

Figure 4.12 Isothermal sections for the three assemblages of Figure 4.11 drawn immediately above (left-hand figures) and immediately below (right-hand figures) the temperatures at which three solid phases equilibrate with liquid. (a) Co-precipitatorial equilibrium of tridymite, enstatite, cordierite and liquid; (b) equilibrium of forsterite, cordierite, spinel and liquid, in which spinel is resorbed down-temperature; (c) equilibrium between sapphirine, spinel, mullite and liquid in which spinel and mullite are resorbed down-temperature.

Co-precipitation
 $L = X + Y + Z$

mono-resorption
 $L + X = Y + Z$

bi-resorption
 $L + X + Y = Z$

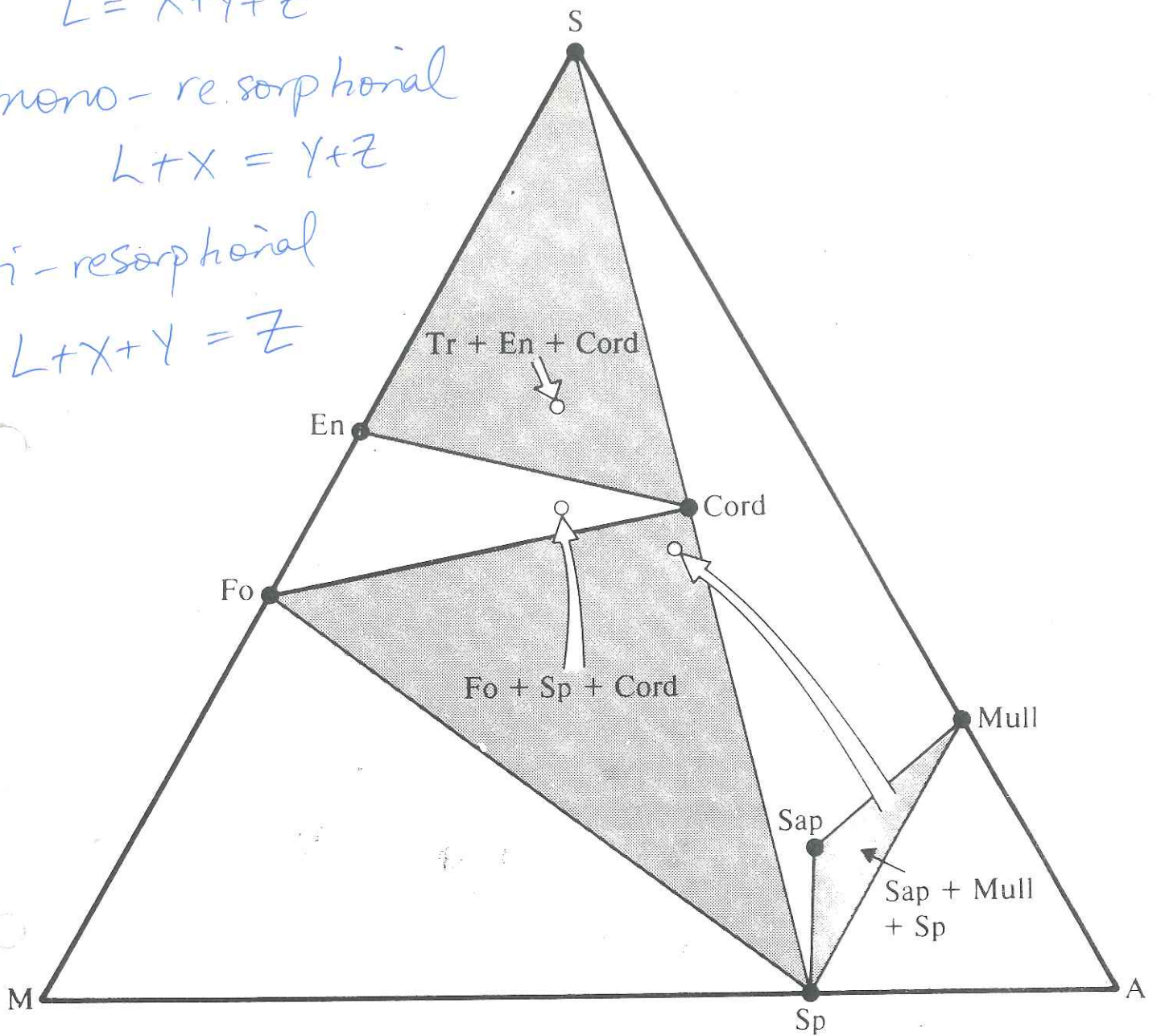


Figure 4.11 Three three-phase sub-solidus assemblages in $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ showing spatial relationships to their equilibrium liquids (small circles). Large arrows link sub-solidus triangles to the appropriate liquid.

shows the way in which the three-phase triangles may be arranged in non-overlapping sets for the three equilibria considered in Figure 4.11. The three-phase triangles of $L + X + Y$ type have been drawn according to the principles illustrated in Figure 4.8 and 4.9, the intervening fields of $L + X$ type having been reduced to infinitesimal width because of the convergence of the boundary curves on their point

intersection. Further, since the garnet join (pyrope–grossular) runs from M_3AS_3 to C_3AS_3 , this intersection point must lie on it, one third of the way along the join from pyrope to grossular for:



The above discussion is concerned with geometrical relations only and these two examples should suffice to illustrate the principles of the method. Further applications are considered later in the chapter.

Complexities introduced by solid solution have not been included in the above discussion. Clearly the complete sub-solidus diagram for a quaternary system consists of a number of sub-tetrahedra each representing the co-existence of four solid phases, and these are separated by three-end-member stable joins. In the absence of solid solutions the latter are planar triangles but if solid solution is present they develop into three-dimensional forms. Two-end-member joins may also occupy three-dimensional space if solid solutions are themselves ternary or quaternary.

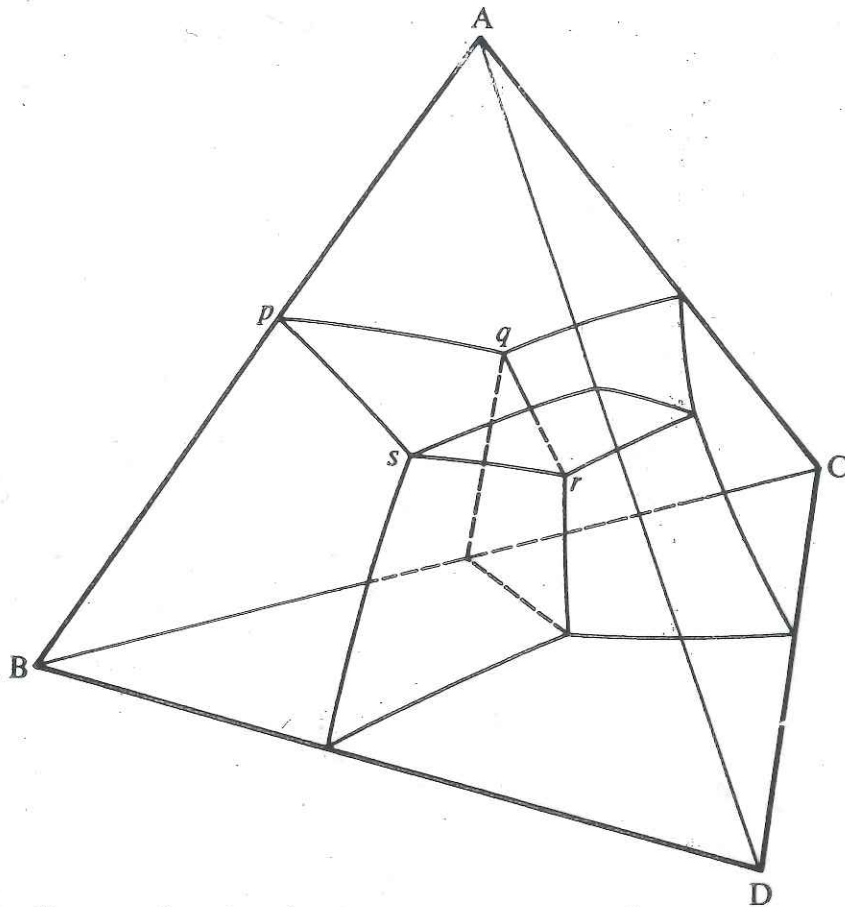


Figure 8.3 Perspective sketch of the simple quaternary system A–B–C–D. The upper part of the diagram is occupied by the A + L volume. This comes into contact with the B + L volume at the surface $p-q-r-s$ which represents A + B + L. This surface meets the A + C + L surface in the boundary curve $q-r$ which represents A + B + C + L. All four primary phase fields meet at the point r representing A + B + C + D + L.

Liquidus diagrams

In quaternary systems primary phase fields (i.e. the loci of liquids in equilibrium with one solid phase) become volumes which meet in surfaces representing liquid composition in equilibrium with two solid phases. Similarly any three primary phase volumes meet in a boundary curve representing liquids in equilibrium with three solids, while four primary phase fields must meet in a point. This point is a unique liquid equilibrating with four solids and represents a univariant (isobarically invariant) equilibrium.

A simple quaternary illustrates these features in Figure 8.3. Isotherms within primary phase fields are curved surfaces (Fig. 8.4) which can only properly be represented in three-dimensional models. Isothermal surfaces in adjacent primary phase fields meet at the boundary surface representing the locus of liquids in equilibrium with both solid phases and create thermal contours across it. The intersection of three such sets of isothermal surfaces obviously implies a specific temperature for each point on the boundary curve representing the locus of liquids in equilibrium with three solid phases. Isobaric invariant points where such boundary curves meet represent equilibria having specific and fixed temperatures.

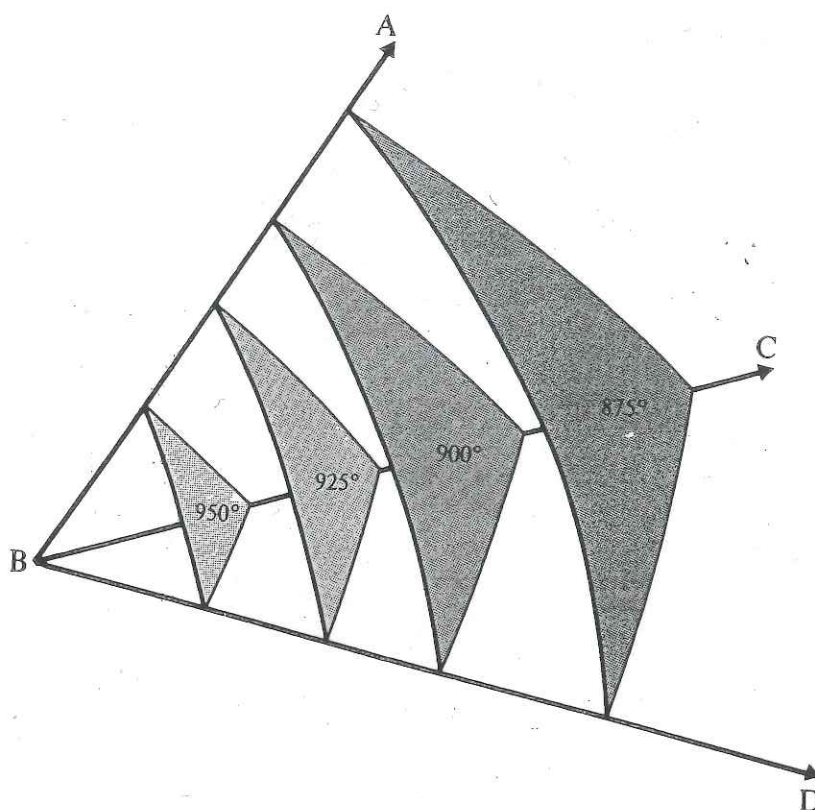


Figure 8.4 Perspective sketch of isothermal surfaces within the B + L volume of the system A-B-C-D (Fig. 8.3).

diagram looks superficially like a ternary liquidus projection, but there are several important differences.

Firstly, the crystallisation behaviour of a composition such as P can be read only if P lies in the primary phase field from which projection is made. The composition P' in Figure 8.10 is coincident with P in projection but lies in a different primary phase field and therefore must show a significantly different crystallisation behaviour. In this case given the single projection (Fig. 8.9) and the information that P lies in the primary phase field of A the crystallisation behaviour can be read as follows:

- (1) On cooling, P begins to crystallise A, but it is not possible to specify with the information given the temperature at which A appears. As A crystallises the residual liquid (in the absence of solid solution) will move directly away from A so that its position in projection *does not change*.
- (2) When the temperature reaches 1150 °C (Fig. 8.9) the residual liquid will meet the surface representing the equilibrium A + B + L. Crystals of B will now appear and the residual liquid will move away from the point on the A–B join which represents

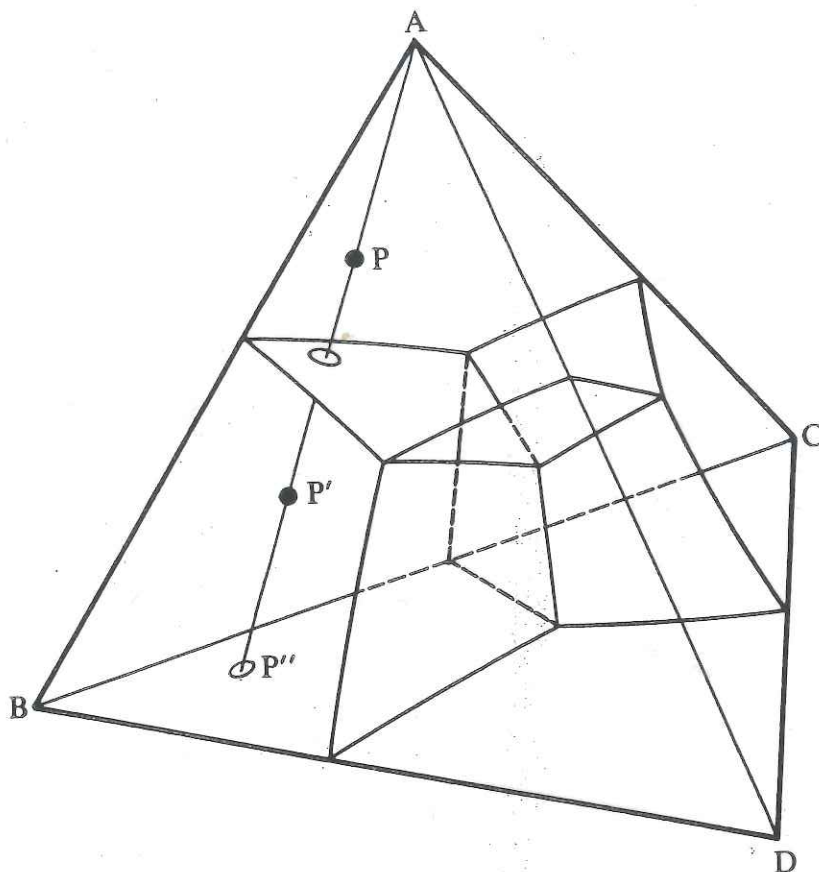


Figure 8.10 Projection of composition P from A (see Fig. 8.9). P and P' coincide in their projected position P''.

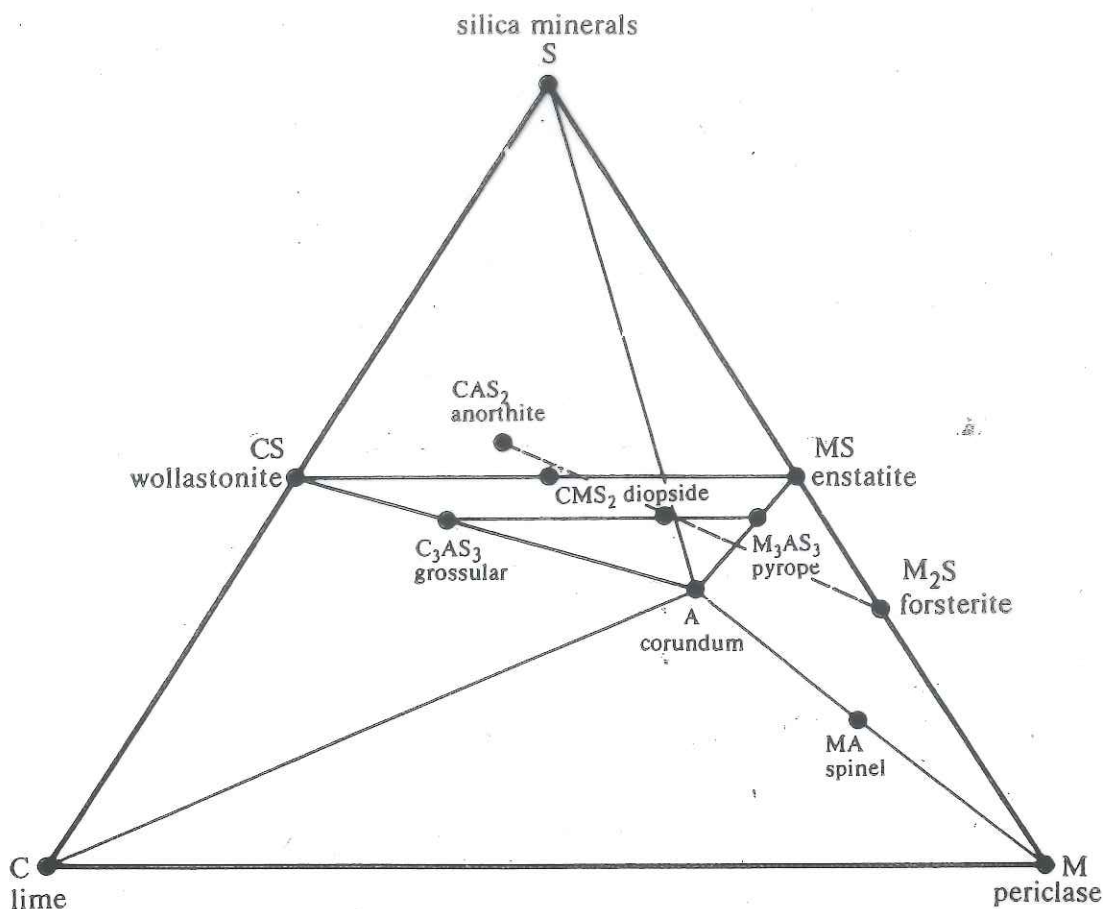


Figure 8.2 The system CaO–MgO–Al₂O₃–SiO₂ showing some important phases. Shorthand notation used is C = CaO, M = MgO, A = Al₂O₃, S = SiO₂. Hence, for example, MA (spinel) signifies MgAl₂O₄.

(b) Where does the join CAS₂ (anorthite) – M₂S (forsterite) cut the plane CS (wollastonite) – MS (enstatite) – A (alumina)? The composition of the point of intersection must be expressible in terms of CAS₂ + M₂S in some proportion, and in terms of CS + MS + A. Hence, using *p*, *q* etc., to express the unknown coefficients we can write the equation:

$$pCAS_2 + qM_2S = rCS + sMS + tA$$

and in order that the equation shall balance for each component:

$$\begin{aligned} \text{for C} \quad p &= r \\ \text{for M} \quad 2q &= s \\ \text{for A} \quad p &= t \\ \text{for S} \quad 2p + q &= r + s \end{aligned}$$

Since we are concerned only with proportions, let *p* = 1, then from the above, *r* = 1, *t* = 1, *q* = 1 and *s* = 2. Hence both sides of the equation sum to CM₂AS₃ which is the composition of the point of

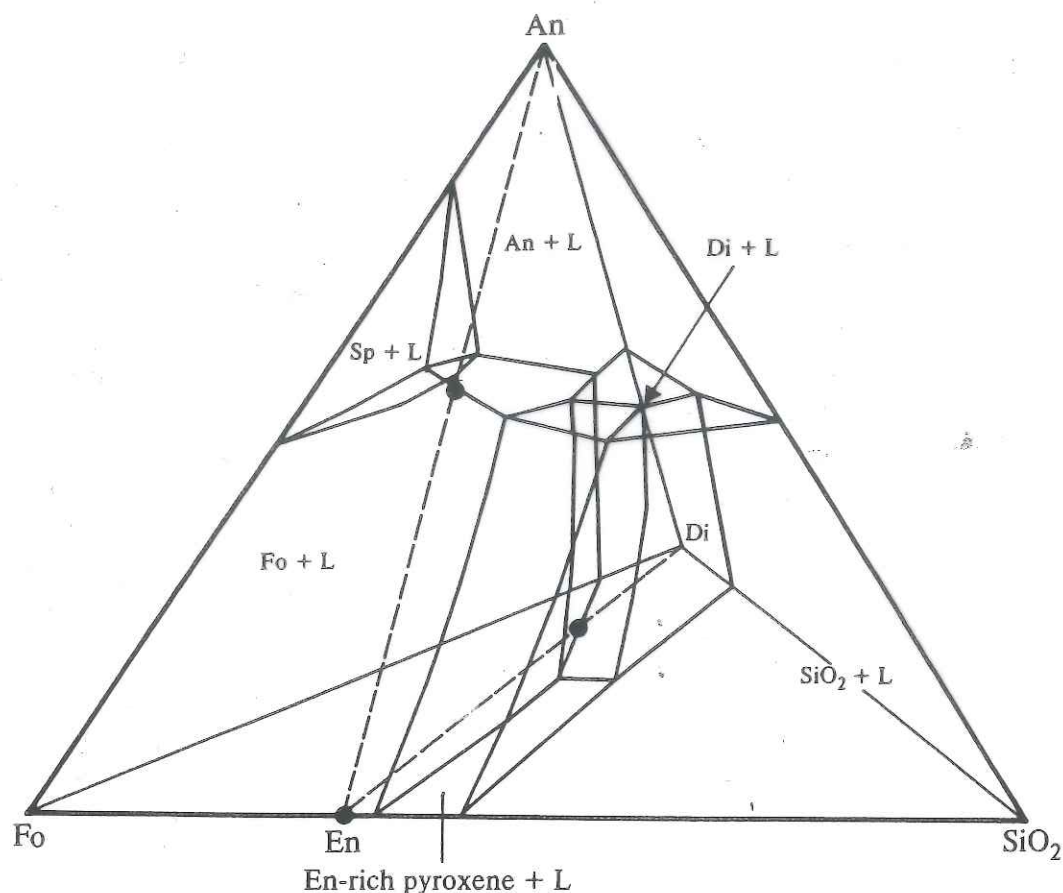


Figure 8.13 Schematic perspective drawing of Fo–Di–An–SiO₂.

diagram of the quaternary to be constructed as in Figure 8.13. Phase relations have been somewhat simplified compared with published literature in respect of the pyroxene fields (e.g. in Fo–Di–SiO₂).

One of the most important features of the system is the pseudo-ternary nature of the En–Di–An join which contains a large field of Fo + L but no En-rich pyroxene field (the latter being the analogue of orthopyroxene or pigeonite in natural rocks). This implies that the entire En-rich pyroxene + L field lies on the SiO₂-rich side of the join and thus the reaction relationship Fo + L = En noted previously in ternary systems (e.g. Fig. 4.20) persists into the quaternary. As will be seen in Chapter 9 this relationship probably disappears with increasing pressure as the olivine field contracts. However, its presence at low pressures implies that solid mixtures of magnesian olivine, enstatite, diopside, and basic plagioclase (plagioclase peridotites or olivine–orthopyroxene gabbros) should give SiO₂-oversaturated liquids as their initial melting products. Similarly, because of the reaction relationships, basaltic liquids originating in the olivine field (as long as they do not lie on the SiO₂-poor side of Fo–Di–An) are capable of fractionating to SiO₂-bearing end products.