

Introduction to Metamorphic Geology

Notes for Mineralogy and Petrology 2

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Abstract

The aim of the course is to provide

- an introduction to the recognition of metamorphic rocks and minerals, and
- an introduction to the physical and chemical processes responsible for metamorphism within the Earth's crust.

A basic requirement is familiarity with the main types of metamorphic rocks and minerals, an appreciation of the *thermal* and *baric* significance of the main mineral associations, and an appreciation of the significance of metamorphic textures. These notes outline the basic content of the lecture course. Italicised words are part of the essential vocabulary of metamorphic geology and need to be understood.

1 The scope of metamorphic Geology

Metamorphic geology is concerned with the *mineralogical* and *textural* changes that occur in response to elevated temperatures and pressures as well as deviatoric (or tectonic) stress that may be experienced by rocks during deep burial within the earths crust.

The main factors that influence the mineralogical makeup of a metamorphic rock are:

- the *bulk composition* of the rock,

- the *pressure (P)* and *temperature (T)* conditions at the time of crystallisation,
- the composition of the *fluid phase* in the rock during metamorphism.

The bulk composition of the metamorphic rock may be inherited from the original sedimentary or igneous precursor, or may be chemically altered by *metasomatic* activity during the metamorphic process. The PT conditions during metamorphism may be evaluated by comparison of the mineral assemblages occurring in metamorphic rocks with the results of *experimental studies* and through the application of *equilibrium thermodynamic* principles. Both techniques are used to establish the PT stability range of metamorphic minerals and mineral associations, and provide the basis for the subdivision PT space into distinct *metamorphic facies*. Most types of sedimentary rocks contain minerals with significant quantities of structurally bound H₂O (clays) and/or CO₂ (carbonates) and progressive metamorphism generally results in the production of significant quantities of *metamorphic fluid*. The *advection* of metamorphic fluids is extremely important in the formation of many ore deposits.

The main factors that influence the texture of a metamorphic rock are:

- the temperature or *grade* of metamorphism,
- the deformation history.

In general there is a correlation between temperature and grain size, although grain size and shape are influenced by many other factors, such as the *strain rate* during the deformation regime at the time of metamorphic recrystallisation. The *preferred orientation* of crystals is common within metamorphic rocks, and directly reflects the deformation regime during crystallisation. Inclusion trail geometries within *porphyroblasts* often provide evidence of complex deformation histories and illustrate the important link between metamorphic crystallisation and tectonic deformation. *Dis-equilibrium* textures such as *coronas* and *symplectites* represent incomplete reaction induced by changes in the physical (PT) or chemical environment of the rock and therefore may provide important information about the nature of *PT path* at the time of reaction.

The environments in which metamorphism occurs are diverse and give rise to characteristic styles of metamorphism :

- the burial and elevated temperatures associated with active deformation of the continents in fold belts such as *the Himalaya* gives rise to *regional metamorphism*,
- the elevated temperatures in the immediate vicinity of shallow level plutons gives rise to *contact metamorphism* with characteristic *metamorphic aureoles* defined by closely spaced *isograds*,
- the large-scale circulation of hot fluids through rocks such as occurs at the *mid-ocean ridges* gives rise to *hydrothermal metamorphism*,
- the deep burial of sediments within deep basins can lead to a distinct type of *burial metamorphism* without any attendant deformation. Burial metamorphism represents a transition from the very low temperature mineralogical and textural changes that occur in newly deposited sediments (that are collectively referred to as *diagenesis*), and represents an important phase in the maturation of organic matter to oil and gas,
- the very large tectonic stresses that occur in the deep crustal extensions of fault zones produces *dynamic metamorphism* the products of which are characterised by texturally distinct suite of rocks termed *mylonites* and *cataclasites*.

It is important to note that these subdivisions are somewhat arbitrary, and many examples occur where the influence of more than one metamorphic style is apparent. For example, *skarns* are metamorphic rocks formed by the interaction of hydrothermal fluids with the rock sequences in the *contact aureoles* of plutons. Similarly, in the Mount Lofty Ranges the effects of regional metamorphism associated with deformation and localised contact effects associated with *syn-tectonic* granite emplacement resulted in a type of regional-contact metamorphic effect during the Delamerian Orogeny approximately 500 Ma ago.

Since ancient metamorphic rocks formed deep in the crust, they provide a means of investigating the types of process that must be occurring deep within the modern earth. Importantly, it is now recognised that the succession of PT conditions, or *PT paths*, experienced by rocks during burial are characteristic of very specific tectonic settings:

- subduction zones are characterised by high-P, low-T *facies series* such

as *blueschists* and *eclogites*, reflecting the very rapid burial to, and excavation from, great depth in these settings,

- collisional fold belts formed by convergence of continental fragments such as *the Himalaya* are characterised by intermediate- and low-P, intermediate- to high-T metamorphic assemblages (giving rise to so-called *Barrovian* and *Buchan* facies series, respectively),
- very high-T rocks termed *granulites* are abundant in Precambrian metamorphic terrains such as the Antarctic Shield and may be forming in the lower crust in the modern earth in *collapsing* mountain belts such as *Tibet* and the *Basin and Range Province* in the western USA as well as in the deep levels of magmatic arcs such as the *Andean belt* of South America.

These observations suggest that ancient metamorphic rock sequences provide a very important tool in reconstructing the past tectonic evolution of the earth.

2 Progressive metamorphism: the effect of bulk composition

The *bulk composition* of the rock is of paramount importance to the mineralogical reaction history during metamorphism. Some bulk compositions are essentially unreactive because the minerals they develop have very large PT stability ranges. For example, pure quartz sandstones are transformed without mineralogical change to quartzites no matter what PT conditions are experienced (actually, the high-P SiO₂-polymorph *coesite* has recently been reported from a number of rare high-P metamorphic terrains such as the Dora Maira Complex in the Italian western Alps, and the ultra-high-P SiO₂-polymorph *stishovite* occurs in some rocks that have suffered shock metamorphism during meteoritic impacts). In contrast, some bulk compositions undergo extensive reaction in response to relatively small changes in P and T, or fluid composition, and therefore are very important in reconstructing the metamorphic history of the host sequence. The rock types that are particularly important are:

- *pelitic* rocks,
- *basic igneous (basaltic)* rocks, and
- *calcareous* sediments.

Many metamorphic terrains show spatial variation in the grade of metamorphism and therefore may be used to understand the effects of progressive metamorphism. Such sequences can be subdivided into *zones* characterised by the appearance of distinct metamorphic minerals or mineral assemblages; each zone being marked by an *isograd* defined by the appearance or disappearance of an *index* mineral. In sequences where isograds cross cut the stratigraphy the effects of pressure and temperature can be readily separated from the effects of bulk composition.

2.1 Progressive metamorphism of pelitic sediments

Pelitic rocks are metamorphosed argillaceous sediments. The detrital clay content of argillaceous sediments gives a characteristic siliceous and aluminous bulk composition (total SiO₂ typically 55-60 % by weight and Al₂O₃ typically 14-20 wt%), with significant potassium (K₂O typically 2-5 wt%), iron (FeO typically 2-5 wt%), magnesium (MgO typically 2-5 wt%) and crystallographically bound water (H₂O 4-6 wt%), with lesser CaO, Na₂O, TiO₂ making up with the remainder of the major elements. Note that pelitic rocks derived from fine-grained, clay-rich sediments may show a range in compositions depending the amount of calcite (CaCO₃) present (carbonate-rich argillites are termed marls). We begin by considering carbonate free- pelitic rocks.

The progressive metamorphism of such pelites is characterised by a series of dehydration reactions involving the following phases (listed with the substitutions and appropriate end-member names that express the compositional range of these phases in pelitic rocks):

- muscovite (mu); key : $K_2Al_4^i(Al_2Si_6)^{iv}O_{20}(OH)_4$
substitutions : $(Mg, Fe)^{iv}Si^viAl_{-1}^{iv}, Al_{-1}^{vi} > phengite$
- chlorite (chl); key : $(Mg_5Al)^{vi}(AlSi_3)^{iv}O_{10}(OH)_8 > chlinochlore,$
substitutions : $FeMg_{-1} > chamosite, Al^{vi}Al^{iv}(Fe, Mg)_{-1}^{vi}Si_{-1}^{vi} >$

- biotite (bt); key : $K_2Mg_6^{vi}(Al_2Si_6)^{iv}O_{20}(OH)_4 > phlogopite$
substitutions : $FeMg_{-1} > annite$, $Al^{vi}Al_{iv}Mg_{-1}^{vi}Si_{-1}^{vi} > eastonite$
- garnet (gt); key : $Mg_3Al_2Si_3O_{12} > pyrope$
substitutions : $FeMg_{-1} > almandine$, $MnMg_{-1} > spessartine$
- staurolite (st); key : $Mg_2Al_9Si_4O_{22}(OH)_2$,
substitutions: $FeMg_{-1}$
- cordierite (cd); key : $Mg_2Al_4Si_5O_{18}$
substitutions $FeMg_{-1}$
- K-feldspar (kf); $KAlSi_3O_8$
- plagioclase (pl); key : $NaAlSi_3O_8 > albite$
substitutions : $CaAlNa_{-1}Si_{-1} > anorthite$
- the aluminosilicate polymorphs, andalusite (and), sillimanite (sill),
and kyanite (ky); Al_2SiO_5 ,
- quartz (qtz); SiO_2
- ilmenite (ilm); $FeTiO_3$
- rutile (ru); TiO_2

Apart from plagioclase, the Fe-Ti oxides, ilmenite and rutile, and the spessartine component in garnet, most of the compositional variation of the important reactive minerals developed during progressive metamorphism of pelitic rocks can be approximated by the system K_2O - FeO - MgO - Al_2O_3 - SiO_2 - H_2O (KFMASH) which serves as a *model pelite* system. The order in which minerals appear depends on:

- the way pressure varies with increasing temperature, which is termed the *piezothermal array*;
- the ratio of Fe to Mg or X_{Fe} (where $X_{Fe} = Fe / (Fe + Mg)$) of the rock.

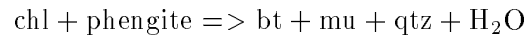
The sequence of minerals that develop during progressive metamorphism (that is, metamorphism at progressively higher temperature) define a *facies series* and depend on the pressure, or range of pressures, at which the progressive metamorphism occurred. The intermediate- and low-pressure facies series are named after the sequences in the Scottish Highlands from which they were first documented:

- the intermediate-pressure (5-10 kbar) *Barrovian facies series*, and
- the low-pressure (3-5 kbar) *Buchan facies series*

2.1.1 The transition from diagenesis to low grade metamorphism

The transition from diagenetic assemblages consisting of various clay group minerals, notably illite, to very low grade metamorphism is a complex process involving the gradual ordering and coarsening of the clays and chlorite, and the eventual breakdown of illite to sericite (a muscovite rich in the *phengite* substitution $\text{Si}^{vi}(\text{Fe},\text{Mg})^{iv}\text{Al}_{-1}^{vi}\text{Al}_{-1}^{iv}$). The degree of crystallinity of illite, as measured by *X-ray Diffraction (XRD)*, is correlated with temperature and can be calibrated against the *illite crystallinity index*.

The assemblage *chlorite-muscovite-quartz* is the typical *greenschist facies* pelitic assemblage characteristic of slates and defines the *chlorite zone*. With increasing temperature the chlorite and phengite component of the muscovite react to form biotite according to



The first appearance of biotite at the *biotite-in isograd*, marks the lower boundary of the biotite zone.

2.1.2 Intermediate temperature metamorphism

Above the biotite zone, the zonal succession, together with the appropriate isograds, in the typical Barrovian succession is:

- garnet zone (+ bt, mu, chl, qtz),
garnet-in isograd,
- staurolite zone (+ bt, mu, chl, gt, qtz),
staurolite-in isograd,
chlorite-out isograd,
- kyanite zone (+ bt, mu, gt, st qtz),
kyanite-in isograd,
staurolite-out isograd,

- sillimanite zone (+ bt, mu, gt, qtz)
sillimanite-in isograd,
kyanite-out isograd.

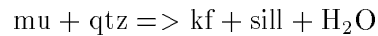
whereas in the Buchan zones the typical sequence is:

- garnet zone: (+ bt, mu, chl qtz),
garnet-in isograd,
- andalusite zone (+ bt, mu, gt, qtz)
andalusite-in isograd,
chlorite-out isograd,
- cordierite zone (+ and, bt, mu, gt, qtz),
cordierite-in isograd,
- sillimanite zone (+ cd, bt, mu, gt, qtz),
sillimanite-in isograd,
andalusite-out isograd.

Chloritoid is a rare component of both Barrovian and Buchan facies series where the *chloritoid-in* isograd occurs above the *garnet-in* isograd while staurolite may occur in some higher pressure Buchan facies series such as in the Mount Lofty Ranges.

2.1.3 Pelites at very high temperatures

Muscovite does not occur in pelites (or any other compositions) at very high temperatures. Instead all potassium is accommodated in K-feldspar, biotite or in silicate melt. The archetypal K-feldspar producing reaction is:



and is characteristic of mid-upper amphibolite facies temperatures. At still higher temperatures, in the *granulite facies*, biotite no longer occurs in any appreciable amount and the typical pelite assemblage is composed of quartz, K-feldspar, plagioclase, along with sillimanite, garnet, cordierite and, in rare cases, spinel and sapphire. Pelitic granulites are consequently almost entirely depleted in H₂O relative to the primary sediment, and may also show a number of other distinct geochemical features reflecting the extraction of considerable proportions of melt of approximately granitic

composition. As such pelitic granulites provide one possible candidate for the source region and residuum following the generation and extraction of *S-type granites* in the deep crust.

2.1.4 High pressure facies series

At the high pressures appropriate to the *blueschist* and *eclogite* facies the extent of solid solution of the phengite substitution in muscovite is very large. An important consequence being that high pressure pelites typically only contain a di-octahedral, phengite-rich, mica with the trioctahedral (biotite-group) micas absent. Other significant characteristics of the high pressure pelites are the occurrence of Mg-rich chloritoid and Mg-rich (or pyrope-rich) garnet (at lower pressures, pelitic garnets are dominantly almandine-rich) and talc, which in association with kyanite and quartz, form rocks that are referred to as *whiteschists*.

2.1.5 Textural changes associated with progressive metamorphism of pelites

The processes of deposition and early diagenesis frequently result in the development of a bedding-parallel *fissility* in unmetamorphosed argillaceous sediments. This fissility is due to the *mechanical anisotropy* imparted by the *preferred orientation* of detrital clays and *phyllosilicates* parallel to the sedimentary layering. With the onset of metamorphism the coarsening of the clays and growth of new phyllosilicates may enhance this bedding parallel fissility or, more typically, result in the development of a new preferred orientation related to the tectonic stress field during metamorphism. *Pencil structure* is a fabric developed by the superimposition of a tectonic preferred orientation on a bedding parallel fissility at very low grades of metamorphism.

With increasing grades of metamorphism and replacement of clays by phyllosilicates, the preferred orientation of chlorite and sericite/muscovite leads to the development of the cleavage characteristic of slates. Typically, this *slatey cleavage* occurs as an axial planar feature to fold structures and thus represents a *tectonic foliation* and as such is representative of the strain accumulated in the rock during tectonic deformation. In more

quartz-rich sediments such as metamorphosed greywackes or *psammites* at the same grade (i.e., chlorite zone) the cleavage is typically a *spaced cleavage* defined by alternating domains rich in quartz (Q-domains) and phyllosilicate (P-domains), respectively. Such chemical differentiation during the metamorphism highlights the role of *pressure solution* as a deformation mechanism under greenschist facies conditions. Pressure solution involves dissolution and precipitation of relatively soluble minerals such as quartz in an aqueous fluid and thus provides important evidence for the existence of a metamorphic fluid at these grades. At least some of the quartz dissolved during the development of P-domains and in the formation of slatey cleavage and crenulation cleavage (see below) is likely to have ended-up in quartz-veins that are ubiquitous in deformed greenschist facies pelite/psammite sequences.

Multiply deformed slates (and schists) develop a characteristic fabric called *crenulation cleavage*, in which early formed slatey cleavage has been deformed and variably overprinted by a new foliation. In the extreme case, crenulation may lead to complete obliteration of the earlier formed fabric, the evidence for which is only preserved within the inclusion trail geometry of *poikiloblasts*.

In the biotite zone coarsening of the phyllosilicates gives rise to *schistose* fabrics defined by the preferred orientation of the micas. Pelitic schists of the andalusite-, staurolite-, and kyanite-zones are very frequently *prophyroblastic* with the index minerals frequently forming poikiloblasts with complex inclusion trail geometries. The inclusion trail geometries provide a record of the foliation geometry at the time of prophyroblast growth and often testify to the important role of crenulation in the textural development of mica schists. Since prophyroblasts grow over a finite time interval, inclusion trail geometries may be used to reconstruct the intricate details of the foliation evolution and thus have important implications for the *kinematics* of deformation.

The onset of partial melting in pelitic rocks, at temperatures appropriate to the *amphibolite - granulite facies* boundary results in the distinctive rock fabric termed *migmatite* in which coarse grained quartz-feldspar veins or *leucosomes* are often separated from the rest of the rock (*neosome*) by biotite rich selvages, termed the *melanosome*, which may represent the residual component of the partial melting reaction. The dehydration reactions associated with the formation of migmatites and granulites involve the breakdown of micas and lead to a transition from *schistose* fabrics, in which foliation is defined by the preferred orientation of platy minerals, to *gneissic* fabrics which are typically coarse-grained and *granoblastic* with layering defined predominantly by differences in rock composition and, hence, differences in the modal proportions of the constituent phases. Coarse grained granoblastic rocks without layering are referred to as *granofels*.

2.2 Progressive metamorphism of basic igneous rocks (basalts)

Basic igneous rocks such as basalts have bulk compositions rich in silica (SiO_2 typically 45-50 % by weight), alumina (Al_2O_3 typically 14-20 wt%), calcium (CaO typically 8-12 wt%), iron (total FeO and Fe_2O_3 typically 8-12 wt%), magnesium (MgO typically 8-11 wt%), and sodium (Na_2O typically 1-3 %), with minor potassium and titanium making up with the remainder of the major elements. Many of the minerals developed during metamorphism result from hydration of the relatively anhydrous igneous precursor, and thus a useful *model basalt system* is NCFMASH.

The metamorphism of basic igneous rocks shows far less mineralogical variation than pelitic bulk compositions with many of the important changes represented by changes in the individual mineral compositions in mineral groups which show an extensive range of the *solid solution*. The main important mineral groups are:

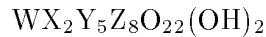
- amphibole,
- plagioclase,
- pyroxene,

- epidote,
- zeolite.

The detailed mineral chemistry of these groups as it pertains to metamorphosed basic igneous rocks is described below.

2.2.1 Monoclinic amphibole group

Amphiboles found in metamorphosed basic igneous rocks exhibit a wide range of chemical substitutions. The basic formula for the monoclinic amphibole group is:



where W represents the content of the large A site which may be occupied by Na, Ca or K but is frequently vacant; X (Ca, Na, K, Mg, Fe) is the content of the M4 site with either 6-fold (octahedral) or 8-fold co-ordination; Y (Mg, Fe²⁺, Fe³⁺, Al) is the content of the octahedral M1, M2, M3 sites, and Z (Si, Al) the content of the tetrahedral sites.

Tremolite, Ca₂Mg₅Si₈O₂₂(OH)₂, and its Fe-end member equivalent *actinolite*, has a vacant A site, M4 occupied by Ca, M1-3 occupied by Mg and all tetrahedral site occupied by Si. Natural *hornblendes* (including edenites, pargasites and tschermakites) are related to tremolite by the edenite (NaAlSi₋₁) and tschermak (Al₂Mg₋₁Si₋₁) substitutions, while the sodic amphiboles such as glaucophane can be related by the substitution of Na for Ca and Al for Mg on the M sites (Na₁Ca₋₁Al₁Mg₋₁). A schematic representation of the calcium-sodium (or potassium) amphibole compositional space is shown in Figure 1.

2.2.2 The plagioclase group and miscibility gaps

While solid solution between the end members of the plagioclase group, albite and anorthite, is more or less complete at high temperatures, plagioclases are characterised by a series of important *miscibility gaps* or *solvii* at low temperature. Miscibility gaps occur due to the intolerance of the crystal lattice to distortion at low temperatures, typically where the substituting ions are of significantly different size (see Figure 2). The main solvii in the plagioclase series include:

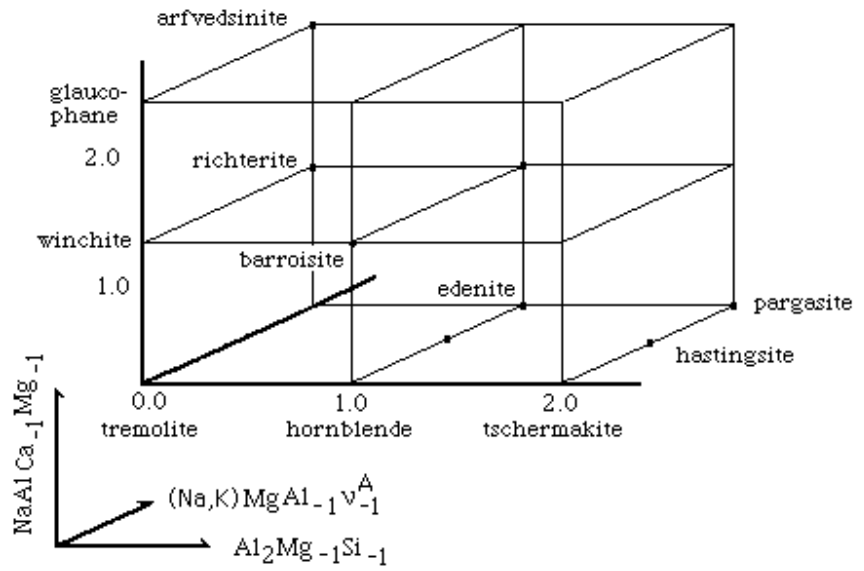


Figure 1: The compositional space for the Ca-Na amphiboles. Note that a fourth dimension includes the exchange vector FeMg_{-1} common to all amphiboles in metamorphosed basic rocks. A further exchange, $(\text{MgCa}_{-1})^A$, that is not shown relates tremolite to the Ca- and Na-free monoclinic amphiboles of the cummingtonite-grunerite series.

- the *peristerite solvus* between An_5 and An_{15} (where An_x represents the molar proportion of anorthite in the plagioclase solid solution).
- the *Bogild solvus* between An_{45} and An_{60} ,
- the *Huttenlocher solvus* between An_{70} and An_{90} .

So-far-as metamorphism of basic igneous rocks is concerned the most important of these is the peristerite solvus which, with a solvus crest at about 500°C , effectively restricts plagioclase compositions in the greenschist facies (see below) to albite.

2.2.3 Pyroxene group

Pyroxenes are stable minerals during crystallisation of basaltic melts, commonly occurring as phenocrysts, and form in the metamorphic environment at high temperatures. The compositions of the metamorphic pyroxenes varies with pressure. At low to intermediate pressures, in the *granulite facies* (see below) pyroxenes compositions are restricted to the "quadrilateral" defined by $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ - $\text{Fe}_2\text{Si}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$ (diopside-hedenbergite-ferrosilite-enstatite). The crest of the solvus between the

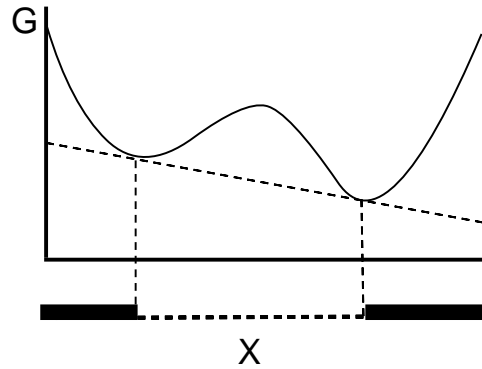


Figure 2: Schematic representation of a miscibility gap in a solid solution such as plagioclase caused by the increase in Gibbs energy due to increasing lattice distortion in the intermediate part of the solid solution range.

calcium-rich monoclinic pyroxenes and calcic-free orthorhombic pyroxenes occurs only at temperatures in excess of about 1000°C and thus sub-calcic clinopyroxenes such as *sub-calcic augite* and *pigeonite* are extremely uncommon in metamorphic rocks, although not completely unknown. The characteristic high pressure clinopyroxene, *omphacite*, found in the *eclogite facies* represents considerable solid solution between the calcic pyroxenes and the Na- and Al- pyroxene *jadeite* through the substitution $\text{NaAlCa}_{-1}\text{Mg}_{-1}$.

2.2.4 Epidote group

The epidote group minerals consist of

- *epidote* with general formula $\text{Ca}_2\text{Fe}^{3+}\text{Al}_2\text{Si}_3\text{O}_{12}(\text{OH})$
- *clinozoisite* with general formula $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$

with considerable natural solid solution. Clinozoisite, and its orthorhombic polymorph *zoisite*, are more typical of metamorphosed calcareous sediments than basic igneous rocks.

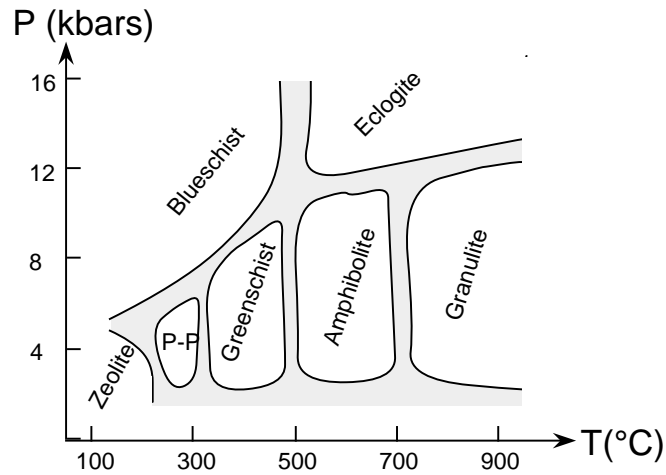


Figure 3: The metamorphic facies defined by assemblages in mafic igneous rocks. PP stands for the prehnite-pumpellyite facies.

2.3 Mineralogy of metamorphosed igneous rocks and the metamorphic facies

On the basis of the characteristic composition of the amphiboles, and the presence or absence of plagioclase and pyroxene diagnostic PT facies may be distinguished (Figure 3):

- *greenschist facies* characterised by amphiboles of the tremolite-actinolite series and albite-rich plagioclase. The characteristic greenschist facies assemblage is albite + actinolite + epidote +/- chlorite.
- *amphibolite facies* characterised by aluminous calcic amphiboles, termed hornblendes, and intermediate plagioclase. The characteristic assemblage is hornblende + plagioclase +/- garnet +/- epidote (An_{30-50}).
- *blueschist facies* characterised by the sodic amphibole *glaucofane*. The hydrated calcium aluminosilicate *lawsonite* occurs instead of calcic plagioclase, while *jadeite* may occur instead of sodic plagioclase.
- *eclogite facies* characterised by the sodic pyroxenes *omphacite* together with calcic garnet and by the absence of plagioclase. The characteristic assemblage is omphacite + garnet +/- kyanite.
- *granulite facies* characterised by "quadrilateral" (Ca-Fe-Mg) pyroxenes and intermediate plagioclase. The characteristic assemblage is

clinopyroxene-orthopyroxene + plagioclase (An_{30-70}) +/- garnet.

At very low temperatures (less than about 300°C), below the greenschist facies, metamorphosed basic igneous rocks may develop the hydrated calc-silicate minerals, prehnite and pumpellyite, while at still lower temperatures zeolite group minerals may develop. The appearance of such minerals has been used to define the *prehnite-pumpellyite facies* and the *zeolite facies*, respectively.

3 Mineral reactions and compatibility relations in Barrow's zones

In the previous section we described the characteristic mineral associations developed during progressive metamorphism of pelitic rocks. In this section we discuss the nature of the isograd reactions that mark zone boundaries during prograde metamorphism, concentrating on the the garnet-staurolite-zone boundary of the Barrovian facies series. We begin with an outline of a convenient *compatibility diagram* that allows the graphical representation of the mineral assemblages and reaction sequences in pelitic schists.

3.1 A compatibility diagram for pelitic assemblages

An important aspect of the mineralogy of pelitic schists is that the phase assemblage is very sensitive to small changes in bulk composition, for example the X_{Fe} , and it is useful to devise a way of graphically portraying this dependence of assemblage on bulk composition. *Compatibility diagrams* show the way in which the phase assemblage varies with bulk composition at specific PT conditions.

The main problem with compatibility diagrams is how to represent the variation in compositionally complex rock systems, such as the model pelite system (KFMASH), given the inherent limitations imposed by the 2D nature of graphical representation. The solution is to make use of the fact that the main function of a compatibility diagram is to show what phases are present at a particular PT condition, and not the relative proportions of these phases (although good compatibility diagrams may give some information about relative proportions). Therefore, it is not necessary to portray the compositional variation that controls the proportion of phases always present during metamorphism; the presence of such phases can be assumed. For example, at low to intermediate temperatures all *true pelites* contain muscovite, quartz and, presumably, a H₂O-rich fluid. Consequently, no matter how much we change the proportion of SiO₂ within the limits allowable in natural pelitic rocks, there will always be some

quartz. All other things being equal, adding more SiO_2 makes more quartz and removing SiO_2 makes less quartz but never enough to entirely remove quartz. Thus, in-so-far as we are concerned with the compatibility relations in the model pelite system we can effectively ignore variation in the proportion of SiO_2 as an important compositional control. Similarly, given the knowledge that muscovite is always present, and the assumption that a H_2O -rich fluid is always present we can also ignore the proportion of K_2O and H_2O . The effective compositional variation is therefore given by the reduced three-component system Al_2O_3 - FeO - MgO or *AFM* which is typically drawn as a ternary diagram. The phases that are always assumed present in constructing compatibility diagrams are termed *saturating phases*.

The procedure of constructing compatibility diagrams involves a projection which can be achieved by simple algebraic methods and illustrated schematically as in Figure 3.1 in which biotite is projected from the saturating phase muscovite in the reduced system K_2O - Al_2O_3 - FeO - MgO (the reduced system can be readily obtained by carrying out the analogous projection from quartz and H_2O in the full KFMASH system). Note that each projection reduces the dimensionality of the reduced system by one-degree (this explains why three saturating phases are required to reduce KFMASH to AFM). As discussed in the practical course, the co-ordinates of any phase we wish to project onto the AFM diagram are obtained by writing a balanced reaction between the phase to be plotted, the compositions of the three apices of the plot (Al_2O_3 , FeO and MgO for AFM) and the saturating phases (muscovite, quartz and H_2O fluid for AFM). The plotting co-ordinates are then given by the three coefficients for Al_2O_3 , FeO and MgO normalised to unity.

In order to understand the reaction sequence marking the appearance and disappearance of phases in pelitic schists it is necessary to understand the the role of the FeMg_{-1} substitution in the ferro-magnesian minerals like garnet, biotite, staurolite, cordierite and chlorite. These minerals represent solid solutions between Mg- and Fe-end members (i.e., pyrope and almandine in garnet), and thus the full compositional range of these minerals represent lines parallel to the FM join in AFM space (see Figure 3.1). ferro-magnesian phases partition Fe and Mg between the co-existing phases in a systematic fashion. This is because the sites on which the two divalent

Figure 4: Schematic representation of the projection of biotite onto the AFM plane form muscovite in the KAFM system

Figure 5: Schematic representation of the compositional ranges of the main ferromagnesian phases found in pelitic schists. Note that solid solution in garnet and staurolite is restricted to relatively Fe-rich compositions, while biotite, chlorite and cordierite are relatively more magnesian.

Figure 6: Schematic representation of partitioning of Fe and Mg between the phases garnet-chlorite-biotite consistent with $X_{\text{Fe,gt}} > X_{\text{Fe,bt}} > X_{\text{Fe,chl}}$. Circles represent projected compositions of the relevant phases while *tie-lines* connect compositions of coexisting phases.

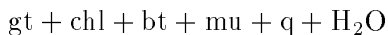
cations sit are of slightly different configuration and size in the different minerals. Fe, which has a larger atomic size than Mg, is partitioned into those phases with a relatively large site such as garnet, relative to those phases with relatively small sites, such as chlorite. Indeed, the order of partitioning amongst the various ferro-magnesian phases found in pelites is typically:

$$X_{\text{Fe,gt}} > X_{\text{Fe,st}} > X_{\text{Fe,bt}} > X_{\text{Fe,chl}} > X_{\text{Fe,cd}}$$

In view of this systematic relationship the typical garnet zone assemblage, consisting of garnet+ chlorite + biotite (+ mu, + qtz, + H₂O) the AFM relations must be of the general form shown in Figure 3.1.

3.2 Reaction sequence at the garnet-, staurolite-zone boundary

As mentioned in the previous section the characteristic assemblage in the garnet zone is :

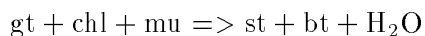


It is important to note that this characteristic garnet-zone assemblage does not occur in all true pelites in the garnet-zone. In rocks with very high X_{Fe} , chlorite is typically absent while in rocks with intermediate to low

Figure 7: Schematic representation of the AFM compatibility relations for the garnet-zone. Rocks with projected compositions in the region of A consist of various proportions of garnet + biotite (+ mu + qtz + H₂O), rocks with projected compositions in the region B consist of the phases garnet + biotite + chlorite (+ mu + qtz + H₂O), while rocks with projected compositions in the region of C consist of chlorite + biotite (+ mu + qtz + H₂O). The stippled region indicates the range of projected compositions in which three AFM phases are expected. Rocks with compositions projecting in other regions contain only two AFM phases. Note typical pelites project onto AFM with compositions less aluminous than garnet.

X_{Fe} is typically absent. The full AFM diagram representing all possible assemblages the range of possible bulk compositions of *true pelites* is shown in Figure 3.2.

The boundary between the garnet- and staurolite-zones is marked by the first appearance of staurolite. In rocks with the assemblage garnet + chlorite + biotite (+ mu + qtz + H₂O) this is marked by a decrease in the proportion of garnet, chlorite and muscovite and increase in the proportion of biotite and, obviously, staurolite. Consequently the reaction can be written :



Note, H₂O is evolved during this reaction (as can be demonstrated by trying to balance the reaction) which is consequently a dehydration reaction. The AFM compatibility relations beyond the reaction are as shown in Fig-

Figure 8: Schematic representation of staurolite zone compatibility relations in AFM

ure 3.2. During the staurolite-producing reaction, garnet and chlorite are used in fixed proportion which can readily be calculated by balancing the reaction. Let this proportion be x . Since the reaction can only proceed when both phases are present, the resulting assemblage after reaction depends on the initial proportion of garnet and chlorite immediately prior to reaction x_i . If x_i is greater than x then chlorite will be exhausted prior to garnet leaving the assemblage garnet + staurolite + biotite (as indicated by the composition A in Figure 3.2). Contrawise if x_i is less than x then garnet will be exhausted prior to chlorite leaving the assemblage chlorite + staurolite + biotite (as indicated by the composition C in Figure 3.2). Only in the case where x_i is equal to x will chlorite and garnet be exhausted simultaneously leaving the assemblage staurolite + biotite (as indicated by the composition B in Figure 3.2).

Note that in the staurolite-producing reaction muscovite is also consumed, in a proportion that must be fixed by the stoichiometry of the reaction. In rocks of true pelitic composition muscovite is always present in greater proportion than used in the reaction and thus will never be exhausted during reaction. We note that this is an essential attribute of a saturating phase in a compatibility diagram and validates the use of muscovite as a saturating phase in the AFM compatibility diagram.

4 Why do reactions occur ?

Metamorphism is about transformation. Mineral transformations entail reaction between existing minerals to form either

- new minerals, or
- change the proportion of existing minerals.

In either case the reaction must be driven by some fundamental chemical "force". This driving force is, as is so often the case in physics and chemistry, related to *energy minimization* (in mechanical systems equilibrium is dictated by minimization of potential energy). In metamorphic geology we are concerned largely with the relationships amongst phases in systems in which pressure and temperature can be considered as part of the environment of the system; i.e., they can be considered as superimposed on the system. In such systems the thermodynamic function which is minimized at equilibrium is the Gibbs energy (or Gibbs free energy).

To understand the notion of Gibbs energy minimization we can consider as the simplest case a system consisting only of *polymorphs* of the one compound, for instance, andalusite, sillimanite and kyanite which are polymorphs of Al_2SiO_5 . Figure 4 is an isobaric (or constant pressure) T-G diagram showing, schematically, the the Gibbs energy of the polymorphs as a function of temperature for a pressure below the Al_2SiO_5 triple point. The stable mineral at any given temperature is given by the curve which minimizes the Gibbs energy at that temperature and in Figure 4 is indicated by the thick parts of the T-G curves. Metastable parts of the T-G curves are indicated by the dashed lines. Figure 4 is similar to Figure 4 but constructed for a pressure higher than the Al_2SiO_5 triple point.

The extension of the concept of Gibbs energy minimization into more complex systems consisting of more than one distinct phases is simple. The molar Gibbs energy of the system, G_s , is simply the sum of the Gibbs energies of the individual phases multiplied by the molar proportion of the phase, for j phases:

$$G_s = \sum_{i=0}^{i=j} G_i X_i \quad (1)$$

where G_i is the Gibbs energy of the i^{th} phase and X_i its molar proportion.

Figure 9: Schematic isobaric G-T diagram constructed for the three Al_2SiO_5 polymorphs at a pressure below the triple point. At temperatures below T_1 kyanite has the lowest Gibbs energy and therefore is the stable phase, between T_1 and T_3 andalusite is stable and above T_3 sillimanite is stable. T_2 is the temperature of the kyanite-sillimanite transition which at this pressure is metastable with respect to andalusite.

Figure 10: Schematic isobaric G-T diagram constructed for the three Al_2SiO_5 polymorphs at a pressure above the triple point.

4.1 G-X Diagrams

All metamorphic minerals show some degree of compositional variation or solid solution, with many mineral groups, such as the amphiboles and micas showing extensive solid solution. The Gibbs energy of a phase is a continuous function of its composition as well as pressure and temperature (discontinuities in the Gibbs energy function for a given composition indicate a phase transition due to abrupt changes in the crystal structure). If we represent the compositional variation by the parameter X , such that:

$$G = \mathcal{F}(P, T, X)$$

then we can represent the variation of Gibbs energy as a function of composition (at constant P and T) on a G-X diagram.

Given the 2-dimensional limitations of paper, it is difficult to illustrate G-X diagrams in greater than binary systems: Figure 4.1 shows an attempt to represent the types of G-X relationship that might exist in AFM. It is somewhat easier to look at what happens by considering the profiles of the G-X curves in Figure 4.1 when viewed from the perspective of the base of the biotite G-X loop, as represented in Figure ??.

Reactions are easily understood in terms of G-X diagrams. In Figure 4.1, the assemblage garnet + chlorite clearly has a lower Gibbs energy than assemblages staurolite for a specific range of bulk compositions that in the range between the intercepts of a common tangent between the G-X curves for garnet and chlorite. However, since Gibbs energy is a function of pressure and temperature as well as composition there will be a pressure and temperature where the G-X curves for garnet, staurolite and chlorite all have a common tangent (Figure 4.1). This is the temperature and pressure of the reaction:



For any given pressure there is a unique temperature at which the G-X curves for the three phases can have a common tangent. However, with any small change in pressure there will be a new temperature at which the G-X curves for the three phases maintain the common tangent. The trace of the pressures and temperatures for which the common tangent

Figure 11: Schematic G-X diagram showing the Gibbs energy as a continuous function of composition (X) in the AFM space at constant pressure and temperature for the phases staurolite, garnet, chlorite and biotite

is maintained in P-T space (necessarily a line) delineates the equilibrium position of the reaction (Figure ??).

4.2 PT phase diagrams

Figures 9-12 show that in some profound way phase diagrams represent the mappings of the G-X relations onto the PT plane. Specifically PT phase diagrams show the PT distributions of the minerals or mineral assemblages that minimize Gibbs energy.

In order to quantify the exact positions of reactions in PT space it is necessary to quantify Gibbs energy. For any phase *Gibbs energy* may be expressed in terms of the *thermodynamic parameters, enthalpy, entropy, and molar volume* as well as P and T, with these parameters able to be extracted from the results of laboratory *experiments* designed to reproduce reactions of the type shown in Figure 12. The main problem with the exper-

Figure 12: Illustration of the profile of the G-X loops as viewed from the base of the biotite G-X curve in Figure 8. These G-X profiles are appropriate to the stability of the garnet-chlorite assemblage.

Figure 13: G-X relationships appropriate to the reaction garnet + chlorite = staurolite (+ biotite).

imental approach is the extreme "sluggishness" of many reactions, which makes the process extremely painstaking. Also, the large compositional range of many of the important metamorphic mineral groups implies an inordinate number of experiments would need to be carried out to understand the thermodynamics of full compositional range. To date the thermodynamic properties of most of the important mineral end-members are constrained by experiment, and theoretical approaches based on the application of *activity models* are used to extend this thermodynamic data to mineral compositions within the solid-solution range.

The sluggishness of metamorphic reactions which so infuriates and frus-

Figure 14: G-X relationships appropriate to temperatures above the reaction garnet + chlorite = staurolite (+ biotite).

trates experimentalists is due to important *kinetic* barriers to reaction. Kinetics plays an important role in understanding why partially completed reaction textures may be preserved in metamorphic minerals, and indeed, why high grade metamorphic rocks may be preserved during excavation to the surface of the earth with little or no apparent back, or *retrograde*, reaction.

Figure 15: Schematic PT (phase) diagram shown the PT trace of the reaction garnet + chlorite = staurolite, with relative positions of the GX diagrams shown in Figures 9 - 11 shown by the labels 1, 2 and 3, respectively. Note that the full reaction is garnet + chlorite + muscovite = staurolite + biotite + quartz + vapour. Note that a PT diagram shows the PT distribution of the mineral assemblages that minimize Gibbs energy.

5 Shape and texture in mineral aggregates

Many metamorphic minerals show characteristic shapes in mineral aggregates suggesting the existence of important principals governing mineral shapes. In this section we outline these controls on the shapes of minerals (and fluids) in metamorphic aggregates and consider some important implications. We begin with a discussion of the shape of single crystals grown in an artificial environment independent of any other crystals, and then extend the discussion to the shapes, and 3-dimensional distribution, of individual crystals and phases in polycrystalline aggregates.

5.1 Single crystals

The shape of single crystals grown in an artificial environment independent of any other crystals is dictated by the crystallographic structure, with crystal faces in the developing crystallite favouring lattice orientations with the highest density of lattice points. In *face centered cubic* (fcc) crystals the faces which have the highest density of lattice points are $\{1,1,1\}$ followed by $\{1,0,0\}$ where the curly brackets $\{\}$ signifies the set of faces of that form. Thus $1,1,1$ includes the faces $(1,1,1)$, $(1,-1,1)$, $(1,-1,-1)$, $(1,1,-1)$, $(-1,1,1)$, $(-1,-1,1)$, $(-1,1,-1)$ and $(-1,-1,-1)$. Crystals with all faces of the form $\{1,1,1\}$, (e.g. spinel-group minerals such as magnetite) typically form *octahedra*. In *body centred cubic* (bcc) crystals the faces with the highest density of lattice points are $\{1,1,0\}$ followed by $1,0,0$ (Figure 5.1).

5.2 Surface energy and the nature of grain boundaries in crystals

To understand constraints on the shapes of individual grains in aggregates of one or more phases we need to consider the nature of the grain boundaries between separate crystals and, in particular the nature of the energy associated with crystal surfaces. Crystal structures exist in nature because these structures provide a configuration of low energy compared to any other conceivable configuration for the mixture of elements that

Figure 16: Schematic illustration of faces with the highest density of lattice points in fcc and bcc crystals, respectively.

make up the crystal (if this were not so, the crystal would not exist). Normally, when we refer to the energy of a crystal structure, for example the Gibbs free energy, we refer to energy appropriate to an interior part of a hypothetical, perfect crystal of infinite size. Specified in this way it is the energy associated with part of an electronically neutral crystal with all bonds intact. Real crystals are neither perfect nor infinite, containing both point and line *defects* (see next section) and surfaces. Defects and surfaces entail broken, or unsatisfied, bonds within the crystal lattice and thus are associated with an excess energy. The excess energy associated with the defect or surface can be expressed as the energy needed to break the bonds appropriate to the formation of the defect or surface.

The surface orientations within a crystal structure which disrupt the structure the least are those with the highest density of lattice points, since bonds within the plane of the surface remain connected. Consequently, surfaces parallel to lattice planes with a high density of lattice points have a lower excess energy than surfaces of any other orientation. Thus, following the principle of *energy minimization*, the reason for the formation of characteristic crystal morphologies is that these shapes minimize the surface energy for the particular phase.

The excess energy of a surface, γ , is necessarily a function of the properties of both of the phases juxtaposed across the surface. Where crystal surfaces are involved, as in mineral aggregates, the γ is also dependent on

Figure 17: Schematic representation of nature of grain boundaries between crystals of the same phase. With little or no misorientation across the boundary most bonds remain intact and thus the excess energy of the boundary is very little (left hand figure). With increasing misorientation the number of broken bonds at the grain boundary rapidly increases causing an increase in the associated surface energy.

the orientation of the crystal lattice with respect to the structure.

5.3 Shapes in crystal aggregates

Just as at equilibrium the rock chooses the assemblage that minimizes Gibbs energy, the shape of mineral aggregates at equilibrium is governed by the tendency to minimize the surface energy. Clearly the surface area per unit volume decreases within increasing crystal grain size, and thus there is always energetic favour in increasing grain size. However crystals in real rocks do not grow without bound. In real aggregates an effective limiting grain size is provided by the rate at which the components needed for the growth of the mineral can be transported (usually by diffusion) to the growing surfaces.

Figure 18:

5.4 Digression on the connectivity of minor phases

An important aspect of grain shape concerns the 3-dimensional arrangement of minor phases in poly-phase aggregates, and particularly the connectivity of the minor phase. This is important for the role of metamorphic fluids and melts, since in order for fluids to move and melts to segregate from their matrix they must form a 3-dimensionally interconnected *porosity*.

At equilibrium, the angle made at the triple point between a minor phase bounded by two grains of a major phase is termed the dihedral angle, θ . The dihedral angle is clearly a function of the relative surface energies of the minor/major phase interface and major/major phase interface. If these energies are the same then the dihedral angle is 120° . For such large dihedral angles the minor phase will form small grains distributed at some of the junctions between major phases, with no connection between individual grains of the minor phase. As $\theta \rightarrow 0^\circ$ the minor phase becomes smeared out along the major phase grain boundaries eventually completely wetting all grain boundaries and thus forming a 3-dimensionally interconnected porosity. There is a critical value, $\theta = 60^\circ$, at which the minor phase first achieves this 3-dimensionally interconnected porosity, independent of the proportions of the phases. Clearly for a minor fluid phase to segregate from, or flow through, its host at very low proportions, such as basaltic melt in a peridotite host, the minor phase must form a 3-dimensionally interconnected porosity.

Figure 19: Schematic representation of the effect of dihedral angle, θ , on the distribution of a minor phase in a two phase aggregate.

5.5 The problem of nucleation and the origin of porphyroblasts

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6 Deformation of mineral aggregates

Metamorphism and deformation are intimately related, since in many environments it is tectonic burial which causes the rock sequences to be subject to elevated temperatures. Deformation occurs in response to a *non-hydrostatic* (or equivalently, deviatoric or directed) stress field, which can be characterised by the maximum (σ_1), intermediate (σ_2) and minimum (σ_3) stresses, respectively. (Note that like the optical activity of crystals which can be characterised by three principal optic axes, the stress field is a *tensor* property). The non-hydrostatic part of the stress tensor, $\tau = (\sigma_1 - \sigma_3)/2$ (or stress deviator), is independent of the magnitude of the pressure, $P = (\sigma_1 + \sigma_2 + \sigma_3)/3$.

The ways in which mineral aggregates deform are manifested in a number of characteristic microstructural features. The dominant modes of deformation at the crystalline level in the metamorphic environment are

- brittle fracture,
- pressure solution creep,

- dislocation creep.

The most important controls on the deformation mode are the :

- temperature, and
- rate of deformation or *strain rate*.

At the crystalline level the deformation mode often varies between different crystal types. The conditions favouring each of these deformation modes and the characteristic microstructural features are described briefly below.

6.1 Brittle fracture

At low temperatures and/or high strain rates deformation of the crystal lattice occurs by fracture. The characteristic microstructural feature of brittle failure at the crystalline level are healed fractures. These are usually recognisable by planar arrays of fluid inclusions. Veins and tension gashes are also characteristic features of brittle failure.

6.2 Pressure solution creep

Many common metamorphic minerals, particularly quartz and carbonates, show appreciable solubility in metamorphic fluids. The solubility of a mineral in a fluid increases as the stress state on the mineral increases, and thus highly stressed grain boundaries are more susceptible to dissolution than less-stressed grain boundaries. In fluid-mineral aggregates subject to deviatoric stress the equilibrium concentration of the solute in the fluid will vary with the stress state at the grain boundary thus setting up solute concentration gradients in the surrounding fluid. Diffusion of solute in the fluid will operate to annihilate such a concentration gradient, thus perturbing the equilibrium solute concentration in such a way as to induce

- oversaturation with consequent precipitation at grain boundaries with little resolved compressive stress,
- undersaturation and consequent further dissolution at boundaries with high resolved compressive stress.

Boundaries with the highest resolved stress are necessarily at a high angle to the principal compressive stress and will undergo continual dissolution

Figure 20: Schematic representation of the stress in aggregate of spherical grains subject to horizontal principal compressive stress, σ_1 . Shaded areas in spherical grains signify stress concentration at boundaries at a high angle to σ_1 .

during deformation (Figure 6.2).

Pressure solution is a characteristic deformation mode of low to intermediate temperatures in the greenschist facies. It is an important process involved in forming compositionally differentiated cleavage fabrics in psammites, such as P-Q fabrics, and crenulated cleavage in greenschist facies metasediments. The characteristic pressure solution structure in limestones and marbles are *stylolites*.

6.3 Defects and the nature of dislocation creep

At elevated temperatures and relatively low strain rates crystals may deform by pervasive shape changes. Such shape changes are achieved by the movement of defects through the crystal lattice. Defects may be of two types

- point defects or vacancies,
- line defects or dislocations.

At metamorphic temperatures deformation by movement of dislocations, known as dislocation creep, is the most important of these two modes. Dislocations represent line defects marked by an extra half lattice row. Dislocations are able to sweep through a crystal leaving behind a perfect

Figure 21: Schematic illustration of nature of dissolution and precipitation aided by solute transfer during pressure solution

crystal structure displaced, or *slipped*, one lattice spacing. The cumulative effect of repeated dislocation movement is to produce substantial shape changes.

Dislocations are generated throughout crystals at discrete sources, but frequently organize themselves into discrete walls. Dislocations of opposite sign will annihilate each other thus walls quickly develop a dominance of dislocations of one sign over another and thus separate crystal domains or subgrains of slight different orientation. The characteristic microstructure resulting from this aggregation of dislocations into walls is undulose extinction. With increasing misorientation across dislocation walls, individual crystals begin to recrystallize into discrete smaller grains.