

Geochemistry exam for the 3rd level students
(Geology & Chemistry) May 2013.

Answer the following questions

1. Write short notes for the following:
 - a) Calc-alkaline basalt
 - b) Mid-Oceanic Ridge Basalt
 - c) The "Rare Earth" elements
 - d) An incompatible element
 - e) Compatible elements
 - f) High Field Strength Elements
 - g) K₂O concentration (classification of Gill, 1981)
 - h) Fractional crystallization
2. Discuss the geochemical characteristics of Andesite and Basalt as the most common volcanic rocks?
3. Write a summary of the differences (Geochemical characterization, Petrography and Geologic Setting) between Calc-alkaline and Tholeiitic fractionation trends?
4. Discuss in detail Bowen's Reaction Series?

Good Luck
Dr. M. M. Mogahed

Model Answer

1. Write short notes for the following:

a) Calc-alkaline basalt. Basalts found in Orogenic Andesite series, showing the characteristic continental fingerprint with anomalously low Nb-Ta and Ti with (at least in continental and matures arc series) relatively high Cs, Rb, Ba, Th, U, K. CAB's are not that common in continental arcs, one can work for years without seeing one.

b) Mid-Oceanic Ridge Basalt. A general term for those low K, tholeiitic basalts erupted along the oceanic ridge spreading centres

NMORB: The "normal" or more common type of Oceanic Ridge basalt, (see above), strongly depleted in the LILE elements Cs, Rb, Ba, Th, U and formed by a relatively high degree of melt of the uprising mantle. Not always associated with the faster spreading centres, Kolbeinsey and Reykjanes Ridge spread at only 4cm/yr but are VERY depleted, eg Nd=>Ce.

EMORBS are the more enriched (50-100 ppm La) MORB variants, compared to the 1-5 ppm seen in the most depleted NMORBS. Found usually in very slow-spreading centres (< 1 cm per year) or at some distance from the median trench in the faster spreading centres usually in off-lying seamounts.

c) The "Rare Earth" elements, mainly trivalent and of common properties. Includes La, Ce, Nd, Pr, Sm, Eu etc down to Lutecium. Eu is divalent and goes into feldspar, the others do not. Strong feldspar fractionation creates a "Europium anomaly" as seen in commendites. Other REE, eg Ce, form trichlorides and seem to have variable valency.

d) An incompatible element is a term used in petrology and geochemistry to describe an element that is unsuitable in size and/or charge to the cation sites of the minerals, and is defined by the partition coefficient between rock-forming minerals and melt being much smaller than 1 Incompatible elements - these are elements like K, Rb, Cs, Ta, Nb, U, Th, Y, Hf, Zr, and the *Rare Earth Elements* (REE)- La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, & Lu. Most have a large ionic radius. Mantle minerals like olivine, pyroxene, spinel, & garnet do not have crystallographic sites for large ions. During the fractional crystallization of magma and magma generation by the partial melting of the Earth's mantle and crust, elements that have difficulty in entering cation sites of the minerals are concentrated in the melt phase of magma (liquid phase).

- e) Compatible elements - these are elements like Ni, Cr, Co, V, and Sc, which have smaller ionic radii and fit more easily into crystallographic sites that normally accommodate Mg, and Fe.
- f) High field strength elements, ie, those with high charge, small ionic radius etc which are the first to form crystals in a cooling magma. Including, Cr, Ni, Mg, the heavy REE, Y, Ca, etc
- g) K₂O concentration (classification of Gill, 1981)

The concentration of K₂O in subduction zone rocks range from ~0.5 to ~2.5 wt.%. There are low-K, medium-K and high-K suites. The tholeiitic series is mostly low-K, whereas the calc-alkaline series is mostly medium to high-K. The high concentration of K₂O in calc-alkaline melts may be related to its enrichment in the source region during fluxing by water.

Thus, compared to the tholeiitic series magmas, the calc-alkaline series magmas have

- higher water contents, indicated by the presence of abundant hydrous minerals;
 - higher K₂O concentrations;
 - on average, somewhat higher SiO₂ concentrations;
 - is the dominant series in andesitic-type subduction zones, where the tholeiitic series is not very common.
- h) Fractional crystallization is one of the most important geochemical and physical processes operating within the Earth's crust and mantle. Fractional crystallization is the removal and segregation from a melt of mineral precipitates; except in special cases, removal of the crystals changes the composition of the magma. Fractional crystallization in silicate melts (magmas) is complex compared to crystallization in chemical systems at constant pressure and composition, because changes in pressure and composition can have dramatic effects on magma evolution. Addition and loss of water, carbon dioxide, hydrogen, and oxygen are among the compositional changes that must be considered. For example, the partial pressure (fugacity) of water in silicate melts can be of prime importance, as in near-solidus crystallization of magmas of granite composition. The crystallization sequence of oxide minerals such as magnetite and ulvospinel is sensitive to the oxygen fugacity of melts, and separation of the oxide phases can be an important control of silica concentration in the evolving magma, and may be important in andesite genesis.

Experiments have provided many examples of the complexities that control which mineral is crystallized first as the melt cools down past the liquidus.

One example concerns crystallization of melts that crystallize to mafic and ultramafic rocks. MgO and SiO₂ concentrations in melts are among the variables that determine whether forsterite olivine or enstatite pyroxene is precipitated, but the water content and pressure are also important. In some compositions, at high pressures without water crystallization of enstatite is favored, but in the presence of water at high pressures, olivine is favored.

Granitic magmas provide additional examples of how melts of generally similar composition and temperature, but at different pressure, may crystallize different minerals. Pressure determines the maximum water content of a magma of granite composition. High-temperature fractional crystallization of relatively water-poor granite magmas may produce single-alkali-feldspar granite, and lower-temperature crystallization of relatively water-rich magma may produce two-feldspar granite.

During the process of fractional crystallization, melts become enriched in incompatible elements. Hence, knowledge of the crystallization sequence is critical in understanding how melt compositions evolve. Textures of rocks provide insights, as documented in the early 1900s by Bowen's reaction series. Experimentally-determined phase diagrams for simple mixtures provide insights into general principles. Numerical calculations with special software have become increasingly able to simulate natural processes accurately.

2. Discuss the geochemical characteristics of Andesite and Basalt as the most common volcanic rocks?

Andesite

The most common volcanic rock found in island arcs and sectors of continental margins above an active or now defunct subduction zone. Originally defined as having an andesine feldspar, (An 30-50), but as the feldspars are often oscillatory zoned, or may not have even formed in very fine grained rocks, it is more common to use the Normative feldspar composition as calculate by a NORM program from the chemical analysis. Andesites (and all continental rocks) are characterised by their anomalously low Nb-Ta content, and low Ti ,(see fingerprint diagrams diagrams in "Andesite Series"). Sometimes in a calc-alkaline series (an old term defined by their Calcium-soda ratio at specific silica) andesites may be defined on their silica

content only, usually 58 – 63 %, those of 53 – 57% being "Basaltic Andesites". Above 63% the rocks are "Dacites" with rhyolites above 70%. A rock with an andesine feldspar and 52% silica would probably be called an "andesine basalt". The plutonic intrusive equivalents are granodiorites.

In a variation diagram, orogenic andesite series are easily distinguished by their high Al₂O₃ (16-18%) compared to the low FeOT and CaO. OIB's and ORB's have lower alumina and higher FeOT, CaO. See diagrams in the relevant chapters.

Basalt

The most common and most abused rock name in petrology. A dark mafic rock of 5 – 10% MgO with a labradorite modal or normative feldspar. Always with associated clinopyroxene as well as plagioclase, possibly with <10% olivine, orthopyroxene or pigeonite, in which case are "olivine basalts", or "hypersthene basalts" or "pigeonite basalts". Basaltic rocks with more than 10% olivine may be termed "picritic basalts" those with more (and MgO from 12 to as much as 35%) are "Picrites". With fractionation and increasing iron and titanium, basalts with more than 14% FeOT are termed "Ferrobasalts". The plutonic, coarse grained equivalents are "gabbros" and "Ferro-gabbros".

"Tholeiitic" basalts have commonly 48 to 52% silica and the alkalis Na and K are low enough that mineralic is quartz found in the matrix or in the interstitial glass. With lower SiO₂ and increasing alkalis and with normative olivine but no nepheline, basalts become "Transitional" and when modal or normative "nepheline" appears they are termed "Alkali basalts". With more than 10% nepheline, they become "Basanites". At less than about 36% silica and high alkalis, melanite and nepheline may form instead of pyroxene – plagioclase and the rock may be a "melanite-nephelinite".

"Tholeiitic" basalts (or "tholeiites") and their derivatives ferrobasalt –icelandite - tholeiitic rhyo-dacite, make up the oceanic lithosphere. "Alkali" basalts occur as volcanic oceanic island chains (OIB's) or follow fracture zones in continents.

3. Write a summary of the differences (Geochemical characterization, Petrography and Geologic Setting) between Calc-alkaline and Tholeiitic fractionation trends?

Calc-alkaline magma series

The calc-alkaline magma series is one of two main magma series in igneous rocks, the other magma series being the tholeiitic. A magma series is a series of compositions that describes the

evolution of a mafic magma, which is high in magnesium and iron and produces basalt or gabbro, as it fractionally crystallizes to become a felsic magma, which is low in magnesium and iron and produces rhyolite or granite. Calc-alkaline rocks are rich in alkaline earths (magnesia and calcium oxide) and alkali metals and make up a major part of the crust of the continents.

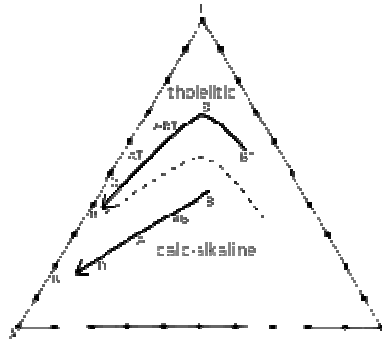
The diverse rock types in the calc-alkaline series include volcanic types such as basalt, andesite, dacite, rhyolite, and also their coarser-grained intrusive equivalents (gabbro, diorite, granodiorite, and granite). They do not include silica-undersaturated, alkalic, or peralkaline rocks

Geochemical characterization

Rocks from the calc-alkaline magma series are distinguished from rocks from the tholeiitic magma series by the redox state of the magma they crystallized from (tholeiitic magmas are reduced, and calc-alkaline magmas are oxidized). When mafic (basalt-producing) magmas crystallize, they preferentially crystallize the more magnesium-rich and iron-poor forms of the silicate minerals olivine and pyroxene, causing the iron content of tholeiitic magmas to increase as the melt is depleted of iron-poor crystals. (Magnesium-rich olivine solidifies at much higher temperatures than iron-rich olivine.) However, a calc-alkaline magma is oxidized enough to (simultaneously) precipitate significant amounts of the iron oxide magnetite, causing the iron content of the magma to remain more steady as it cools than with a tholeiitic magma.

The difference between these two magma series can be seen on an AFM diagram, a ternary diagram showing the relative proportions of the oxides of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (A), $\text{FeO} + \text{Fe}_2\text{O}_3$ (F), and MgO (M). As magmas cool, they precipitate out significantly more iron and magnesium than alkali, causing the magmas to move towards the alkali corner as they cool. In the tholeiitic magma, as it cools and preferentially produces magnesium-rich crystals, the magnesium content of the magma plummets, causing the magma to move away from the magnesium corner until it runs low on magnesium and simply moves towards the alkali corner as it loses iron and (relic) magnesium. With the calc-alkaline series, however, the precipitation of magnetite causes the iron-magnesium ratio to remain relatively constant, so the magma moves in a straight line towards the alkali corner on the AFM diagram.

Calc-alkaline magmas are typically hydrous, and also typically are more oxidized, with higher oxygen fugacities.



This is an AFM diagram, a ternary diagram showing the relative proportions of the oxides of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (A), $\text{FeO} + \text{Fe}_2\text{O}_3$ (F), and MgO (M). The arrows show the path of the magmas in the tholeiitic and the calc-alkaline magma series.

Geologic Setting

Calc-alkaline rocks typically are found in the arcs above subduction zones, commonly in volcanic arcs, and particularly on those arcs on continental crust.

Petrologic origin

Rocks in the series are thought to be genetically related by fractional crystallization and to be at least partly derived from magmas of basalt or andesite composition formed in the Earth's mantle. Trends in composition can be explained by a variety of processes. Many explanations focus on water content and oxidation states of the magmas. Proposed mechanisms of formation begin with partial melting of subducted material and of mantle peridotite (olivine and pyroxene) altered by water and melts derived from subducted material. Mechanisms by which the calc-alkaline magmas then evolve may include fractional crystallization, assimilation of continental crust, and mixing with partial melts of continental crust.

Tholeiitic magma series

The tholeiitic magma series, named after the German municipality of Tholey, is one of two main magma series in igneous rocks, the other magma series being the calc-alkaline. A magma series is a series of compositions that describes the evolution of a mafic magma, which is high in magnesium and iron and produces basalt or gabbro. The International Union of Geological Sciences recommends that *tholeiitic basalt* be used in preference to the term "tholeiite" (Le Maitre and others, 2002).

Geochemical characterization

Rocks in the tholeiitic magma series are classified as subalkaline (they contain less sodium than some other basalts) and are distinguished from rocks in the calc-alkaline magma series by the redox state of the magma they crystallized from (tholeiitic magmas are reduced; calc-alkaline magmas are oxidized). When the parent magmas of basalts crystallize, they preferentially crystallize the more magnesium-rich and iron-poor forms of the silicate minerals olivine and pyroxene, causing the iron content of tholeiitic magmas to increase as the melt is depleted of iron-poor crystals. However, a calc-alkaline magma is oxidized enough to precipitate significant amounts of the iron oxide magnetite, causing the iron content of the magma to remain more steady as it cools than with a tholeiitic magma.

The difference between these two magma series can be seen on an AFM diagram, a ternary diagram showing the relative proportions of the oxides $\text{Na}_2\text{O} + \text{K}_2\text{O}$ (A), $\text{FeO} + \text{Fe}_2\text{O}_3$ (F), and MgO (M). As magmas cool, they precipitate out significantly more iron and magnesium than alkali, causing the magmas to move towards the alkali corner as they cool. In the tholeiitic magma, as it cools and preferentially produces magnesium-rich crystals, the magnesium content of the magma plummets, causing the magma to move away from the magnesium corner until it runs low on magnesium and simply moves towards the alkali corner as it loses iron and any remaining magnesium. With the calc-alkaline series, however, the precipitation of magnetite causes the iron-magnesium ratio to remain relatively constant, so the magma moves in a straight line towards the alkali corner on the AFM diagram.

Petrography

Like all basalt, the rock type is dominated by clinopyroxene plus plagioclase, with minor iron-titanium oxides.^[1] Orthopyroxene or pigeonite may also be present in tholeiitic basalt, and olivine, if present, may be rimmed by either of these calcium-poor pyroxenes. Tridymite or quartz may be present in the fine-grained groundmass of tholeiitic basalt, and feldspathoids are absent. Tholeiitic rocks may have a fine, glassy groundmass, as may other types of basalt.

Geologic Setting

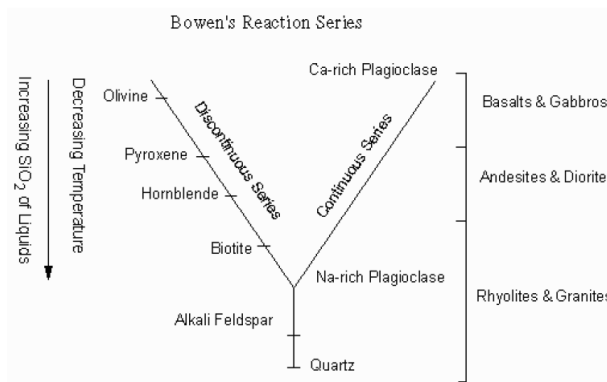
Basalt magmas are partial melts of peridotite (olivine and pyroxene) produced by decompression melting in the Earth's mantle, a process described for igneous rocks. Tholeiitic basalts are the most common volcanic rocks on Earth, as they are produced by submarine volcanism at mid-ocean ridges and make up much of the ocean crust. MORB, the acronym for typical mid-ocean-ridge basalt, is a type of tholeiitic basalt particularly low in incompatible elements. In contrast, alkali basalt is not typical at ocean ridges, but is erupted on some oceanic

islands and on continents, as also is tholeiitic basalt.^[1] Because the Moon is extremely reduced, all of its basalt is tholeiitic.

4. Discuss in detail Bowen's Reaction Series?

Bowen's Reaction Series

Norman L. Bowen, an experimental petrologist in the early 1900s, realized this from his determinations of simple 2- and 3-component phase diagrams, and proposed that if an initial basaltic magma had crystals removed before they could react with the liquid, that the common suite of rocks from basalt to rhyolite could be produced. This is summarized as Bowen's Reaction Series.



Bowen suggested that the common minerals that crystallize from magmas could be divided into a continuous reaction series and a discontinuous reaction series.

- The continuous reaction series is composed of the plagioclase feldspar solid solution series. A basaltic magma would initially crystallize a Ca-rich plagioclase and upon cooling continually react with the liquid to produce more Na-rich plagioclase. If the early forming plagioclase were removed, then liquid compositions could eventually evolve to those that would crystallize a Na-rich plagioclase, such as a rhyolite liquid.
- The discontinuous reaction series consists of minerals that upon cooling eventually react with the liquid to produce a new phase. Thus, as we have seen, crystallization of olivine from a basaltic liquid would eventually reach a point where olivine would react with the liquid to produce orthopyroxene. Bowen postulated that with further cooling pyroxene would react with the liquid, which by this time had become more enriched

in H_2O , to produce hornblende. The hornblende would eventually react with the liquid to produce biotite. If the earlier crystallizing phases are removed before the reaction can take place, then increasingly more siliceous liquids would be produced.

This generalized idea is consistent with the temperatures observed in magmas and with the mineral assemblages we find in the various rocks. We would expect that with increasing SiO_2 oxides like MgO , and CaO should decrease with higher degrees of crystal fractionation because they enter early crystallizing phases, like olivines and pyroxenes. Oxides like H_2O , K_2O and Na_2O should increase with increasing crystal fractionation because they do not enter early crystallizing phases. Furthermore, we would expect incompatible trace element concentrations to increase with fractionation, and compatible trace element concentrations to decrease. This is generally what is observed in igneous rock suites. Because of this, and the fact that crystal fractionation is easy to envision and somewhat easy to test, crystal fractionation is often implicitly assumed to be the dominant process of magmatic differentiation.