forming the individual crystal lattice.
- 7.3 Crystal systems... Again, a crucial definition of crystals, this time focusing on the threedimensional arrangement of atoms in space, which has to posses symmetry of structures in three dimensions with translational symmetry in three directions (as shown in the inset below). The seven main groups of crystal systems are shown together with the best known mineral examples. Except for the hexagonal figure, most crystal figures appear as variations on a common blueprint: the cubic system. Indeed, if we pull the cube in one direction of another, we get all the other five crystal systems: this is because the lattice parameters enjoy six degrees of freedom and they differ only by the relative lengths and faces angles. In the orthorhombic system, the lengths a-b-c are all different, but the angles α - β - γ are the same (90°). On the triclinic crystal, all the angles are different from 90° but the lengths are the same.
- 7.4 Nesosilicates... The name stands for island silicates which refers to the fact that the minerals in this family contain independent $[SiO_4]^{-4}$ tetrahedral. Olivine(s) are the best known mineral phase examples and they are mostly iron-magnesium silicates that formed early in the history of the solar system. Their presence has been detected on the surfaces of all terrestrial planets (except for Venus), most satellites, and asteroids. Olivine (and its high-pressure polymorphs) also makes up most of the Earth's mantle's composition (along with the aluminium-rich mineral garnet). Zircon is an ultra-stable compound and it is used to date very ancient rocks (thanks of its uranium inclusions that is).

- 7.5 Olivine crystal structure... 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). The inset shows an alternative description of the olivine lattice and gives an example of a way a three-dimensional arrangement of points in space can be represented according to the point of perspective.
- 7.6Inosilicates... In chain-silicates, two or two and a half oxygens are shared by adjacent tetrahedra. Most minerals in this group are called single chain silicates because the $[SiO_4]^{4}$ tetrahedra are linked together to form chains of composition $[SiO_3]^{2}$. These are bonded together by cations such as Mg^{2+} , Fe^{2+} , Ca^{2+} , and Na^+ . There is complete solidsolution between Mg and Fe members. There is also some Ca^{2+} in most pyroxene structures that becomes distorted by the large calcium ion. The classification of pyroxenes relates to the type and ratio of cations linked to the [SiO₃]² chain: most have either or both iron and magnesium ions within their structure, but the large cation calcium has the largest influence on the crystalline structure of the mineral. When its concentration is <5% we have orthopyroxenes; up to about 18%, pigeonite, and finally, up to, but not over 50%, we have clinopyroxenes. In a real planetary environment, the range of compositions are potentially infinite but they tend to cluster around certain compositional clusters relating to specific geomorphologic settings; Augite, the most common cpx, has a variable calcium content between 26 and 46 % and magnesium between 10 and 50 %: it occurs mainly in igneous rocks and represents an essential mineral constituent of gabbros, dolerites and ba<mark>salts. In plutonic</mark> gabbros augites frequently occur with opx. Pigeonite instead occurs only in rapidly chilled rocks, otherwise, in slow cooling geological environments it would invert to orthopyroxene.
- 7.7 Pyroxene crystals... The pyroxene group is composed of minerals of the general formula $XY(SiO_3)_2$. If X and Y are small-radius divalent cation like Fe^{2+} or Mg^{2+} the resultant structure is commonly 'undistorted' or orthorhombic and the pyroxene is classified as a orthopyroxene; if X and/or Y are two divalent cations and X is a large-radius cation like Ca^{2+} , the structure is monoclinic and we have a clinopyroxene. The image shows the effect of the large calcium cation within the pyroxene SiO₃ crystalline structure.
- 7.8 Tectosilicates... Or framework silicates; here all four oxygens are shared with other tetrahedra. If composed entirely of silicon and oxygen, such framework will have the composition of SiO₂, as in quartz. These silicates are divided into two main mineral groups: Alkali and Plagioclase Feldspars. Feldspars are the most important constituents of many rocks found at the Earth's surface. The plagioclase series (of composition) ranges from anorthite (low Na) to albite (low Ca) and they form a solid-solution series, so called because all intermediate compositional abundances (from 100 % Ca to 100 % Na) are possible in various geological settings. This is possible because calcium and sodium have comparable sizes, unlike the orthoclase (K-rich) and albite series (the so-called alkali feldspars, or K-feldspars) where, giving the difference in sizes between potassium (larger) and sodium ionic substitution is limited and the two minerals form separately.
- 7.9 *Quartz et al....* Back to the structure: here we have a (solid) crystal framework built around the oxygens in the silica tetrahedra shared with other oxygens of other tetrahedra, in effect creating a close framework where the ratio of silicon to oxygen is 1:2: in this case

the mineral is quartz or one of its (pressure related) polymorphs. But, as we saw in the section about sizes we noted that aluminium (6.7) can also 'shrink' to an ionic radius comparable to silicon (0.39 and 0.26 respectively), hence is able to 'fit' a fourfold symmetry (a tetrahedral, as in AlO₄ instead of SiO₄). When this happens the potential energy of Al-O-Al becomes greater than that of an Al-O-Si linkage, in a sense weakening the inherent strength of the 'purer' framework silicates (i.e. quartz); significantly, if one out of four of the Si⁺⁴ ions is replaced by Al⁺³ two things happen: aluminium, as we have seen, being larger than silicon 'expands' or distorts the framework structure, and, crucially, creates a charge unbalance allowing for the cations K⁺, Na⁺, and Ca²⁺ to be incorporated and substituted into void spaces. Let's take it step by step starting from 'perfect' quartz: [Si⁺⁴0⁻²] (or times four = [Si⁺⁴]⁺¹⁶₄[0⁻²]⁻¹⁶₈); if we substitute one Al every

four Si then we have $Al^{+3}[Si^{+4}]_3^{+12}[0^{-2}]_8^{-16}$; the compound charge is unbalanced so, it can

accommodate alkalis, hence giving the alkali feldspar series: $[K^{+1},Na^{+1}]_1^{+1}Al^{+3}[Si^{+4}]_3^{+12}[0^{-2}]_8^{-16}$; now it is balanced! Similarly, when two aluminium ions

substitute two silicon ones, to maintain charge balance the (idealised) elemental composition will be: $Ca^{+2}[Al^{+3}]_{2}^{+6}[Si^{+4}]_{2}^{+8}[0^{-2}]_{8}^{-16}$; this represents the chemical formula of

the calcium rich plagioclase feldspar end member anorthite.

7.10 Metal Oxides... Metal oxides (mainly iron and/or titanium oxides) are present when the ingredient materials making silicate rocks are silica-deficient or the metals present are surplus to the needs of silicates. Iron-titanium oxides 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.

LESSON 8 - ENERGY, SILICATES, AND PHASE DIAGRAMS

- 8.1 A mineral genesis?... Hazen et al. (2008) have compiled a useful table proposing a timescale of 'Mineral evolution', as they titled their paper. Here again, we see that primary chondritic materials (the most primitive dust-grains materials to solidify within the solar nebula) are mainly magnesium olivines and pyroxene along with iron sulphide and Fe-Ni metals. Within a few million years these basic compounds within planetesimals were already subject to various alteration processes (aqueous/thermal) and differentiation, producing the next most common mineral phases, including phyllosilicates, hydroxides, carbonates, halite, albite, feldspathoids, quartz, K-feldspar, titanite, zircon, transition metal sulphides and phosphates. These differentiation processes increased considerably when the young planets achieved a more stable 'life': the terrestrial mantle developed a primordial crust where fractionation and volcanism intensified and doubling the number of mineralogical species within half billion years. The next half billion years witnessed an expansion of the fractionation process which produced much of the lighter rock types and minerals typical of an evolved planetary environment, such as quartz, hornblende, micas, tourmaline and others. As the Earth surface expanded and floated atop a plastic mantle basement, dynamic (P-T) processes produced the first metamorphic rocks (i.e. kyanite, jadeite, etc.); vapour and water also started they process of hydrothermal alteration of the existing rocks, producing mineral sulphides, sulphosalts, etc. Carbonates, sulphates, and evaporates, within their petrological settings were started depositing and accumulating in thick strata all over the planet's surface. >2.5 Ga oxygen production by early photosynthesising life gave rise to more than 2000 new oxide/hydroxide species by oxidation processes of surface rocks, resulting, for instance, in the banded iron formation exploited today as the most important iron ore. For half-billion years the Earth experienced a 'snowball Earth' climate which was followed by an extensive post-glacial oxidative weath<mark>ering phase of all surfac</mark>e rocks. The phanerozoic era begun with an explosion and diversification of life forms which started a process of bio-mineralization and bio-weathering of the terrestrial surface which is still going on today (extensive skeletal biomineralisation of calcite, aragonite, dolomite, opal, clay minerals, soils etc.).
- 8.2 Too hot to handle... We have been dealing so far with minerals being formed and aggregate into rocks, for being then dismantled, reorganised, and even reborn as different phases and rock types. But what energy sources drive this micro to macro processes? The Earth receives heat from the Sun at the rate of around 200 watts per square meter. This is enough to drive the terrestrial water cycle and ultimately allow complex life forms to exist. Indeed, the heat source budget from the interior of the Earth is 'only' around 0.08 Wm², or twenty-five hundred times weaker than the solar input, not enough to keep complex life-forms going for sure! But still, this on a planetary scale is a lot of heat escaping from below our feet. Where does it come from and how is it produced? The energy stored, produced and released form the interior of the Earth is sufficient to split gigantic slabs of terrestrial crust and move them around (plate tectonics), create chains of erupting volcanoes, and make the earth shake and crack (earthquakes). OK, as usual let's start from the beginning: we know that the making of the Earth must have included a time when the whole planet was in a molten state: we can estimate several heat sources: 1] Heat of accretion, just a measure of the KE transfer from colliding bodies; 2] Heat of compression, gravity-led self compression of the planet as it grew in size; 3] Core formation, as we saw this earlier, the 'iron rain' gravitationally segregating towards the Earth's core would have generated a considerable amount of heat, in the order of one

magnitude smaller than the accretion output; 4] Short-lived radioactive isotopes, as the planet grew in size, short-lived radioactive isotopes input a considerable amount of energy into the system; 5] along with long-lived isotopes like uranium and potassium that are still fuelling the internal heat flow of the planet; 6] Tidal dissipation due to the gravitational interaction with our 'sister planet', the Moon. Billions of years ago our satellite was much closer to the Earth and its gravitational pull stretched the whole solid body towards it. The energy dissipation further heated up the Earth and caused a slowing of its rotation. As the Moon progressed towards today's synchronous orbital, it progressively moved (as it is still moving) away from us and with it its energy input to our planet has since decreased considerably. Now, before we explore the possible sources of today's terrestrial heat output, we need to remind ourselves that rocks are poor conductors of heat, i.e. they possess 'low thermal conductivity'. Indeed, on any point on Earth, there are no seasonal variations below 20 meters; furthermore, daily temperatures changes are already less that one degree Celsius at a depth of one meter! On average, and away from igneous centres, the geothermal gradient near the Earth's surface is around 30 K per kilometre, which means that three kilometres down the temperatures are already near 100 degrees. Back to the origin of this heat: Calculations have suggested that the four heat-producing radioactive isotopes $^{\rm 235\text{-}238}\text{U},~^{\rm 232}\text{Th},~^{40}\text{K},$ 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. In short, we don't have precise data, but, as most things in geology, plausible, but also discordant, models.

- 8.3 Back to silicates... This table collects all the facts that we have encountered so far on the three fundamental mineralogical families of silicates: feldspars, pyroxenes and olivines. The importance of these three groups of minerals in planetary geology cannot be underestimated: peridotite, an ultramafic rock said to be a candidate for the bulk composition of the terrestrial mantle, has an average compositional mode of 45% pyroxene, 45% olivine, and 10% feldspar; Garnet Peridotite 32% pyroxene, 63% olivine, and garnet 5% garnet; gabbro and basalt, the main igneous rocks have on average 55% pyroxene, 10% olivine, and 35% plagioclase; when these rocks, and their mineral constituents within, are exposed to changing physical environments (temperature and pressure), chemical exposure (to volatiles such as CO_2 , OH^{-1} , H_2O , etc.), physical weathering (mechanical, thermal expansion, etc.) they, so to speak, develop and change into secondary (as opposite to primary) mineral products.
- 8.4 But attention!... Life and minerals are never as simple as we would like them to be! For instance the mineral phase hedenbirgite, a ferrous end member of the clinopyroxene family, can be described by the relatively idealised formula $CaFeSiO_3$ or Di_{10} - Di_0 , but in the real world of rocks, a chemical analysis of a given standard sample would be more accurately represented by a formula such as: $Ca_{0.95}Fe^{2+}_{0.77}Fe^{3+}_{0.08}Mg_{0.20}Si_{1.92}Al_{0.08}O_6$. Let's just keep this in mind when given a 'simple' compositional norm of a rock...
- 8.5 *Phases and phases...* To understand in full the genesis of the mineral constituents in rocks, and thus gaining insight into the thermal, chemical, and physical conditions of the source materials, we need to make one concept very clear in our minds: the model of (mineral) phases: for instance when quartz crystal melts it undergoes a change in phase, from solid to liquid. No problems. But when we completely melt a rock, let's say comprising of discreet solid phases such as feldspar and pyroxene, we get *one* phase only: a liquid phase

(basalts in this case), and possibly an exsolved gas phase. When a rock 'becomes' liquid, the pyroxene and feldspar phases cease to exist as distinct mineral crystals and revert, ideally one must stress, to their oxide components (i.e. their basic constituent elements). Now, if we allow the melt to re-solidify within the same physical conditions and rates, in principle we should produce the same mineral phases, and in the same ratios, as we started with (the elemental 'ingredients' staying the same that is). It is also obvious that if this rock of, let's say 30% pyroxene and 70% plagioclase is melted completely, but before we let it crystallise again we remove some of the, say, early formed plagioclase crystals, the mineral ratio in the final rock would differ in composition from the original mineral assembly. But life is much more complicated than that: here we need to completely understand that a melted rock, or magma, has the (chemical) potential of 'having' i.e. 30% pyroxene and 70% plagioclase composition and this is a convenient to describe the melt mineralogy... but, and I stress again, this is a theoretical and probabilistic assumption. The physical constrains and time frame of solidification will dictate if this potential is reached... This is even more complicated when the potential minerals (as I will call the melt constituents from now on), in the form of elements/oxides, belong to a so called Complete Solid Solution. First let's have a look at the plagioclase series, comprising of a range of alumino silicates with varying chemical composition ratios Si/Al and Ca/Na. As we have seen, the crystal structure between end members is essentially the same given the comparable ionic sizes of the interchangeable elements. The availability of each element at any given point in the phase change process (i.e. from melt to solid or viceversa) will be crucial to the type of rock we get at the end. A phase diagram shows the chemical behaviour of the phases within their specific thermal environment of solidification/melt. Usually, in a complete solid solution series we see not one but two phase boundaries, one called liquidus and the other solidus: above the liquidus boundary all the melt is liquid, below the solidus there is no liquid (melt) left. In between there is the 'purgatory' <mark>range, dict</mark>ated but the different melting/solidification points of the constituent minerals (and potential) in the rock. Let's take our plagioclase example, a liquid which derived from a mineral component of composition 'x' An70, if allowed to solidify again in the same physical regime, will give us again anorthite 70. But its journey from 'x' liquid to 'x' solid can become quiet tortuous...

8.6 *Plagioclase is made...* A liquid of composition X (*potential* An61 or Ab39 if you prefer) cools to the liquidus, a temperature threshold below which crystals start forming, in this case around 1490°C. What would be the composition of the first crystals, An61? No, at this temperature (and pressure we must add) the composition of the crystal allowed to solidify is An87; what this means, practically, is that this is the only solid phase achieving 'structural' integrity and stability at this temperature, starting from the abundance of elements/oxides X. But let's look at the chemical composition now: the crystals that are forming are relatively calcium rich, i.e. the crystals are segregating from the melt more calcium (and aluminium) than sodium (and silica). This unbalance leads to the melt composition to become relatively more sodium rich, or sodic. This process continues with a dynamic compositional exchange between crystals and melt until, at temperature $\sim 1340^{\circ}$ C all the liquid has solidified, and the last crystals produced have the same composition as the original pre-melt minerals, given that we can't create new elements out of thin air. But wait a moment: we said that if the crystal solidified with different compositions as the temperatures dropped, we should have a complete collection of crystals from An61 to An87 and this is not obviously possible, because to obtain elemental/oxide balance, we should find more sodic crystals along calcium rich ones (in comparison to original rock). Let's investigate further:

- 8.7 Mystery solved:... Remember, we can't create matter out of nothing: if the melt contained so much i.e. calcium and sodium, the end product (minerals/crystals) must have the same amount of elements. So, two things can happen: the crystals react continuously with the surrounding melt, so the calcium-rich An87 would react with the (now) more sodic liquid, and 're-equilibrate' towards the X composition. Unsurprisingly, this process is named Equilibrium Crystallisation and it implies a stable geophysical environment with no or little mineral segregation (i.e. removal or either solid or melt, mostly in plutonic settings). The other possible scenario is that 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: the crystals become (compositionally) zoned (usually from Ca- to Na-richer layers). This process is called Fractional Crystallisation (FC) and it is typical of rapid cooling environments, as those producing volcanic rocks.
- 8.8 Get real!... Again and once more... life in the geochemical world is not as simple as we would like it to be... Now that we are familiar with the plagioclase series, let's have a look at a more realistic phase diagram and introduce two variables that are typical of terrestrial settings, i.e different pressure environments and the presence of volatiles (in this case water). The diagram at 1 GPa looks similar to the one we have studied, but here we can see that at high temperatures, but in a volatile poor environment, the first solid phases to crystallise (providing a An-rich potential melt composition) will include the mineral Corundum (Al₂O₃). At pressures of around 2 GPa (top graph) Corundum becomes one of the most important solid phases, even in relatively low-Ca melt compositions. With the presence of water the liquidus temperatures (at 0.5 GPa) fall by ~500°C, and the phase regime becomes somewhat less 'complicated' with the 'disappearance' of the solid aluminium oxide phase.
- 8.9 Another example: olivine... The binary phase diagram obviously also works the other way round, i.e. from rock to melt. This time we look at another 'textbook' example, the olivine binary system, or the forsterite solid solution (Fe-rich to Mg-rich). One thing to keep in mind at this point: geology is a 'messy' science; things rarely are 'black and white'. Most of times, both Equilibrium and Fractional Crystallisation will occur within a certain geological setting, resulting in an even more complex crystal phases population, and more headaches for the petrologist/geologists trying to interpret their origin and evolution!
- 8.10 Phase diagrams zoo!... So far we have looked at binary systems relating to the same crystallographic and mineralogical family (plagioclase and olivine). Binary systems come, as they say, in all shapes and sizes. But, obviously, a real life melt has the potential of yielding minerals phases belonging to different species, as for the chemically comparable Forsterite (olivine) and Diopside (clinopyroxene): they are both calcium rich silicates, but, at least as idealised end-members, one contains magnesium in its structure and the other aluminium (respectively). The diagram shows a liquid of composition X, containing calcium, magnesium, silica, and aluminium oxides. This time the composition of the crystals will not show a solid solution trend: they will be either plagioclase or olivine crystals: i.e. two phases will be present at subsolidus temperatures. The most 'interesting' facts will be that depending on the composition X, either anorthite or olivine will crystallise before the temperature falls to a certain point (called eutectic point) where three phases coexist (solid Di, An, and liquid). Let's look at this process in a little more detail...

- 8.11 The journey of AnDi:... OK, here we go again: temperatures drop to 1450°C and the first anorthite crystals appear. Beware; this solid matter is made up of 'pure' anorthite, not a mix or compound of anorthite and pyroxene! When the temperature drops to 1274°C the physical and chemical conditions to form a stable form of Diopside are reached: basically, all the anorthite that could be formed has crystallised and the melt yields only Diopside crystals. Once all the melt has solidified, temperatures are allowed to drop and the mineralogy of this (idealised) rock would be 30% anorthite and 70% Diopside (as per the potential X composition).
- 8.12 Let's combine the two!... We have so far encounter two types of phase diagrams, one for the plagioclase Ab-An series (complete solid solution), the other for Di-An (binary system with an eutectic point). Let's now have a look at an even more realistic mineralogical and petrological scenario, where the actors are plagioclase feldspar (Ab-An series) and pyroxene (cpx). This is a tertiary diagram and in effect represents a two-dimensional transposition of a three-phase diagram. We need to think of the middle line as a bottom of a valley running between three (compositional and temperature related) peaks. Depending on the compositional starting point of the melt, with descending temperatures, the crystallisation path will follow the isometric temperature lines until they 'reach' the bottom of the valley, but more of this later. For now we need to understand how a composition plots on this type of diagram.
- 8.13 A good example... This is a great phase diagram to wrap this topic up. Three phases, the most common silicate minerals in the solar system and the focus of this introduction course: calcic plagioclase (anorthite, An), an Mg-olivine (forsterite, Fo), and a clinopyroxene (Diopside, Di). We start with bulk composition liquid X, roughly of composition $Di_{44}Fo_{40}An_{16}$ at 1600°C. As forsterite begins to crystallise, liquid composition moves directly away from Fo. Liquid composition reaches cotectic (a eutectic point with more than two phases). Diopside begins to crystallise along with forsterite. Crystallisation of these two phases causes the liquid composition to move down the cotectic curve. The liquid composition reaches the ternary eutectic at 1270°C and anorthite begins to crystallise with Di and Fo. When all the liquid is consumed, the minerals cool below 1270°C.

LESSON 9 - LET'S ROCKI

- 9.1 *From minerals to rocks?...* We have seen that the mineralogical description of a rock, or a mineral assemblage, is far from being intuitive and straightforward. Rocks are aggregates of minerals, usual several, but sometimes only one or two. Similarly, minerals are either free, native elements or elemental compounds.
- 9.2 Let's get native... Our choice of a native element example here is not ideal, because silicon is not found in nature in its native form, i.e. it is always oxidised. Minerals which are found as native elements are the precious metals (platinum, gold, and silver), but often also copper, sulphur and carbon (as graphite or diamonds).
- And now let's (igneous) rock... Before we dwell into the actually assembling of rocks, let's 9.3have a look at the most common igneous rocks. Igneous means born from fire, which betrays the origin of these stones, i.e. from a molten magma. A bit of jargon first: Magma is the name for molten rock in general, Lava is magma that reaches the surface and may flow (or pond...), a Volcanic rock is one formed from erupted magma; this can be in flowing in nature (with varying flow rates), or pyroclastic (violent and with air-borne materials); plutonic refers instead of rocks solidified slowly below ground. Composition, volatile content, and speed of cooling are crucial elements in dictating the type of rock we get: mineralogical composition (and in particular silica content) will produce either felsic, intermediate, or mafic rocks; plutonic rocks tend to have larger crystals within the matrix giving their slower rate of cooling within the insulation of surrounding rocks; on the other end of the cooling rate spectrum we found the glassy volcanic rocks that solidified from air born dust and ashes; obsidian represents extremely quick cooling of igneous materials into a glassy or crystalline form. Erupting magma is often rich in volatile content (H₂O, CO₂, etc.) and these often contribute to the explosive nature of some phases of eruptions; evidence of these gases can be seen in the vesicular ('with holes') nature of some basalts (haha). As always, igneous rocks belong to the messy real geological world, so it is common to find volcanic rocks with porphiritic texture, i.e. inclusions of larger crystals formed at depth and brought to the surface by the ascending magma; often, especially in aqueous conditions, vesicular basalts' spaces are filled with salts and minerals (i.e. calcite and zeolites) deposited out from the water.
- 9.4 It all starts here... So, where are these primary rocks produced on Earth? Volcanic rocks vary greatly in composition, because they can be produced in different environments, geological settings, and physical conditions: the sketch shows the three most common types of rocks. As we have seen in the previous slide, basalts, the silica-poor rocks, are those more closely related to the composition of mantle (or primitive) geological materials; it is clear to see why by looking at the main production centres of these rocks, the Middle Ocean Ridges and Hot Spots, said to originate as deep as from the mantle/core boundary. Here hot materials from the lower lithosphere/upper mantle 'escape' through cracks or linear openings produced by diverging plate boundaries, thus producing even more ocean basin crust. The overall surface extent of the Earth is obviously fixed, so this 'surplus' of lithospheric rocks 'returns' deep into the Earth's interior at destructive plate margins (as in the western side of South America) where, by now enriched with seawater, re-melts at more shallow depths giving rise to more 'evolved' (multi-generational) magma (i.e. silica-rich).

- 9.5 And then the cycle... These new surface or oceanic rocks, both primary and secondary, then become part of the rock cycle where they undergo a complex and diverse process of mechanical and chemical breaking down and metamorphosis. Atmospheric gases and water all combine to dissociate, alter or even dissolve the individual minerals from the igneous rocks.
- 9.6 New life from old rocks...Only a very small number of minerals can resist nearly indefinitely: zircon $(ZrSiO_4)$ and gold. Quartz is the most enduring silicate, that's why most beaches in the world are made of quartz crystals. They have been probably being recycled many a times from the original igneous rock, to metamorphic and sedimentary rocks (such as sandstones). Nevertheless, given enough time even quartz breaks down to silicic acid, H_4SiO_4 . Olivine, pyroxenes and amphiboles react with water and leave behind rusty iron hydroxides. These do not commonly associate as solid minerals but they are still important ingredients in soils and often add colouring (brown/red) to sedimentary rocks. Water reacts with the cations present in plagioclase (i.e. Si, Ca, K, and Na) except for aluminium. What is left behind are hydrate aluminosilicates: clays. Clays are made of sheets of silica (SiO_4) and sheets of magnesium or aluminum hydroxide $[Mg(OH)_2]$ and $Al(OH)_3$]. Clays plus quartz make up the overwhelming majority of surface minerals; together they make mud, which ranges from visible particles constituents (sands) to invisible (clay). These minerals collect at the bottom of the sea, large lakes and inland basin. Gravity and tectonics forces compress these materials, eventually given us the clastic ('made out of bits of rock') sedimentary rocks: sandstones, mudstones and shales. In our mineralogical and petrological analysis we have left behind a major constituent element of rocks and life: calcium. This is an important element in the make up of igneous rocks (cpx and anorthite for instance), and it does not enter the 'clay' cycle. Instead the cations remain in water, where it affiliates with the carbonate ion (CO_3) . When the concentration in water is high enough, it precipitates as calcite (CaCO₃). Living creatures use it to build their calcite shells, which in turn will also become part of sea floor sediments. Sulphur, again when is abundant, will combine and precipitate with calcium to form gypsum (CaSO₄·2H₂O) or pyrite (FeS₂) with iron. Sodium (Na) stays in water solution until its concentration reaches high levels, as in a drying water body, and joins chloride to form common salt, or halite. Finally, our silicic acid finds its way underground and concentrate as the rock chalcedony (SiO_2) . This is it. All the other elements present in igneous rocks, from copper to tin, will eventually concentrate in particular hydrothermal geological settings, forming important extraction ore materials. From volcano to rocks to clay. Have we left anything behind? Sure, we don't know where the prime materials behind the erupting magmas come from and their initial composition, in short, how we go from mantle (chondritic) material to crustal magmas and lavas...
- 9.7 First, let's shake the planet... We have seen that we can infer the overall composition of the bulk Earth assuming a comparable and homogeneous composition of Solar System bodies, hence the terrestrial chondritic model. This model gives us a plausible compositional and mineralogical estimate of the materials at depth, and obviously we have worked out the average density of our planet (rocks) millennia ago. Furthermore, we have seen that samples (xenoliths) from the deep Earth reach the surface through fast rising magma (kimberlite and lamproite) from deep sources. But how do we know were and possibly why the Earth is layered as it is presumed? Rocks can be elastically deformed by natural occurrences (i.e. deep earthquakes, tsunami, landslides) or manmade actions (explosions, collapse of disused mines, atomic experiments etc.). Rocks can sustain two general forms of deformation: one is a change in volume, through compressional waves, and the other in

shape (shear waves). Compressional waves, or P, for Primary, are similar to sound waves, and they consist of alternating pulses of material compression and expansion acting in the direction of wave travel. 'P' waves are called primary for a number of reasons, but mainly because of their greatest speed (6 km/s in the uppermost crust) and because they will traverse, and hence carry information, about matter through all physical states. Shear waves ('S' for secondary) instead deform materials by changing shape, like shaking a rug, but not their volumes and they travel slower through rocks (3.5 km/s in the top crust). Surface waves are another type of energy transfer through solid and pass around the Earth rather than through it. There are two kinds of surface waves, one kind behaving similarly to S-waves, and the other that causes a back and forth shaking. These shock waves do not penetrate the Earth, so they are less useful in helping to probe the interior of our planet.

- 9.8 Waves through the Earth... Seismic body waves behave like light waves and sound waves, in so much that they can also be reflected and refracted through a medium. Refraction is characterised by a change in the speed and direction of the travelling wave. Wave speeds are a function of rock density. In a simple model of homogeneous Earth composition, increase in density due to pressure would cause seismic waves to curve. Inside the Earth the wave paths are indeed curved but they are also refracted ($P_{\rm K}P$) and reflected (PcP) by several zones of sudden density changes. Note how the P-waves are both bent (due to changes and density) and reflected on the Earth's surface and the outer core boundary. S-waves cannot penetrate and transit through the liquid outer core, offering further evidence (apart from inference from the Earth's magnetic field) of a deep liquid layer in the Earth. The (secondary) points of emergence of waves are used to calculate the depth of density/phase changes.
- *Reading the waves...* The seismogram of a 'typical' earthquake looks somewhat like this: 9.9 from time zero t<mark>he fir</mark>st waves to arrive are the P-waves; after a time interval related to the distance of the instrument from the epicentre, the S-wave arrives. Later on, the surface waves also arrive. Knowing the estimated rock density of crustal rocks, we can estimate the distance travelled by the difference wave from the different arrival times. Obviously, this can work the other way round: by generating seismic waves artificially (from a mallet striking a metal plate on soil up to 'an atomic explosion') where we know the distance from the focus and an array of seismographers, we can work out the densities of the rocks between. If the sampling stations are positioned far enough (maybe even the other side of the planet) and the magnitude of the seismic wave strong enough, we can read the inner layering and rock types of the inside of the Earth. This works as an equivalent of a mammogram or sonogram as used in the medical field. Today, using ever more sophisticated instruments, 3-D tomographic structures of the mantle can be resolved (seismic tomography can map out lateral variability in seismic wave speeds throughout the globe).

LESSON 10 - THE MOTHER MANTLE

- 10.1 Let's have a look inside... We have seen that seismic waves offer a unique opportunity to build an understanding of the interior of our planet. Indeed, the classic major divisions of the Earth, crust, mantle, and core, are defined seismologically. We will come back shortly to a description and formalisation of the constituents of the mantle layers, but for now, let's have a look at the seismic evidence.
- 10.2 Waves' tortuous travels... The mantle is divided into an upper part (Upper Mantle down to 660 km) and a lower part (Lower Mantle, ~2900 km). As we can see from the lower graph, both Vp waves and Vs waves feature increases in velocity with depths, but these are punctuated by sudden 'jumps' in speed. The major velocity changes occur at the upper and lower boundaries of a mantle layer (shell) called 'transition zone' (between 410 and 660 km). The compressional and shear velocities throughout the Lower Mantle increase progressively with depth, which is consistent with a model of relatively uniform materials experiencing raising pressures. As we noted, Vs waves, or shear waves, are seismic waves that are transmitted only through solid materials. The absence of evidence of these waves from depths between \sim 2900 and 5100 km indicate the presence of a liquid layer, as understood to represent the liquid outer core, principally composed of iron with a convecting mobility that gives rise to the Earth's magnetic field. Vs waves 'reappear' towards the centre of the planet indicating a change of state from liquid to solid again. As a footnote of this very succinct introduction to the layers, we need to remember the 'loose' definition of a solid layer. Indeed, we have plenty of evidence (e.g. plate tectonics) that even the 'solid' mantle is actually mobile and convecting. A better word to describe the mantle would be 'plastic' rather than solid. Anyhow, all these jumps in seismic wave velocities mean only one thing: a change in rock densities. But are materials with different densities automatically translate into rocks made up of different elements, minerals, crystal structure etc.? As always, the geological picture is rather 'messier' and more complicated than a simple 'change in phase with depth' would describe. The good news is that we have evidence that the composition of the mantle is, overall, rather simpler than surface rocks, and becomes even simpler with increasing depths. The inset shows the latest consensus model of mantle composition. Just below the solid surface (crust, making up most of the lithosphere) the composition is strongly mafic, made up nearly entirely of Nesosilicates (olivine + garnet) and Inosilicates (pyroxenes). Before we start unravelling the petrological and mineralogical jargon here presented, we need to clarify some confusing terms in the geological 'tongue': olivine, garnet, pyroxenes, etc. are mineral, the basic constituent of rocks such as peridotite, pyroxenite, eclogite, and, importantly, perovskite. Perovskite is a general petrological term used to describe rocks of widely varying composition and mineralogy. Indeed, a perovskite is any material with the same type of crystal structure as calcium titanium oxide (CaTiO₃), known as the 'perovskite structure'. Going back to lower crust / upper mantle, kimberlite sources believed to tap into depths of 200 km or more indicate an olivine-rich magma source, with lesser amount of eclogite (a rock composed of garnet and Na-rich opx, omphacite). Olivine undergoes fundamental phase changes at two crucial depths (i.e. pressure thresholds): one at 410 km depth, where it turns into β -phase olivine (called wadsleyite) and around 520 km, where again it transforms into γ -phase olivine (ringwoodite, with a cubic structure related to spinel, $MgAl_2O_4$). These two phase changes of one of the major upper mantle mineral olivine could account for the seismic discontinuity transition zones between these depths. So, are the sources of the 'common' magmas (MORB) mostly the

result of partial melting of olivine-rich rocks? Laboratory experiments and comparative rock density characteristics indicate the presence of accompanying minerals such as orthopyroxene (Enstatite), clinopyroxenes (Diopside or Augite), and an aluminous phase (garnet and spinel depending on depth). As pressures and temperature increase, garnet and pyroxenes form a single solid solution at depths of 450-500 km, characterised by the garnet structure (garnet-majorite solid solution). The lower mantle is dominated by the crystalline phase perovskite with smaller contributions from Ca-perovskite and ferropericlase. Aluminium has obviously not disappeared, but could be incorporated within the perovskite crystal structure. As a curiosity, albeit perovskite represents the most abundant phase on Earth, can not be classified as a mineral because it has not being found in nature.

- 10.3 The mother of all rocks... Most magma is generated at depths no greater than 200 km, with only circumstantial evidence that some melts may originate deeper in the mantle down to the CMB (hot spots). What do we have then? Most, and here we emphasise the word most since there are many types of basalts erupting on Earth, basalts can be described as the result of equilibrium partial melting of an olivine-rich rock called pyrolite. Let's try and unravel the geological jargon: pyrolite describes a garnet-lherzolite rock; the 'garnet' prefix indicates that the lherzolite is the name of the rock and garnet is the accessory mineral. Back to lherzolite: this is the most common type of peridotite with composition dominated by the mineral olivine (55-60%) and the rest by pyroxenes. All the main elements to make up most rocks on Earth are here represented: Mg, Fe, Si, O, Ca, and Al. Clearly, all the other elements believed to make up the bulk of the planet, including those found on the surface (titanium, gold, sodium, etc.) are there as minor element components and are incorporated within the crystal structures of silicates and the metal oxides.
- 10.4 Let's rise to the surface... OK, we have pyrope, i.e. peridotite and garnet in the upper 200 km of the upper mantle. But both the rock and the mineral are not found in magmas erupting at the surface (apart from xenoliths). So, how do we go from them to basalts, for instance those erupting in the Middle Ocean Ridges (MORB) to form new oceanic crust? And why melting in the first place? We understood that the mantle is essentially solid, although it flows and convects plastically due to high temperatures at depth. Well, the melting behaviour of any material is dependent on two factors: temperature, obviously, but also pressure, or better expressed, the melting point of a material rises with pressure. On top of Everest water boils at 60 degrees C, for instance. 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. In diverging plate settings the upward movement in the mantle to pressure and temperature conditions above the solidus is caused by the space vacated by crustal movements. In the much rarer settings of hot spot volcanic eruptions, mantle upwelling is driven by hot buoyant magma rising towards the surface from deep within the mantle (perhaps, as noted earlier, originating as deep as from the CMB). Rock samples from ophiolites complexes (tectonically re-surfaced oceanic floors) shows varying compositions for lherzolite samples believed to originate at different depths. Why? Because different mineral phases are more stable (or vice versa, become unstable) under different pressure environments. The mineral structure can respond to higher pressures in two ways: structurally, rearranging its atoms in a more tightly packed structure (like carbon-diamonds or olivine- β - γ -olivines), or compositional readjustment involving chemical reactions between the minerals in a rock to produce a different and denser mineral assemblage. In lherzolite, the aluminium bearing phases

react with more mafic silicates and free cations to produce minerals stable at certain pressure/temperatures conditions. Here we see that at lower pressures the aluminosilicate garnet (pyrope) reacts with olivine (forsterite) to produce spinel and 'two' orthopyroxenes (enstatite); note this 'ideal' reaction is chemically balanced. At even lower pressures spinel, enstatite, and diopside rearrange their atomic fractions into 'back' into olivine and the plagioclase anorthite. This explains the presence in the lower crust of (plutonic) feldspar-rich rocks (i.e. gabbros and granites) and, on the surface, extrusive basalts and other alumino-rich rocks. It is crucial to understand that decompression, and the consequent lowering of the melting temperature threshold (the liquidus) of rocks is the driving force leading to partial, or indeed complete, melting of rocks, nevertheless other factors, especially the volatile content of the host rock (H₂O, CO, and CO₂), are fundamental in altering (raising or, as in most cases lowering) the melting points and the actually physical dynamics of eruptions.

- 10.5 We are melting... So, the production of MORBs starts with an upwelling of mantle material of pyrolitic composition, its partial melting, and the ascent of the liquid fraction (lower density than the surrounding materials) towards the surface. At constructive plate margins, dense oceanic crustal plates move away from each other, dragged down below continental crustal plates by gravity, causing the central crust to stretch and thin, allowing the mantle to rise to take its place. This results in a decrease in the pressure experienced by the mantle and can lead to partial melting of the upwelled peridotite. According to the lherzolite phase diagram in the previous slide, at around 1500 °C peridotite will undergo partial melting when its pressure falls below ~3 GN m⁻² (the equivalent of around 90 Km and above). As we can see from the diagram on the left, the solidus of mantle peridotite and calculated geotherm beneath typical (younger than cratons) continental/oceanic crust. The geotherm does not cross the mantle solidus, suggesting that the mantle will not normally contain any melt. But as the crust is thinned the geotherm is crossed at a certain depth ('D', around 50 km in this example) and melting may occur.
- 10.6 The melting and fractionation... Now we are having a look at the actual chemical consequence of the separation of the basaltic melt from the primitive pyrolite. As we can see, the silica content is only partially segregated between the melt and the residue, with the basalt becoming more silica rich than the lherzolite. More drastic is the partition of other key mineralogical elements: Al, Ca, Na, Ti, and K are all strongly preferentially incorporated in the liquid fraction, while magnesium is the main 'loser' and stays behind incorporated in the harzburgite minerals. Now, these rocks do not contain constituent oxides as such as reported here (these are chemical descriptions), but their constituent elements are part of crystalline structures, i.e. minerals. The chemical description reflects the modal distribution in the different rocks: the typical lherzolite contains 45% pyroxene, 10% feldspar, and 45% olivine in comparison to gabbro/basalt with 55%, 35%, and 10% respectively. Indeed, by looking closer at the data we see where the magnesium is 'gone' (from the basaltic melt, that is): what is left behind from the removal (fractionation) of melt is an enriched residue (harzburgite) in the olivine forsterite phase (Mg-rich) and high-Mg pyroxene (orthopyroxene).
- 10.7 Opera Magna... Now our melt is on the move and ready to reach the surface. We have followed the journey of mantle materials undergoing partial melting and the liquid commencing its upward journey. Where the melt will end up depends on the physical conditions of ascent: some will not reach the surface as lava and slowly solidify within

magma reservoirs (magma chambers) directly below crustal fractures (mid oceanic ridges). Slow(er) solidification will result in the growth of larger mineral grains, still of MORB compositions, and forming gabbros. We all should be quiet familiar nowadays with the concept of plate tectonics, i.e. the partition of the terrestrial crust into distinct and relatively autonomous regions or plates. These interact dynamically driven by a relative ductile and convecting basement, the asthenosphere (a portion of the upper mantle, between 100-200 km). These plates constantly collide, converge, diverge, or slide pass each other given rise to familiar geological phenomena as earthquakes, orogeny (mountain building), volcanic activity, etc. Before we go 'deep' again into the composition and classification of igneous rocks of basaltic composition (as per the MORB so far focused on), it is important to be aware that not all the volcanic activity and indeed plutonic mass production is due to fractionation of lherzolite materials. Indeed, whole volcanic regions, such as the Andean volcanoes, originate from the fractional melting of sub-crustal materials triggered by the release of volatiles, mainly from seawater-derived hydroxides released by the melting of the subducting oceanic pacific crust. Water lowers the melting point of the descending rocks causing them to partially melt at relatively low temperatures, hence the production of magmas within 'cold' crustal layers. The melt has obviously a different composition from the MORBS, since they originate from already fractionated (i.e. evolved) rocks. Furthermore, the production of melts within a 'wet' environment promotes the assembly of certain minerals unlike those from drier settings. Finally, the degree of melting also influences the mineralogical make up. MORBs tend to be rather uniform in composition given the relatively comparable compositional sources. On the other hand, volcanic arc magmas and continental hot spots tend to display a wider range of compositions.

- 10.8 Igneous rocks... Continental crust compositions can be explained by its stepwise extraction from the mantle of the Earth: primitive mantle, depleted mantle, continental crust: primitive mantle has the necessary 'components' to make the present crust enriched in mantle incompatible elements (K, Ti, Rb, Sr, Ba, REE, Th, U, P, H₂O, CO₂, etc.). Depleted mantle is now the source of MORB (tholeiitic). The table gathers most of the generic facts relating to the classification of igneous rocks: as we can see the main division is between silica-saturate and silica-under-saturated rocks (alkaline). The main difference is that the alkaline rocks represent the 'second' or third generation melts and are found mainly in Oceanic Island settings (OIB, hot spots), but also in intra-continental volcances. Subalkaline rocks include calc-alkaline rocks, this time found above subduction zones, commonly on volcanic arcs, and in particular on those arcs on continental crust (VAB). In mature island arcs there is a progression from the tholeiitic to the calc-alkaline series starting from the oceanic to the continental side.
- 10.9 The TAS diagram... There are (too) many ways of classifying the rocks found on Earth's surface. This is one encompassing the majority of both volcanic and plutonic rocks. The tholeiitic and calc-alkaline series account for nearly 90% of all rocks found on the surface of the Earth and some names might sound familiar by now. It must be stressed that both fine grained extrusive rocks and coarse grained intrusive rocks the do not necessarily share the same petrogenesis, albeit showing very similar compositions. In particular, granitic rocks (e.g. granodiorite and granite) can be formed in a variety of geological settings and can be also be generated in metamorphic processes. So the tempting simplification "rhyolite=fine-grained granite" should not be automatically assumed. Nevertheless, the diagram offers many clues on the mechanisms of petrogenesis and differentiation of igneous rocks, and the fundamental role of silica in particular.

- 10.10 More diagrams... Really, there are probably as many rock types on Earth as there are people, each with its own particular physical and chemical characteristics and subtly unique settings of formation. Even a common rock like granite will display a wide array of mineral mixes (within certain compositional parameters though!), grain sizes, colours (from pink to white), etc. Here there are some nearly-random classifications of rock types fished out of petrological books. Some of these classifications have real importance and uses, especially in a planetary geology context (where igneous rocks are dominant). Take the Plag-Opx-Cpx phase diagram: here we found a clear graphical representation of two common plutonic rocks found on most planets: gabbro and norite, mainly differing on the type of pyroxene present (Ca-rich or -poor). Plag-Ol-Px: this phase diagram 'zooms out' from the subdivision of pyroxenes to include olivine in the classification; this is a good diagram for catching a compositional snapshot of common rocks on Earth (since these three minerals represents its most common mineralogical constituents...): ultramafic rocks with little plagioclase phases, gabbros, with a 'blend' of the three, and up to anorthosites, the alleged light-constituent of a planetary magma-ocean. Other diagrams (i.e. bottom left) are used to explain compositional trends in terms of oxides, note the unspecified trend of a number of magmas in terms of iron, magnesium and alkalis and their relevance to the classification between tholeiitic and calc-alkaline igneous rock series. Finally, the 'diamond' type diagram could not be omitted here, and on the top right we see the Quartz-Alkali-Plagioclase-F(eldspath)oid (QAPF) classification according to those mineral constituents. Mafics are conspicuous by their absence and this diagram only works with mafic (M) < 10%. So you have it.
- 10.11 Mineral constituents and rocks... All rocks were once molten (i.e. magmas) but the solidification process, if complete, or the partial solidification and extraction of melt (magmatic differentiation – crystal fractionation) occur along well-defined physical and chemical constrains. As we have seen, in partially crystallised magma, the coexisting crystal and liquid rarely have exactly the same composition, and so if the crystals are separated from magma, the remaining melt will differ from the original magma. The end products are solid cumulates (accumulation of crystals) and residual liquids. Primitive magmas are characterised by being rich in constituents with high melting temperatures (e.g. ferromagnesian minerals and calcic plagioclase) and have high Mg/Fe ratios and high liquidus and solidus temperatures. In the early 1900's N. L. Bowen and others determined the crystallisation sequence of silicate minerals with decreasing temperatures. The diagram shows two distinct trend lines: a continuous 'plagioclase' branch showing that the early formed plagioclase crystals will be more calcic than the melt from which they crystallise, and the residual liquid will be more sodic. But the range of compositions, as we saw early in the course, is continuous, i.e. it can take any intermediate values. On the other hand, the mafic minerals on the right form a discontinuous series, where, as Bowen noticed, at a certain temperature a magma might produce olivine, but if the same magma was allowed to cool further, the olivine would 'react' with the residual magma and change into the next mineral on the series (in this case pyroxene). Olive itself, when considering the Fo-Fa system, shows that early formed olivine crystals are more Mg-rich than the melt, and their residual liquid will be enriched in iron. At lower temperatures, the branches merge and crystallisation of the more felsic mineral occur. As always, the real-world situation is somewhat more complicated than this and factors such as crustalliquid separation mechanisms (i.e. gravitational settling, flow differentiation, etc.) would interfere with the idealised Bowen model and create melts showing a more complex formation trend. How does it all translate into a real rock sample? Well, first let's have a

look at these tables. The upper part shows a 'typical' chemical breakdown of the typical subalkaline rock sequence. These numbers are far too precise but they are often quoted in this way in much literature. Nevertheless, they offer at a glance a convenient way in classifying igneous rocks and tiding them up together into neat groups of origin. The modal classification in the lower part instead deals with the average mineral assemblages found in a given type of rock. Here we see the modal percentages given are rather more generic because, as stated before, they vary greatly even between rock and rock. The picture below gathers all these data into a graphical format and reminds us on the arbitrary nature in the choice of rock names, i.e. the continuous overlapping and fading of mineralogical phases between ultrabasic and acidic rocks. Please also note the correct nomenclature here: strictly speaking a felsic (as per feldspathic) rock is given this name because of its qualitative appearance, not composition, which should be described in this case as 'acidic', like granite.

10.12 CIPW diagram... We saw in a much earlier lesson that we can analyse a rock composition relatively easily nowadays using techniques such as X-ray spectrometry, but this gives us a chemical description of the overall mineral assemblage, and not a breakdown in mineralogical phases. In 1931 four petrologists devised a method to 'translate' absolute chemical compositions (expressed as oxides) into modes, or modal classification of mineral phases (i.e. as observed in a real rock). This method relies on the predictable assembly of minerals based on compositional variations of the melt. So, how does it work in practice? The logic of calculation a norm is simple, albeit the steps are tedious, i.e. an ideal job for a computer! This is the general method: first the most predictable elements are allocated, such as the substitution elements to major elements: "nickel and manganese with ferrous iron, strontium and barium with calcium. Then allot minor elements to accessory minerals: i.e. phosphorous to Apatite, sulphur to Pyrite, chromium to Chromite, Fluorine to Fluo<mark>rite,</mark> and CO₂ to calcite. Titanium is allotted to ilmenite or sphene. Later on, Ti may need to be allotted to perovskite or rutile. Calcium and Aluminium 'goes' to anorthite. Provisionally form silica-saturated silicates. Provisionally allot alkalis and aluminium. Begin allotting iron and magnesium. Create provisional pyroxenes. Silica excess forms quartz. Important: if there is no silica deficit, calculation is complete. Otherwise... convert provisional minerals to remove silica deficit; convert hypersthene (opx) to olivine, sphene to pervskite, albite to Nepheline, and orthoclase to Leucite." That's it: what can go wrong? We are going to find discrepancies with the observed mineral assemblages if the formation of the minerals have undergone disequilibrium (i.e. zoned minerals), varying temperatures and pressures, alteration, water content (identical rocks might contain biotite, amphibole, or pyroxene, depending on water content), or the presence of other minor constituents, for instance excess sulphur or chlorine might cause scapolite to form instead of feldspar. Here you have it. The circle is closed. From the given mix of physical elements (dictated by nuclear physics laws), to oxides, to minerals, to rocks, to planetary bodies. The journey of the igneous rocks is complete, or is it?

LESSON 11 - THE MISSING GEOLOGY

- 11.1 Amphiboles anyone?... Back to the Bowen's reaction series, we have encountered a few new igneous minerals not mentioned previously, such as amphibole, biotite, and muscovite. Why and what are they? Well, if we go back to slide 7.1 showing the general formula for silicates, some of you would have noticed a 'W' element which was not dealt with, the hydroxyl (OH⁻¹) site. Amphiboles belong to the Inosilicates family, with pyroxenes as the main phases, and they possess a double chain silicate structure (Si_4O_{11}) which allows for a large number of elemental substitution: i.e. the general formula can become very complicated... Most common representative minerals of this group make up the Hornblende series, with the varying amount of sodium dictating the phase type. Common hornblendes are primary minerals, particularly found in intermediate plutonic igneous rocks, although they can occur in other rock types. Hornblende is stable under a wide range of pressure and temperature conditions in metamorphism. Both biotite and muscovite belong to the Mica group: this is part of a silicate family that have not being introduced so far, the Phyllosilicates. Micas contain sheets of cations such as Fe, Mg or Al (the octahedral sheets), which are linked to two sheets of linked tetrahedra (SiO_4) . These are themselves linked to similar unit by weakly bonded K. Na or Ca cations. The general formula is '*cations*' $[Si_6Al_2O_{20}](OH,F)_4$. As hinted by the Reaction Series, biotite is the more 'mafic' mica phase (including both Mg and Fe in its structure), while muscovite is richer in aluminium (not incidentally, biotite is 'reddish' and biotite 'whitish'). Biotite is a common mineral in a variety of rocks, occurring in most metamorphic rocks but it becomes unstable at high temperatures $(>600^{\circ}C)$. So, why were these minerals not given the same 'exposure' as the other silicates? Because, as you might have noticed, they incorporate in their formula the hydroxyl phase, i.e. they can only form in hydrous environment, wh<mark>en water is present. They cann</mark>ot form in high temperatures and depths, so they are not found in the lower crust or mantle (especially micas); they have not being found on most extraterrestrial planetary bodies (i.e. the Moon, Mercury, most meteorites); on the crust they are mainly produced by metamorphic events, i.e. they cannot be considered 'primary' minerals and they are late products of fractional crystallisation processes.
- 11.2 Sedimentary rocks... Well, this is the place where most 'proper' geological' lessons usually start from. The reason is obvious: the majority of rocks that people will come across during their lifetime will be of sedimentary origin. These rocks originate from as many different scenarios that are possible to imagine, debris from previous rocks, which themselves might have been sedimentary, or igneous, metamorphic, etc. They range from chalk to coal, sandstones to clay, from conglomerate to travertine... most permutations are possible and found: the Earth's surface is a small place when related to the vast geological times a solid crust has existed (>4.4 Ba!). Anyhow, this slide is an incredibly succinct attempt to offer a 'flavour' of this rock family, most geological books and online resource offer a bewildering amount of information and detail beyond the scope of this course. For this brief course, it is sufficient to realise that sedimentary rocks are classified both on grain size characteristics and obviously compositional and origin. The tertiary phase diagram gives a fairly good representation of the most common rocks, based on their broad chemical composition: silicate (mainly quartz as in sands and argillaceous rocks), carbonates (limestones and dolomites), and hydroxides (...rust etc.), most found in nature, except for silica-poor carbonate with high content of oxides. Sandstones are also classified by their origin settings, where we found Clastic rocks, as the name implies,

a cemented collection of rock fragments of various sizes; Biogenetic rocks, sharing an organic origin mainly from deposition of living forms' hard parts (skeletons or shells), these can be either carbon or silica based, or plant material (i.e. coal); finally, some sedimentary rocks are the result of slow but continuous deposition of suspended minerals (i.e. carbonates producing limestones) or salts (the common rock salt, halite, NaCl, or gypsum, calcium sulphite).

- 11.3 Metamorphic rocks... "Metamorphic rocks form from the alteration of pre-existing rocks. Contact metamorphism is caused by direct heat, and the resulting rock is usually crystalline. Regional metamorphosism is due to heat and pressure, and produces foliation, or cleavage, in rocks where the mineral have been aligned due to pressure and recrystallisation. Dynamic metamorphism is associated with the alteration of rocks along major thrust zones (fault planes)" [sic. Rocks & Minerals – Chris Pellant ©]. The 'classic' example of rock metamorphism is the mud-clay (shale)-slate-schist progression with burial of strata and subsequent higher pressures and temperatures. The metamorphosis from granite to gneiss occurs within high pressure and temperature settings. Gneiss can also be produced from all other rock types, such as sediments, sandstones and shales, and igneous rocks. This rock is thought to comprise much of the lower continental crust. When calcite, the principle component in limestone, is heated next to a contact aureole (igneous intrusions) it becomes metamorphosed into a variety of marbles, and when relatively pure, into the highly prized white marble. Within the same geological setting, another metamorphic rock forms, the hornfels, a rock containing a variety of minerals, including quartz, mica and pyroxene. The high degree of crystallisation that occurs removes any original sedimentary structures.
- 11.4 Volcanoes... Here is where many igneous petrology books start from, and it is here were we end (well, nearly...). Volcanology is an important branch of the geological field and surely deserves a much more in-depth analysis, but the implications for the pure mineralogy are not fundamental; in fact, it is the magma's composition, volume of eruption, depth of origin, and geographical/tectonic settings that will command the type and development of intrusive or extrusive igneous phenomena. The top left sketch introduces the main types and nomenclature of magma expressions: large underground 'reservoirs' of molten materials are named 'batholiths' and may extend for hundreds of kilometres deep below the surface. From these batholiths 'stocks' protrude upwards and may represent conspicuous volumes of magma. Magma bodies may continue their journey towards the surface through dikes, which, if they meet impenetrable strata, might expand horizontally and form 'sills' intrusions or 'laccolith' bodies. If a dyke succeeds in reaching the surface and erupt, they become (as per their given name, that is) volcanic pipes. Now, the type of volcanoes which these lavas will form depends on a number of factors, but mainly the volume of liquid, its viscosity, density, and volatiles content (CO_2 and H_2O principally). The 'shape' of a volcano edifice again, will relate to the physical and volumetric magma characteristics, and in particular, chemically, the silica (i.e. viscosity) content (the higher, the more viscous the liquid, the least 'travel' before cooling). Mafic melts will tend to form wide and relatively flat shield volcanoes, but more acidic magmas will build more imposing edifices. Lavas are not the only products of eruptions. Volatiles mixed in the melt will decompress and come out of solution as pressure drops while ascending to surface causing violent explosions and ejection of materials high into the troposphere. Eventually, the ash and cinder will find their way down to the ground and contribute to the building of volcanic strata . These fine volcanic sediments will eventually form another type of volcanic-igneous rocks called pyroclastic (tuff, ignimbrite, etc.).

11.5 Plates are on the table... A final look of the whole Earth system, governed on the surface by plate tectonics. This is a unique characteristic of this planet at least within our solar system (albeit some equivalent icy versions might be occurring on some Jovian satellites). Soon after the gradual solidification of the planet's surface, fractures appear along lines of weakness as the planet gradually cooled and contracted over a plastic and convecting mantle layer (called asthenosphere, which includes most of the upper mantle and some crustal basement). These rocky tassels, called plates, still ride on top of convecting mantle cells and consequently collide ('convergent plates'), diverge ('divergent plates'), and slide past each other (transform). When they collide they might pile against each other or the relatively heavier plate might slide (subduct) below the lighter one. This dynamic crustal regime has played a fundamental role in the birth and development of life on this planet. Vastly increased volcanic output along plate margins, i.e. trenches and rift zones, have allowed the early development of a thick CO₂ and H₂O atmosphere, raising global temperatures well above those granted early in the history of the planet by a still weak solar output. Deep oceanic vents, screened by kilometre of water from deadly UV rays probably facilitated the assembly of early life forms at the bottom of the oceans. Much later, shifting environments and global climate changes (where the distribution of landmass played a key role in ocean circulation) pushed and facilitated evolution along paths leading to our present world and ecosystem.



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