

Course outline – Igneous Petrology

8h of lectures and 16h of practicals

Dr. V. R. Troll

- Lecture 1:** Classification of igneous rocks, differentiation mechanisms, the course of crystallisation, Bowen's reaction series, and chemical evidence for fractional crystallisation.
- Lecture 2:** Phase diagrams and the evolution of basalt magmas, binary systems, peritectic systems, solid solutions, and ternary systems.
- Lecture 3:** Origin of basalt magma, composition of the mantle, mantle melting, melt extraction and formation of the oceanic crust.
- Lecture 4:** Mantle melting II, melt extraction and flood basalt petrogenesis.
- Lecture 5:** Magmatic differentiation: fractional crystallisation in magma chambers, liquid immiscibility, crustal contamination, and magma mixing.
- Lecture 6:** Granites, the granite controversy, granite petrography, the Ab-Or and Qz-Ab-Or-H₂O systems, calc-alkaline and alkaline granites, I-type and S-type granites, and granite emplacement mechanisms.
- Lecture 7:** Rhyolites, calcalkaline versus alkaline rhyolitic melts, rhyolite domes, caldera volcanoes, ignimbrite eruptions and compositionally zoned shallow-level magma chambers.
- Lecture 8:** Rhyolites and Granites and associated ore deposits.
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Recommended Textbooks

- H. U. Schmincke; Volcanism, ISBN 3-540-43650-2
 - Wilson M; Igneous Petrogenesis, ISBN 0-412-53310-3
 - Hall A; Igneous Petrology; ISBN 0-470-20781-1
 - Hibbard MJ; From Petrography to Petrogenesis; ISBN 0-02-354145-8
 - MacKenzie W.S., Donaldson C.H. and Guilford C.; Atlas of igneous rocks and their structures; ISBN 0-470-27339-9
 - M. Best and E. Christiansen; Igneous Petrology; ISBN 0-86542-541-8
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Practical No 1

1. Draw the Streckeisen diagram into your lab-book and classify the rock specimen handed out. Note you first have to estimate the percentage of all minerals present. Then subtract the percentage of the mafic phases and recalculate the felsic minerals to 100%.
2. Draw the TAS diagram into your lab-book and plot the compositions given in page 1. Also plot P₂O₅ vs. SiO₂. Can you explain the trend?
3. Thin section descriptions (mafic volcanic rocks).
 - Draw annotated sketch of thin section view.
 - Briefly describe the texture (see glossary).
 - What minerals are present and in what percentage?
 - What is the nature of the groundmass?
 - What was the sequence of crystallisation?
 - Can you see evidence for fractional crystallisation?



The Rocks Display'd

Igneous Petrology

Rocks are a collection of minerals (mineral phases), stuck together by various forms of cement and/or matrix or just by the interlocking of grains. The minerals themselves are collections of atoms and molecules arranged in crystal lattices. Thus a rock is a chemical system and can be described in terms of chemical thermodynamics.

The atoms in minerals are arranged in crystal lattices characteristic for each mineral phase (i.e. a mineral may have more than one phase, each with its own lattice structure). E.g. quartz occurs as a high and a low temperature phase where low-T α -qtz is trigonal and high-T β -qtz is hexagonal.

The chemical composition of a rock is therefore the sum of chemical components (minerals and matrix). Most rocks are formed by a relatively small number of minerals known as the "rock forming minerals" and most of which are silicates. There is usually a large proportion of a small number of elements common in 99% of all igneous rock on Earth. These elements are known as the major elements and they make up 95-99% of an igneous rock. They are:

O, Si, Al, Fe, Mg, Ca, Na, K, Ti, Mn, P

Traditionally these elements are reported as oxides though they actually occur mainly as silicates.

<i>Element (wt %)</i>	<i>Basalt/Gabbro</i>	<i>Andesite/Diorite</i>	<i>Rhyolite/Granite</i>
SiO ₂	49	62	71
TiO ₂	1	0.7	0.5
Al ₂ O ₃	18	16.5	14.5
FeO	6	4	2
Fe ₂ O ₃	3	3	1.5
MgO	7	2.5	1
CaO	11	5.5	2
Na ₂ O	2.5	3	3.5
K ₂ O	1	2	4
P ₂ O ₅	0.25	0.5	0.2

Further constituents of igneous rocks are minor and trace elements. These are recorded as ppm (parts per million or $\mu\text{g/g}$) and not as oxides. There is a wide variety of trace elements, usually hidden in the lattices of minerals as substitutes for the major elements, except where they form their own minerals (e.g. zircon, ZrSiO₄)

Trace elements: Ba, Cr, Cu, Ni, Rb, Sr, Y, Zr, Nb, Pb

Rare Earth Element: (REE, minor elements): La, Ce, Sm, Nd, U, Th, Yb

Igneous rocks also contain volatile components, notably compounds of C, H, S (but also Cl and Br) that form the main volcanic gases CO₂, SO₂ and H₂O. Magma loses these gases on cooling and/or eruption and igneous rocks generally contain very little dissolved gaseous components.

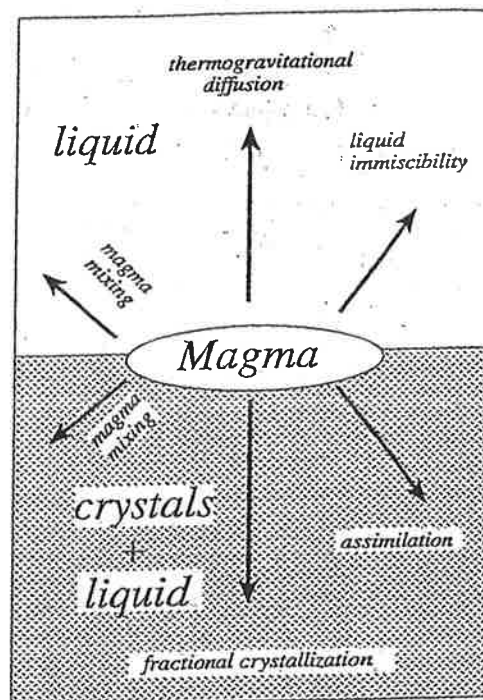
Classification of Igneous rocks

Various methods of classification of igneous rocks are found in the literature and each scheme has a particular advantage. We discuss only the most widely used ones.

- *Streckeisen classification* → using modal mineral proportions; thin section
- *TAS (total alkali vs. silica)* → using major oxide chemistry; XRF data
- *Flemming classification* → using trace element chemistry; ICPMS data

Origin of igneous rock suites

The wide range of different igneous rock suites found on Earth (e.g. calc-alkaline, peralkaline, tholeiitic) are caused by (a) different magma sources, (b) different degrees of melting of the source, (c) the process of differentiation, and (d) the degree of assimilation. The occurrence of individual rock series (e.g. at a single volcano) where all members are related requires, in turn, a mechanism to produce the whole series from just a single parent magma. This is termed differentiation. Over the last 150 years a large range of differentiation mechanisms was invoked which may be subdivided into differentiation mechanism in the liquid state and crystal liquid fractionation.



Differentiation in the liquid state:

- liquid immiscibility
- thermogravitational diffusion
- magma mixing

Crystal liquid fractionation

- assimilation
- fractional crystallisation
- magma mixing

From these processes only fractional crystallisation appears able to produce a whole series of derivative magmas from a single parent and is considered the most important process of magmatic differentiation. However, the other processes mentioned above are also relevant and will influence magmatic evolution to various extents. Hence, they have to be assessed for each rock suite individually !!! (See also Wilson M. 1993, JGS London, vol. 150, p 611-624).

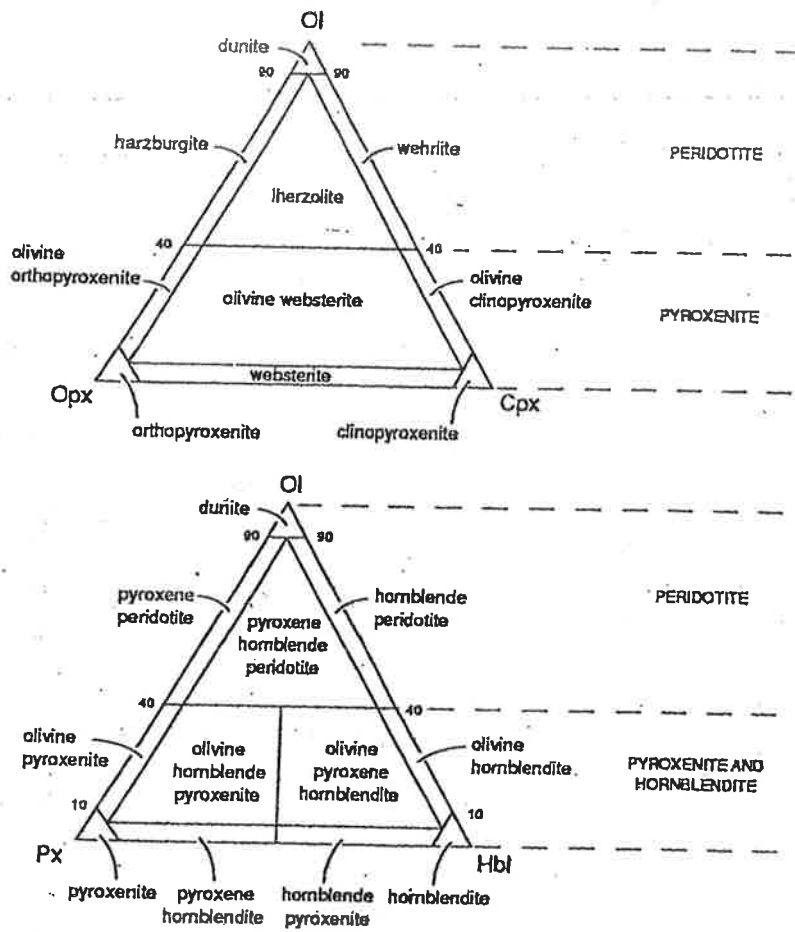


FIGURE V-2. Classification of ultramafic rocks ($M > 90\%$) based on the relative abundance of olivine (ol), orthopyroxene (opx), clinopyroxene (cpx), and hornblende (hbl) (Le Maitre, 1989). Reprinted by permission of Blackwell Science Ltd.

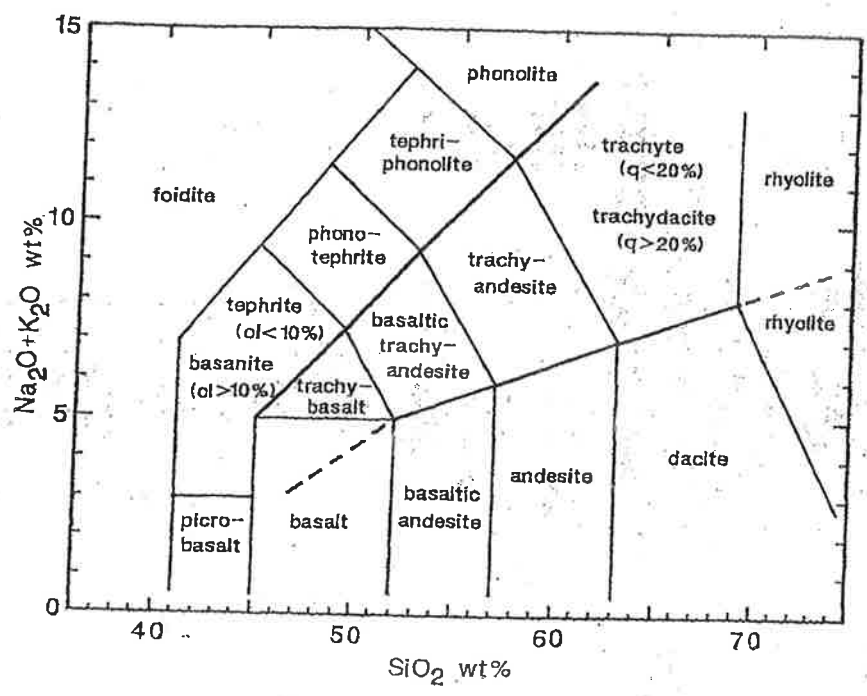
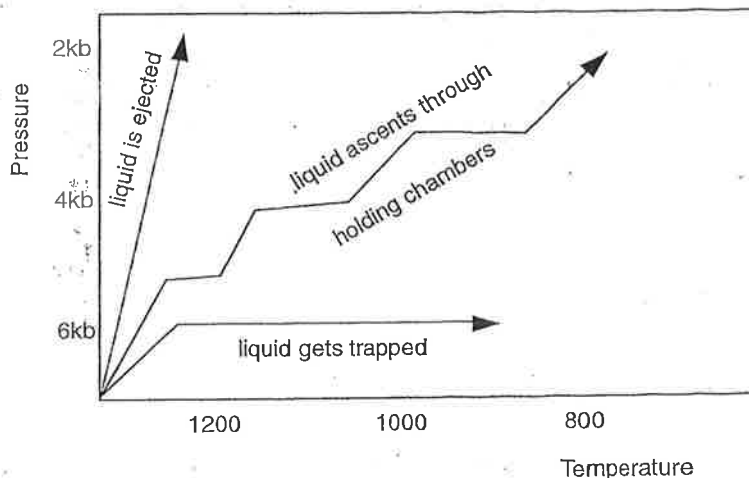


FIGURE V-3. Classification of volcanic rocks based on the weight content of SiO_2 and $\text{Na}_2\text{O} + \text{K}_2\text{O}$.

The course of crystallisation

The course of crystallisation of an igneous melt is the history of cooling of a silicate liquid: from the liquid a succession of crystals will appear as their freezing (=melting) points are reached. They grow as long as their components are available, and as long as they are stable at the temperature and pressure, and are not physically removed or isolated from the melt (e.g. crystal settling, dyke intrusion, etc.). The sequence in which they appear (crystallisation) and disappear (removal or resorption) is governed by the composition, the temperature and the pressure. The history of an igneous magma can be plotted in P-T space:



Changing melt chemistry

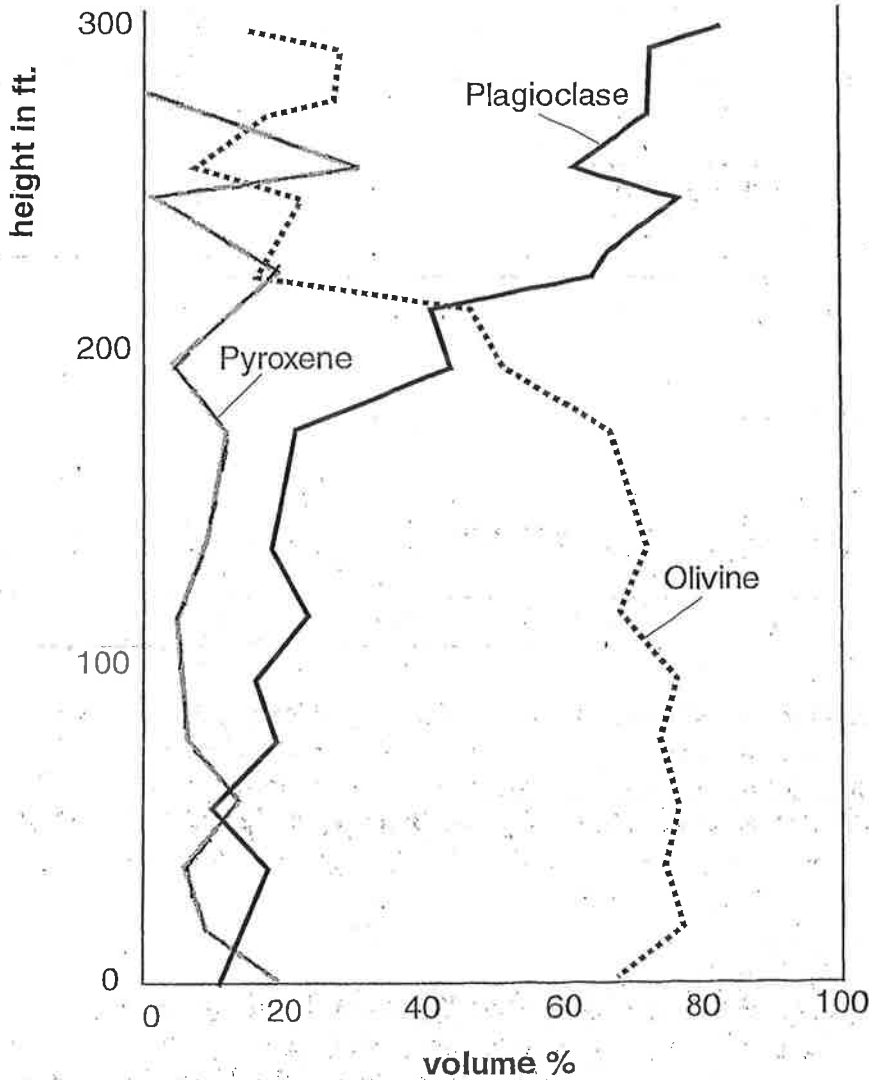
As various minerals crystallise the composition of the liquid changes (try to put wine in the freezer), particularly when crystals are removed or become isolated. The liquid then evolves towards a more felsic composition (felsic= feldspar and silica; also called acidic or silicic). The end-product is a residual liquid that is chemically very different from the initial magma composition and produced various crystal assemblages during the course of fractional crystallisation. The process of crystal removal/isolation is inferred from several natural examples:

- ★ Darwin 1844: olivine crystals accumulate at the base of some lava flows.
- ★ Walker 1940: olivine cumulates in Palisade sill.
- ★ Wager and Brown 1939: layered cumulates in the Skaergaard and the Rum intrusions.
- ★ Zoned feldspar crystals also support the theory of fractional crystallisation as the core of a crystal will be isolated from the melt during overgrowth. This produces an increasingly Na+K rich feldspar composition towards the crystal rim.

The theoretical background to the phenomenon of fractional crystallisation was experimentally investigated by Bowen in the 1920's (Bowen N.L. *The evolution of igneous rocks*, 1928). His results can be summarised in the **Bowen reaction series**.

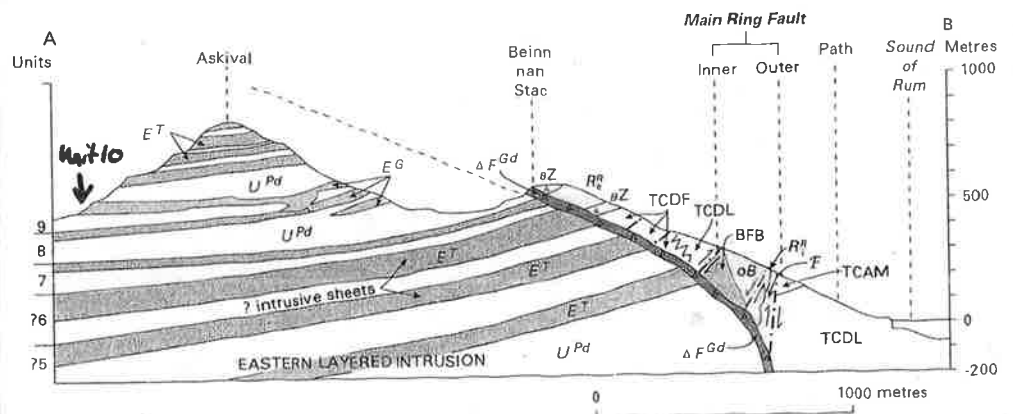
Evidence from Layered Intrusions

Unit 10, Rum intrusion, NW-Scotland



Modal variation in the ultrabasic rocks of Unit 10 of the Rum layered intrusion (based on Brown 1956)

RUM LAYERED INTRUSION



● Bowens reaction series:

<i>Rock type</i>	<i>Discontinuous</i>	<i>Continuous</i>
Basalt	olivine ↓	bytownite ↓
↓	pyroxene ↓	labradorite ↓
Andesite	amphibole ↓	oligoclase ↓
↓	biotite ↘	albite ↙
Rhyolite	Alk-fsp, muscovite, qtz	

Discontinuous series: Crystals react with liquid to form different type of mineral

Continuous series: Crystals change composition during growth: continuous reaction with liquid

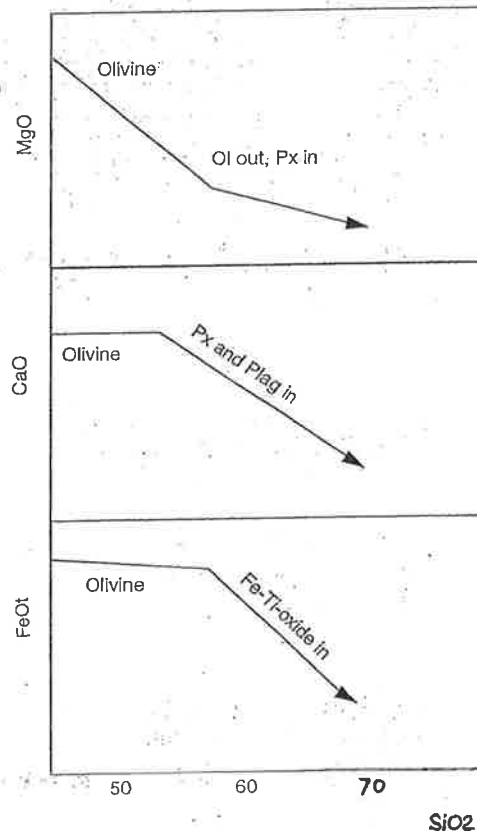
Chemical evidence for fractional crystallisation

Fractional crystallisation can also be inferred from the chemical changes through a genetically related rock suite and not only from petrographic observations. This is most clearly reflected in so called variation diagrams where a major element concentration is plotted against the progress of crystallisation which indicates the degree of evolution of the melt. The principle variant for this purpose is silica. SiO₂ is most abundant in igneous rocks and fractional crystallisation changes the melt composition from silica poor to silica rich (TAS diagram is such a variation diagram !). This type of diagram was first used by Harker at the beginning of the 20 th century and is still referred to as Harker diagram.

However, it must be understood that SiO₂ does not increase at a regular rate throughout a rock suite. In fact SiO₂ increases very little in the mafic spectrum (basalt) and may in some cases even decrease (e.g. opx crystallisation, as opx has more silica than cpx and plag). In fact more than half a basalt magma can crystallise before there is any major increase in SiO₂ and high silica rocks represent perhaps a 5% residual liquid from the initial basalt magma.

In general, the effects of continuous fractional crystallisation is to lead to a system strongly

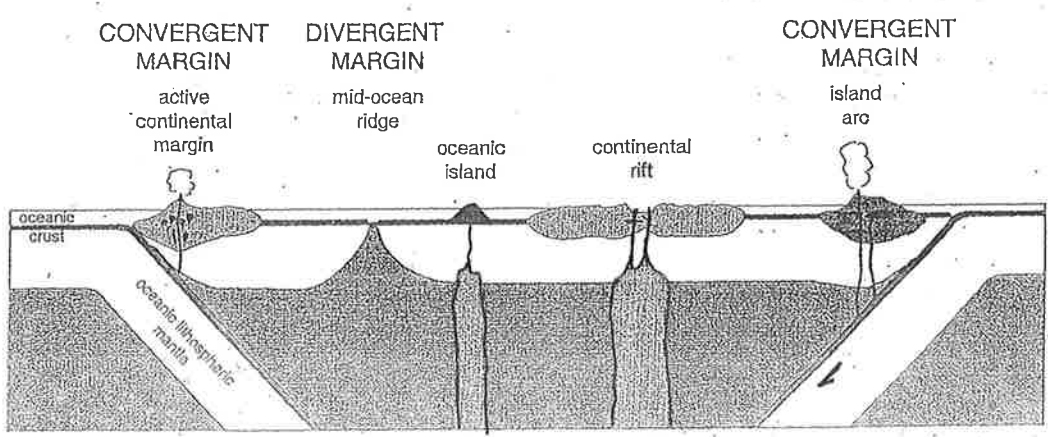
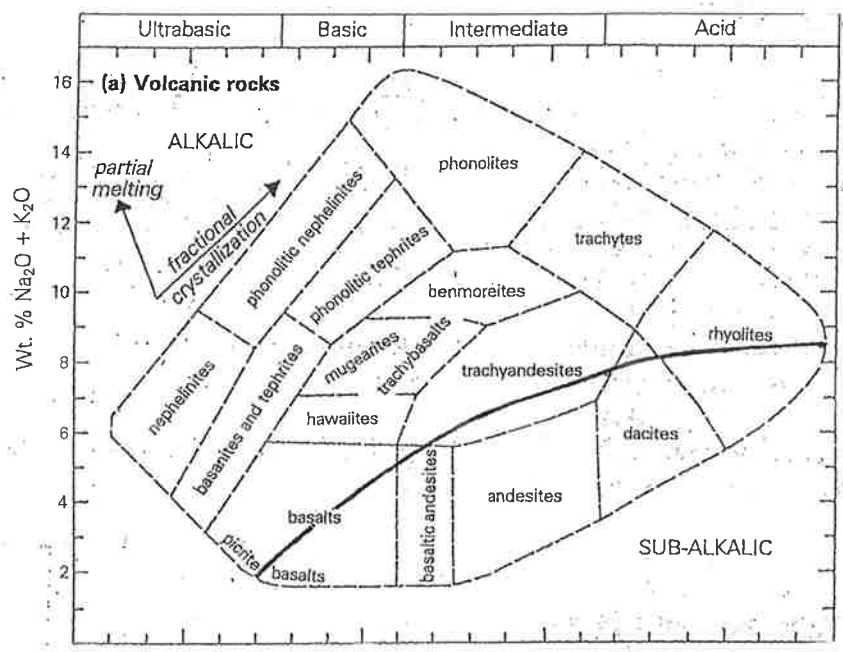
depleted in CaO, MgO, FeO and enriched in Na₂O, K₂O and SiO₂ – a system that will ultimately crystallise only qtz, Alk-fsp (Na,K)AlSi₃O₈ and mica (rhyolite composition).



Abundance on Earth

THE FIVE MAGMA SERIES

ALKALINE	0.5%	}	nephelinite - (phonolite) magma series
	3.5%		basanite - (phonolite) " "
SUB ALKALINE	84%		alkali olivine basalt - (trachyte) " "
	12%		tholeiitic (basalt) - (rhyolite) " "
			(calc-alkaline) basalt - (rhyolite) " "



"WHAT'S IN A NAME? THAT WHICH WE CALL A ROSE BY ANY OTHER NAME WOULD SMELL AS SWEET."

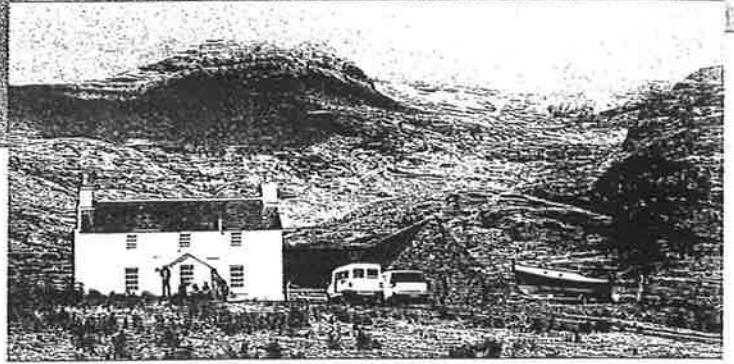
—WILLIAM SHAKESPEARE

The names of magmatic rocks give igneous petrologists a secret pleasure. They are magical passwords into a world of minerals, textures, chemistry, associations and histories accessible only to those who have studied enough to understand what the names imply. We relish using them – *absarokite*, *kakortokite*, *jacupirangite* – and their obscurity binds our tribe together, excluding those who have not acquired the magic. Unlike minerals, whose names have to be approved by the hard-working members of the IMA Commission on New Minerals and Mineral Nomenclature, rock names can be introduced willy-nilly, as they were, mainly in the 19th and early 20th centuries. Discussion of their etymology reached its apotheosis in *A Descriptive Petrography of the Igneous Rocks* by Albert Johannsen, published in four volumes between 1931 and 1938 by the University of Chicago Press. Look up 'basalt' and you will be treated to four pages, with long quotations in Latin, French and German, and words printed in the Ethiopic, ancient Egyptian, Greek and Hebrew scripts. Johannsen concludes, 'The term *basalt* is of uncertain origin', but of the alternatives offered I prefer: 'Worm said the word comes from the Ethiopic *bselt* or *bsalt*, the feminine of the adjective *bsul* (*bsul* [here printed in the Ethiopic script – ed.] is the Ethiopic word for cooked)'. There we are, transported by a single word to East Africa, a cooked rock in a cooked terrain.

Unlike minerals, which are often named after people, rocks are predominantly named after regions or places. There are striking differences in the scale of these sources, even when the rocks are closely related. For example, take the series *alkali basalt* – *hawaiiite* – *mugearite* – *benmoreite* – *trachyte*, volcanic rocks related primarily by crystal fractionation in deep magma chambers. The relationship is mainly expressed by increasing proportions of alkali feldspar at the expense of plagioclase, which simultaneously becomes richer in sodium, poorer in calcium. *Trachyte* was (according to Johannsen) named by Haüy, perhaps in 1813, and is an allusion to the Greek word for 'rough'. The other three are named after places, all of which I visited in 2008.

Hawai'i is the greatest, most magnificent volcanic edifice on Earth, measuring at sea level 160 by 140 km. The highest of its five volcanic centres, Mauna Kea, rises 4205 m above sea level and 17 km above its base on the ocean floor. The centre most active at present, Kilauea, has been almost continuously active for 600,000 years. Its flanks, streaked by overlapping flows, their young, glassy surfaces iridescent in the tropical sun, give an overwhelming impression of inexorable growth. Hawai'i truly deserves to have a rock type named after it, and *hawaiiite* was defined by Iddings in 1913. Johannsen is dismissive of the name, which was based on the feldspar composition calculated from chemical analysis (the CIPW norm, of which Iddings was the 'I'); it therefore 'has no place in a mineralogical classification'.

Benmoreite is named after Ben More on the island of Mull, which is off western Scotland and part of the North Atlantic Large Igneous Province. The Hebridean sub-province is built around four famous volcanic cen-



Palaeogene traps, Ben More, Isle of Mull

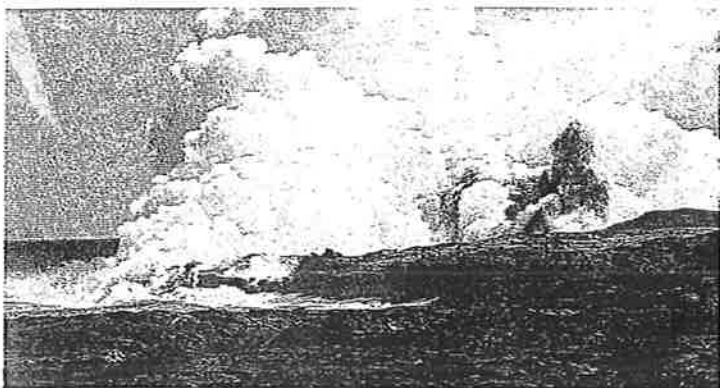
tres, Mull, Ardnamurchan, Rum and Skye, and with their associated lava fields has a north-south dimension of 150 km, similar to the size of Hawai'i. But erosion since the Palaeogene lets us see into the magma chambers that lay below volcanic superstructures of which only fragments are preserved. The Mull volcano has a central position in the history of igneous petrology because it was here in 1924 that Bailey and others first recognized the two magma types that we now call the 'alkaline' and 'tholeiitic' series. Ben More (it simply means 'big hill' – there are lots of Ben Mores in Scotland) is a handsome 966 m mountain, rising from the sea, the piled lavas with their distinctive 'trap' topography forming the western flank of a plutonic centre with a central caldera. The evolved lavas form paler horizons near the top of the peak. The name *benmoreite* was given by Tilley and Muir in 1963 and thus escaped Johannsen's scrutiny, but Kerr in 1995 analysed samples from the type locality and found them to be trachyte!



Mugeary, Isle of Skye

Which leaves us with *mugearite*. The rock was named, from its mineralogy, by Harker in 1904 after Mugeary (pronounced moog-ary, with a hard 'g') in Trotternish, a windswept peninsula of flat-lying flows that forms the northernmost extension of the Isle of Skye. I went there towards the end of November, when the high ground of the Cuillin gabbro centre to the south was snow covered. Mugeary is a solitary, small farmhouse, at the end of a twisting single-track road, in an expanse of peat bogs enlivened by occasional jointed-basalt cliffs. While I was taking photographs the farmer arrived on his quad bike, accompanied by the inevitable super-intelligent black-and-white dog. I asked if he knew that his house had given its name to a rock type. 'Aye, I looked it up on the web', he replied. Mugeary is a long way from Hawai'i, in many senses, but to have an igneous rock type named after your home – how cool is that!

Ian Parsons, University of Edinburgh



Lava entering the Pacific from Kilauea, Hawai'i, July 2008

Igneous Petrology - Lecture 2

Phase diagrams and the evolution of basaltic melts

Textbook: Cox, Bell and Pankhurst, *The Interpretation of Igneous Rocks*, Chapman & Hall

To describe the crystallisation of a melt it is usual to simplify things by assuming that crystallisation is keeping pace with cooling i.e. there is equilibrium, and there is constant pressure (stable magma chamber situation). This is certainly not always applicable to natural rocks but gives nevertheless a reasonable estimate of the crystallisation history of a magma. Leaving pressure (P) unconsidered we focus on the effects of temperature (T) and composition (X). In these circumstances we can describe the crystallisation by reference to phase diagrams, which are a simplified way of evaluating the effects of thermodynamic equilibrium.

Phase diagrams are based on the phase rule: $F = C + 2 - P$

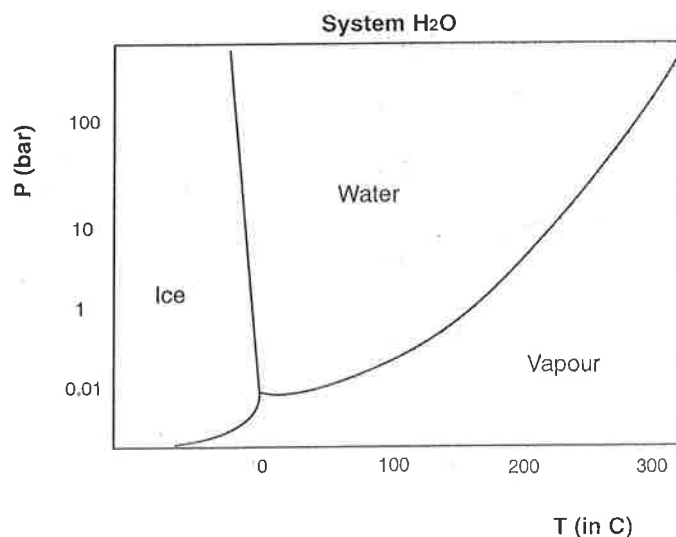
F = number of degrees of freedom

C = components (chemical units, e.g. $MgSiO_3$)

P = phases (solid minerals or liquid), e.g. diopside

Phase diagrams can be constructed with numerical values that define the actual amounts as well as the phases involved in a crystallisation sequence. Binary diagrams plot 2-component compositions against temperature. Ternary diagrams show the crystallisation of a 3-component system projected as a 2D map view.

The process of crystallisation is—in plain language—the freezing of particular minerals (solid phases) from a liquid (single liquid phase). A good example is the crystallisation of ice from water, where the freezing point is also the melting point. For pure components freezing from a liquid of its own composition (ice + water) this is a fixed temperature for any given pressure, i.e. changing the pressure changes the freezing/melting point.



Binary systems

System diopside-anorthite (Di-An)

If the liquid has more than one component (magma is at least a two component mixture: more realistically its a multi-component mixture) then the temperature at which the liquid begins to freeze is neither the melting point of component A nor that of component B. For example the system diopside-anorthite (basalt) shows freezing of diopside or anorthite at a higher temperature than the melting point of diopside (Di) and anorthite (An). This binary phase diagram can show the course of crystallisation and that of melting of a whole series of mixtures of the two components.

The melting curve (univariant curve= start of crystallisation) is the liquidus and the line marking the completion of crystallisation is the solidus. Below the solidus all compositions are solid, above the liquidus all belong to one homogeneous liquid. In between crystals and liquid co-exist in equilibrium.

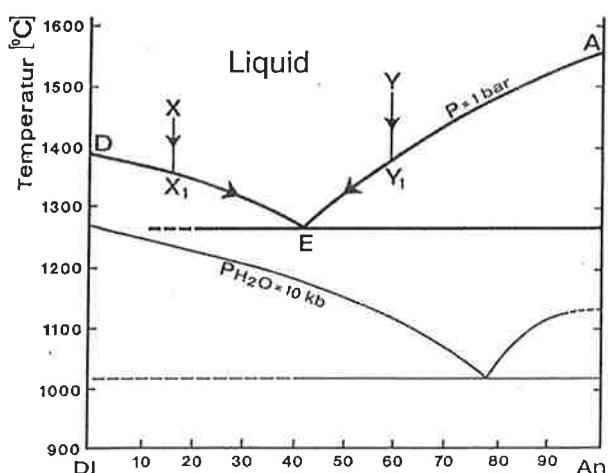
The first crystals to form will always be either diopside or anorthite depending on the starting composition of the liquid, and will appear at a temperature that is lower than that of a single component system (e.g. pure diopside liquid). If the system is left to cool as a closed system it will eventually crystallise a mixture of diopside and anorthite crystals in proportion to the original mixture.

Composition X contains mostly diopside. When cooled to the intersection point of X and the liquidus (X_1) diopside crystals begin to form. Due to diopside crystallisation the liquid gets depleted in this component (wine in the freezer \rightarrow liquid gets depleted in H_2O) and moves towards more An rich composition. The melting point on the univariant curve D-E is now lower and more Di crystals form. If equilibrium is maintained, the temperature and X_{liquid} follows the curve towards the eutectic minimum (E). At E ($X = 58\%Di:42\%An$ at $1200^\circ C$) An begins to crystallise and both mineral crystallise happily until all liquid is used up. The result is an eutectic

mixture of pure Di and pure An in the proportions of the starting composition.

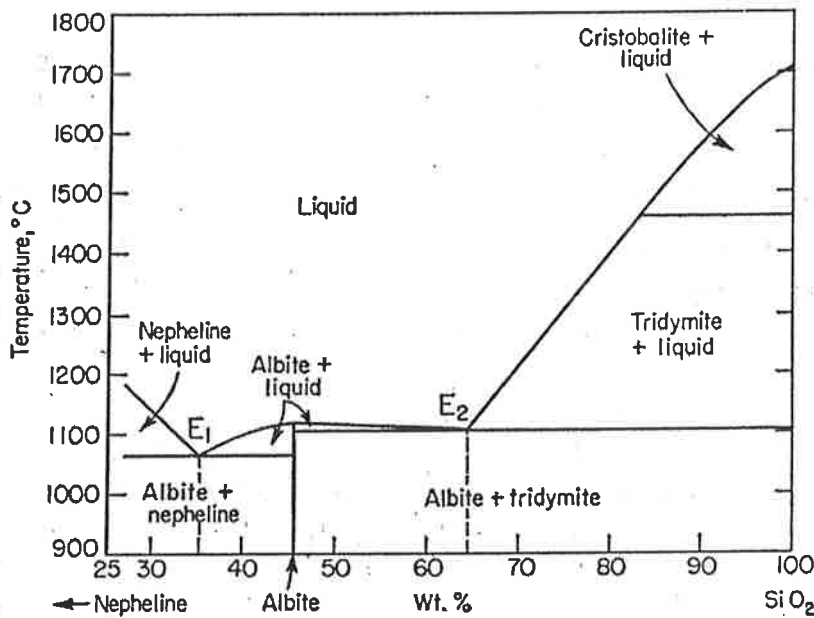
If some crystals are removed during the process, the end mixture would not be that of X_1 , i.e., the initial liquid would have been fractionated to (a) a solid that is rich in diopside and an end product that is depleted in diopside relative to X_1 .

Simple eutectic mixtures are rare in nature. More common are systems in which the end members can produce a different intermediate compound, a third mineral phase.



System nepheline – silica (Ne-Si)
with the intermediate compound: albite

This is simply two binary eutectics side by side. The melting point of the intermediate compound is a thermal maximum on the liquidus. This inflection point is in effect a thermal divide. Crystallisation can take place with cooling on either side of it but cannot cross the thermal divide. Hence, nepheline and quartz can never exist in the same system ($\text{Na}[\text{AlSi}_3\text{O}_8] + 2\text{SiO}_2 \rightleftharpoons \text{Na}[\text{AlSi}_3\text{O}_8]$; $\sim \text{Ne} + 2\text{Si} = \text{Ab}$).

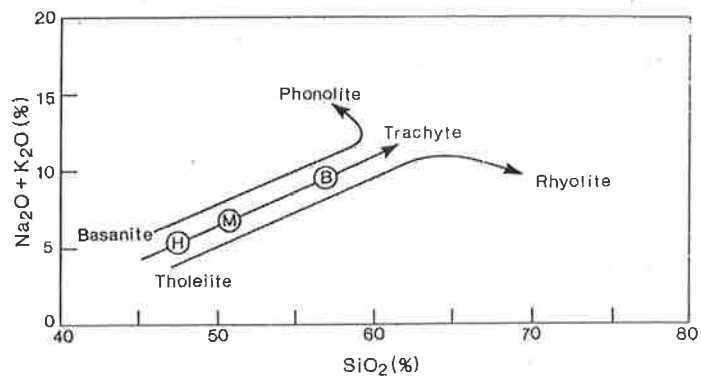


Fractional crystallisation:

If crystals are removed during the process of crystallisation, the liquid changes composition continuously down the slope of the liquidus.

There are only two possibilities, however, depending on the initial starting composition.

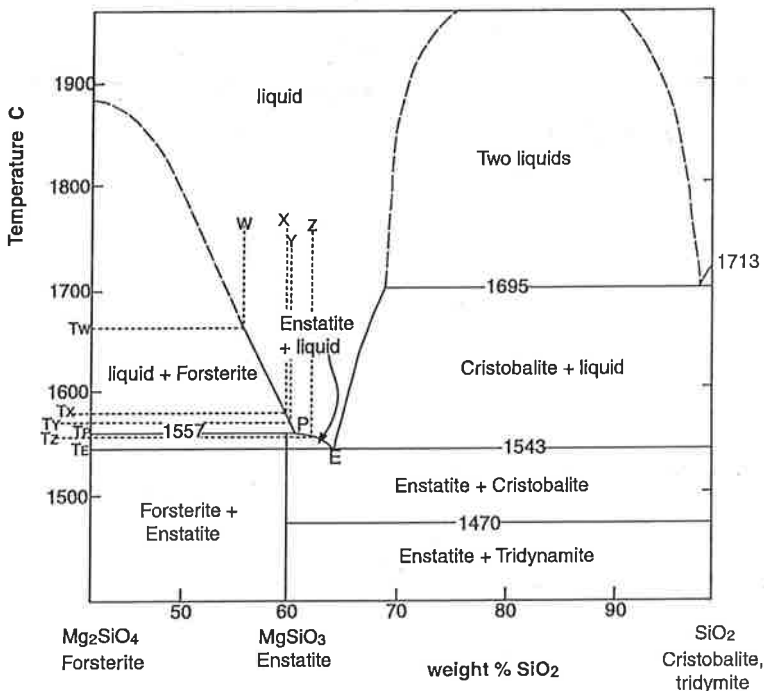
The liquidus on either side of the albite thermal divide crystallise both albite but the liquid composition moves in opposite directions to one of the two eutectic points. In nature this is reflected by a trachyte magma that crystallises alkali-feldspar and can end up as either rhyolite (fsp+qtz) or as phonolite (fsp + ne) (Remember the TAS diagram !).



Peritectic systems

System forsterite-silica (Fo-Si)

In peritectic systems once formed crystals react with the progressively evolving melt to produce another type of mineral (remember Bowen's discontinuous crystallisation series). For example in the system forsterite-silica an intermediate phase is formed; enstatite. At high temperatures and low pressures silica is present as cristobalite or tridymite and enstatite as protoenstatite. For simplicity we may consider these phases as quartz and pyroxene. If a liquid with composition X (see diagram) cools to ca. 1600°C forsterite crystals form and the liquid moves down the peritectic line towards an inflection point (peritectic point P) where enstatite becomes stable. Once formed forsterite is now reacting with the more silicious liquid according to the peritectic reaction $Mg_2SiO_4 + SiO_2 \rightleftharpoons 2MgSiO_3$ to form enstatite. If the system has sufficient time to equilibrate all Fo will be used up by this reaction until no Fo is left. As this reaction uses all remaining liquid the end product would be 100% enstatite. If a starting composition W is considered (less silica rich) the remaining liquid in P is not enough to convert all Fo to enstatite and the end product would be a rock with both Fo and En possibly with olivine crystals mantled by pyroxene.

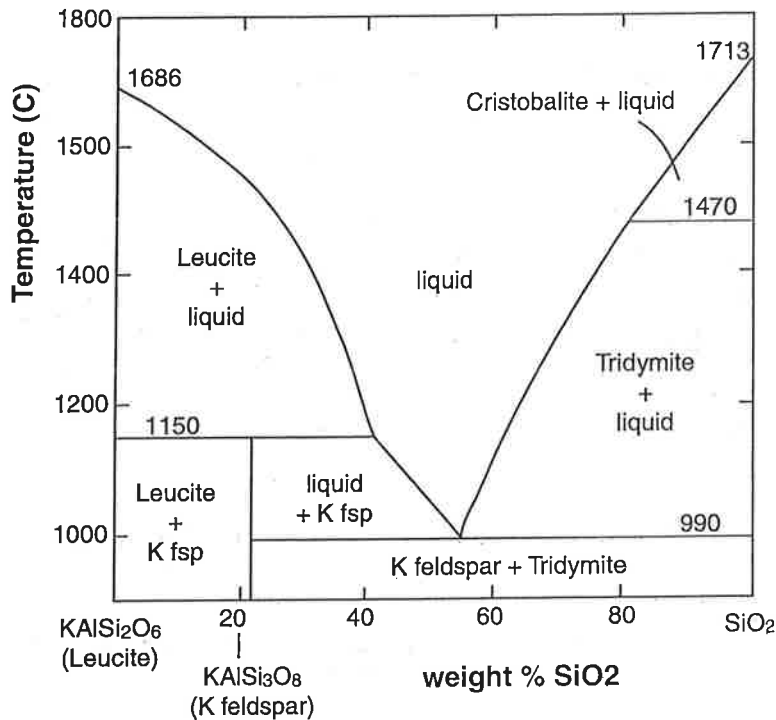


The binary system Fo-SiO₂ at 1 atmosphere pressure
(after Bowen and Anderson 1914 and Greig 1927)

If the starting composition is more silica rich the liquid would evolve from point P towards E while Fo is converted to En. The end product expected would be a rock that contains pyroxene and quartz with no olivine left. However, the reactions may be too sluggish to convert all olivine and a rock with olivine, pyroxene and quartz may be expected, reflecting an incomplete peritectic reaction (disequilibrium).

System Leucite-Silica

Another peritectic system is the leucite- SiO_2 system with the intermediate phase K-feldspar. This system is in principle similar to the Fo-Si system where leucite forms first and reacts with the melt to form K-fsp.



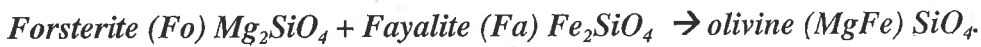
The KAISi₂O₆ (Leucite) - SiO₂ binary system at 1 atmosphere pressure (after Schairer and Bowen 1948)

Fractional melting in peritectic systems: There are two types of fractional melting. Congruent and incongruent melting. Congruent melting is essentially the reverse of crystallisation with a liquid that starts with eutectic composition and evolves towards the starting composition. Incongruent melting involves an intermediate compound that is not on the liquidus of the two end members. E.g. in the system forsterite-silica. There melting produces a liquid that is not its own composition + a new solid phase (solid A → solid B + liquid). Enstatite melts to a liquid more siliceous, and forms crystals more mafic. This takes place at a reaction point which is not immediately above the phase composition and is not a peak but an inflection point on the liquidus.

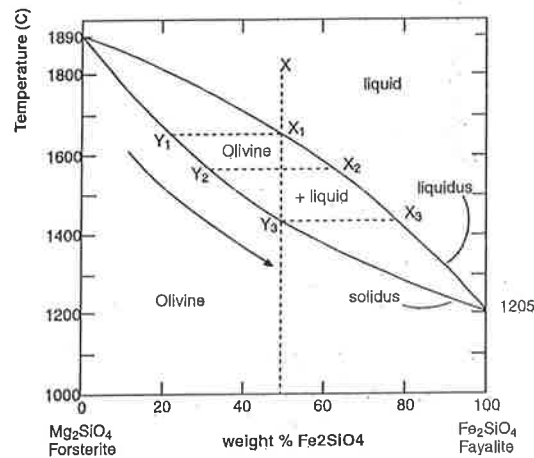
Solid solutions

So far we have considered the crystallisation of minerals with fixed compositions. However, many petrologically important minerals such as olivine and plagioclase have compositions which range between two end members and belong to a solid solution series.

Olivine (ol)



There is a complete range of substitution of Fe^{2+} for Mg^{2+} and the composition is usually expressed in % endmember e.g. $(Fa_{10}Fo_{90})$. It has become common to just use the Fo value e.g. (Fo_{90}) as an expression of the Mg content in ol. Note the higher the Fo % in olivine the more mafic its parental liquid!



The Mg_2SiO_4 (forsterite)- Fe_2SiO_4 (Fayalite) binary system at 1 atmosphere pressure (after Bowen and Schairer)

Plagioclase (plag)

Plagioclase has a more complex substitution with end members albite ($Ab = NaAlSi_3O_8$) and anorthite ($An = CaAl_2Si_2O_8$). The substitution is coupled: one (Ca,Al) for one (Na,Si). Note that plagioclase compositions are reported similar to olivine compositions (e.g. An_{80}). The higher the An value the more mafic the parental liquid !

Consider a liquid with a starting composition L ($An_{50}:Ab_{50}$). At the intersection of falling temperature with the liquidus (P) plagioclase with the composition W begins to form. The liquid will evolve downslope along the liquidus and at liquid composition Q plagioclase with a composition X begins to form. The liquid then evolves further along the liquidus (increase in Ab) and crystals become increasingly more Ab rich. At R crystals of the composition Y form and all liquid is used up. Now the composition of the crystals is that of the starting composition with a liquid that is always more evolved than the crystals, reflecting the course of the continuous crystallisation series of Bowen.

If the crystals are removed they are prevented from reacting and An is removed from the system. The liquid is now depleted in An and the whole system is even more strongly enriched in Ab. The result is a batch of crystals richer in Ab than the starting composition. E.g. crystal composition Z, with a liquid of composition S.

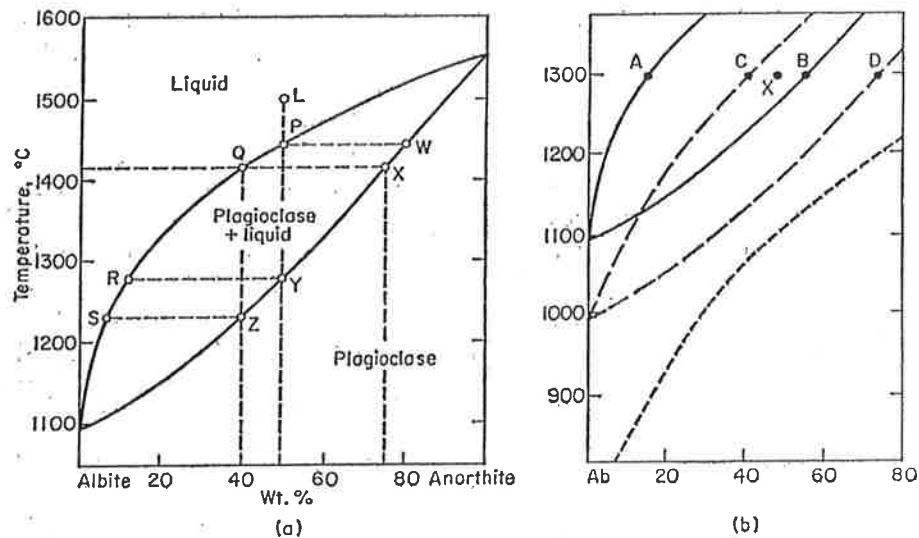


FIG. 5. Phase diagrams for the system albite-anorthite. (a) The anhydrous system at atmospheric pressure. (After N. L. Bowen.) (b) Anhydrous system (full lines) compared with system at water pressure of 5,000 bars (finely dashed line, lower right). (After H. S. Yoder, D. B. Stewart, and J. R. Smith.) Broken lines represent hypothetically some intermediate water pressure.

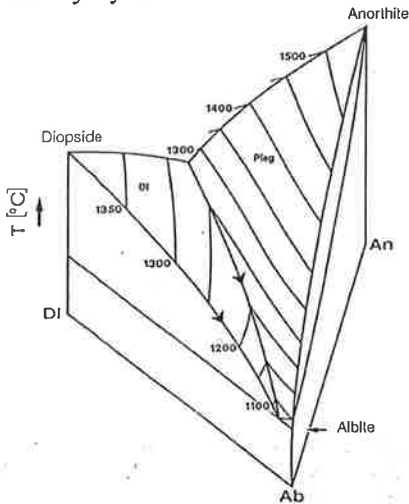
Note : the plagioclase system is pressure depended. Increasing the pressure will lower the solidus and conversely reducing the pressure will raise the solidus. This may cause shifts in mineral composition, for example when magma ascends, the chamber pressure is reduced or increased by eruption or replenishment, or when convective motion in the reservoir occurs.

Ternary Systems

Whilst binary systems are useful to show the crystallisation of minerals, whole rocks usually have more than two components. It turns out that many real rock systems can be more accurately depicted with three binary systems (ternary systems). Ternary systems can show the essential course of crystallisation of both basalts and granites. These systems have three components which are located in the corners of a triangle, where the temperature information is given in the third dimension. In other words ternary systems are a map projection of a 3D system where the temperature is given in isotherms (like contour lines on a topographic map).

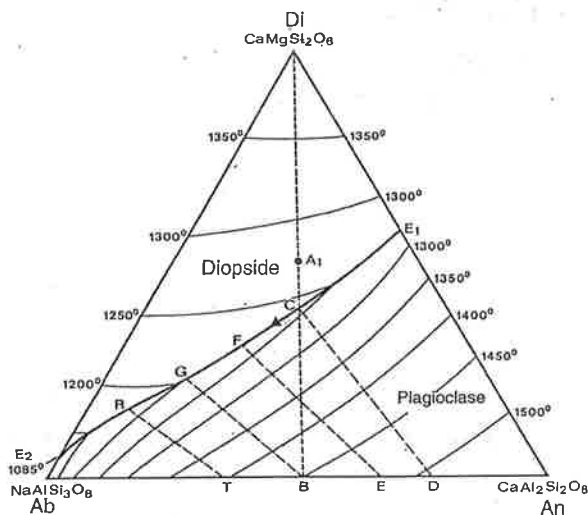
System Di-Ab-An

This is the system that most closely describes basalt crystallisation. The 3D image gives you a feel how the system looks when all four variables are considered. If you want its two hills with a valley in between where the two hill surfaces represent liquidus surfaces. The sides of the system are represented by binary phase diagrams, two of which are introduced above (Ab-An and Di-An). In other words this is a combination of three binary systems, each makes one side of the ternary system.



The valley is a low temperature trough that extends from the binary eutectics of the Di-An system to the binary eutectic of the Di-Ab system and is called the cotectic curve. In contrast to binary systems the liquid composition moves down to the thermal valley (binary eutectic) but does not freeze there, rather is continues moving down the valley floor (along the cotectic) until all liquid is used up. The compositions in this system are given as percentage of the three components recalculated to 100% (e.g. Di₃₀, An₆₀, Ab₁₀).

Lets first consider crystallisation of a composition of 50% An₅₀Ab₅₀ and 50% Di (A₁). This composition lies in the Di field so it will start crystallising Di as soon as a temperature of 1275 °C is reached.

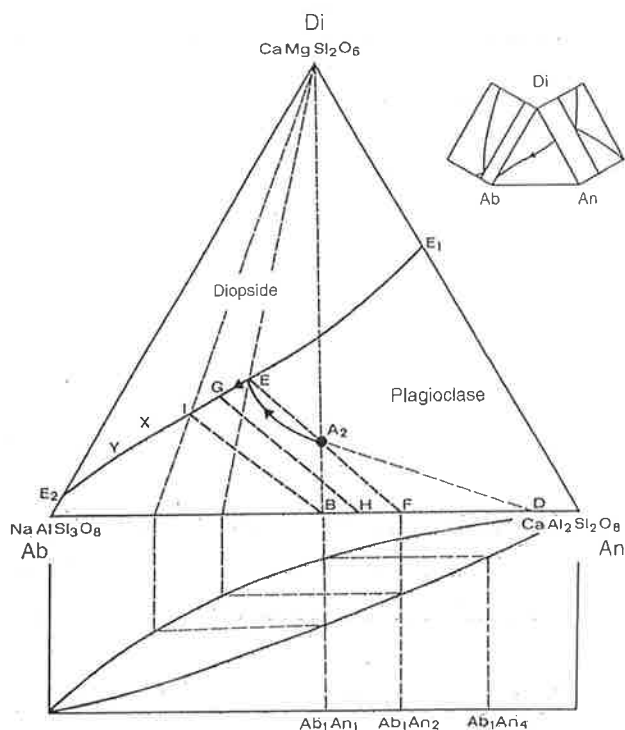


1275 °C is reached. The liquid then evolves towards the cotectic (E₁-E₂) and intersects E₁-E₂ at C (ca. 1235°C). Here plagioclase joins diopside as a crystallising phase.

The first plagioclase to crystallise is of composition D (remember the An-Ab diagram → plag is more An rich than the liquid). The liquid then moves down the thermal valley towards E₂. At F the plagioclase crystallising is of composition E. When the liquid reached G the crystallising plag is of composition B and hence similar to the starting composition, implying that all liquid is used up at this stage. Fractional

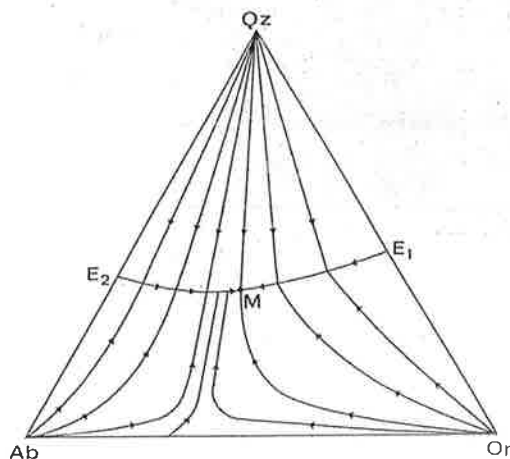
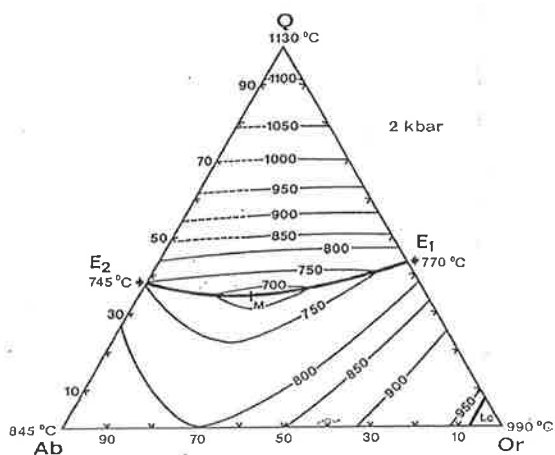
crystallisation, in turn, would allow the system to move further and reach a liquid composition of e.g. R, crystallising plagioclase of composition T.

Lets now consider a starting composition that plots in the plagioclase field (A2). This is a bit more tricky. The starting composition is now 85% of $Ab_{50}An_{50}$ and 15% Di. When such a liquid cools down it will first crystallise plagioclase. However, this time the evolution from the starting composition towards the cotectic follows a slightly curved path with plagioclase of composition D crystallising. As soon as the liquid reached the thermal valley at E, it is back to normal crystallising a plag with composition F. From E the liquid evolves then towards G and I, crystallising plagioclase of compositions H and B, respectively. At B the plagioclase crystallising is the same as the An-Ab component in the starting composition implying no more liquid left. Fractional crystallisation would again shift melt compositions further along the cotectic (X,Y) and produce plagioclase that is more evolved than the starting composition.



System Qtz-Ab-Or

This system works the same way as the Di-An-Ab system only with different endmember compositions resembling the whole rock composition of granites. Depending on starting composition either plagioclase or K-fsp crystallises first followed by qtz at the cotectic. The system will then evolve towards the minimum composition M (valley bottom). However, more about this when we discuss granite petrogenesis.

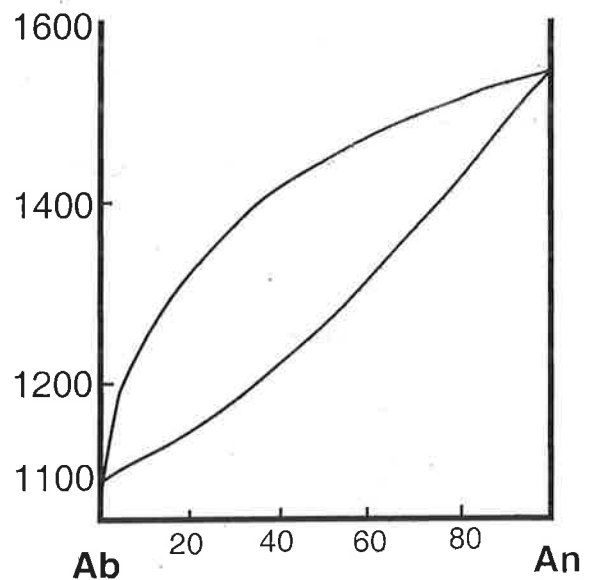
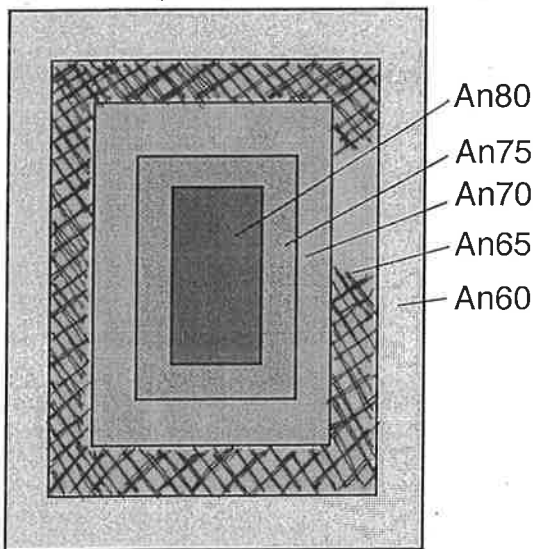


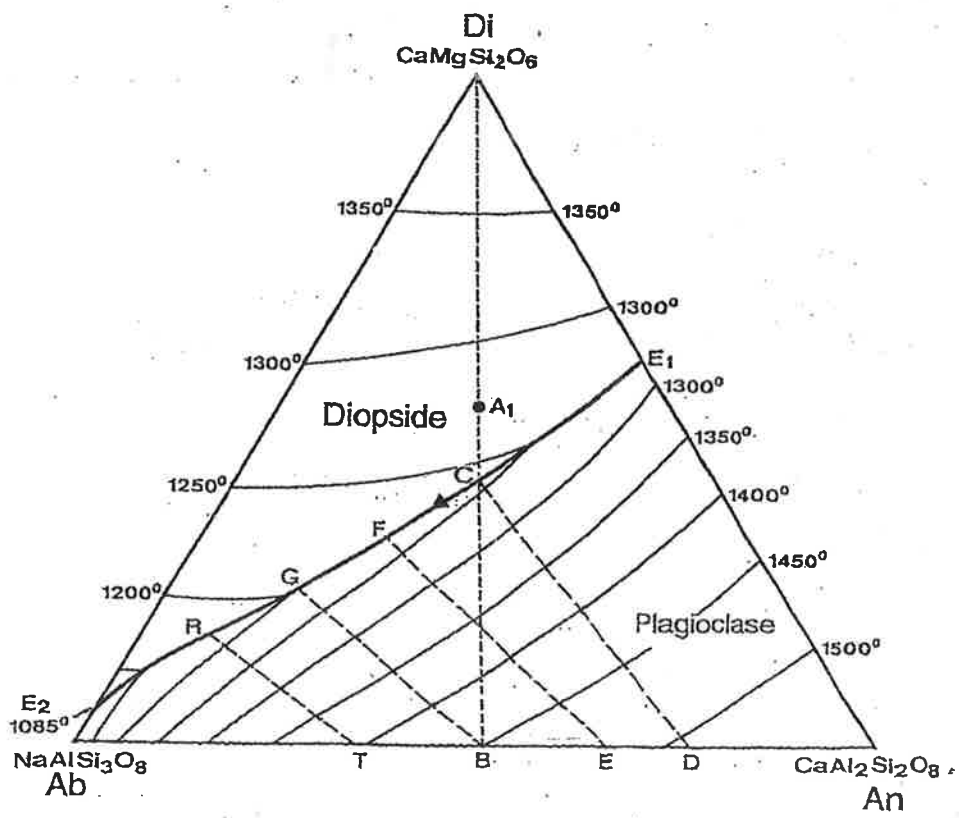
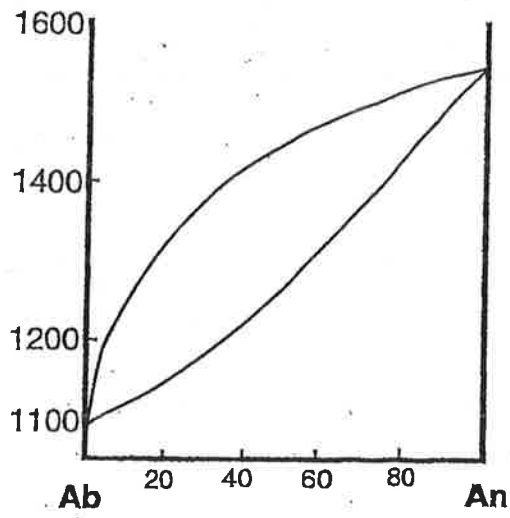
Addenda: Construction of ternary diagrams are based on experimental petrology where petrologists melt a mixtures of compositions all over the triangle and cool them down. The occurrence of crystals as well as the composition of the liquid at any given temperature are recorded so that a 3D diagram can be constructed from the experimental results.

- Practical 2 -

1. Describe the history of crystallisation the plagioclase crystal below has experienced (by using the adequate phase diagram). What was the starting composition of the liquid and what would be the final composition of the melt from which the crystal grew?
2. Consider equilibrium crystallisation of a starting composition 70% $An_{70}Ab_{30}$ and 30% Di in the system Di-An-Ab. What is the composition of the final liquid ?
3. Thin section work. See handouts of practical 1.

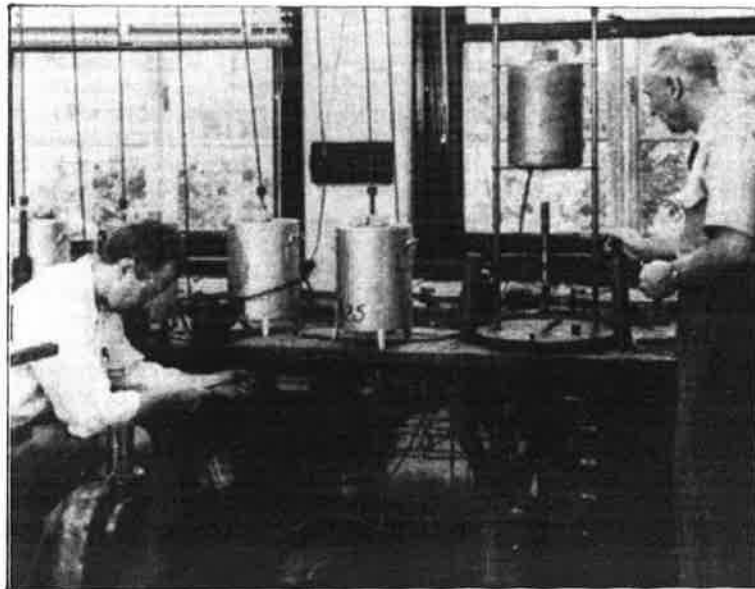
Plagioclase No 1







N.L. Bowen (left) and O.F. Tuttle (right), 1950s



*N.L. Bowen's Laboratory, Carnegie Inst.
Washington, USA*

Origin of basalt- mantle melting

In the last two lectures we discussed equilibrium crystallisation and fractional crystallisation as probably the most important mechanisms of differentiation. Also noted in lecture 1 was the influence of the source on the composition of a basalt magma. Before we discuss processes - other than fractional crystallisation - that potentially influence and modify magmas during their evolution, we should evaluate the impact of mantle melting, that produces the basaltic magmas in the first place.

Mantle melting

Composition of the mantle

The mantle consists of ultramafic rocks that are rich in olivine and pyroxene (cpx+opx) called peridotites. Peridotites also contain a small percentage of an Al compound that occurs as different phases according to pressure. At depth > 80 km this Al compound occurs as garnet, below 80km it occurs as spinel and yet shallower than ca. 20 km it occurs as plagioclase. Mantle nodules are sometimes brought up by lava and with the information on the Al-compound we can tell from what depth the nodule is derived.

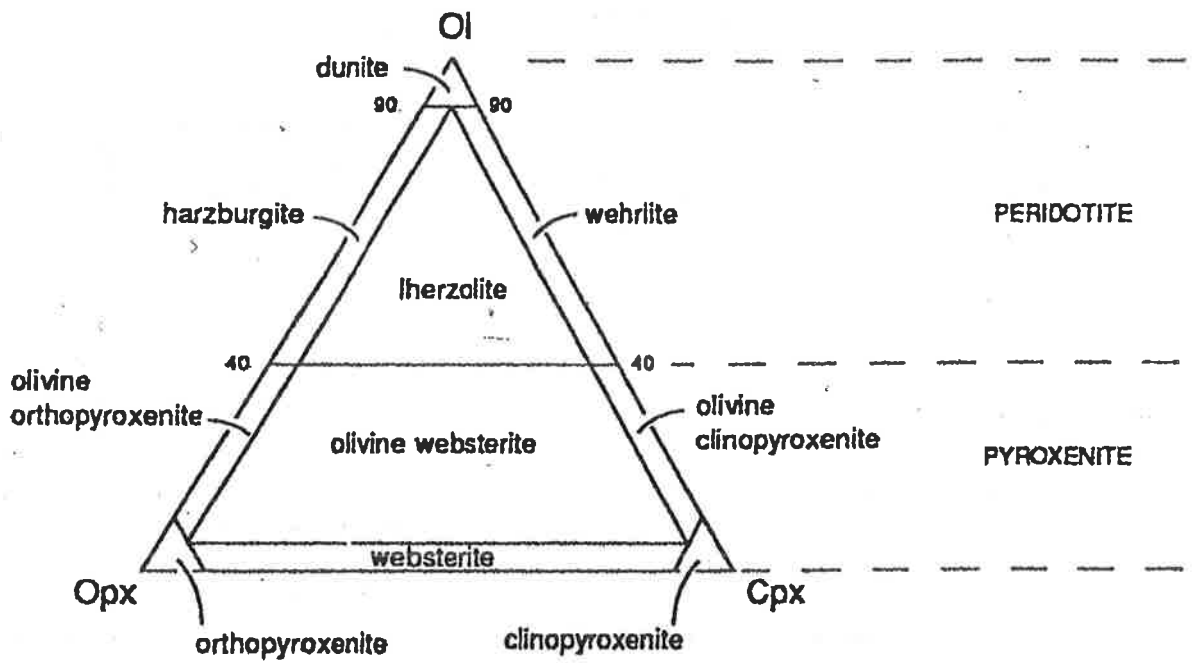
To produce basalt we have to melt the mantle peridotite and in experiments it was shown that an average basalt can be produced by melting a peridotite to ca. 30%. In the 1960's it was still believed that mantle derived basalt can be produced by melting of eclogite. However a almost 100% melting degree is required to get a basalt out of an eclogite and thus it is more likely that the mantle consists of peridotite which, when partially melted gives basalt.

When mantle rock begins to melt (normally by decompression) the first liquid to form will be a minimum melt fraction and this can segregate by a process of filter pressing to collect as a magma (leaving a residue of non-melted but depleted minerals). This collected liquid is a partial melt of the mantle, i.e. it is compositionally different to mantle rocks, but if the liquid gathers at the place where it formed it will be in equilibrium with the mantle. That means it will contain the same chemical components but in different proportions. Once the liquid moved away, T and P changes and the phase assemblage changes too.

Extraction of melt from the mantle

It has been questioned if very small degrees of mantle melting can actually produce a magma volume sufficient to be extracted from the crystal framework of a mantle lherzolite (Lac du Lherz, France). A recently proposed model by MacKenzie suggests that melt forms first at grain boundaries, preferably where three minerals come together - at triple junctions. With increasing degree of partial melting the rock melts along grain boundaries and forms a interconnected network of melt that increases the permeability of the mantle rock to an extent that melt can move. Since the newly formed melt is specifically less dense (by ca. 10%) it will have the tendency to rise. If the rock comes under additional pressure (e.g. mantle convection) the melt may even be squeezed out.

Depending on the degree of melting the partial melt will have a different composition. The very first melt to form and the melt produced during low degrees of partial melting is

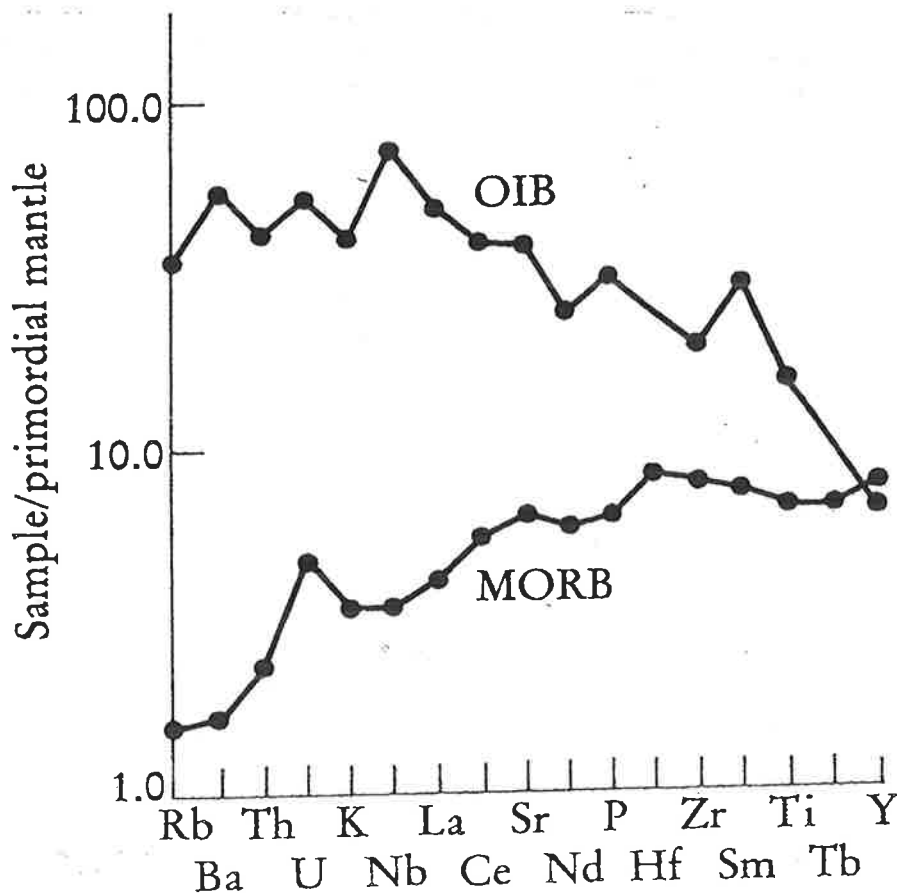


Peridotite subtypes → increasing melt extraction !

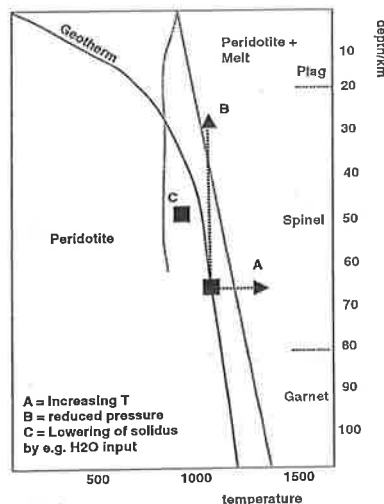
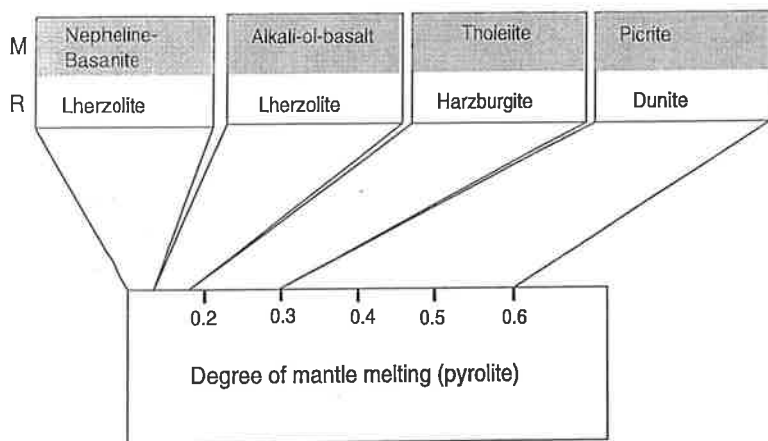
	Olivine	Enstatite (opx)	Diopside(cpx)	Al- compound
Lherzolite	60-70%	20%	5-10%	5-10%
Harzburgite	70-80%	20%	0-5%	5%
Dunite	95%	-----	-----	0-5%

Mineralogical differences between tholeiitic and alkali olivine basalts

	ALKALI OL. BASALT	THOLEIITIC BASALT
<i>Olivine</i>	in groundmass and as phenocrysts, if present phenocrysts are commonly zoned	if present, only as phenocrysts phenocrysts are unzoned
<i>Orthopyroxene</i>	not present	may form reaction rims on olivine phenocrysts
<i>Augite</i>	the only pyroxene present. in section are brownish-purplish (<i>faint</i>)	may be accompanied by opx and/or pigeonite. Augite is colourless in section. Exsolution texture may occur
<i>Alkali feldspar</i>	may occur as narrow rim on plag. groundmass crystals. (but difficult to see)	no alkali feldspar rims on plag.
<i>Analcite</i>	may be present in spaces between plags in groundmass	not present
<i>Glass</i>	very uncommon	intersertal patches may occur, or be replaced by quartz + alkali feldspar micrographic intergrowth

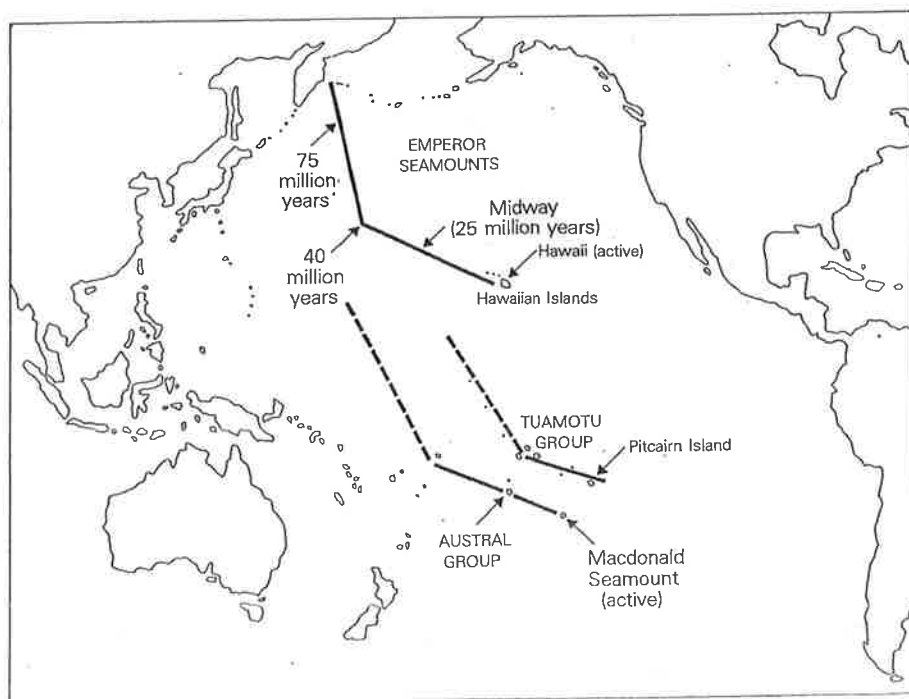


enriched in alkali and LILE relative to a melt produced during large degrees of partial melting that is e.g. an average tholeiitic basalt. Therefore, small degrees of partial melting leave behind a residual rock that lost only several percent of its original composition and is still richer in e.g. LILE elements than the residue of large degrees of partial melting where the residue is strongly depleted in e.g. LILE.



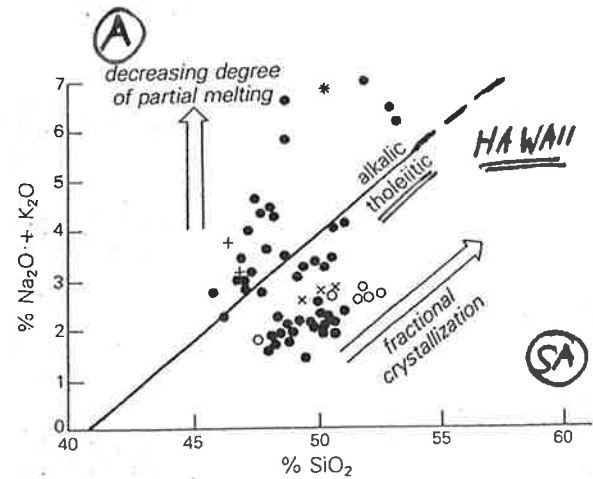
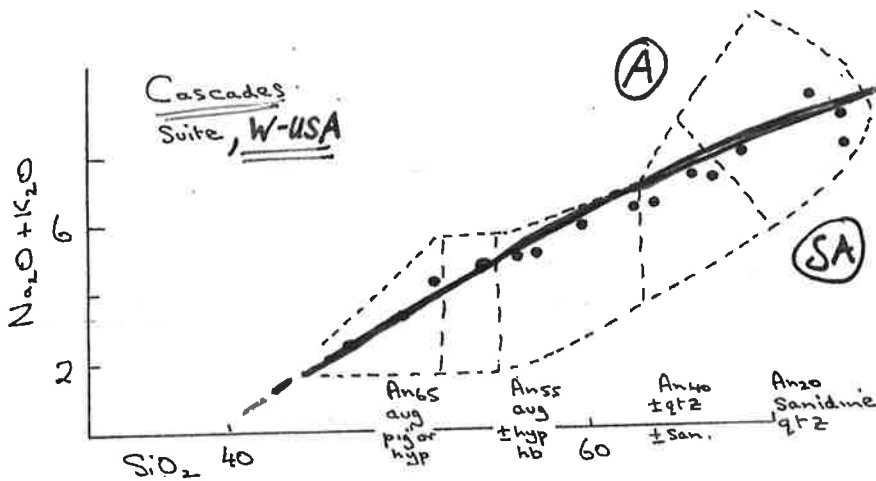
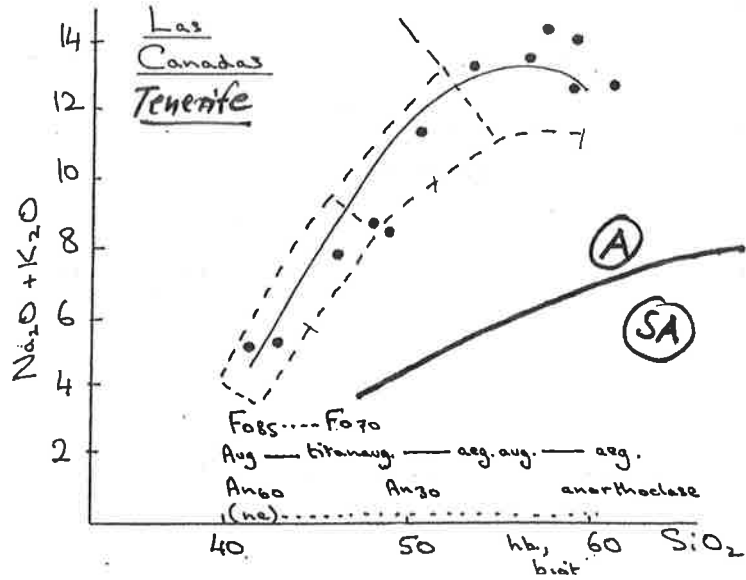
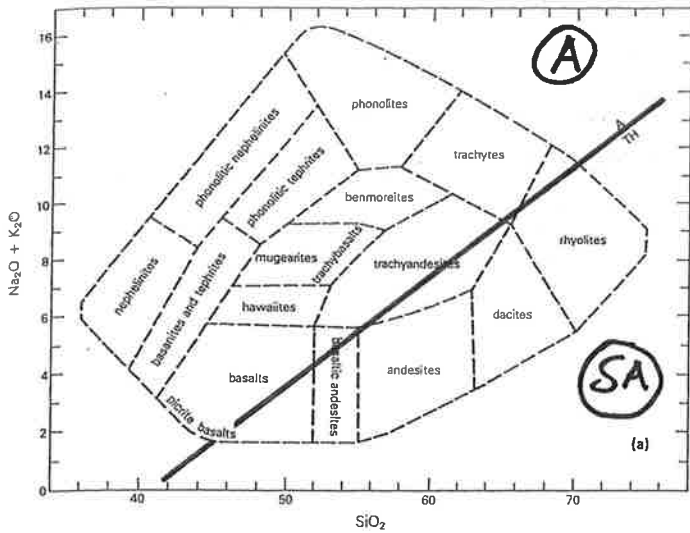
Whereas ocean islands often show alkaline rocks that probably formed by low degree of partial melting, MOR basalts are substantially less alkaline (subalkaline or tholeiitic) and are likely to have formed from large degree of partial mantle melting. MORBs are thus depleted relative to ocean island basalts. However, low degree of partial melting of a rock that was previously deprived in a melt will also produce a sub-alkaline suite although no large degrees of melting are required.

For hot-spot volcanoes we commonly assume mantle melting by a temperature increase coupled with reducing the pressure. In MORB settings decompressional melting is commonly assumed and in arc settings a shift of the solidus due to H₂O increase is made responsible for melting of mantle peridotite.



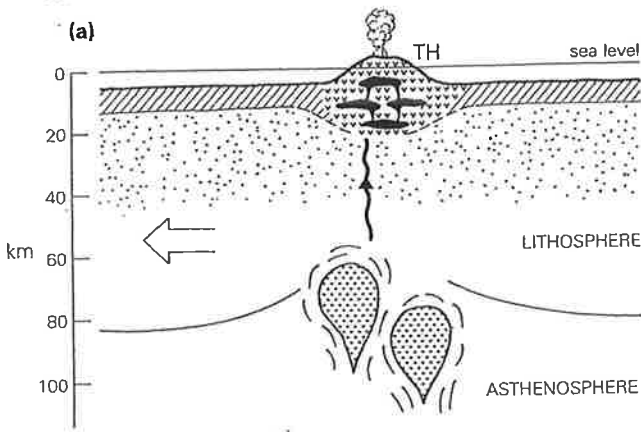
Distribution of linear volcanic island chains in the Pacific Ocean. Dashed lines indicate linear seamount chains extending to the north from the Austral and Tuamotu groups, subparallel to the Emperor seamount chain, the age progression of which is not adequately documented (after Burke & Wilson 1976, p. 34).

TAS-DIAGRAM



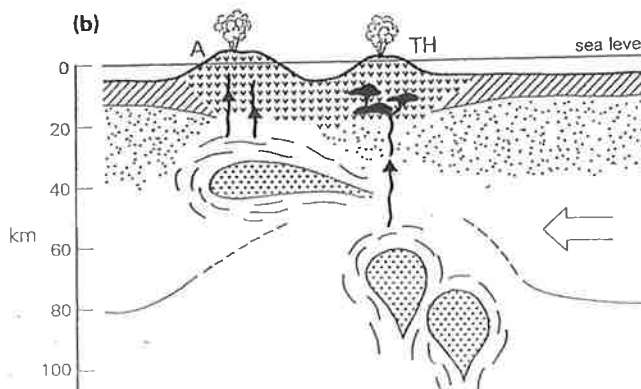
Data sources

- Kohala
 - + Hualalai
 - * Mauna Kea
 - x Kilauea
 - Mauna Loa
- Feigenson et al. (1983)
Basaltic Volcanism Study Project (1981)



Key

- volcanic and plutonic rocks of the oceanic island crust
- oceanic crustal layer (MORB)
- depleted asthenosphere - source of N-type MORB
- depleted N-type source mantle - further depleted by magma extraction at the mid-oceanic ridge crest
- enriched plume component mantle
- partially melted asthenosphere in the envelope of the rising diapir
- high-level magma storage reservoirs



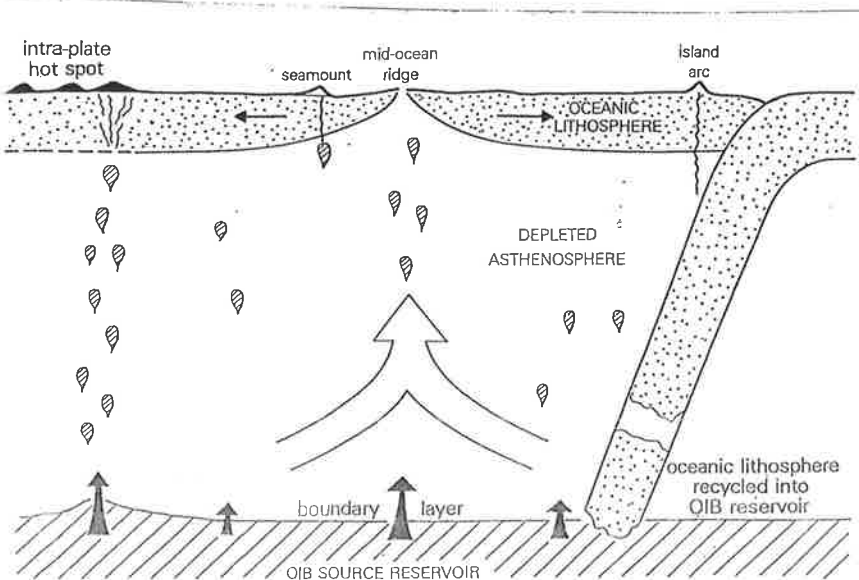
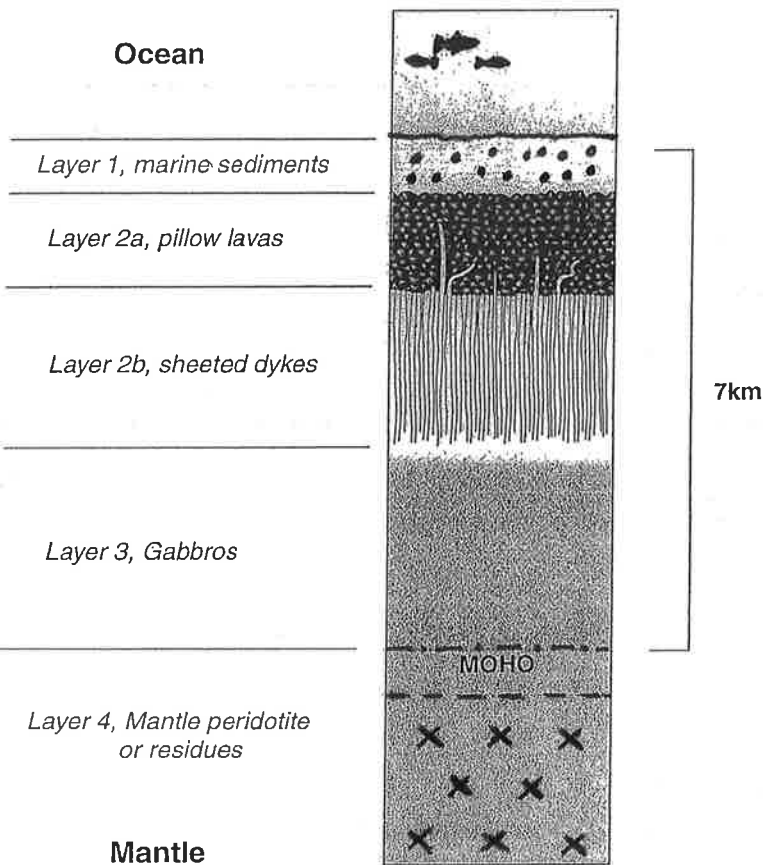
arrows show the relative vector of motion in the lithosphere with respect to the underlying asthenosphere

Hawaii, temporal evolution from alkaline to tholeiitic, back to alkaline!

Oceanic crust

Melt formed in the mantle rises up and collects in shallow magma chambers. The highest magma production worldwide is at Mid-Ocean Ridges, about 95% of all volcanism takes place there. Large parts of the major magma chamber systems solidify below the surface and form gabbro. From the reservoir that feeds the gabbros and more commonly from the residual liquid in the gabbros dykes are feed that shoot of towards the surface. Where they make it to the ocean floor, they erupt submarine lavas with characteristic pillow structures. This sequence of events is reflected in the typical profile through ocean crust. Gabbro is overlain by sheeted dykes (dykes intruded into dykes which are, in turn, intruded by dykes). The sheeted dyke complex is overlain by pillow lavas often intermixed or overlain by marine sediments. The gabbros that form the base of the oceanic crust are underlain by mantle rocks (peridotites, lherzolites, harzburgites and dunites). The transition between the gabbros and the mantle rocks represents the Moho and is located at only 6-7km depth beneath the ocean floor.

Section through Oceanic Crust



Further differentiation mechanisms

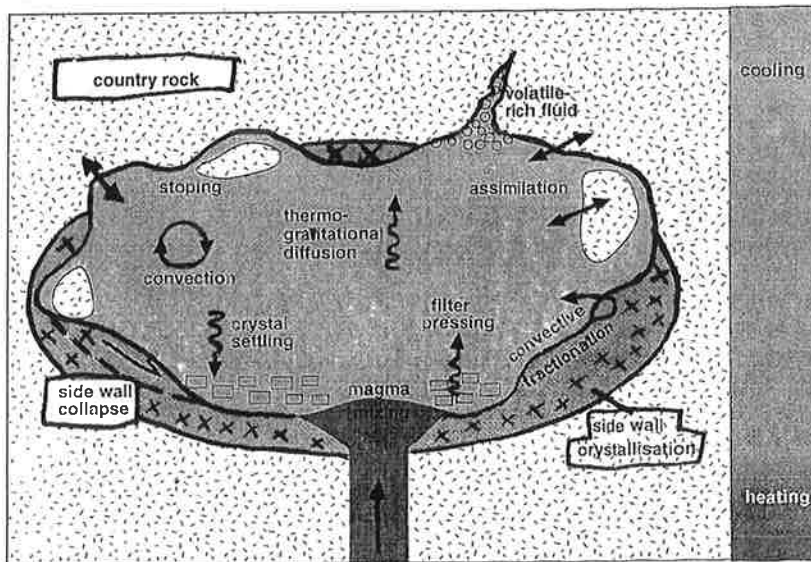
After the initial processes which produce the melt from the source region, there are various different mechanisms. Broadly speaking there are two types, those concerned with differentiation in the liquid state (liquid immiscibility, thermogravitational diffusion, magma mixing) and those concerned with crystal-liquid fractionation (fractional crystallisation, assimilation).

Fractional Crystallisation in a static magma chamber.

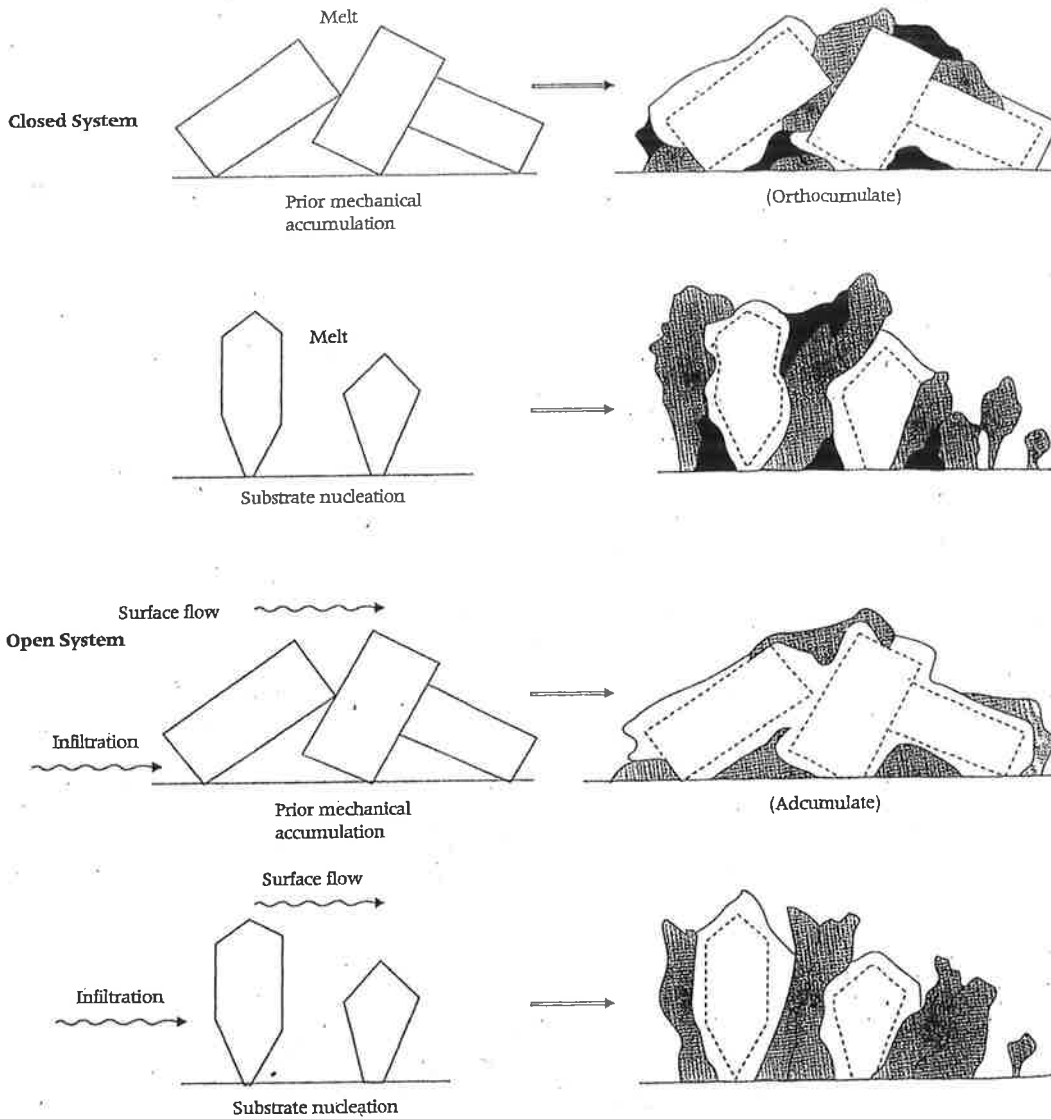
A magma moving up through the mantle and crust will be subjected to progressively lower pressure - the temperatures of crystallisation of individual minerals change with pressure, and different mineral phases will appear on the liquidus at different pressures. Again crystal fractionation is the most important mechanism, and an essential feature of producing different rock types is the physical separation of crystals and liquid.

The classic model (largely evolved from work in Skaergaard by Wager and Deer), was of crystals sinking through the liquid because they are of greater density, to form an accumulation on the floor of the magma chamber; many such cumulates have been recognised in gabbro plutons. Modern studies of fluid dynamics now show that this process is possibly not so common, nor so simple. There is a separation but more usually by convective fractionation driven by compositional change (the residual liquid being lighter than the primary magma) or by thermally induced convective currents. The undoubted bedding characteristics seen in many cumulates appears to be at least partly produced by the slumping of crystals accumulated on the chamber's walls and roof.

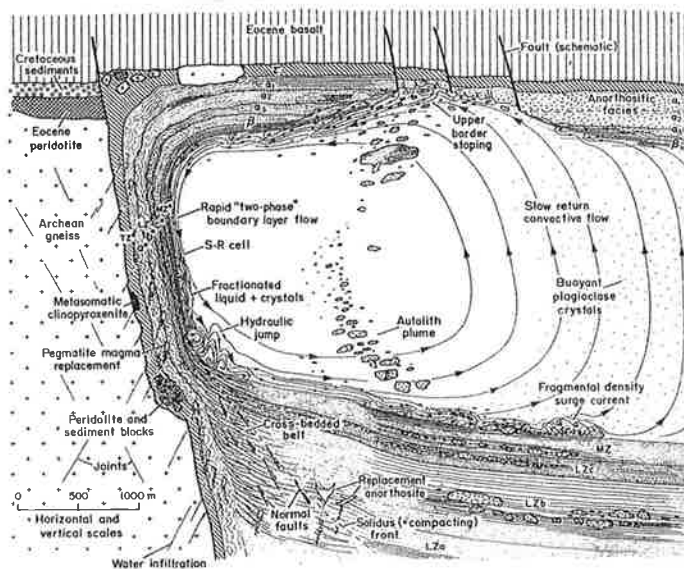
There are other possibilities for splitting the primary magma composition within the magma chamber. As the liquid evolves, it becomes more volatile rich (volatiles have a low Distribution Coefficient). Eventually the magma will become saturated in the principal volatile, water, and a hydrous phase will separate from the silicate liquid phase.



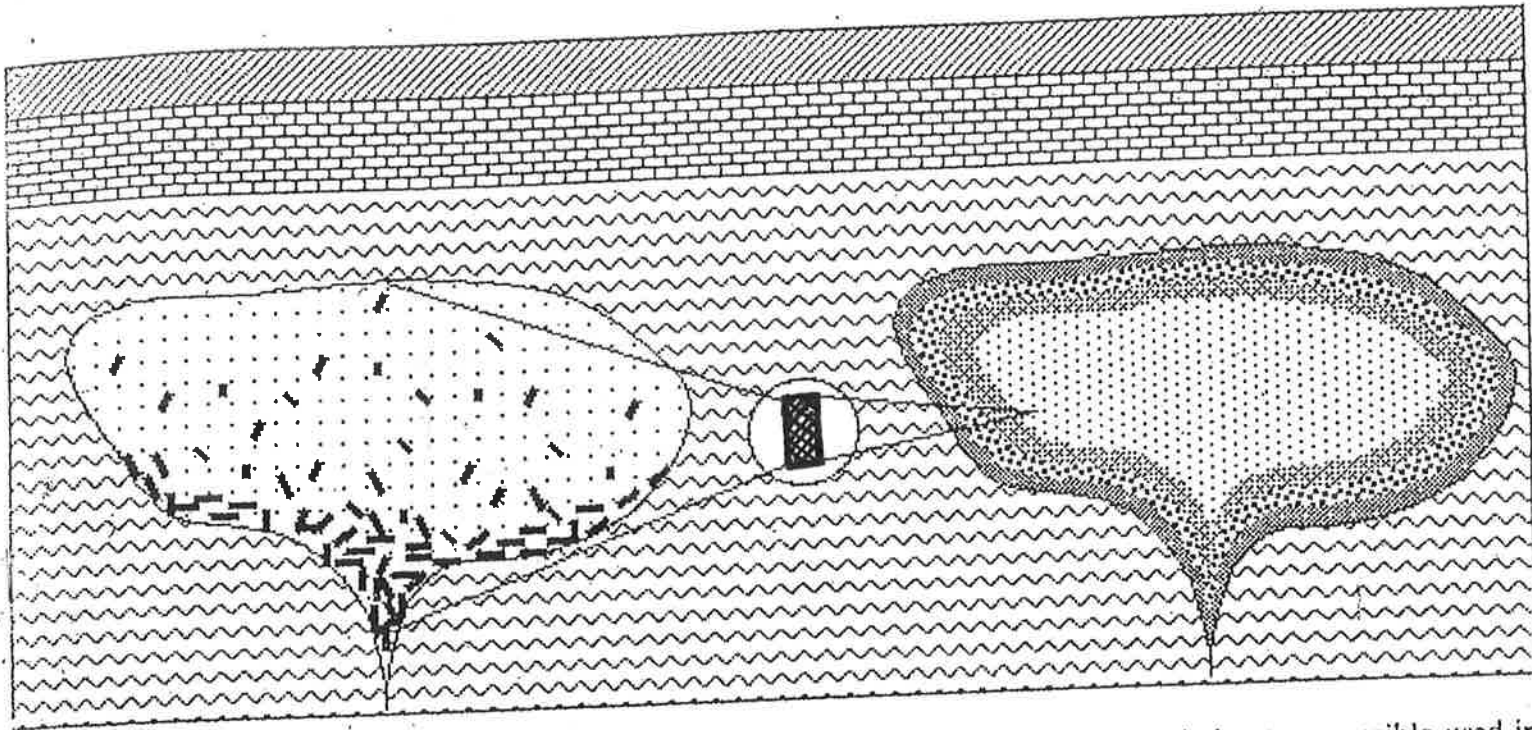
Idealised crustal magma chamber (no scale)



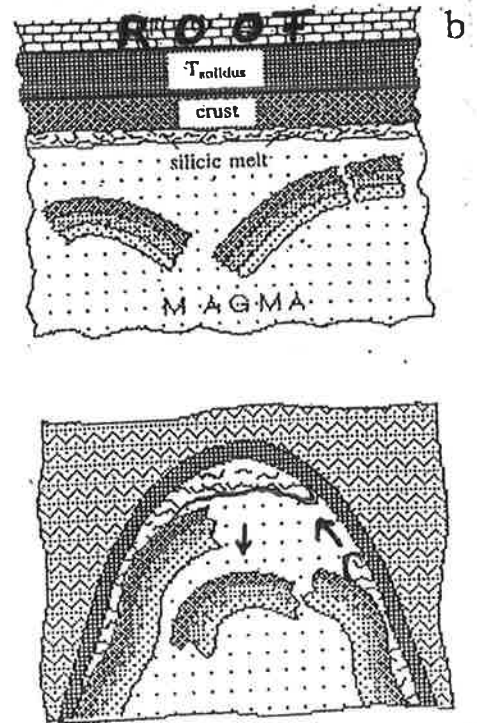
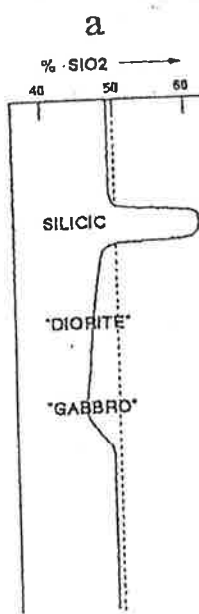
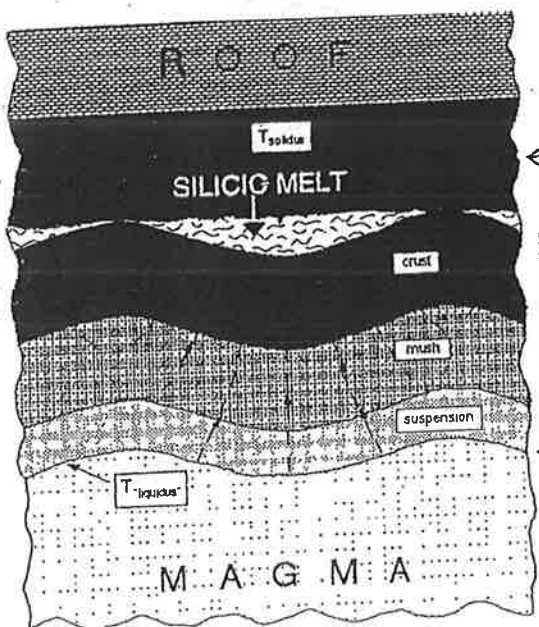
Representation of mechanical accumulation compared with chemical accumulation of mineral phases in magmatic rock. Fractionation occurs in closed systems, forming three mineral-phase orthocumulates in mechanical accumulations. Only two mineral phases form in open systems because of melt resupply.



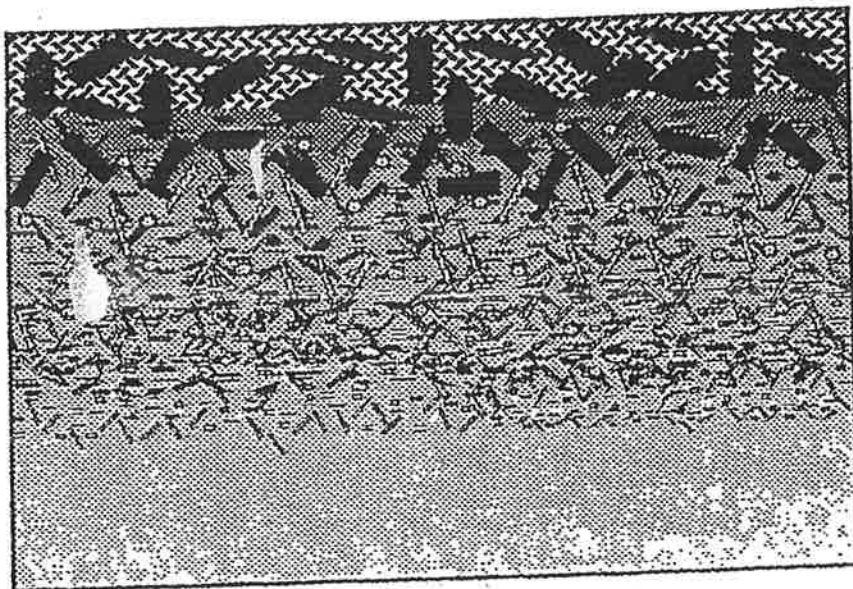
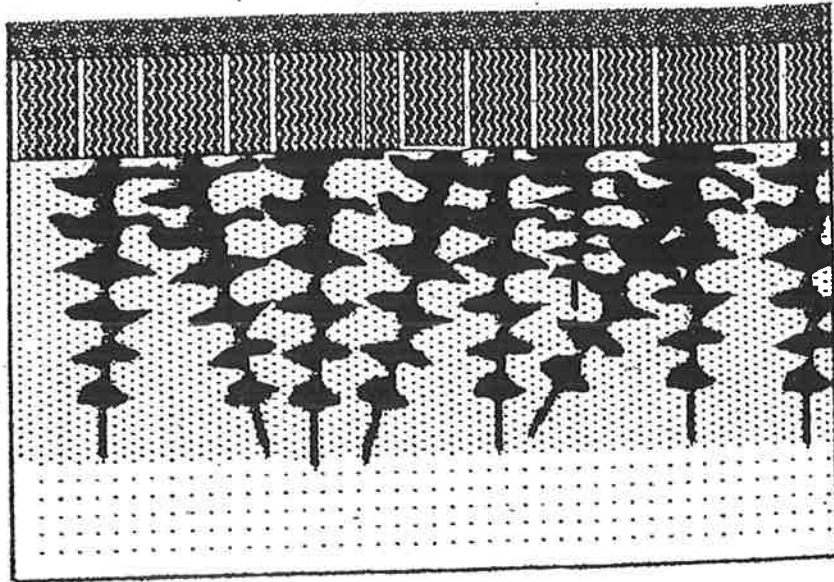
Schematic synthesis of magmatic processes in the western part of the magma chamber of the Skaergaard Intrusion, East Greenland, during the Middle Zone stage of differentiation. From *Geological Society of America Bulletin*, v. 110, pp. 1398-1447. Irvine, T. N., Andersen, J. C. Ø., and Brooks, C. K. (1998). Reproduced with permission of the publisher, The Geological Society of America, Boulder, Colorado, USA. Copyright (c) 1998, The Geological Society of America, Inc. (GSA).



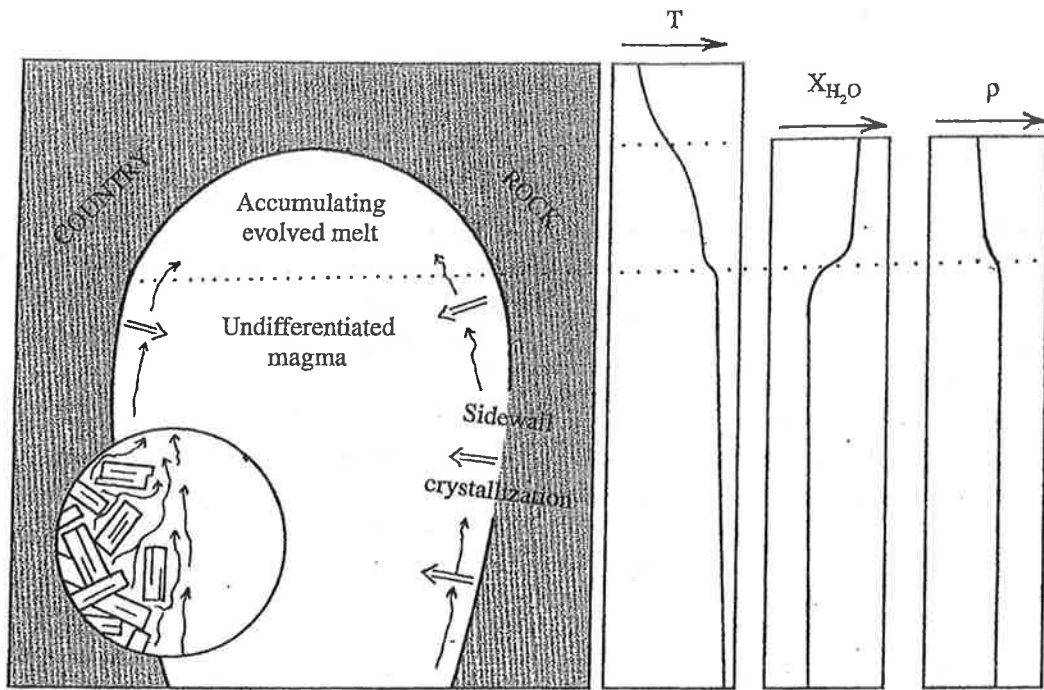
A schematic illustration of two ideas of magma chambers and their conceptual relation to a crucible used in experimental studies of phase equilibria (inset). The chamber on the left crystallizes throughout and deposits crystals on the floor; it cools mainly from the roof and crystallizes from the floor up. The chamber on the right is surrounded by mushy solidification fronts, cooling and crystallization are approximately evenly distributed about the margins of the body; thick piles of crystals on the floor, should they arise, come from phenocrysts injected with the magma itself.



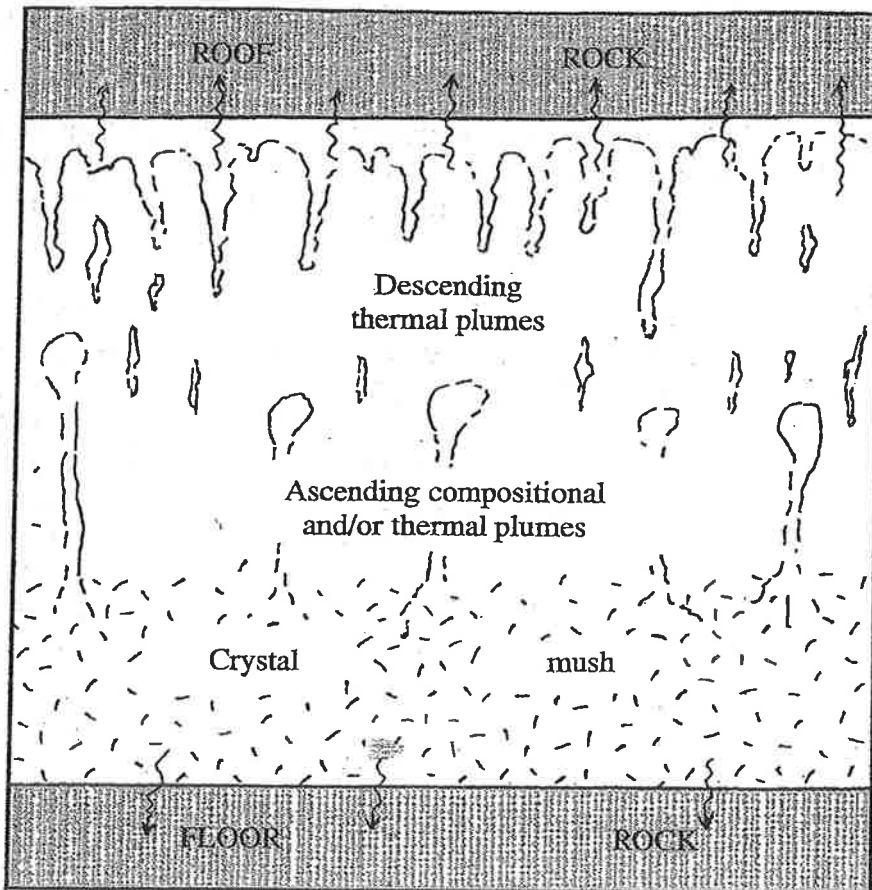
Solidification front instability (SFI) whereby siliceous interstitial melt is segregated into lenses through the sagging or internal tearing of the upper solidification front under the influence of gravity. The ensuing silicic segregations are chemically and spatially separated from the underlying magma, and new melt entering the leading edge of the front makes this region relatively more primitive. (b). Later stages in the solidification front instability where the front may wholly detach from the roof, freeing the still molten silicic segregations to collect along the roof (upper). When this process occurs along a sloping roof, the silicic melt may migrate upwards and form a separate magma.



Two examples of solidification fronts. The upper example is a dendrite front common in singly saturated aqueous and metal alloy solutions. The lower example is dominated by many small crystals and is typical of multiply-saturated magmas. Melt can flow freely in and amongst the crystals of the dendrite front but not in the magmatic front.



Thermochemical convection in a crystallizing bottle-shaped calc-alkaline magma chamber. Pronounced compositional stratification can be produced in an initially homogeneous magma chamber. **Sidewall crystallization** (double-line arrows) yields less dense, silica- and water-enriched residual melt that can separate from the associated mush of crystals adhering to the chamber wall (inset circular diagram at enlarged scale). This melt buoys upward and accumulates in a gravitationally stable, growing cap zone. Schematic properties of the stratified chamber are shown in three graphs on right. Continued heat loss from the magma body allows inward advance of the crystallizing wall so that the final solidified pluton can be concentrically and vertically zoned in composition. Explosively erupted silicic magmas are derived from the upper volatile-rich parts of such stratified chambers.



Thermochemical convection in a flat slab of crystallizing magma. Compare Figure 8.21. In contrast to magma unmixing in a bottle-shaped chamber (Figure 8.22), the magma in this slab tends to be homogenized and mixed by the descending and ascending plumes.

Liquid Immiscibility:

If the separation takes place at pressures above the "critical pressure" for water vapour, then the new phase will be a liquid, and the remaining components in the magma will have to partition and distribute themselves between the two immiscible fluids. Such a fractionation process can produce a silicate liquid from which pegmatites crystallise, and a hydrous fluid from which hydrothermal minerals crystallise.

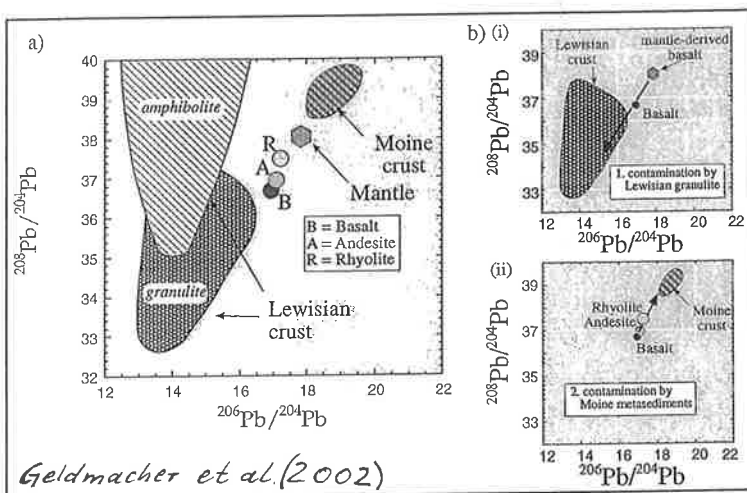
At some alkaline volcanoes a very weird type of magma erupts termed carbonatite. This magma contains largely carbonate minerals and was previously considered as molten limestone. Recent research however showed that carbonatite magmas are true mantle magmas forming from CaO and $\text{CO}_2 \rightarrow \text{CaCO}_3$ and separate from silicic magmas due to immiscibility. Type examples of carbonatite volcanism are Oldoinyo Lengai volcano in Kenya and the Kaiserstuhl volcano in SW Germany (both associated with continental rifts). Very small occurrences of carbonatite are also found in the Canary Islands.

Another occurrence of immiscibility happens much earlier in magmatic evolution and that is the separation of sulphides from ultramafic melts. This is then seen as sulphide droplets that are found in mafic rocks (chalcophile vs. lithophile element affinities).

Assimilation

Interaction with wall/country rocks is particularly effective in high-level chambers emplaced in crustal rocks composed largely of quartz and feldspar. At such shallow depths the wall rocks tend to be brittle, easily fractured, and stoped off into the magma. The minimum-melt fraction of such stoped blocks will join the magma, making it somewhat richer in those components, whilst the unmelted residue will be dispersed as individual crystals or clumps of crystals through the magma (xenocrysts or xenoliths). This is particularly common in granites and rhyolites. Well documented example of crustal assimilation are the centres of the British Tertiary Province where ancient basement was incorporated into the ascending magmas allowing

to trace back the crustal domains the magma passed through.



assimilated crustal material (O'Hara, 1998). Moreover basalts with isotope ratios that differ from average mantle compositions are also very likely to have incorporated a fair amount of crust. This phenomenon is meanwhile also documented for Gran Canaria where the early shield basalts seem to have assimilated several percent of oceanic crust and marine sediments.

Magma Mixing

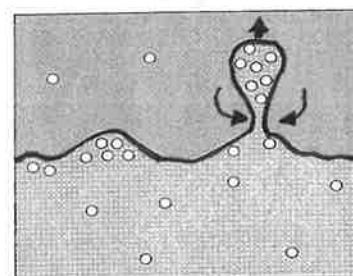
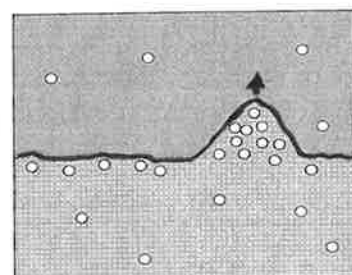
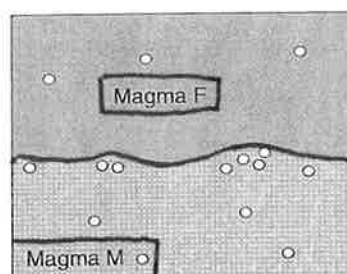
Although magma mixing does not by definition differentiate a melt it may do so when a mafic and a felsic melt mixes. Then the output is a hybrid. This is compositionally more evolved than the mafic end member but less evolved than the felsic end member. Magma mixing is a very common phenomenon and we will explore this in some more detail:

Magma mixing produces only in very few cases complete hybrids. Often the mixing process is incomplete, i.e. bits of one magma enclosed in another. In granite petrology this is referred to as enclaves or inclusions. For example mafic enclaves in granite.

When mafic magma enters a shallow-level felsic reservoir, the mafic magma is a) hotter, b) denser and c) less viscous. The result is spreading of the basic magma along the chamber bottom. The first mafic magma that comes in contact with the felsic melt will chill against the cooler, less dense liquid which produces chilled enclaves often also referred to as microgranular enclaves. The magma that resides at the chamber bottom will also cool down and possibly partially crystallise. The felsic magma above will be superheated which reduces the viscosity of the felsic magma and ultimately the mafic and the felsic melt will thermally equilibrate. This is a fairly rapid process and may take less than a week even in large magma chambers. As soon as the two magmas approach thermal equilibrium chemical exchange will occur. This starts with trace elements and isotopes (similar to assimilation) and later follows major element exchange.

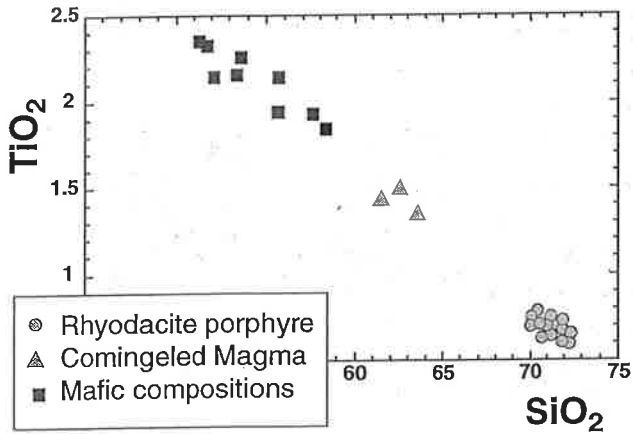
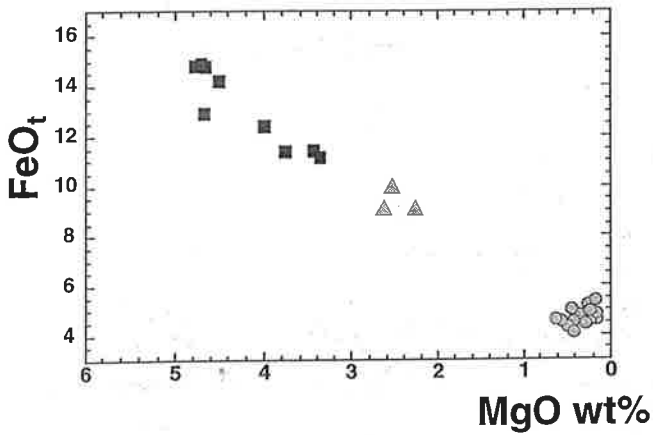
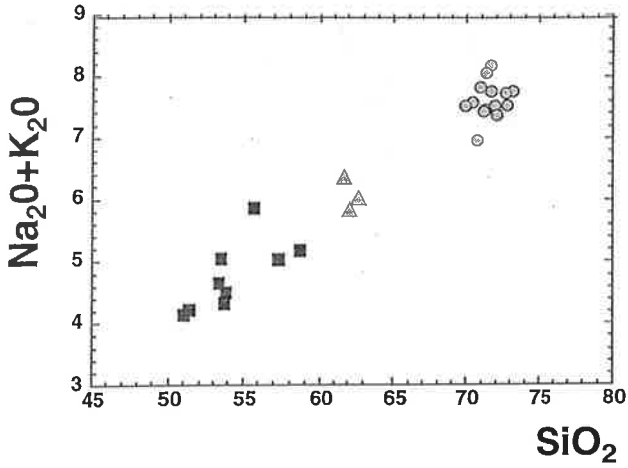
Due to cooling of the basalt a volatile enrichment may be achieved that leads to vesiculation within the upper parts of the mafic magma. Vesiculation reduces the specific density of the mafic magma and blobs of it may rise up into the felsic part of the chamber that is now reduced in viscosity due to the reheating event and may distribute the blobs in the entire chamber by convective motion (Eichelberger 1980). The end result is theoretically a hybrid formed from blending the two magmas, but the common occurrence of mafic enclaves in granites and rhyolites testifies the process to be generally very ineffective. However, chemical interaction between the magmas can often be determined on the basis of mineralogy, and/or geochemistry.

Formation of Mafic enclaves



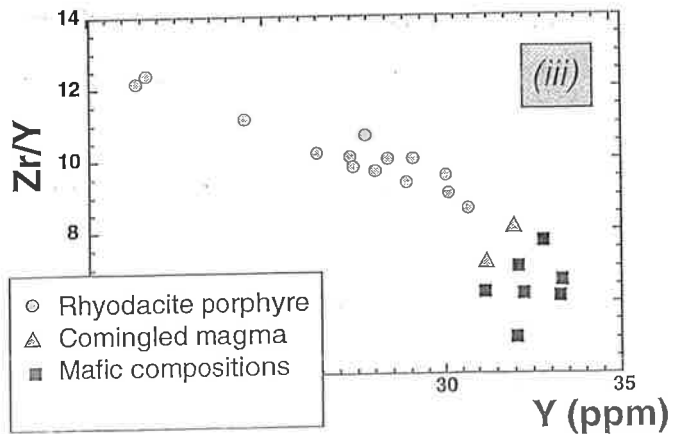
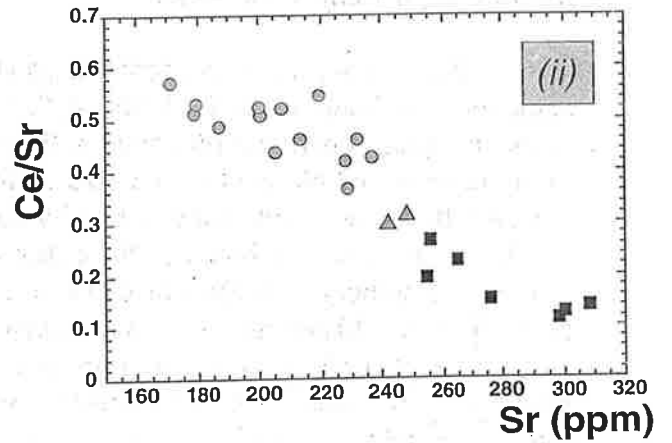
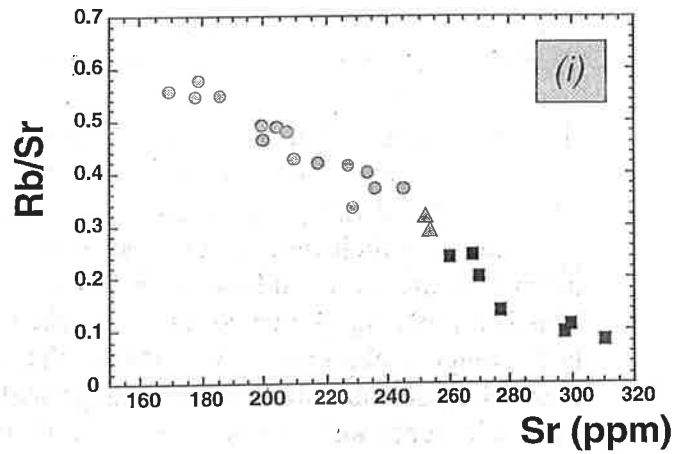
Eichelberger, 1980

Major Elements



○ Rhyodacite porphyre
 ▲ Comingled Magma
 ■ Mafic compositions

TRACE ELEMENTS



○ Rhyodacite porphyre
 ▲ Comingled magma
 ■ Mafic compositions

Examples taken from Trol et al (2004).

Volume 150 Celebration Paper

Magmatic differentiation

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Abstract: During the past 150 years, a wide range of processes have been invoked to explain the mechanism by which magmas differentiate. These may be divided into those which operate essentially in the liquid state, such as liquid immiscibility and thermogravitational diffusion, and those which involve some form of crystal–liquid fractionation. It is now generally accepted that the latter are the most important. Many of the models developed during the past twenty years to explain *magmatic differentiation* have their roots in ideas first proposed in the early years of this century. This review presents some of the historical background to the subject and attempts to summarize some of the more recent developments.

Alfred Harker's perceptive study of in-situ crystallization within a high-level intrusion (Carrock Fell in the English Lake District), published in volume 50 of the *Quarterly Journal of the Geological Society* in 1893, clearly laid the foundations for many modern theories. In 1900 he introduced the oxide–oxide variation diagram, which is still widely used to depict the geochemical variations within suites of cogenetic igneous rocks. Studies of phase equilibria in synthetic and natural systems by Bowen and his contemporaries, during the 1920s and 30s, provided the theoretical background needed to understand the complex processes involved in fractional crystallization of magmas. In the past decade mathematical modelling has allowed a more quantitative approach to the problem.

In 1909, in his seminal publication *The Natural History of Igneous Rocks*, Harker commented that 'the most fundamental problem in modern petrology (is) that of the origin of the great diversity of rock types actually found'. Eighty one years later Nielsen (1990) was to note that 'one of the primary goals of igneous petrology is the definition and evaluation of the roles of the processes responsible for chemical differentiation'. In the past century an immense number of publications have appeared on the subject of magmatic differentiation, a brief, but by no means comprehensive review of which will be presented here. Have we actually made any real progress? Of course the answer to this must be 'yes'. Have we built on the work of our predecessors? To this the answer must be 'sometimes'. In the past decade there has been an ever-increasing tendency to dismiss anything published in the preceding decade as 'out of date', let alone anything produced in the early part of this century. Clearly the present generation of petrologists cannot read everything previously published on a particular topic. However by dismissing older publications there is a grave danger that inadvertently we may 're-invent the wheel'. Reading the classic works of Harker (1909) and Bowen (1928) does not leave one feeling trapped in a time warp; rather with an impression that these were men light years ahead of their time. What kind of progress would they have made had they had access to the vast geochemical databases presently available? This of course is entirely philosophical. However, it should serve to remind us all to conduct thorough literature searches as a precursor to new research projects.

A wide range of processes have, over the past 150 years, been advocated as potential causes of magmatic differentiation (Fig. 1). As we shall see in subsequent sections some (e.g. thermogravitational diffusion, liquid immiscibility, assimilation) have gone in and out of fashion,

while others (e.g. fractional crystallization) appear to have stood the test of time. Other processes, such as gaseous transfer, are probably only significant during the latest stages of magmatic differentiation and will not be considered further here.

Early ideas about the causes of magmatic differentiation

By the turn of the century, it was already well established (Harker 1909) that the great diversity of igneous rocks and the compositional variation within many individual rock bodies was mainly attributable to processes of differentiation. This had been a common basis for discussion for more than 60 years, since Darwin's classic 1844 publication *Geological observations on the volcanic islands*. . . Harker's ideas about magmatic differentiation were profoundly influenced by his studies of the Carrock Fell gabbroic intrusion in the English Lake District, reported in 1894 in volume 50 of the *Quarterly Journal of the Geological Society*. He was clearly aware of two different types of differentiation: the in-situ differentiation of a single magmatic body; and the differentiation, prior to intrusion or extrusion, responsible for the production of cogenetic suites of intrusives or extrusives. In the latter case Harker (1909) reasoned that, as we only see the finished product, we have to speculate about the processes involved. However, in the in-situ case both the stages of the variation and to some extent the nature of the processes themselves may be studied directly. The significance of this was to gain fundamental importance, more than thirty years later, in studies of the great layered mafic intrusions (e.g. Wager & Deer 1939). Harker, however, was uncertain as to how conclusions based on a study of in-situ differentiation could be applied to the more obscure question of the

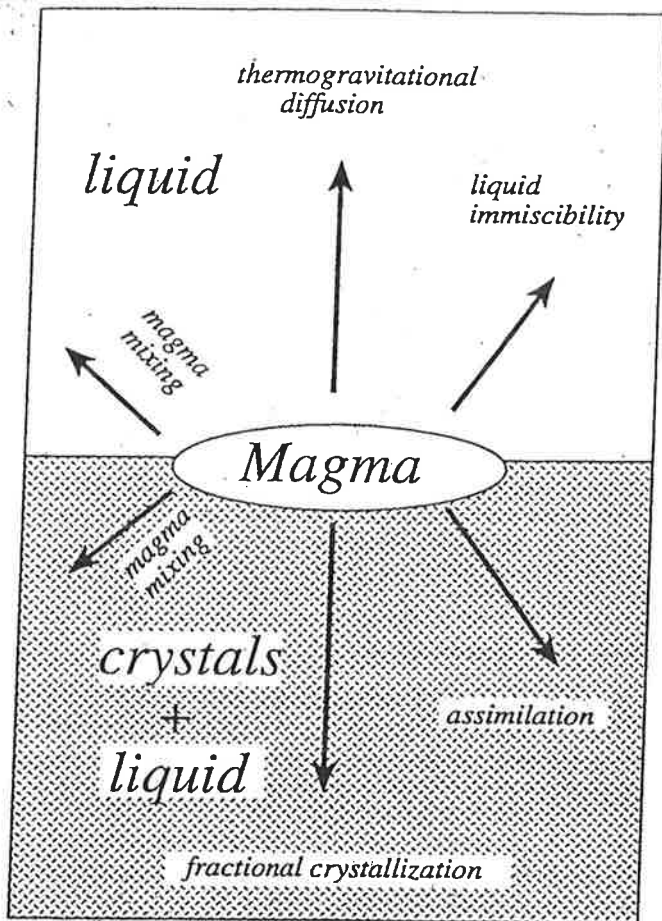


Fig. 1. A summary of the major processes responsible for magmatic differentiation.

differentiation of magmas in an unknown deep-seated magma reservoir. It may be argued that this is still as true today as it was in 1909!

In the early part of this century ideas about magmatic differentiation were divided between processes of differentiation in the liquid state and those of crystal-liquid differentiation or *fractional crystallization* (Fig. 1).

Differentiation in the liquid state

As part of his studies of the Carrock Fell intrusion, Harker (1894) discussed the possibility that gravitational stratification of denser components might occur in magma bodies, but concluded that such a process was incapable of explaining the symmetrical nature of the compositional zonation which he observed in the gabbro. He also considered (and dismissed) the possibility for differentiation in the liquid state due to temperature differences between the central and marginal parts of the intrusion (the *Soret effect*). By 1909, he had extended his ideas to much larger scale phenomena, envisaging the possibility of large crustal magma chambers, in which denser (more mafic) magma underlay less dense (more acidic) magma, from which simultaneous eruptions of contrasting magma compositions might emanate. Models involving such stratified magma bodies were to come back in vogue more than seventy years later (e.g. Huppert & Sparks 1980). Silicate liquid

immiscibility was widely discussed as a potential liquid state differentiation mechanism at this time (e.g. Harker 1909; Bowen 1928) but was not considered to be particularly important. Magma mixing was also viewed as a significant process in contributing to the chemical diversity of magmatic systems, although, as noted by Harker (1909) it is actually a 'reverse differentiation mechanism' in that two different magma compositions become mixed to form one.

Crystal-liquid fractionation

Whilst agreeing that liquid state differentiation mechanisms could generate localized compositional variations within magma bodies, both Harker (1894, 1909) and Bowen (1928) strongly favoured processes of crystal-liquid fractionation as the main cause of magmatic differentiation. Bowen noted that 'differentiation in a crystallising mass may be brought about in two ways: through the localisation of the crystallisation of a certain phase or phases and through the relative movement of crystals and liquid'. Eighty five years later we are still debating about the precise mechanism which this occurs!

Harker (1894, 1909) explained his ideas about the mechanism of fractional crystallization in the context of progressive crystallization in a dyke. He envisaged that as a result of crystallization at the margins of the intrusion the remaining magma would become progressively depleted in those components incorporated into the solid phase, as long as diffusion could keep pace with crystallization. Clearly this model depends very heavily on the ability of components to diffuse through a silicate melt, which we now know is actually a very slow process (e.g. Hofmann 1980). Indeed as early as 1928, Bowen argued that the rates of diffusion are too slow to have any significant effect in producing compositional gradients in silicate melts. Harker, however, believed that diffusion would be important in the early stages of crystallization but would decrease with falling temperature as the residual magma became more viscous. He (Harker 1909) placed great importance on crystallization in the marginal zones (walls, roof) of magma chambers as a major mechanism for differentiation. Becker (1897) first introduced the term *fractional crystallization* to describe this mechanism of igneous differentiation, but, unlike Harker, dismissed diffusion in favour of transportation of components in the liquid phase by convection currents. Seventy five years later Sparks *et al.* (1984) were to reach a similar conclusion, though based on rather different reasoning, using the term *convective fractionation*.

The gravitational settling of minerals in a fluid magma had already been proposed by Darwin (1844) as a principal cause for magmatic differentiation, based upon his observations of phenocryst accumulations in the bases of lava flows. The viability of the process was to remain a matter of debate for the next 150 years! Harker (1909) realized that the viscosity of a magma might be sufficient to overcome the natural tendency of crystals to sink by virtue of their greater density and as a consequence did not regard crystal settling as a particularly important mechanism of differentiation. However, he was well aware of the time element which meant that while crystal settling to the base of a small sill might not be very important, it could be in a large crustal magma chamber cooling very slowly.

Harker had studied the layered mafic-ultramafic igneous complex of the island of Rhum in the Tertiary volcanic

province of NW Scotland (Harker 1908, 1909) but did not recognize the cumulate origin of these rocks and thought that the banding was due to repeated intrusion combined with deformation. Had he been aware of the spectacular evidence for crystal accumulation, which would be provided by the layered rocks of the Skaergaard intrusion, Greenland (not to be discovered by Wager and co-workers until thirty years later), might he have concluded otherwise? It is interesting to note in this context how our ideas can sometimes come full circle. Eighty years after Harker's original study, Bedard *et al.* (1988) concluded that his ideas about the origin of layering in the Eastern Layered Series of Rhum were broadly correct, overturning the models of the previous 25 years, which proposed crystal accumulation on the floor of a periodically refluxed magma chamber (e.g. Wager & Brown 1968).

By the early 1930s (Daly 1933) ideas that layering in some plutonic bodies was the product of gravitational crystal settling were gaining widespread acceptance and these were reinforced by Wager & Deer's classic description of the Skaergaard intrusion in 1939. However it was not until after the Second World War that the implications of these layered mafic intrusions for models of magmatic differentiation really became apparent (e.g. Wager & Brown 1968). Gravitational crystal settling models were to dominate most discussions of magmatic differentiation during the 1960s and 1970s. However, since McBirney & Noyes (1979) re-evaluation of the evidence for crystal settling in the Skaergaard intrusion, more recent models have favoured in-situ crystallization. This is yet another illustration of the ways in which our ideas have come full circle.

Like many of his fellow scientists, Harker (1909) considered that assimilation of crustal rocks could be an important process in the compositional diversification of magmas, particularly in deep crustal magma reservoirs where extensive melting of wall rocks might occur. However 'the enormous amount of heat needed to raise the solid (wall) rocks to the point of melting and to melt them' and the lack of evidence for superheated magmas to provide the necessary heat source concerned him. Bowen (1928) was also impressed with the amount of superheat necessary to assimilate significant quantities of crustal rocks and, whilst accepting that limited assimilation undoubtedly did contribute to the compositional variability of magmatic rocks, doubted 'whether the presence of foreign matter is ever essential to the production of any particular type of differentiate'. In the 1980s and 90s, models of wall rock assimilation have come back into favour with the recognition of assimilation coupled with fractional crystallization (AFC) as an important process in the petrogenesis of many continental magmas.

Bowen (1928), building on the earlier ideas of Harker, stressed the importance of developing models for magmatic differentiation that were consistent with the fundamental principles of physical chemistry. He showed how a knowledge of phase equilibria in synthetic silicate systems, when used in conjunction with detailed field observations and mineralogical studies of igneous rocks, could be helpful in interpreting their petrogenesis. In addition, building on the work of Fenner (1926), he developed the use of the oxide-oxide variation diagram, first introduced by Harker (1900, 1909), as a graphical means of interpreting the chemical relationships within cogenetic suites of rocks. Bowen also introduced the idea of a *Reaction Principle* to

explain the mineralogical changes which occur during the progressive crystallization of mafic magma. Fifty years after the publication of Bowen's classic book *The Evolution of Igneous Rocks* (1928), Osborn (1979) reviewed the Reaction Principle and concluded that the basic idea was still valid.

Whilst the war years (1939–45) undoubtedly slowed the pace of research, by the time Tilley gave his presidential address to the Geological Society of London in 1950 on 'Some aspects of magmatic evolution', it was clear how our understanding of magmatic differentiation processes had developed since the 1930s. Major steps in establishing the concept of magmatic differentiation series related to different parental basalt compositions (alkali and tholeiitic) had been made by Bailey *et al.* (1924) in their classic study of the Tertiary and post-Tertiary geology of the Isle of Mull, Scotland. These ideas were developed further by Kennedy (1933). Tilley (1950) believed that the alkaline magma series could be derived from a tholeiitic basalt parent by fractional crystallization. However, Yoder & Tilley (1962) were later to show that a low pressure thermal divide precludes this and a fractionation relationship between these two primary magma compositions is not generally considered today. Tilley clearly demonstrated the different evolutionary trends of the tholeiitic and alkaline magma series on a total alkalis v. silica Harker variation diagram, still widely used today to classify volcanic rocks (Le Bas *et al.* 1986). He discussed the variable nature of the iron-enrichment trends which could be generated by differentiation of tholeiitic basaltic magma in contrast with the trend of iron-depletion displayed by the calc-alkaline series. As we shall see in subsequent sections, this remains a subject for debate. Additionally he was concerned about the role of crustal contamination in the petrogenesis of the calc-alkaline association of orogenic belts; again a subject at the forefront of discussion in the 1980s and 90s.

Mechanisms for magmatic differentiation: a review of current ideas

Magma-mixing processes in open system magma chambers

Magma mixing is clearly an important differentiation process contributing to the overall geochemical and petrological diversity within and between magmatic suites (Philpotts 1990). First proposed by Bunsen (1851), it was considered to be an important petrogenetic process by many workers during the later part of the nineteenth century and the beginning of this (e.g. Harker 1909; Bowen 1928). One of the more extreme theories was that all magmas were mixtures of basalt and rhyolite (e.g. Fenner 1938). A wide range of phenomena have been recognized ranging from incompletely mixed magmas (Furman & Spera 1985) to hybrids in which mixing appears complete (e.g. Sparks & Marshall 1986; Oldenburg *et al.* 1989). Clearly, in nature, magma mixing must be common but we rarely see its effects. For example, repeated injections of new batches of primitive magma into long-lived, open magma chamber systems undergoing crystal fractionation undoubtedly controls the variety of eruptive products we observe at many volcanic centres. This was recognized at the turn of the century by Harker (1909). Osborn (1959) showed that oxidation state plays a fundamental role in the course of

magmatic differentiation and that this may be directly related to whether the chamber is open or closed to new magma batches.

In theory, a series of magmas generated by mixing of two parental liquids should define straight lines on oxide-oxide (i.e. Harker) variation diagrams, so long as they were not concurrently fractionating. In contrast, suites of rocks related by crystal fractionation should, in general, define curved trends on Harker variation diagrams. Complex mineralogical relationships can occur if two partially crystallized magmas are mixed and equilibrium is not completely re-established in the mixed magma.

The chemical diversity of the 1959 eruptions of Kilauea Iki, Hawaii, have been cited by many workers as a classic example of magma mixing (e.g. Murata & Richter 1966; Wright 1973; Helz 1987). Recently, however, Russell & Stanley (1990) have suggested that crystal sorting is sufficient to explain the range of chemical compositions observed. Eichelberger (1975) proposed that many andesites and dacites in the western USA are the products of mixing of primary basaltic and rhyolitic magmas; reviving an idea more than 100 years old. However McBirney (1980) critically evaluated the concept and claimed that most of the petrographic and chemical features proposed as evidence for magma mixing (e.g. disequilibrium) could be explained by the eruption and mixing of magmas from compositionally zoned magma chambers.

The idea that most magma chambers are episodically replenished by new pulses of magma is widely accepted and based on a range of evidence from both volcanic and plutonic rocks. A number of workers have shown that a variety of phenomena may occur during replenishment, depending upon the relationships between the densities and viscosities of the incoming and chamber magmas and the input rate of new magma (e.g. Huppert & Sparks 1980; Campbell & Turner 1986; Huppert *et al.* 1983, 1986). O'Hara (1977) and O'Hara & Mathews (1981) developed mathematical models to predict the course of magmatic differentiation in magma chambers which are periodically replenished with new batches of primitive magma, periodically tapped and continuously fractionated. Over the past decade a range of more complex models have been devised (e.g. Nielsen 1988, 1990). These will be discussed further in a subsequent section. Russell (1990) presents a comprehensive review of the thermodynamics of magma mixing, using a forward modelling approach to calculate synthetic data sets for mixed magma systems. The model data can then be compared against data for natural systems as an aid in interpreting their petrogenesis.

Nielsen (1990) has shown, on the basis of model calculations that, in a magmatic system undergoing paired recharge and fractionation, the liquid line of descent (LLD) for major elements is similar to that produced by fractional crystallization. In recharged systems the magma chamber fractionates only the liquidus phases, and the liquid is constrained to evolve along the cotectics in some n -dimensional phase diagram. As an example, in a simple ternary system (Fig. 2), if the magma in a chamber is crystallizing ol + cpx + plag, adding a pulse of more primitive magma will push it back into the olivine phase field from which it will evolve back towards the ol-cpx cotectic. In such a situation the long term amount of ol + cpx removed from the system will be greater than that in a closed system.

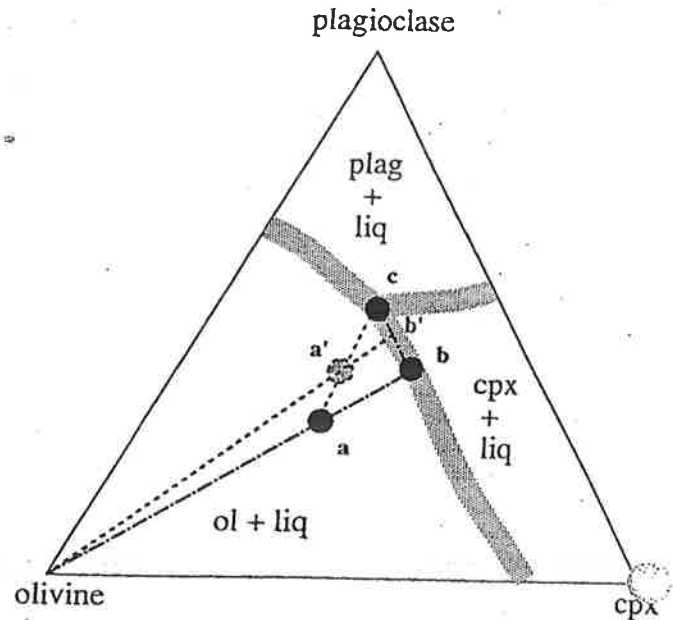


Fig. 2. Magma mixing viewed in the context of a simplified ternary system. If the magma in the chamber was crystallizing the assemblage ol + plag + cpx it would lie at the ternary eutectic c . Re-fluxing the chamber with a new batch of primitive magma (a), followed by complete mixing, would generate a new chamber magma composition a' which would then evolve back towards the eutectic c along the liquid line of descent (LLD) $a'-b'-c$. The path $a-b-c$ represents the initial LLD of magma a .

Fractional crystallization

Gravitational crystal settling and differentiation in layered mafic intrusions. Much of our understanding of the differentiation of basic magmas is based on the record of crystallization preserved in layered mafic intrusions (e.g. Skaergaard, East Greenland; Stillwater, Montana; Bushveld, S Africa). Our knowledge of the petrogenesis of these bodies is grounded in the classical works of Wager & Brown (1968), Jackson (1961) and Hess (1960). However, in recent years, it has become clear that many of the petrographic, chemical and textural features of layered intrusions cannot be modelled adequately using the classic assumptions of gravitational crystal settling on to the floor of a magma chamber (McBirney & Noyes 1979; Shirley 1987). Many of the controversies have revolved around the site of crystallization. Throughout the 1960s and 1970s models were dominated by ideas of cumulus crystallization within the main body of magma and sedimentation by convection currents (e.g. Wager & Brown 1968). However McBirney & Noyes (1979) proposed that the layering is actually produced by in-situ crystallization on the floor (and walls) of the chamber; a complex process involving both chemical and thermal diffusion, nucleation and crystal growth.

One of the oldest controversies in igneous petrology (Bowen 1928; Morse 1980) concerns the path of differentiation in tholeiitic magmas. It is generally accepted that a tholeiitic magma crystallizing at constant bulk composition (i.e. in a closed system) will generate an extreme iron-enrichment trend on an AFM diagram (Fig. 3) depicting the compositions of its derived liquids (Osborn

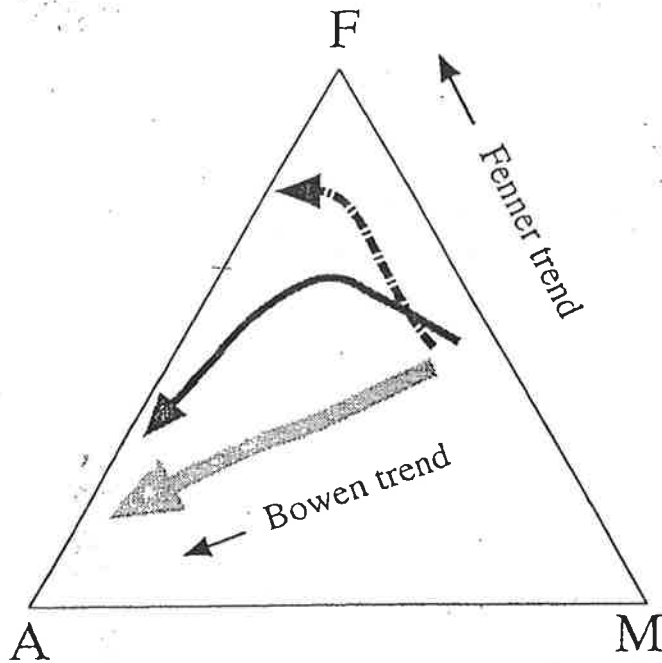


Fig. 3. A $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ -F $(\text{FeO} + \text{Fe}_2\text{O}_3)$ -M (MgO) diagram to show the contrasting Bowen and Fenner trends of magmatic differentiation, of alkali and of iron enrichment respectively.

1959, 1962; Yoder & Tilley 1962). Such a trend is known as the *Fenner trend* and is characteristic of large, apparently closed, intrusive systems such as Skaergaard. In contrast, if the magmatic system is open to oxygen, in particular if f_{O_2} is maintained at a constant value during crystallization (Ghiorso & Carmichael 1985), such that the system becomes progressively more oxidized with falling temperature, fractional crystallization of a tholeiitic liquid is presumed to generate a residuum rich in silica and low in Fe (the *Bowen trend*), due to the precipitation of large quantities of spinel.

The classic study of Osborn (1959) demonstrated that the difference between the Bowen and Fenner trends appears to be controlled by the timing of the onset of magnetite fractionation, which is, in turn, controlled by the oxidation state of the system. Simplistically we can think of the oxidation state of a magma in terms of the oxidation-reduction equilibrium: $4\text{FeO} + \text{O}_2 = 2\text{Fe}_2\text{O}_3$. From the thermodynamic equilibrium relation for this reaction we can deduce that the fugacity of oxygen (f_{O_2}), which is a measure of the degree of oxidation of the system at a given temperature, should be proportional to the amount of Fe_2O_3 .

During closed system crystallization the early extraction of olivine and pyroxenes, which contain no appreciable Fe_2O_3 , should increase the concentration of Fe_2O_3 in the residual liquid relative to FeO , leading to an increase in f_{O_2} (Juster *et al.* 1989). However, once magnetite begins to crystallize the $\text{Fe}_2\text{O}_3/\text{Fe}_{\text{total}}$ ratio should decline in the more evolved liquids. The magnitude of the effect will clearly depend upon the composition of the magnetite as well as that of the other iron-bearing phases in the crystallizing mineral assemblage. If olivine is in a reaction relationship with the magma to form pigeonite, FeO will be added to the liquid as the olivine dissolves which will counterbalance the tendency for f_{O_2} to increase as olivine + cpx + plagioclase crystallize (Juster *et al.* 1989).

In certain circumstances the oxygen fugacity of a magma may be buffered by the surrounding country rocks (e.g. Ghiorso & Carmichael 1985). This probably involves hydrogen diffusion; the fugacity of hydrogen being linked to that of oxygen through the breakdown of water. Oxygen fugacity may also be internally buffered by magmatic oxidation-reduction equilibria, for example S_2 - SO_2 and CO - CO_2 . Ghiorso (1985) calculates that for crystallization along an oxygen buffer (e.g. quartz-fayalite-magnetite (QFM) or nickel-nickel oxide (NNO)) the ratio of ferric to total iron in the residual liquid should remain approximately constant. Ghiorso & Carmichael (1985) suggest that, to generate the typical Fenner differentiation trend, a tholeiitic basalt must crystallize essentially along an oxygen buffer. In contrast the Bowen trend is generated by continuous oxidation of the melt (maintenance of constant f_{O_2} as temperature decreases) which results in early magnetite saturation in the evolving liquid.

The Skaergaard intrusion, East Greenland, has, for the past 50 years been cited as the classic example of in-situ differentiation of basic magma. This was first described by Wager & Deer in 1939 (after its discovery in 1930) and subsequently by Wager & Brown in 1968 in their classic book on *Layered Igneous Rocks*. Useful reviews of the structure and average composition of the Skaergaard Layered Series are given by McBirney & Noyes (1979) and McBirney (1989).

Wager & Deer (1939) proposed that convection currents of variable velocity played a significant role in the cooling and differentiation of the intrusion, reintroducing the idea (proposed by Darwin 1844 and by Bowen 1928) that magmatic differentiation could be induced by crystal settling. The nature of convection in high-level magma chambers has occupied the minds of workers in this field ever since and our ideas have been strongly influenced by studies of the Skaergaard. However in more recent years several authors (e.g. McBirney & Noyes 1979; Naslund 1984) have come to question the importance of crystal settling, and have proposed new models to account for the development of layering, so spectacularly developed in the Skaergaard intrusion.

Wager (1960) proposed that the differentiation of the tholeiitic Skaergaard parent magma was characterized by a trend of iron enrichment throughout, with very little silica enrichment until very late stages (Fig. 4). This is in marked contrast to the normal trend of differentiation observed in tholeiitic volcanic suites. However, Hunter & Sparks (1987) triggered a controversial series of short papers (McBirney & Naslund 1990; Morse 1990; Brooks & Nielsen 1990; Brooks *et al.* 1991) by proposing that earlier calculations of the Skaergaard differentiation trend (e.g. Wager & Brown 1968) were incorrect, and that the magmatic differentiation sequence actually follows the more normal eruptive trend of early iron-enrichment (Fig. 4), with magmas evolving from tholeiitic basalt to ferrobasalt in the Lower Zone (LZ), from a ferrobasalt to an iron-rich tholeiitic andesite (icelandite) from the Middle Zone (MZ) to the Upper Zone (UZ) and from icelandite to an iron-rich rhyolite at the Sandwich Horizon. Hunter & Sparks argued against the Fenner-type of differentiation for Skaergaard partly on the grounds that iron-rich magmas are rare as eruptive compositions. However Brooks *et al.* (1991) pointed out that iron-rich silica-poor dykes and plateau lavas do in fact occur in the area of the Skaergaard and cited additional examples from

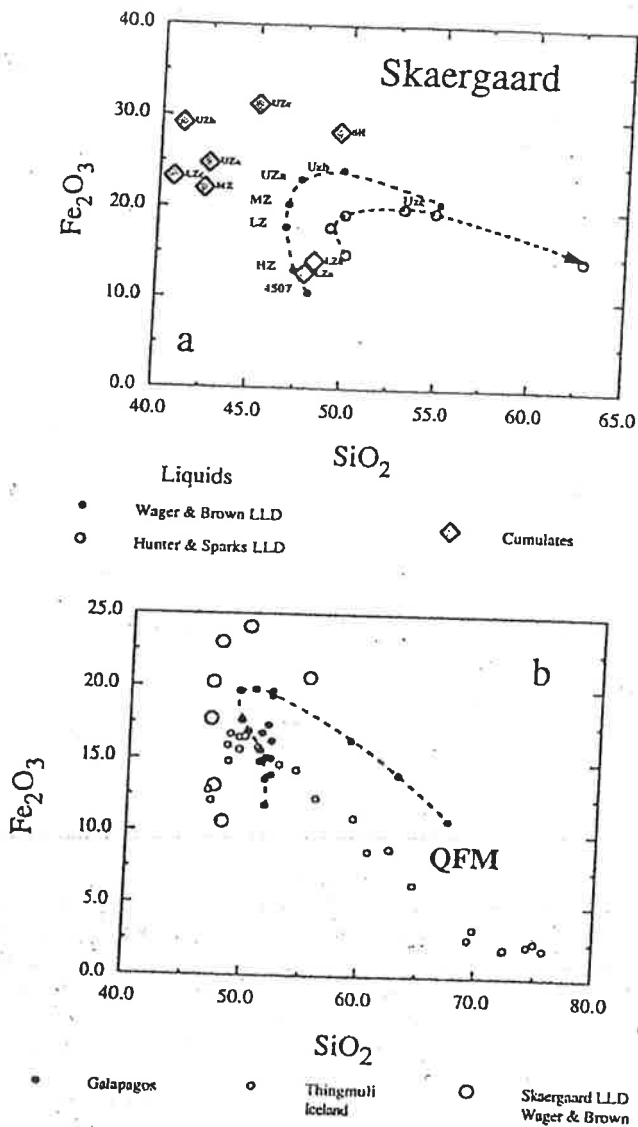


Fig. 4. (a) Fe_2O_3 (total Fe) versus SiO_2 wt % variation diagram for the Skaergaard intrusion, Greenland, showing the liquid lines of descent for the chamber magma predicted by Wager & Brown (1968) and Hunter & Sparks (1987). Also shown are the average compositions of the cumulates from each of the major zones of the Layered Series from McBirney (1989). Abbreviations: HZ, Hidden Zone; LZ, Lower Zone; MZ, Middle Zone; UZ, Upper Zone; SH, Sandwich Horizon. (b) Fe_2O_3 (total Fe) versus SiO_2 wt % variation diagram showing the liquid line of descent (LLD) of the Thingmuli tholeiitic volcanic series, Iceland (Carmichael 1964) and an experimentally determined LLD for a tholeiitic basalt from the Galapagos (Juster *et al.* 1989). Both evolved in a relatively oxidizing environment, close to the QFM oxygen buffer. Also shown for comparison is the Skaergaard LLD from (a).

oceanic environments (e.g. Melson & O'Hearn 1986; Sinton *et al.* 1983).

Brooks *et al.* (1991) proposed that the Skaergaard iron-rich liquids evolved from a MORB-like tholeiitic parent magma by simple crystal fractionation in a closed or nearly closed system. They concluded that the iron-rich Fenner differentiation trend may actually be the normal liquid line of descent of tholeiitic magmas, and that the Bowen trend of silica enrichment arises only when magmas come under the

influence of oxidizing conditions in near surface (probably open) magma chambers. This has been confirmed in experimental studies on material from the Galapagos arc by Juster *et al.* (1989). Thus the requirement of close system differentiation may be essential to develop the Fenner trend. Indeed Morse (1990) suggests that plutonic processes will tend to enhance the Fenner trend of iron enrichment, and thus that we should expect to see differences in the differentiation trend of tholeiitic magmas between the volcanic and plutonic environment. Problems arise of course because layered intrusions such as the Skaergaard predominantly preserve the crystal extract whereas the volcanic successions preserve the liquids. Indeed the more efficient the process of crystal-liquid fractionation the more difficult it is to define the liquid line of descent of the magmas from which a series of plutonic rocks has formed. This is one of the major points of contention between Hunter & Sparks (1987) and their opponents. Brooks *et al.* (1991) raised the possibility that liquid lines of descent constructed from volcanic sequences may not actually represent the fractionation path of the magmas in the underlying chambers, even though least-squares modelling calculations can be performed which give good residuals. Magma compositions may depart from the theoretical liquid line of descent as a consequence of open-system magmatic processes, including magma chamber refluxing and in-situ differentiation. This is a view echoed in the theoretical modelling of magmatic differentiation processes by Nielsen (1990). If correct, this may challenge many of our traditional perceptions of magmatic differentiation based on Harker diagrams and studies of volcanic rocks.

Hunter & Sparks (1987) suggested that the Skaergaard magma chamber might not have been completely closed and could have lost significant volumes of silicic magma to the surface by eruption or lateral intrusion. Since most of the roof rocks of the intrusion have been removed by erosion, there is no way of knowing whether there was indeed any connection to the surface. In addition Stewart & DePaolo (1990) have measured the Nd-Sr isotopic composition of the cumulates from the Layered Series, which reveals that the Skaergaard magma was actually assimilating small amounts (2-4%) of Precambrian gneissic wall rock, at least during the early stages of crystallization. Thus even the type example of closed system magmatic differentiation was probably not completely closed to external influences.

Defant & Nielsen (1990) noted that for simple systems undergoing fractional crystallization the instantaneous bulk composition of the fractionating mineral assemblage begins to approach the bulk composition of the magma from which it is crystallizing when the magma becomes multiply saturated i.e. when it reaches a eutectic. In simple terms this means that at the mafic end, the extracted cumulates should be most different in composition from the crystallizing magma, and at the evolved (acidic) end most similar. Such relationships may change, however, if the system becomes open to recharge or assimilation. This could have important implications with respect to the interpretation of the composition of the Skaergaard cumulates (McBirney 1989; Fig. 4). The isotopic evidence for assimilation (Stewart & DePaolo 1990) may mean that the early cumulates are not what would normally fractionate from an evolving tholeiitic magma. Addition of the assimilant would probably have driven the magma composition off the cotectic along which

it was evolving, changing the fractionating mineral proportions as well as the mineral assemblage (Nielsen 1989).

Marsh (1988) and Sparks (1990) have continued the debate about whether the plutonic and the volcanic record reveal fundamentally different styles of magmatic differentiation. Marsh investigated the dynamic evolution of a sheet-like basaltic magma chamber and concluded that most of the crystallization should occur near the roof, but that descending plume-like convection currents would transport crystals down to the chamber floor. In this model the more differentiated liquids are always trapped in the downward crystallizing roof zone and therefore the residual magma never differentiates to any considerable extent. In many respects the physical aspects of this model have strong similarities to that proposed originally by Wager & Deer (1939) for the Skaergaard intrusion. However Sparks (1990) argues that this model is not applicable to large magma chambers in which crystallization occurs predominantly at the floor, while cooling occurs predominantly through the roof. It is clear that this remains an area for further study!

Convection in magma chambers

Until the late 1970s our ideas about the physical processes that allowed fractional crystallization to take place were based on very simple concepts and differed little from those of Bowen (1928). Crystals were considered to nucleate and grow within a magma and then to settle out under the influence of gravity to form cumulate rocks. Although many other processes potentially responsible for magmatic differentiation had been recognized by the turn of the century (e.g. Harker 1909), including in-situ crystallization on the margins of the magma chamber, magma mixing, crustal contamination, immiscibility and liquid state diffusion, by the late 1920s these were all regarded as subordinate to crystal settling.

In the past decade, the dynamics of magma chamber processes have become an important theme, with increasing importance attached to the role of convection in fractional crystallization. This represents a considerable shift of emphasis from previous studies of magmatic differentiation, based on experimental determinations of phase equilibria in silicate systems (e.g. Hess 1989). It is interesting to note that the idea of thermal convection in magma chambers was first proposed by Becker (1897).

The convective system established in a particular magma body is necessarily a transient condition, because convection will enhance the rate of cooling. Thus the life span of a convection system depends on the amount of heat that is lost by conduction through the walls and roof and the amount of new magma (if any) periodically injected into the chamber. Flow rates calculated for magmas undergoing convection are comparable to, if not higher than, the settling velocities predicted by Stokes Law. Thus convection will either cancel out or enhance the effects of crystal settling. It is important to remember, however, that Stokes Law relates to the movement of small spheres in Newtonian fluids. Magmas that contain more than a few percent crystals and those that are highly polymerized are more likely to behave as non-Newtonian or Bingham fluids which have a finite yield strength (McBirney & Noyes 1979).

From recent studies (for reviews see Sparks *et al.* 1984; Turner & Campbell 1986) it is clear that heat and mass

transfer processes in multicomponent fluids such as silicate melts are complex. Calculated thermal Rayleigh numbers range between 10^9 for viscous rhyolite to 10^{23} for basaltic magmas. Thus given a value of 10^3 for the onset of turbulent convection, we might conclude that all magmas, regardless of their chemical composition, stored in high-level magma chambers should be in a state of vigorous thermal convection (Hess 1989). This should have fundamental implications for models of crystal settling in magma chambers for, as pointed out by Sparks *et al.* (1984), the convective motions are usually sufficiently vigorous to keep crystals in suspension. However crystal settling may occur from within boundary layers at the margins (floor, walls) of the magma chamber. In recent years most models for crystallization in magma chambers have favoured in-situ growth on the floor and walls of the chamber (McBirney & Noyes 1979; Irvine 1980 *a, b*; Turner & Campbell 1986; McBirney *et al.* 1985; Nilson *et al.* 1985). However, Sparks *et al.* (1993) have recently returned to gravitational crystal settling models to explain the modal and rhythmic igneous layering which typifies many large layered mafic intrusions. They propose that each mineral phase has its own critical concentration which must be exceeded before sedimentation can occur.

Sparks *et al.* (1984) proposed a mechanism for magmatic differentiation, termed *convective fractionation*, in which in a crystallizing boundary layer the less (or more) dense liquid fraction convects away from the residual crystals (Fig. 5). Langmuir (1989) and Tait & Jaupart (1990) propose that the evolved melt from the boundary layer may then be mixed back into the main body of the magma (Fig. 6). This means that magma in the central part of the chamber may exhibit the effects of differentiation without ever having crystallized directly itself. Nielsen (1990) has incorporated this concept into a complex mathematical model of in-situ crystallization. His results show that the course of differentiation (liquid line of descent) can be strongly influenced by the amount of crystallization in the boundary layer and on the mineral

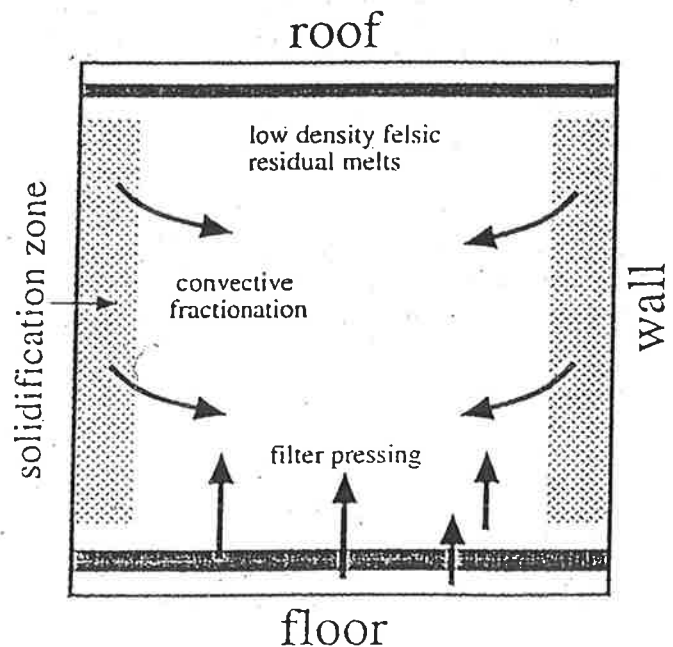


Fig. 5. Schematic model for convective fractionation in a magma chamber.

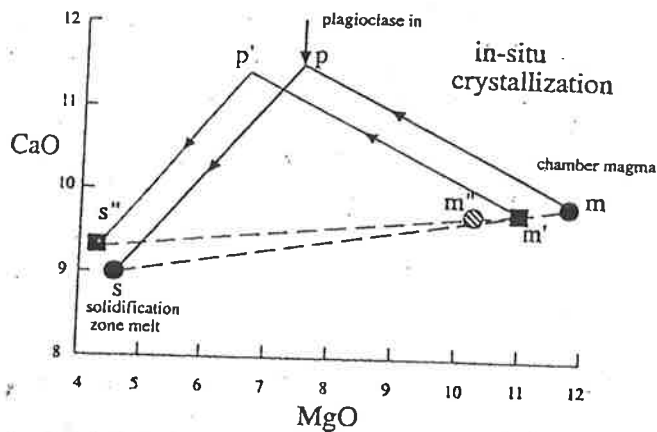


Fig. 6. Schematic weight % CaO versus MgO variation diagram to show the effects of in-situ crystallization. For the case of perfect fractional crystallization the initial chamber magma m evolves along the LLD m - p - s . The marked inflection corresponds to the point at which plagioclase becomes a major fractionating phase. Highly fractionated melt evolving in-situ in the *solidification zone* (Fig. 3) has the composition s . If a small amount of s mixes back into the main body of magma (m) the new chamber magma will have a composition m' . This will then evolve along a slightly different LLD (m' - p - s). Mixing-in of the new solidification zone melt s' with m' will yield a new chamber magma m'' . The chamber magma thus evolves along a path m - m' - m'' which contrasts markedly with the LLD predicted for perfect fractional crystallization.

assemblage crystallizing. A consequence of in-situ fractionation is that the system evolves by mixing in a small amount of magma with an extreme composition (Fig. 6), particularly with respect to its trace element characteristics. This simple graphical representation demonstrates that the magma chamber composition will evolve towards the composition of the solidification zone liquids, not along any specific cotectic. Rather surprisingly models of convective fractionation are not new. In 1918, Grout proposed a two phase model of convection in which crystal laden melt from the chamber roof sinks to the floor where crystals settle, and residual liquid rises as it is less dense and is recycled into the zone of crystallization. Integration of this effect could result in the gravitational differentiation of considerable volumes of magma.

An important property of multicomponent fluids such as silicate melts is that individual components (including heat) can have different diffusivities. As a consequence such fluids may become vertically stratified with respect to density, composition and temperature (Irvine 1980a; McBirney & Noyes 1979; Rice 1981; Sparks *et al.* 1984; Turner & Campbell 1986). If opposing gradients of two (or more) components with different diffusivities are set up, the system may separate into a series of independently convecting layers, bounded by sharp diffusive interfaces, across which heat and chemical components are transported by molecular diffusion. This phenomenon is known as *double (multiple)-diffusive convection*, and Sparks *et al.* (1984) consider that this will inevitably occur in silicate magmas. Indeed Irvine (1980a) considered that multi-diffusive convection is probably one of the principal mechanisms in the fractional crystallization of magmas. This process may also be effective in transmitting the effects of magma mixing and assimilation through a cooling body of magma. There is substantial evidence to suggest that many silicic magma chambers are

both compositionally and thermally zoned (e.g. Hildreth 1979, 1981) and that in such systems multiple-diffusive convection may be important.

Thermogravitational diffusion

The diffusion of chemical species in silicate melts governs the kinetics of most magmatic processes including partial melting, fractional crystallization, magma mixing and crystal growth. Hofmann (1980), Watson & Baker (1990) and Leshner & Walker (1991) give excellent reviews of this complex subject and the reader is referred to these articles for a more detailed discussion of the principles and governing equations.

In the late nineteenth century a particular type of diffusion known as *Soret diffusion* was regarded as being one of the main causes of magmatic differentiation. This refers to the tendency of non-convecting homogeneous solutions to develop concentration gradients when subjected to a temperature gradient. Hess (1989) presents an excellent review of the phenomenon.

The governing equation has the form:

$$(C_C - C_H)/C_0 = \sigma \Delta T$$

where C_C and C_H are the temperatures at the cold and hot ends of the system respectively and C_0 is the initial concentration. σ is the *Soret coefficient* and ΔT is the temperature difference between the two ends of the system. The compositional gradient which can develop in a system will depend upon the magnitude of the Soret coefficient, which can vary in both sign and magnitude from component to component, and on the temperature gradient. Components with positive Soret coefficients accumulate at the cold ends of temperature gradients whereas those with negative coefficients concentrate at the hot ends.

Harker (1894), in his study of the Carrock Fell intrusion, gave careful consideration to the possibility that Soret diffusion could have been responsible for the chemical variation he observed. He came to the conclusion that diffusion controlled gradients in a liquid magma were not the major control, favouring instead a model which combined crystallization and diffusion. However it must be noted that Harker had only one complete major element chemical analysis and one partial analysis of the gabbro on which to base his ideas. Additionally, since he was basing his interpretations on Soret's original model of diffusion in saline solutions, he did not consider the possibility that different components of a silicate melt might diffuse in different directions in the same temperature gradient.

In 1981, Walker *et al.* demonstrated experimentally that a basalt magma held at several hundred degrees above its liquidus and subjected to a steep temperature gradient developed strong chemical gradients in about a week, becoming broadly andesitic at the hot end and a low silica basalt at the cold end (Fig. 7). It is interesting to note that this is the converse of normal crystal-liquid differentiation trends, in which the low temperature differentiation products are silica rich. These experiments triggered renewed interest in the potential for the development of diffusion controlled chemical gradients in magma bodies.

Large temperature gradients are likely to exist at the margins of magma chambers and these will control the effective role of thermal diffusion in the fractionation of chemical species within the boundary layer (Carrigan & Cygan 1986; Cygan & Carrigan 1992). Numerous researchers (e.g. Hildreth 1979, 1981; Koyaguchi 1989) have

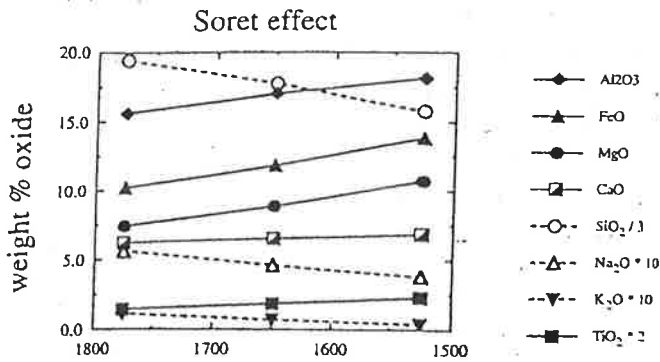


Fig. 7. Weight % oxide variations as a function of temperature, generated as a consequence of the Soret effect in an experimental charge. Data from Walker *et al.* (1981). The mid-points of each curve represent the initial starting composition of the system.

suggested that thermal diffusion (Soret fractionation) may be a significant process contributing to chemical zonation in magma bodies, particularly silicic ones. However other workers (e.g. Michael 1983; Stix *et al.* 1988) have argued that crystal fractionation processes and not Soret diffusion can account for the observed chemical gradients in silicic magmas. Indeed recent experimental determinations of the Soret coefficients for a variety of silicate melt compositions (e.g. Leshner 1986; Leshner & Walker 1988) have suggested that the effect would be small and often of the opposite sense to that observed in natural magmatic systems. In addition, processes of crystallization, crystal settling and convection will tend to destroy any large scale chemical gradients developed by diffusion within the liquid magma. However in stagnant boundary layers near the walls and roof of a magma chamber, Soret diffusion may locally modify the pattern of magmatic differentiation (Hess 1989).

Cygan & Carrigan (1992) have developed a numerical model to examine the effect of non-linear and time dependent temperature fields upon the mass flux associated with thermal diffusion. Their results suggest that thermal diffusion of magma in a time-dependent thermal field is minimal and thus that this cannot be considered a significant chemical fractionation process. It is interesting to note, however, that their predicted changes in the silicate melt induced by thermal diffusion in a boundary layer are orders of magnitude lower than those observed in experimental (e.g. Walker *et al.* 1981; Leshner 1986) and field (Hildreth 1979) studies.

Assimilation and fractional crystallisation

Since the classic work of Bowen (1928), it has generally been accepted that crystallizing magmas may simultaneously assimilate the surrounding wall rock. Even Harker (1909) conceded that extensive melting may occur adjacent to magma reservoirs in the deep crust, although he did not envisage that the effect would be significant due to the absence (as he thought) of sedimentary strata in the deep crust. The heat required for assimilation must clearly be derived from the heat contained within the magma itself and from the heat of crystallization liberated by mineral precipitation. Most authors now agree that assimilation, combined with fractional crystallization, is an important mechanism of magmatic differentiation in all continental magmatic settings, particularly in zones of thickened continental crust.

As noted by McBirney (1984) the major element

composition of a contaminated magma does not necessarily reflect the effect of an added component in any simple way. In many cases the evolving magma will continue to follow its original liquid line of descent. However a magma assimilating felsic crustal rocks will differentiate to produce much larger volumes of more evolved products than if it had not assimilated any crust.

Increasingly complex theoretical models to describe the trace element and isotopic evolution of systems undergoing paired assimilation and fractional crystallization (AFC) have been devised since the late 1970s (e.g. Allegre & Minster 1978; Taylor 1980; DePaolo 1981; Ghiorso & Kelemen 1987; Nielsen 1989, 1990). The older models (e.g. DePaolo 1981) involve several important simplifying assumptions, the most critical of which is that all partition coefficients (D) are constant over the range of fractionation being modelled, and that there is a constant ratio (r) between the rate of assimilation and the rate of fractional crystallization. The recent development of phase equilibria based differentiation models (e.g. Ghiorso & Kelemen 1987; Nielsen 1988) has allowed formulation of more complex, and more realistic, models of AFC processes. The most recent (Nielsen 1989, 1990) permit calculation of liquid lines of descent for Sr and Nd isotopes and evaluation of the effects of assimilation on temperature, fractionating mineral proportions and melt composition. Nielsen (1989) has demonstrated that in systems undergoing AFC the bulk partition coefficients for Sr and Nd are strongly dependent on the chemistry of the assimilate and on the rate of mixing. Virtually all silicic assimilants will increase the bulk partition coefficient for network modifying cations. Additionally he has confirmed that assimilation will generally cause a change in the fractionating mineral proportions. For example, a peraluminous assimilant will increase the proportion of plagioclase crystallizing from a mafic magma, while a peralkaline assimilant will increase the proportion of augite.

Liquid immiscibility

Silicate liquid immiscibility occurs whenever a single melt splits into two coexisting melts in response to changes in pressure, temperature or composition. The idea of liquid immiscibility as a differentiation mechanism was probably first proposed by Scrope (1825) and given serious consideration by Harker (1909), Daly (1914) and Bowen (1928). In 1951 Roedder reported the results of experiments which demonstrated the existence of a large field of silicate liquid immiscibility in the system $K_2O-FeO-Al_2O_3-SiO_2$. Experimental evidence for the existence of a miscibility gap between carbonatite and silicate magmas was presented by Freestone & Hamilton (1980) and Kjarsgaard & Hamilton (1988).

Roedder (1979) reviewed the evidence for liquid immiscibility in a wide range of magmatic rocks including low-K ultrabasic and basic komatiites, high-K feldspathoid-bearing basalts, high-Al olivine-bearing subalkali basalts, normal and high Fe subalkalic basalts, nephelinites and high Ti Lunar mare basalts. He suggested that immiscibility in silicate systems usually yields a felsic alkali-aluminosilicate melt and a mafic melt rich in Fe, Mg, Ca and Ti. Philpotts (1982) considered that immiscible liquids are present in sufficient amounts that this should be considered a viable means of magmatic differentiation during the late stages of crystallization of common magmas. Indeed McBirney & Nakamura (1973) proposed that immiscibility in the later

stages of differentiation of the Skaergaard intrusion was responsible for the formation of granophyres.

Petrologists have from time to time postulated that the common association of basalt and rhyolite, without transitional rock types, is evidence for silicate liquid immiscibility. However the simple juxtaposition of two contrasting magma types is obviously insufficient to prove them immiscible. As noted by Bowen (1928), coexisting immiscible liquids should be in equilibrium with a common mineral assemblage. Le Bas & Handley (1979) used this logic to demonstrate an immiscible relationship between ijolites and sovites from the East African Rift.

The experimental approach to understanding magmatic differentiation

In a review of this brevity it is impossible to describe the experimental approach to studies of magmatic differentiation in any detail. Bowen (1928) was clearly one of the pioneers of modern experimental petrology, although his work concentrated largely on phase equilibria in synthetic binary and ternary systems. Such data have provided a tremendous insight into phase equilibria in silicate systems, although they have little quantitative application to the understanding of magmatic differentiation processes. Excellent reviews of the interpretation of phase equilibria data may be found in Cox *et al.* (1979), Yoder (1979) and Hess (1989) and will not be reiterated here.

Over the past 30 years, experimental studies have provided important constraints on the nature of the crystallizing phases in basaltic systems as a function of pressure and temperature (e.g. Yoder & Tilley 1962; Green & Ringwood 1967; Holloway & Burnham 1972; Bender *et al.* 1978; Elthon & Scarfe 1984; Gust & Perfit 1987; Baker & Egger 1987; Longhi & Pan 1988). Such data provide the experimental basis for the most recent quantitative models of magmatic differentiation (e.g. Ghiorso & Carmichael 1985; Nielsen 1988). Milestones in the interpretation of experimental data are the classic papers of Yoder & Tilley (1962) and O'Hara (1968).

Representing the data: variation diagrams

Harker diagrams

Oxide-oxide weight percent variation diagrams illustrating the compositional variation within magmatic suites have been in use, essentially unmodified, for almost a century. They were first introduced by Harker (1900, 1909) and for this reason bear his name. It was Bowen (1928), however, who realized their full potential for interpreting the processes of magmatic differentiation and their physical meaning in the context of experimental phase petrology. Bowen showed how effective variation diagrams are in illustrating the chemical relationships among the members of a rock association. They enable us to explore in a simple graphical way the compositions and quantities of phases that have to be added or subtracted from an evolving magma to produce the next magma in the liquid line of descent (LLD). Cox *et al.* (1979) present an excellent review of the interpretation of major and trace element variation diagrams which should be compulsory reading for anyone unfamiliar with the subject.

Pearce element ratio diagrams

In 1968 T.H. Pearce introduced a new method for the representation of chemical data on variation diagrams, in

part to overcome the constant sum effect inherent in oxide-oxide weight percent variation diagrams. At the time the method received little attention in the literature. However there has recently been a resurgence of interest in their use (Pearce 1987; Ernst *et al.* 1988; Nicholls 1988; Russell & Nicholls 1988; Russell & Stanley 1990; Pearce & Stanley 1991), although admittedly restricted to a group of Canadian geoscientists closely associated with their originator.

Pearce element ratios provide an interesting way of using major element data for cogenetic suites of volcanic rocks to test hypotheses on liquid lines of descent in evolving magma chambers. The method is based on the conversion of weight per cent oxide data for a suite of rocks to element fractions:

$$e_i = W_i A_i / MW_i$$

where W_i , A_i and MW_i are the weight percentages, the number of cations in the oxide formula and the molecular weight of oxide i . The Pearce element ratio (r_i) of an element i is then defined as:

$$r_i = e_i / e_z$$

where z is a conserved element whose amount does not change during the differentiation process being investigated. Typically P, Ti and K are chosen as conserved elements, at least during the initial stages of differentiation of basaltic magmas. Complex ratio diagrams using axes constrained to be sensitive to the fractionation of a particular mineral (e.g. 0.5 (Mg + Fe)/K versus Si/K for olivine) are used to evaluate the role of that mineral in the petrogenesis of a suite of cogenetic rocks related by fractional crystallization.

The supporters of the method argue that Pearce element diagrams can yield insights into igneous processes that are not obvious or quantitatively expressed when portrayed on other variation diagrams (e.g. Harker diagrams). All agree that the method is sensitive to analytical error and to the assumption that the chosen conserved elements are effectively excluded throughout the entire crystallization sequence. Defant & Nielsen (1990) have used a forward modelling approach to generate synthetic data sets with which to evaluate whether Pearce element ratio diagrams can correctly predict the proportions of phases involved in magmatic differentiation. Their results show that for cases of homogeneous crystallization and in-situ crystallization, with or without magma chamber recharge, Pearce element ratio analysis gives quite consistent results. However the method breaks down when any kind of assimilation has occurred.

Differentiation indices

Running through much of the older geological literature is the idea that analyses of igneous rocks, if plotted on the appropriate type of variation diagram, can be arranged in an evolutionary sequence. To this end a variety of differentiation indices have been devised. The *Harker index* (SiO₂ as abscissa) depends upon the commonly observed increase in SiO₂ in successive liquids with progressive fractional crystallization and has been widely used for much of this century. Similarly, for basaltic compositions MgO is commonly used as the abscissa in variation diagrams. In addition indices based upon the magnesium-iron ratio have been widely used (e.g. 100MgO/MgO + FeO or Mg²⁺/Mg²⁺ + Fe²⁺). More complex differentiation indices, including the *Solidification Index* of Kuno (1959) and the *Differentiation Index* of Thornton & Tuttle (1960), have been devised but are rarely used these days. For a more

complete discussion of this subject the reader is referred to Cox *et al.* (1979) and Ragland (1989).

Modelling magmatic differentiation

Over the past 20 years a number of attempts have been made to model the process of differentiation mathematically. Quantitative models for the geochemical evolution of magma chambers have become increasingly more complex since the basic Rayleigh fractionation equation was first applied to the problem of fractional crystallization (Neumann *et al.* 1954). Models may be divided into two groups: (a) those based upon graphical analysis of synthetic systems or projections (e.g. Presnall *et al.* 1979; Walker *et al.* 1979; Grove *et al.* 1982) and (b) those based on a numerical approach (e.g. Allegre *et al.* 1977; Minster *et al.* 1977; Allegre & Minster 1978; Nathan & Van Kirk 1978; Hostetler & Drake 1980; Langmuir & Hanson 1981; O'Hara & Mathews 1981; DePaolo 1981; Nielsen & Dungan 1983; Ghiorso 1985; Ghiorso & Carmichael 1985; Nielsen 1988, 1989, 1990; Defant & Nielsen 1990).

Early numerical models (pre-1985) were based on statistical evaluation of experimental data to derive empirical expressions to describe the phase equilibria. In contrast the later models (e.g. Ghiorso 1985; Nielsen 1988, 1989, 1990) are all based on a thermodynamic approach. Most of the pre-1985 models rely on assumptions which are known to be invalid over extended periods of differentiation. For example partition coefficients (D) were generally assumed to be independent of pressure, temperature and system composition. The more recent models of Nielsen (1988, 1989) use variable partition coefficients, which are functions of temperature and composition, to simulate liquid lines of descent in differentiating magma systems.

The simplest models have their roots in Harker-type major element variation diagrams, using a linear least squares approach to deduce the proportions of minerals (of specified composition) which might fractionate from a particular magma composition to yield a more evolved daughter (e.g. XLFRAC, Stormer & Nicholls 1978; GENMIX, Le Maitre 1981; Wright & Doherty 1974). It is however, important to note that such mass balance calculations are able to produce a number of arithmetically feasible solutions (all with low sums of squares of residuals, σ^2). For meaningful results, it is essential that in the system being modelled there are fewer mineral phases than chemical components (oxides).

In general, while major element modelling can provide some useful insights into the nature of magmatic differentiation processes; the variation of major elements can tell us little about more complex processes such as refluxing of magma chambers with batches of more primitive magma or crustal assimilation (Nielsen 1990). In such cases isotopic and trace element behaviour may be much more sensitive. Nielsen (1990) has developed one of the most complex simulations of magmatic differentiation thus far. No doubt even more complex models will emerge in due course. At present, such models are limited by an inadequate experimental data base, with which to constrain the crystallization behaviour of the complete spectrum of magma types under crustal and mantle conditions. They are also limited by our lack of understanding of the thermodynamics of silicate melts.

One of the most useful aspects of these numerical

calculations is the ability to forward model a particular petrogenetic process or series of processes. Starting with a chosen parental magma composition, different liquid lines of descent can be modelled for combinations of homogeneous (perfect) fractional crystallization, in-situ fractionation, refluxing of the chamber, crustal assimilation and periodic eruption. In addition the oxygen fugacity of the system can be varied. These theoretical models can then be compared to an actual data set, for example for a suite of cogenetic volcanic rocks. This forward modelling approach may be particularly useful for evaluating complex petrogenetic models which cannot be evaluated by experimental techniques. Nielsen (1990) also uses this forward modelling approach to evaluate the effectiveness of other modelling techniques (e.g. linear least squares calculations, trace element ratio diagrams and Pearce element ratio diagrams) with some rather interesting results. For example he shows that linear least squares mass balance calculations and Pearce element ratio diagrams, for systems which have evolved by in-situ fractionation, reveal the phase assemblage crystallizing in the solidification zone. This may explain those cases where the phase assemblage predicted by least squares modelling is inconsistent with observed phenocryst assemblages. Nielsen (1990) also uses this approach to demonstrate that log-log trace element diagrams (Allegre *et al.* 1977) used in the analysis of fractional crystallization processes are only valid if fractional crystallization is the only process responsible for differentiation.

Summary

It is as clear today, as it was a century ago to Harker, that magmatic differentiation must be the result of a complex series of processes. Most petrologists now agree that some form of crystal-liquid fractionation is the dominant driving mechanism, although the manner in which this occurs remains a subject for debate. Nevertheless, liquid-state differentiation mechanisms, including thermogravitational diffusion, liquid immiscibility and magma mixing are clearly capable of generating significant compositional variations within magma bodies.

As noted by Harker (1894, 1909) it is important to differentiate between the in-situ differentiation of a single magma body and the processes of differentiation in deep seated magma reservoirs responsible for the formation of cogenetic suites of intrusives or extrusives. Layered mafic-ultramafic intrusions provide unique natural laboratories in which to study the former. The latter, by comparison, are in some respects almost as elusive now as they were to Harker in the 1890s. However, unlike Harker, we clearly have a much greater understanding of the physico-chemical processes which must operate in high-level magma bodies.

Accepting that some form of crystal-liquid separation provides the dominant control for magmatic differentiation, one of the major controversies remaining is the mechanism by which this actually occurs. Is it primarily induced by localized crystallization at the walls, roof and floor of a magma reservoir (in-situ differentiation) or through the relative movement of crystals and liquid (gravitational crystal settling). In the past hundred years we have seen gravitational crystal settling go in and out of favour several times. It dominated most discussions of magmatic differentiation during the 1960s and 70s. In contrast, in the 1980s models involving in-situ crystallization gained

popularity, following McBirney & Noyes (1979) re-evaluation of the evidence for crystal settling in the Skaergaard intrusion. Currently (e.g. Sparks *et al.* 1993) gravitational crystal settling seems to be back in vogue, but one may wonder for how long?

Geochemical and Sr-Nd-Pb isotopic studies of cogenetic suites of magmatic rocks have provided powerful support for models of magmatic evolution by the combined processes of crustal assimilation and fractional crystallization (AFC). This must be a common cause of magmatic differentiation in most high-level magma chamber systems. However it is most easily detected within the continental crust when the chamber magma and the wall rocks have strongly contrasting isotopic and trace element characteristics.

From the classic studies of Bowen in the 1920s up to the 1970s most discussions of magmatic differentiation relied heavily upon interpretations of phase equilibria in natural and synthetic systems (e.g. Bowen 1928; Philpotts 1990). While this approach greatly enhanced our understanding of the processes involved, it was limited in its ability to make quantitative predictions about the course of evolution in natural magmatic systems. In contrast, in the past decade increasingly sophisticated thermodynamic modelling techniques have been applied, allowing predictions to be made about the liquid line of descent for a given magma composition, evolving under a specified set of conditions. Unfortunately too few petrologists have adopted this forward modelling approach in petrogenetic studies of cogenetic suites of igneous rocks. This is clearly one of the most powerful ways in which we can quantify the various processes involved in magmatic differentiation and will undoubtedly dominate discussions for the remainder of this decade.

Looking back over the past century, we can identify several distinct periods when rapid advances were made in our understanding of the processes involved in magmatic differentiation. In many instances these resulted from detailed field based studies. The description of igneous layering in the Skaergaard intrusion, Greenland, by Wager *et al.* in the 1930s and its re-interpretation in the late 1970s by McBirney & Noyes (1979) were clearly important milestones. In addition the tremendous increase, during the past thirty years, in the volume of high quality geochemical and isotopic data available for cogenetic suites of magmatic rocks has been of fundamental importance. During the past decade quantitative modelling of these data has enabled us to evaluate the viability of the various differentiation mechanisms which have been proposed over the years, although this is not an easy task given the number of variables involved. In this respect it is interesting to note how many of the 'new' models proposed during the past decade to explain magmatic differentiation have actually been around for more than seventy years, some for more than a hundred.

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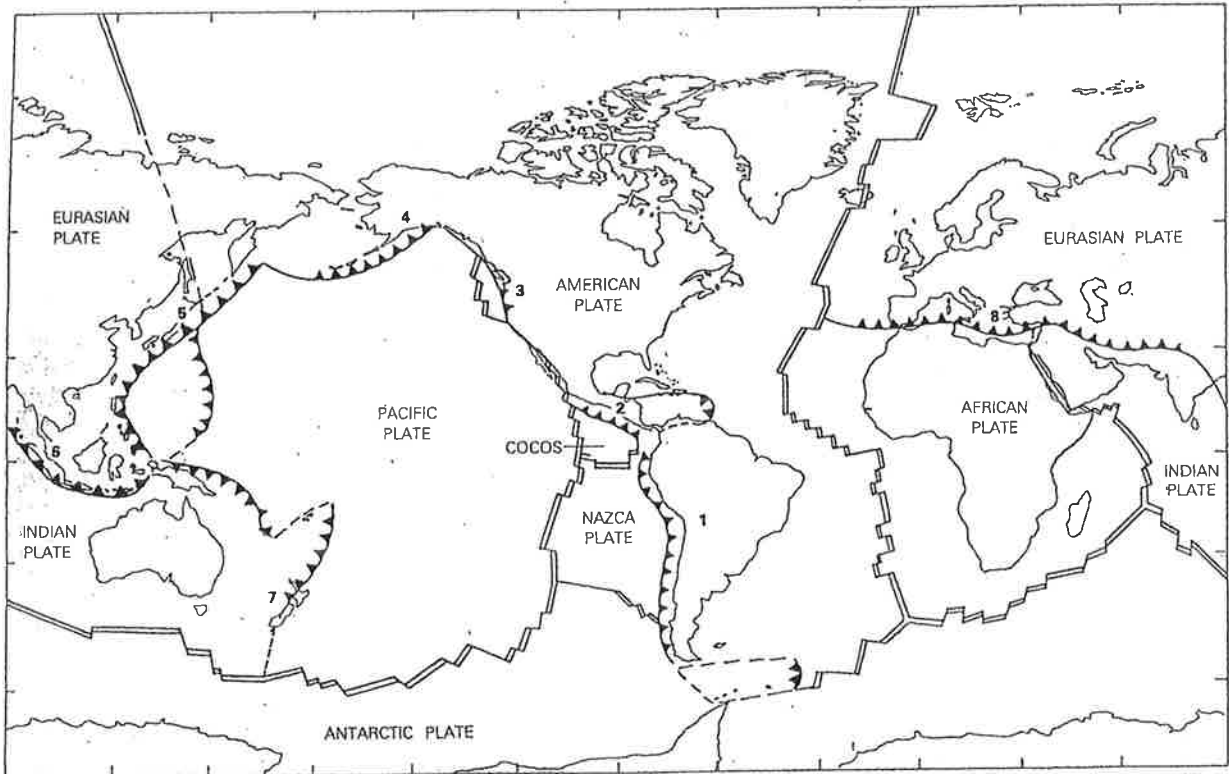
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Subduction Zone Volcanism – Andesites



- | | | | |
|-----------------------------------|------------|---------------------------------|---------------|
| <i>Active continental margins</i> | | <i>Continental micro-plates</i> | |
| 1 Andes | 3 Cascades | 5 Japan | 7 New Zealand |
| 2 Central America | 4 Alaska | 6 Sumatra | 8 Aegean |

Figure Location of the major active continental margins and subduction systems involving continental micro-plates.

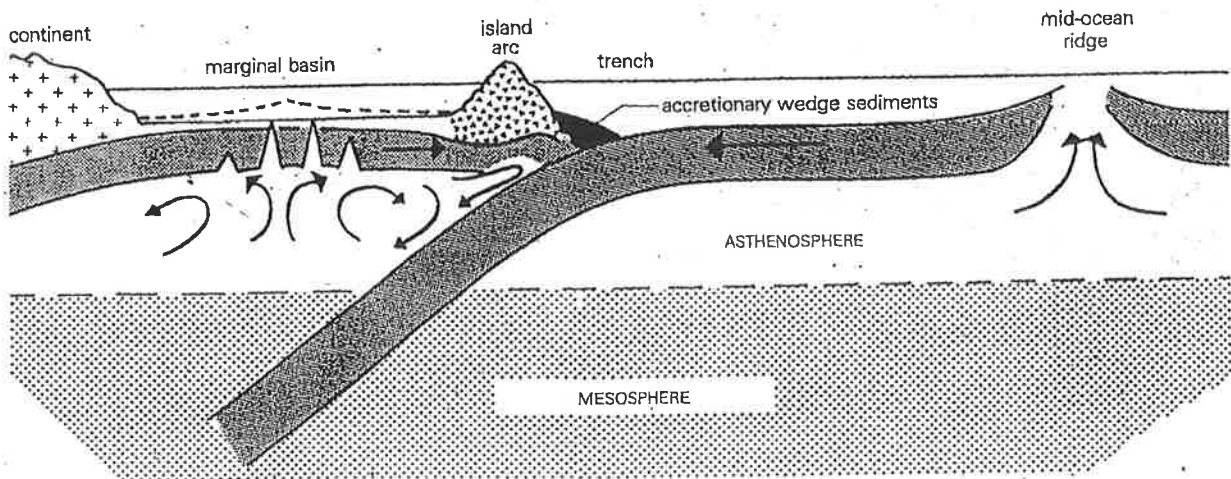


Figure The formation and subduction of oceanic lithosphere. New oceanic lithosphere is created at the mid-oceanic ridge and a deep trench is formed where the lithospheric plate descends into the mantle. Secondary convection currents in the asthenosphere cause a small spreading centre, a marginal basin, to develop behind the arc.

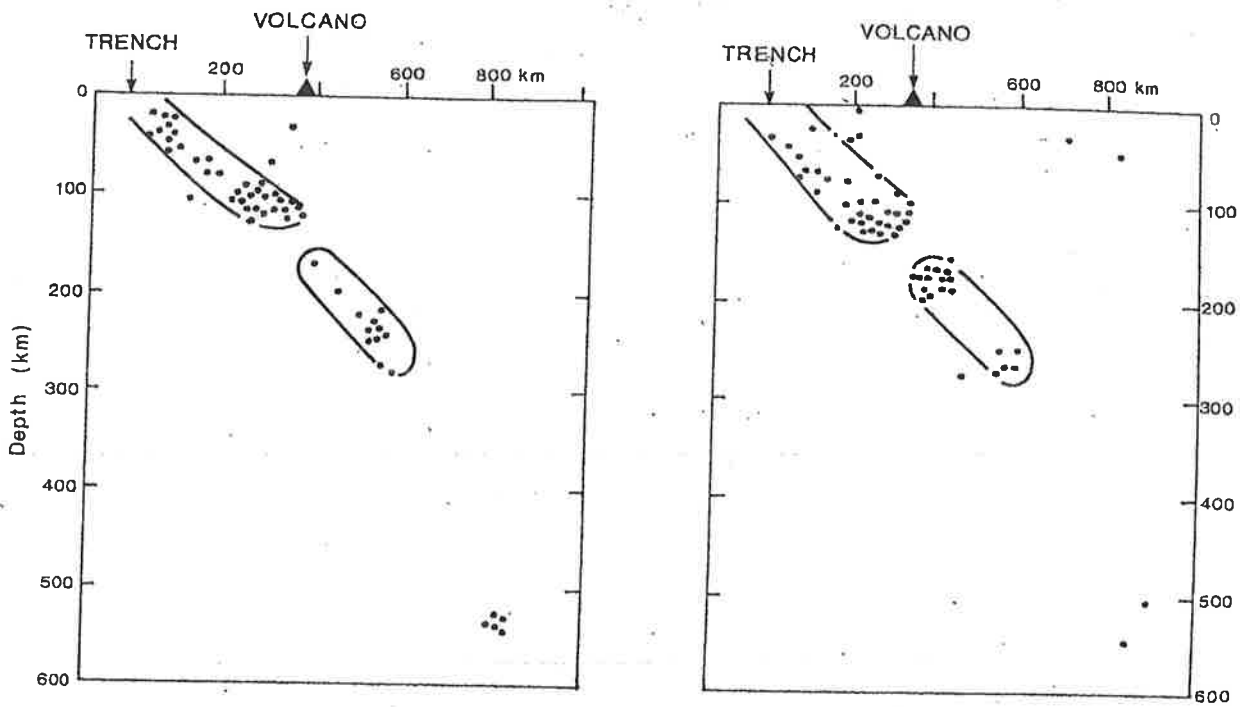


Figure Two sections through the inclined seismic zones of western South America which show a seismic hiatus immediately underneath actual volcanoes (after Hanuš and Vaněk 1978). Dots show the foci of earthquakes > ISC magnitude 4.

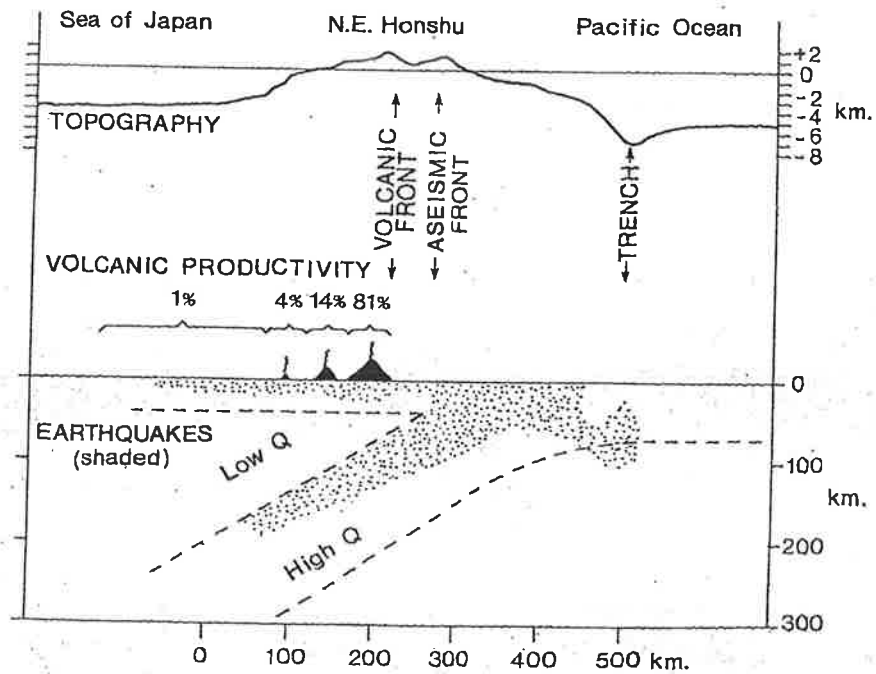


Figure Cross-section through Japan showing the position of the oceanic trench, the distribution of seismic activity, and the location and relative intensity of volcanic activity (after Aramaki and Ui 1982).

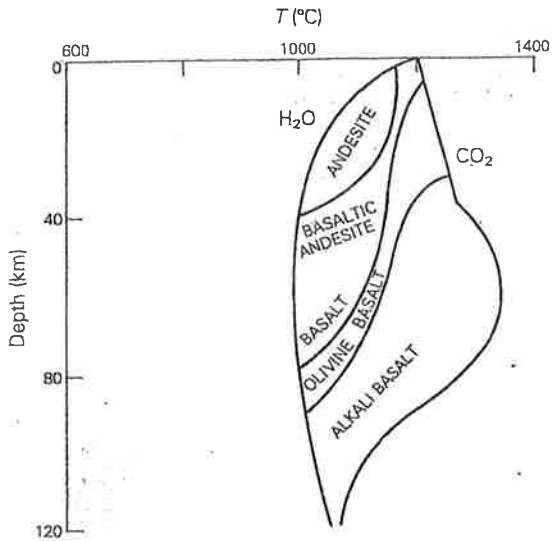
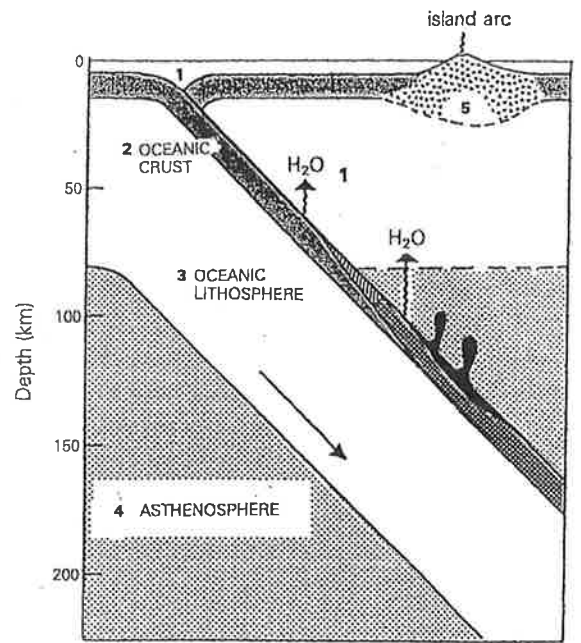
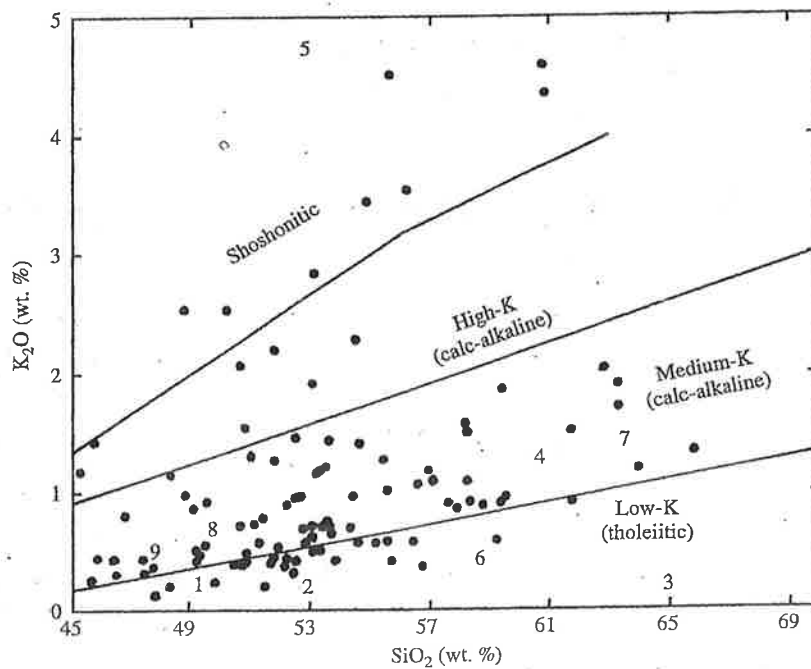


Figure Compositions of near-solidus partial melts in the system lherzolite-H₂O-CO₂ (modified after Wyllie 1982, Fig. 6).



- Key**
- greenschist
 - amphibolite
 - eclogite
 - partial melt
 - 1 sea water
 - 2 oceanic crust
 - 3 mantle of the oceanic lithosphere
 - 4 asthenospheric upper mantle
 - 5 oceanic crustal rocks depressed at the base of the island-arc crust



Basalt | Basaltic andesite | Andesite | Dacite

Volcanic rocks of the Mariana oceanic arc. Numbers 1–8 are analyses from Table 13.6. Compare with volcanic rocks in the Tonga oceanic arc that are low-K tholeiitic (Figure 2.18). (Data from Woodhead, 1989 and Bloomer et al., 1989.)

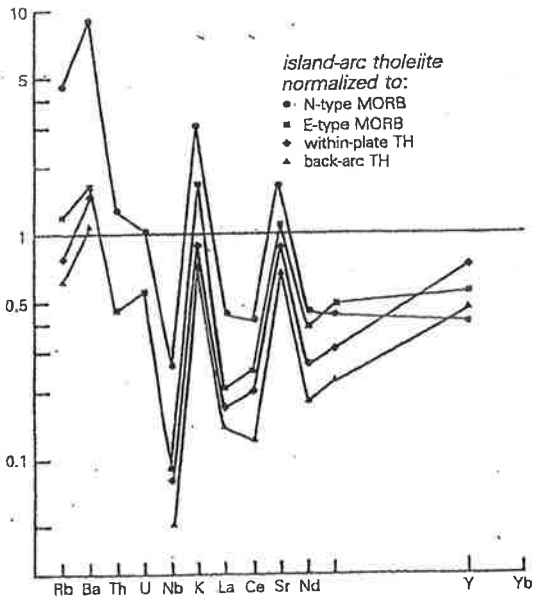


Figure 1 Incompatible element abundances in an island-arc tholeiitic basalt, normalized to a range of tholeiitic basalts from other tectonic settings (data from Table 6.7).

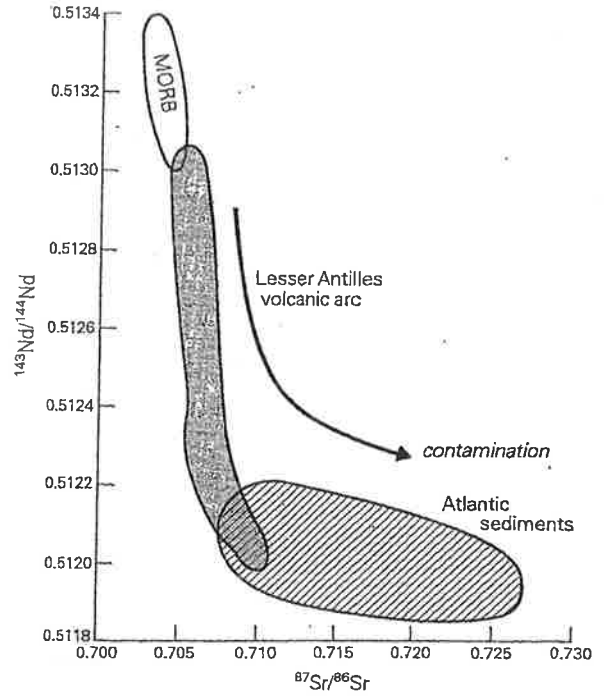


Figure 2 $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for volcanic rocks from the Lesser Antilles island arc (Davidson 1986), relative to the field of Atlantic sediments (White *et al.* 1985) and MORB.

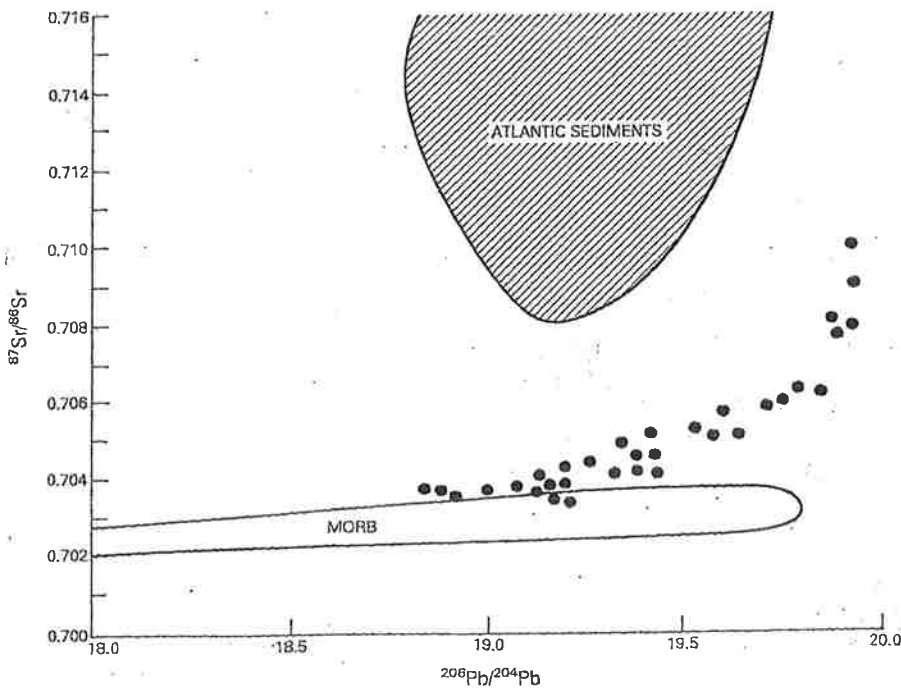


Figure 3 Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for volcanic rocks from the Lesser Antilles. These data reveal the apparent contamination of the magmas with a sedimentary component with $^{206}\text{Pb}/^{204}\text{Pb} \sim 20$, which is slightly more radiogenic than analysed Atlantic sediments. Fields of Atlantic sediments and MORB from White & Dupré (1986); Lesser Antilles data from Davidson (1986) and White & Dupré (1986). (After White & Dupré 1986, Fig. 4.)

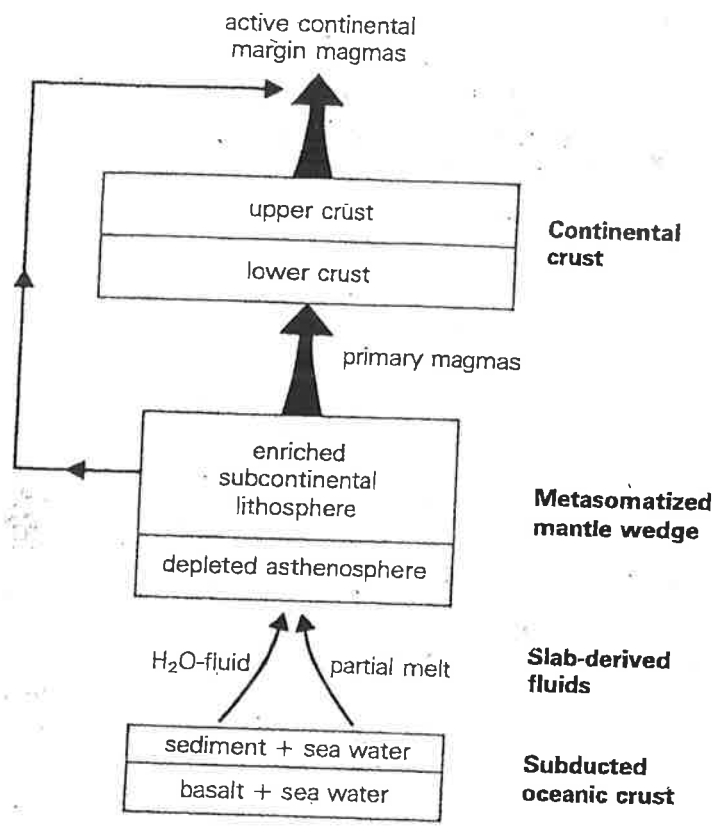


Figure Flow diagram to summarize the source components involved in the petrogenesis of active continental margin magmas.

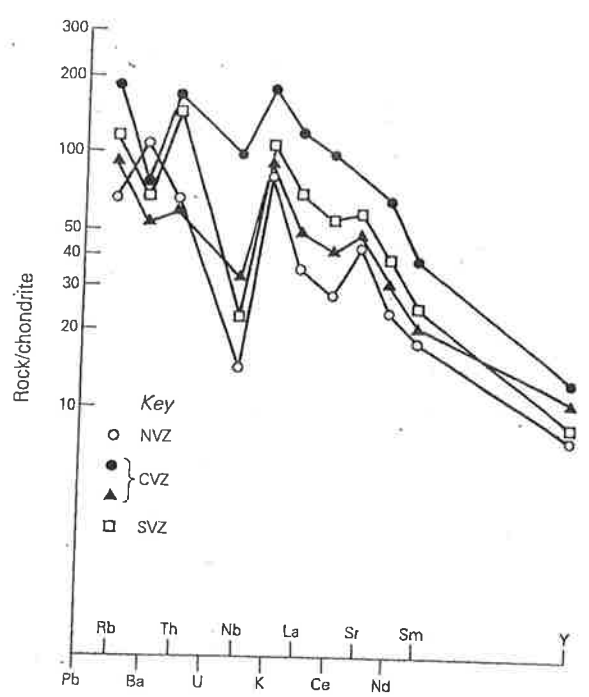


Figure Spiderdiagrams for basaltic andesites from the northern (NVZ), central (CVZ) and southern (SVZ) active volcanic zones of the Andes. Data from Thorpe *et al.* (1984) and Hickey *et al.* (1986). Normalization factors from Sun (1980).

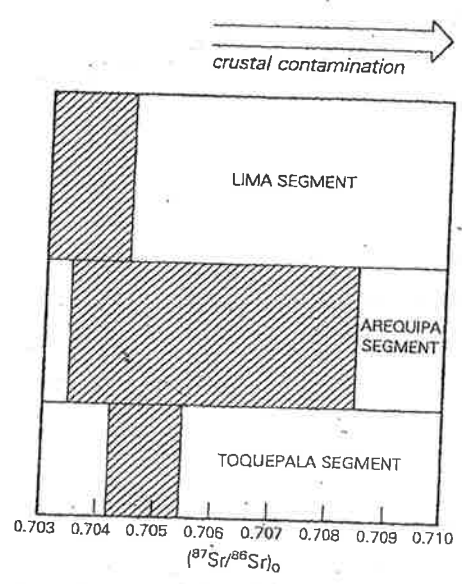


Figure Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio for plutonic rocks from the Lima, Arequipa and Toquepala segments of the Coastal Batholith of Peru (data from Beckinsale *et al.* 1985).

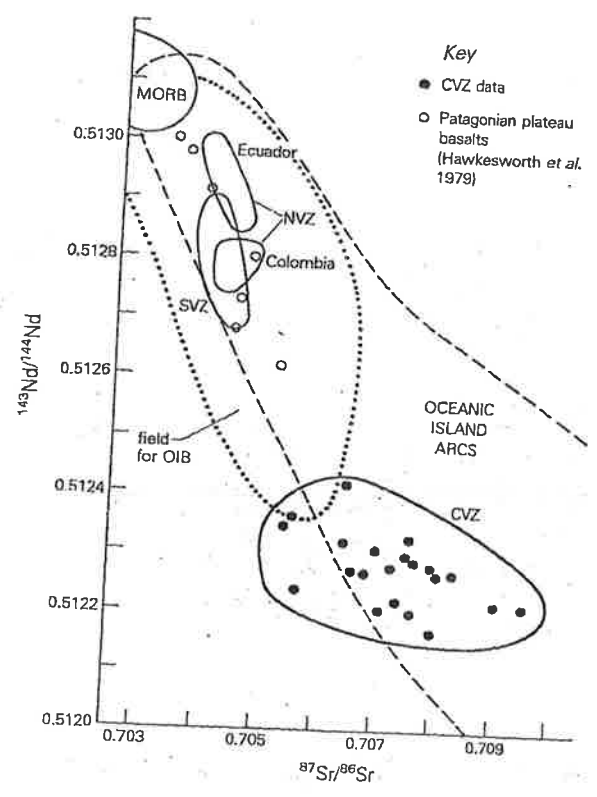


Figure Plot of $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for volcanic rocks from the northern (NVZ), central (CVZ) and southern (SVZ) active volcanic zones of the Andes. Data from Hawkesworth *et al.* (1982), James (1982), Thorpe *et al.* (1984) and Hickey *et al.* (1986). Field of oceanic island-arc volcanic rocks from Figure 6.46 and field of oceanic-island basalts (OIB) from Figure 9.23.

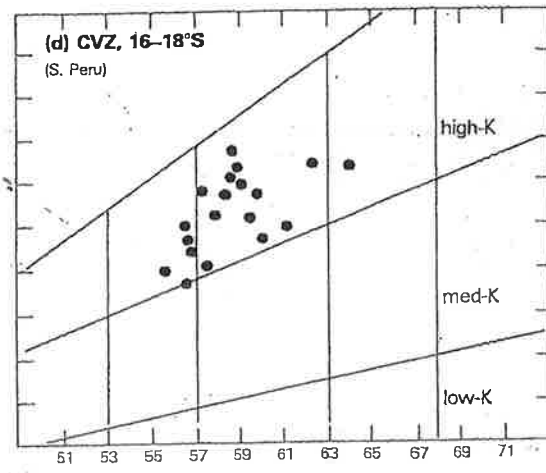
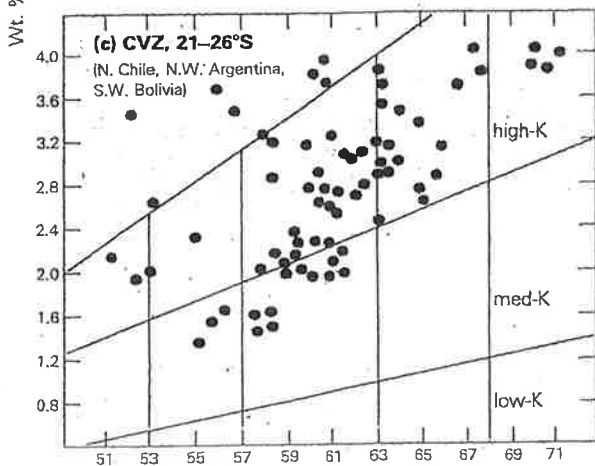
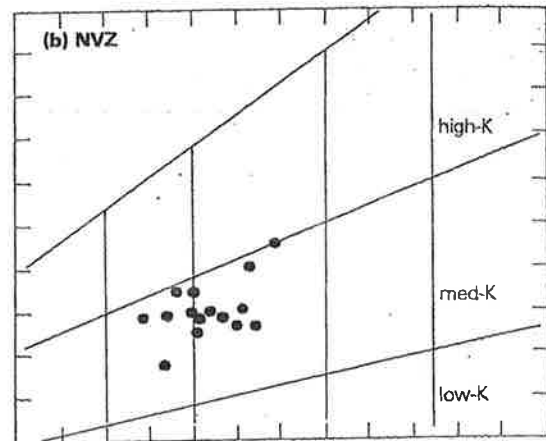
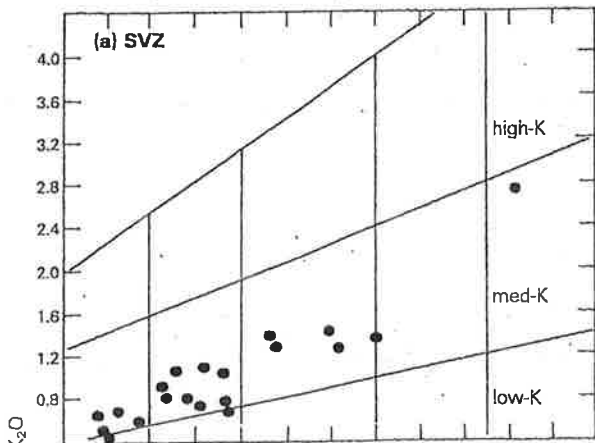
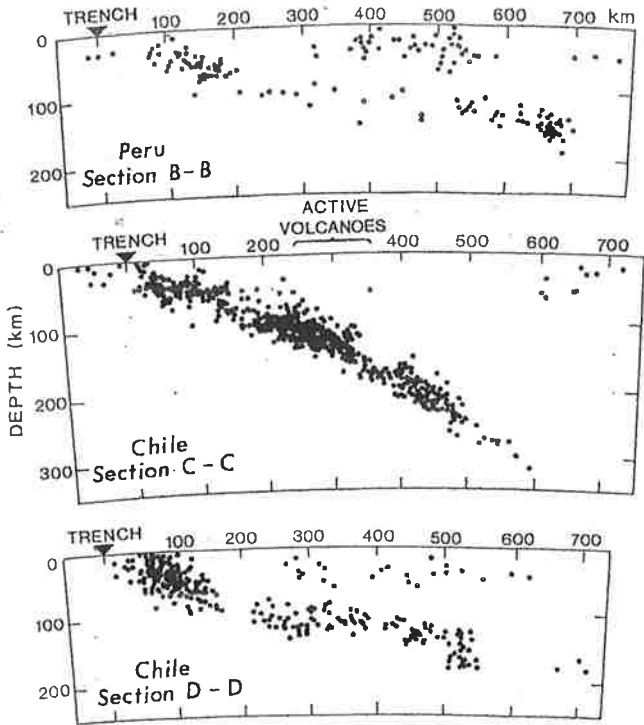
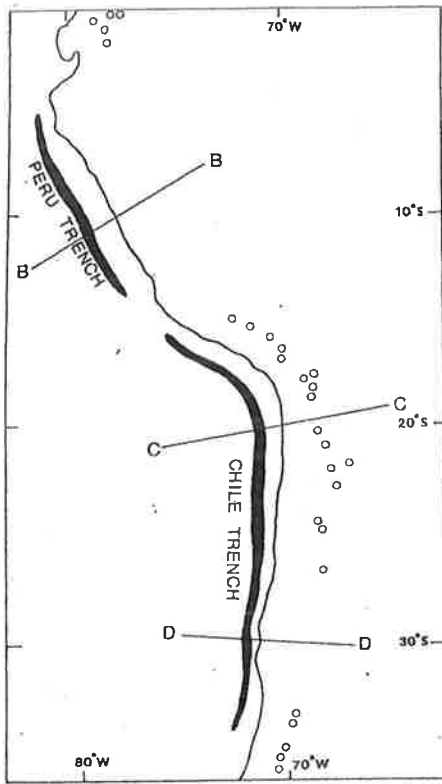


Figure Plots of wt.% K_2O versus wt.% SiO_2 for young volcanic rocks from the northern, central and southern volcanic zones of the Andes. The boundaries between the low-, medium- and high-K fields are those of Peccerillo & Taylor (1976) (after Hannon *et al.* 1984, Fig. 2, p. 810).

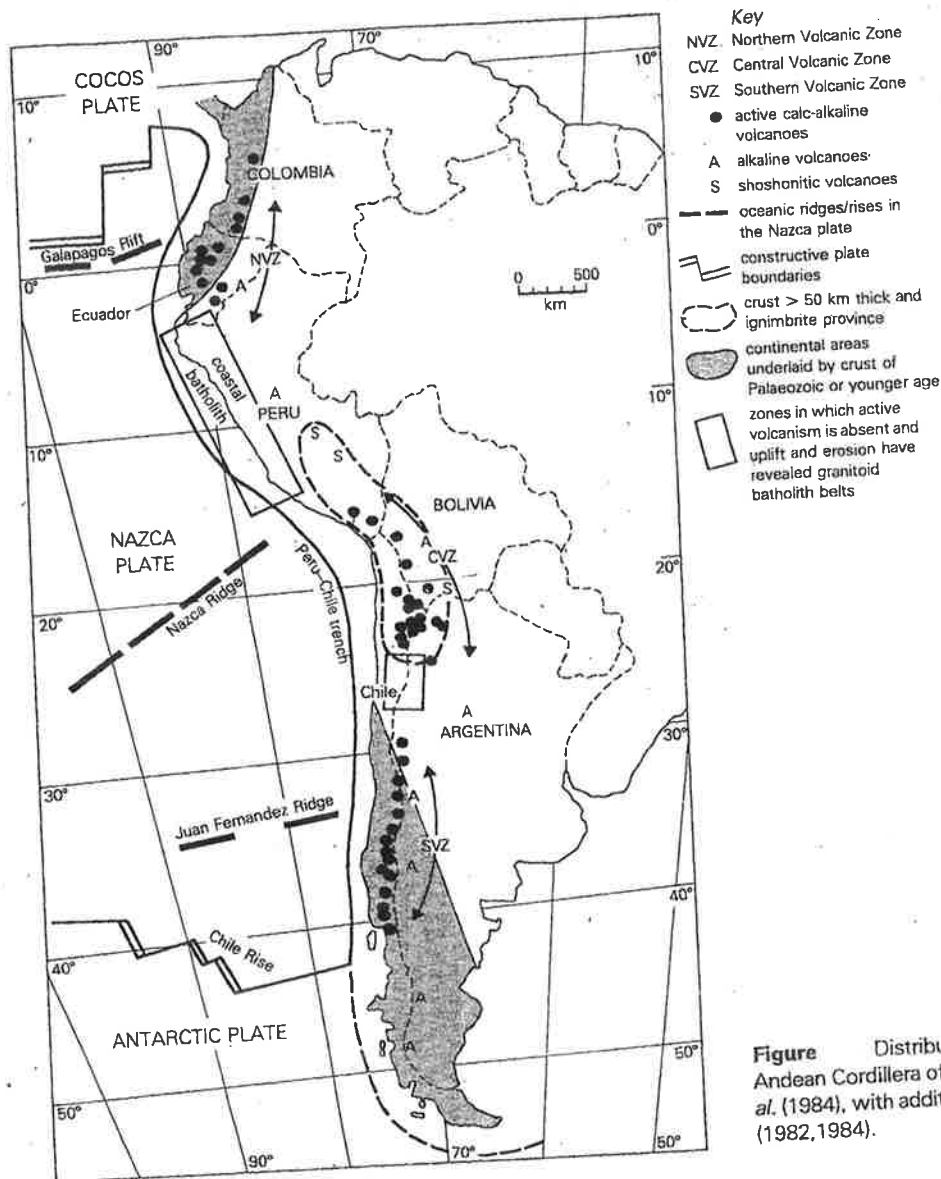
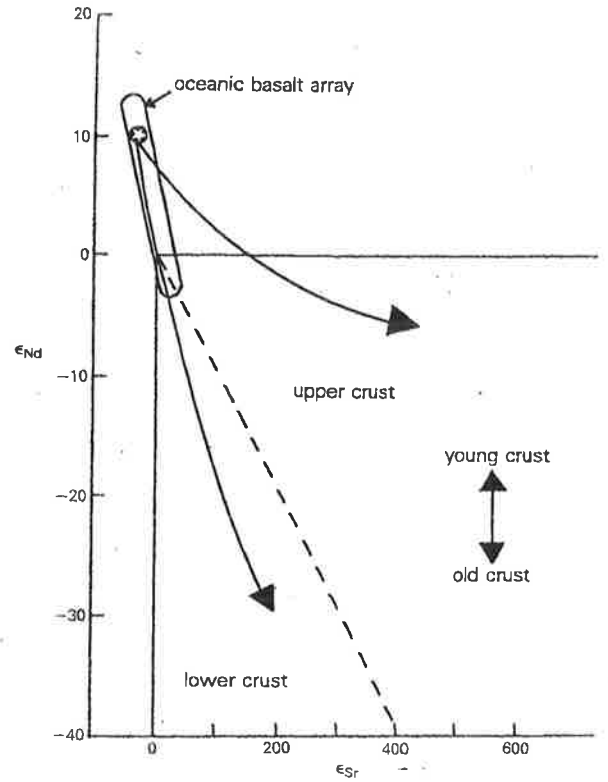
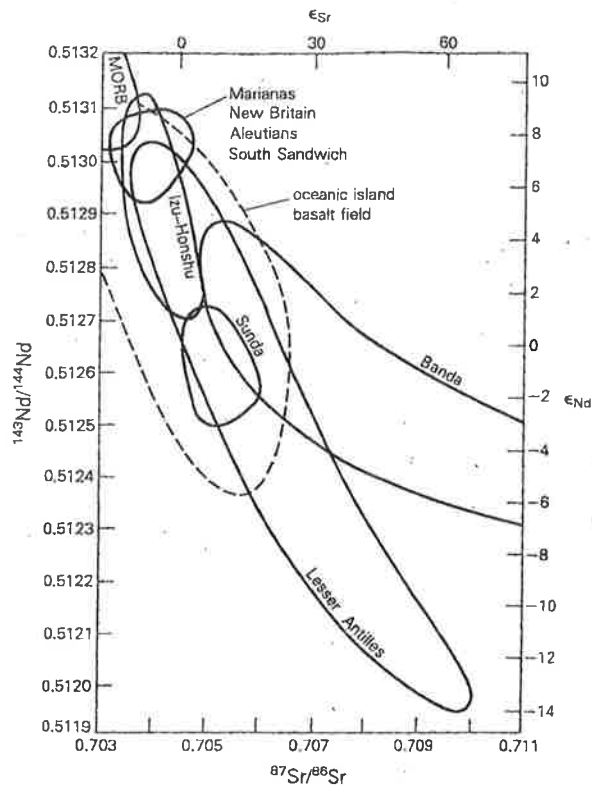


Figure Distribution of active volcanoes along the Andean Cordillera of South America (after Harmon *et al.* (1984), with additional data from Thorpe *et al.* (1982, 1984).

Table Tectonic and geological characteristics of the late Cenozoic volcanic zones of the Andes (after Harmon *et al.* 1984, Table 1, p.805).

	SVZ (45–33°S)	CVZ (26–18°S)	NVZ (2°S–5°N)
dip of seismic zone	<25°	c. 25–30°	c. 20–30°
depth to seismic zone	c. 90 km	c. 140 km	c. 140 km
maximum crustal elevation	2000–4000 m	5000–7000 m	4000–6000 m
crustal thickness	30–35 km	50–70 km	40 km
crustal age	Mesozoic–Cenozoic	Precambrian–Palaeozoic	Cretaceous–Cenozoic
composition of volcanics	basalt with minor andesite and dacite	andesite–dacite with dacite–rhyolite ignimbrites	basaltic andesite to andesite
SiO ₂ (wt.%)	50–69	56–66	53–63
K ₂ O (wt.%)	0.4–2.8	1.4–5.4	1.4–2.2
δ ¹⁸ O	medium-K series	high-K series	medium-K series
⁸⁷ Sr/ ⁸⁶ Sr	5.2–6.8	6.8–14.0	6.3–7.7
²⁰⁶ Pb/ ²⁰⁴ Pb	0.7037–0.7044	0.7054–0.7149	0.7036–0.7046
²⁰⁷ Pb/ ²⁰⁴ Pb	18.48–18.59	17.38–19.01	18.72–18.99
²⁰⁸ Pb/ ²⁰⁴ Pb	15.58–15.62	15.53–15.68	15.69–15.68
	38.32–38.51	38.47–39.14	38.46–38.91



Variation of $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for oceanic island-arc volcanic rocks compared to the spectrum of oceanic basalts (MORB + OIB) (after Arculus & Powell 1986, Fig. 4, p. 5916).

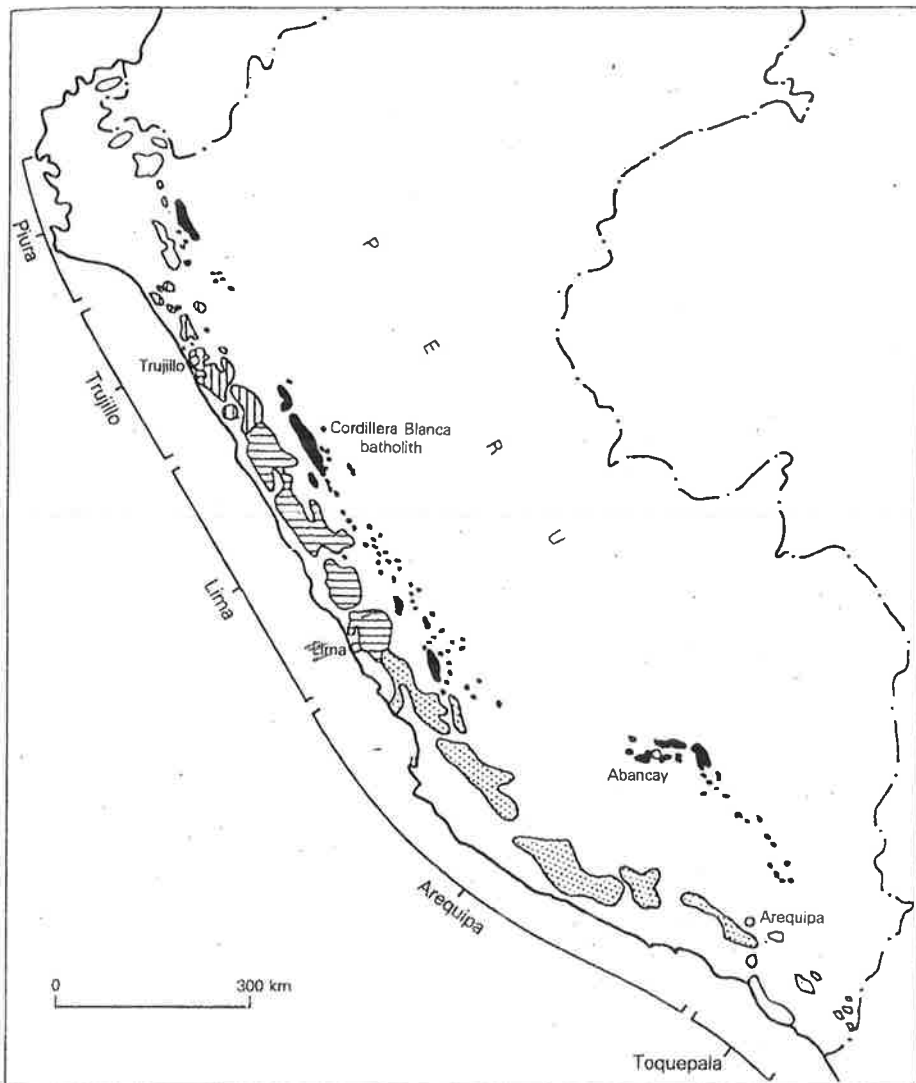
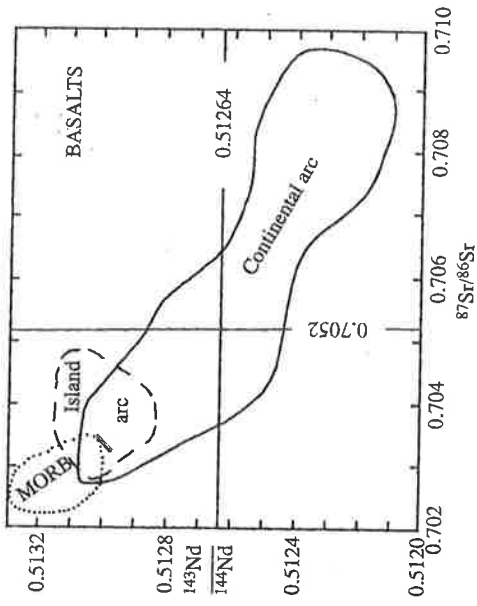
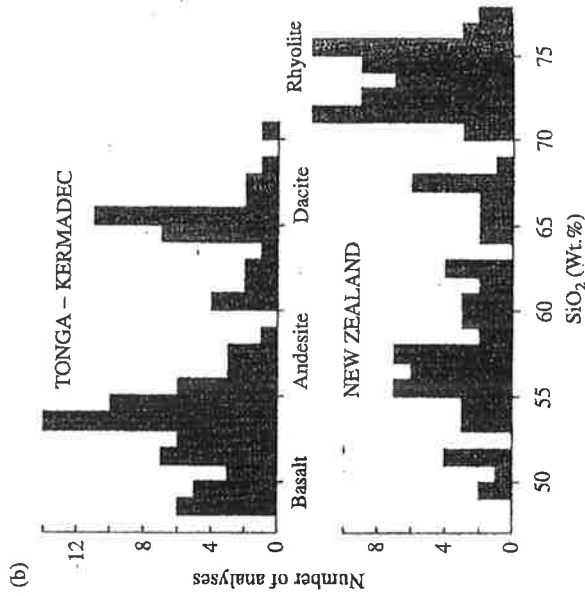


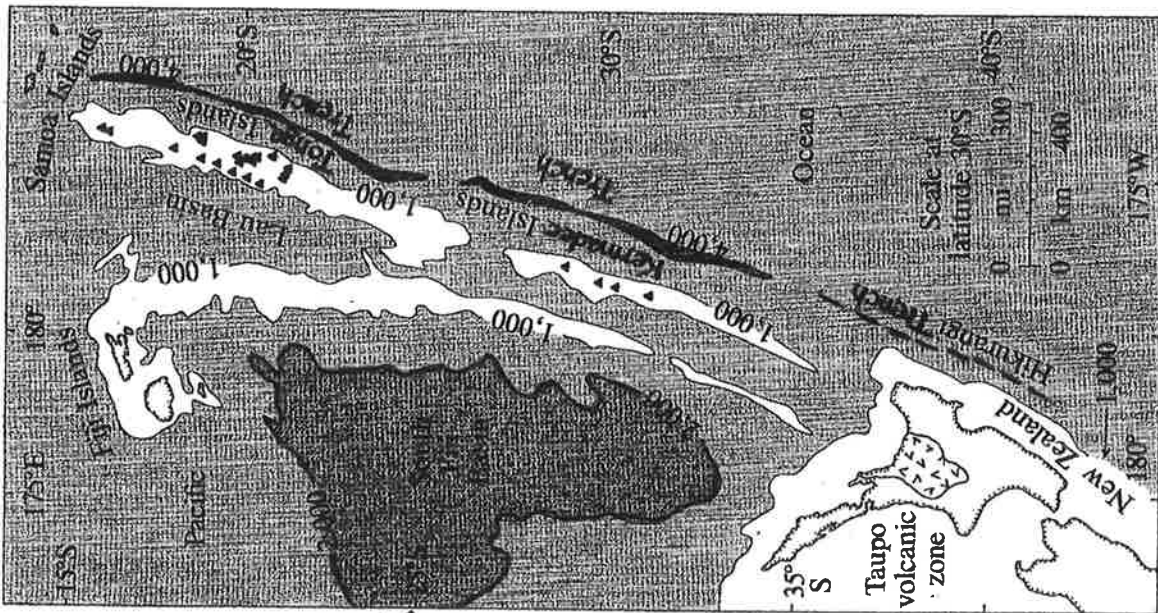
Figure The segmentation of the Cretaceous Coastal Batholith of Peru (shown by various ornaments or blank): Also shown in black is a belt of Cenozoic stocks and batholiths paralleling, but to the landward side of, the Coastal Batholith (after Pitcher & Cobbing 1985, Fig. 3.2, p. 22).



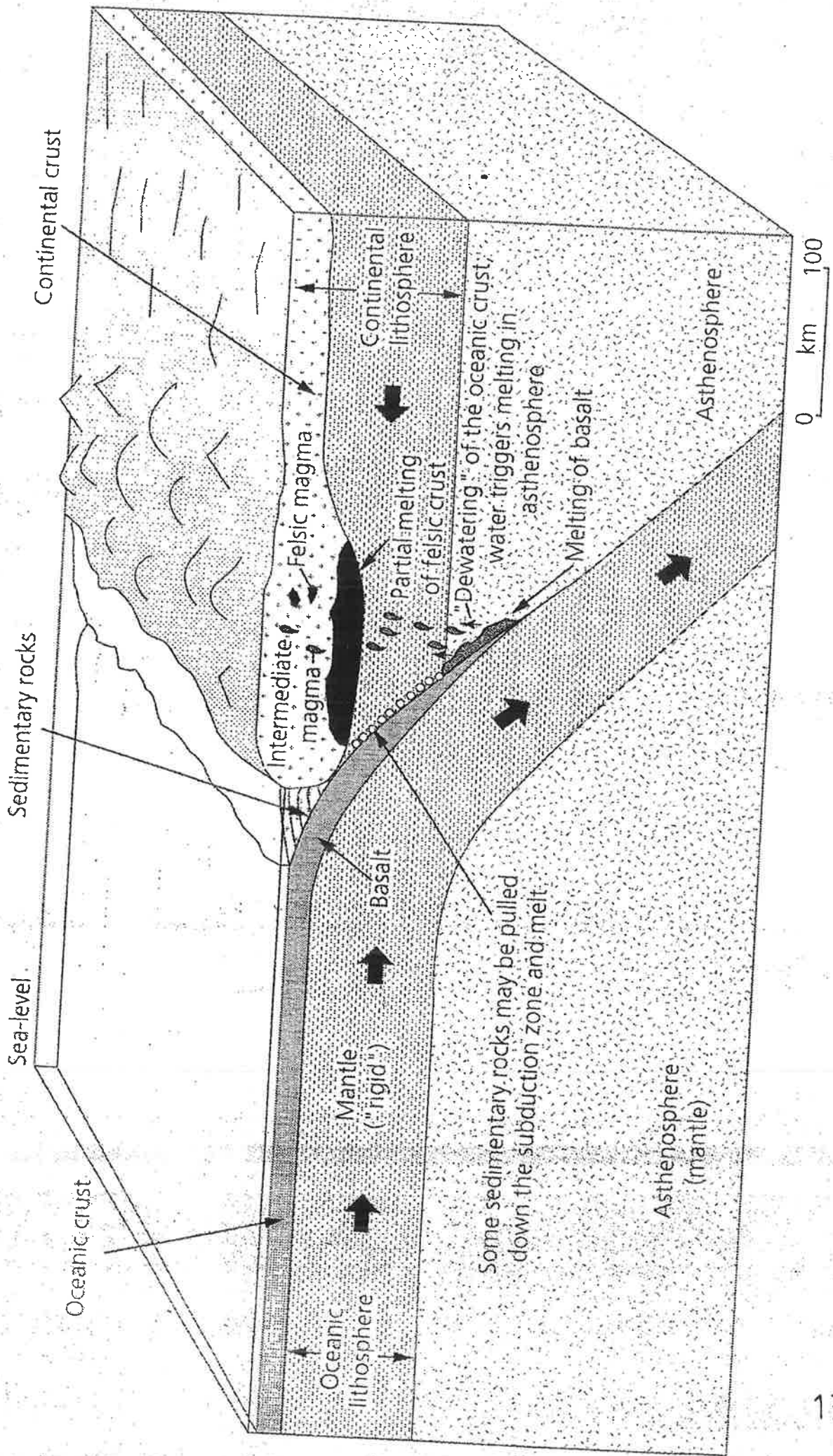
12.31 Nd and Sr isotope ratios in arc basalts compared to MORB. Basalts from western Pacific island arcs are slightly more radiogenic than MORB because of the slab-derived aqueous fluid component, whereas continental arc basalts (Japan, Philippines, New Zealand, Ecuador, Central America, Lesser Antilles) range to much more radiogenic ratios because of interaction with highly radiogenic old continental crust in which $^{143}\text{Nd}/^{144}\text{Nd}$ can be 0.5110 and $^{87}\text{Sr}/^{86}\text{Sr}$ 0.900. (Redrawn from Tatsumi and Eggin, 1995.)



(b) Tonga-Kermadec-New Zealand volcanic arc and arc rocks in the southwestern Pacific. (a) Volcanic islands indicated by filled triangles. Bathymetric contours are in fathoms (1 fathom = 1.83 m). For a more detailed, larger-scale map of the North Island of New Zealand see Figure 13.27. (b) Frequency distribution of silica in analyzed rocks from the Tonga-Kermadec island arc and from the North Island of New Zealand. Tonga is chiefly basalt and andesite; sparse dacite is overrepresented. In New Zealand, rhyolite is estimated to be about 20 times more voluminous than andesite. (Redrawn from Ewart et al., 1977.)



→ Fijian basin



Evolved igneous rocks- Granites and Rhyolites

The bulk of the continental crust is made up of crystalline rocks rich in Si + Al, with minor Fe, Mg, Ca. (Because of this it used to be called the **sial**, to distinguish it from the ocean crust - **sim** - which contained much more Mg). It was generally called **granitic**, but really has a more intermediate composition, with an average chemistry of a granodiorite.

The granite controversy - "Granites and Granites"

Throughout the history of geology these great masses of granite have caused controversy, because of their extent, and the fact that they appeared to grade into metamorphic rocks (gneisses) with no recognisable intrusive contacts. Much of the debate in the 20th Century was between those who believed granite was a metamorphic rock (metamorphosed sediment) which had got hot enough to melt, and those who thought it crystallised directly from an igneous magma. It was not until 1958 that Bowen and Tuttle proved conclusively that granite (*sensu stricto*) is a minimum-melt composition, which will be produced from the melting of any suitable assemblage of mineral grains, if the temperature is that of the melting point of quartz+feldspar. This liquid contains Si+Al+K+Na+H₂O, and is the same composition as the residual melt from basalt fractionation. Therefore, granite can be either the residual product of a fractionated igneous magma, or the first-formed liquid from melting of continental crust.

Granite petrography

Granite is a holocrystalline rock (completely crystallised) with a texture known as "hypidiomorphic = subhedral" - which means that none of the crystals have their own shapes (idiomorphic or euhedral) - all are subhedral to anhedral because they all crystallise at the same time and each interferes with the growth of its neighbours. The result is a mosaic with completely irregular boundaries between crystals.

Both mineralogy and chemistry support a distinction between: calc-alkaline granites and alkaline granites:

Granite (*sensu stricto*) is made up largely of alkali feldspar and essential (more than 30%) quartz, with minor mafic minerals, mica and hornblende, with a restricted chemical composition rich in SiO₂ and alkalis (K₂O + Na₂O). It ranges from the common **calc-alkaline granite** [which generally carries two feldspars - a K-feldspar (microcline) and a Na-feldspar (albite/oligoclase)] to the much rarer **alkaline granite**, the latter rocks containing one mixed (K+Na) feldspar which has unmixing to a perthite, together with an alkali amphibole such as riebeckite, or alkali pyroxene such as aegirine or aegirine.

Calc-alkaline granites

Calc-alkaline granite is found in association with a wide range of other calcalkaline plutonic rocks, in the series - Diorite, Tonalite, Granodiorite, Granite, all holocrystalline with dominant feldspar and minor ferramagnesian minerals, and with varying quantities of quartz. Rocks of this series make up huge Batholiths which may cover hundreds of km².

Calc-alkaline granites are wet (high H₂O content), and therefore cooler (H₂O lowers the solidus). As a consequence they usually have two feldspars (microcline and albite) besides mica, and hornblende.

The feldspar phase diagram shows the reason: the liquidus for wet granite melts is at a lower temperature than that of dry ones, thus the field of a single mixed Na+K feldspar is intersected by the solvus curve, and two feldspars crystallise from the start.

Alkaline granites

Alkaline granites are dry (little H₂O), hotter (above solvus temperature) with only one feldspar, Na-amphibole and Na- pyroxene. Granite intrusive complexes in continental crust are usually of this type. Intrusives on ocean islands are also alkaline (e.g. Gran Canaria !)

The feldspar phase diagram shows that dry liquidus is at a higher temperature, and the first feldspar to crystallise is anorthoclase, a single Na+K feldspar. On cooling this composition passes through the solvus and the crystals exsolve into two components, one K-feldspar, the other Na-feldspar. This perthite may have more of either the K or Na feldspar, with veinlets of the other in it.

Classification of granites

The accepted mineralogical classification is that of Streckeisen, which is based on proportions of quartz, K-feldspar and plagioclase. This classification does, however, little to help identification of the source of the granite. The first modern advance in this was by Chappell and White (1974). Their study of granites in SE Australia showed it was possible to distinguish melts derived from igneous sources (**I-type**) in the mantle or lower crust-, from those derived from upper crustal rocks which had been through a sedimentary cycle (**S-Type**).

Since then other types have been added: **M-Type** from mantle sources with no or very little crustal input, and **A-Type** (anorogenic, often alkaline), found in continental crust away from subduction zone influence.

I-type granites:

S-type granites

high Na ₂ O > 3.2%	low Na ₂ O < 3.2%
Mol Al/ C+N+K < 1.1	Mol Al/C+N+K > 1.1
CIPW-norm < 1% norm. corundum	> 1% norm. corundum
low ⁸⁷ Sr/ ⁸⁶ Sr	high ⁸⁷ Sr/ ⁸⁶ Sr
low δ ¹⁸ O	high δ ¹⁸ O
H ₂ O poor	often gnt present, H ₂ O rich

I-type are, for example, the Cordilleran Batholiths emplaced in the closing phases of active subduction under continental plate margins. The magmas are produced by partial melting of the underplated continental crust - underplated by basalts rising from the subduction zone and the mantle above it. Their source rocks have igneous signatures in mineralogy, chemistry and isotopic ratios.

S-Type granites: Commonly in orogenic settings; Melting owes nothing to mantle melting but is all crustal due to heat equilibration of the thickened crust. Such magmas are water-rich and they have a high proportion of felsic minerals (leucogranites = fsp+ muscovite +/- garnet) and are per-aluminous because much of the source rock is sedimentary (e.g. Himalayan leucogranites → continent/continent collisions). Sometimes relics of the protolith are found in S-type granites which are termed 'restites'.

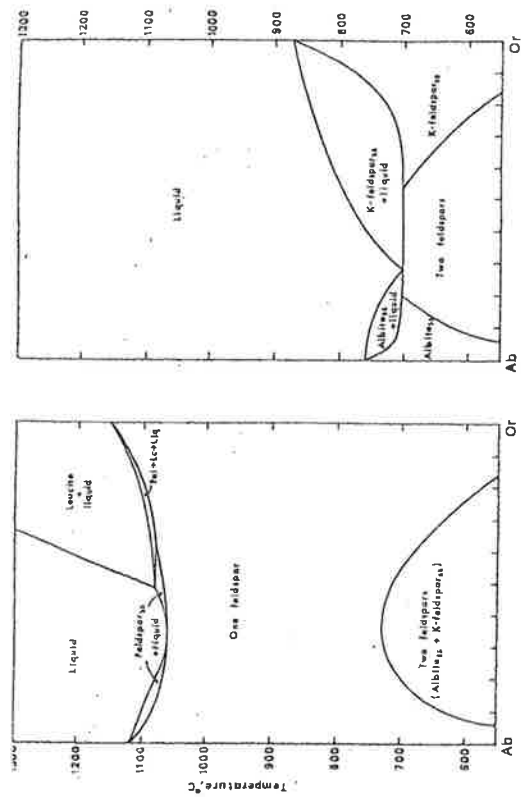


Figure 253. The system quartz-orthoclase-albite-water at $P_{H_2O} = 1$ kilobar and 5 kilobars (after Tuttle and Bowen 1958; Luth et al. 1964).

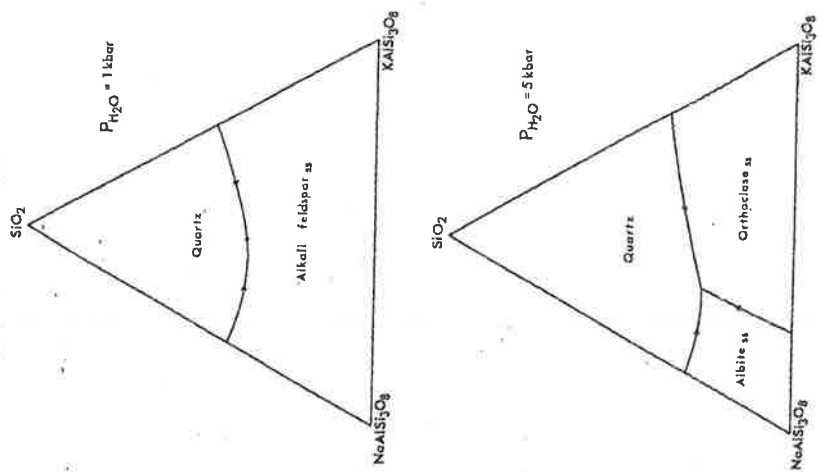
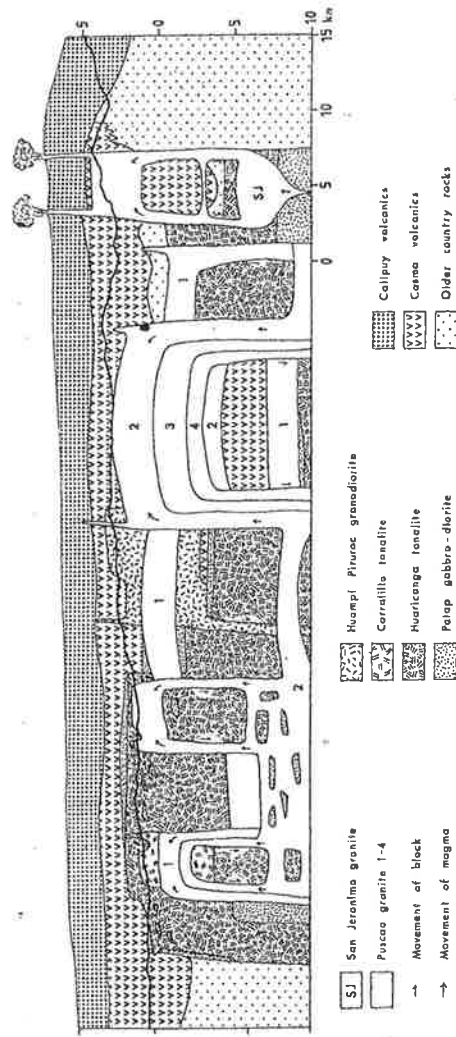
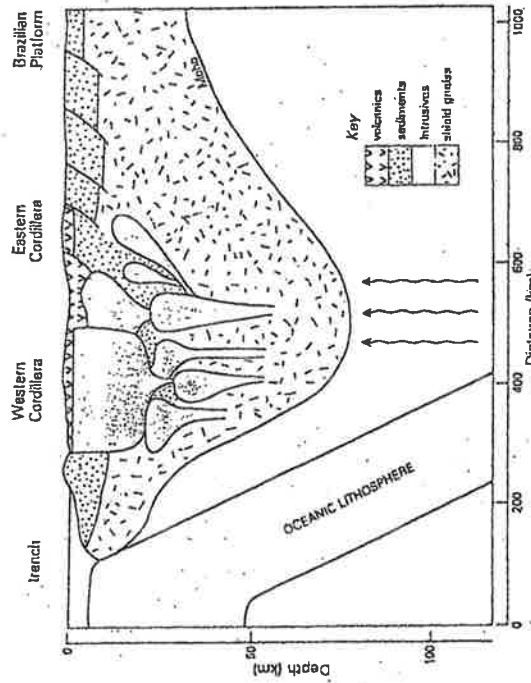


Figure 7.7 Schematic cross section through the central Andean active continental margin to show the crustal structure (x5 vertical exaggeration). Arrows indicate the direction of magma and volatile streaming from the downgoing plate (after Brown & Mussel 1981, Fig. 9.6, p. 166).



- [SJ] San Jeronimo granite
- [Pattern] Huampí Piruro granodiorite
- [Pattern] Carrizillo tonalite
- [Pattern] Huacacanga tonalite
- [Pattern] Patac gabbro-diorite
- [Pattern] Callipuy volcanics
- [Pattern] Canoa volcanics
- [Pattern] Older country rocks
- [Arrow] Movement of block
- [Arrow] Movement of magma

I+S Types may occur together e.g. as post-collision Batholiths - such as the Scottish and Irish Caledonide plutons. Following the plate closure there is commonly a mantle decompression with uprise of heat plus basic magmatism which re-melts the lowest crustal rocks. Some of these are metasediments which have been at the earth's surface in contact with the atmosphere, and undergone weathering, erosion and deposition from water. These have different chemistries and isotopic signatures, and produce melts with distinctive S-type characters. The combination of fresh igneous and reworked sedimentary sources give the I+S character.

A-Type - Anorogenic granites - are much smaller, occur in central complexes as ring dykes and stocks or plugs, are associated with rhyolitic eruptives, and tend to be alkaline in chemistry. They are found on continental crust and appear to relate to incipient cracking and rifting of the crust, which is often a precursor to the opening of new oceans. The heat source is probably plume related and the magma may be generated by melting of the sub-continental incompatible-enriched mantle followed by prolonged evolution in high level sub-volcanic magma chambers.

M-Types are characterised by isotopic compositions that resemble mantle values. They are generally associated with oceanic settings (MORB) and there they occur as plagiogranites. Some Island Arc plutons also exhibit M-type chemistry. These granites are purely derived from mantle melts.

Emplacement and field relations

Many of the problems of interpretation encountered in mapping granite bodies arose from the many settings in which granitic rocks appear - ranging from sharply intrusive bodies, often with contact-metamorphic (thermal) aureoles, to apparently conformable patches of granite in high-grade metamorphic rocks of similar composition but quite different texture (migmatitic gneisses). To the early workers it was apparent that one was being converted into the other. In general there was a view that the metasediments were metasomatised and "granitised". This process solved the difficulty of explaining how large masses of granite could be emplaced without disturbing (pushing aside) the host rocks.

Uprise and emplacement of Granitoid Batholiths

First it is necessary to correct the old concept of Batholiths being enormous masses of magmatic rock diapirically displacing huge volumes of crust. This was the space problem that troubled so many geologists in the past.

Until very recently, profiles of gigantic batholiths like the Californian Sierra Nevada or Peruvian coastal batholiths, were given depths of thousands of feet - sometimes extending continuously almost down to the base of the crust with roots of migmatite in high grade metamorphic crustal rocks.

However, modern detailed mapping aided by air photography has shown that they are not huge uniform masses but are made up of aggregates of numerous smaller plutons - and furthermore, these have a discoid or sheet-like form. They have collected at shallow crustal depths, sometimes so near the surface that cauldron collapse and rhyolite lava and ash eruption has occurred (as in the Peruvian batholiths). They still represent huge quantities in total, and various mechanisms have been proposed to explain how the magmas could rise so abundantly.

Forceful emplacement vs permitted emplacement

Permitted emplacement

One suggestion was that deep penetrative shear zones extending to the lower crust/mantle melt zone would provide conduits. The ability of these shear zones to provide pathways for magma was not clear, but seemed feasible in the deeper ductile crustal zones where the difference between the viscosities of magma and country rock were not great.

The concept was refined by Donny Hutton (1988, *Trans.Roy.Soc.Edin.*) who showed that in addition to the deep shears, fractures in the cool brittle upper crust could also provide space. Suitable structures were produced during the Caledonide orogeny in Scotland and Ireland.

Other modern workers have confirmed the importance of pre-existing structures such as strike-slip faults and shears (Holdsworth et al 1999, *J.Geol.Soc.*).

Forceful emplacement

Where the viscosity contrast is slight - as in partial melt zones, there is little difficulty in moving magma masses upward as the wall-rocks can close behind them on the "lava lamp" principle.

However, higher in the crust the wall rocks become cooler, less ductile, (more viscous), less able to deform and spread into the spaces. At the same time the magma cools, crystallises and becomes more viscous. Here the governing factors are buoyancy and increasing volatile partial pressure in the magma which exerts a stress on the wall rocks. Repeated injection of granite often enlarge granite plutons by a process called ballooning, i.e. the successive pulses of granite that blow up a pluton and produces a characteristic chemical zonation across a granite complex. Then massive wall rock updoming can occur (e.g. the Arran granite).

Stoping

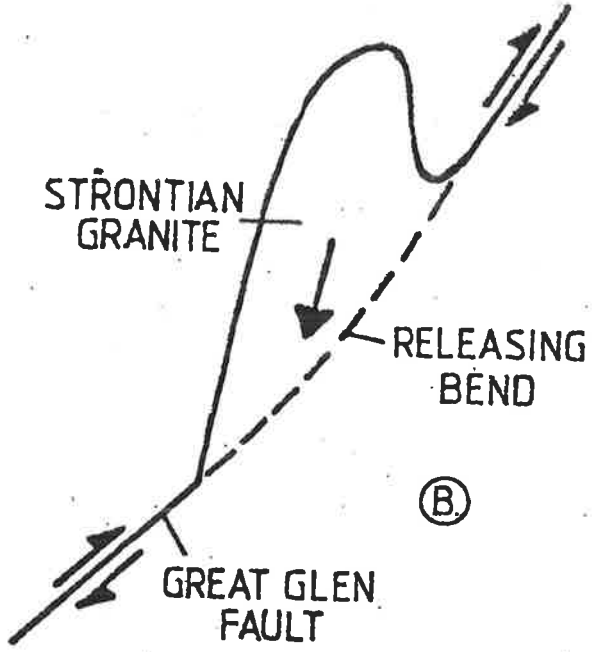
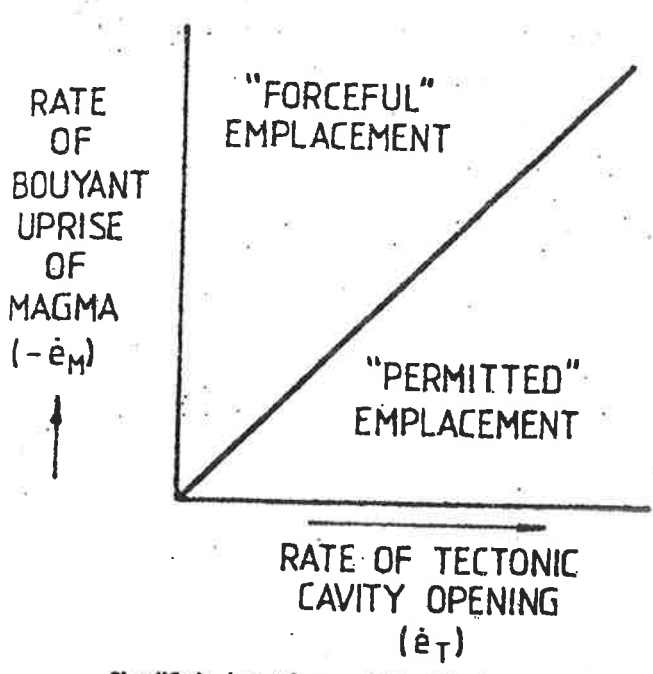
At very high levels the crust can often only deform in a brittle manner by fracturing, and the magma, now a plastic mass of crystals and some residual liquid, can only advance by occupying tectonic cavities, and by cracking off and enclosing blocks of the wall and roof (stopping).

Rhyolites

Rhyolites are essentially the extrusive equivalents of granites. Shallow level magma chambers that form granite at depth may erupt a percentage of the contained magma as rhyolites or zoned rhyolite-mafic deposits. These magmas are often very viscous and can no longer erupt as lava - they erupt as ash-flows or ignimbrites.

Ignimbrites are often vertically zoned. This is thought to be a function of withdrawal depth that increases with the proceeding eruption. Evacuation of such a reservoir commonly leads to caldera subsidence.

The mineralogy and geochemistry of rhyolites reflects the composition of granites in many ways but differs in that crystallisation was interrupted by eruption. Hence, the crystallisation is incomplete but shows a very similar phase assemblage than associated granites.



Simplified view of the relationship between magma related buoyancy forces and strain rates and tectonic 'cavity creating' rates leading to a spectrum of emplacement types with two basic end members.

(A) Summary diagram of bitotite granite emplacement mechanism showing diminution of dextral shear northwards into arcuate extensional zone of sheeting; (B) general siting model for the Strontian complex (tonalite, granodiorite and biotite granite): dextral shear on the Great Glen Fault creates an extensional component at a releasing bend; this pulls a flat segment out of the core of a pre-existing Caledonian synform; magma comes up the releasing bend hole and emplaces sideways into the synform cavity.

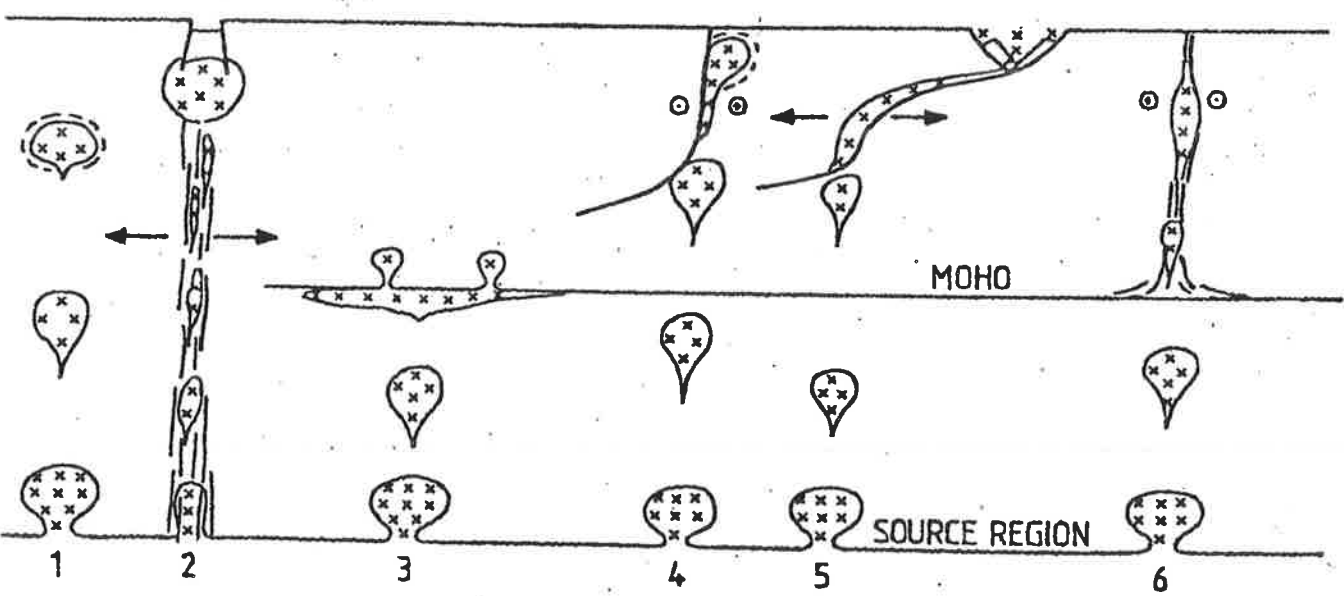
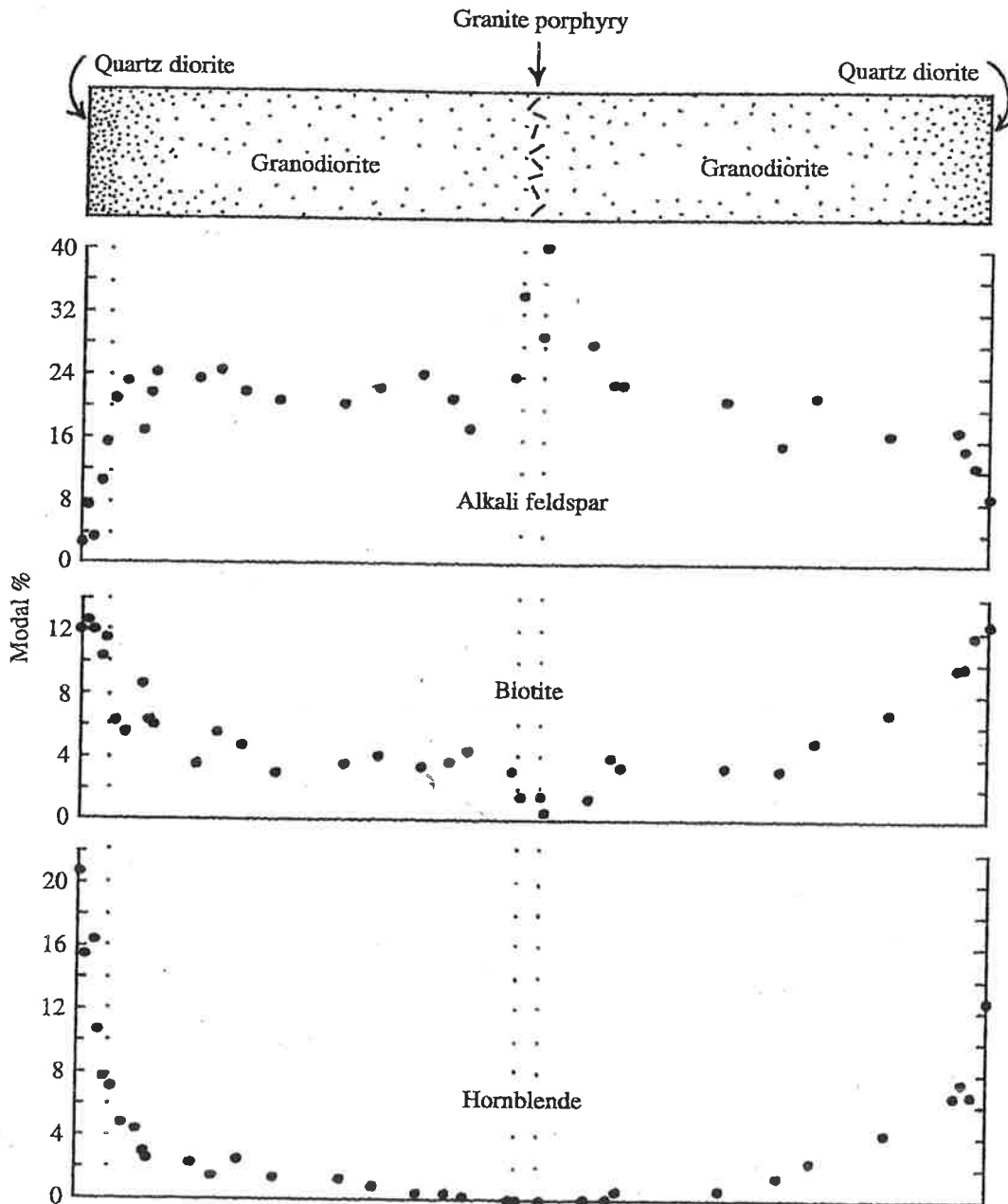
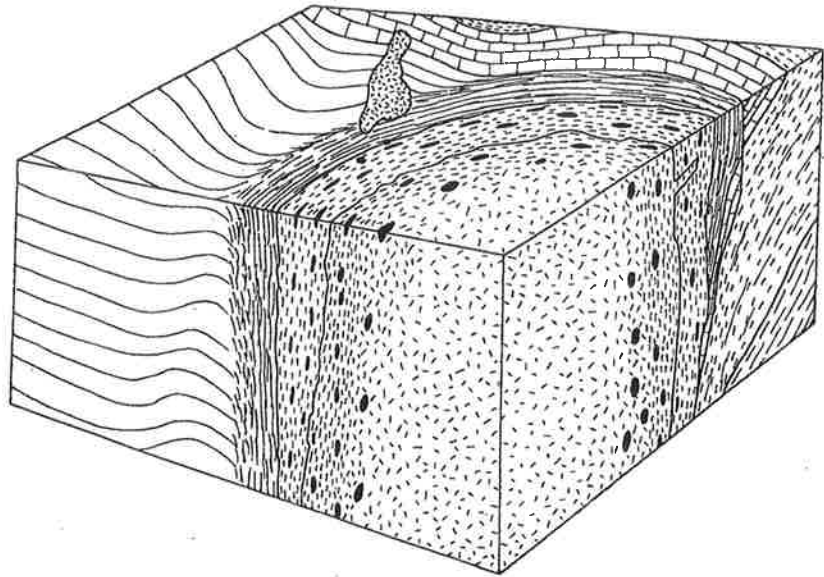
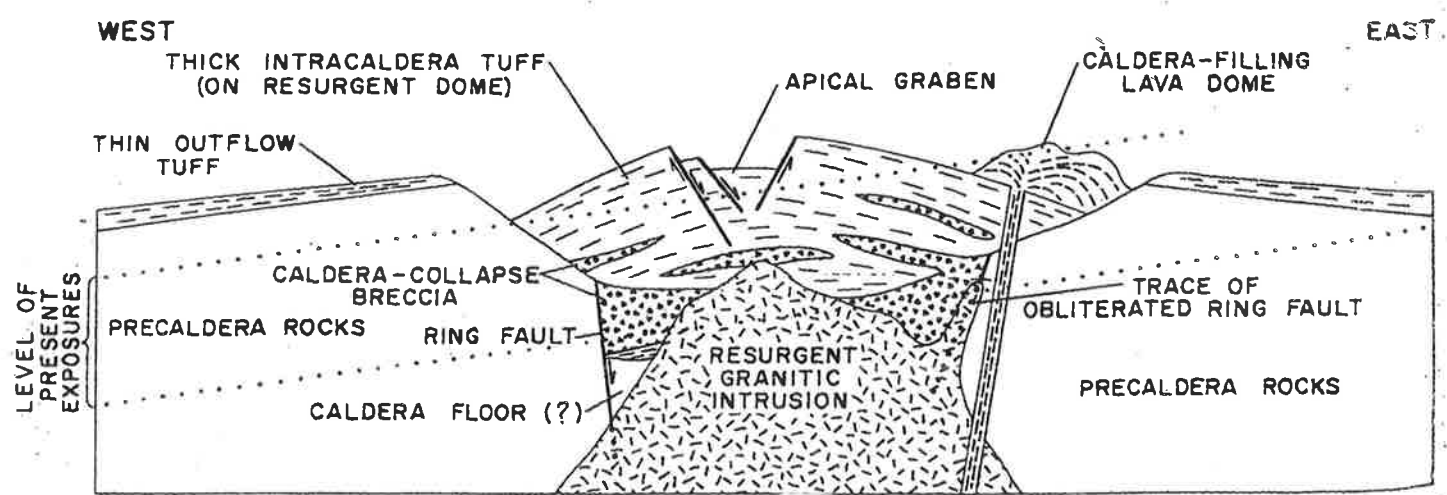
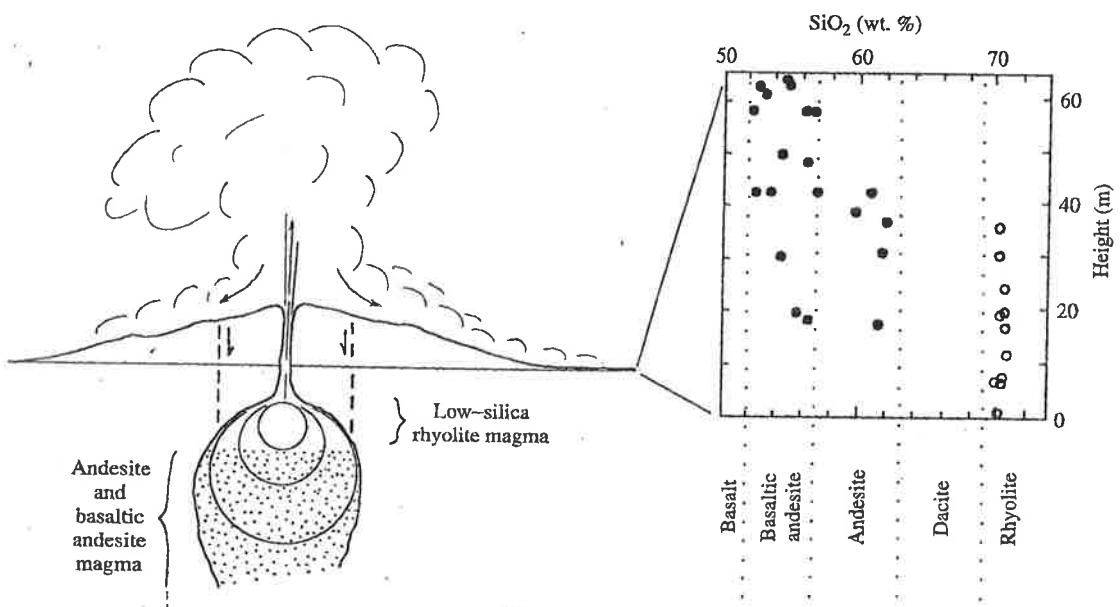
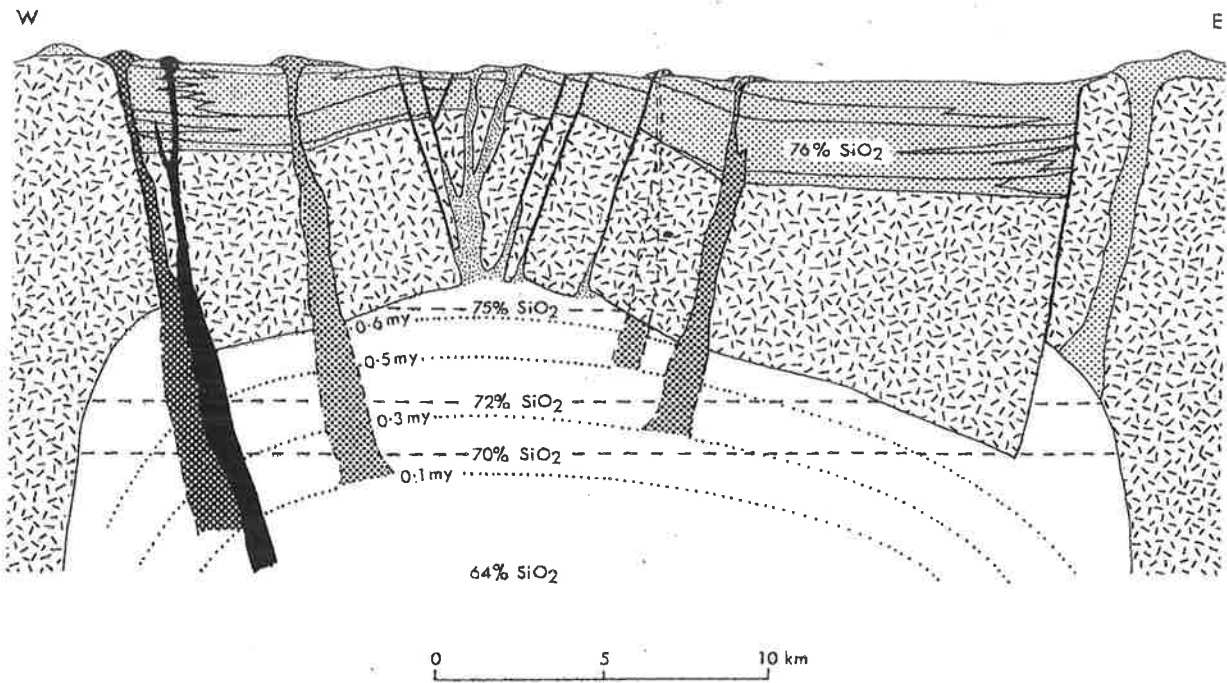


Figure 7 Six generalised modes of ascent and emplacement of granitoids; all begin with initial diapiric detachment and uprise of melts: (1) continued diapiric uprise, in the absence of tectonics, leading to final arrest due to density equilibration followed by late ballooning; (2) uprise into major vertical tectonic extensional fault system, magmas rise to high levels, with uppermost crustal ponding and cauldron/caldera behaviour; (3) diapiric uprise arrested by viscosity/strength changes at Moho—this leads to lateral spreading with possible late spawning of crustal plutons; (4) diapiric rise into middle crust, intercepting an intra-crustal strike slip fault zone leading to elongate plutons with late ballooning; (5) diapiric uprise intercepting intra-crustal listric extensional fault/shear zone leading to listric granite sheets and possible generation of asymmetric cauldrons and calderas; (6) uprising melts intercept trans-crustal vertical transcurrent fault/shear zone—jogs, pull apart and large tension gash features, etc., create space for magma ponding; note that in all these scenarios the "source region" is arbitrarily located in the lithospheric mantle.

Generalized section through the north-western part of the Ar dara pluton, showing the structures associated with diapiric intrusion. Within the pluton, foliation intensifies and xenoliths are progressively flattened as the outer contact is approached. Outside the pluton, the country rocks show intense deformation parallel to the contact (after Pitcher and Berger 1972).





Granite Practical: A/CNK ratios

Using the information given below, calculate the A/CNK value for the three samples listed.

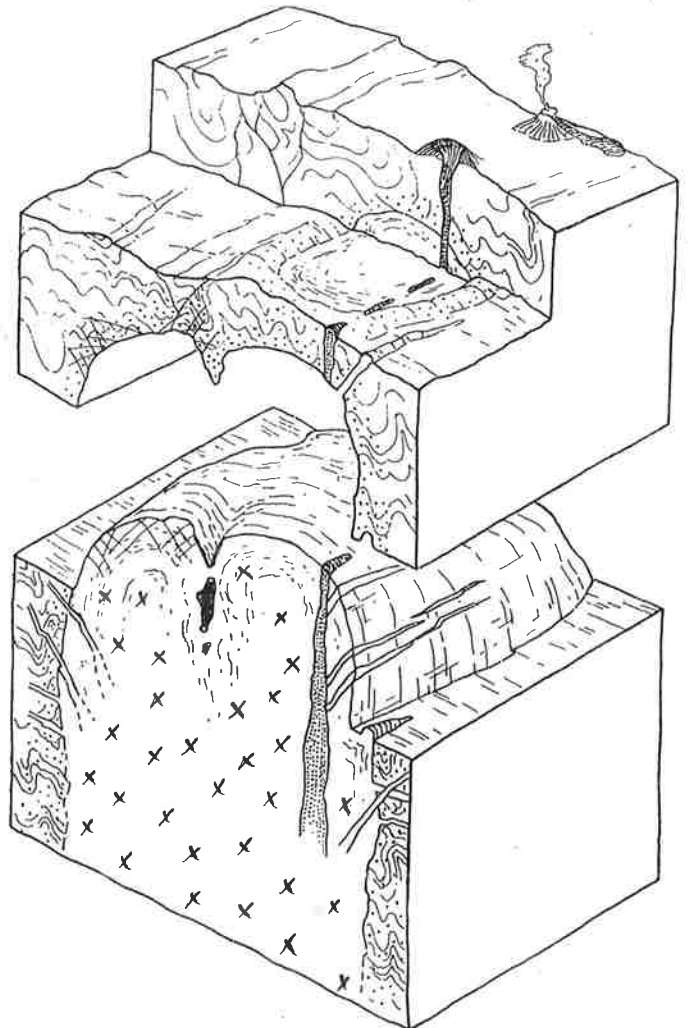
$$A/CNK = Al_2O_3 / (CaO + Na_2O + K_2O)$$

All data have to be converted from wt% oxides to mol% oxides first! This is done by division of the raw analytical data by formula weights (see table attached).

The A/CNK ratio is used to distinguish how dominant alkali elements are, when compared with alumina. If A/CNK is < 1 then the rock is peralkaline, if it is > 1 then the rock is peraluminous. An A/CNK of about 1 (± 0.1) means the rock is metaluminous.

Sample	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	CaO
G1	75.67	13.07	2.79	5.16	0.55
G2	76.13	12.99	4.31	4.51	0.53
G3	65.63	16.39	4.49	4.78	4.08

Results:



PERIODIC TABLE OF THE ELEMENTS

The periodic table displays elements from Hydrogen (1) to Oganesson (118). It is organized into groups (IA-VIIIB, IIIA-III) and periods (1-7). The lanthanide and actinide series are shown below the main table. A diagram at the bottom illustrates the principal shells (1-7) and sub-shells (s, p, d, f) with their respective electron capacities.

Symbol	Name	Atomic Number	Atomic Weight	Symbol	Name	Atomic Number	Atomic Weight
A or Ar	Argon	18	39.948	Mg	Magnesium	12	24.312
Ac	Actinium	89	227	Mn	Manganese	25	54.938
Ag	Silver	47	107.868	Mo	Molybdenum	42	95.94
Al	Aluminum	13	26.98154	N	Nitrogen	7	14.0067
Am	Americium	95	243.13	Na	Sodium	11	22.9898
As	Arsenic	33	74.9216	Nb	Niobium	41	92.906
At	Astatine	85	—	Nd	Neodymium	60	144.24
Au	Gold	79	196.967	Ne	Neon	10	20.183
B	Boron	5	10.811	Ni	Nickel	28	58.71
Ba	Barium	56	137.34	No	Nobelium	102	—
Be	Beryllium	4	9.0122	Np	Neptunium	93	237.00
Bi	Bismuth	83	208.9808	O	Oxygen	8	15.9994
Bk	Berkelium	97	—	Os	Osmium	76	190.20
Br	Bromine	35	79.904	P	Phosphorus	15	30.97376
C	Carbon	6	12.01	Pa	Protactinium	91	231.0
Ca	Calcium	20	40.08	Pb	Lead	82	207.19
Cd	Cadmium	48	112.40	Pd	Palladium	46	106.40
Ce	Cerium	58	140.12	Pm	Promethium	61	—
Cf	Californium	98	—	Po	Polonium	84	210.05
Cl	Chlorine	17	35.453	Pr	Praseodymium	59	140.907
Cm	Curium	96	—	Pt	Platinum	78	195.09
Co	Cobalt	27	58.9331	Pu	Plutonium	94	242
Cr	Chromium	24	51.996	Ra	Radium	88	226.0254
Cs	Cesium	55	132.9054	Rb	Rubidium	37	85.47
Cu	Copper	29	63.546	Rh	Rhodium	45	186.2
Dy	Dysprosium	66	162.50	Rn	Radon	86	102.905
Er	Erbium	68	167.28	Ru	Ruthenium	44	101.07
Es	Einsteinium	99	—	S	Sulphur	16	32.064
Eu	Europium	63	151.96	Sb	Antimony	51	121.75
F	Fluorine	9	18.99840	Sc	Scandium	21	44.956
Fe	Iron	26	55.847	Se	Selenium	34	78.96
Fm	Fermium	100	—	Si	Silicon	14	28.086
Fr	Francium	87	—	Sm	Samarium	62	150.35
Ga	Gallium	31	69.72	Sr	Strontium	38	118.69
Gd	Gadolinium	64	157.25	Ta	Tantalum	73	180.948
Ge	Germanium	32	72.59	Tb	Terbium	65	158.924
H	Hydrogen	1	1.00797	Tc	Technetium	43	—
He	Helium	2	4.0026	Te	Tellurium	52	127.60
Hf	Hafnium	72	178.49	Th	Thorium	90	232.038
Hg	Mercury	80	200.59	Ti	Titanium	22	47.90
Ho	Holmium	67	164.930	Tl	Thallium	81	204.37
I	Iodine	53	126.9044	Tm	Thulium	69	168.934
In	Indium	49	114.82	U	Uranium	92	238.03
Ir	Iridium	77	192.20	V	Vanadium	23	50.942
K	Potassium	19	39.09	W	Tungsten	74	183.85
Kr	Krypton	36	83.80	Xe	Xenon	54	131.30
La	Lanthanum	57	138.91	Y	Yttrium	39	88.905
Li	Lithium	3	6.939	Yb	Ytterbium	70	173.04
Lu	Lutetium	71	174.97	Zn	Zinc	30	65.38
Lw	Lawrencium	103	—	Zr	Zirconium	40	91.22
Md	Mendelevium	101	—				

Data abstracted from Handbook of Chemistry and Physics 55th edition, 1974-75, The Chemical Rubber Company, Cleveland, Ohio.