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Chapter I

Metamorphic Processes

I.I Introduction

Metamorphism refers to the mineralogical and structural alteration of rocks in Earth's crust, and excludes alteration at or just beneath the surface, such as weathering and early diagenesis. However, diagenetic changes grade into metamorphic changes in *burial metamorphism*. In fact, metamorphism may occur in several geological environments, because assemblages react to changes in temperature (T), pressure (P) and activities of mobile chemical components, regardless of the geological processes responsible for the changes. For example, identical or very similar assemblages can be formed by (1) deuteric alteration in an igneous intrusion, (2) wallrock alteration around a hydrothermal orebody, (3) low-temperature alteration around an igneous intrusion, (4) burial metamorphism of sedimentary/volcanic successions and (5) alteration, both local and regional, in geothermal areas (Vernon, 1976).

Metamorphic geologists try to: (1) infer what the rocks were before metamorphism (the parent or precursor rocks) and (2) work out what has happened to them during metamorphism (the metamorphic-deformation history). Most effort goes into the second aspect (see Chapters 1 to 6), in the form of inferring: (1) compatible metamorphic mineral assemblages; (2) the combinations of pressure (P), temperature (T) and fluid composition (X) implied by those assemblages; (3) changes in P-T conditions with time, (4) metamorphic reactions, including partial melting reactions; (5) relating metamorphic minerals and assemblages to deformation events (D) and (6) suggesting P-T-time (t) paths for the region of Earth's crust under consideration. However, careful determination of parent (source) rocks is also important (see Chapter 7), for (1) providing the necessary field control on laboratory-based interpretations; (2) completing the metamorphicdeformation history of a terrane and (3) identifying pre-metamorphic rock-types, which is necessary for ore search models in metamorphic terranes.

The classification of metamorphic rocks is simple, with the result that metamorphic petrology is not cluttered with a large number of rock-type names. Nine basic terms (Table 1.1) cover nearly everything, apart from a few specialized compositional terms, such as 'eclogite', 'skarn', 'peridotite', 'serpentinite' and 'rodingite'. More detailed naming is achieved by qualifying the nine basic terms with mineral adjectives. For example, various

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Table 1.1. Metamorphic rock names	
hornfels:	typically granoblastic rock, generally non-foliated ('massive'), occurring in contact metamorphic aureoles; may be foliated where the contact metamorphism overprints earlier regional metamorphism
slate:	fine-grained, low-temperature regional metamorphic rock with a slaty cleavage (see Chapter 6)
phyllite:	similar to slate, but with larger chlorite and white mica grains, resulting in a less perfect cleavage
schist:	regional metamorphic rock, coarser-grained than phyllite, with schistose foliation (see Chapter 6) and commonly (though not necessarily) with porphyroblasts (large metamorphic grains)
gneiss:	coarse-grained, generally high-temperature regional metamorphic rock with a gneissic (commonly lenticular and discontinuous) foliation (see Chapter 6)
granofels:	granoblastic, non-foliated rock, commonly (though not necessarily) high-grade; may be contact or regional metamorphic; useful non-genetic term
amphibolite:	special compositional term for a metamorphic rock (typically regional) composed largely of amphibole (especially hornblende) and plagioclase
marble:	special compositional term for metamorphosed pure or nearly pure limestones or dolomites; metamorphosed impure (clay and/or quartz-bearing) limestones or dolomites are called 'calcsilicate' rocks
quartzite:	special compositional term for metamorphosed pure or nearly pure quartz-rich rocks, such as quartz sandstones (orthoquartzites) or cherts; the term 'metaquartzite' is technically preferable, but not always used

hornfelses and schists may be distinguished by mineral prefixes, such as hornblende hornfels, biotite-andalusite hornfels, garnet-wollastonite hornfels, mica schist, biotite-garnet schist and muscovite-cordierite-andalusite schist. The prefix 'meta-' is also useful (e.g., metasandstone, metapelite, metagabbro, metarhyolite), provided the parent rock is known.

The most direct evidence of metamorphism in Earth's crust is observation of a transition from unaltered to strongly altered rocks. The variation may be due to progressively increasing *T* and *P*, which is called *prograde metamorphism* or it may be due to decreasing *T* and *P*, which is called *retrograde metamorphism*. The degree of alteration is loosely referred to as the *metamorphic grade* or *grade of metamorphism* (e.g., Tilley, 1924). Rocks are referred to as being of 'low grade', 'medium grade' or 'high grade' informally, with no well-defined *P*-*T* boundaries between them. Grade is commonly related mostly to temperature (e.g., in low-*P* metamorphism), though pressure also has an effect, and dominates over *T* in high-*P* metamorphism (Fig. 1.1).

Because chemical reactions proceed faster at higher *T*, most prograde reactions tend to go to completion, whereas retrograde reactions, are commonly incomplete (showing evidence of partial replacement of high-grade

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Three 'geotherms' superimposed on a simple phase diagram that shows the approximate *P*-*T* positions of the Al_2SiO_5 reaction curves and the line for the reaction Ab = Jd + Qtz. Geotherm 1 (characterized by andalusite at lower grades) represents a low-pressure terrane; geotherm 2 (characterized by kyanite at lower grades) represents a medium-pressure terrane; and geotherm 3 (characterized by the assemblage Jd + Qtz at higher *P*) represents a high-pressure terrane.

minerals), owing to decreasing T and restricted access of H_2O and/or CO_2 that was lost during earlier prograde metamorphism (e.g., Vernon, 1969; Vernon & Ransom, 1971; Corbett & Phillips, 1981). Exceptions occur in high-strain zones (shear zones, mylonite zones), where the retrograde reactions tend to go to completion, owing to the catalytic effect of strong deformation, which facilitates neocrystallization by inducing plastic strain in the original grains and by opening transient pores for fluid access (Vernon & Ransom, 1971; White & Clarke, 1997; Vernon, 2004). Outside such high-strain zones, rocks may show evidence of both prograde and retrograde metamorphism (Vernon, 1969; Vernon & Ransom, 1971). Both the prograde and retrograde metamorphism can belong to the same metamorphic cycle ('event'), or the retrograde metamorphism can occur much later, the rock then being referred to as *polymetamorphic*. This term is also applied to rocks subjected to more than one period of prograde metamorphism.

Experiments have shown that low-grade metamorphic minerals are stable at about 100°C–300°C and that common high-grade minerals are stable at about 700°C–850°C. Higher temperatures (in excess of 1000°C) occur in exceptionally hot regional metamorphic terranes (e.g., Ellis *et al.*, 1980; Harley, 1989) and around some high-temperature (mafic-ultramafic) intrusions (e.g., Willemse & Viljoen, 1970; Nell, 1985). Pressures range from very low (in high-level metamorphism around igneous intrusions) to in excess of 30 kbar (approximately 100-km depth) in high-pressure metamorphism (Chopin, 2003).

Conventionally, metamorphism is divided into *contact* ('thermal') metamorphism, occurring around igneous intrusions, and regional metamorphism, in which metamorphic rocks are produced on a regional scale. However, the same minerals can be formed in both types of metamorphism, and so the distinction has no serious genetic importance, though the terms are widely used for convenience. In fact, the intensity of regional

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metamorphism at low pressure is commonly related to proximity to granite intrusions (e.g., Vernon *et al.*, 1990; Clarke *et al.*, 1990; Collins & Vernon, 1991; Vernon *et al.*, 1993a; Williams & Karlstrom, 1996; Vassallo & Vernon, 2000), and a useful distinction can be made between *contact aureole granites*, around which metamorphism is very localized, and *regional aureole granites*, around which occur metamorphic aureoles of regional extent (White *et al.*, 1974), as in the Cooma complex, south-east Australia. It is also often useful to refer to *low-P*, *medium-P* and *high-P* metamorphism, based on broad pressure differences (Fig. 1.1), as discussed in more detail in Section 1.7.2.

The minerals in chemically compatible coexistence in a metamorphic event constitute a *mineral assemblage* or *paragenesis*. A problem is to ascertain that the members of an inferred mineral assemblage really did coexist stably (Section 2.3).

The metamorphic process is profoundly asymmetrical. Metamorphic rocks formed at deep crustal or even upper mantle depths are exposed at Earth's surface, and yet their high-grade minerals do not reflect their current physical conditions (1 atmosphere, 25°C). Thus, they are metastable, in the sense that they are thermodynamically unstable, but persist because of kinetic barriers to their reaction. The metastable persistence of metamorphic rocks at Earth's surface can be explained mainly by the role of a minor but important constituent, H₂O. Sediments being actively deposited have high proportions of hydrous pore fluid (up to 30%); yet their metamorphosed equivalents contain only small amounts of H₂O, which is mostly structurally bound in hydrous minerals (0%-12%). Though hydrous minerals dominate low-grade (low-T) metamorphic rocks, only small proportions of hydrous minerals occur in high-grade (high-T) metamorphic rocks. One of the main reasons high-grade metamorphic rocks are exposed at Earth's surface without being converted to low-temperature mineral assemblages during cooling is that hydrous fluid lost during the previous prograde metamorphism needs to be returned to the rocks in order to cause retrograde metamorphism, as mentioned earlier.

The mass of rock overlying most metamorphic environments imposes a *confining pressure*, which depends on the density and thickness of the overlying material, and which reduces the porosity. Plastic deformation and consequent *recrystallization* (see Sections 6.2 and 6.3) of minerals during metamorphism, growth of new mineral grains (*neocrystallization*) and movement of grain boundaries to reduce interfacial energy (e.g., Vernon, 1976, 2004) all contribute to porosity reduction. An analogous environment occurs in glacial ice sheets, where the weight of successive snow accumulation compacts underlying snow into nevé (firn) and then ice, with the progressive reduction of extensive porosity by grain-boundary movement, as illustrated by Vernon (2004, fig. 4.43).

These processes ensure that metamorphic rocks generally contain very little pore fluid, probably only up to about 2 weight percent (Yardley & Valley, 1997, 2000). The excess pore water is initially squeezed out, owing to the confining pressure, and H_2O released by prograde metamorphic reactions migrates as supercritical fluid in microfractures formed by local fluid pressure increase and by tectonic deformation. Despite the inability of metamorphic rocks to hold much free fluid, substantial amounts of fluid may pass though rocks undergoing deformation with time, especially in fracture networks and shear zones, in which space for the fluid is made by the opening of transient microfractures and pores caused by the different

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responses of adjacent minerals to the local stress system, as discussed in Chapter 5.

Pore fluid in most metamorphic environments cannot be observed directly, as most is lost during metamorphism. Vestiges may remain as small primary fluid inclusions in minerals, and indications of fluid composition can be obtained from deep crustal drilling. However, limits to drilling technology restrict sampling to the upper 10 km or so of the crust (i.e., above most regional metamorphic terranes), and fluid inclusions are prone to the partial loss of mobile material (decrepitation). Therefore, much information concerning pore fluid in metamorphic rocks must be gleaned indirectly (see Chapter 5).

Up to 12 weight percent H_2O may be structurally bound as hydroxyl $(OH)^-$ in common hydrous minerals, such as mica, amphibole or lawsonite. These solid H_2O reservoirs convey fluid deep into Earth during subduction, and fluid released consequent to their breakdown during prograde metamorphism may contribute to partial melting and the formation of some arc magmas.

Though most metamorphic rocks experience a dynamic history involving burial, metamorphism and exhumation, they commonly preserve *P*-*T* evidence of only the maximum or *peak* conditions. Working out the *P*-*T* history of the burial and exhumation stages (Chapter 2) may be difficult or impossible. However, many terranes partially record evidence of their *P*-*T* history, and so metamorphic petrologists attempt to suggest plausible models by combining these partial records with *P*-*T* information obtained on other rocks or from experiments.

On the way to reaching peak conditions, a rock undergoes a series of *devolatilization* (dehydration and/or decarbonation) reactions, with products that are commonly denser and less hydrous than the original minerals (reactants). The inability of rocks to store fluid, owing to restricted or absent porosity, means that H_2O or CO_2 released as fluid by mineral breakdown is lost. Having lost a key potential reactant, the products cannot react to reverse the prograde reactions during cooling, preserving peak assemblages, as mentioned previously.

1.2 Effect of rock composition: The ACF diagram

Most metamorphic processes are considered to be essentially isochemical, apart from loss of volatile components, such as H₂O in the metamorphism of pelites and mafic igneous rocks and CO₂ in the metamorphism of carbonate rocks (Harker, 1893; Leake & Skirrow, 1958; Pattison & Tracy, 1991, p. 118; Barton et al., 1991; Greenfield et al., 1998), although some have challenged this generalization (see Section 5.13). However, regardless of the extent of inferred chemical change during prograde metamorphism of metasedimentary rocks, the essential chemical composition (e.g., pelitic character) is preserved. So it is fair to say that the major and trace element composition of most metamorphic rocks largely reflects the protolith (parent rock) composition, enabling us to 'see through' the effects of metamorphism (see Chapter 7). Major exceptions to the generalization of approximately isochemical metamorphism involve special circumstances, in which large fluid-rock ratios and chemically complex fluids profoundly influence a rock's chemical composition in a process referred to as metasomatism (Chapter 5).

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A simple example of at least approximately isochemical metamorphism is an orthoquartzit with ripple cross-bedding delineated by magnetite or hematite: metamorphism produces a metaquartzite by recrystallization of the detrital quartz, magnetite and hematite grains, without chemically modifying them. A more complex example is a low-grade metamorphic rock rich in chlorite and biotite, as well as feldspar and quartz. The chemical elements now forming chlorite and biotite probably were deposited as clay minerals in a mud-rich sediment. Clay minerals are only stable up to a few hundred degrees Celsius, and react to form new minerals, such as chlorite and biotite, which are stable at the elevated temperatures of metamorphism. Large proportions of chlorite tend to occur in low-grade metamorphic rocks, but react with other minerals to form new minerals such as garnet, cordierite and staurolite with biotite, in response to increasing temperature.

In some areas of extensively exposed metamorphic rocks, individual sedimentary layers can be traced through grade variations (e.g., Harte & Hudson, 1979; Stewart, 1981). This illustrates another important principle, namely that minerals in a metamorphic rock reflect both the whole-rock chemical composition *and* the metamorphic grade. This is well exemplified by amphiboles formed in the metamorphism of ocean-floor basalts. At the comparatively low-*T* conditions of subduction metamorphism, metabasalts are dominated by glaucophane, whereas at higher-grade conditions, the same rock-composition is dominated by hornblende. At the highest grade, the metabasalt may lack amphibole, and instead contain the anhydrous chemical equivalent, pyroxene (e.g., Vernon *et al.*, 1990).

Metamorphic rocks exposed at Earth's surface can be subdivided chemically in many ways, but for the purpose of field identification, can be initially divided into a few main compositional types. Mafic (basic) rocks form the largest proportion of Earth's surface, as basaltic material floors most oceans. Most metamorphosed mafic rocks (amphibolites, greenschists) have basaltic or gabbroic protoliths; they are widespread and define key assemblages for several metamorphic facies (Section 1.7). Ultramafic rocks are commonly mantle derived, low-Si, high-Mg rocks, composed chiefly of mafic minerals. Quartzofeldspathic (felsic) rocks may be of (1) sedimentary origin, namely sandstones (psammites, arenites), such as feldspathic sandstone ('greywacke') or felsic tuff, or (2) igneous origin, namely granitoids or metavolcanic rocks. Pelitic rocks (shales, claystones, mudstones) are finegrained clastic sediments with appreciable clay and quartz; they are commonly carbonate-poor, and their metamorphic equivalents (metapelites) are sensitive indicators of the greenschist, amphibolite and granulite facies (discussed in Section 1.8.1). Carbonate rocks are sedimentary rocks formed by organic or inorganic precipitation from aqueous solution of carbonates of calcium, magnesium or iron. Marls are sedimentary rocks containing both carbonate and clastic (clay and quartz) components, and may be dominated by either.

Metamorphic minerals are of two types, namely those with fixed composition, such as quartz (SiO₂) or calcite (CaCO₃), and those with variable composition, such as garnet or amphibole. Variations in mineral composition are caused by cations of similar charge and size exchanging on sites in the crystal lattices, a process called *solid solution*. For example, garnet is commonly a solid solution of almandine (Fe₃Al₂Si₃O₁₂) and pyrope (Mg₃Al₂Si₃O₁₂), the ratio of Fe²⁺ to Mg²⁺ being temperature-dependent (for



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hornblende-biotite-diopside field. As the compositions of most metabasalts are close to that of hornblende, these rocks are dominated by hornblende. Relationships between metamorphic whole-rock compositions and mineral assemblage are discussed in more detail in Sections 1.7 and 2.2.

a given rock composition). Plagioclase shows coupled (Na⁺Si⁴⁺ = Ca²⁺Al³⁺) substitution, and more complex minerals, such as micas or amphiboles, may show multiple solid solution series.

In rocks dominated by few minerals, the composition of the minerals can provide much useful information concerning variations in metamorphic grade. For example, greenschist facies metabasalts are commonly dominated by the amphiboles actinolite and hornblende, the transition from actinolite to hornblende being a chemical (and crystallographic symmetry) change controlled by temperature (Section 1.7).

Though metamorphosed ocean-floor basalts tend to be uniform in chemical composition, the wide variety of sedimentary environments at Earth's surface generates considerable diversity in the composition of clastic deposits. The variation in compositions is best shown graphically, which is commonly done using ternary diagrams. In Fig. 1.2A, the proportions of 7

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hypothetical variables A, B and C are simultaneously plotted, the base of the triangle representing 0% A and the top apex 100% A. Equal proportions of all three variables are represented by the star in the middle of the triangle. For example, variation in common whole-rock (bulk-rock) composition can be simplistically represented on an ACF diagram (e.g., Turner, 1981), in which $A = Al_2O_3(AlO_{3/2}) + Fe_2O_3(Fe_{3/2}) - (Na_2O + K_2O), C = CaO - 3.3P_2O_5$ and F = (FeO + MgO + MnO), as shown in Fig. 1.2B. Before plotting rack compositions on this diagram, K₂O and Na₂O are subtracted from Al₂O₃ to remove from consideration the amount of Al₂O₃ tied up in common felspar, and so more accurately reflect excess Al available for other minerals. Similarly, enough P₂O₅ is subtracted from CaO to reflect calcium locked away in apatite. Pure limestones are almost pure CaCO₃ and hence plot at the C apex of the ACF diagram (carbon not being considered). Contamination of a pure limestone by variable proportions of clastic material (such as quartz or clay minerals) results in a spread of rock types plotting between the C apex and the clastic contaminant (Fig. 1.2B), the exact position depending on the proportions of the mixture and the composition of the clay minerals. Claystones and sandstones are typically carbonate-poor or carbonate-free, and have a spread of compositions, depending on the proportions of clay and quartz (Fig. 1.2B).

At metamorphic conditions in the mid-amphibolite facies (discussed in Section 1.7.1), namely about 10-km depth and c. 550°C, the elements in clay minerals in sedimentary rocks or glass in basalt form metamorphic minerals that broadly reflect the original elemental proportions. Figure 1.2C shows a series of metamorphic minerals common at such temperature conditions plotted on an ACF diagram, their positions depending on the proportions of elements forming them. These minerals subdivide the diagram into a series of chemical domains, diagrammatically shown by joining different minerals by tie-lines. The positions of the lines depend on the physical conditions (P,T), as discussed in more detail in Section 1.8. For the chemographic relationships shown in Fig. 1.2C, a sandstone with composition x plots in a ternary sub-field bound by sillimanite, anorthite and biotite, so that this rock has these minerals at the metamorphic conditions considered. A marl with composition y plots in a field defined by calcite, anorthite and diopside; so the metamorphosed equivalent of the marl (a calcsilicate rock) is composed of these minerals. As the composition lies close to where calcite plots, the rock is mostly formed from calcite, with substantially less diopside and anorthite. The compositions of most basalts lie close to the position of hornblende; consequently they are mostly formed from this mineral at amphibolite facies conditions (see Section 1.8). The plotted metabasalt with composition z has the assemblage hornblende, diopside and biotite. At higher temperature conditions, the appearance of orthopyroxene in metabasalt defines the lower limit of the granulite facies (see Section 1.8), and the configuration of the tie-lines in the lower right of the diagram would need to be redrawn with a line between hornblende and hypersthene.

A weakness with the ACF diagram is that most rocks contain large proportions of elements in addition to those explicitly considered in Fig. 1.2, such as SiO₂, Na₂O, K₂O and TiO₂. The adjustment of Al₂O₃ values by subtracting Na₂O and K₂O content primarily addresses the role of plagioclase in metabasalts, and works less well for alkali content in, for example, actinolite, hornblende or biotite. Though the ACF diagram is a good starting

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point for considering metamorphic changes, it is unable to handle compositional detail.

Some rock compositions are better indicators of metamorphic grade than others. Mafic and pelitic compositions show marked mineralogical changes with changing grade, whereas felsic compositions commonly do not. For example, subdivisions of the blueschist and eclogite facies (Section 1.8.1) are largely based on metabasic mineral assemblages, and subdivisions of the amphibolite and granulite facies (Section 1.8.1) are largely based on metapelitic mineral assemblages. This is because metabasic rocks commonly have high-variance equilibria (involving few minerals) that are less useful for subdividing the amphibolite and granulite facies. However, continuous changes in the more calcic high-variance metabasic equilibria can be sensitive indicators of relative pressure variations. Mineral changes in metapelitic equilibria are dominated by low-variance dehydration reactions involving many minerals (e.g., Fig. 1.10), which mostly occur over restricted temperature intervals, and so are useful for subdividing the greenschist and amphibolite facies. Therefore, P-T analysis of most metamorphic terranes is best done using information from as many rock types as possible.

1.3 Metamorphic phase diagrams

Phase diagrams, such as the ACF diagram (Fig. 1.2B), are graphical representations of the chemical (mineral) and physical (*P* and *T*) variables that control metamorphic reactions. Inferred relationships are based on experimental data, direct field observations and theoretical calculations. Much effort has been exerted in determining phase relationships in metapelitic rocks, as they are the most sensitive indicators of common crustal metamorphic conditions, and can be used to subdivide the amphibolite facies into 'subfacies' (e.g., Harte & Hudson, 1979; Pattison & Harte, 1985). In this section, we address the modelling of metapelitic equilibria in a qualitative sense, with a simple example of how maps of mineral equilibria called *pseudosections* can be used to predict *P-T* conditions for major mineral assemblages (e.g., Hensen, 1988). Chapter 2 covers more complex methods for the quantitative modelling of mineral assemblages.

Single-component systems are the simplest, and H₂O is a good example. At conditions near Earth's surface, H₂O exists as the three phases ice, water and gas, the P-T relationships of which are shown in Fig. 1.3A. The three independent variables required to define the system are P, T and the chemical component H₂O. Increasing T by heating at constant P can result in a successive change from ice to water to gas, as indicated by the horizontal blue arrow in Fig. 1.3A. Increasing P at constant T can result in the change from ice to water, as indicated by the vertical blue arrow; this happens at the bottom of large glaciers and enables them to slip on the underlying rocks. An example more relevant to metamorphic petrology is provided by the aluminosilicate phase diagram (Fig. 1.3B). Three solid polymorphs of Al₂SiO₅ occur at common crustal conditions. Kyanite has the greatest relative density and hence occurs at the highest-pressure conditions. If only one phase is stable, there is considerable freedom in choosing P or T conditions (i.e., the mineral occupies a P-T area or divariant field, in which two variables, P and T, can be varied independently).

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Fig. 1.3 (A) *P*-*T* diagram for the one-component system, H₂O. The vertical blue arrow indicates a phase transition from solid to liquid with increasing *P*, such as occurs at the base of large glaciers. For pure H₂O, the point at which ice, water, and vapour all coexist is fixed or invariant. (B) *P*-*T* diagram for the one-component system Al₂SiO₅, showing the relative stability ranges of the three minerals andalusite, sillimanite, and kyanite. The *P*-*T* conditions at which two of the minerals can coexist are univariant reaction lines, and the *P*-*T* condition at which all three phases coexist is an invariant point. (C) Diagrammatic three-dimensional illustration showing the three parameters (*P*, *T*, *X*) needed to define solid–liquid relationships in the two component system Fe₂SiO₄-Mg₂SiO₄ (fayalite-forsterite), where X = mole fraction of one of the end-member components. (D) Two-dimensional slice, at constant *P*, through Figure, I.3C. For a colour version of this figure, please go to the plate section.

If two phases are present in a one-component system, for example, ice and water, or andalusite and sillimanite, the system has less freedom to vary *P* or *T*, so that the two phases can coexist only on a *univariant line* that represents the reaction from one phase to another (Fig. 1.3B). The line is called univariant because it permits only one degree of freedom; once *T* is stipulated, *P* is defined, and vice versa. If three phases coexist, the system has no degrees of freedom, and is fixed or *invariant* (Fig. 1.3A), because the invariant point occurs at only one *P* and *T*, which are the only conditions at which the three phases can coexist. In the system H₂O, the presence of NaCl reduces the freezing point of water to below 0°C, showing that adding more chemical components enables greater freedom in the system being considered. Aluminosilicate minerals can accommodate small proportions of F_2O_3 or Mn_2O_3 , displacing the otherwise 'invariant'