

The Uppermost Nappes in the Asterousia Mountains - Coast Road Kali Limenes to Chrysostoms



View of the coastline looking east from the top of the mountain ridge near the village of Chrysostoms. At the top of the ridge there is coarse grained white marble underlain by metapelites (paragneiss) and metagranite (orthogneiss). Lower down near sea level the crystalline nappe is thrust on top of slightly metamorphic rocks consisting of grey phyllite, basalt, red slates/ marl and limestone.

Compiled by George Lindemann, MSc.

Berlin, August 2024

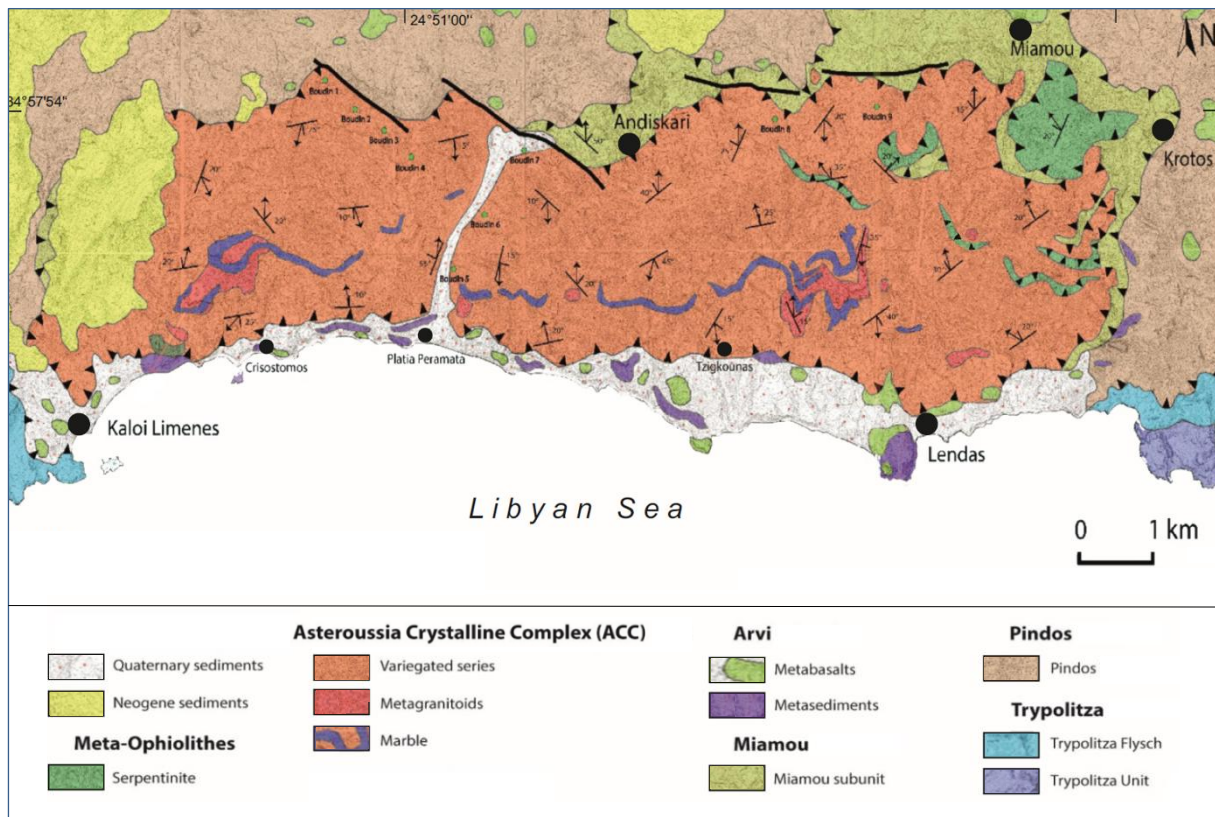
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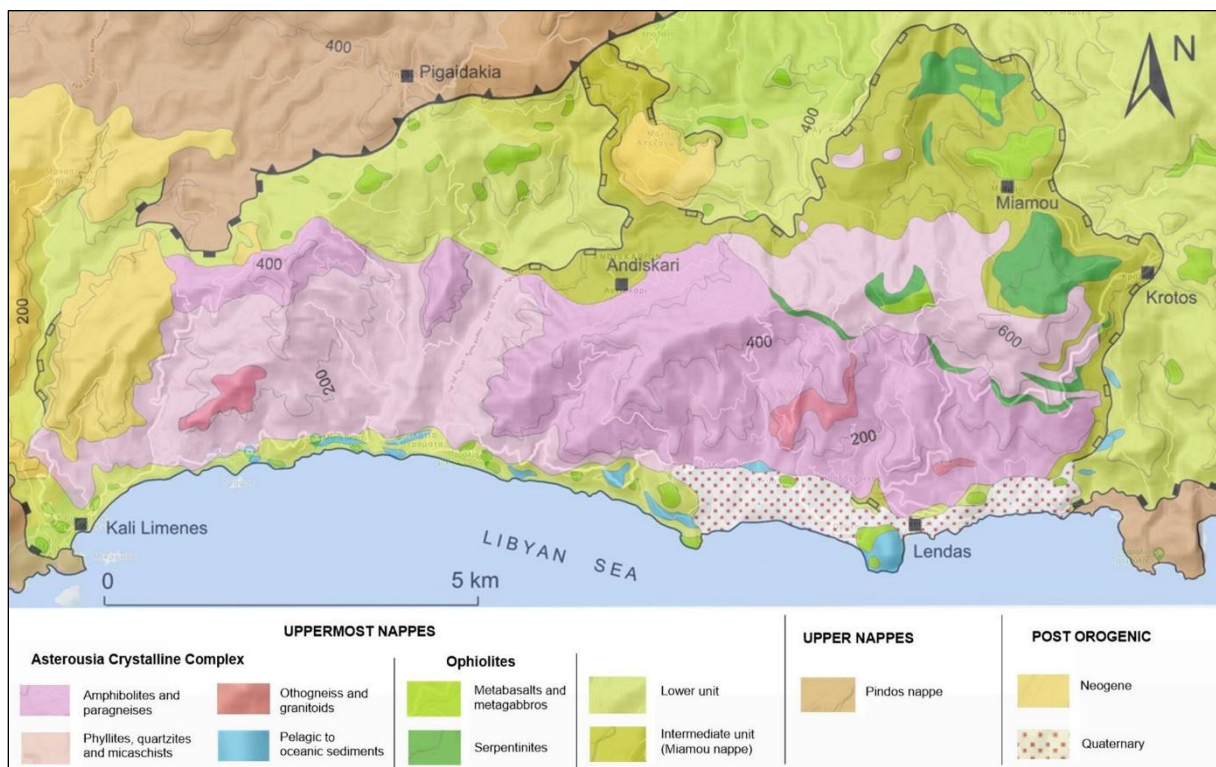
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1 Introduction to the Astrousia Mountains



Geological map of the western part of the Astrousia Mountains showing the area between Kaloi Limenes and Lendas. Source: Zulauf G. et al., 2023, (modified after Davi and Bonneau 1972; Thorbecke 1987; Tortorici et al. 2012; Neuwirth 2018).



Geological map of the western part of the Asterousia Mountains showing the area between Kali Limenes and Lendas. Source: Tortorici L. et al., 2011

On Crete, the Uppermost Unit has been subdivided into several subunits differing in their lithology and in the grade and timing of metamorphism (e.g. Bonneau, 1972; Krah, Herbart & Katzenberger, 1982; Tortorici et al. 2012). Amphibolite facies metamorphic rocks, intruded by Late Cretaceous granitoids (Kneucker et al. 2015; Martha et al. 2016, 2017), are referred to as the Asterousia Crystalline Complex (ACC; Bonneau, 1972), which is usually correlated with the southern margin of the Pelagonian domain and therefore with the Internal Hellenides (e.g. Aubouin & Dercourt, 1965; Bonneau, 1972; Martha et al. 2017). Other tectonometamorphic nappes ascribed to the Uppermost Unit include the prehnite-pumpellyite facies Arvi Unit, which is interpreted as a Maastrichtian seamount at the northern margin of the Pindos realm (Palamakumbura, Robertson & Dixon, 2013), and the Greenschist Unit, consisting of fine-grained epidote-amphibole schist with a mid-ocean ridge basalt (MORB) -type signature (Reinecke et al. 1982; Martha et al. 2017). The provenance, tectonostratigraphy and metamorphic evolution of the Uppermost Unit and its subunits are only poorly understood and far from consensus. Recent studies have shown that the Uppermost Unit has undergone polyphase metamorphism and deformation during Late Cretaceous and Paleocene time (Tortorici et al. 2012; Martha et al. 2017). Understanding the tectonometamorphic evolution of the Uppermost Unit is therefore confronted with unravelling its polymetamorphic history. [Martha S. et. al., 2018]

One of the largest occurrences of Late Cretaceous crystalline rocks is exposed in the Asterousia Mountains along the southern coast of central Crete, between the villages of Kali Limenes and Lendas (Fig. 2). The crystalline rocks comprise meta-plutonic rocks and a variegated metamorphic sequence consisting of metapelites, calcsilicate rocks, marbles and amphibolites, as well as meta-ultramafics. Intrusive rocks in the Asterousia Mountains are restricted to two relatively small areas. Mainly felsic granitoids are found in the hills 24 km east of Kali Limenes, while most of the more mafic plutonic rocks are exposed about 2 km NNW of Lendas, close to the road from Gerokampos to Agios Kyrillos. The Asterousia plutonic rocks display a foliation which is mostly faint, but in some cases conspicuous. Frequently, the contacts between granitoids and the country rocks are sharp and obviously of intrusive origin. However, blurred contacts to migmatitic paragneisses occur as well, and there is apparently no clear distinction between granitic dikes and leucosomes, suggesting a granite formation by in-situ anatexis. The paragneisses forming the country rock are of amphibolite-facies and have preserved ages of high-temperature metamorphism around 72 Ma. A granite from this area yields an identical age suggesting that magmatism and metamorphism occurred contemporaneously. Metamorphic assemblages, e.g. quartz-plagioclase-K-feldspar-sillimanite-biotite-garnet-cordierite in pelitic paragneisses, correspond to P-T conditions of the upper amphibolite facies, i.e. 650 to 700 °C and 4 to 6 kbar (Koepke and Seidel 1984). [Langosch A. et al., 2000]

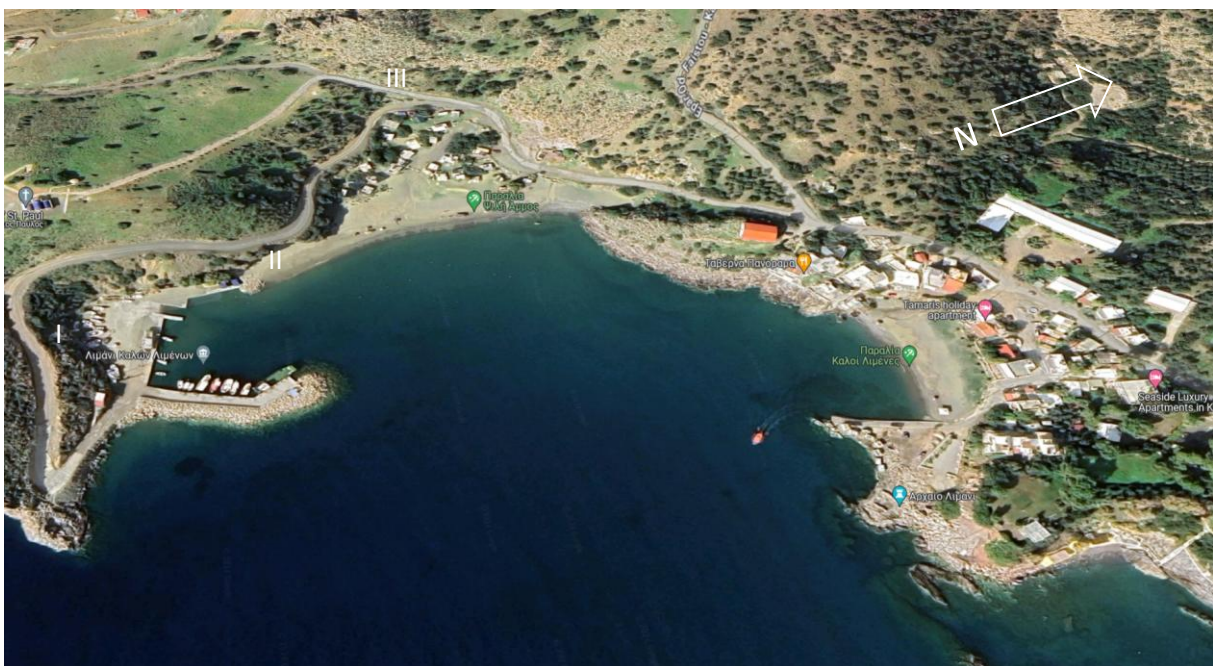
The granites and granodiorites of Kali Limenes include mafic dikes, which are dissected but not foliated. In their mineralogy and geochemistry (see below), the dissected mafic dikes correspond to orthoamphibolites in the metamorphic country rock sequence. Both rock types have preserved porphyritic textures with plagioclase phenocrysts. The plutonic rocks, mafic dikes and metamorphic country rocks of the Asterousia Mountains have been intruded by tourmaline-rich pegmatite dikes. Locally, these pegmatites contain aggregates of large muscovite flakes, lath-shaped biotite and isolated crystals of spessartine. [Langosch A. et al, 2000]

Langosch A. et al, suggest that the Late Cretaceous plutonic rocks in the uppermost tectonic unit of Crete formed in a supra-subduction zone setting or, alternatively, during continental lithospheric extension from a depleted mantle. The granitoid compositions can be modelled by an assimilation-fractional crystallization process in which a diorite magma underwent fractional crystallization, accompanied by assimilation of (meta)sediments similar in composition to the amphibolite-facies metapelites in the area. The intrusion of mafic melts at depth might have acted as a heat source, elevating mid-crustal regions to amphibolite-facies temperatures and causing the formation of migmatitic paragneisses. [Langosch A. et al, 2000]

Refer to My GeoGuide “No. 17: Sellia to Asomatos and the Cretan Detachment” for an introduction to the general geology of Crete.

2 Kali Limenes

After crossing the Asterousia Mts. from Pombia you reach the coastal road and initially follow it in a westerly direction to Kali Limenes. Drive through the village to the beach in the SW and walk along the beach to the rocks on the south side of the bay.



Location of outcrops at Kali Limenes [Source of image: Google Maps]

2.1 Basalt/andesite



Outcrop I, Volcanic rock probably of andesitic composition.



Outcrop I, the medium grey colour indicates that this may be an andesite and not a basalt, which is normally darker. The flow textures and gas “bubbles” (arrow) is a sure sign for lava.



Outcrop II, shear zone within meta-pelitic rock underlying basaltic/andesitic rock displaying several faults and scaly cleavage (SC/SCC'-type shear textures).

2.2 Mélange

In geology, a mélange is a large-scale breccia, a mappable body of rock characterized by a lack of continuous bedding and the inclusion of fragments of rock of all sizes, contained in a fine-grained deformed matrix. The mélange typically consists of a jumble of large blocks of varied lithologies. Both tectonic and sedimentary processes can form mélange.

Mélange occurrences are associated with thrust faulted terranes in orogenic belts. A mélange is formed in the accretionary wedge above a subduction zone. The ultramafic ophiolite sequences which have been obducted onto continental crust are typically underlain by a mélange. Smaller-scale localized mélanges may also occur in shear or fault zones, where coherent rock has been disrupted and mixed by shearing forces [Wikipedia].



Outcrop II, tectonic mélange consisting of a mixture of phyllitic and basaltic/andesitic rock. Notice the many veins that are filled with quartz (?) that have been sheared apart within the shear zone.

2.3 Ultramafic Rocks

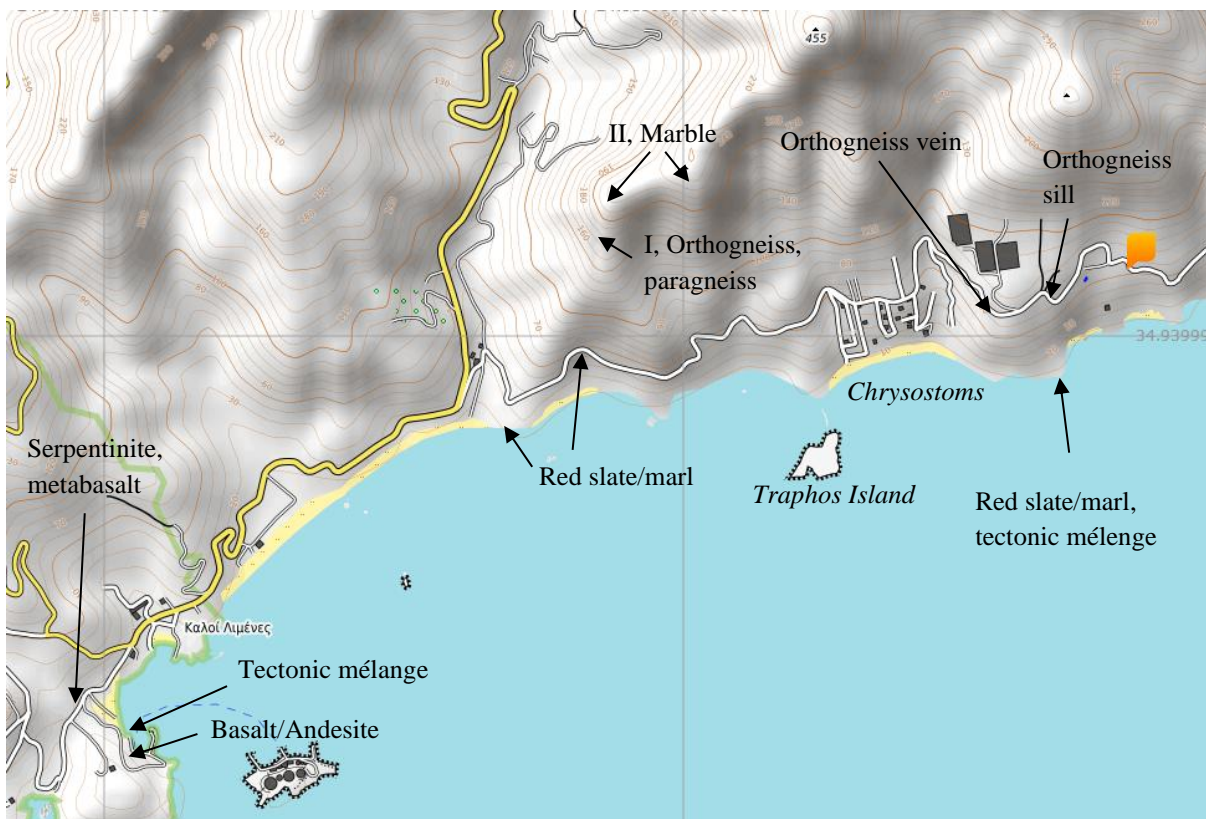


Outcrop III, shear zone in serpentinitized ultramafic rock.



Outcrop III, closeup of serpentinite sample

3 Chrysostoms



Overview of the area between Kali Limenes and Chrysostoms. Coordinates of orange arrow: N 34° 56,51; E 24° 50,12

Red marly limestones, grey pelites and psammities as well as volcanic rocks (basalts) belong to the tectonic mélange of the Uppermost Nappes and correspond to those of the Arvi unit south of the Dikte Mts. 70 km farther east. To the east and west of the junction with the main road to Pombia, red slates/marls as well as paragneiss are occasionally exposed along the coastal road.

At the small island of Traphos there is an ancient Hellenistic-Roman harbour, which can be seen from the road. Remains of the harbour wall are still visible between the island the coast. Based on archaeological findings, it is assumed to have subsided by 1.2 m since Roman times. The harbour wall is locally included in a formation of beach rock, which is now also under water (Mourzas & Marinos 1994). The rock of Traphos Island consists of limestone from the Arvi unit.



Former Hellenistic-Roman submerged harbour at Taphros Island as seen from near the top of the mountain ridge.

The Outcrops I and II are not easily accessible and require approx. one hours hike up the mountain ridge. The top of the mountain presents a good view of the landscape. Near the top one encounters orthogneiss, diorite dykes, paragneiss and white marble all of which belong to the Asterousian Crystalline Complex (ACC).



Location of outcrops I and II [Source of image: Google Maps]

3.1 Orthogneiss



Outcrop I. Gneiss showing signs of anatexis (i.e. melting). 1: leucosome, the felsic minerals such as quartz and feldspar are the first part of the rock to melt when exposed to adequately high temperatures. Based on the existing geological maps (Davi and Bonneau 1972, Tortorici et al. 2012) it is indicated to be an orthogneiss – therefore a granitoid igneous rock that has been subjected to metamorphism.



Outcrop I. Close up of the previous picture showing the texture of the orthogneiss. The texture of the surrounding country rock, which is a paragneiss is different. However, the orthogneiss appears to be part of a small vein rather than a larger intrusion.



Outcrop I. Fresh sample of the orthogneiss. Quartz (qu) can be distinguished from feldspar (fl) by its greasy lustre, irregular cleavage and its transparency that makes it appear grey. Feldspar in this sample is white and has fair cleavage.

3.2 Diorite Dykes



Outcrop I. Dolerite dyke cross cutting the paragneiss. The texture is porphyritic owing to the plagioclase phenocrysts.



Outcrop I. Closeup of the dolerite dyke displaying phenocrysts of plagioclase. The rock texture is called porphyritic due to the texture with larger crystals embedded in a much finer matrix. This indicates that part of the magma had already crystalized prior to it being transported to the earth's surface. Dykes occur where tectonic strain causes fissures and faults that extend to a magma chamber.

3.3 Marble



Outcrop II, 1: Marble, 2: Paragneiss partly showing signs of anatexis.



Outcrop II: Marble escarpment at the top of the mountain ridge



Outcrop II, Marble sample. High temperature metamorphism is indicated by the coarse-grained structure. The marble is quite white and homogeneous.



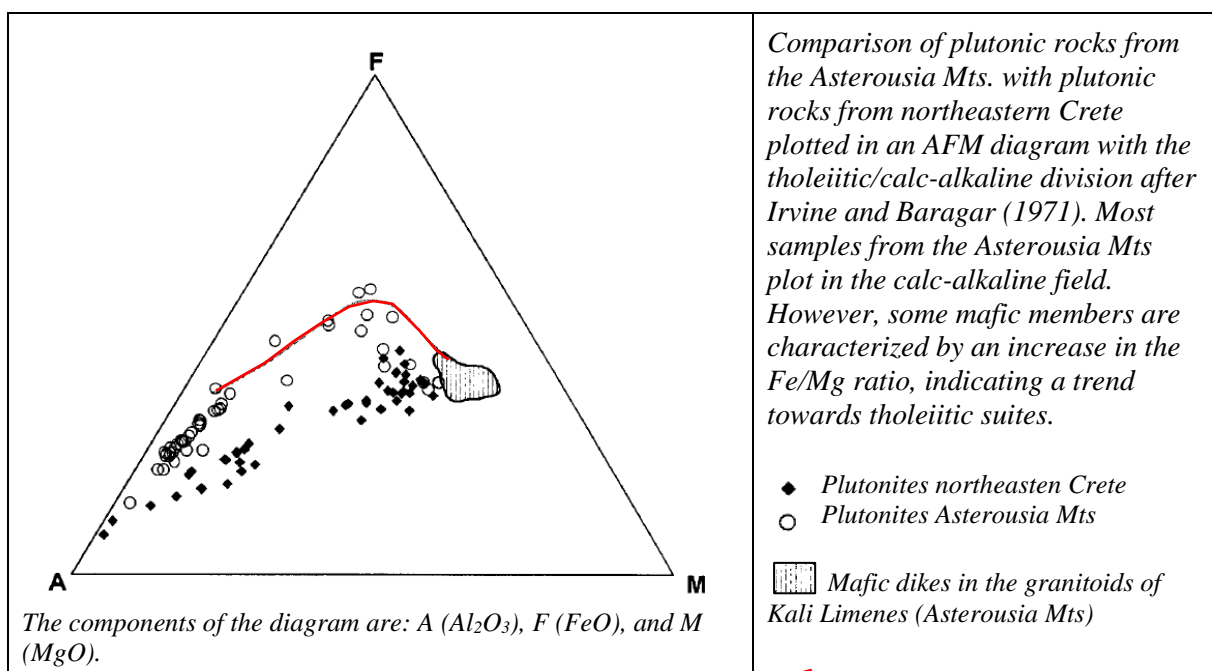
Outcrop II, Paragneiss located below the marble escarpment. Notice the different texture to the orthogneiss.

3.4 Petrology of the Granitoids and Granodiorites

In the plutonic suite of the Asterousia Mts. the most abundant rocks are granites and granodiorites, which are more or less deformed and highly metamorphic; some even appearing as augen-gneisses. Owing to their metamorphic overprint they are occasionally referred to as orthogneisses in the following text. Plagioclase zoned from An₃₈ (core) to An₁₅ (rim) and microcline (displaying perthite exsolution) form large phenocrysts, which are surrounded by a fine-grained matrix consisting of quartz and both feldspars. Especially in strongly deformed samples, quartz is recrystallized and may occur as ribbons. Several of the granitoids contain only biotite as mafic mineral, while others include both biotite and Ca-amphibole. The preferred orientation of biotite and/or amphibole enhances the foliation of the orthogneisses. In weakly deformed samples, Ca-amphibole may not be aligned and displays euhedral shape. The Ca-amphiboles are green in colour and range in composition from ferrohornblende to ferroedenite, which is an Al-containing hornblende (Al_{tot} 1.25±1.50 per formula unit). The Al-in-hornblende barometer of Anderson and Smith (1995) yields pressures between 2.5 and 4 kbar (at 700 °C) for the granites and granodiorites. Accessory phases are, in order of decreasing abundance, apatite, ilmenite, zircon, titanite and allanite. [Langosch A. *et al.*, 2000]

Most of the microstructural features, such as rounded feldspar grains, quartz and feldspar recrystallization, quartz ribbon structures, myrmekites and a low strain location, indicate ductile medium-to-high temperature solid-state deformation of the granitoids (Tullis and Yund 1985; Gapais 1989; Paterson *et al.* 1989; Tribe and D'Lemos 1996). Rare microplites and myrmekite in feldspar fractures may be interpreted as deformation of an incompletely crystallized magma (Hibbard 1987).

In the Asterousia Mountains, only a very few amphibole-free granites contain garnet in varying amounts from <1±10 vol%. These samples are distinctly peraluminous with molecular Al₂O₃/(CaO + Na₂O + K₂O) ratios >1.1. The garnets in the granites correspond to those of adjacent paragneisses in their chemical composition. Some of the garnet grains in granites are regarded as xenocrysts. Clusters of small euhedral garnets are thought to have crystallized from a granitic melt rich in assimilated pelitic material. The occurrence of garnet-bearing granites is restricted to marginal parts of the intrusions, where migmatitic paragneisses are present. Assimilation of these gneisses may have modified the composition of the intruding magmas. [Langosch A. *et al.*, 2000]



	tholeiitic/calc-alkaline division after Irvine and Baragar (1971)
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The AFM diagram shows the varying composition (mineral assemblages) of samples collected by Langosch A. et al. Each marking represents an analyzed rock sample. The components of the diagram are A (Al_2O_3), F (FeO), and M (MgO). Each of these components has to be modified slightly to account for the presence of other, minor components in the rock, leading to: A ($\text{Al}_2\text{O}_3 - 3\text{K}_2\text{O}$); F($\text{FeO} - \text{TiO}_2 - \text{Fe}_2\text{O}_3$); and M (MgO). The minerals quartz and albite are assumed to be present in the rocks but are not shown on the diagram. [Langosch A. et al., 2000]

3.5 Mafic Dykes

The dissected, nonfoliated mafic dikes occurring within the granites and granodiorites of Kali Limenes in the Asterousia Mountains display a tholeiitic affinity in the AFM diagram (see figure above) and are classified as high-Mg tholeiitic basalts using the cation plot of Jensen (1976).

In their trace element contents (i.e. Zr, Nb, Y, Hf, Th, U, Zn) the mafic dikes differ significantly from the diorites of the Asterousia Mts found near Gerokampos. Geochemically the mafic dykes resemble the orthoamphibolites further east located near Lendas (see My GeoGuide “No. 24: The Uppermost Nappes in the Asterousia Mountains – Miamou to Lendas).

4 Outcrops Near “Sinifas Apartments”

Follow the road eastwards as far as ‘Sinifas Apartments’. Roadcuts near the “Sinifas Apartments” reveal interesting orthogneiss outcrops [Kull U., 2012].

The Granitoids near the ‘Sinifas Apartments’ are more like granite rather than the orthogneisses described above. According to Langosch (1999) they are of Upper Cretaceous age (approx. 71 million).



Overview of geological features near 'Sinifas Apartments' [Source of image: Google Maps]

4.1 Granite/Orthogneiss Veins 1



Outcrop I. Granite/Orthogneiss vein at road cutting



Outcrop I. Closeup of previous picture.



Outcrop I. Granite/orthogneiss vein above road cutting



Outcrop I. Granitoid orthogneiss displaying a phanerite texture (i.e. the microstructure is made up of crystals large enough to be distinguished with the naked eye). The main minerals are quartz, feldspar and a minor content of mafic minerals such as amphiboles. This particular sample also contains a minute amount of euhedral red garnet (gr), which is normally a metamorphic mineral. According to Langosch A. et al. (2000) additional magma modification through assimilation of the country rock (paragneiss) is thought to have taken place.



Outcrop II. Small granite/orthogneiss vein in country rock consisting of paragneiss. The granite magma appears to have chemically interacted with the paragneiss creating a diffuse contact. 1: granite/orthogneiss, 2: paragneiss (metapelite)



Outcrop II. 1: granite/orthogneiss vein in paragneiss, 2: xenoliths i.e., pieces of assimilated country rock.



Outcrop III. 1: granite/orthogneiss body, 2: Pegmatite vein cross cutting the granite/orthogneiss body. Pegmatite veins have also intruded into the paragneiss as well as the diorite rock occurring further East near Lendas.



Outcrop III. 1: Coarse grained granite/orthogneiss body, 2: assimilated country rock, 3: pegmatite vein



Outcrop III. Closeup of pegmatite vein. fl: feldspar /K-feldspar, qu: quartz



Outcrop III. Closeup of pegmatite sample. fl: Feldspar /K-feldspar, mu: white sheet silicate (muscovite). Notice the almost perfect idiomorphic hexagonal-shape of the muscovite crystal.

4.2 Diorite Porphyry



Outcrop III. Dolerite/diorite dyke next to granite body displaying phenocrysts of plagioclase in fine-grained mafic matrix. The orange colours are due to oxidization of Fe-containing minerals

4.3 Granite/Orthogneiss Veins 2



Outcrop IV. 1: country rock consisting of paragneiss (metapelite), 2: Pegmatite vein cross cutting the country rock.



Outcrop IV. Country rock consisting of paragneiss next to granite/orthogneiss body. Granitoid magma was intruded along a fault or fissure within the country rock and later exposed to high temperature / low pressure metamorphism. The emplacement of magma is reported to have taken place during folding of the paragneiss and is therefore syn-metamorphic. [Langosch A. et al., 2000, Seidl]. 1: granite/orthogneiss, 2: country rock, 3: pegmatite vein.



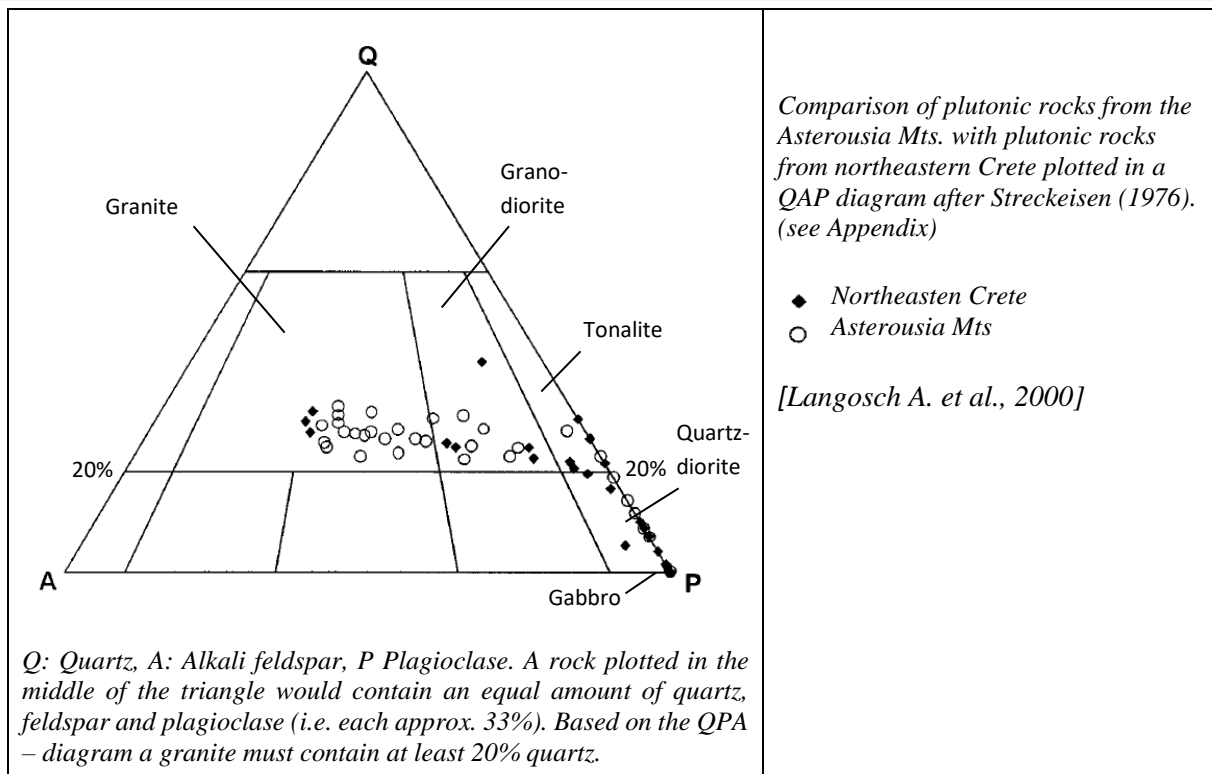
Outcrop IV: Closeup, of the transition from country rock (paragneiss) to the granite/orthogneiss. In this case the contact is diffuse indicating assimilation of country rock. 1: country rock, 2: granite/orthogneiss.



Outcrop IV: Closeup of granite/orthogneiss containing quartz, feldspar and probably garnet (other mafic minerals could not be determined on a macro scale). The small garnets indicate chemical interaction with the paragneiss. gr: garnet



Outcrop V. Granite/orthogneiss sill

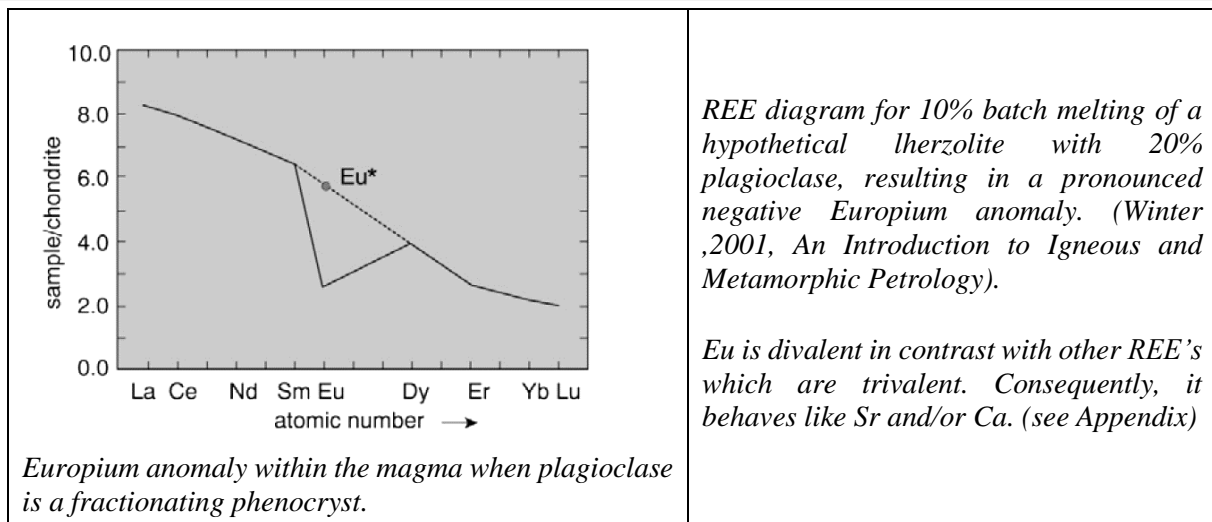


4.4 Rare Earth Elements (REE) and Incompatible vs Compatible Elements

Elements in igneous rocks and magmas can be divided into two groups: those that tend to remain in a magma until the later stages of crystallization (and consequently become enriched in the magma as crystallization takes place), and those that are easily incorporated into early growing crystals (and consequently become depleted in a magma quickly). Elements that tend to remain in the magma are said to be *incompatible*, and those that enter crystals quickly are *compatible*. Some elements behave as compatible elements in some magma types, but incompatible in others, because the specific minerals that crystallize vary with magma composition. Trace elements, however, both compatible and incompatible, are especially useful as trackers of magma evolution. Incompatible elements include the rare earth elements, elements (atomic No. 57 – 71, La – Lu). [Open Geology]

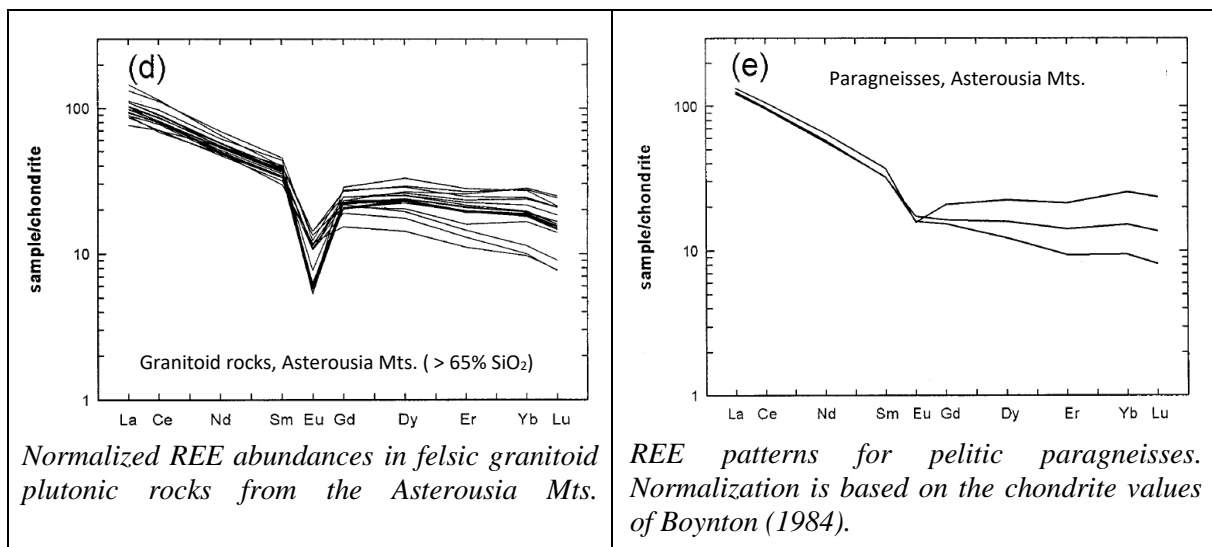
The europium anomaly is the phenomenon whereby the europium (Eu) concentration in a mineral is either enriched or depleted relative to some standard, commonly a chondrite or mid-ocean ridge basalt (MORB). In geochemistry a europium anomaly is said to be "positive" if the Eu concentration in the mineral is enriched relative to the other rare-earth elements (REEs), and is said to be "negative" if Eu is depleted relative to the other REEs. While all lanthanides form relatively large trivalent (3+) ions, Eu and cerium (Ce) have additional valences, europium forms 2+ ions, and Ce forms 4+ ions. In the case of Eu, its reduced divalent (2+) cations are similar in size and carry the same charge as Ca^{2+} , an ion found in plagioclase and other minerals. [Wikipedia]

Therefore, the enrichment or depletion Eu is generally attributed to europium's tendency to be incorporated into plagioclase preferentially over other minerals. If a magma crystallizes plagioclase, most of the Eu will be incorporated into this mineral, causing a positive anomaly. The rest of the magma will then be relatively depleted in Eu with a concentration of Eu lower than expected versus the concentrations of other REEs in that magma. If the Eu-depleted magma is then separated from its plagioclase crystals and subsequently solidifies, its chemical composition will display a negative Eu anomaly (because the Eu is locked up in the plagioclase left in the magma chamber). Conversely, if a magma accumulates plagioclase crystals before solidification, its rock composition will display a relatively positive Eu anomaly. [Wikipedia: https://www.wikiwand.com/en/Europium_anomaly]



4.4.1 Investigation of REE Content by Langosch A.

Several granites/orthogneisses are characterized by a strong negative Eu anomaly ("d" in following figure). Pelitic paragneisses from the Lendas and Kali Limenes areas ("e" in following figure) have REE patterns similar to the granites with the exception of their negative Eu anomalies being less pronounced ("e" in following figure). The development of a negative Eu anomaly requires the fractionation of plagioclase at an early stage of magma evolution. The similarity between the REE patterns of the paragneisses and granitoids is consistent with a major contribution from a (meta)sedimentary protolith (i.e. assimilation of country rock). Note that the negative Eu anomalies of the granitoids are much more pronounced than those of common sediments worldwide.



The conclusion from the major and trace element chemistry is that either the metasediments are not the parent rocks of the granitoids or the primary melts (of the migmatites) were modified by crystal fractionation, in particular by removal of plagioclase. The granitoid compositions can be modelled by an assimilation-fractional crystallization (AFC) process in which a diorite magma underwent fractional crystallization, accompanied by assimilation of (meta)sediments similar in composition to the amphibolite-facies metapelites. However, Langosch A. also states that there was probably some contribution of melts from lower-crust sources. [Langosch A. *et al.*, 2000]

4.5 Isotope geochemistry

Rb-Sr isotope analyses has been carried out by Langosch A. et al. (2000) to constrain the origin of the granitoids and mafic magmatic rocks. Due to the abundance of biotite in the meta-sedimentary and felsic to intermediate igneous rocks, the Rb-Sr system is particularly suitable for dating purposes of high temp metamorphic and igneous rocks. The results confirm the existence of a Late Cretaceous thermal event for Crete. The homogeneous paragneiss, migmatitic paragneiss and the granite/orthogneiss all have consistent biotite-whole-rock ages of about 72 Ma. Note that radiometric dating generally yields the age of metamorphism, but not the age of the original rock. Moreover, the homogeneous and the migmatitic paragneiss have almost identical initial $^{87}\text{Sr}/^{86}\text{Sr}$ (approx. 0.715). [Langosch A. et al. , 2000]

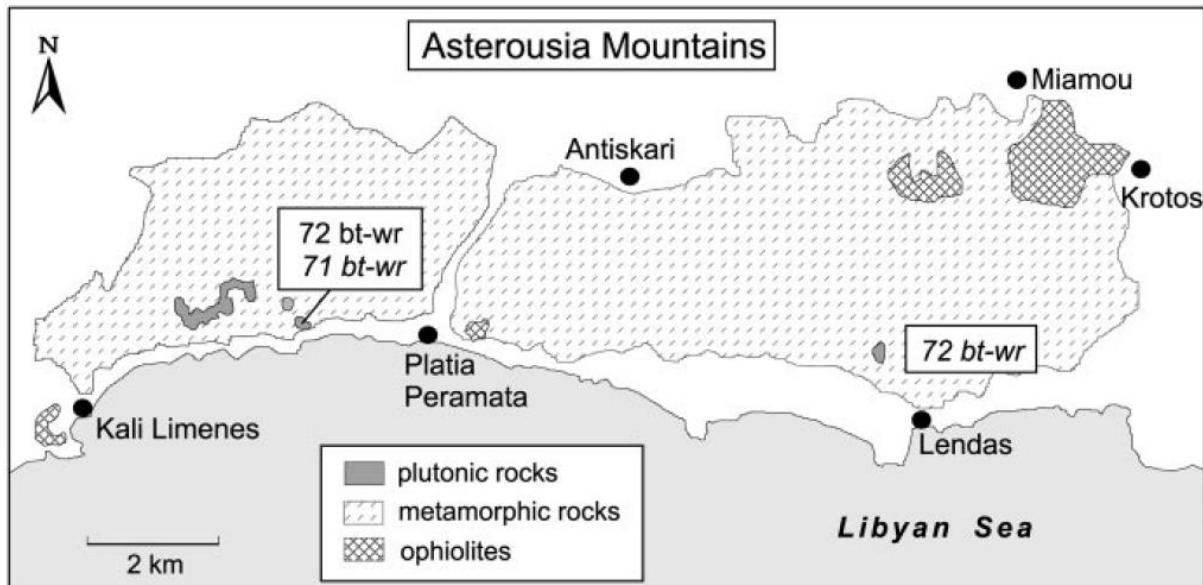


Fig. 2 Sketch map of the outcrops of Late Cretaceous plutonic rocks in central Crete based on a map of the Asterousia Mountains after Davis and Bonneau (1985), with modifications. Only the crystalline rocks and ophiolites are considered; other geological units are not specified (white areas). Numbers in boxes are Rb±Sr ages for biotite±whole-rock (bt-wr) in million years (for plutonic rocks shown in regular type, for paragneisses in italics). [Langosch A. et al. , 2000]

5 Sfinias Beach



Location of outcrops at the Sfinias Beach [Source of image: Google Maps]

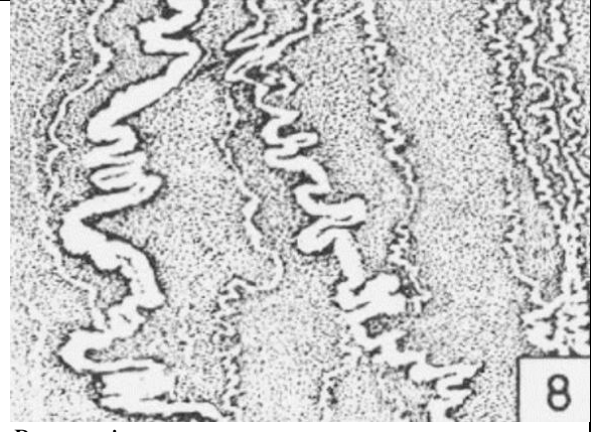
5.1 Migmatite and Orthogneiss Boulders

Migmatites are crystalline coarse-grained rocks that display signs of melting. They have clear distinguishable features with different mineral compositions and structures - one part belonging to the original metamorphic rock, and the other part having characteristics of melted rock (anatexis). In detail migmatites have the following textures:

- the mesosome (or palaeosome), which represents the unaltered, metamorphic parent rock,
- the leucosome, which is usually significantly lighter in colour compared to the mesosome, i.e. it contains more quartz and feldspar and shows no favoured orientation of its mineral grains
- the melanosome, which is enriched in dark (mafic) minerals, such as biotite or amphibole, and which usually occurs at the boundary between mesosome and leucosome.



Schlieren structure



Ptygmatic structure

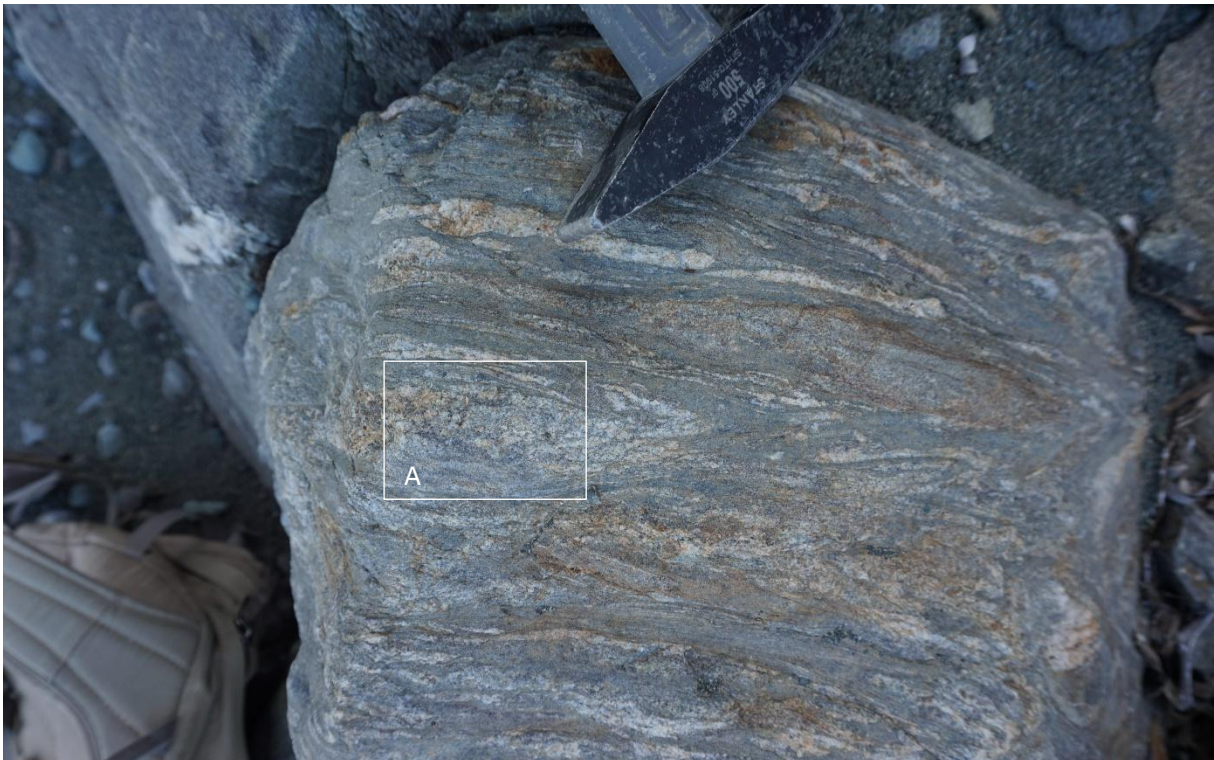
Anatexis occurs when metamorphic rocks deep within the earth's continental crust become heated reaching a critical temperature (solidus -liquids boundary). The first minerals to melt are the felsic minerals such as quartz and feldspar.



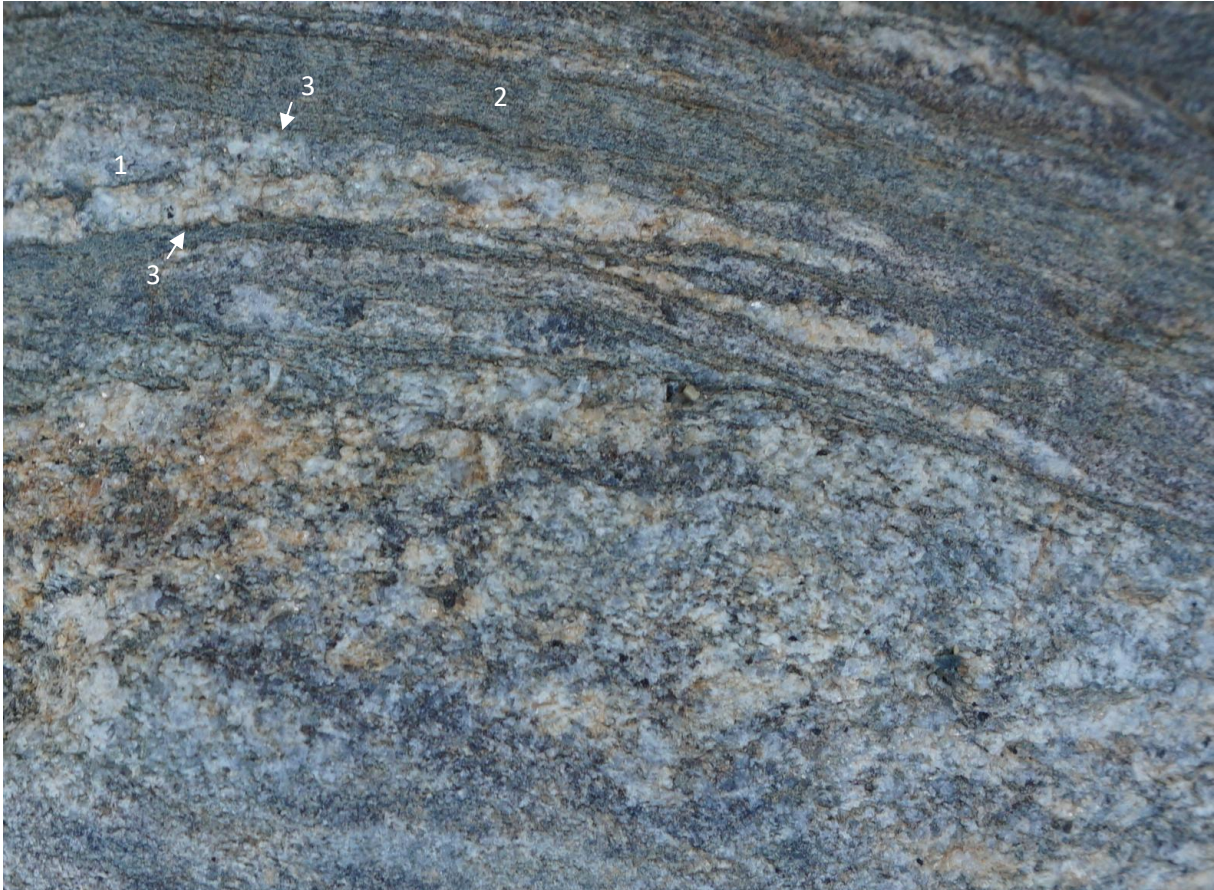
Outcrop I, Migmatite. 1: metamorphic texture more or less representing the original rock prior to anatexis – in this case an amphibolite, 2: migmatite texture representing melted rock by anatexis. The amphibolite is characteristically green indicating intermediate to mafic composition.



Outcrop II, Migmatite developed from amphibolite displaying schlieren and ptigmatic structure. 1: schlieren structure; 2: fine grained mesosome thought to represent the unaltered, metamorphic parent rock; 3: ptigmatic structure that is superimposed on "1 & 2". This could indicate two different phases of HT/LP conditions.



Outcrop II, Greenish migmatite boulder with schlieren structure thought to have developed from a mafic fine-grained amphibolite.



Outcrop II, Box A, 1: leucosome recognizable by coarse grained felsic minerals, in this case feldspar, 2: mesosome representing the original metamorphic rock, 3: the melanosme in this case is made up of very fine layers of mafic minerals that fringe the leucosome.



Outcrop II. Green schist boulder



Outcrop III, Migmatite displaying a fold structure



Outcrop III. Slightly brownish granite/orthogneiss with predominantly homogenous structure.



Outcrop III. Light grey orthogneiss displaying foliated texture.



Outcrop III. Orthogneiss displaying foliation of mafic minerals and lighter coarser grained vein. Note that there is no visible melanosome at the border of the vein, which excludes it from being a leucosome and ultimately a migmatite. The vein is assumed to be a secondary pegmatite/aplite intrusion.



Outcrop III. Closeup of previous picture



Outcrop III. Contact of orthogneiss with country rock indicating that magma once intruded into a cavity probably during folding and later became foliated due to metamorphic conditions.



Outcrop III. Closeup of previous picture. There appears to have been some chemical interaction between the granitoid magma and the country rock owing to the fine veins of felsic minerals mingling with the paragneiss (white arrow) and the white fringe around the paragneiss (black arrow).



Outcrop III. Orthogneiss containing xenoliths. 1: xenolith - a xenolith is a fragment of country rock that has been enveloped by magma during the magma's ascent and emplacement. Xenoliths may be assimilated from the margin of a magma chamber and influence the magma's composition.



Outcrop III. Closeup of previous picture indicating the xenolith itself to have undergone metamorphose. The orthogneiss displays round dark brown spots that could be weathered garnet. Garnet is a mineral that forms solid solutions meaning that its composition changes depending on the T/P conditions and the chemistry of its surroundings. In some cases, zoning of garnet presents a method of determining the evolution of a rock.



Outcrop III. Boulder displaying mafic xenoliths. The fringes of felsic minerals around the xenoliths indicate chemical interaction with the magma.



Outcrop III. Closeup of previous picture showing mafic xenoliths in orthogneiss. Notice the coarse grained feldspar around the mafic xenolith, which consist mainly of biotite.

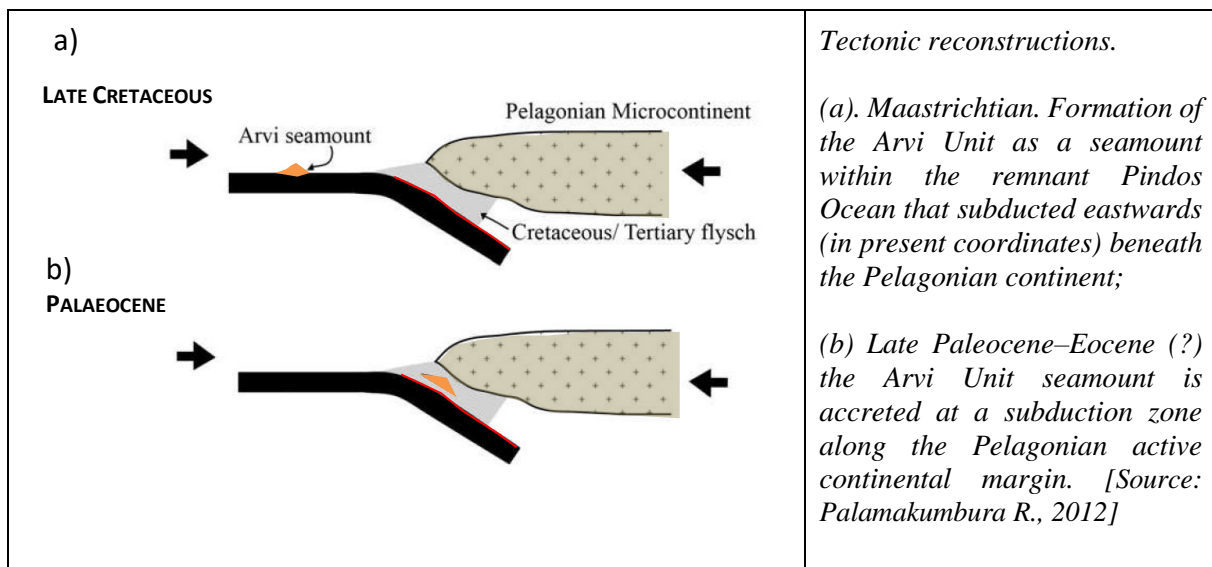
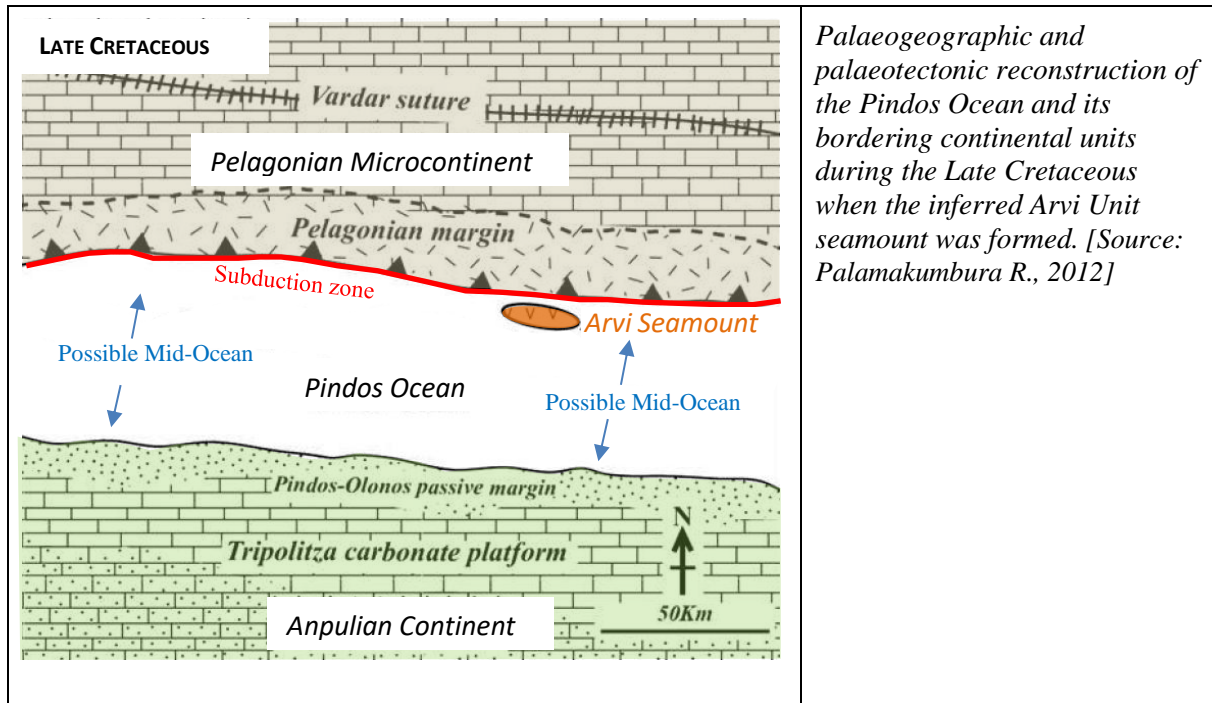
6 Red Slates/Marl, Limestone and Basalt (Arvi Unit)

As part of the Uppermost Unit the Arvi Unit is exposed along the southern margin of the Asterousia Crystalline Complex (ACC) along the southern coastline of central Crete. Tectonostratigraphically it is overthrust by the ACC nappe. Between Kali Limenes and Lendas the Arvi Unit, which is slightly metamorphic (prehnite-pumpellyite facies) displays pillow and sheet lavas, limestones, red slates/marls, and grey phyllites. The Arvi unit has been divided by Davi and Bonneau (1985) into the following sequence: Late Triassic pink or grey limestones, a flyschoid series (probably Late Jurassic), Late Cretaceous creamy limestones, pillow basalts with their sedimentary cover constituted by red micritic limestones and shales (Cenonian?-Maastrichtian) [Stampfli, 2010].

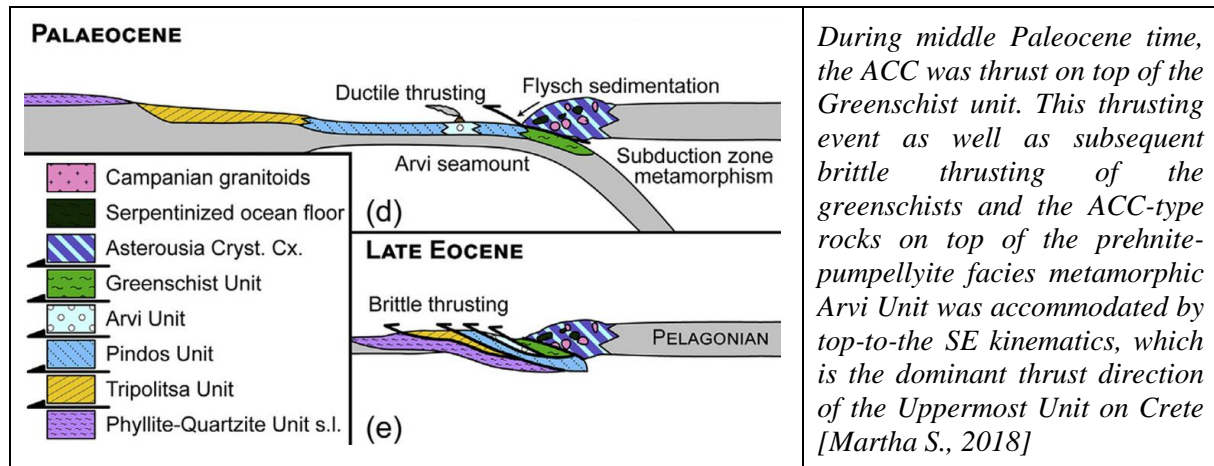
Rock Type	Age	Section
Red micritic pelagic limestones and shales	Cenonian? - Maastrichtian	
Pillow and sheet basalts		
White (creamy) pelagic limestones	Late Cretaceous	
Sandstones and pelite (flyschoid ser.)	Late Jurassic	
Micritic and cherty limestones	Not exposed at this location	
Intraformational breccias	Late Triassic	
Micritic and cherty limestones		

Source: Stampfli, Vachard D.

The geochemical analysis of the basalts by Payer (2001) show that the basalts have a within-plate signature (Payer, 2001). According to Bellini (2002), the Arvi unit occupies a structural position between the Tripolitza and the Pindos units. It is therefore indicated to have been emplaced within the Pindos basin between the Tripolitza platform and the Pelagonian Microcontinent in form of isolated volcanos/ seamounts [Stampfli, 2010].



A notable feature of the lava sequence is the presence of peperites that are composed of variably mixed basalt and pelagic carbonate (see Appendix). The style of the textures varies between blocky and fluid like. Peperite formation involves the fragmentation and intermingling of erupting lava with fluid-rich sediments (Skiing et al., 2002). South of the Dikti Mts. two samples of carbonate rock associated with pillow lava are reported to have been dated using planktic foraminifera. One sample came from peperites within the lavas and the other from the succession of pelagic limestone above the lavas. Both of these samples were shown to be of Late Maastrichtian age. [Palamakumbura R., 2012]



View of Sfinias beach looking westwards. Location of outcrops. V: tectonic *mélange*, VI: green metamorphic or hydrothermally altered lava, VII: Pink and white pelagic limestone, VIII: Red slate/marl, IX: "Violet" volcanic rock in tectonic *mélange*.

6.1 Basalt/andesite and tectonic Mélange



Outcrop IV, andesite or basalt lava partly displaying pillow structures



Outcrop IV, the grey colour of the lava indicates it to be of intermediate composition. Notice the small phenocrysts of plagioclase.



Outcrop V. Tectonic mélangé (see Appendix for description of tectonic mélangé)



Outcrop V. Tectonic mélangé consisting of grey schist with quartz "Augen". Tectonic mélangé is the result of extensive shearing and is characteristic of thrust planes



Outcrop VI: bright green metamorphic or hydrothermally altered lava.



Closeup of previous picture. Sample with dark mafic minerals embedded in a green matrix.

6.2 Pink and White Limestone Associated with Basaltic Lava (Arvi Unit)



Outcrop VII: white and pink limestone that is not metamorphic (i.e. not marble)

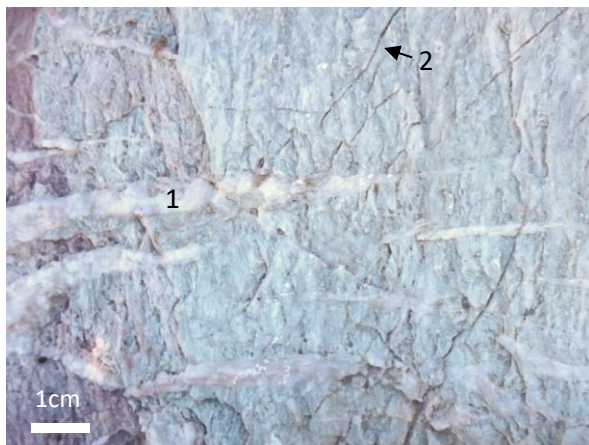


Outcrop VII: white and pink limestone displaying kink band approx. vertical to bedding.



Outcrop VII: closeup of the white part of the limestone

Work by Palamakumbura R., et al (2012) conducted within the Arvi Unit south of the Dikti mountains about 50 km further East describes pelagic carbonates associated with pillow lava and sheet lava. Based on the existence of pelagic foraminifera the limestone there is reported to be of Upper Maastrichtian age. Note that the limestone there is pink whereas the limestone at the Sinifas Beach consists of pink and white layers. A mutual feature is the existence of peperite, which is formed when lava mixes with wet sediments in this case limy muds.



Weanereu surface of the pink and white limestone. 1: Veins at right angles to bedding planes are filled with calcite and represent a phase of brittle deformation. 2: A younger phase of deformation is indicated by the diagonal fissures.



Close up of the pink and white limestone probably showing manganese dendrites (arrow). They are thin, branching crystals that grow over a surface in a rock or mineral. Often, they are found in cracks or along bedding planes. The dendrites are usually some variety of manganese oxide.

6.3 Red slates and Peperites



Closeup of red “slate/marl”. The slates are in reality marls as they fizz when tested with diluted hydrochloric acid.



Outcrop VII: Intermingled rock layers cropping out at the seashore. 1: pink and white limestone, 2: red slate/marl, 3: hydrothermally altered violet lava.



Outcrop VIII: red slates/marl, overlying hydrothermally altered basaltic rock



Outcrop VIII: Red slates/marl, overlying hydrothermally altered volcanic rock. The chaotic texture consisting of intermingled volcanic rock and pink limestone is indicated to be the result of lava mixing with wet sediment. The sediment clasts are called peperites (see Appendix for details).



Outcrop VIII: Closeup of previous picture. Volcanic rock displaying peperite texture. 1: “violet” lava 2: intermingled pink limestone, 3: green hydrothermal mineral that is not calcareous (probably containing epidote).



Outcrop IX. 1: Hydrothermally altered volcanic rock displaying a network of calcite veins and partly peperite texture, 2: highly sheared lava, 3: red slate/marl, 4: fine network of calcite in softer red slate/marl (see next picture). The rock sequence red slate/marl (and/or limestone) repeats itself in this section



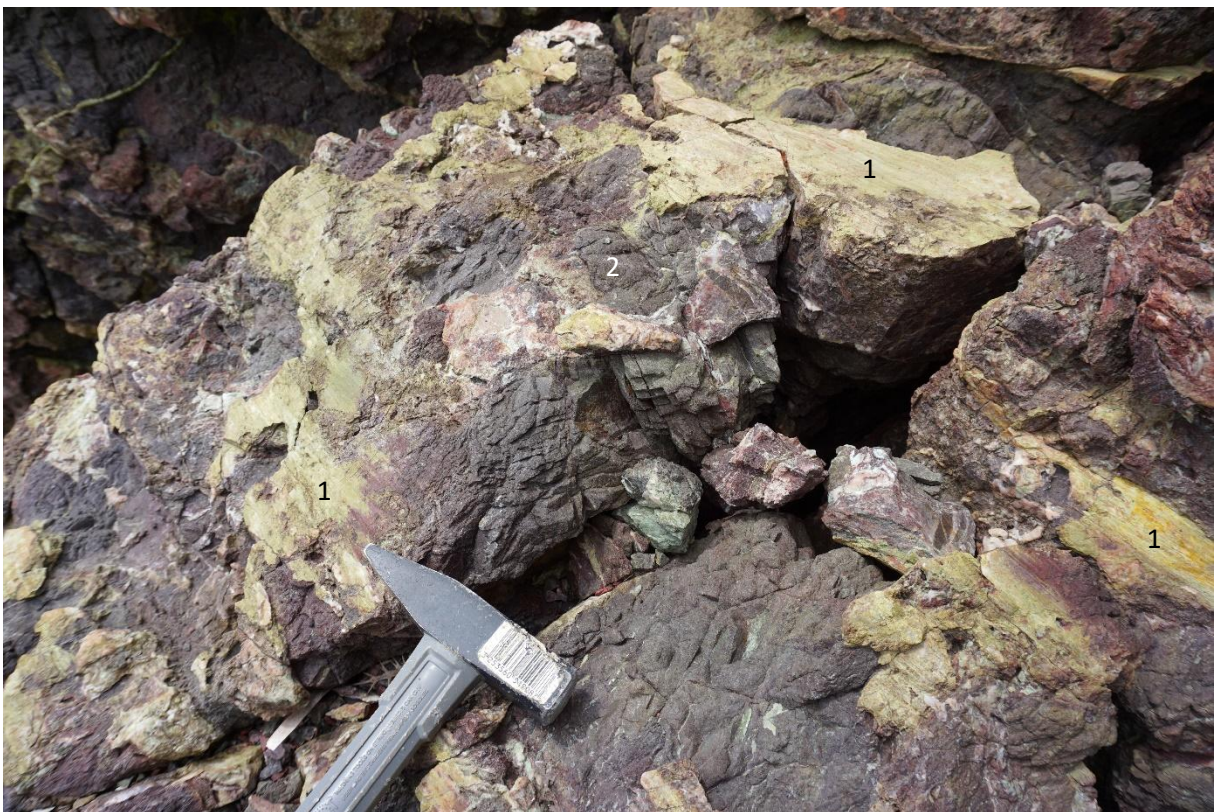
Outcrop IX, Closeup of previous picture. Fine network of calcite veins in red slate/marl. Weathering has produced a relief between the slightly harder calcite and softer slate/marl. 4: Kink band structures are now filled with calcite.



Outcrop IX: Boulder composed of violet and white limestone layers as well as red slate/marl. The upper part of the boulder is underlain by red slate/marl, which has numerous calcite veins. Notice that the veins are curved and pass from the red slate/marl into the limestone indicating that the different layers were deformed simultaneously resulting in fissures that were later filled with calcite.



Outcrop IX: A boulder displaying “violet” volcanic rock embedded in calcite and grey limestone. 1: clast of volcanic rock. It contains phenocrysts probably of plagioclase.

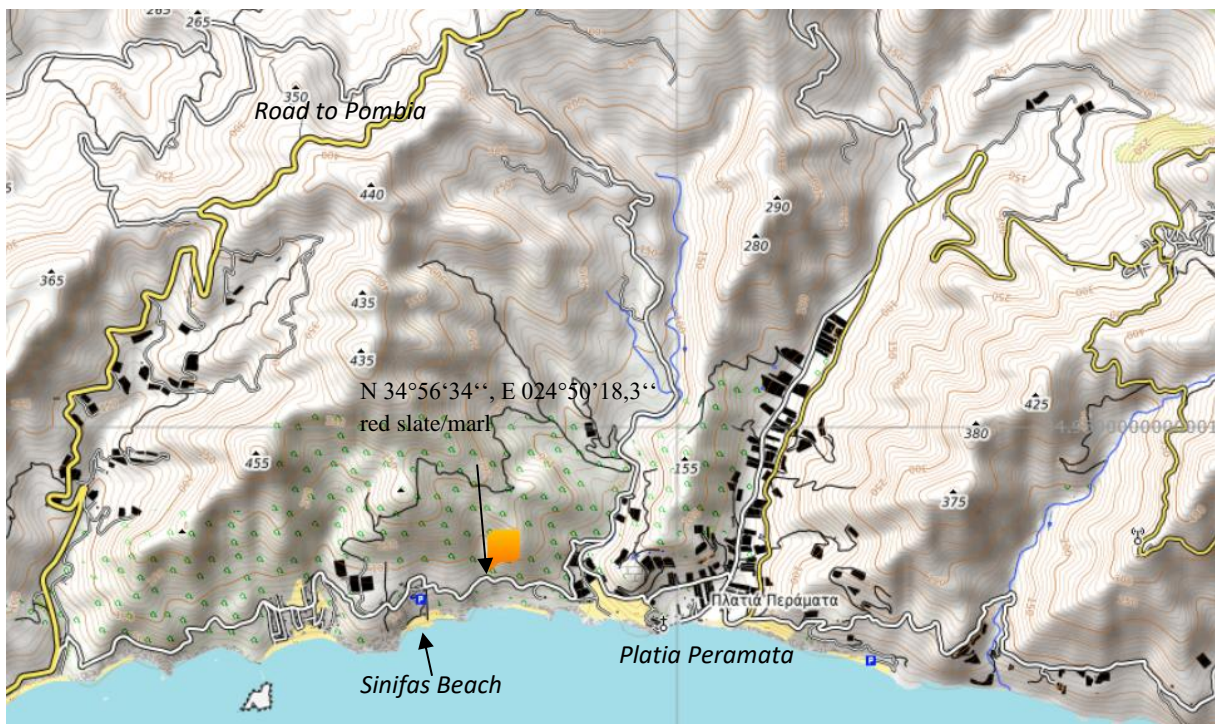


Outcrop IX: Volcanic rock displaying slickensides. Slickensides surfaces are formed along fault planes, whereby the direction of movement along the fault is indicated by the lineation. Epidote is thought to be a major component to the slickenside surfaces owing to the green colour and it being a common secondary mineral. 1: slickenside, 2: blocks of volcanic rock with peperite texture.



Outcrop X: “Violet” volcanic rock with pink micritic limestone. In this example, at an outcrop approx. 50m west of the Sinifas Beach, mixing of the lava appears not to be so extensive. An interesting feature are the hexagonal shapes that is reminiscent of basalt columns. The hexagonal shape originates from contraction when basaltic lava cools. Notice that the micritic lime mud and the volcanic rock both display secondary white calcite veins. This indicates tectonic activity after cooling of the lava and after diagenesis of the lime mud. 1: pink micritic limestone (once wet limy mud), 2: hexagonal column-shape as seen from the top of the column (once basaltic lava).

7 Sinifas Beach to Platia Peramata



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9 Appendix

Geological Time Scale

Eonothem/ Eon	Erathem/ Era	System/ Period	Series/ Epoch	Stage/ Age	mya ¹
Phanerozoic	Cenozoic	Neogene	Pliocene	Piacenzian	2.58
				Zanclean	3.600
			Miocene	Messinian	5.333
				Tortonian	7.246
				Serravallian	11.63
				Langhian	13.82
				Burdigallian	15.97
				Aquitanian	20.44
					23.03
		Paleogene	Oligocene	Chattian	27.82
				Rupellian	33.9
			Eocene	Priabonian	37.8
				Bartonian	41.2
				Lutetian	47.8
				Ypresian	56.0
					59.2
			Paleocene	Thanetian	61.6
				Selandian	66.0
				Danian	66.0
	Mesozoic	Cretaceous	Upper	Maastrichtian	72.1 ± 0.2
				Campanian	83.6 ± 0.2
				Santonian	86.3 ± 0.5
				Coniacian	89.8 ± 0.3
				Turonian	93.9
				Cenomanian	100.5
					113
			Lower	Albian	~125.0
				Aptian	~129.4
				Barremian	~132.9
				Hauterivian	~139.8
				Valanginian	~145.0

Eonothem/ Eon	Erathem/ Era	System/ Period	Series/ Epoch		Stage/ Age	mya ¹		
Phanerozoic	Mesozoic	Jurassic	Upper		Tithonian	~145.0		
					Kimmeridgian	152.1 ± 0.9		
					Oxfordian	157.3 ± 1.0		
			Middle		Callovian	163.5 ± 1.0		
					Bathonian	166.1 ± 1.2		
					Bajocian	168.3 ± 1.3		
					Aalenian	170.3 ± 1.4		
						174.1 ± 1.0		
			Lower		Toarcian	182.7 ± 0.7		
					Pliensbachian	190.8 ± 1.0		
					Sinemurian	199.3 ± 0.3		
					Hettangian	201.3 ± 0.2		
		Triassic	Upper		Rhaetian	~208.5		
					Norian	~227.0		
					Carnian	~237.0		
			Middle		Ladinian	~242.0		
					Anisian	247.2		
			Lower		Olenekian	251.2		
		Induan		251.902 ± 0.024				
	Paleozoic	Permian	Lopingian		Changhsingian	254.14 ± 0.7		
					Wuchiapingian	259.1 ± 0.5		
			Guadalupian		Capitanian	265.1 ± 0.4		
					Wordian	268.8 ± 0.5		
					Roadian	272.95 ± 0.11		
			Cisuralian		Kungurian	283.5 ± 0.6		
					Artinskian	290.1 ± 0.26		
					Sakmarian	295.0 ± 0.18		
					Asselian	298.9 ± 0.15		
						298.9 ± 0.15		
			Carboniferous	Pennsylvanian ²	Upper		Gzhellian	303.7 ± 0.1
							Kasimovian	307.0 ± 0.1
		Middle				Moscovian	315.2 ± 0.2	
		Lower			Bashkirian	323.2 ± 0.4		
				Mississippian ²	Upper		Serpukhovian	330.9 ± 0.2
		Middle			Visean	346.7 ± 0.4		
Lower			Tournaisian		358.9 ± 0.4			

Peperites

<https://www.wikiwand.com/en/Peperite>



White (2000) defines peperite as "a genetic term applied to a rock formed essentially in situ by disintegration of magma intruding and mingling with unconsolidated or poorly consolidated, typically wet sediments. The term also refers to similar mixtures generated by the same processes operating at the contacts of lavas and other hot volcaniclastic deposits with such sediments".

Formation

When magma comes into contact with wet sediment several processes combine to produce the mixture of sedimentary and igneous clasts which is characteristic of a peperite. These processes are required to produce both the disintegration or fragmentation of magma to form juvenile clasts and the mingling of these clasts within the sediment. Mechanisms proposed for the fragmentation of the magma include; fracturing due to the stresses associated with quenching, autobrecciation due to continuing flow in the cooling magma, pore-water steam explosions and magma-sediment density contrasts. The main mechanism suggested for mingling of the igneous clasts with the sediment is fluidisation, in the sense of particle support and transport by a fluid.

Example Tennant Creek porphyry, Australia

‘Upward from the contact of the porphyry sill, tongues and irregular bodies of porphyry, some apparently detached from the main mass, penetrate several metres into the sandstone.

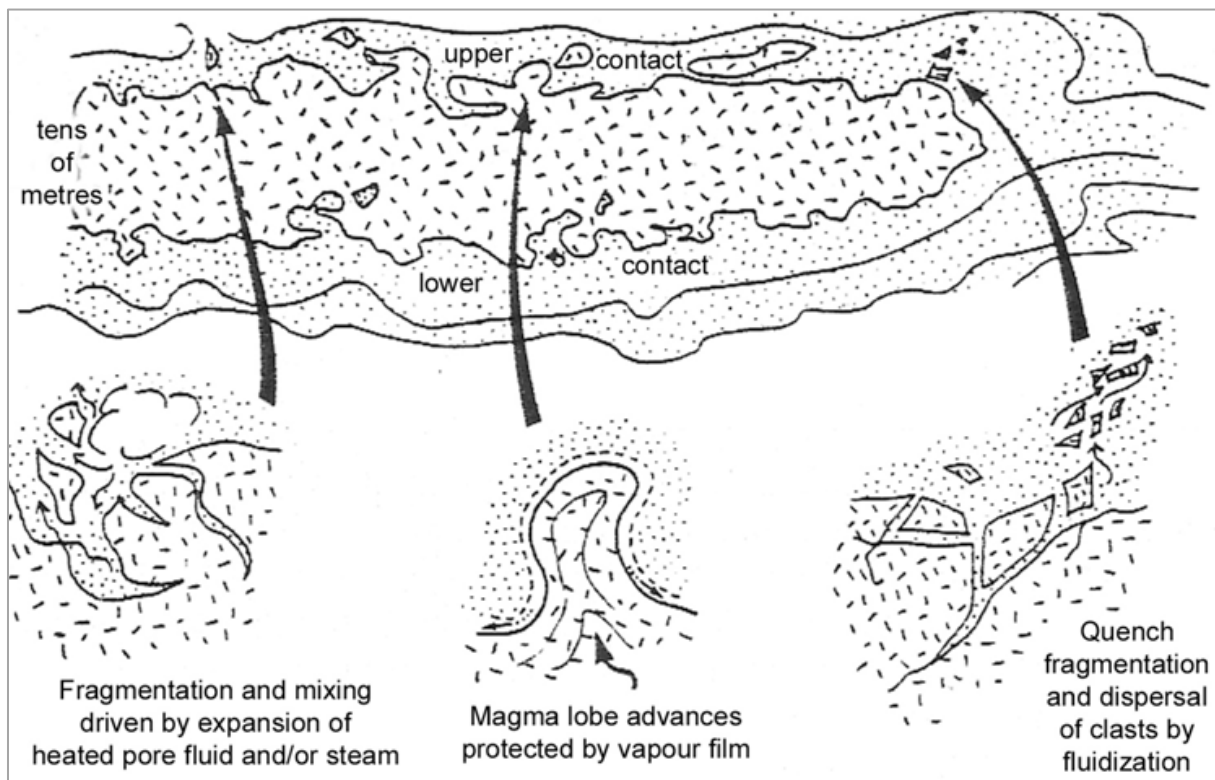


Diagram illustrating the processes involved in peperite formation at the sill margins. The important

processes for the Tennant Creek porphyry appear to be a tearing of the magma into fluid-shaped clasts and quench fragmentation (from McPhie).¹

All these textures convinced Jocelyn McPhie that the Tennant Creek porphyry was emplaced *within* the sediments while they were still unconsolidated and still filled with water. She was not able to determine the thickness of the sediments when the porphyry was emplaced, but she suggested that they were of the order of 100s of metres thick at the time.

Sedimentary and Tectonic Mélanges

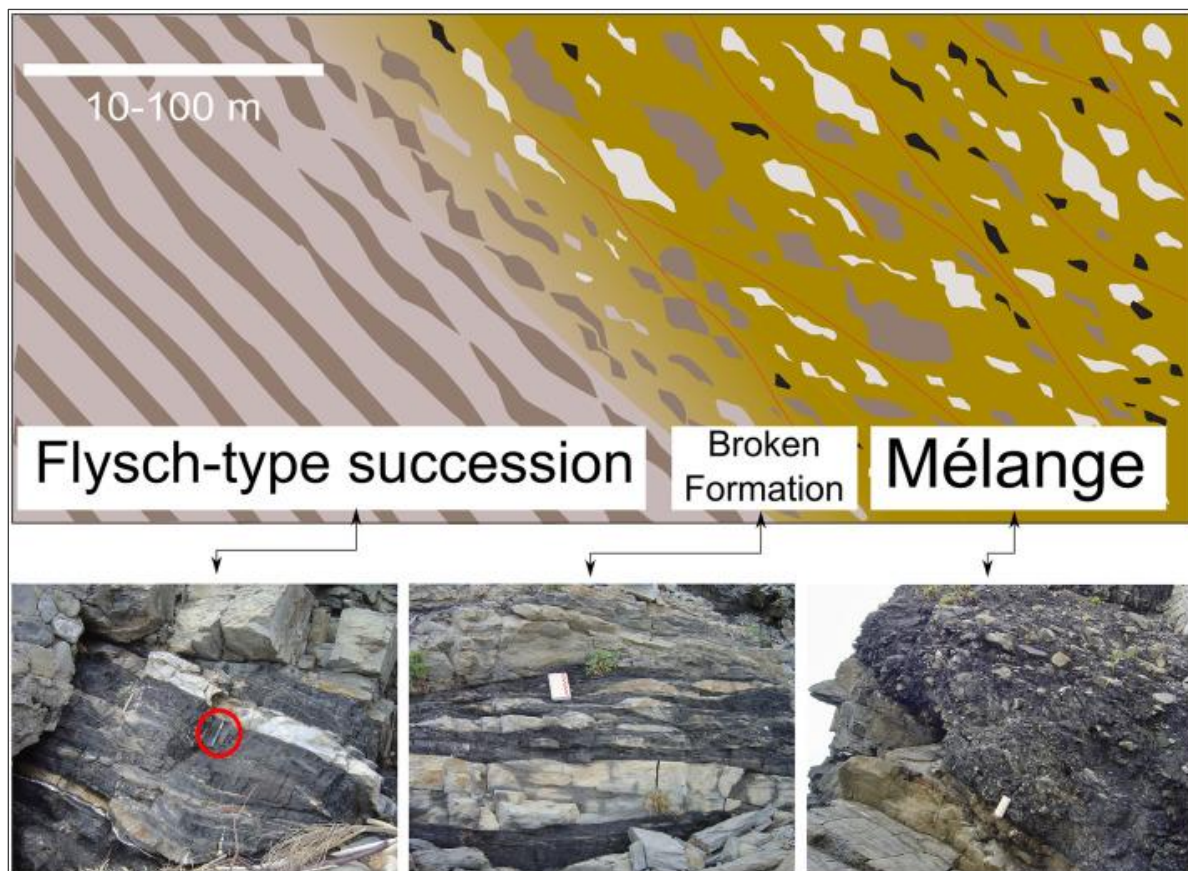


Fig. 1. Conceptual diagram showing a gradual transition from an undeformed, flysch-type lithology to a mélangé (mixed rock) passing through a broken formation (un-mixed rock; modified from Festa et al., 2019). Outcrop examples are from the Eocene Canetolo Formation exhumed at the Cinque Terre, La Spezia (Northern Apennines, Italy). [Ogata K. et. al., 2013]

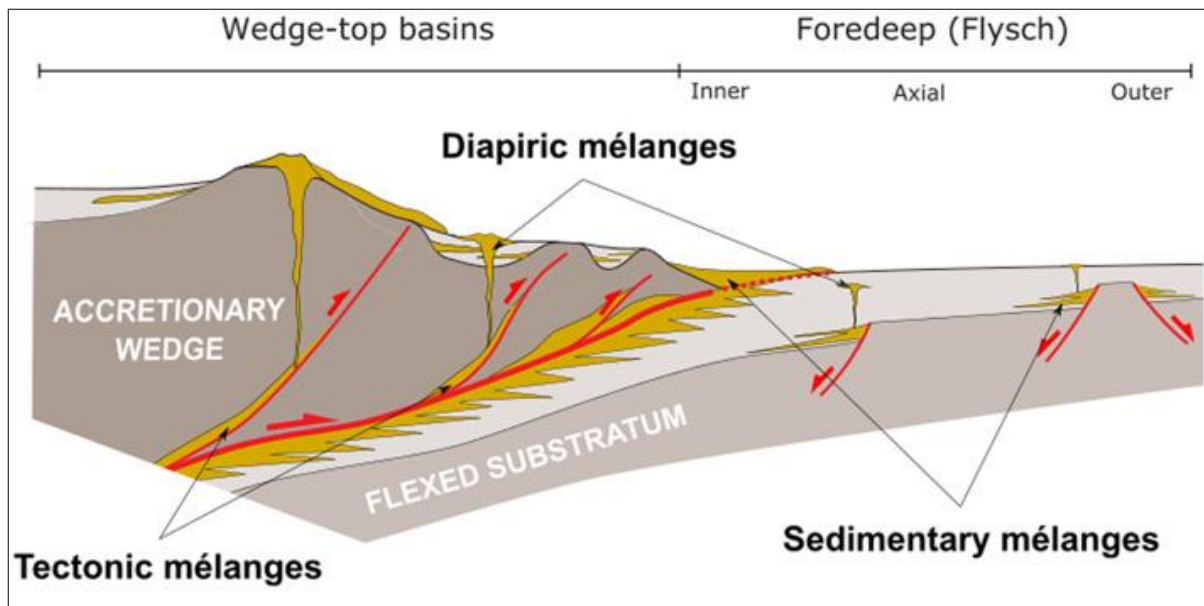


Fig. 2. Schematic cartoon illustrating a profile across an ideal Alpine-type foreland basin (flysch to molasse) with subdivision of the depositional settings and the typical localisation of sedimentary, tectonic and diapiric mélange units. Note the reworking and recycling of these processes and products through time (modified from Festa et al., 2019). [Ogata K. et. al., 2013]

QAPF diagram

A QAPF diagram is a doubled-triangle plot diagram used to classify intrusive igneous rocks based on their mineralogy. The acronym QAPF stands for "Quartz, Alkali feldspar, Plagioclase, Feldspathoid (Foid)", which are the four mineral groups used for classification in a QAPF diagram. The percentages (ratios) of the Q, A, P and F groups are normalized, i.e., recalculated so that their sum is 100%.

Pegmatites



<https://geologybase.com/pegmatites/>

Pegmatites are intrusive or plutonic igneous rocks with wholly crystalline, unusually large, or coarse crystals that may sometimes interlock. These rocks form from a low-viscosity fluid phase rich in volatile compounds formed during the crystallization of the last magma portion. Usually, pegmatitic rocks will have crystals that are at least 0.4 inches (1 cm) in diameter, with the larger ones more than 1.2 inches (3 cm) and some as large as 10 m (33 feet). Pegmatites host the largest crystals, like mica, microcline, spodumene, beryl, quartz, and tourmaline. Most pegmatites have quartz, feldspar, and mica, with a silicic composition similar to granites. However, they can be also of mafic composition such as gabbro, syenite.

Pegmatite or pegmatitic texture only describes the texture, not the mineral composition. Therefore, the rock name may be used as a prefix to indicate the mineral composition. For instance, granite pegmatite, diorite pegmatite, or gabbro pegmatite suggest that the said rock has granite, diorite, and gabbro composition, respectively.

Pegmatite bodies are smaller than usual magma intrusion and may be pod-like, tubular, cigar-shaped, inverted teardrop, or irregular-shaped. They can occur as segregated small pockets or bodies within a large intrusive rock body or extrude into country rock, forming sills, lenses, or even pegmatite dike.

Complex pegmatite mineral composition

Most complex pegmatites have a composition like granite but are enriched with some incompatible elements and minerals not typically found in most igneous rocks. Some may also be of intermediate to mafic composition. Incompatible elements are those with a too-large or small atomic number or very high or low ionic charge or size. So they cannot participate in the rock formation. Instead, they will remain dissolved in water and eventually form their minerals. Examples of incompatible elements in pegmatites are uranium (U), niobium (Nb), boron (B), yttrium (Y), phosphorus (P), fluorine (F), lithium (Li), zirconium (Zr) and beryllium (Be). Others are Strontium (Sr), Barium (Ba), scandium (Sc), Tantalum (Ta), thorium (Th), cesium (Cs), Tin (Sn), Titanium (Ti), Bismuth (Bi), and some Rare Earth Minerals (REEs).

These incompatible elements may form minerals such as pollucite (Cs), spodumene (Li), Beryl (Be), tantalite-columbite (Ta, and Nb), tourmaline (Li, B), cassiterite (Sn). Also, complex pegmatites may also have beryl, lepidolite, topaz, apatite, garnet, emerald, spodumene, tourmaline, mica, monazite, and fluorite. Other minerals are amblygonite, triphylite, molybdenite, scapolite, columbite etc. These minerals are not typical in ordinary igneous rocks.

Formation of pegmatites

Pegmatitic rock is generally thought to form from the low-viscosity superheated fluid phase that separates from the last portion of magma melts to crystallize and does not necessarily have a slower cooling rate than the rest of the magma. Of course, the cooling is slow, being intrusive. At the initial stages following a significant magma intrusion, minerals with higher melting points will start crystallizing and slowly be depleted from the magma. As the process continues, remaining magma increasingly remains with minerals with lower melting, water, and volatiles. These volatile compounds include carbon dioxide, boron, fluorine, chlorine, and phosphorus.

Also, any incompatible minerals or elements will remain in this melt, specifically in water. At the final stage of magma crystallization, the exceptionally high amount of dissolved water causes a phase separation resulting in the last magma melt and fluid phase or superheated water pockets rich in silica, alkalis, volatiles, and incompatible trace elements. The fluid phase is what forms pegmatites. The presence of volatiles, i.e., water, carbon dioxide, chlorine, and fluorine, will tremendously lower the viscosity of the fluid phase (hydrous fluid). So, ions or molecules can move, migrate, or diffuse quickly to the crystal growth site. Also, the crystal growth rate (ions or molecules joining a growing crystal) exceeds nucleation (formation of new nuclei or sites for crystallization). Otherwise, you will end up with many smaller crystals.

Lastly, pegmatite formation isn't only associated with intrusive rocks or magma. For example melting or anatexis of metamorphic rock under high pressure and temperature may produce pegmatites. The melting will make fluids, volatiles, and trace elements sweat out, forming a fluid phase pocket seen in felsic gneiss.

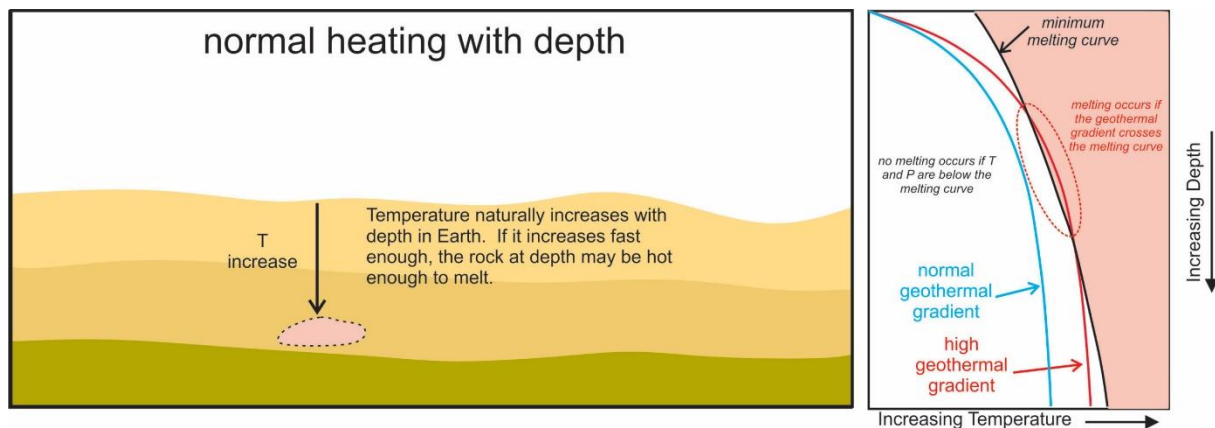


Emeralds (green), schorl tourmaline (black), and garnet (pinkish-reddish) in quartz (medium-brown glassy) and feldspar (grayish) Crabtree Pegmatite from Devonian of North Carolina, USA. Photo credit: [James St. John](#), Wikimedia, [CC BY 2.0](#).

<https://opengeology.org/petrology/03-magma/>

Origin of Magma

Just as ice melts when temperature goes above 0 °C, rocks will melt if heated to temperatures above their melting temperatures. To accomplish this rock melting requires extra heat, and that poses a problem. Where is the extra heat to come from? Although radioactive decay of potassium, uranium, thorium, or other radioactive elements may create small amounts of heat, most of Earth's heat is left over from the original time of formation. This residual heat flows from Earth's interior to dissipate at the surface, and Earth has been cooling for more than 4.5 billion years. In some places, flowing magma delivers extra heat, but the origin of the heat necessary to initially create the magma is problematic.

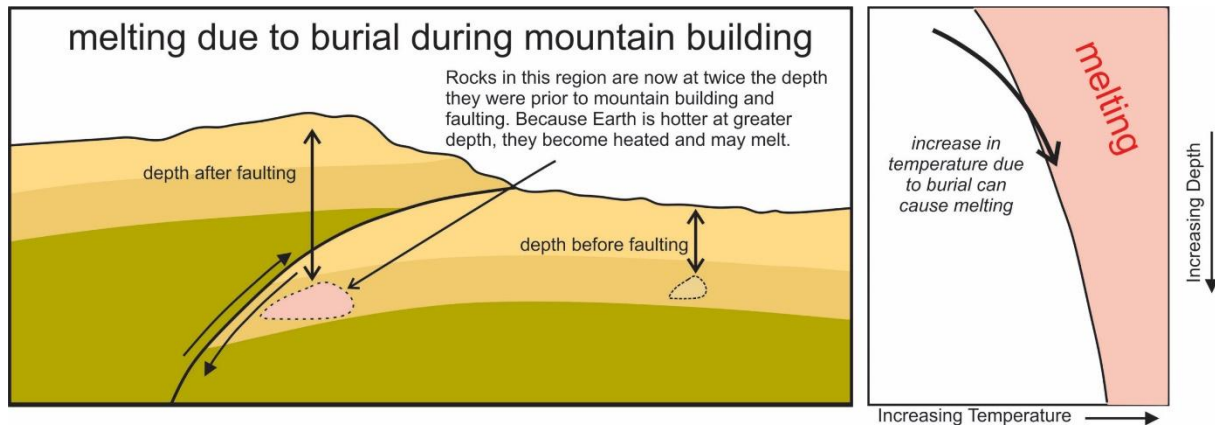


3.18 Heating with depth in Earth

Earth's average *geothermal gradient* (the rate at which temperature increases with depth in Earth) is about 25 °C/km near the surface. It is not the same everywhere – some places, such as mid-ocean ridges or hot spots like Yellowstone, have very high gradients, sometimes exceeding 50 °C/km. Other places, such as centers of old continents, have low gradients. The blue and red lines in the temperature-depth diagram on the right of Figure 3.18 are *geotherms*. The geotherms show schematically how temperature increases with depth for a place with an average gradient and for a place with a high gradient.

The solid black curve in the temperature-depth diagram of Figure 3.18 is a typical *melting curve*; it shows the minimum temperatures at which melting can occur. If temperature-depth conditions plot in the red part of the diagram, rocks will melt. The minimum melting temperature increases with depth but so do temperatures along the geotherms. In principle, if the geothermal gradient is high enough, the temperature may exceed the melting curve (shown where the red “high” geothermal gradient line crosses the black melting curve in Figure 3.18). Yet, even at mid-ocean ridges or hot spots, the gradient is generally insufficient for this to happen and cause melting. Consequently, most of Earth's mantle is unmelted.

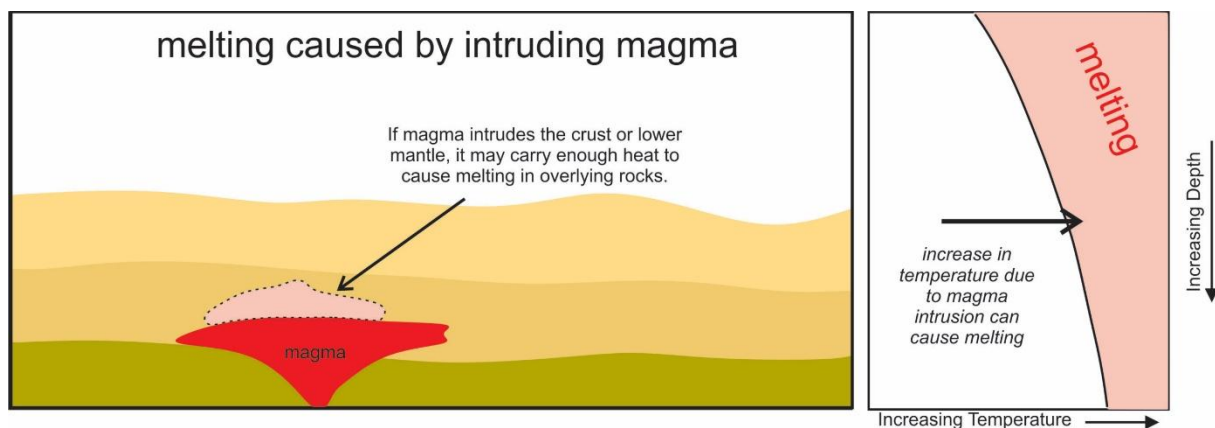
Melting Caused by Mountain Building



3.19 Melting during mountain building

Because a normal geothermal gradient cannot lead to melting, other mechanisms must be responsible in most cases. For instance, *tectonism* associated with mountain building can occasionally cause melting when rocks are buried by folding or faulting – because heating naturally accompanies burial (Figure 3.19). The pressure-temperature diagram on the right side of this figure shows that if burial-induced heating is great enough, melting may occur when temperatures cross into the melting field (shown in pink). Some granites in continental regions undoubtedly form by melting of sediments and sedimentary rocks, once at or near the surface, that melted after being carried to depth.

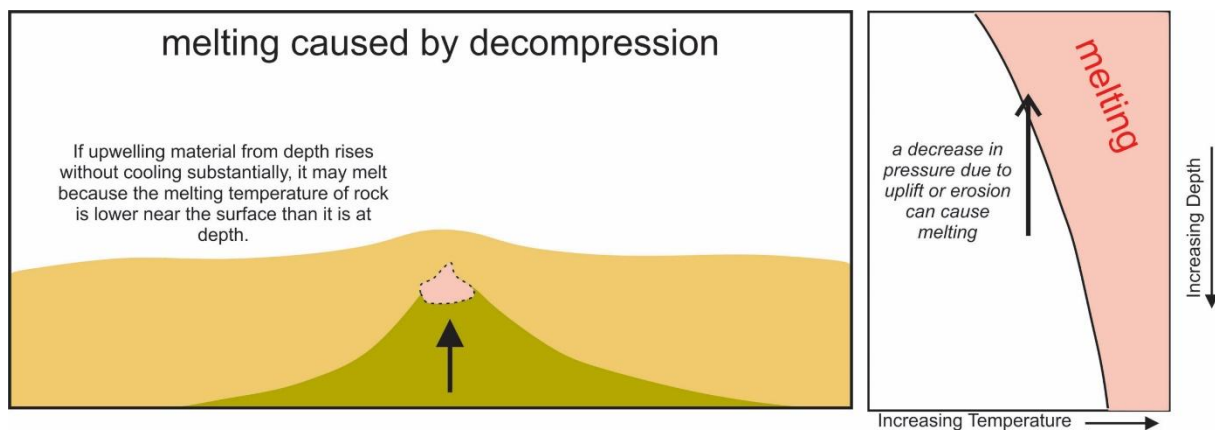
Melting Caused by Intruding Magma



3.20 Melting caused by magmatic intrusion

Intruding magma is a very efficient mechanism for delivering heat that can cause melting (Figure 3.20). As shown by the black arrow in the pressure-temperature diagram, heat from magmas can cause temperature to increase without any increase in pressure. In subduction zones, magmas rising above a subducting plate may cause melting in the overlying continental lithosphere, creating silicic magmas that erupt in subduction zone volcanoes or crystallize underground to become plutons.

Decompression Melting



3.21 Melting caused by decompression

The processes described above may all cause melting, but they do not account for the widespread melting that occurs at mid-ocean ridges. There, an additional, and very significant, mechanism promotes melting – a decrease in pressure (Figure 3.21). Rising mantle moves up to fill the void created by sea floor spreading. As shown by the black arrow in the pressure-temperature diagram, the resulting pressure decrease leads to melting because rock melts at lower temperature when at low pressure, compared with high pressure. This process, called *decompression melting*, generates more magma than any other Earth process.

So, decompression melting is the key mechanism producing magmas at mid-ocean ridges, which, although we don't generally see them, are the most active volcanic settings on Earth. In these settings, partial melting of rising solid rocks produces basaltic lavas that erupt on the ocean floors, and upon cooling, are added to the spreading oceanic lithosphere.

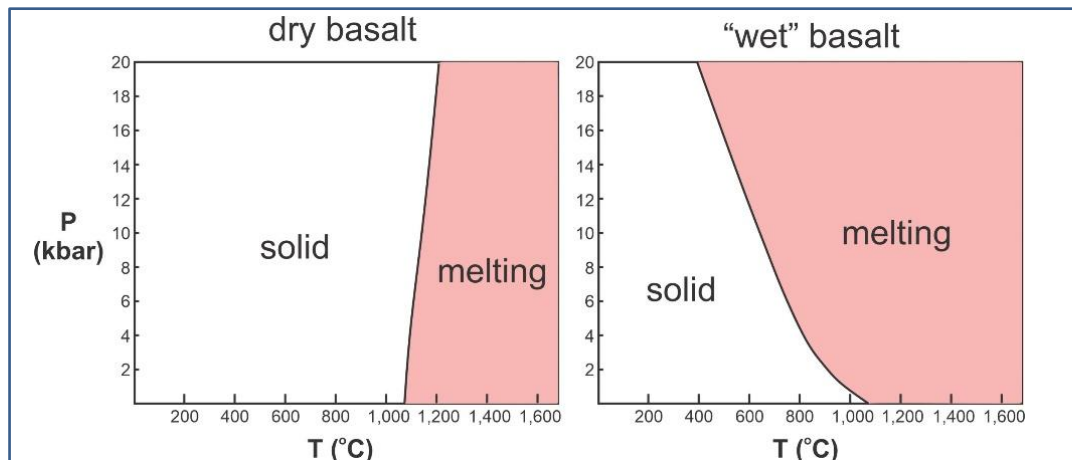
Decompression melting also leads to igneous activity where continental rifting occurs, for example along the East African Rift. The East African Rift is an elongate zone that includes the Kenyan Rift and the Main Ethiopian Rift (Figure 3.23). Along this narrow zone, the African continent has begun to split apart; the rift may eventually be the site of a new ocean basin similar to the Red Sea or the Gulf of Aden, also shown in Figure 3.23. Besides causing melting at rift zones, decompression contributes to the melting associated with more localized hot spots, like those under Yellowstone, where warm rocks move upwards due to buoyancy.

Flux Melting

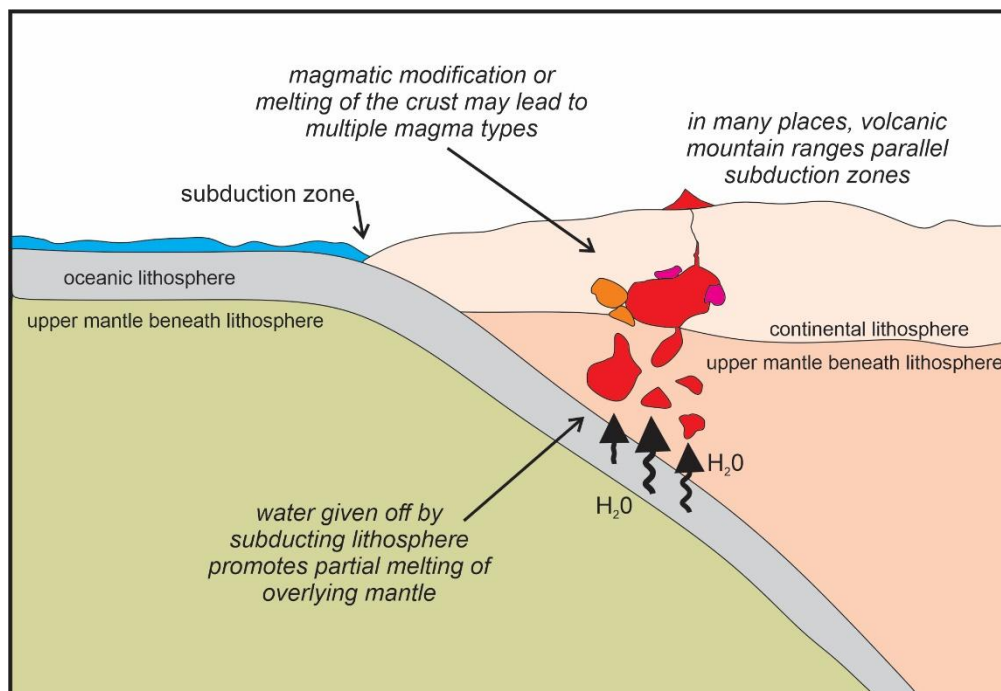
Principles of thermodynamics tell us that two things combined will often melt at a lower temperature than they would individually. An analogy is a mix of ice and salt, which we all know melts at a lower temperature than ice alone. Similarly, rocks will melt at lower temperatures when they contain water, CO₂, or another volatile compared to when dry.

The presence of a small amount of water can change magma melting temperatures by hundreds of degrees. Figure 3.24 compares the conditions that cause melting (shown in red) of a basalt that contains no water and one saturated with a small amount of water. "Dry" basalt begins to melt at temperatures in excess of 1,000 °C. Depending on pressure, melting of "wet" basalt may begin at temperatures significantly lower. Because water and other volatiles lower melting temperatures in the same way that a *flux* is used to lower the melting temperature of metals, this additional mechanism for melting is called *flux melting*. If a rock is already hot, addition of only

a small amount of water can promote melting. Water is the most important geological flux, but CO₂ and other gases also promote melting in some settings.



3.24 The effects of water on melting temperature of basalt

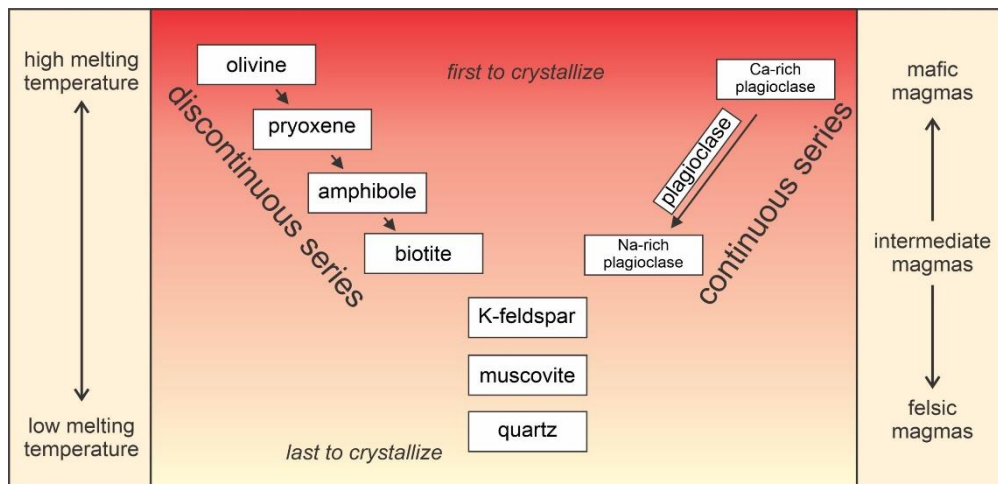


3.25 Flux melting in a subduction zone

Flux melting is especially important in subduction zones (Figure 3.25). Subducting oceanic lithosphere contains hydrous minerals that react during metamorphism to form anhydrous minerals. Consequently, water is released and migrates upwards into hot overlying mantle. This water lowers the melting temperature, causing partial melting of the ultramafic mantle to produce mafic (basaltic) magma. This magma then migrates upwards and may reach Earth's surface. It may also promote additional melting in the uppermost mantle or crust, or may become modified to produce magmas of different compositions.

Bowen's Reaction Series

When rocks melt or magmas crystallize, things are generally more complicated than when a single mineral melts or crystallizes. Most rocks contain more than one mineral, and different minerals melt or crystallize at different temperatures. N. L. Bowen, an early 20th century petrologist, conducted many laboratory experiments and was the first to compare melting and crystallization temperatures of common igneous minerals in rocks.



3.33 Bowen's Reaction Series

Bowen's Reaction Series (Figure 3.33) depicts Bowen's fundamental findings. It is called a reaction series because during melting (or crystallization) solid minerals continuously react with surrounding liquid.

Mafic magmas crystallize at high temperatures and felsic magmas at lower temperatures. Bowen's series shows the relative liquidus temperatures for common minerals for magmas of different compositions. As shown by the series, olivine crystallizes at the highest temperature (from mafic magmas) and quartz at the lowest temperature (from felsic magmas).

One sometimes confusing thing about this series is that it depicts liquidus temperatures for minerals when they crystallize from magmas of complex chemistry. Crystallization temperatures are different for the individual minerals if they are by themselves. For example, ignoring minor complications involving polymorphs, quartz may not begin to crystallize from a granitic melt until other minerals have formed and temperature drops to less than 1,275 °C. In contrast, quartz will crystallize from a melt of 100% SiO₂ composition at a much higher temperature (in excess of 1,700 °C).

Plagioclase melts incongruently over a range of temperature depending on its composition; Bowen called the plagioclase side of the diagram the *continuous series*. Most other minerals, also depending on their compositions, melt sequentially over more restricted temperature ranges (*discontinuous series*). Bowen found that (mafic) minerals common in ultramafic and mafic rocks have the highest liquidus and solidus temperatures, and (silicic) minerals that are common in silicic rocks have the lowest. Consider a cooling magma: as temperature decreases, minerals higher up in the series crystallize first followed by minerals lower down. We call minerals that melt and crystallize at high temperatures *high-temperature minerals*; those that

melt and crystallize at low temperatures are *low-temperature minerals*. The specific minerals that crystallize, however, vary with magma composition.

Although melting and crystallization in the order depicted by Bowen's Reaction Series seems straightforward, there are many complications. No magmas follow the entire series – most crystallize only one or a few of the minerals in the series – and some magmas crystallize minerals that are not part of the series. Furthermore, some minerals melt (and crystallize) congruently and some do not. Additionally, many melting and crystallization reactions involve more than one mineral reacting together. For example, at Earth's surface, anorthite melts at about 1,560 °C and diopside melts at about 1,390 °C. A rock that contains both anorthite and diopside, however, will begin to melt at around 1,270 °C, a much lower temperature than the melting point of either individual mineral.

Partial Melting and Fractional Crystallization

Incomplete Melting

Melting can only occur if temperature exceeds the solidus, and temperatures rarely, if ever, reach the liquidus. Because the geothermal gradient is different in different places, this means that partial melting occurs but does not occur everywhere. So, magmas generally form by melting of an originally solid *parent rock* that does not melt completely. When a rock melts only partially, producing a melt that contains melted low-temperature minerals and leaving behind solid high-temperature minerals, we call the process *anatexis*. In the mantle, for example, anatexis of ultramafic rock produces basalts.



3.34 Metasedimentary migmatite

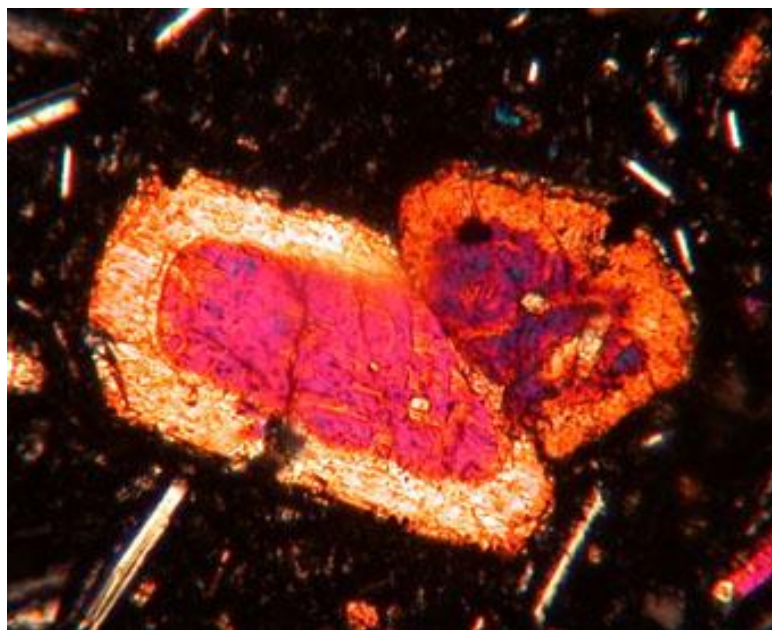
Migmatites (from the Greek *migma* meaning *mixture*, and *ite*, referring to *rock*) are rocks composed of two different components that are mixed, or swirled, together. Typically migmatites contain a light colored segregation that in many cases appears to have formed by partial melting of the darker surrounding material. In the crust, many migmatites, such as the

one seen in Figure 3.34, are thought to have formed by anatexis associated with metamorphism of a parental sedimentary rock. The result is a mixed rock that contains both metamorphic and igneous components. The melt that develops eventually cools and crystallizes just like any other magma does, and will sometimes contain large crystals (phenocrysts) after completely solidified. If the melt migrates away from where it was produced, identifying its origin may become problematic, and the residual material left behind will not resemble the original sedimentary parent. It seems apparent, nonetheless, that large scale anatexis of crustal rocks can produce large volumes of granitic melts that later form granitic plutons. The plutons may contain xenoliths (included unmelted pieces) of the original rock that melted to form the granitic magma.

Equilibrium or Not?

In an equilibrium melting process, the melt and solid remain in contact and in chemical equilibrium as melting occurs. The system is “closed” – the overall composition does not change – so the melt and remaining solid material add up to the starting composition. Consider the melting process that may occur when a rock is heated. Melting begins at the solidus temperature, and the first melt is formed by the melting of low-temperature minerals, singly or in combination. The rest of the minerals remain unmelted. Melting progresses as temperature increases, and different minerals melt at different temperatures.

As the amount of melting increases, the melt composition evolves to be more like its original parent rock until everything has melted. During this process, the minerals present will change, and the compositions of solid solution mineral crystals will change as atoms migrate in and out of the solid crystals. It does not matter if the rock melts partially or completely; if melt and solids continue to react, chemical equilibrium is possible as compositions change in response to temperature changes. The same concept of equilibrium applies to crystallization. If equilibrium is maintained during crystallization, crystals will be homogeneous in composition and will change proportions and compositions systematically as temperature decreases. However, disequilibrium can occur if the migration of atoms through the solid crystals, or through a viscous melt, is not fast enough to keep up with cooling.

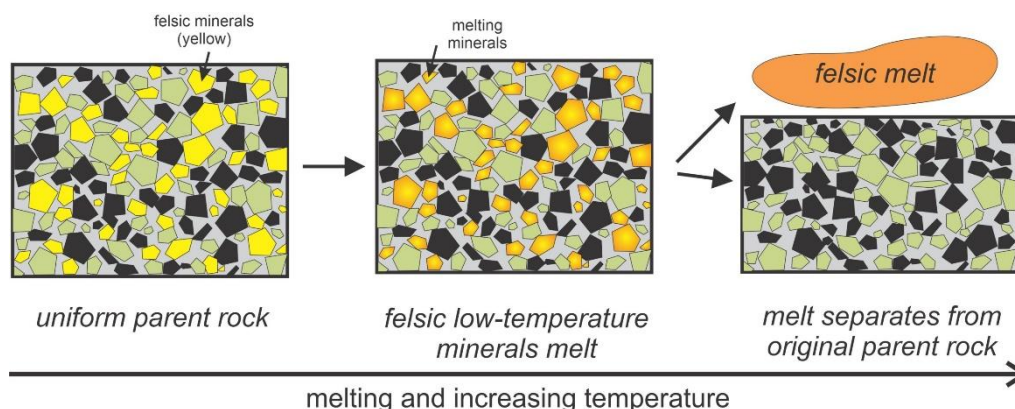


3.35 A zoned clinopyroxene crystal in a basalt

When studying rocks, petrologists may find it difficult to decide if crystals and melt stayed in equilibrium. Some volcanic rocks, however, contain zoned crystals that are evidence of disequilibrium. Figure 3.35 shows a polarizing microscope view of a large compositionally zoned grain of clinopyroxene in a basalt. The dark material surrounding the clinopyroxene is mostly volcanic glass, and the needle-shaped light colored crystals are plagioclase. If the clinopyroxene grain was homogeneous, the colors induced by the polarizers would be the same in all parts of the grain. Zoning of this sort is evidence that the melt and crystals did not stay in equilibrium during crystallization. The center of the crystal grew at high temperature, and as temperature decreased the crystals grew larger. If the minerals and melt stayed in equilibrium, the grain (no matter the size) would have a homogeneous composition. But in zoned crystals the crystal cores have compositions formed at higher temperature than the rims did. The outer zones have compositions that formed at lower temperature because atoms could not migrate into and through the crystals fast enough to maintain compositional homogeneity. Thus, only partial equilibrium was maintained. Many volcanic mineral crystals have broad homogeneous centers but are zoned near their rims, suggesting that they stayed in equilibrium with the melt until the latest stages of crystallization.

Partial Melting

Large scale disequilibrium melting occurs if a melt and a solid do not continue to react together, but instead become chemically isolated due to physical separation. For example, if a rock melts partially and the magma escapes upwards, the melt and remaining solid material cannot react to stay in chemical equilibrium.



3.36 Partial melting

Figure 3.36 shows melting of an original parent rock that contains several different minerals. The first minerals to melt are (generally Si-rich) low-temperature minerals (shown in yellow). So, initial melting produces a relatively silicic magma (shown in orange). This melt may subsequently become separated from the leftovers of the original rock. Consequently, a melt of different composition from the parent has been produced and may move upwards in Earth.

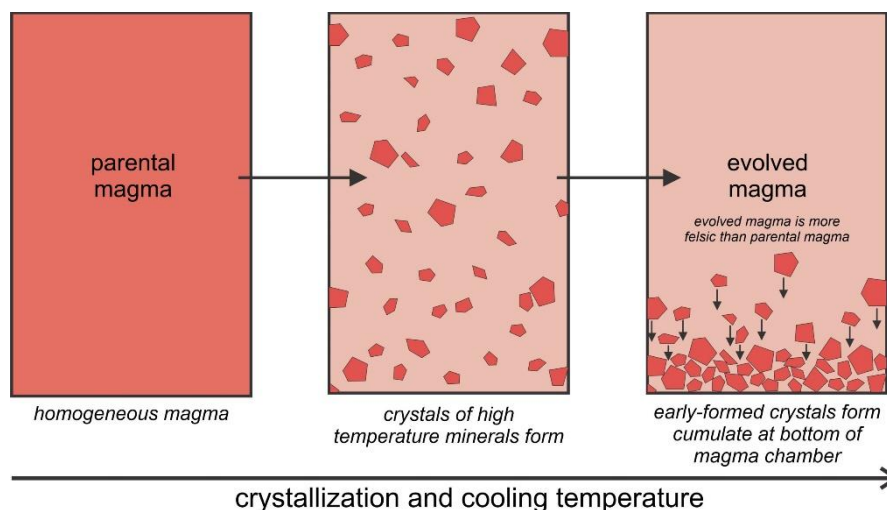
Partial melting is a widespread and important process that occurs in the source region for most magmas. Low-temperature minerals always melt first, either individually or in consort with others. They are relatively silica-rich minerals compared with others in a rock, so when partial melting occurs, the melts are more silicic than the parent rock is. The remaining rock becomes depleted in silicic components and, therefore, more mafic than its parent. When this happens, silicic melts migrate upwards, leaving more mafic residue behind. So, partial melting explains, in part, why the Earth has differentiated into a more silicic crust and more mafic mantle during

its 4.6 Ma year lifetime. These generalizations always apply, but the specific products of partial melting depend on the starting material composition and the amount of melting. Furthermore, the results will be different if the parent rock is already depleted.

Earth's mantle is ultramafic; if it melted completely it would produce ultramafic magma, but, as discussed previously, complete melting cannot occur because there is no known mechanism for heating the mantle to the very high temperatures needed to melt it completely. Partial melting, however, is common, and the upper mantle is the source of many magmas that move within the crust and sometimes reach the surface. Because the upper mantle has a relatively uniform composition, partial melting of mantle produces similar magmas worldwide, almost all mafic, equivalent to basalt compositions. More silicic magmas may also be generated in the mantle, but they are uncommon. Similarly, partial melting of subducted ocean crust, which is basaltic everywhere, generally produces magmas of intermediate composition, and partial melting of lower continental crust produces silicic magmas (equivalent to granite).

Fractional Crystallization

Fractional crystallization, the opposite of partial melting, occurs when a magma partially crystallizes and the remaining magma becomes segregated from the crystals. In these circumstances, the new *evolved magma* will have a different composition from its *parental magma*. The evolved magma, which is more silicic than its parent was, may move upwards, leaving the high-temperature (mafic) minerals behind. Fractional crystallization, like partial melting, has been a key process contributing to differentiation of Earth.



3.37 Diagram showing fractional crystallization

Fractional crystallization may occur when newly formed crystals sink to the bottom of a magma chamber and no longer stay in equilibrium with the melt. Figure 3.37, a schematic diagram, shows the principles involved. While cooling, a parental magma crystallizes some high temperature minerals. These minerals eventually sink to the bottom of the magma chamber, leaving an evolved magma above. Because high-temperature minerals are mafic, the evolved melt is more silicic (less mafic) than the original parent magma. During this process, a *cumulate* rock forms at the bottom of the magma chamber, and the evolved magma may move upwards and become completely separated from the cumulate. Fractional crystallization explains the origins of cumulate rocks like the chromite cumulates.

Other Processes Explaining Variations in Magma Composition

Fractional crystallization is undoubtedly the most important process that changes magma composition after a magma forms. Other mechanisms, however, also lead to changes. For example, in some settings, hot magmas may melt surrounding rocks and assimilate them into the magma. Generally, we think of this *assimilation* occurring when mafic magmas encounter more silicic rocks, because mafic magmas may be hotter than the silicic rock's melting temperature is. So, assimilation can make magma more silicic and is most likely to occur in the (silicic) crust. Some volcanic rocks contain crustal xenoliths, inclusions of rock fragments incorporated as solid pieces into the melt; often the xenoliths show evidence of partial melting. It is no stretch to assume that sometimes xenoliths melt and mix in completely. Some geochemical data, too, supports the idea that crustal material has been incorporated into a mantle-derived melt.

Different magmas may also combine to produce hybrid magmas of different compositions. However, *magma mixing* is unlikely to happen if magma compositions are too different because different magmas have different melting temperatures, densities, and viscosities. Although some evidence suggests that magma mixing occurs on a small scale, most petrologists believe it is generally a minor contributor to magma diversity. A third process, *liquid immiscibility*, has also been proposed as a process that may lead to change in magma composition. Immiscible liquids unmix in much the same way that chicken soup separates into broth and fat upon cooling. Experimental evidence suggests, for instance, that sometimes a sulfide-rich melt may unmix from mafic silicate magma – a potential important process forming ore deposits, or that alkali-rich magmas may unmix from less alkaline ones. Some petrologists have invoked this last process to explain the origin of *carbonatites*, that are unusual carbonate-rich magmas.

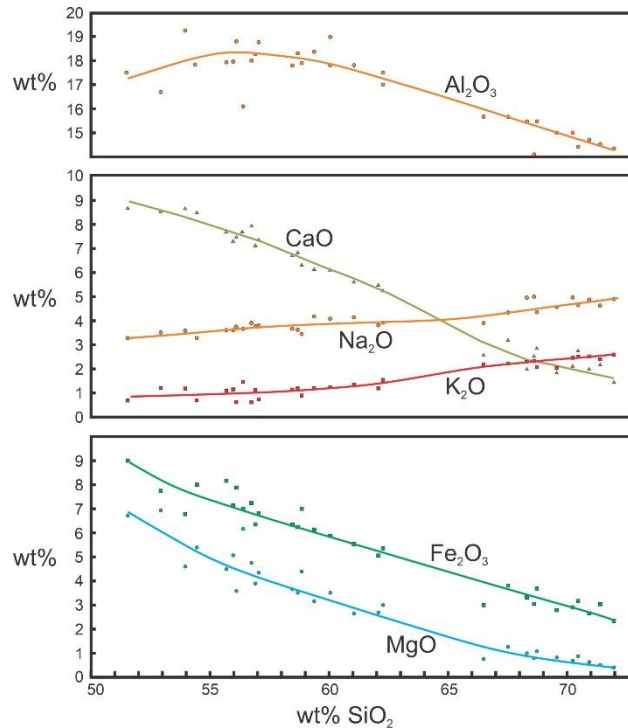
Parental Magmas and Differentiation

Only a few rare magmas may not be evolved. For example, the white veins (termed *leucosomes*) in migmatites that form by partial melting of sedimentary rocks may not have changed composition after they formed (Figure 3.34). The leucosomes appear to have been created by partial melting of metasedimentary rock, and the melt has remained local and has not differentiated.

The majority of magmas, however, evolve from some parental magma. They are evolved melts, not melts having the composition created during initial melting. Subsequently, as crystallization progresses, magma compositions follow what is called a *liquid line of descent*, producing a series of magmas of different compositions as fractional crystallization removes specific minerals from the melt.

If solid mantle melted directly, either partially or completely, to create magma, the magma would be called a *primary magma*. Primary magmas have undergone no differentiation and have the same composition they started with. Specifically, if they come from the ultramafic mantle, and were not subsequently modified, they must have a very high Mg:Fe ratio and be enriched in Cr and Ni just like mantle rocks, and petrologists use these and other characteristics to test if magmas could be primary magmas. Most magmas fail the tests, and primary magmas are exceptionally rare, or may not exist at all. Some magmas and rocks, however, come close to being primary, and petrologists describe them as *primitive*, meaning they have undergone only minor differentiation.

Parental magmas may be primary or primitive. The only requirement is that they lead to magmas of other compositions. If a collection of melts with different compositions evolve from the same parent, they form a *magma series*. Although the melts have different compositions, they will share some chemical characteristics, especially trace element compositions and isotopic ratios. A challenge for petrologists is to study the compositions of an inferred magma series to learn the composition and source of the original parent.



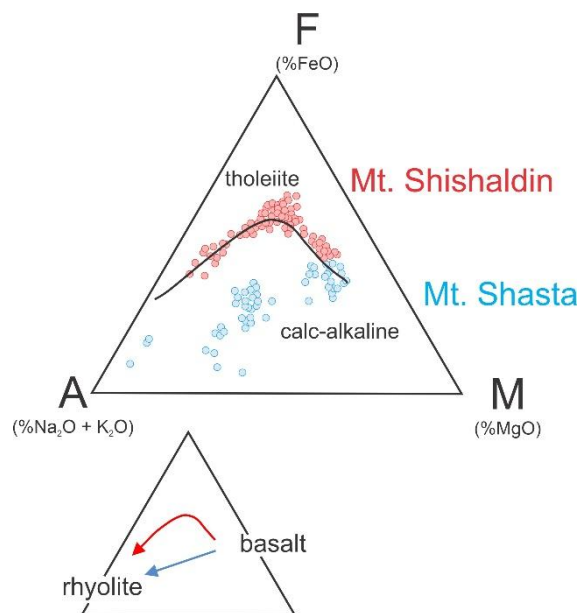
3.40 Harker diagram for volcanic rocks of the Crater Lake region, Oregon

Typically, petrologists begin their quest by obtaining analyses of the rocks and plotting the results on different kinds of *composition diagrams*. For example, *Harker diagrams*, first used in 1902, have SiO_2 content as the horizontal axis and other oxides plotted vertically (Figure 3.40). SiO_2 is chosen as the abscissa because it generally shows the most variation of all oxides, and because it relates closely with magma temperature and the amount of fractional crystallization.

When looking at Harker diagrams, the principles are that (1) if derived from a common parent, rock compositions should trend smoothly across a diagram; and (2) the most mafic composition is closest to the parent magma composition. So, if a Harker diagram reveals smooth trends, it is possible that all the magmas derived from the same parent and that the low SiO_2 end of the graphs are closest to the magma's parent composition. Harker diagrams are only one kind of composition diagram; many others with different oxides on the axes are commonly used.

Figure 3.40 shows a well-studied Harker diagram for volcanic rocks from near Crater Lake, Oregon, based on the data of Howell Williams (1942). Each point represents a different volcanic rock from the same region; the horizontal axis shows the SiO_2 content of the rock and the vertical axis the amount of other oxides present. The solid lines show the smoothed trends. The smooth trends are evidence that the different rocks may have derived from the same original parental magma. The Crater Lake magmas range from *basalt* (on the left side of the diagram) to *rhyolite* (on the right side). Based on the trends shown, Williams concluded that the magmas

all came from a common parent magma and that they evolved by fractional crystallization. The basalt composition is closest to that parent.



3.41 AFM diagrams for rocks from Mt. Shishaldin, Alaska, and from Mt. Shasta, California

A second commonly used way to look at magma composition is to plot compositions on an AFM diagram (Figure 3.41). AFM diagrams ignore SiO_2 and instead look at alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$), iron as FeO (assuming it is not Fe_2O_3), and MgO content. The triangle corners are: A = alkali oxide weight %, F = FeO weight %, and M = MgO weight %. Many studies have found that magma series follow one of two trends, the *tholeiite* trend or the *calc-alkaline* trend, and we easily see these on an AFM diagram. Figure 3.41 is an AFM diagram comparing rocks from Shishaldin Volcano (Aleutian Islands) and Shasta Volcano (California). Each point represents an analysis of an individual rock. Shishaldin is an island arc volcano associated with an oceanic plate subducting under another oceanic plate. Shasta is a continental margin volcano where an oceanic plate is subducting under a continental plate. The Shishaldin data follow a tholeiite trend, depicted by the solid line and red arrow that initially moves toward the F-corner before curving downward toward the A-corner. The Shasta data follow a calc-alkaline trend (depicted by the blue line that heads directly toward the A-corner).

Whether tholeiitic or calc-alkaline, originally mafic magmas can produce rocks ranging from basalt to rhyolite, as the bottom triangle in Figure 3.41 shows. At both Shishaldin and Shasta Volcanos, more primitive parental magmas were mafic and the later evolved magmas were silicic. They differ, however, because tholeiitic magmas become iron-rich as they evolve, moving initially toward the F apex of the triangle. Calc-alkaline trends go directly from basalt to rhyolite.

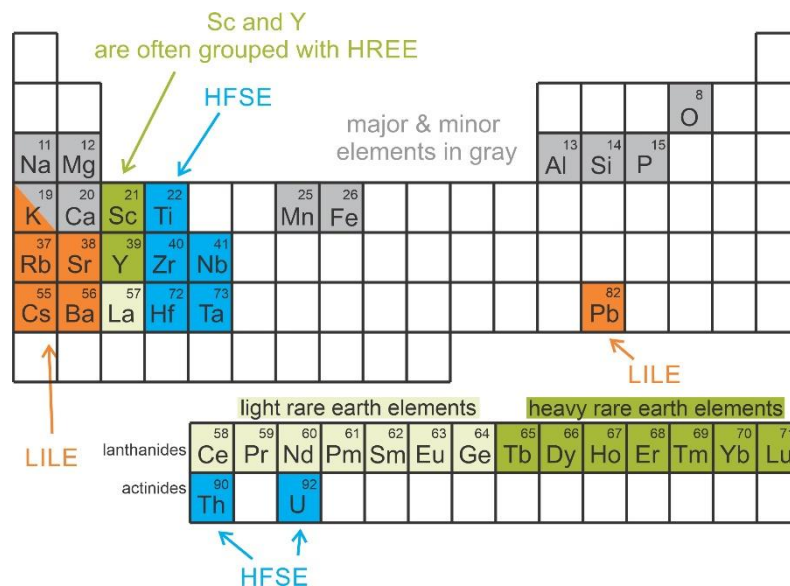
The trends on an AFM diagram reveal clues about the environments in which the magmas differentiated. The difference between calc-alkaline and tholeiite trends is due to the oxidation state of iron. If iron is mostly oxidized, magnetite (Fe_3O_4), a mineral that contains oxidized iron (Fe^{3+}), crystallizes early from a melt. If the iron is mostly reduced (existing as Fe^{2+}), magnetite does not crystallize. In calc-alkaline magmas, the iron is oxidized, leading to crystallization of magnetite. Consequently, when mafic minerals crystallize, iron is removed from the magma as fast as magnesium and the melt's Fe:Mg ratio remains about constant during differentiation. In tholeiitic magmas, olivine and pyroxene crystallize first and magnetite may not crystallize at

all. Olivine and pyroxene have high Mg/Fe ratios compared with melt, and the magma becomes enriched in iron during the initial stages of crystallization. Calc-alkaline magmas are dominant in *andesitic-type* subduction zones, such as California's Cascade Mountains. Mt. Shasta is an example. Tholeiitic trends occur mostly in island arcs, such as the Aleutian Islands, and Shishaldin Volcano is an example.

Magma Chemistry

Major and Minor Elements

Major elements, typically present at levels exceeding 1 weight %, determine most magma properties and eventually the minerals that may form. Typical major elements in igneous rocks include O, Si, Al, Fe, Ca, Na, K, and Mg. In some rocks, Ti, Mn, P, and perhaps others may be considered major elements. Rocks also contain *minor elements*. Minor elements, typically comprising 0.1 to 1 weight % of a magma or rock, substitute for major elements in minerals but are selective about which minerals they enter. For the most part, they do not affect magma properties.



3.42 Periodic chart showing some key elements in igneous rocks

Figure 3.42 shows some key elements in igneous rocks. Major and minor elements are shaded gray. The other shaded elements are *incompatible elements* in mafic minerals (discussed in detail below). The incompatible elements include large ion lithophile elements (LILE) shaded orange, heavy rare earth and related elements shaded dark green, light rare earth elements shaded light green, and high field strength elements (HFSE) shaded blue. Potassium (K) is considered both a major element and an LILE element.

Trace elements are elements present in very small amounts, amounts even smaller than amounts of minor elements. The amount of any trace element that can enter a growing crystal depends mostly on ionic charge and radius. Some trace elements enter growing crystals in the early stages of crystallization, but others may remain in a magma until the latest stages of crystallization. Trace elements are even more selective than minor elements about the minerals they enter and generally have insignificant effects on rock and mineral properties. Because trace elements are present in very small amounts, petrologists commonly report them in parts per million (ppm) or parts per billion (ppb) instead of weight % (wt %). 1 ppm = 0.0001 wt %.

Furthermore, when plotting trace element analyses, petrologists normalize the raw data by dividing by the composition of some reference standard. Normalization means that the range of values becomes small enough so that we may plot all trace elements on a single graph.

*Table 3.3 Analysis of a Hawaiian Basalt**

major and minor elements		trace elements	
element	wt%	element	ppm
O	44.66	V	292.00
Si	23.27	Cr	238.00
Fe	8.59	Zr	129.90
Ca	8.28	Sr	129.10
Al	7.20	Ni	102.60
Mg	4.27	Zn	85.40
Na	1.81	Cu	63.30
Ti	1.64	Y	40.60
K	0.46	Ba	18.40
Mn	0.13	Ce	8.30
P	0.11	Nb	4.30
		Rb	1.30
Total	100.42	Total	1113.20

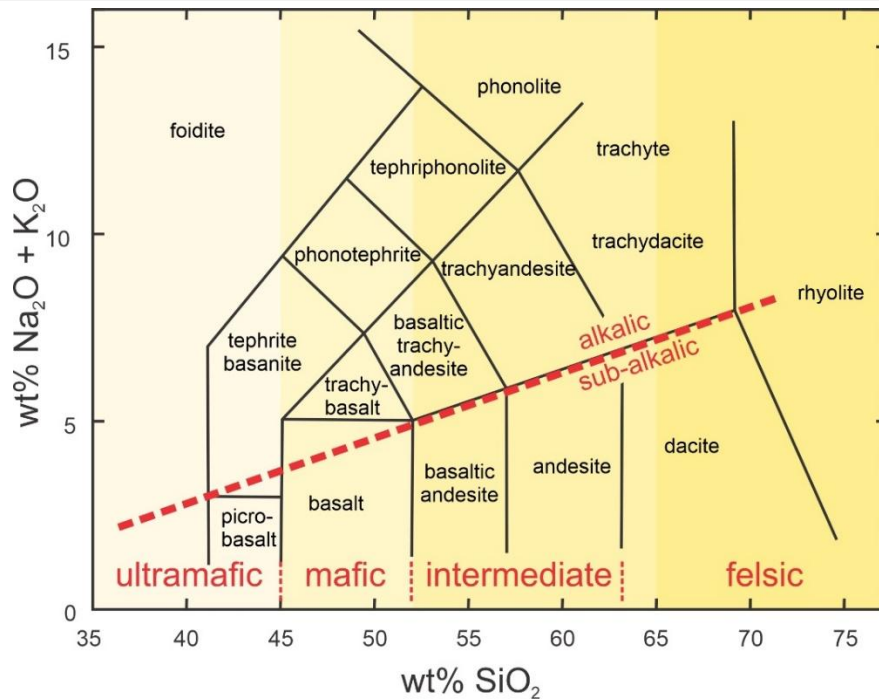
**Data are from Duncan, et al. (1990)*

Table 3.3 contains an analysis for a Hawaiian basalt.

The analysis does not distinguish between major and minor elements (because the distinction between the two is a fuzzy one), but Mn and P together comprise only about 0.2 weight % of the rock and would be considered minor elements by most petrologists. K, too, might be considered a minor element in this rock. The analysts listed trace elements separately, reporting them in ppm instead of weight %, and the total of the trace elements is about 1,113 ppm, which is equivalent to 0.1113 weight %. Many other trace elements are undoubtedly present in the Hawaiian basalt, but were not analyzed because they were not important to the study being conducted. Although Mn and P are minor elements in the Hawaiian basalt (and most other basalts), they may be concentrated in other kinds of rocks. The alkalis, major elements in silicic rocks, may be nearly absent in mafic rocks, although in the Hawaiian basalt they add to about 2.25 weight %. So, minor elements in some types of rocks can be major elements in others and vice versa.

We can classify and name igneous rocks based on the minerals they contain, but magmas, because they contain no minerals, must be classified in another way. Additionally, many volcanic rocks may contain glass instead of minerals or may be too fine grained for mineral identification. Thus we often classify magmas and many igneous rocks based on their chemical composition instead of their mineralogy.

Although igneous rock chemistry varies in many ways, the silica content and alkali content of volcanic rocks form the basis for one of the most commonly used classification schemes. It is not that other compositional variations are unimportant, but that many other possible variations correlate with alkali and silica content and so the classification system captures well the variation in rock compositions.



3.43 The total-alkali-silica (TAS) classification system

Using the *total alkalis versus silica* (TAS) system (Figure 3.43) is straightforward, and the weight percentages of silica (SiO_2) and alkali oxides ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) in a rock are used to obtain a rock name. The vertical axis is the total alkali oxide content, and the horizontal axis is the silica content. In the TAS diagram, ultramafic compositions (low silica content) plot on the left and silicic compositions (high silica content) on the right, with mafic and intermediate compositions between. The diagonal red line divides the diagram into two parts. Compositions that plot in the upper part of the diagram are *alkalic*; they are relatively rare in nature. Those plotting in the lower part of the diagram are termed *sub-alkalic* and are much more common. By far, the most common volcanic rocks are sub-alkalic: basalt, andesite, dacite, and rhyolite. Although the names in Figure 3.43 are names of volcanic rocks, they are often used to describe magma types. A dacite magma, for example, is one that could erupt to form a dacitic rock.

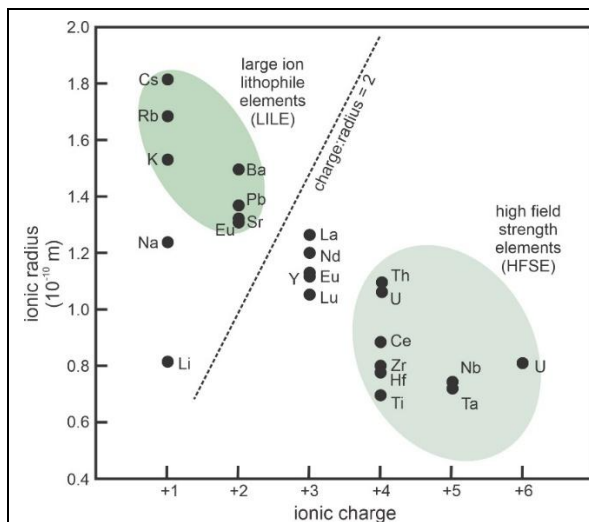
Table 3.4 Properties of Different Kinds of Magmas

magma type	ultramafic	mafic	intermediate	felsic
extrusive rock name	komatiite	basalt	andesite	rhyolite
intrusive rock name	peridotite	gabbro	diorite	granite
silica content (wt% SiO_2)	40-45	← →		71-75
mafic content (wt% $\text{FeO} + \text{MgO}$)	high	← →		low
ratio alkali earth/alkali (wt% $\text{CaO}/\text{Na}_2\text{O} + \text{K}_2\text{O}$)	high	← →		low
eruption temperature	up to 1,500 °C	← →		800 °C or less
viscosity	low	← →		high

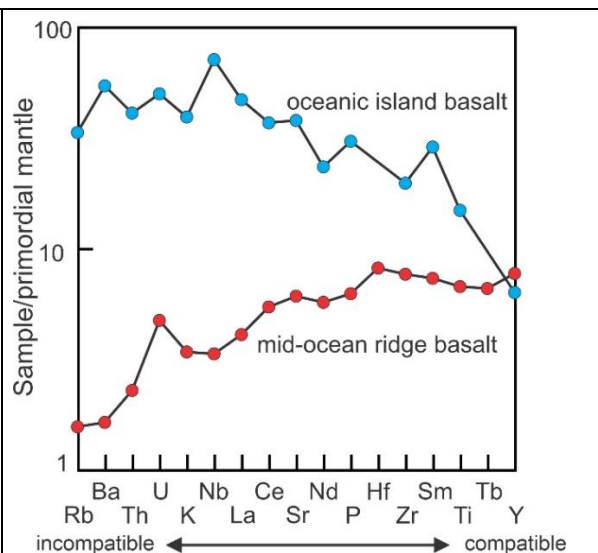
Although both silica and alkali content are keys when classifying magmas or volcanic rocks, silica content alone explains many variations in magma properties (Table 3.4). It is also the basis for a rock-naming scheme that is simpler than the TAS system is: simply calling rocks ultramafic, mafic, intermediate, or silicic. Variations in magma properties with silica content are profound. The more silicic a magma, the lower its eruption temperature but the greater the possibility for explosive eruptions due to high viscosity and gas content. Note that in this simpler classification scheme, alkali content correlates with silica content. This correlation is not always the case, as shown in the TAS diagram, but is the case for sub-alkalic rocks. Similar to the names in the TAS system, the rock names in Table 3.4 are often used to describe magma composition. For example, we might describe a magma as granitic if it could crystallize to form a granite.

Incompatible and Compatible Elements

We can divide elements in igneous rocks and magmas into two groups: those that tend to remain in a magma until the later stages of crystallization (and consequently become enriched in the magma as crystallization takes place), and those that are easily incorporated into early growing crystals (and consequently become depleted in a magma quickly). Elements that tend to remain in the magma are said to be *incompatible*, and those that enter crystals quickly are *compatible*. Petrologists use these terms, incompatible and compatible, most commonly to describe trace elements, but they apply equally well to major and minor elements. Some elements behave as compatible elements in some magma types, but incompatible in others, because the specific minerals that crystallize vary with magma composition. Trace elements, however, both compatible and incompatible, are especially useful as trackers of magma evolution. Incompatible elements include the rare earth elements, elements 57 through 71 (La – Lu), but their degree of incompatibility varies with atomic number. The rare earths, and other incompatible elements are highlighted in the periodic chart of [Figure 3.42](#).



3.44 The two groups of incompatible elements



3.45 Comparing the trace element chemistry of an oceanic island basalt with a mid-ocean ridge basalt

Incompatible elements fall into two main groups, a group that has large ionic radius, and a group that has large ionic charge (Figure 3.44). The first group includes alkali and alkali earth elements, notably K, Rb, Cs, Sr, Ba, and several other elements. Elements that tend to

concentrate in Earth's crust and mantle are called *lithophiles*. So, the alkalis and alkali earths, and elements with similar properties, are collectively termed *large ion lithophiles*, or *LILE* for short (Figure 3.44). LILEs do not fit into crystallographic sites in most minerals, and the charge attracting them to growing crystals is small, so they tend to remain in a melt.

Elements that form ions with small radii and high charge are called *high field strength elements* (*HFSE*) (Figure 3.44). This group of incompatible elements includes Zr, Nb, Hf, Th, U, and Ta. HFSEs have high ionic charge (+4 or greater), which means that, if they enter crystals charge balance is hard to obtain. Consequently, HFSEs tend to remain in a melt. For some purposes, HFSE are defined as those whose ions have a charge to radius ratio greater than 2 (to the right of the dashed line in Figure 3.44).

Figure 3.45 compares the trace element content of an oceanic island basalt with that of a mid-ocean ridge basalt. In diagrams of this sort – sometimes called *spider diagrams* – the most incompatible elements are on the left, and elements are increasingly less incompatible moving to the right. The mid-ocean ridge basalt is depleted in incompatible elements compared with the oceanic island basalt. However, both have about the same concentrations of the compatible elements. This diagram, therefore, suggests that mid-ocean ridge magmas, associated with active plate spreading centers, derive from regions that have undergone significant amounts of partial melting. In contrast, the oceanic island magmas come from regions that are more primitive.

Evidence of this sort allows petrologists to conclude that the upper oceanic mantle – the source region for mid-ocean ridge basalts – is an area of active melting and recycling of material. The source of oceanic island basalts, such as those that reach the surface in Hawaii, is deeper in the mantle where melting has not removed incompatible elements. Note that the data for both basalts were normalized by dividing the analyses by an estimated composition for the primordial mantle (to keep numbers on scale). Additionally, the vertical scale is a log scale; if it were not, the trends would not be as easily seen.

Some transition elements – including nickel, cobalt, chromium, and scandium – are also important trace elements. They have small radii, and (usually) +2 or +3 ionic charge, and are incorporated into mafic minerals during the earliest stages of crystallization and tend to remain there. So, they are compatible when melting occurs in the mantle and, consequently, melts from the mantle contain them in very low amounts. They are often used as markers that determine where in Earth a magma originated.

The concept of compatible versus incompatible elements depends on rock type, because different rocks contain different minerals that incorporate elements in different ways. Scandium may enter pyroxenes, but not enter olivine. Zirconium is easily accommodated in zircon. Phosphorus concentrates in apatite, but neither zirconium nor phosphorous go into olivine. Earth's mantle is primarily composed of olivine and pyroxene, and these minerals become enriched in scandium, nickel, titanium, chromium, and cobalt as fractional melting occurs. So, melts derived from the upper mantle are enriched in these elements, and the amount of melting that has occurred can be estimated based on trace element abundance.

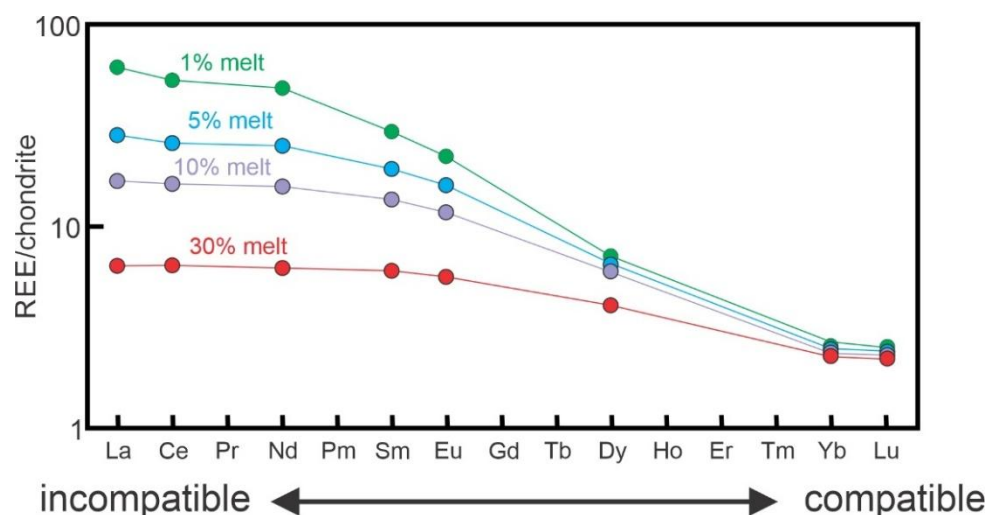
Rare Earth Elements

The *lanthanide elements*, also called the *rare earth elements* (REE), having atomic numbers 57 (La) to 72 (Lu), are very important trace elements with high field strength (Figure 3.44). Elements 57 through 64, La through Gd, are considered *light REEs*; 65–71, Tb through Lu, are

heavy REEs. Y and Sc are sometimes grouped with the *heavy REEs* due to similar properties. The REEs all have a large ionic radius and, except Eu, they are trivalent (+3). Ionic radius decreases with increasing atomic number, so La and other light REEs (largest) are more incompatible than Lu and other heavy REEs (smallest) are. If garnet crystallizes, it incorporates heavy REEs (Ho-Lu) easily, making them especially compatible.

During fractional crystallization of a magma in the mantle or the crust, incompatible elements stay preferentially in melts and, so, tend to move up and concentrate in Earth's outer layers. The original source region is *fertile* if there has been little removal of incompatible elements, but fertile rocks become *depleted* rocks when melting occurs. Rocks or magmas that are rich, or only slightly depleted, in light rare earth elements are fertile, and those with strong depletions in LREE are depleted, because their chemistry indicates the degree to which they have melted. This is why trace elements are powerful indicators of magma origin. Magmas that originate in upper levels of Earth are richer in incompatible elements than those that come from pristine mantle sources. Additionally, petrologists distinguish both fertile and depleted magma source regions within the mantle.

When a rock melts, the incompatible elements enter the melt quickly. Consequently, the concentration of incompatible elements will be very high after just a little bit of melting. With more melting, the concentrations decrease because most incompatible elements are already in the melt and get diluted with further melting. This effect is especially true for elements present in rocks and magma in very small amounts, which explains why trace elements are such powerful indicators of magma origin. So, trace elements tell us how much melting has occurred to produce a magma and, although a bit more complicated, they also monitor how much crystal fraction occurs when a magma cools.



3.46 Calculated rare earth concentrations for melts derived from a garnet peridotite

Figure 3.46 shows rare earth patterns for melts derived from a garnet peridotite. If only a small amount of melting occurs, concentrations of incompatible elements are high because they enter the melt first. With increased melting, other elements enter the melt and the concentrations of incompatible elements goes down. In this diagram, the compositions were normalized by dividing by the standard composition of a chondritic meteorite, and the scale is a log scale.

Rubidium–strontium dating



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The rubidium–strontium dating method (Rb–Sr) is a radiometric dating technique, used by scientists to determine the age of rocks and minerals from their content of specific isotopes of rubidium (^{87}Rb) and strontium (^{87}Sr , ^{86}Sr). One of the two naturally occurring isotopes of rubidium, ^{87}Rb , decays to ^{87}Sr with a half-life of 49.23 billion years. The radiogenic daughter, ^{87}Sr , produced in this decay process is the only one of the four naturally occurring strontium isotopes that was not produced exclusively by stellar nucleosynthesis predating the formation of the Solar System. Over time, decay of ^{87}Rb increases the amount of radiogenic ^{87}Sr while the amount of other Sr isotopes remains unchanged.

The ratio $^{87}\text{Sr}/^{86}\text{Sr}$ in a mineral sample can be accurately measured using a mass spectrometer. If the amount of Sr and Rb isotopes in the sample when it formed can be determined, the age can be calculated from the increase in $^{87}\text{Sr}/^{86}\text{Sr}$. Different minerals that crystallized from the same silicic melt will all have the same initial $^{87}\text{Sr}/^{86}\text{Sr}$ as the parent melt. However, because Rb substitutes for K in minerals and these minerals have different K/Ca ratios, the minerals will have had different starting Rb/Sr ratios, and the final $^{87}\text{Sr}/^{86}\text{Sr}$ ratio will not have increased as much in the minerals poorer in Rb. Typically, Rb/Sr increases in the order plagioclase, hornblende, K-feldspar, biotite, muscovite. Therefore, given sufficient time for significant production (ingrowth) of radiogenic ^{87}Sr , measured $^{87}\text{Sr}/^{86}\text{Sr}$ values will be different in the minerals, increasing in the same order. Comparison of different minerals in a rock sample thus allows scientists to infer the original $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and determine the age of the rock.

In addition, Rb is a highly incompatible element that, during partial melting of the mantle, prefers to join the magmatic melt rather than remain in mantle minerals. As a result, Rb is enriched in crustal rocks relative to the mantle, and $^{87}\text{Sr}/^{86}\text{Sr}$ is higher for crust rock than mantle rock. This allows scientists to distinguish magma produced by melting of crust rock from magma produced by melting of mantle rock, even if subsequent magma differentiation produces similar overall chemistry.[1] Scientists can also estimate from $^{87}\text{Sr}/^{86}\text{Sr}$ when crust rock was first formed from magma extracted from the mantle, even if the rock is subsequently metamorphosed or even melted and recrystallized. This provides clues to the age of the Earth's continents.[2][3]

Development of this process was aided by German chemists Otto Hahn and Fritz Strassmann, who later went on to discover nuclear fission in December 1938.

Uses

Geochronology

The Rb–Sr dating method has been used extensively in dating terrestrial and lunar rocks, and meteorites. If the initial amount of Sr is known or can be extrapolated, the age can be determined by measurement of the Rb and Sr concentrations and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. The dates indicate the true age of the minerals only if the rocks have not been subsequently altered.

The important concept in isotopic tracing is that Sr derived from any mineral through weathering reactions will have the same $^{87}\text{Sr}/^{86}\text{Sr}$ as the mineral. Although this is a potential

source of error for terrestrial rocks, it is irrelevant for lunar rocks and meteorites, as there are no chemical weathering reactions in those environments.

Isotope geochemistry

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are a useful tool in archaeology, forensics and paleontology because the $^{87}\text{Sr}/^{86}\text{Sr}$ of a skeleton, sea shell or indeed a clay artefact is directly comparable to the source rocks upon which it was formed or upon which the organism lived. Thus, by measuring the current-day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (and often the ^{143}Nd – ^{144}Nd ratios as well) the geological fingerprint of an object or skeleton can be measured, allowing migration patterns to be determined.

Strontium isotope stratigraphy

Strontium isotope stratigraphy relies on recognised variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater over time.[5] The application of Sr isotope stratigraphy is generally limited to carbonate samples for which the Sr seawater curve is well defined. This is well known for the Cenozoic time-scale but, due to poorer preservation of carbonate sequences in the Mesozoic and earlier, it is not completely understood for older sequences. In older sequences diagenetic alteration combined with greater uncertainties in estimating absolute ages due to lack of overlap between other geochronometers (for example U–Th) leads to greater uncertainties in the exact shape of the Sr isotope seawater curve.[6]