Phil. Trans. R. Soc. Lond. A **328**, 529–646 (1989)
Printed in Great Britain

THE PRECURSOR PRINCIPLE AND THE POSSIBLE SIGNIFICANCE OF STRATIFORM ORES AND RELATED CHEMICAL SEDIMENTS IN THE ELUCIDATION OF PROCESSES OF REGIONAL METAMORPHIC MINERAL FORMATION

By R. L. STANTON

Department of Geology and Geophysics, University of New England, Armidale,
New South Wales 2351, *Australia*

(*Communicated by S. E. Moorbath, F.R.S. – Received* 13 *April* 1988)

[Plates 1–8]

CONTENTS

[Published 25 August 1989

This contribution is concerned with the regional metamorphism of fine-grained (pelitic) sedimentary materials, and with the pelitic components of coarser sediments. It emphasizes the possible importance of purely chemical sedimentary rocks, and the preservation of chemical patterns within them, in the elucidation of some regional metamorphic mineralogical processes. The materials and examples used come largely from the category of exhalative sediments, of which stratiform metallic sulphide orebodies and their associated exhalites are important members. A few examples come from volcanic rocks that have been altered by exhalative processes.

The special significance of chemical sediments stems from their propensity for the development of highly complex metamorphic silicate mineral assemblages within relatively minuscule volumes of rock, and from their commonly sharply defined chemical bedding and chemical sedimentary facies patterns. As the primary nature of such chemical bedding and chemical layering and zoning in completely unmetamorphosed materials is observable and known, and as their sharp boundaries and other well-defined features can be examined in a full range of unmetamorphosed to highly metamorphosed environments, they may be used as extremely sensitive markers for the detection and measurement of any chemical movement that may have taken place during regional metamorphism.

Detailed examination of such evidence appears to indicate a general lack of diffusion and reaction, and a common lack of attainment of mineral equilibrium, in the development of the regional metamorphic silicate assemblages of a number of such stratiform ore deposits and their associated exhalative materials. This, together with the common interbedded nature of metamorphic silicate, sulphide, carbonate, etc., and the faithful maintenance of primary sedimentary chemical facies patterns within many exhalative metasediments suggests that the silicates, like the accompanying sulphides and associated compounds, may derive directly and *in situ* from early-formed precursor materials rather than from extensive elemental diffusion and metamorphic reaction.

That particular clays and zeolites derive from specific precursors in many instances

has been recognized for a long time. That many metamorphosed bedded oxides (including quartz), together with carbonates, sulphates, sulphides and authigenic silicates such as the feldspars, have derived from sedimentary:diagenetic precursors is self-evident and unavoidable, and establishes precursor derivation for at least some regional metamorphic minerals as a principle, not an hypothesis. What is not known, however, is the extent to which this principle applies to the broader spectrum of metamorphic silicates. The present contribution examines this problem.

The evidence of 'metamorphic' silicates in a range of unmetamorphosed and little-metamorphosed rocks, in present ocean-floor sediments, in unmetamorphosed volcanic alteration products and in modern geothermal systems is examined. The preservation of possible precursor materials in a variety of rocks, and the synthesis of a number of 'metamorphic' minerals by low-temperature solution experimentation and in low-temperature industrial products is considered. It is deduced that most of the well-known regional metamorphic minerals may in fact be produced directly from low-temperature sedimentary/diagenetic/alteration materials, and that such precursors may be of simple or complex kind.

It is suggested that the direct derivation of regional metamorphic silicates from precursors may resolve the problem of the elusive metamorphic mineral reaction, and that the principal regional metamorphic grade indicators may be the temperatures of precursor transformations rather than temperatures of reactions.

Several implications of the precursor principle are then examined: its significance in the interpretation of zoning of regional metamorphic mineral assemblages and mineral chemistry; in considerations of metamorphic grade and the development of grainsize; in the identities of certain metamorphic equilibria, intergrowths and 'retrograde' materials; and in the deduction of earlier environments of rock formation and alteration. In this general connection it is proposed that the overall regional metamorphic process may be substantially indigenous: that through their primary nature certain materials, e.g. some andesitic–dacitic volcaniclastic rocks, may be predisposed to metamorphose themselves, and that this may be accentuated by the petro-tectonic setting in which they form, e.g. island arc – eugeosynclinal provinces, with their characteristically inter-related calc-alkaline volcanism, rift-related palaeogeographical features and highly patterned heat flow. Effects of climate may be superimposed on this: some of the more highly developed regional metamorphic zoning may arise in calc-alkaline volcanic sediments deposited in tropical island arc shelf areas, and in sediments laid down in large saline lakes of continental volcanic rift provinces.

From all this it is proposed that the ambit of regional metamorphic petrology may be much wider than currently visualized. Just as precursor-derived oxides, carbonates, sulphates, graphite, pyrite, etc., of high-grade metasedimentary rocks may give clear indications concerning the nature and environments of formation of the original sediments, so the metamorphic silicates may yield subtle insights into palaeoprovenance, palaeogeography, palaeoclimate and a variety of weathering, volcanic alteration, sea-floor hydrothermal and other régimes. The application of metamorphic mineralogy and mineral chemistry to the search for stratiform ores in metamorphosed terranes may constitute one of the major advances in mineral exploration in the near future.

It appears that there is considerable scope for further searching for possible precursor material in a variety of rocks and modern sediments (especially those of the present-day volcanic–sedimentary milieu), extension of clay and mixed-layer clay–chlorite–zeolite mineral synthesis in low-temperature–pressure laboratory experiment, and for the investigation of the behaviour of these synthetic products at metamorphic temperatures and pressures.

1. INTRODUCTION

(a) *Sulphides and silicates in the metamorphic milieu*

During the past 25 years it has become well established that sulphide ores have formed, here and there, by all of the major rock-forming mechanisms, and a wide variety of ore types, stemming variously from igneous, sedimentary and metamorphic processes, is now universally recognized.

The geological process responsible for the development of some of the world's most spectacular ores (from the point of view of richness, coarseness and textural beauty) is that of contact metamorphism. Deposits of this type commonly exhibit coarse-grained sulphides set in matrices of similarly coarse-grained metamorphic silicates and marblized carbonate. The materials involved are partly indigenous, partly introduced. The intruded sedimentary rock – usually largely carbonate, but also containing fine silicate and perhaps some minor sulphide – is coarsened and becomes the site of metamorphic reactions between indigenous carbonate and silicate, and between these and fluids introduced from the intruding igneous mass. Ore metals are emitted from the cooling melt, probably largely as halides, and metallic sulphides are formed by reaction with sulphide ions and the replacement of the host carbonate. Introduction of fluorine and boron leads to the formation, again by reaction and replacement, of minerals such as fluorite and tourmaline. (Ca, Fe, Mg, Mn) carbonates react with SiO_2 to form a variety of hedenbergitic pyroxenes, actinolitic amphiboles, fayalitic olivines and numerous related mineral species. The whole contact metamorphic milieu is one of thermally – and chemically – induced reaction, and perhaps its most notable outcome is the development, by a whole series of metamorphic reactions, of spectacular suites of metamorphic silicates.

A geological process responsible for the development of some of the world's largest orebodies is that of hydrothermal sedimentation. Sub-aquatic exhalative activity and resulting localized chemical precipitation is now well recognized as the process by which large numbers of stratiform sulphide orebodies have formed. Hydrothermal solutions, probably of a variety of derivations, are variously contributed to the floors of seas, lakes and lagoons. As a result of the sharp change in conditions accompanying emission, the solutions precipitate their load of dissolved materials in areas adjacent to, or at least not far from, the vents concerned. This in turn leads to the progressive accumulation of beds composed of varying proportions of iron, zinc, copper, lead and other sulphides, barium and calcium sulphates, (Ca, Fe, Mg, Mn) carbonates, hydrous silica (subsequently quartz-rich 'cherty' beds) and a variety of silicates such as clays, chlorites, mixed layer clay/chlorites and zeolites.

Such stratiform accumulations inevitably pass through the various stages of diagenesis and many in due course undergo regional metamorphism. In some cases this is unaccompanied by significant deformation and very fine bedding is preserved with great delicacy. As metamorphism proceeds the various sulphides undergo grain growth and coarsen *in situ*. Some phase changes doubtless occur, such as transformation of early-formed wurtzite to sphalerite, primitive $FeS.nH_2O$ compounds to pyrrhotite, and so on. Bedded barium and calcium sulphates coarsen *in situ* to layers of barite, anhydrite and gypsum. Similarly layers of hydrous silica dehydrate, crystallize to fine quartz and undergo grain growth *in situ* to form chert or sacharroidal quartzose beds. Any associated magnetite, derived from the authigenic dehydration–reduction sequence $FeO.OH \rightarrow Fe_2O_3 \rightarrow Fe_3O_4$, also coarsens *in situ*. The same is the case with the apatite that derives from the phosphate so commonly deposited as part of these accumulations, and fluorite where this occurs.

Thus in contrast to the materials of the contact metamorphic ore-forming milieu, where sulphides, silicates, sulphates, fluorides, oxides and so on are formed substantially by *reaction* and *replacement* processes, the sulphides, sulphates, fluorides and oxides of metamorphosed stratiform ores develop by simple *transformation* and *grain growth* of pre-existing sedimentary/diagenetic materials *in situ*.

What, however, of the *silicates* of metamorphosed stratiform ores? Have they, unlike their associates, formed by metamorphic mineral reactions, or have they, like the accompanying sulphides, sulphates, carbonates, etc., simply developed *in situ* from pre-existing sedimentary/diagenetic materials? The answer to this question, which is encapsulated in figure 1, plate 1, may have substantial relevance to the wider problem of regional metamorphic mineral formation in general.

(*b*) *Brief examination of the problem*

It is now almost universally accepted that metamorphic silicate minerals such as biotite, garnet, staurolite, pyroxene, amphiboles, feldspars and the aluminium silicate polymorphs are formed, in the regional metamorphic milieu, more-or-less exclusively by the mechanisms of metamorphic reaction. This view, generally adopted for at least 100 years, holds that with rise in temperature and pressure pre-existing materials destabilize and break down; the chemical components so released then diffuse through the relevant rock mass and react with each other to form new minerals, stable under the new conditions and grouped in accordance with the 'Phase Rule'.

According to this hypothesis, further increase in temperature–pressure may in due course induce these newly formed minerals and mineral groupings to themselves destabilize, giving way in turn to yet newer assemblages. With such progressive change in physical conditions, the metamorphic silicates may progress through the stability fields of a continuous succession of mineral assemblages, inducing what is currently conceived as progressive regional metamorphism. Such progression may manifest itself through substantial volumes of rock, leading in turn to the development of zones of progressive regional metamorphism, the various characteristic mineral assemblages of which have been interpreted since the time of Barrow (1893) to indicate ranges of metamorphic grade.

This rather simple view involving extensive diffusion and progressive reaction has not, however, always prevailed entirely unquestioned. That it might not was perhaps anticipated by Harker as long ago as 1893. The latter noted (Harker 1893, p. 575) 'that within the mass of a rock undergoing thermal metamorphism any transfer of material (other than volatile substance) is confined to extremely narrow limits, and consequently...the mineral formed at any point depends only on the chemical composition of the rock mass within a very small distance around that point'; and in the same year he and J. E. Marr estimated this distance to be '$\frac{1}{20}$ or $\frac{1}{25}$ inch†' (1893, p. 369). If this were correct – and much recent work suggests that it is at least a close approach to the truth – the volume of rock from which the components of any new metamorphic mineral could be drawn would be small; in many cases little or no larger than the grain size of the final crystal. That is, the new grain would develop largely from materials that already occurred within the domain that that grain was to finally occupy.

The contentions of Harker & Marr are, in effect, assertions of what is nowadays referred to as isochemical metamorphism. Such assertions that regional metamorphism has, here and there, been isochemical are common in modern literature, and far too numerous to document

---

† 1 inch = 2.54×10^{-2} m.

(see, for example, Winkler 1976, p. 16). This is particularly the case with metamorphosed chemical sediments such as Precambrian iron formations (see, for example, Laajoki & Saikkonen 1977) for which primary sedimentary (i.e. premetamorphic) compositions, and patterns of compositional variation, are particularly consistent and very well known.

In this connection, recent investigation of a related type of chemical sediment – the stratiform sulphide ores and their small 'exhalite' accompaniments – has not only indicated that regional metamorphism here is also substantially isochemical, but has yielded some quite precise information concerning distances of metamorphic diffusion, incidence of mineral reactions and the attainment of equilibrium.

(i) *Diffusion distances*

The evidence provided here by metamorphosed chemical sediments ranges from the scale of a formation boundary (commonly close to a knife edge, even in highly metamorphosed terranes) through the fine bedding of chemical sediments and adjacent grains, to the patchy compositional variation of small, unzoned, individual grains. The preservation of sharp boundaries between well-bedded iron formations and sillimanite gneiss, between iron-rich amphibolites (impure silicate iron formations) and quartzo-feldspathic gneisses and other sharply contrasted pairs of rock types in many highly metamorphosed terranes (Stanton 1976) indicates lack of diffusion on this scale. Maintenance of distinct mineral compositions from one fine bed (less than 0.1 mm) to the next – involving a single mineral embedded in a uniform matrix e.g. bedded garnets enclosed in quartz (Stanton & Williams 1978; see figure 7) – demonstrates lack of diffusion to an even smaller scale. Preservation of patchy compositional variation within single unzoned grains of minerals such as sphalerite, epidote, grandite garnet and metamorphic amphibole in exhalites of 'amphibolite grade' terranes indicates restriction of diffusion to distances of a very small fraction of a millimetre (less than 0.01 mm) in at least some cases of high-grade metamorphism (Stanton 1979, 1982).

Similar indications of close restriction (or absence) of regional metamorphic diffusion are provided by other materials, and there are a number of recently documented examples. For example Yudin & Plotnikova (1983) showed that metamorphosed sedimentary apatite deposits, interbedded with biotite–garnet–sillimanite gneisses of the Slyudyanka series of the Archaean of the Baikal region of Russia, retain original sedimentary rare earth patterns and oxygen and carbon isotope abundances. These authors conclude that the sedimentary–metamorphic apatite-bearing deposits 'inherit the geochemical features which are peculiar to the sedimentary phosphate-bearing formations from which they are formed' (1983, p. 172). Cliff *et al.* (1985), in investigating Sr isotope abundances in tillites involved in biotite to kyanite metamorphism in the Precambrian to Lower Palaeozoic metasediments of the Ogcheon Belt, South Korea, noted that 'Sr-isotopic disequilibrium between clasts and matrix persists up to the higher grade...' (1985, p. 346). Substantial homogenization of Sr isotope abundances had occurred throughout the matrix, which was attributed to gross passage of fluids. The isotope ratios of the clasts, however, varied grossly from one clast to another and from clast to immediately adjacent matrix. Cliff *et al.* concluded that their study had emphasized 'the limited range' of *diffusion induced* transport at metamorphic temperatures up to approximately 550 °C. Wickham & Taylor (1986) investigated $^{18}O/^{16}O$ and D/H systematics in some of the 'basal gneisses' (amphibolite to granulite facies) and overlying Palaeozoic pelitic metasediments of the Pyrenees. Although the basal gneisses were estimated to have undergone regional metamorphism at pressures of 4–7 kbar† (14–20 km depth), it was found that they were isotopically heterogeneous and preserved steep gradients in ^{18}O (as much as 10‰ (by mass) over a few centimetres) at the margins of metacarbonate layers.

Although this consideration of evidence on diffusion distances is extremely brief, it does indicate that there is considerable evidence, ranging from a scale of centimetres to that of small fractions of millimetres, indicating that diffusion paths in regional metamorphism are commonly on a millimetre to micrometre scale.

(ii) *Metamorphic reactions*

The paucity and ambiguousness of textural evidence of metamorphic reactions is well known and has been remarked upon by many investigators. Kwak (1974) observed that the most important, but most poorly understood, aspect of metamorphic petrology is the form metamorphic reactions take. In addition to the scarcity and ambiguity of reaction textures Kwak noted that few investigators gave justification for all of the product and reactant minerals indicated, nor for the ratios involved, and that in consequence many of the equations, as written, were seriously open to doubt. He went on to point out that there appeared to be little evidence, in some cited reactions, for including all of the postulated mineral participants, nor for their amounts, and that this was conspicuously the case when the common imbalance of minor elements was taken into account. He cited in particular the example of relatively abundant zinc in many staurolites, and its absence from the staurolite 'reaction products'.

Yoder (1952) and Kwak (1974) in particular have cast doubt on the reality of many proposed reactions, leading Yoder (1952, 1955) and Atherton (1965) and others to suggest that metamorphic rocks may attain their mineral assemblages directly, rather than by a series of mineral reactions, and hence without passing through a succession of grade-dictated mineralogies.

As emphasized earlier (Stanton 1979), many stratiform ores and their associated exhalites exhibit a wide range of prograde metamorphic silicates and silicate assemblages, spanning a wide range of metamorphic grade indicators within a few metres or tens of metres. For example, in the Mount Misery stratiform deposit of North Queensland unreacted prograde chlorite–muscovite aggregates occur within a few metres of quartz–biotite–almandine–staurolite–sillimanite assemblages. There is no indication of chlorite and muscovite reacting to form biotite or, more importantly, of any texture indicating that biotite has formed by such a reaction. Indeed any suggestion that biotite has formed in this way in these particular rocks would be no more than an act of faith (Carmichael 1969).

From the point of view of metamorphic mineral formation by metamorphic mineral reaction, stratiform ore and related exhalite environments thus appear to provide two important lines of evidence.

(*a*) Given that they commonly possess a very wide range of prograde metamorphic minerals within volumes of a few cubic centimetres, it might have been expected that textural indications of such reactions would be found here even if they could be found nowhere else. I have been unable to observe such indications, and am unaware of any documentation of a metamorphosed stratiform orebody in which they have been described.

(*b*) Given that in some instances they exhibit high-grade assemblages *coarsely and abundantly developed*, it would have been expected that any associated low-grade assemblages would have

---

† 1 kbar = 10^8 Pa.

been eliminated by reaction, whether or not any textural evidence of this remained. However, in the case of Mount Misery biotite occurs in the previously mentioned quartz–biotite–garnet–staurolite–sillimanite assemblages, but nearby chlorite-muscovite aggregates show no sign of reacting to form biotite (Stanton 1979). At Broken Hill, New South Wales, garnet occurs abundantly, but adjacent muscovite–biotite aggregates show no sign of a reaction yielding garnet; sillimanite is also abundant but many quartz–muscovite aggregates may be seen showing no sign of reaction yielding sillimanite and K-feldspar (Stanton 1976).

Such evidence combined with the concern of Kwak (1974) and others that the complement of 'reaction products' observed is commonly less or more than that indicated by experiment, that they often appear in incorrect proportions, and that minor elements (such as the zinc of staurolite) are generally not in balance as between reactants and products, suggests that, *as natural phenomena*, many postulated metamorphic reactions have little factual basis. This is not to say that mineral reactions cannot occur. Far from it: many have been induced in the laboratory. However, it must be kept in mind that many compounds may be formed in more than one way and under widely different conditions, e.g. K-feldspar may be produced by a variety of routes including crystallization from a melt at $T > 800$ °C, or precipitation from an aqueous solution at $T < 80$ °C. What is now proposed is that while many metamorphic minerals can indeed be readily synthesized by mineral reactions in the laboratory, there is considerable evidence to indicate that they do not – or at least frequently do not – form by these reactions in the natural regional metamorphic milieu.

(iii) *Metamorphic equilibrium*

Turner (1968) noted that the classical writers on metamorphic petrology since the time of Williams (1890) had seen each common metamorphic mineral assemblage as a system approximating to internal equilibrium controlled by a limited range of temperature and pressure conditions. He reflected prevailing modern opinion when he went on to say the following.

> There is abundant cumulative petrographic evidence to support this contention as a *first approximation*. Minerals belonging to most isomorphous series tend to be remarkably uniform in composition within domains ranging from a thin section to a metamorphic zone. Optical measurements made in hundreds of grains of plagioclase in schists of the chlorite and biotite zones of Otago, New Zealand (an area of 30000 km^2 in extent) indicate compositional variations no greater than An_0 to An_7. Even this limited range probably reflects error in measurement rather than variation in anorthite content. Perhaps the true range is no greater than An_0 to An_1,...The chlorite series is one in which there is a wide range of possible substitution between Mg^{2+}, Fe^{2+}, Al^{3+} and between Al^{3+} and Si^{4+}. Yet such chlorites of New Zealand and Japanese greenschists as have been analyzed are highly restricted in compositional range: they are prochlorites in which the ratio FeO/MgO is about 0.8 to 1.1. Optically recognizable zoning in plagioclase and amphibole crystals, although by no means unknown, is relatively rare in metamorphic rocks. Garnet of pelitic schists, however, is commonly zoned. (1968, pp. 54, 55.)

After giving further, more refined data on consistencies of composition between single and coexisting species, Turner observed that 'generalizations such as these collectively constitute strong evidence for approximate internal equilibrium in metamorphic rocks.' (1968, p. 55.)

In considering the effects of the superimposition of a later episode of metamorphism on an earlier one, Turner did, however, refer to small-scale compositional variations then already being detected by the electron probe: '...on a very small scale compositional variation within optically homogeneous grains is being increasingly revealed by means of the electron probe microanalyzer...Some of this variation probably represents the expectable small-scale adjustments to postmetamorphic conditions in microsystems sufficiently small for ionic diffusion to be effective during postmetamorphic time' (1968, p. 55).

Turner's brief reference to the electron probe foreshadowed what was to become a deluge of fine-scale information on mineral compositions to derive from application of this instrument. The real significance of the electron and ion probes and related instruments is, however, only now becoming apparent: it is not simply that they are capable of accurately analysing very small domains, but that in doing so they are revealing widespread, very small-scale, compositional heterogeneities, and hence demonstrating that the sizes of the domains over which equilibrium has been attained are commonly orders of magnitude smaller than previously thought.

Present consideration of metamorphic equilibrium involves the features already discussed under (i) and (ii): preservation of short-range constitutional differences, the occurrence of discordant mineral (e.g. garnet) zoning patterns, and the maintenance of what appear to be unequilibrated mineral assemblages.

It also involves considerations of physical equilibrium, an aspect of regional metamorphic polycrystalline aggregates only occasionally alluded to in silicate metamorphic literature (exceptions are, for example, Voll 1959; Vernon 1978 and numerous other contributions by the same author).

It has been shown earlier (by means of electron probe analyses) that garnet compositions within and adjacent to stratiform ore deposits may vary greatly (Stanton & Roberts 1978; Stanton 1979, 1982; Vaughan & Stanton 1986). Figures 2 and 3 show variation in garnet composition (FeO and MnO; CaO and MgO respectively) in a single diamond drill core transecting the Mount Misery orebody already referred to (Stanton 1982). The distance between samples 9 and 48 is approximately 32 m. Any suggestion that garnet compositions here could be used to determine physical conditions of metamorphism must surely be unsustainable. Figure 4 shows variation in aluminium contents of amphiboles and pyroxenes associated with the garnets of the same interval of Mount Misery core. Figures 5 and 6 depict variations in almandine and fayalite compositions respectively in single drill cores through the periphery and centre of the Pegmont metamorphosed stratiform Pb–Zn deposit of Queensland. The full length of core involved in figure 5 is approximately 1 m, and extensive variation in the garnets clearly occurs on the scale of an individual thin section (Stanton 1979; Vaughan & Stanton 1986). Figure 7 shows almandine composition variation across-bedding and along-bedding in a well-bedded garnet quartzite intersected in drill core at Broken Hill, New South Wales. The pattern of across-bedding variation and along-bedding uniformity appears to reflect the very delicate preservation of an original sedimentary feature through high-grade metamorphism (adapted from Stanton & Williams 1978).

Figure 8 shows variation in almandine zoning patterns within only 23 cm (interval 357.03–357.26 m) of the same diamond drill core as that depicted in figure 5 (Stanton 1979; Vaughan & Stanton 1986). Such patterns could hardly be applied to determine the *P–T* history of the relevant metamorphic episode, as suggested by Spear *et al.* (1984).

The extensive metamorphic assemblages exhibited by a number of well-known stratiform orebodies and their associated exhalites have already been referred to, and some examples are given in table 1. The preservation of prograde chlorites in high-grade metamorphic assemblages

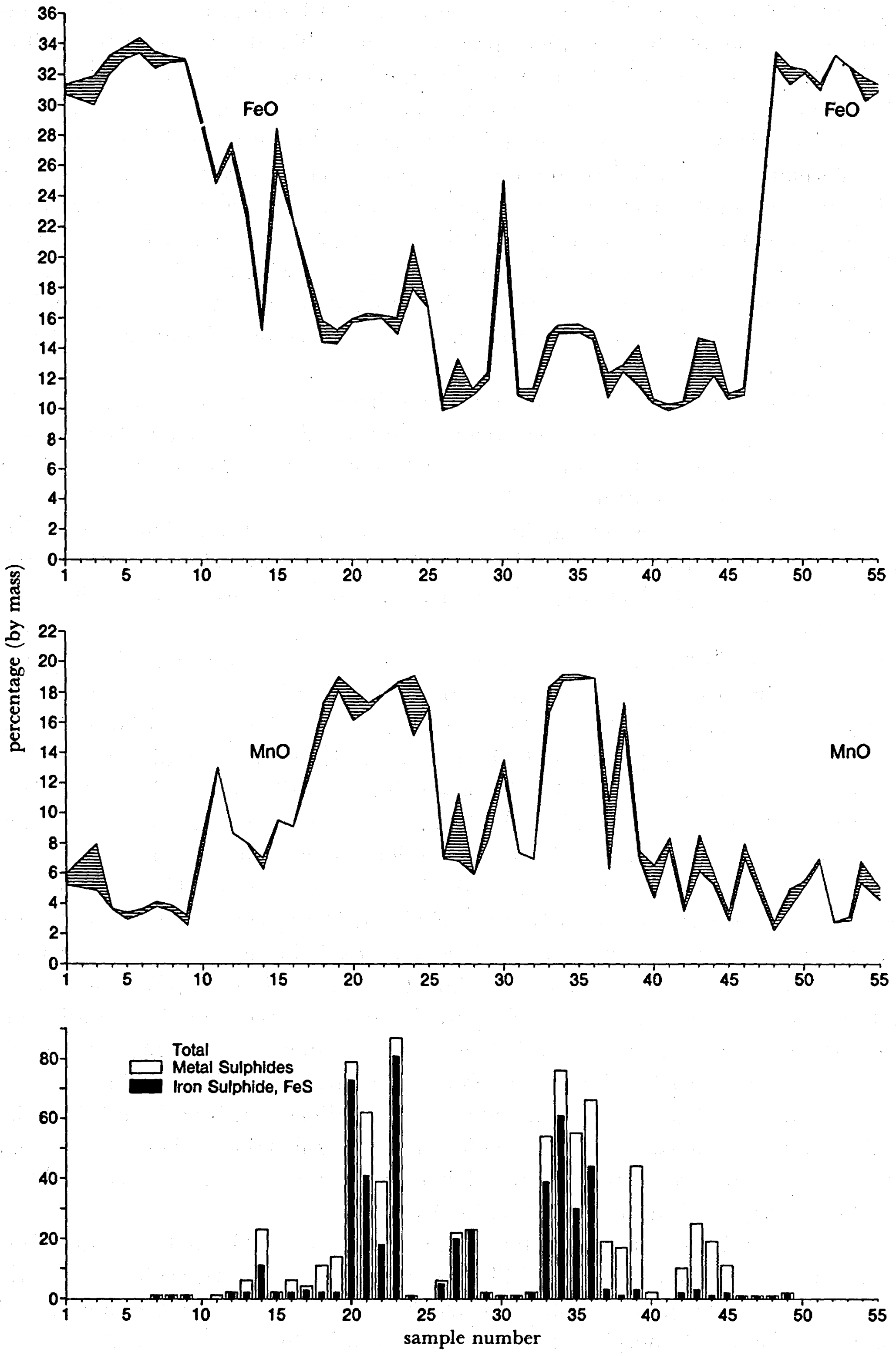


FIGURE 2. Variation in FeO and MnO content of aluminous (almandine-type) garnet along the length of diamond drill core 77MD8 intersecting the stratiform sulphide-bearing deposit of Mount Misery, North Queensland. Shading indicates compositional variation within single electron probe sections. The interval from sample 9 to sample 48 is 32 m (samples shown evenly spaced for convenience; see Stanton 1982*b*).

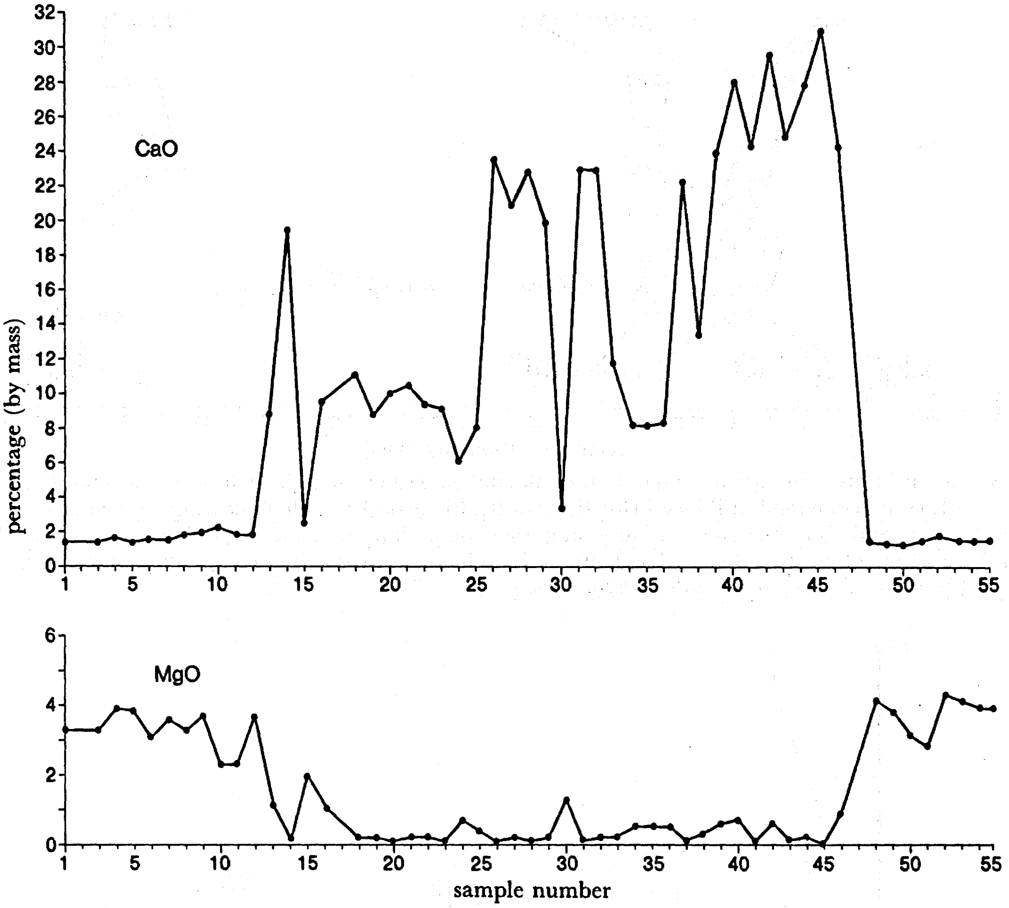


FIGURE 3. Variation of CaO and MgO in the garnets of figure 2 (from Stanton 1982*b*).

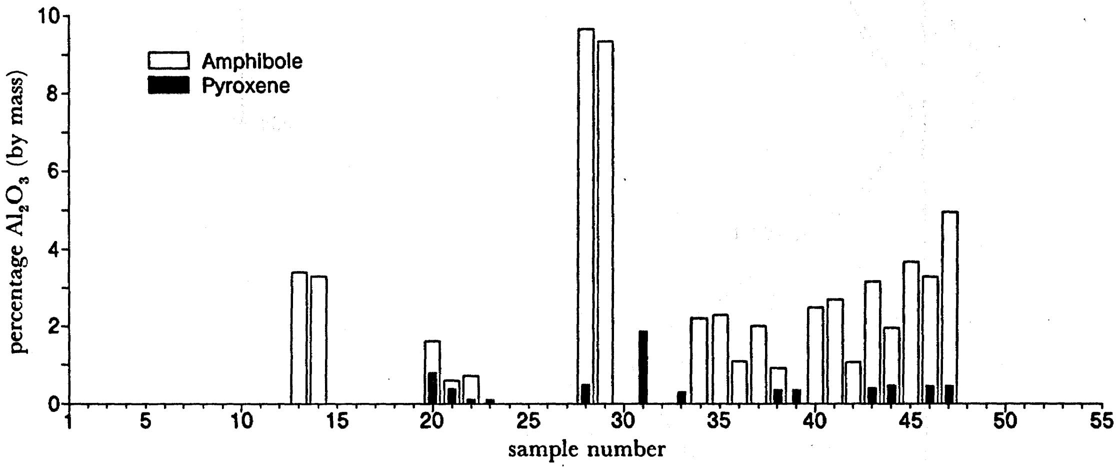


FIGURE 4. Variation in Al_2O_3 in the amphiboles and pyroxenes associated with the garnets of the Mount Misery core interval depicted in figures 2 and 3.

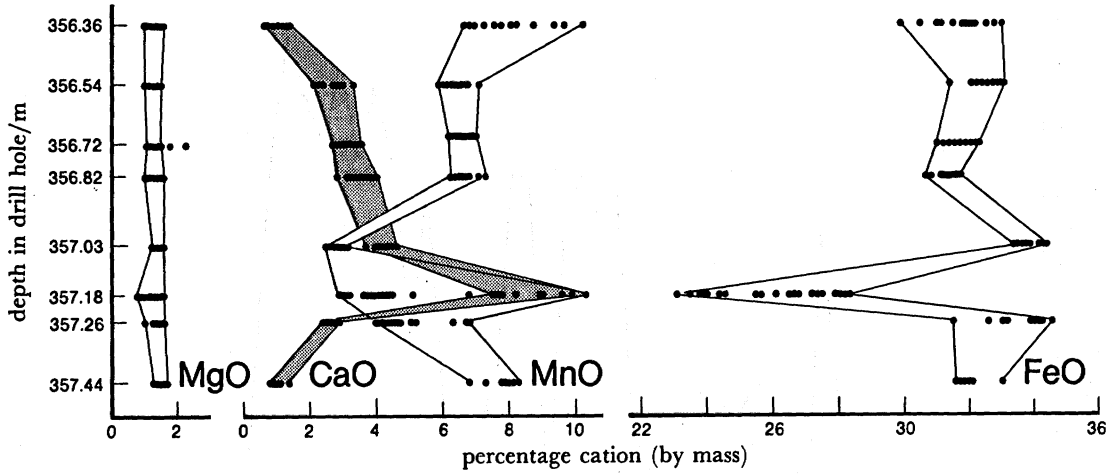


FIGURE 5. Variation in divalent cation composition of almandine garnets at eight points over a total down-core distance of 1.08 m in diamond drill hole PD31 through the fringe of the sulphide-bearing horizon at Pegmont, Western Queensland. Note the gross variation in garnet composition over the 23 cm interval from 357.03 m to 357.26 m. Rows of filled circles at each depth position indicate variation in composition observed in each individual probe section. (From Stanton 1979, 1982*a*.)

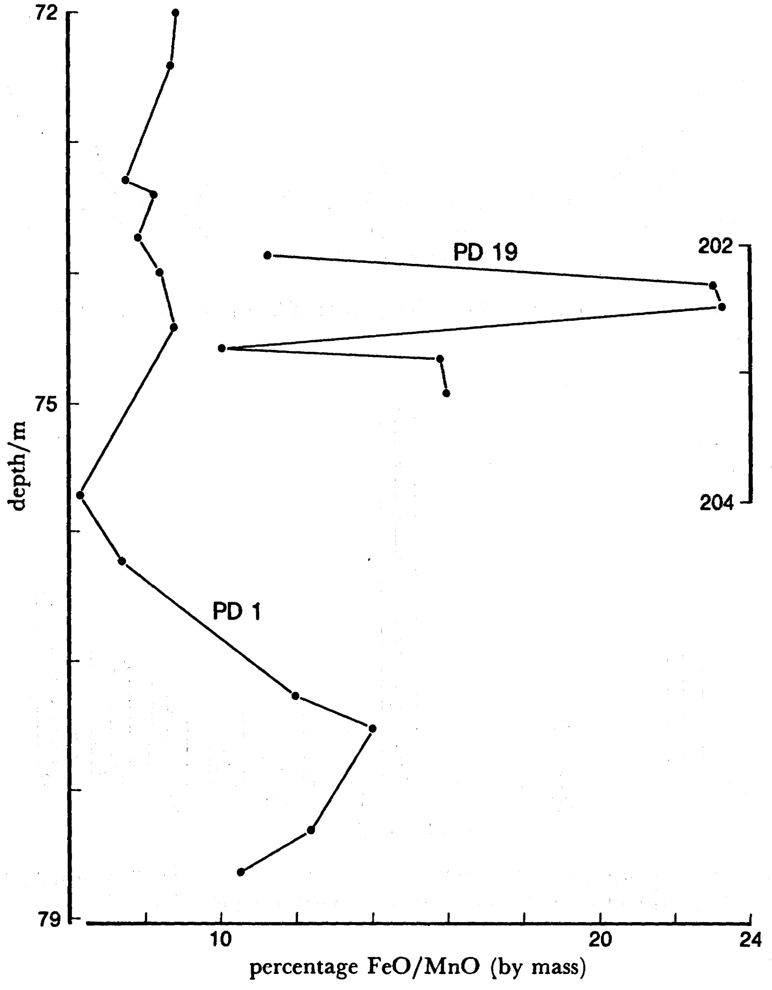


FIGURE 6. Variation in FeO/MnO in the manganiferous fayalitic olivine encountered over distances of 6.6 m in diamond drill core PD1 and 1.05 m in PD19 at Pegmont (from Stanton 1979, 1982*a*).

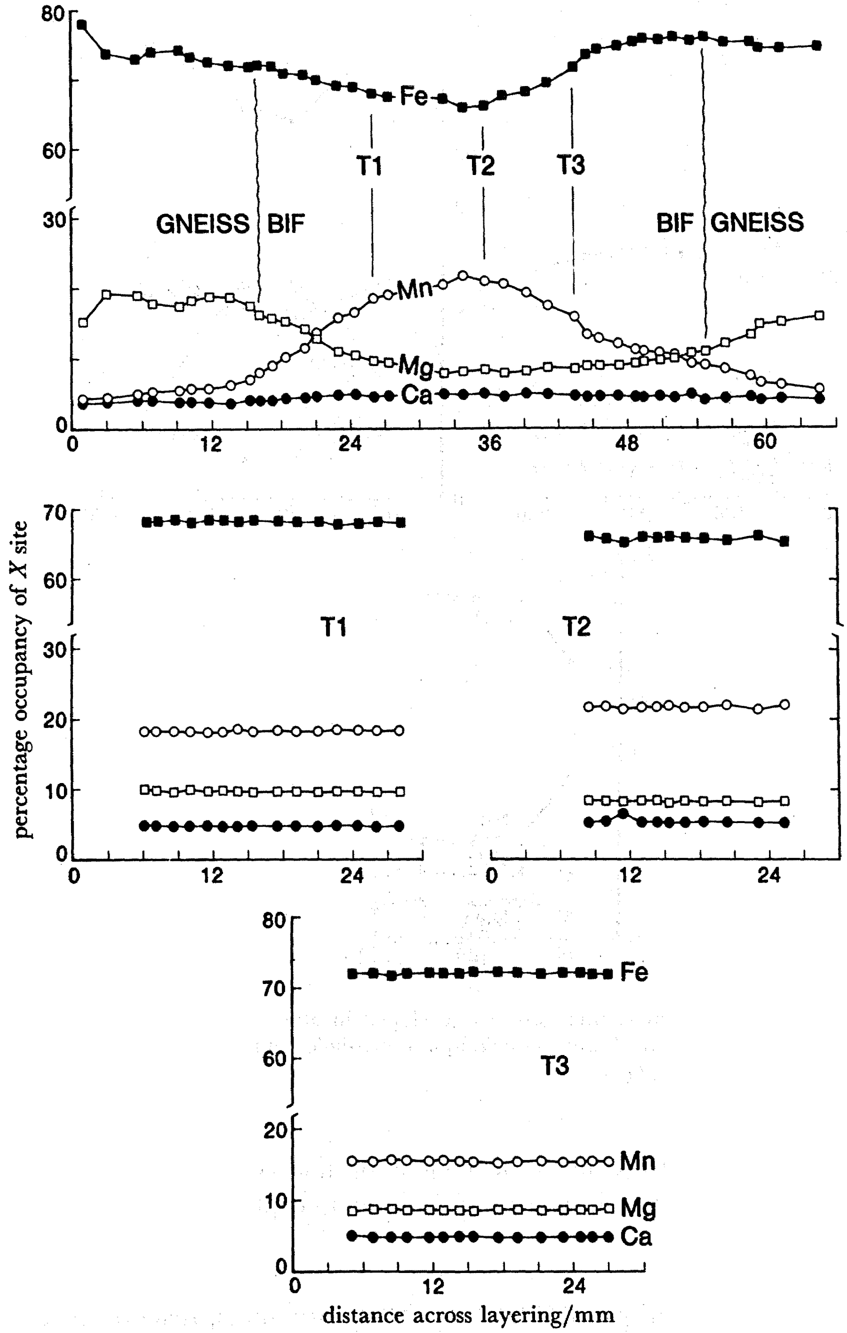


FIGURE 7. Variation in divalent cation composition of almandine across and along layering in a finely bedded 4 cm thick garnet quartzite enclosed within high-grade sillimanite gneisses of diamond drill core from Broken Hill, New South Wales. T1, T2 and T3 are along-bedding traverses in positions shown. (From Stanton & Williams 1978.)

appears to be common (and of prehnite less common, but by no means rare) and has also been referred to in connection with the Ducktown (Tennessee) orebodies by Nesbitt & Essene (1980) and Nesbitt & Kelly (1980).

Clearly a number of these features devolve from apparent lack of metamorphic diffusion considered in (i) above, but equally clearly such lack of diffusion – evidence of which remains

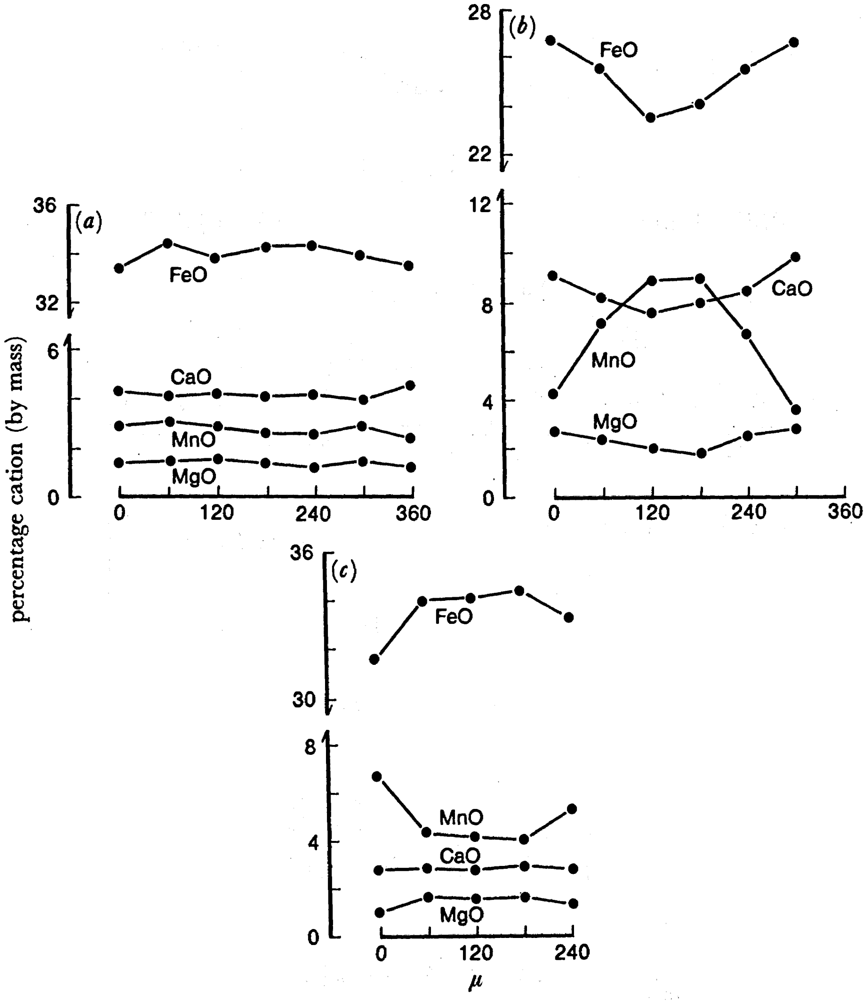


FIGURE 8. Variation in compositional zoning patterns developed in almandine garnets 15 cm and 8 cm apart respectively at (*a*) 357.03, (*b*) 357.18 and (*c*) 357.26 m down-hole depth in diamond drill core PD31 from Pegmont (from Stanton 1979, 1982*a*).

well-preserved – carries with it the inevitable conclusion that equilibrium, of even very short-range kind, has not been attained in these regional metamorphic milieux.

(iv) *Synthesis*

All of these detailed observations concerning diffusion distances, reaction textures and the approach to mineral equilibria in metamorphosed stratiform exhalite environments return us to the prognostications of Harker (1893) and Harker & Marr (1893). In at least some cases 'transfer of material' during regional metamorphism appears to have been restricted to distances of no more than a small fraction of a millimetre. Largely as a result of this, concentration equilibrium of the elements has commonly not been attained. As might have been anticipated from these two points there is no clear, tangible evidence of metamorphic mineral reactions; and indeed the circumstantial evidence indicates that these have not occurred.

All this leads us to the inevitable conclusion that, at least in the cases examined,

TABLE 1. METAMORPHIC SILICATE ASSEMBLAGES OF SOME EXHALATIVE STRATIFORM OREBODIES AND THEIR SHEATHS

Gorob	Gamsberg	Broken Hill (A-lode)	Pegmont	Einasleigh	Geco
sillimanite	sillimanite	sillimanite	sillimanite	sillimanite	sillimanite
K-feldspar	K-feldspar	K-feldspar	andalusite	staurolite	K-feldspar
kyanite	olivine	olivine	K-feldspar	andesine	staurolite
staurolite	clinopyroxene	staurolite	staurolite	scapolite	hornblende
cordierite	orthopyroxene	hornblende	clinopyroxene	clinopyroxene	cordierite
anthophyllite	pyroxenoids	hedenbergite and related pyroxenoids	hornblende	hornblende	gedrite
almandine	grunerite	grunerite	grunerite	andradite	biotite
biotite	cordierite	almandine	biotite	almandine	muscovite
muscovite	almandine	biotite	muscovite	actinolite	chlorite
chlorite	andradite	muscovite	chlorite	epidote	kaolinite
prehnite	biotite	chlorite	greenalite	biotite	sudoitic chlorite
quartz	zoisite	quartz	quartz	muscovite	quartz
	clinozoisite			chlorite	
	muscovite			stilpnomelane	
	chlorite			prehnite	
	quartz			laumontite	
				chamosite	
				quartz	

metamorphism has been static (isochemical) down to the scale of a grain, the state of affairs clearly implied by Harker & Marr some 94 years ago.

If and where this is the case, one is forced to conclude that, for any rock volume of the order of the present grain size, those chemical components observed to be present now must precisely reflect the chemical composition of that domain before the onset of metamorphism. That is, the chemical components of a metamorphic mineral now occupying any given small domain must have derived directly from those chemical components occupying that domain immediately before the onset of metamorphism. The implication of this is that each metamorphic mineral grain now present represents the *in situ* growth and/or transformation of a pre-metamorphic material of similar overall composition, or that it is one of two or more products of the *in situ* breakdown of a pre-metamorphic material of appropriate composition. These may be referred to as *precursors*, and, at this stage, the postulate may be referred to as the *precursor hypothesis*.

It may now be appropriate to view the problem in another way, by examining some simple analogies.

2. THE PRECURSOR HYPOTHESIS

(*a*) *Possible significance of some chemical sediments: simple examples*

A conspicuous feature of all of the world's Precambrian terranes are numerous and sometimes extensive chert units. Many of these, including the cherts associated with the great Lower Proterozoic banded iron formations, exhibit delicately preserved fine bedding. This is commonly well preserved even where it has been involved in high-grade metamorphism.

Most of these cherts represent chemically sedimented silica. They were originally deposited, in many cases as products of seafloor hydrothermal exhalation, as a hydrous form of SiO_2, probably a gel. With diagenesis and ageing this material dehydrated and transformed, *in situ*, to quartz. Metamorphic heating then induced variable grain growth and coarsening but usually not in such a way as to obliterate bedding. (It may be noted here that what appears to be distinctly hydrous 'quartz' has been detected in well-bedded quartz–muscovite biotite–almandine–spinel rocks of Lower Proterozoic age drilled to the west of Broken Hill, New South Wales, by CRA Ltd. The quartz, analysed with a Cameca electron microprobe, occurs chiefly as fine quartz-rich beds, glows conspicuously under the beam, and consistently yields totals ranging from 89 % to 95 %, and most frequently in the interval 90–93 %. It seems remarkable that silica of this age, *ca.* 1800×10^6 years, and relatively high-grade metamorphic mineralogical context should still retain such a notably hydrous nature.)

Where they occur in metamorphosed terranes there can be no doubt that these finely bedded, essentially monomineralic chert units are metamorphic rocks. In its present form the quartz is a product of metamorphism: a metamorphic mineral. However, it has not been produced by any metamorphic reaction. It has been derived directly from an ancestral hydrous form of silica.

That is it has been derived directly, *in situ*, from a premetamorphic *precursor material.*

The same clearly holds for most of the bedded carbonate of metamorphosed Precambrian and Phanerozoic terranes. Numerous high-grade metamorphic Precambrian provinces such as the Grenville of North America and the Karelian of Finland possess abundant carbonate which represents metamorphosed sedimentary 'limestone'. Many metamorphosed Phanerozoic carbonate rocks still exhibit fossil organisms, and the origin of their constituent calcite (and related Ca–Fe–Mg–Mn carbonates) is plain: it has been precipitated, commonly as aragonite which transforms to calcite, during sedimentation and diagenesis, and subsequently involved in metamorphism. The carbonate grains as they now occur are metamorphic products. However, no one would suggest that the carbonate has been formed as a result of metamorphic breakdown, diffusion and reaction: the carbonate has always been carbonate, and the present grains are simply coarsened derivatives that have grown, *in situ*, from sedimentary:diagenetic precursor 'limestone'.

If we turn now to stratiform ores, several simple analogies immediately present themselves. The bedded barite of many of these deposits is universally accepted as being exhalative sediment. This is indicated by its bedded form and also by abundant evidence of the modern deposition of finely precipitated barite around seafloor hydrothermal orifices. The present barite of highly metamorphosed stratiform ores, 'metamorphic barite', is therefore unquestionably derived directly from pre-existing hydrothermal sedimentary material of the same composition.

A similar state of affairs clearly holds for the sulphides of such orebodies. Stratiform layers of sphalerite, conformable with relict sedimentary layering in associated high-grade metapelites as at Broken Hill, New South Wales, Balmat, New York and Gamsberg in Namaqualand, are not ascribed to metamorphic diffusion and reaction. As indicated by geological evidence in older deposits and by direct observation of modern accumulations such as those of the Red Sea deeps and the East Pacific Rise, the zinc sulphide originates as a chemical sediment. Its initial accumulation may be as the hexagonal, wurtzitic form, but with ageing and elevation of temperature this inverts, *in situ*, to sphalerite (*vide* aragonite → calcite). With the onset of metamorphism such sphalerite may coarsen, deform, anneal and, in some cases, develop local discordances to original bedding. However, the sphalerite was never a product of metamorphic reaction: it derives directly from a fine, sedimentary/diagenetic zinc sulphide precursor.

These very simple examples lead us to a slightly more complex process: the conversion of limonite to magnetite as in the Atlantis II deep of the Red Sea (Hackett & Bischoff 1973).

According to these authors this process begins by the precipitation of amorphous iron hydroxides (limonite) at the interface of the 56 °C and 44 °C brines. Following precipitation the fine limonite settles through the 56 °C brine and is deposited on the sea-floor where it dehydrates to goethite:

$$\underset{\text{limonite}}{Fe(OH)_3} \rightarrow \underset{\text{goethite}}{FeO.OH} + H_2O.$$

Locally further dehydration results in the transformation of goethite to haematite:

$$\underset{\text{goethite}}{2\,FeO.OH} \rightarrow \underset{\text{haematite}}{Fe_2O_3} + H_2O.$$

In turn haematite converts to magnetite by the reaction:

$$Fe_2O_3 + H_2O + Fe^{2+} \rightarrow Fe_3O_4 + 2H^+.$$

Hackett & Bischoff (1973) observe that magnetite coexists with haematite in the sediment and appears to form at the latter's expense, and that 'The well-crystallized nature of both minerals indicates that diagenetic modification is occurring in place.' Thus the bedded iron oxide forms and develops during sedimentation and diagenesis: limonite is the precursor to goethite, goethite to haematite, and haematite to magnetite. Once limonite is formed the materials of the transformations are essentially indigenous. This is doubtless the kind of sequence responsible for the development of the magnetite of many banded iron formations. It is slightly more complex than the simple growth of calcite from marine carbonate, of apatite from marine phosphate, or the dehydration reaction $SiO_2.nH_2O \rightarrow SiO_2 + nH_2O$, but it clearly represents the development of a mineral, which may later constitute a component of a high grade metamorphic assemblage, directly from a precursor rather than via a metamorphic reaction series.

In such cases as these, the development of much regional metamorphic quartz, carbonate, sulphate, sulphide, graphite, phosphate, etc., the original sedimentary and present metamorphic compositions of the materials are known and the direct derivation of the metamorphic minerals from precursors is self-evident and unavoidable. The mechanism is relatively simple and is accepted without question. Is it, however, too simple to have any relevance to metamorphic silicate formation? Is there some fundamental difference between the development of the silicates and, say, the development of metamorphic pyrite from primitive sedimentary/diagenetic iron sulphides? Is there any evidence of authigenic silicates from which their metamorphic counterparts might derive?

There is: authigenic K-feldspar, albite and other members of the plagioclase series are known to occur in abundance in both modern and young unmetamorphosed sediments (see later in this contribution) and all have been synthesized from aqueous gels at temperatures between 0 °C and 80 °C (Flehmig 1977). Simple regional metamorphism of such authigenic feldspars must, as in the case of quartz or pyrite, lead to the development of metamorphic counterparts.

Albite provides a simple example. This mineral forms by a wide variety of processes, from igneous crystallization to low-temperature hydrothermal replacement of pre-existing minerals and even precipitation from aqueous solution. It is an important constituent of many metamorphic rocks.

One of the important pathways for the formation of albite, however, is diagenetic. During burial, felsic volcanic glass may be attacked by pore-space water and converted to clays, chlorite, a variety of zeolites, analcite and silica. The two latter may combine,

$$\underset{\text{analcite}}{NaAlSi_2O_6} + SiO_2(aq) \rightarrow \underset{\text{albite}}{NaAlSi_3O_8},$$

to produce authigenic albite.

It may be said that this is a 'reaction'. However, there are two aspects that distinguish the process from the diffusion-reaction régime to which metamorphic mineral formation is normally attributed. First, the authigenic process may be initiated virtually with the beginning of burial, and take place under P–T conditions very much lower than that of normal metamorphism. Second, the materials of the albite are indigenous: they are derived directly and *in situ* from the glass that then constitutes the *precursor* to the albite, and whose place the latter takes.

This is no more than one example. Evidence provided by geological occurrence in unmetamorphosed materials, and by low-temperature aqueous experiment indicates that both K-feldspars and members of the plagioclase series may develop as authigenic entities both by the conversion of precursor materials such as glass and by the neoformation of appropriate gels. It thus appears that in the present context there is no difference in principle between the metamorphic oxides, carbonates, sulphides, phosphates, etc., on one hand and the silicates on the other: the silicates, like the simpler compounds, may form initially as low-temperature authigenic compounds, which, with later metamorphism, are converted directly to the relevant regional metamorphic counterparts.

(*b*) *Extension to the case of almandine*

This brings us to the case of the abundant almandine garnet that commonly occurs as a conspicuous constituent of the small banded (bedded) iron formations now recognized as an almost-ubiquitous component of stratiform ore environments in regionally metamorphosed volcanic settings. Examples are widespread in the Willyama (Broken Hill) Province of New South Wales (Richards 1966; Stanton 1972, 1976), the Grenville (Adirondacks) Province of northern U.S.A. (Buddington 1966), the Karelian terrane of Finland (see, for example, Isokangas 1978), the Appalachian–Caledonide Province of North America and Norway respectively (McAllister 1960; Stanton 1984) and in many other stratiform ore provinces.

These small banded iron formations range from sparsely garnetiferous or magnetite-bearing cherts to well-bedded quartz–magnetite rocks, quartz–garnet rocks, and, in many cases, quartz–magnetite–apatite–garnet rocks. All of these lithologies, especially the quartz–magnetite–apatite–garnet members as typified by the occurrences at Broken Hill, are virtually invariably characterized by the delicate preservation of bedding laminations (down to less than 0.05 mm in thickness), other assorted sedimentary features, and pre-lithification deformation structures.

These rocks are now well recognized as 'exhalites'; like the stratiform ores they accompany, products of sea-floor exhalation and its consequent chemical sedimentation. The quartz layers represent, in principle, chert, presumably originally laid down as a hydrous form of silica as already discussed. The apatite layers, usually containing some admixed quartz but in some cases almost pure granular apatite, appear to have been laid down quite simply as fine beds of hydrothermally derived calcium fluo-phosphate. At Broken Hill this apatite of the banded iron formations appears to be entirely similar to the apatite well-known to be abundantly co-extensive with the associated exhalative sulphide ores. In an analogous way the magnetite (and, where it occurs, haematite) are universally accepted as finely sedimented exhalative iron oxide; original precipitation has probably been in the form of hydrous goethitic oxide, which has undergone dehydration and variable reduction to haematite and/or magnetite during diagenesis as described above (Hackett & Bischoff 1973).

Although many of the terranes in question, and certainly Broken Hill, have undergone conspicuously 'high-grade' metamorphism, no metamorphic petrologist suggests that the quartz, apatite and magnetite are the products of high-grade metamorphic reactions. Each is the simple, direct, *in situ* derivative of a precursor material whose composition was essentially similar to that of the mineral (quartz, apatite or magnetite) now observed.

What, then, of the garnet that occurs so abundantly, and in bedded arrangement apparently completely analogous to that of the associated quartz, apatite and magnetite, in so many of these iron formations? This is one of the important metamorphic index silicates, and in most other milieux – especially those of metapelitic rocks – would be ascribed to metamorphic reaction. The fact that it is a *silicate*, that it is the index mineral of one of Barrow's zones of progressive thermal metamorphism, together with the now-established interpretation of garnet-bearing assemblages as metamorphic grade indicators, leads us immediately to assume that the garnet is the product of a metamorphic reaction; that its formation has resulted from a process quite different from that universally accepted as being responsible for the intimately associated quartz, apatite and magnetite, all of which have manifestly developed by simple *in situ* transformation of precursors.

But does this particular garnet *necessarily* owe its formation to metamorphic diffusion and reaction; processes that would not only have had to provide copious quantities of aluminium (in precisely appropriate proportions) in an otherwise Al-deficient rock, but which would also have had to induce in the garnet a bedded arrangement precisely similar to that of three other minerals derived by different means?

As suggested earlier (Stanton 1976, 1982; Stanton & Williams 1978), the answer must be no. The whole mode of occurrence of the garnet in these banded iron formations suggests that it was produced in a way generally similar to that responsible for the formation of the intimately associated quartz, apatite and magnetite: from some precursor material that formerly occupied the space now occupied by the garnet. The fact that the latter is a *silicate* arouses our prejudices to deflect us from such a conclusion, but brief consideration of the problem suggests that there is no reason why it should not be so. As the Broken Hill banded iron formations are chemically almost identical with many younger ironstones that have as an important component the iron-rich chlorite chamosite, it has been proposed (Stanton 1976) that a sedimentary/diagenetic iron silicate such as a siliceous chamosite – perhaps rendered unstable by the presence in its structure of minor Mn – constituted a simple precursor to the almandine. As will be shown further on, the constitutional similarities between siliceous chamosite and some almandines are so close that an appropriate solid–solid transformation could convert one to the other.

Thus by following through a series of minerals from the very simple to the more complex ('metamorphic' quartz, carbonate, barite, sphalerite, magnetite, authigenic K-feldspar, authigenic albite to almandine garnet) it may be shown by simple steps of logic that a mineral, garnet, generally regarded as a product of metamorphic reactions might well develop through 'within-domain re-ordering' of an early-formed precursor material.

The fact that such minerals as quartz, magnetite, apatite, sphalerite and K-feldspar, all of which commonly constitute components of high-grade metamorphic mineral assemblages, may derive directly from specific domains of early-formed materials establishes the development of metamorphic minerals from precursors as a *principle*. It is no longer an hypothesis. What is in question is the extent to which this principle may apply to the broader spectrum of regional metamorphic silicates; a problem encapsulated by the above case of almandine garnet in regionally metamorphosed fine-grained sediments.

From this point it is therefore the purpose of the present contribution to consider not the validity of the principle, but how far it may be extended.

(*c*) *Earlier suggestions concerning precursors*

The idea that silicate metamorphic minerals might grow from materials indigenous on a fine scale is by no means new, and the principle of precursor derivation has long been accepted for clay, primitive phyllosilicate and zeolite mineral formation during sedimentation, diagenesis and 'burial metamorphism'.

The deduction of Harker to which reference has already been made – that '...the mineral formed at any point depends only on the chemical composition of the rock mass within a certain very small distance around that point' (1893, p. 575) and his accompanying observation that 'In the cases examined this is about one twentieth of an inch...' (1893, p. 577) – appears, as already pointed out, to have carried the implication that a given metamorphic mineral grain is derived from the substance of the material formerly occupying the present site of that grain. While the idea is no more than implied here, Harker's statement is a close, and perhaps the first, approach to an enunciation of the precursor principle.

Perhaps the next suggestion that particular metamorphic minerals might result from compositional features on a fine scale was that of Emmons & Laney (1910) who attributed the growth of staurolites in particular thin pelitic beds (associated with some of the stratiform orebodies of Ducktown, Tennessee, U.S.A.) to small-scale compositional variation. They noted that 'It is possible...that the staurolitic layers represent beds for which the material contained a considerable but variable proportion of clay...' (1911, p. 158). They continued this theme in a further contribution in 1926 (Emmons & Laney 1926, pp. 18–19). Dunn (1929) in a remarkably prescient contribution on kyanite, sillimanite and corundum in some of the Archaean regional metamorphic rocks of northern India, suggested, *inter alia*, that much of their corundum derived directly from bauxite, and sillimanite from 'bauxitic clay'. He went so far as to say: 'There is, indeed, a temptation to explain even the fine radial structure of some of the sillimanite as resulting from the recrystallization of original pisolitic bauxitic-clay' (1929, p. 246).

Harker (1932; 3rd edn, 1950) again came within a hair's breadth of stating the precursor principle when he drew attention to '*pseudomorphs* of a higher-grade mineral after one proper to a lower grade' affording 'direct evidence of the derivation of one mineral at the expense of another' (1950, p. 192). Harker figured several thin sections in which garnet exhibits textures typical of chlorite, and stated that 'The garnet preserves in many places the shapes of the flakes of chlorite from which it has been largely formed' (1950, p. 192). It may be presumed that Harker considered the chlorite to have lost water of crystallization and to have reacted with enclosing quartz to form garnets, which assumed precisely the same volume and shape as the pre-existing chlorite. Had the requisite SiO_2 been within the body of a 'siliceous chlorite' (see p. 574, table 7), derivation of the garnet would have stemmed from a precursor; if a normal chlorite had derived SiO_2 from quartz immediately enclosing it, the garnet would have been the product of mineral reaction. The distinction is a fine one. Whichever was the case, Harker's proposed mechanism involved materials from a highly localized domain closely approximating to the domain now occupied by the garnet. He was coming very close to suggesting the latter's derivation from a precursor.

Yoder (1955) commented that 'It is not known whether a sediment actually passes through each of these stages [of metamorphism] in accord with the concept of progressive metamorphism' and that 'It is possible...that each bed may achieve its metamorphosed state directly and that its state may be conditioned by factors other than rise of temperature or increase of pressure...one of these factors may be bulk composition, specifically the initial water content' (1955, p. 509). Yoder's statements did not allude to distances of metamorphic diffusion, but they did carry the suggestion that 'higher-grade' metamorphic assemblages might derive directly from the primary materials of the pelite rather than through a progressive series of intermineral reactions. Yoder (1957) went on to point out that greenalite and chamosite seemed likely to be common precursors to minnesotaite and stilpnomelane respectively. Blake (1965) noted the close similarity of the compositions of the latter two minerals and suggested that both might derive from a low-Al chamosite.

These various contributions do no more, however, than imply or hint that metamorphic minerals might derive directly from primary materials of the parent rocks and/or that they reflect compositional features of rather small primary domains.

Perhaps the first suggestion that metamorphic minerals might arise directly from specific clay species was that of Segnit (1961) who proposed that sillimanite at Broken Hill had derived *in situ* from kaolinite, and gahnite ($ZnAl_2O_4$) from kaolinite on which Zn had adsorbed *during sedimentation*:

$$\underset{\text{kaolinite}}{Al_2O_3.2SiO_2.2H_2O} \rightarrow \underset{\text{sillimanite}}{Al_2O_3SiO_2} + SiO_2 + 2H_2O$$

and

$$\underset{\text{kaolinite}}{Al_2O_3.2SiO_2.2H_2O} + Zn^{2+} + O^{2-} \rightarrow \underset{\text{gahnite}}{ZnO.Al_2O_3} + 2SiO_2 + 2H_2O.$$

A little later, Berge (1966) proposed that some of the garnets of the Goe Range area of Liberia had been produced by *in situ* transformations of chamosite granules. He observed that the quartz–garnet rocks intercalated with the argillaceous schists of the area are essentially bimineralic rocks 'in which metamorphism has caused the complete conversion of iron–aluminum silicates into garnet' (1966, p. 22). His petrographic studies indicated that there had been no introduction or removal of material during metamorphism, and hence that present constitutional features reflected those of the original iron silicate-bearing quartzose sediment.

> The reason for postulating a pre-metamorphic iron aluminum silicate rather than independent oxides (or hydroxides) or iron and aluminum with quartz is that the apparently uniform composition of the garnet may reflect a pre-metamorphic silicate of a determinate composition. Otherwise, constant proportion of independent oxides of iron, alumina, and magnesium might be considered somewhat fortuitous. Thus it is tentatively proposed that these layers represent a metamorphosed sequence of interstratified layers of iron silicate and chert, or orthoquartzite.... There is a similarity between the garnet and certain chamosite analyses...with the exception of silica. Sedimentary chamosite has been frequently encountered together with carbonate-bearing iron formation in other localities (e.g. Clinton iron ore beds), but also in association with orthoquartzites (1966, p. 22).

Eugster (1969) in a now-famous contribution based on observation of the Lake Magadi area, Kenya, suggested that chert layers of iron formations may have been deposited originally as magadiite $NaSi_7O_{13}(OH)_3 . 3H_2O$, which, when leached by fresh water, lost Na to form a silica gel that later transformed to layers of fine cherty quartz. Sodium thus lost might then react with iron-bearing clays or stilpnomelane to form the Na–Fe amphibole riebeckite as a diagenetic material. Magadiite was thus seen as a precursor to diagenetic and metamorphic quartz, and the diagenetic riebeckite a potential diagenetic precursor to metamorphic amphibole.

Grubb (1971), working on the Dales Gorge Member of the Brockman Iron Formation concluded that the primitive silicate phases of those iron-rich rocks were montmorillonite and greenalite, which, during diagenesis, constituted precursors to stilpnomelane and minnesotaite respectively. Grubb went on to note that the great bulk of the riebeckite in the Brockman Formation occurs as blue, massive riebeckite-rich beds, the riebeckite apparently having formed by diagenetic replacement of stilpnomelane. The fibrous form of riebeckite, crocidolite, was suggested to have formed, at least in part, from 'iron–silica–soda gels' and nucleated on small crystals of magnetite. Earlier Cilliers & Genis (1964) had suggested that the crocidolite of some of the South African banded iron formations had formed directly from a sedimentary/diagenetic 'protoriebeckite' precursor of attapulgite-type crystal structure, and that the fibres had nucleated on associated magnetite.

In their investigation of the contact metamorphism of the Biwabik iron formation, Morey *et al.* (1972) simply referred, without elaboration, to the derivation of the Biwabik almandines from chamosite, presumably assuming an SiO_2 addition. In the same year Kennan (1972) noted hollow, often ellipsoidal, clusters of small manganiferous garnets that constituted a striking feature of the fabrics of garnet–quartz coticules of the Garnetiferous Beds, an important group of metamorphosed manganese-rich sediments occurring within the aureole of the Leinster Granite. Kennan considered the garnet clusters to represent original small sedimentary concretions, perhaps ferromanganese nodules, 'subsequently completely reconstituted' (1972, p. 165).

In his investigation of the sedimentation, diagenesis and low-grade metamorphism of the Sokoman iron formation, Klein (1974) noted that among the more important products of original sedimentation were hydrous Fe-silicate gels of greenalite-type composition, and, locally, hydrous Na-, K-, Al-rich iron–silicate gels which approximated to stilpnomelane compositions. He considered that during diagenesis H_2O was lost from the more open gel structures because of compaction, and that the amorphous silicate gels became somewhat less disordered structures: 'For example, amorphous greenalite-type compositions may tend toward very fine-grained, somewhat ordered greenalite and hydrous Na-, K-, Al-rich iron silicate gels may tend to acquire the structural arrangement of a possible precursor to stilpnomelane' (1974, p. 495).

Klein went on to conclude that all of the phases (oxides, carbonates and silicates) now observed in the Sokoman iron formation 'have sedimentary precursors in terms of gels, precipitates or oozes' (1974, p. 496).

Although they worked, again, on the almost-unmetamorphosed material of the Sokoman iron formation, Klein & Fink (1976) concluded that all of the phases they observed were 'recrystallization products of sedimentary precursors' and they interpreted the Sokoman textures and assemblages 'in terms of possible sedimentary precursors' (1976, p. 453).

Unaware of Berge's thoughts or the suggestions of Morey *et al.* and of Kennan, the present author (Stanton 1976), working on the small Broken Hill banded iron formations already referred to, found evidence indicating that metamorphic diffusion distances in those rocks had been very small.

> ...one is therefore forced to conclude that, for any rock volume of the order of the present grain size, those chemical components observed to be present now must precisely reflect the chemical composition of that domain immediately prior to the onset of metamorphism...The principal implication appears to be either that each mineral now present represents the *in-situ* transformation of a pre-existing mineral of similar composition or that it is one of two or more products of the *in-situ* breakdown of a pre-existing mineral (1976, p. B127).

Accordingly Stanton proposed that the almandine of the Broken Hill banded iron formations and their immediate environments derived from a sedimentary/diagenetic manganiferous chamosite,† biotite from glauconitic material, muscovite from illite and sillimanite from kaolinite. He noted that such a precursor hypothesis and its implications appear '...so simple that it seems naive to propose them; however, if metamorphic changes have occurred in closed systems of small scale, considerations of this kind appear inescapable' (1976, p. B127).

Following a similar line of reasoning, Valliant & Barnett (1981) identified garnets underlying the Bousquet stratiform pyritic gold orebody of Quebec as metamorphosed equivalents of Archaean manganese nodules that had accumulated near the sea-floor hydrothermal vent that later generated the ore deposit. They noted that the garnet occurs in a distinctive garnet-rich lens beneath the orebody, and in its distribution, abundance and composition exhibits close ties with the latter. Garnet constitutes only 3% of the rock within muscovite-rich layers near the east and west ends of the ore lens, increasing to about 12% beneath its centre. In addition, garnet MnO is greatest near the centre and stratigraphic top of the garnetiferous lens, decreasing systematically towards the east and west and stratigraphic base. Trace Pb, Zn and Ba in the whole rock behave in similar manner. They stated that

> well-preserved bedding contacts, preservation of fine sedimentary laminations in the garnet-bearing rock, microstratigraphic control of garnet distribution, lack of a Mn-depleted domain in the matrix surrounding garnet grains, numerous silicate, carbonate and sulphide inclusions in garnet, and the large MnO content of garnet rims provide extensive evidence against the presence of large diffusional domains, fractionation, and depletion of Mn in the rock matrix during garnet growth. It therefore appears that the composition of garnet grains must reflect the original composition of the particular volume of sediment that is now garnet.
>
> Garnet at Bousquet is believed to have overgrown primary nodular accumulations of Mn-oxide minerals that contained a sufficient quantity of clay to provide the Al necessary for garnet growth. Inclusions of detrital or chemically precipitated quartz, carbonate, pyrite and sphalerite within these primary nodules remained as post-metamorphic inclusions in garnet. The primary nodules were analogous to modern hydrothermal, seafloor Mn-nodules (1981, p. 1007).

As had been pointed out by Stanton & Williams (1978) for the Broken Hill garnets, Valliant & Barnett noted that the wide variability in Mn and Fe contents of the Bousquet garnets indicated that temperature and pressure could not be the factors controlling garnet growth in this case.

---

† Whole-rock chemical studies of the banded iron formations had shown a close similarity of these to younger 'ironstones' (James 1966) not only in Fe, Si and Al content but also in the incidence of Mn and P. This added substance to the view that the finely bedded quartz, magnetite and apatite of the iron formations were simple *in situ* derivatives of exhalative/sedimentary/diagenetic hydrous silica, goethite-haematite and fine calcium fluorphosphate respectively. The fact that the chemical features of the iron formations were almost identical with those of younger *chamositic* ironstones constituted an immediate indication that the relevant garnets might have derived from chamosite grains.

More recently the present writer has put forward evidence indicating that several other silicates (epidote, sillimanite, cordierite and grossular–andradite) may arise, at least in some cases, directly from precursor materials during regional metamorphism (Stanton 1982, 1983, 1984 and 1987 respectively).

That it would ultimately be suspected that metamorphic silicates could derive directly from specific clay, clay-type and zeolitic precursors has been inevitable if for no other reason than that many of the clays and zeolites themselves are known to be derivatives of yet earlier precursors.

The development of certain clays from specific precursor substances has been known for a long time, and it is being recognized increasingly that zeolites, which commonly constitute precursors to components of metamorphic rocks, may themselves derive from particular precursor material. For example, Iijima (1978) in considering the development of zeolites and their daughter minerals in marine volcanic rocks of Japan, observed that the identity and compositions of the zeolites were influenced by the composition of precursor glass. He went on to note that the composition of analcite derived from such zeolites '...is principally controlled by the composition of precursor zeolites, clinoptilolite and mordenite'; and:

> Authigenic albite of burial diagenetic origin is slightly different in composition depending on the nature of its precursor mineral. In Tertiary and Cretaceous silicic tuffs in Japan, the albite replacing plagioclase is nearly ideal in composition, whereas that replacing analcime contains appreciable amounts of Ca and K...This suggests that the composition of albite is not only the function of temperature but also affected by composition of precursors (1978, p. 183).

Of the zeolites Hay (1978) noted that phillipsite is commonly derived from low-silica, generally basaltic, tephra whereas clinoptilolite is derived from more siliceous tephra and that, in turn, 'Early formed zeolites (e.g. clinoptilolite and phillipsite) are commonly precursors to other zeolites (e.g. analcime, heulandite, laumontite' (1978, p. 135). He went on to observe of diagenesis in saline, alkaline environments: '...glass alters to zeolite such as phillipsite, which may alter to analcime and which in turn may be replaced by K-feldspar' (1978, p. 138).

These and many other investigators of clay–zeolite formation appear to accept a precursor concept as well-established and virtually self-evident, and use the term precursor as a normal item of their technical vocabulary.

(*d*) *Precursor mechanisms*

Three potentially important mechanisms of regional metamorphic mineral development thus present themselves.

1. The simple ordering and coarsening of compounds formed during sedimentation and diagenesis, e.g. sedimentary/diagenetic carbonates, sulphides, barite, neoformed chlorite.

2. Nucleation and growth of ordered crystal structures within amorphous materials (most commonly gels) of generally similar composition formed during chemical sedimentation, e.g. gel silica → cristobalite → quartz; ZnS gel → wurtzite → sphalerite; gel goethite → goethite → haematite.

3. The solid–solid transformation of 'pure' and 'impure' crystal and mixed-layer crystal structures formed during chemical sedimentation and diagenesis, e.g. illite → muscovite; kaolinite–gibbsite mixed layers → sillimanite; siliceous chamosite → almandine garnet.

The starting materials of (1) may be referred to as *simple precursors*; those of (2) and (3) may be referred to as *complex precursors*.

If it is indeed by mechanisms such as these that regional metamorphic minerals develop, the chemical reactions responsible for the formation of metamorphic silicates take place substantially *before* metamorphism. On this basis, although minor chemical change during the early stages of metamorphism cannot be entirely precluded, chemical movement probably ceases essentially as pore spaces close and the pelitic sediment becomes lithified. Following lithification, metamorphic changes are dominantly physical; simple grain growth, or gel–solid/solid–solid transformation followed by grain growth. In due course these processes may be succeeded by all the complexities of polymetamorphism.

The three postulated mechanisms may now be examined. The first, simple ordering and grain growth of substances – *simple precursors* – formed during sedimentation and diagenesis, may be considered through observations on old but essentially unmetamorphosed rocks, and on modern marine sediments and oozes. The experimental background for the direct precipitation of carbonates, sulphides, sulphates, and now for silicates such as clays, chlorites and zeolites, is well-established and, for the non-silicates, elementary.

The second and third processes, gel–solid and solid–solid transformation of early-formed non-crystalline and poorly crystalline substances – *complex precursors* – may be considered through observations of materials partly preserved in metamorphosed and other rocks, and by considering some low-temperature industrial and experimental products.

3. EVIDENCE CONCERNING THE DEVELOPMENT OF METAMORPHIC MINERALS FROM SIMPLE PRECURSORS

(*a*) *Mineral occurrences in old but little-metamorphosed rocks*

(i) *Talc and amphibole in the Archaean stratiform ores of Mattagami Lake, Quebec*

In their extensive investigation of the chemistry of the Archaean Mattagami Lake Fe–Cu–Zn deposit of Quebec, Costa *et al.* (1983) concluded that both Fe-bearing talc and amphiboles (of tremolite ± Mg cummingtonite and actinolite–tirodite groupings) were products of direct precipitation at the time of ore formation. They determined trends of Fe-enrichment in talc both where this was present as single grains in layered pyrite–sphalerite ore and in '...so-called talc-actinolite schist', and concluded that the trends were not related to bulk-rock compositional effects, or to the abundance of talc itself, and could not reasonably be attributed to superimposed metamorphic processes. The authors noted *inter alia* that there was a high degree of acceptance of the chemical precipitation concept when applied to sulphides, carbonates and chert when these display recognized sedimentary features, but that there was a distinct reluctance to ascribe a sedimentary origin to other silicate minerals even where these coexisted with the former phases in sedimentary structures; origins involving diagenetic and, most commonly, metamorphic modifications of presumed precipitated precursors, were generally invoked (1983, p. 1198). In view of the observed compositional variations in talc and solution chemistry considerations, Costa *et al.* concluded that the talc had precipitated directly 'from a dynamic sea-floor brine pool ponded in a sea-floor depression at the top of the Watson Lake Group rhyolite' (1983, p. 1199). Chemical features of the tremolite–cummingtonite–actinolite–tirodite amphiboles indicated that the amphiboles, too, were sedimentary or diagenetic and had formed directly rather than through an intermediate precursor phase.

Costa *et al.* observed that 'actinolite is the second most abundant silicate mineral in the ore zone and together with talc composes most of the silicate gangue in the deposit' (1983,

p. 1198). These silicates are therefore not simply occasionally-observed oddities; they are major components of a major orebody. As has long been accepted for the sulphides, carbonates, etc., of which they are intimate accompaniments, the Mattagami talc and amphibole constitute large-scale occurrences of sedimentary/diagenetic silicate.

(ii) *Pyrophyllite in the Lower Proterozoic Witwatersrand auriferous sequence*

Massive pyrophyllitic beds are known to occur in the sequence of both the Dominion Reef and Witwatersrand systems of the Witwatersrand gold–pyrite–uraninite-bearing sedimentary succession of South Africa. These dominantly arenaceous sediments of Lower Proterozoic age were laid down in the lower braided stream, delta and near-shore facies, and are unmetamorphosed.

The principal pyrophyllite-bearing unit is the Khaki Shale, a soft brown, shaly rock with a pronounced talcose feel, interbedded with quartzites, gritty quartzites, pebble beds and conglomerates of the Upper Witwatersrand succession. The shale is usually separated from the gold-bearing Basal Reef below by a quartzite (sandstone) bed which varies in thickness from about ½in to a little over 3 ft[†] (Coetzee 1960, 1976).

The Khaki Shale itself consists of one or more bands generally not more than a few feet thick overall. However, the zone of pyrophyllitic shale is known to attain a thickness of 30 ft; Coetzee (1960, 1976) notes that in bore-hole 1 on the Hestersrust 29 lease the Khaki Shale unit consists of four separate bands, which, together with the quartzite interbeds, have a total thickness of about 28 ft, the actual shale bands varying from 11 in to 41 in. The unit is extensively developed (though not fully defined) and as its extremities appears to thin out to a quartzose variant of the shale.

An analysis of the Shale (Coetzee 1960) given in table 2, indicates almost pure pyrophyllite.

The pyrophyllite of the Khaki Shale has not developed *in situ* by regional metamorphism; the enclosing thick succession of completely unmetamorphosed gold-bearing sediments of the

TABLE 2. CHEMICAL ANALYSIS OF KHAKI SHALE, WITWATERSRAND, AND TWO PYROPHYLLITES

	(1)	(2)	(3)
SiO_2	61.45	63.36	63.57
TiO_2	0.82	n.d.	0.04
Al_2O_3	29.69	30.16	29.25
Fe_2O_3	0.32	0.64	0.10
FeO	0.22	n.d.	0.12
MnO	0.02	n.d.	nil
MgO	0.09	trace	0.37
CaO	0.54	nil	0.38
Na_2O	0.38	n.d.	0.02
K_2O	1.19	n.d.	trace
P_2O_5	0.07	n.d.	trace
H_2O^+	4.90	5.07	5.66
H_2O^-	0.20		0.66
total	99.89	99.23	100.17

Abbreviation: n.d., not determined.

Columns: (1) Khaki Shale, bore-hole VDH4 on Van Den Heevers Rust 410, depth 4869 ft (Coetzee 1960); Analyst: A. Kruger; (2) high-grade commercial anthophyllite, Newfoundland (Coetzee 1960); (3) pale blue pyrophyllite, Honami Mine, Nagama Prefecture, Japan (Kodama 1958).

[†] 1 ft = 30.48×10^{-2} m.

Witwatersrand goldfields attests to this. The immediate proximity of relatively poorly sorted arenaceous and rudaceous rocks indicate that beds of almost pure pyrophyllite are unlikely to be detrital. It appears most likely that the pyrophyllite developed, during a pause in detrital sedimentation, by neoformation from SiO_2–Al_2O_3 gels, or by low-temperature diagenetic processes.

(iii) *Talc in the Upper Palaeozoic Chu Chua stratiform ores, British Columbia*

The Chu Chua exhalative sulphide deposit occurs in association with basaltic rocks of the Upper Palaeozoic volcano-sedimentary Fennel Formation of south central British Columbia (Arggarwal & Nesbitt 1984). Massive cherts and massive talc rocks occur in the footwall to the sulphides. That the silica and Mg silicate in question might have derived from leaching and alteration of footwall basalts is obviated by their lack of relict textures and their very low content of immobile elements such as Ti and Zr compared with the basalt. From these and related observations Arggarwal & Nesbitt conclude that like the chert, the talc rocks in the footwall of the Chu Chua deposits are chemical precipitates.

As indicated above, these talc units are massive and constitute a large-scale concentrated occurrence of the mineral. Thus, as with the Mattagami Lake talc and amphibole, the Chu Chua talc is not an occasionally observed oddity; it constitutes a major occurrence of early-formed low-temperature, directly precipitated silicate.

(iv) *Clinopyroxene in the Palaeozoic Woolomin ores, New South Wales*

The Woolomin terrane first described by Benson (1913–1918) and analysed more recently by Korsch (1977) and Leitch & Cawood (1980), represents a typical occurrence of the Steinmann Trinity (Steinmann 1927) or Steinmann Association (Stanton 1972*a*). It exhibits abundant fine shaly and siliceous sediments, including radiolarian cherts and jaspers, basaltic lavas (commonly pillowed), alpine-type lenses of serpentinized ultrabasic and basic rocks, and a number of conformable cupriferous pyritic ores of Cyprus type with the usual related stratiform Mn oxide and silicate lenses. The association as a whole appears to represent an early, deep sea-floor, stage of volcanic island arc development.

Grade of metamorphism indicated by the mineral assemblages of the sediments and basic lavas is low; Herbert (1981) has determined a range prehnite–pumpellyite–actinolite–greenschist. Here and there the sulphide–oxide–carbonate silicate assemblages of the Cyprus-type cupriferous lenses are locally superimposed, substantially in bedded form, on these low-grade metamorphic assemblages.

At the Nangarah Creek sulphide occurrence Herbert (1981) found abundant bedded to semi-massive clinopyroxene, a remarkably pure hedenbergite (table 3). There was no indication that this arose from any silica–carbonate reaction, and Herbert concluded that it had formed *in situ* by the ordering and coarsening of a sedimentary precursor. In view of its close association with exhalative sulphides Herbert considered the precursor to have been, quite simply, an exhalative silicate.

(v) *Chlorite, muscovite and talc in Palaeozoic stratiform deposits of S.E. Australia*

McLeod & Stanton (1984) investigated the nature and origin of phyllosilicates associated with nine stratiform sulphide deposits occurring in very low-grade metamorphic sedimentary–pyroclastic rocks of the Cambrian to middle Palaeozoic terrane of S.E. Australia.

TABLE 3. ELECTRON MICROPROBE ANALYSES OF HEDENBERGITES IN CHEMICAL SEDIMENTS OF THE WOOLOMIN SERIES, NEW SOUTH WALES

	(1)	(2)
SiO_2	47.70	48.23
Al_2O_3	0.59	nil
Cr_2O_3	nil	0.19
$FeO^{(a)}$	30.92	31.62
CaO	20.76	19.87
total	99.97	99.91

number of ions on the basis of 6(O)

	(1)		(2)	
Si	1.984		2.004	
Al	0.019	2.00	—	2.00
Cr	—		0.003	
Fe	1.076	2.01	1.099	1.99
Ca	0.930		0.885	

Columns: (1) average core composition (analyst H. K. Herbert); (2) average rim composition (analyst H. K. Herbert).

(a) Total iron as FeO.

The phyllosilicates – principally chlorite, muscovite and talc, with lesser phlogopite – were interbedded with the exhalative sulphides and, like the latter, commonly formed almost monomineralic beds. Individual phyllosilicates frequently exhibited gross compositional variation from bed to bed over very short distances (figure 9). The purity, fineness and chemical (i.e. sulphide-rich) environments of the phyllosilicates precluded a detrital origin. Gross compositional variation from one bed to the next involving distances of the order of a few centimetres appeared to preclude significant metamorphic diffusion and their formation by metamorphic reaction. McLeod & Stanton concluded from such evidence that the phyllosilicates, like the intimately associated, bedded, exhalative sulphides, were formed and accumulated as chemical sediments, the within-bed compositional systematics developed between coexisting phyllosilicates, and between coexisting phyllosiliciate and sulphide (figures 9 and 10) reflecting very early, sedimentary/diagenetic equilibria.

(vi) *Concretionary and colloform epidote-andradite of the essentially unmetamorphosed stratiform zinc occurrence of Brindabella, New South Wales*

The evidence here is substantially textural. Figures 11 and 12, plate 2, show rounded bodies of grandite garnet, bordered in most cases by epidote, occurring in diamond drill core from a stratiform, sulphide-bearing, calc-silicate body at Brindabella, New South Wales. These rounded masses occur in what otherwise appear to be unmetamorphosed, undeformed pelitic sedimentary rocks. Figure 11 also shows preservation of bedding and minor blind faulting in the pelite enclosing the grandite–epidote bodies.

I submitted these materials in hand specimen, and without revealing their nature or context, to several sedimentologists (K. A. W. Crook, P. G. Flood, B. C. McKelvey, personal communications 1984). Independent opinion in each case was that the rounded bodies were diagenetic concretions, corroborating my own, earlier, diagnosis.

In addition, the grandite garnets of many stratiform calc-silicate masses exhibit highly variable zoning. Many of the individual garnets are conspicuously zoned with respect to

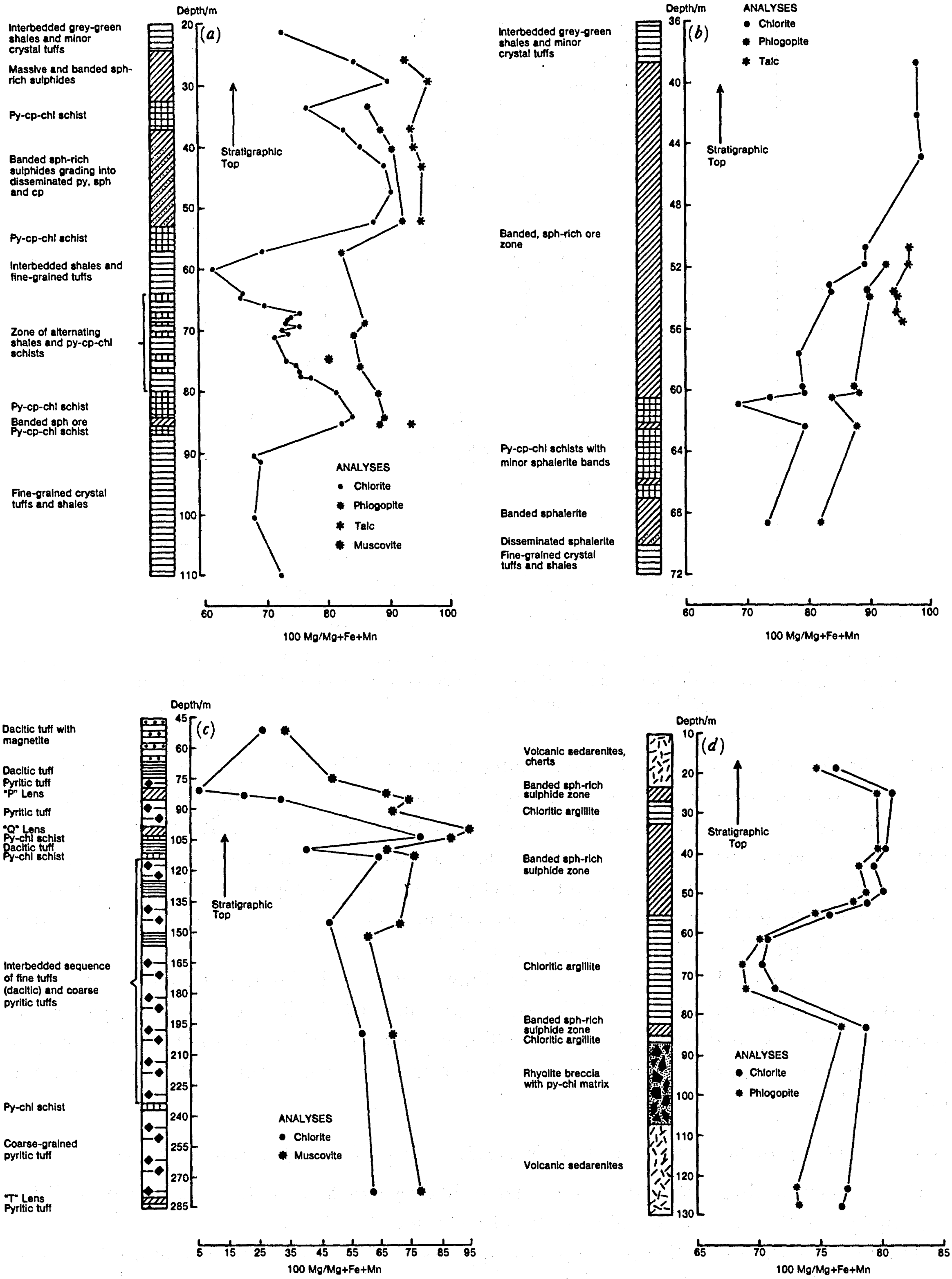


FIGURE 9. Variation in Mg/(Mg+Fe+Mn) ratios of coexisting bedded phyllosilicates in two diamond drill cores from ((*a*) and (*b*)) the Woodlawn stratiform sulphide occurrence near Goulburn, New South Wales, and from (*c*) those of Colo Creek, New South Wales and, (*d*) Que River, Tasmania. (After McLeod & Stanton 1984.)

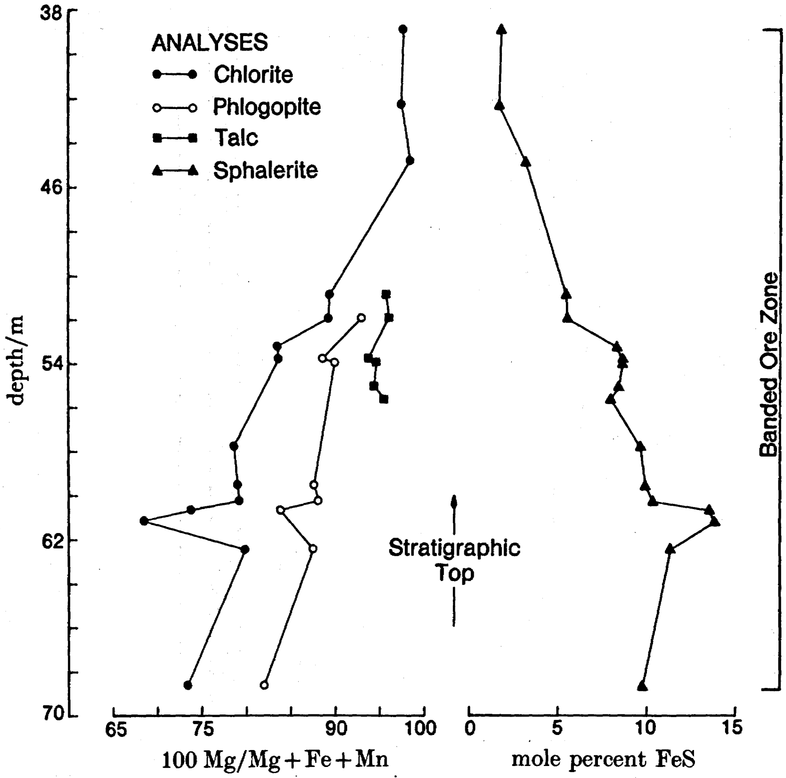


FIGURE 10. Variations in Mg/(Mg+Fe+Mn) ratios of coexisting bedded phyllosilicates and corresponding changes in the iron content of intimately associated bedded sphalerite in diamond drill core across the Woodlawn sulphide horizon (from McLeod & Stanton 1984).

Fe_2O_3/Al_2O_3; others, however, show no zoning detectable either under the microscope or by the use of electron microprobe. One notable feature is a strong tendency to develop 'mass textures' in which large numbers of crystals are involved in a single zone pattern. Each crystal is zoned only on one side of its body, this asymmetrical zoning linking from one crystal to another around the outer sides of curved to rounded clusters of crystals. The whole is very reminiscent of similar shared zoning in the rounded, polycrystalline bodies of pyrite commonly referred to as 'colloform pyrite' of many stratiform ores.

It may be proposed that these polycrystalline, colloform-looking, rounded aggregates of grandite are indeed what the analogy suggests: colloform bodies of garnet developed by substantially free growth at and below the sediment–water interface, substantially by the same kind of authigenic process responsible for the formation of colloform pyrite, sphalerite and other sulphides.

(vii) *Grossular-andradite and hydrograndite in unmetamorphosed and very-low-grade terranes*

Grossular-andradite (grandite) and related hydrogarnets have been observed in little-metamorphosed rocks from a wide variety of localities.

The first description of this phenomenon appears to have been that of Banno (1964) who noted andradite associated with chlorite in pseudomorphs after olivine in basic lavas of the lowest grade ('slightly metamorphosed basalt of zone A_1'; 1964, p. 275) of the Sanbagawa schists of the Bessi-Ino District of Japan. Smith (1969), studying the burial metamorphism of

Ordovician volcanogenic units along the Molong Geanticline in the Lyndhurst district of New South Wales, observed small grains of hydrogarnet in rocks of the prehnite–pumpellyite zone of that area. He noted that the hydrogarnet occurred with chlorite as pseudomorphs after mafic minerals, as a replacement of glass in some volcanic breccias, and as vesicle fillings in some porphyritic basalts. Jolly (1970) in describing burial metamorphism of Cretaceous intermediate lavas and pyroclastic rocks of south central Puerto Rico, considered, *inter alia*, the progressive alteration of the original feldspars and olivines of the volcanic lavas and pyroclastics. He noted that abundant chlorite was the principal early alteration product of olivine, and that commonly associated with this chlorite were sphene and hydrogarnet, both of which occurred as imperfect spheres with diameters up to 0.01 mm.

Yakovleva (1970) described abundant grandite garnet in bedded arrangement in unmetamorphosed jaspers occurring within basic lavas ('greenstones') of the Lower Devonian succession of the Southern Urals. Garnet had been known previously in these rocks, but because of its fineness and very widespread nature, had been loosely identified as 'clayey material'. It occurs most abundantly as minute dark granules 1–3 μm in diameter (occasionallly 5 μm), and in the banded (bedded) jaspers; beds relatively rich in garnet alternate with those that are almost totally devoid of it. In the light of my work (see later section on precursors to grandite) it is interesting to note that the garnets described and illustrated by Yakovleva were black and in large part opaque under the microscope. She also noted of the garnet that 'When illuminated from the side, it is white and flocculent' (1971, p. 136). In some areas Yakovleva found the garnets to be rather coarser (up to 0.05 mm) and to occur as 'skeletal dendritic aggregates'. A recalculated analysis indicated the grandite to be approximately 74% andradite, 13% grossular and 13% spessartine.

In his petrological and geochemical study of spilites and associated volcanogenic rocks of St. John, U.S. Virgin Islands, Hekinian (1971) carried out detailed observation of 1180 ft of diamond drill core which intersected a total of 950 ft of altered mafic (spilitic) lavas of the Water Island Formation of northern St. John. These mid-Cretaceous lavas have undergone no more than mild burial metamorphism (prehnite–pumpellyite–actinolite) and in spite of alteration they retain much of their original igneous texture and undeformed vesicularity. Hekinian notes that in addition to the major minerals, the spilites contain 'minor amounts of prehnite, pumpellyite, sphene, hydrogarnet, actinolite and micas...' (1971, p. 663). He figures (1971, figure 4 [A]) small garnets set in chlorite, which in turn fills the numerous undeformed vesicules within the well-preserved primary intersertal groundmass of the lava.

In a later contribution on regional metamorphic zonation in the Abitibi region of Ontario, Jolly (1974) noted the presence of 'hydrogarnet' in all three of the burial metamorphic zones delineated, in ascending order of apparent grade, chlorite, prehnite and pumpellyite. The host rocks – basic to intermediate lavas and pyroclastics – were undeformed and incompletely altered, exhibiting relict clinopyroxene and plagioclase and, in the rhyolitic lavas, traces of relict igneous biotite. Olivine phenocrysts of the more basic lavas were generally degraded to chlorite, and matrices were devitrified and usually heavily chloritized. Jolly provides little comment on the properties or mode of occurrence of the hydrogarnet, but notes that within the prehnite zone, glassy rocks with abundant amygdules are especially prone to alteration. The most common alteration associations here are chlorite–albite–prehnite and chlorite–albite, both ± quartz, albite, haematite, sericite, hydrogarnet and sphene.

K. A. W. Crook & G. P. Kelly (personal communication, 1975) observed abundant 'hydrogrossular' in the unmetamorphosed sediments of the Namoi Formation of New South Wales, referring to it as 'an unequivocal occurrence of hydrogarnet as an authigenic mineral in a burial metamorphosed plagioclase arenite interbedded in mudstone...' (1975, p. 1).

The Namoi Formation is a unit of the Burindi Series, a component of the Carboniferous marine and marine volcanic sequence of the Werrie Basin in northern New South Wales. The Burindi Series consists of a basal marine conglomerate some 400 ft thick, changing upwards to buff-coloured sandstones, and then to well-bedded dark blue, marly mudstones and tuffs and finally laminated olive-green mudstones. Oolitic and fossiliferous limestone lenses and bands occur in the upper parts of the sequence, which is clearly near shore marine.

The Carboniferous sequence as a whole has undergone only slight warping and mineral textures and assemblages are essentially diagenetic.

Studies of some of the feldspathic arenites of the Burindi sequence by Crook & Kelly (1975) revealed the assemblage albite–calcite–laumontite–grossularite–chlorite, these authors noting that the likelihood that hydrogrossular of diagenetic origin would be found in due course had been predicted just a little earlier by Bliskovskii (1968). The garnet occurs as colourless to transparent, sharply faced, equant euhedra from 0.06 to 0.32 mm in diameter, with a mode at 0.2 mm, and constitutes a trace to 5% (by mass) of the rock. The framework of the latter consists of plagioclase (*ca.* An_5) with minor volcanic rock fragments and biotite. Abundant calcite, minor chlorite and laumontite constitute the major part of the cement, and minor veins of laumontite and stilbite transect the rock. The garnet euhedra occur as a further component of the cement, often as clusters at the contacts between albite grains, against which they show sharp contacts. The garnet is generally in contact with calcite and sometimes also with laumontite. There is no evidence of disequilibrium between the phases. An electron probe analysis (Crook & Kelly 1975) is given in table 4.

Although Crook & Kelly referred to the mineral as hydrogrossular it might be termed a grandite garnet with grossular dominant and a small hydrous component.

Leitch (1975), in examining the zonation of low-grade regional metamorphic rocks of the Upper Palaeozoic Nambucca Slate Belt of north eastern New South Wales, noted the isolated occurrence of garnet in basic lavas bearing the indicator assemblages prehnite–pumpellyite and prehnite–actinolite. The basaltic lavas concerned showed a variety of relict textures ranging from perhyaline to intergranular or intersertal, and from porphyritic to essentially equigranular. Doleritic rocks consisted of hypidiomorphic granular aggregates of clinopyroxene and albitized plagioclase that in many cases exhibited ophitic and sub-ophitic textures. Metamorphic minerals, other than those in veinlets, occurred in patches replacing small areas of the rocks regardless of mineralogy, and as selective replacements of specific magmatic products. The garnets, the nature of which Leitch did not define, were noted in two specimens from the second lowest of four low-grade metamorphic zones. In one, the garnet occupied amygdules in association with prehnite and pumpellyite, and in the other garnet crystals, with epidote, occurred in chlorite patches in an altered dolerite. The very fine grain size and small amount of the garnet precluded its determination.

Coombs *et al.* (1977) found garnets ranging from almost pure andradite through a spectrum of grandites and hydrogarnets in very low-grade regionally metamorphosed rocks of southern New Zealand. The garnets, which commonly were framboidal in habit, were found to be widespread in basic volcanic rocks (both lavas and minor intrusions) and volcanic breccias and sandstones, where these had undergone only very low-grade burial metamorphism:

TABLE 4. ELECTRON MICROPROBE ANALYSIS OF GROSSULAR GARNET OF THE NAMOI FORMATION, NEW SOUTH WALES

SiO_2	38.39
TiO_2	0.33
Al_2O_3	19.08
Cr_2O_3	0.03
Fe_2O_3	4.95
FeO	0.21
MnO	2.29
MgO	0.22
CaO	34.31
Na_2O	nil
K_2O	nil
H_2O^+ H_2O^-	0.20
total	100.01

number of ions on the basis of 12(O)

Si	2.96	
Ti	0.02	2.98
Al	1.73	
Cr	—	2.02
Fe^{3+}	0.29	
Fe^{2+}	0.01	
Mn	0.15	3.00
Mg	0.01	
Ca	2.83	

Analyst: K. A. W. Crook.

prehnite–pumpellyite, pumpellyite–actinolite, and possibly extending into the zeolite facies. In one area andradite occurred as a component of an andradite quartzite. Coexisting phases included, variably, iron-rich epidotes, pumpellyite, prehnite, actinolite, chlorite, quartz, albite, calcite and, in the andradite quartzite, stilpnomelane. As in the case of the Russian garnets described by Yakovleva (1970), those figured by Coombs *et al.* are commonly dark, suggesting the presence of material similar to that investigated by the present writer and considered in the later section on precursors.

In a context rather different from the foregoing Tulloch (1979) investigated secondary Ca–Al silicates developed as low-grade alteration products of granitoid biotite. He found that in granitoids (Devonian/Carboniferous; Cretaceous) of the Victoria Range of the South Island of New Zealand, a number of Ca–Al silicates, including grandite garnet, epidote, pumpellyite and prehnite, were very widespread as low-grade alteration products of biotite, occurring as elongate lenses and pods within the latter. Such lenses of grandite garnet commonly exhibited a prominent parting parallel to the cleavage of the biotite host, presumably inherited from the cleavage of this host. Compositions were generally intermediate between grossular and andradite and in some cases there was a small hydrogarnet component. Tulloch concluded that the alteration process responsible for the development of the garnets and associated minerals was deuteric, and that, in contrast to the prehnite–pumpellyite facies of the nearby Wakatipu metamorphic belt which developed in a high- to intermediate-pressure facies, the prehnite–pumpellyite (and associated grandite) facies alteration in the Tasman Belt granitoids was developed at considerably shallower depths under relatively low-pressure conditions.

Duggan (1986), in a contribution on Fe-rich Ca–Al silicates developed in volcanic detritus occurring in the interstices of basaltic pillow lavas of the Permian Takitumu Group, western Southland, New Zealand, noted the development of babingtonite, Fe-rich prehnite, grandite garnet, quartz, calcite, chlorite and pumpellyite. On the basis of textural and chemical evidence Duggan concluded that 'the babingtonite, Fe-rich epidote, calcite and quartz formed from hydrothermal solutions by direct precipitation in open cavities and by replacement of higher-temperature silicate phases (in particular plagioclase and basaltic glass) in a shallow marine volcanic environment. During subsequent burial and low-grade metamorphism babingtonite was partially replaced by prehnite, less Fe-rich epidote, grandite and chlorite.' (1986, p. 657). Duggan noted that the garnet occurred as very small equant grains (10 μm) in almost every thin section examined, and that it was locally abundant. The grains were commonly dispersed through babingtonite, especially where this appeared to have formed by replacement of volcanic glass or plagioclase, rather than filling vesicles. Elsewhere the garnet occurred as framboidal aggregates up to about 0.5 mm in diameter, usually enclosed in quartz. It was relatively constant in composition around And_{70}–Gro_{30}, and generally gave low analytical totals indicating a hydrous component or the presence of very fine fluid inclusions.

(*b*) *Mineral occurrences of low-temperature régimes of young unmetamorphosed rocks*

(i) *The Green River Formation*

This remarkable sequence of sediments, middle early to early middle Eocene in age, was laid down in four closely related shallow basins within Lake Gosiute which in turn formed part of a string of interior lakes running through Wyoming, Utah and Colorado in Tertiary time. The formation, which accumulated over a period of about 4×10^6 years, is characterized by buff, brown, white and light grey limestone, marlstone and shale (Wolfbauer 1971). Locally, oil shale, trona and associated salts, dolomitic marlstone, volcanic ash, limy sandstone and algal deposits are also prominent. According to Wolfbauer, the clear and for the most part well-oxygenated water of Lake Gosiute was highly favourable for biological activity. Fossil fish, gastropods, pelecypods, ostracodes and algae are preserved in abundance, and fossil crocodiles, turtles, birds and insect larvae are found in the near-shore facies sediments. In the deeper, more stagnant waters of the lake, bacteria flourished; these, together with algae and planktonic organisms, yielded a sapropelic ooze that constituted the precursor to the present oil shale. Climatic changes caused expansion and shrinkage of the lake, with consequent accumulation of evaporitic sediment during the drier periods.

These very young deposits have not been affected by compressional tectonism or metamorphism and their features are quite simply those of lacustrine sedimentation and early diagenesis.

The formation is now famous for its assemblage of authigenic minerals, of which over 70 have been identified (Milton 1971). They include sulphides, halides, a large group of Na–Ca–Mg–Ba–Fe–Sr carbonates, sulphates, phosphates and an extensive suite (at least 28 species) of authigenic silicates. Table 5 lists several species of relevance to the present contribution.

It is clear that of the first group of minerals, albite and orthoclase (and analcite) are present in enormous absolute abundance. Pyroxene and amphibole are not abundant (although they are widespread) and biotite is rare – but these minerals are there – as authigenic components of what is clearly a very low-temperature assemblage.

TABLE 5. AUTHIGENIC SILICATES OF THE GREEN RIVER FORMATION, WESTERN U.S.A.

(From Milton 1971.)

(a) common 'rock-forming' silicates	
albite	ubiquitous and abundant[a]
orthoclase	ubiquitous and abundant
analcite	ubiquitous and abundant
pyroxene (acmite)	local and never abundant
amphibole (magnesio–riebeckite)	local and never abundant
talc	local and sparse
chlorite	local and sparse
biotite	local and extremely sparse
hydrobiotite	local and extremely sparse
(b) associated clays and zeolites	
illite	ubiquitous and dominant
kaolinite	locally abundant
montmorillonite	locally abundant
sepiolite	local and never abundant
stevensite	local and sparse
harmotome	local and sparse
natrolite	local and sparse
clinoptilolite–mordenite	local and sparse

[a] Abundances as given by Milton (1971).

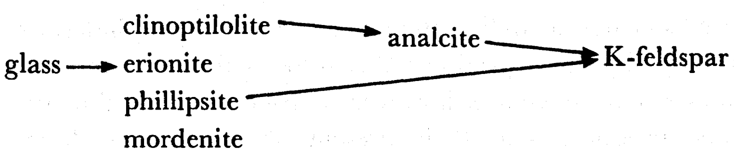
Two facts are of significance in the present context: that (1) minerals such as pyroxene, amphibole, K-feldspar and biotite have formed authigenically at temperatures too low to dissipate associated oil and (2) these minerals occur in association with still well-preserved clays and zeolites.

(ii) *Other alkaline lake deposits of western U.S.A.*

The authigenic development of K-feldspar from volcanic glass via zeolites and analcite is well-illustrated by some of the ancient lake deposits of Arizona and California (Surdam & Sheppard 1978).

The Pliocene Big Sandy Formation of Arizona and the Pleistocene Lake Tecopa deposits (which have been subject to only very shallow burial) of eastern California show well-developed diagenetic mineral zoning (or facies) parallel to the former lake margins. The tuffaceous sediments closest to the old lake shores are characterized by the preservation of fresh glass and are termed by Surdam & Sheppard the 'fresh-glass facies'. The tuffs in the central parts of the lake basins are characterized by K-feldspar and/or searlsite ($NaBSi_2O_6 . H_2O$) and are termed the 'K-feldspar facies'. Those between the fresh glass and K-feldspar facies are characterized by zeolites and are termed the 'zeolite facies'.

This zonation reflects progressive change brought about by the action of saline, alkaline, pore waters on the volcanic glass and then in turn on the zeolites and analcite to finally generate abundant authigenic K-feldspar according to the following scheme (after Surdam & Sheppard 1978).



The resulting K-feldspar, a common constituent of high-grade metamorphic mineral assemblages, is in this case an early-formed, low-temperature, diagenetic product.

(iii) *The Spencer Formation, Corvallis, Oregon*

This, like the Green River Formation, is Eocene in age. It is, however, of normal marine, not lacustrine, origin, and as indicated by lithologies, sedimentary structures and the presence of abundant shallow-water fossils, was deposited in a near-shore zone of current action. Like the Green River sediments, those of the Spencer Formation have not been involved in metamorphism and their features are entirely sedimentary/diagenetic.

According to Enlows & Oles (1966) they contain three principal authigenic silicates: thomsonite, actinolite and clinopyroxene. Analcite is a rare associate. These authors noted that

> silicates such as amphibole and pyroxene long have been considered to be characteristic of magmatic or metamorphic environments rather than sedimentary ones. Where found as authigenic minerals in a sedimentary rock, the environment commonly is assumed to have been of an unusual type, such as the alkaline-brine environment in which were developed the minerals of the Green River assemblage.... It was with some surprise, therefore, that the writers discovered authigenic amphibole and pyroxene which have crystallized as cementing materials in a fossiliferous marine sedimentary rock of an otherwise normal and undistinguished nature (1966, p. 1918).

They emphasized the completely unmetamorphosed nature of the late Eocene rocks by noting that the sandstone beds in which the authigenic amphibole and pyroxene occurred were potential petroleum reservoirs.

Both minerals were closely associated with the thomsonite, the actinolite appearing as columnar and fibrous aggregates and reticulated masses of crystals up to 0.2 mm long, the clinopyroxene as square or octagonal cross sections up to 0.1 mm across or as short laths up to 0.5 mm long. Textural evidence for authigenesis was clear: molluscan fragments, their shapes well-defined, generally retain no original material, but consist entirely of a pseudomorph of thomsonite, actinolite and clinopyroxene. The silicates either fill cavities left by dissolution of the shells, or replace the latter.

Enlows & Oles observed that the best-preserved examples of the authigenic amphibole and pyroxene occur in a graded sedimentary unit rich in molluscan fossil fragments, basic volcanic glass and zeolite concretions. Their reconstruction of the diagenetic environment indicated a temperature of little more than 60 °C, pore solutions somewhat less saline than seawater, a pH slightly less than 7.0 and an oxidation–reduction (redox) potential (Eh) near -0.2.

(*c*) *Mineral occurrences in present ocean-floor sediments*

Chlorite, muscovite and talc have all been found as components of deep sea-floor hydrothermal aprons accumulating at the present day, and their direct precipitation by chemical sedimentary and authigenic processes is thus well-established (see, for example, Costa *et al.* 1983; McLeod & Stanton 1984; Aggarwal & Nesbitt 1984). The recent discovery of substantial quantities of talc precipitating in the hydrothermal aprons of sea-floor vents in the Guaymas Basin, Gulf of California (Lonsdale *et al.* 1980), is noteworthy and indicates that chemically deposited silicates, as well as the more spectacular sulphides, oxides and sulphates, may be volumetrically important products of sea-floor exhalative activity.

All of the silicates noted above are, however, well-known as sedimentary/diagenetic/low-grade metamorphic products, and their present observation as direct, low-temperature precipitates in modern sediments cannot be regarded as a particularly surprising or significant development. On the other hand recent sampling of the sea-floor, particularly (although not exclusively) in hydrothermal or volcanic areas, is beginning to yield examples of spessartine, andradite–grossular, amphibole and pyroxene forming through authigenic processes. Where such minerals occur in metamorphic contexts they are regarded as distinctly 'higher-grade' products than chlorites, muscovites and talc, and their discovery in young unlithified to semi-lithified oozes is therefore highly noteworthy and perhaps of considerable significance to metamorphic petrogenesis.

(i) *Spessartine*

Donnelly & Nalli (1973) described two occurrences of aluminous garnet in sediments drilled in holes 146 and 153 of leg 15 of the Deep Sea Drilling Project. This leg extended, in an essentially E–W direction, almost the full width of the Caribbean and provided a sampling of the axial region of the basin.

The garnets of hole 146 and, tentatively, some of those of hole 153, were identified as authigenic. Other minute garnets of hole 153 were suspected to be of volcanic origin.

The authigenic garnets of hole 146 were found as minute rectangular plates, the largest of which were approximately 50 μm × 30 μm. Mean size was about 20 μm largest dimension. The garnet showed growth striations and appeared to have grown as hopper crystals: it was golden yellow to brown in transmitted light, gave very good X-ray powder patterns and had a unit cell edge of 11.607 ± 0.006 Å†, within observational limits, the value for spessartine.

Donnelly & Nalli commented: 'The occurrence of spessartine garnet, or of aluminous garnet rich in the spessartine end member, in lowest-grade metamorphic rocks is well known...the present sample could indicate that spessartine may actually form during authigenesis rather than earliest metamorphism' (1973, p. 935).

(ii) *Grossular–andradite*

Abundant garnets of hydrogrossular–hydroandradite composition (table 6) have been described from Deep Sea Drilling Project site 251, southwest branch of the Indian Ocean Ridge, by Kempe & Easton (1974) and Cook *et al.* (1974). The garnets occur in a micrite (unit 5 of the stratigraphic sequence revealed in the core) derived from a pelagic, coccolith-bearing, foraminiferal ooze constituting the lowest 18 m of a 450 m thick sequence of nannoplanktonic ooze and chalk. The overlying units 1–4 consist entirely (Kempe & Easton 1974) of white, bluish-white or yellowish nannoplankton ooze and chalk, containing between 0.5 % and 1.1 % of detrital and clay minerals and usually 98–99 % calcium carbonate. Burrows, mottling, and framboidal and finely disseminated pyrite are common in these oozes.

Unit 5, which directly overlies the basement basalt, contains virtually no mineral other than recrystallized calcite and garnet, the latter constituting around 20 % (by mass) of the whole. The garnet crystals are substantially dodecahedral, ranged from 1.5 to 4.5 μm across and averaged 2–3 μm. Colour is a pale honey yellow and the X-ray pattern indicates very well crystallized material; $a = 1.19265$ nm, $n = 1.764$ and SG = 3.54.

Kempe & Easton (1974) concluded that the garnets are products of some kind of pre-lithification metasomatism; that sea-water convection involving not only the basement basalt but also the overlying ooze of unit 5 (at a time before the deposition of units 1–4) transferred

---

† $1\ \text{Å} = 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$.

TABLE 6. CHEMICAL ANALYSIS OF GARNET FROM DSDP SITE 251

SiO_2	38.18
TiO_2	0.42
Al_2O_3	11.89
Cr_2O_3	0.01
Fe_2O_3	11.69
FeO	0.64
MnO	0.26
MgO	1.47
CaO	38.87
Na_2O	0.10
K_2O	0.02
H_2O^+	n.d.
H_2O^-	nil
total	99.55

number of ions on the basis of 12(O)

Si	3.02	3.02
Al	—	
Al	1.11	
Cr	—	1.81
Fe^{3+}	0.60	
Ti	0.03	
Mg	0.18	
Fe^{2+}	0.05	
Mn	0.02	3.23
Ca	2.96	
Na+K	0.02	

Abbreviation: n.d., not determined. Analyst: A. J. Easton (Kempe & Easton 1974).

SiO_2, Al_2O_3 and Fe_2O_3 from the basalt to the ooze, which provided Ca and an appropriate régime for the nucleation and growth of garnet.

However, the impression may be gained from the literature (Kempe & Easton 1974; Easton *et al.* 1982) that metasomatism has been invoked at least partly as a result of preconceptions on the part of the investigators. Garnets are seen as 'distinctly metamorphic' minerals and hence their development as authigenic products has been difficult to contemplate. Such a view might be said to be supported by the oxygen isotope evidence, which indicates temperatures of formation around 170 °C. The authors (Easton *et al.* 1977) observe that such a 'temperature of formation, *ca.* 170 °C, is far too high for such a process to occur in an oceanic environment' (1977, p. 265). However, the now numerous observations made from submersibles since 1979 have demonstrated that temperatures of over 300 °C are attained in the immediate vicinity of some sea-floor hydrothermal vents and temperatures of 170 °C are doubtless commonly achieved at and beneath the sediment–water interface in such areas. In fairness it must be noted that Kempe & Easton remark that 'although the garnets are believed to be metasomatic they must be considered in the context of authigenesis...' (1974, p. 593), and they proceed to consider other possible cases of authigenic garnet growth that might indicate processes by analogy. None the less they consider the site 251 garnets to result from hydrothermal introduction of materials and consequent metasomatic replacement of portion of the carbonate of the then unconsolidated ooze.

On the evidence it appears that there remain two possibilities for the formation of the garnets: (1) that their Si, Al and Fe were introduced, that they grew by combination with and replacement of the unconsolidated ooze, and that they are now confined to unit 5 because their formation occurred before the deposition of unit 4, all as deduced by Kempe & Easton and their collaborators, or (2) that the garnets were deposited directly by sea-floor precipitation and/or by authigenesis in hot oozes accumulating in the vicinity of sea-floor hydrothermal and exhalative activity, and that they are now confined to unit 5 because it was only during the formation of this member that the relevant conditions prevailed.

Whichever is the case, there seems no doubt that the garnets grew at relatively low temperatures, *ca.* 170 °C, and before the consolidation of the host material: a foraminiferal ooze. They thus grew in an authigenic context and are hence now in existence, as potential simple precursors, long before any regional metamorphism that may in the future affect the sediments in which they developed.

More recently small quantities of authigenic andradite have been detected in sediments of the Red Sea brine pools (Zierenberg & Shanks 1983). These garnets appear among the accessory minerals of the haematite–magnetite oozes of drill core 18P. No information on composition is available, but the garnets have developed in what is still an unlithified ooze, and in an environment where authigenic haematite is in the process of reduction to authigenic magnetite.

(iii) *Pyroxene and amphibole*

In view of the observations of Enlows & Oles (1966) on what is clearly authigenic pyroxene and amphibole in the Eocene Spencer Formation of Oregon it was to be expected that these minerals would ultimately be found as authigenic products in modern sediments. This has duly transpired (Zierenberg & Shanks 1983), and their occurrence as major to trace constituents of the Red Sea (Atlantis II Deep) oozes is now well documented.

Occurrences noted so far are in the southwest basin, close to the passage to the west basin, where the iron oxides of the primary 'Central Oxidic' zone metalliferous oozes have crystallized to haematite and coarse-grained magnetite (Hackett & Bischoff 1973; Zierenberg & Shanks 1983). Here clinopyroxenes have been found associated with the haematite–magnetite beds of three cores: 17P, 18P and 492K. Zierenberg & Shanks observe that the pyroxenes occur as radiating or bow-tie aggregates of elongated prismatic crystals 1–3 mm in length, and as euhedral prismatic crystals intergrown with magnetite. Extensive electron microprobe analysis gave pyroxene compositions ranging from low Al aegirine augite to end-member hedenbergite (see Zierenberg & Shanks 1983, fig. 4).

The same authors also observed very fine-grained acicular to asbestiform actinolite associated with pyroxene in cores 17P and 492K. Very minor amounts of the amphibole also occur as overgrowths on pyroxene grains, apparently reflecting the evolutionary trend of the sediment pore fluid to a progressively less oxidizing state. Intergrown with some of the actinolite of core 492K are minor amounts of the uncommon mineral ilvaite ($CaFe_2^{2+}Fe^{3+}Si_2O_8(OH)$), earlier noted in the Atlantis II Deep sediments by Pottorf & Barnes (1978) and Weiss *et al.* (1980).

(iv) *K-feldspar*

The authigenic development of K-feldspar, commonly in association with authigenic clays and zeolites, in modern marine sediments is well known and documented. For example, Donnelly & Nalli (1973), in the Caribbean study already referred to, found abundant

K-feldspar in both pelagic and turbiditic sequences of hole 146. The relevant smear slides showed plagioclase crystals (presumably authigenic albitic material), more or less abundant phillipsite, and K-feldspar occurring as very small, low refractive index (RI), colourless, formless, shreds that were identified by X-ray diffractometry. Donnelly & Nalli noted that phillipsite and clinoptilolite are common zeolites of the Caribbean sediments and that erionite was found in one core. These all occur with authigenic clays with a variety of silica, sulphide, sulphate and other materials. The authigenic K-feldspar is clearly a component of an extensive low-temperature authigenic assemblage.

(*d*) *Mineral occurrence in unmetamorphosed alteration products: the hydrothermal clay deposits of Japan*

During the past 30 years (see, for example, Sudo *et al.* 1957) increasing attention has been paid to hydrothermal alteration and clay–mica–zeolite formation associated with the Miocene Kuroko ores of Japan. This is, however, only one facet of an extensive pattern of hydrothermal alteration developed in Cretaceous, Miocene and Plio-Pleistocene volcanic and associated rocks of the Japanese islands: alteration that has led to the development of extensive clay deposits that now constitute the basis of the country's ceramics industry. The two principal commercial 'clay types' are *Roseki*, which consists predominantly of pyrophyllite, sericite, quartz and kaolinite, and *Toseki*, which is composed chiefly of sericite, quartz and kaolinite.

These, and other, related, clay types have formed by volcanic–hydrothermal alteration of andesitic, dacitic and rhyolitic materials; principally pyroclastic beds, often with a substantial glassy component. A few result from hydrothermal alteration of basaltic rocks.

Some of these hydrothermal clays are considerably more aluminous than immediately indicated by the composition given above, and as well as possessing substantial quantities of kaolinite, also contain varying amounts of halloysite, nacrite, dickite, diaspore, gibbsite, boehmite, dioctahedral (i.e. high Al) chlorites and alunite. In addition, and of particular significance in the present context, some of these high-Al assemblages include corundum and andalusite.

At the Yano–Shokoxan deposit the pyrophyllitic clay has developed by the hydrothermal replacement of a specific volcanic unit of the local Cretaceous terrestrial succession. This unit consists, where unaltered, of dacitic lapilli tuff, spherulitic andesite and andesitic tuff (Fujii *et al.* 1976). According to Matsumoto (1968), the alteration is zoned: an inner pyrophyllitized zone containing as minor components diaspore, corundum and kaolin minerals; an intermediate siliceous pyrophyllitized zone with haematite and/or pyrite; and a 'weakly altered' outer zone. Kinosaki (1963) and Matsumoto (1968) considered the alteration to have resulted from volcanic exhalative activity very close to the contemporary surface. Of the Mitsuishi pyrophyllite deposits Fujii *et al.* (1976) note that '...generally, the whole altered rocks are distributed concordantly to the original rock beds...and they are covered by almost unaltered acid pyroclastics.' (1976, p. 7.)

According to Fujii *et al.* (1976) the hydrothermally altered Miocene volcanic rocks of the Goto area of Kyushu may be ranked with the Mitsuishi and Shokozan as one of the principal sources of pyrophyllite in Japan. Some 10 pyrophyllitic bodies occur within volcanic sediments and an associated porphyritic intrusive, and at the time (1976) these deposits provided over 90% of total diaspore production in Japan. Principal Al minerals of the alteration zones are pyrophyllite and diaspore, accompanied by corundum, sericite, dumortierite $(Al,Fe)_7BSi_3O_{18}$, and andalusite.

Finally, among the Plio-Pleistocene and Recent deposits, the pyrophyllitic bodies of the modern Matsukawa geothermal area (the first geothermal area exploited for the generation of electric power in Japan) contain, as major aluminous components, pyrophyllite, andalusite, diaspore, alunite and kaolinite (Fujii *et al.* 1976).

Although the development of andalusite as a hydrothermal alteration product is certainly not out of keeping with the experimentally determined stability field of this mineral, its formation, with corundum, under near-surface 'exhalative' conditions as evidenced by the Japanese deposits is noteworthy. For the world as a whole, andalusite occurs chiefly as a contact metamorphic, less commonly a low-pressure regional metamorphic, mineral. Corundum is found principally as a constituent of high-Al igneous rocks (e.g. nepheline syenites), contact-metamorphosed high-Al sedimentary rocks and, occasionally, of regional metamorphic (granulite facies) terranes. That is, both minerals are customarily thought of in a contact metamorphic or intrusive igneous context. The Japanese occurrences, on the other hand, reveal them as near-surface phenomena in some cases: products, together with kaolinite, halloysite and other clays, diaspore, boehmite, gibbsite and alunite, of aluminous alteration at hydrothermal temperatures and pressures of little more than atmospheric.

(*e*) *Mineral occurrences in geothermal systems*

Since the contribution of Muffler & White (1969) on the currently active metamorphism of Upper Cainozoic sediments intersected by bore-holes in the Salton Sea Geothermal Field and the Salton Trough of southeastern California, there have been a number of studies of the metasomatic development of metamorphic minerals in present-day areas of geothermal activity (see, for example, McDowell & Elders 1980; Cavarretta *et al.* 1982; McDowell 1983; Bird *et al.* 1984; Schiffman *et al.* 1984). A range of silicates, including clays and zeolites, chlorite, prehnite, epidote, amphibole, clinopyroxene, garnet (chiefly grandite), vesuvianite and wollastonite, have been found to develop at comparatively low temperatures (*ca.* 250–350 °C) and very low hydrostatic pressures.

The literature on this subject is now too extensive and complex for brief, but adequate, summary here. However, among recent contributions, Cavarretta *et al.* (1982) note that in the hottest parts of the Larderello–Travale geothermal field of Italy (250–350 °C) processes of sediment alteration and metasomatism by the circulating geothermal fluids have produced an assemblage including the silicates K-feldspar, epidote, chlorite, sphene, prehnite, datolite, diopside–hedenbergite solid solutions, tremolite–actinolite solid solutions, albite and mica. In their study of the assemblages of the Cerro Prieto geothermal field of southern California, and in their comparison of this with other geothermal fields, Bird *et al.* (1984) noted that '...wairakite occurs to temperatures of 250 °C to slightly greater than 300 °C. The lower temperature occurrences of prehnite, epidote and possibly ferroactinolite overlap with wairakite. Occurrences of clinopyroxene, garnet and wollastonite are predominantly restricted to temperatures greater than 300 °C'(1984, p. 676). In summarizing the metasomatic effects observed in the Cerro Prieto sediments, Schiffman *et al.* (1984) described '...an example of authigenic mineral zonation in the Cerro Prieto field and suggest that a paragenesis of calc-silicates crystallizing at temperatures less than 370 °C represents an extremely low-pressure metamorphic facies series that spans the zeolite to amphibole facies' (1984, p. 12).

4. Evidence concerning development of regional metamorphic minerals from complex precursors

(*a*) *Evidence from natural occurrences*

(i) *Muscovite*

The growth of larger, crystallographically well-ordered, stoichiometric flakes of muscovite from extremely fine-grained impure (phengitic) 'sericitic' material is well known to every microscopist who has worked on metamorphic rocks. This has led to the tacit assumption that at least much of the muscovite of metapelitic rocks has arisen from earlier illitic clays, and the present author (Stanton 1976) suggested that muscovite of the metapelites enclosing the small Broken Hill (New South Wales) banded iron formations might have arisen through the sequence illite → hydromuscovite → muscovite. Since then there has been considerable investigation of relations between muscovite polymorphism and grade of metamorphism at very low grades.

Recently Hunziker *et al.* (1986), using illite and muscovite concentrates from Triassic and Permian claystones, shales, slates and phyllites sampled along a cross section from the diagenetic zone of the Alpine foreland through the prehnite–pumpellyite to the lower greenschist facies of the Helvetic Zone of the Central Alps, showed quite unequivocally the development of muscovite directly from illite. They established that several mineralogical and chemical features of the illite are related to the very low range of metamorphic grade as such grade is indicated by illite 'crystallinity'; the disappearance of expandable layers; the replacement of the low-temperature 1Md illite polymorph by the higher-temperature $2M_1$ form; the shift of a dehydration peak in differential thermal curves; an increase in the total layer charge and of the K-content in the interlayer position; and a decrease in the chemical variability of individual mica grains. The authors showed that K–Ar, Rb–Sr and $^{40}Ar/^{39}Ar$ relations in the illites showed quite substantial changes before any crystallographic reorganization as indicated by the $1Md \rightarrow 2M_1$ polymorphic transformation.

Hunziker *et al.* considered that Ar redistribution and loss involved three stages: a general diffusion of Ar with respect to K; a reordering process that produced 'progressively more homogeneous repartitioning of Ar and K in the illite structure' (1986, p. 378); further crystal restructuring that began in a few mica layers and continued together with volume diffusive loss until all inherited ^{40}Ar was expelled.

However, in spite of this Ar mobility Hunziker and his co-investigators found no change in ^{18}O and D values from the non-metamorphic illites to the greenschist facies muscovites that, they considered, indicated a crystallographic reordering process that does not break bonds within the tetrahedral and octahedral layers of the mica lattice. They interpreted this as indicating a reordering ('restructuration'; 1986, p. 178) rather than a recrystallization mechanism.

Hunziker *et al.* therefore concluded that the change from illite (the sedimentary/diagenetic precursor) to muscovite (the direct metamorphic derivative) involved the principal processes: (1) argon loss, completed before crystallographic reordering; (2) K increase from 6–8% (by mass) in the diagenetic facies to 8.5–10% (by mass) in the prehnite–pumpellyite facies to 10–11% (by mass) at lower greenschist facies, representing a change of total negative layer charge from 1.2 to 2; (3) a prograde solid–solid transformation from 1Md illite to $2M_1$

muscovite involving a continuous lattice reordering without rupture of the tetrahedral and octahedral bands or change of hydroxyl radicals.

Such an illite → muscovite transformation provides an excellent illustration of the precursor principle as visualized by the present author. Although the illite is probably most appropriately regarded as a complex precursor, it constitutes something of a borderline case. It is clearly more complex than simple grain growth, as in diagenetic albite → metamorphic albite, or simple transformations such as wurtzite → sphalerite, aragonite → calcite, gel SiO_2 → cristobalite → quartz, or goethite → haematite → magnetite. However, it is probably considerably less complex than the proposed siliceous chlorite → almandine garnet or sudoitic chlorite → cordierite transformations.

(ii) *Aluminous garnets of pyralspite type*

The garnets considered under this heading incorporate a wide range of cation compositions, and commonly include occurrences with a large spessartite (MnO) component. However, all are characterized by $Al \approx 20\%$ and by Fe essentially exclusively in the ferrous state and the divalent position, as distinct from the ferric iron in the trivalent position of the grossular–andradite ('grandite') series. The latter are considered in the next section.

Perhaps one of the earlier indications that at least some regional metamorphic almandines might have been derived from a specific pre-existing material was the common and abundant occurrences of beds of 'garnet sandstone' associated with the Pb–Zn orebodies of Broken Hill, New South Wales. This rock is not a 'sandstone' in the normal, sedimentary sense: it is a regional metamorphic rock consisting virtually entirely of almandine garnet (commonly with a large Mn and Ca component), and exhibiting a somewhat friable, 'sandy' nature. The principal impurity is quartz, and there is a whole spectrum of types ranging from essentially pure quartzite, through a wide variety of 'garnet quartzites' to essentially pure, bedded, garnet rocks: the 'garnet sandstone'. (Rocks of this general kind are now known to be well developed in association with a number of exhalite sequences in metamorphosed terranes in other parts of the world, e.g. Namaqualand, in South Africa, and the Pyhasalmi area of Finland.)

Based on the assumption that such metamorphic garnet was produced by reaction between a variety of fine-grained components of a pelitic sediment it has, since the early part of this century, been commonly observed at Broken Hill that it was remarkable that the relevant pelites could have been precisely of an overall composition to produce garnet and nothing but garnet. The clear implication of such questioning has always been that the compositional coincidence was indeed so great as to require special explanation. Until 1976 (Stanton 1976) it had not been suggested that the development of this garnet might have been pre-ordained, or pre-determined, by the prior existence of a single, specific sedimentary/diagenetic precursor mineral, but the occurrence had been regarded as suspicious – in terms of the theory of regional metamorphic reactions – for at least 70 years.

Further suspicions were aroused at Broken Hill by the garnets of the already noted, small ore-associated banded iron formations, members of the Broken Hill lithological spectrum that includes the garnet quartzites and garnet sandstones (see pp. 546, 547, 551).

These 'iron formations' are in fact 'ironstones' in terms of the usage of James (1966). Their chemical composition is virtually identical with that of oxide–silicate facies of the unmetamorphosed Mesozoic ironstones of England and Europe, including the minor quantities of manganese and phosphorus present in both. Mineralogically, the important iron-bearing components of each are oxide and silicate: in the unmetamorphosed ironstones, these are goethite (haematite) and chamosite; in the metamorphosed analogues, they are magnetite and almandine. In view of the compositional similarities of chamosite and almandine (see below) it was thus suspected that, in the Broken Hill rocks, the latter might be a direct metamorphic derivative of the former (Stanton 1976; Stanton & Williams 1978).

As noted earlier, the possibility that almandine might, in particular cases, be derived *in situ* from a specific, pre-existing precursor has been suggested by Berge (1966), Morey *et al.* (1972), Kennan (1972), Stanton (1976), and Valliant & Barnett (1981). Berge, Morey *et al.* and Stanton pointed to chamosite as the material probably involved. Kennan postulated 'original ferromanganese concretions', and Valliant & Barnett suggested primary materials analogous to modern hydrothermal sea-floor Mn nodules. Earlier, and in a less direct way, Brindley (1954) had pointed to the possibility that 'a primary iron silicate mineral' had played an important role in the development of the garnets of the Leinster Granite aureole. Yoder (1957) and Miyashiro (1965), among others, had suggested that almandine formed by a reaction of chlorite with quartz, and Yoder (1957) went so far as to comment that 'most field investigators' believed almandine garnets to form by such a process. In the same contribution Yoder (1957, p. 236, fig. 64) identified chamosite as the chlorite involved, and went so far as to specify a composition 'on the join daphnite-thuringite'.

The idea that garnet might derive directly from a primary iron silicate is thus by no means new and if the very tentative suggestion of Brindley (1954) is included, it goes back over 30 years.

The most precise identification of parentage appears to be that of the present author (Stanton 1976, 1979, 1982), who has postulated a chamositic chlorite containing very finely dispersed chemical SiO_2. Dehydration and incorporation of this silica into the chlorite structure induces *in situ* transformation to the garnet structure. Instability induced by Mn, and perhaps small quantities of Ca, in the structure may predispose the chlorite to such transformation (Stanton 1976). Any silica in excess of the requirements of this process aggregates into small rounded particles within the garnet grain: the quartz 'inclusions' that are almost a characteristic feature of the garnets of metapelites.

There are two possible lines of evidence concerning such a transformation; chemical and textural. Is there any indication that such SiO_2-rich chlorites occur? It might be expected that in some instances, through the presence of blocking impurities, such chlorites might be preserved as kinetic effects. Are there any textural relics of a transformed primary material? *In situ* derivation from a chlorite might well be betrayed, here and there, by the preservation of traces of former phyllosilicate cleavages in the daughter garnet.

Chemical evidence. Electron microprobe analyses of several hundred chlorites from metamorphosed stratiform sulphide deposits and their immediate environs reveal the common occurrence of chlorites containing SiO_2 in the 25–30% range, with $Al_2O_3 \approx 16$–21%. Figure 13 illustrates $M^{2+}O$ (i.e. $FeO+MnO+MgO+CaO$) : Al_2O_3 : SiO_2 relations in chlorites and Al_2O_3 (i.e. substantially almandine) garnets from the Geco and Hemlo deposits of Ontario and the Mount Misery deposit of Queensland. Calculation of the proportions of the three components effectively presents the chlorites on an anhydrous basis and brings into sharper focus the general similarity of garnet and chlorite compositions. Variation in the garnet field

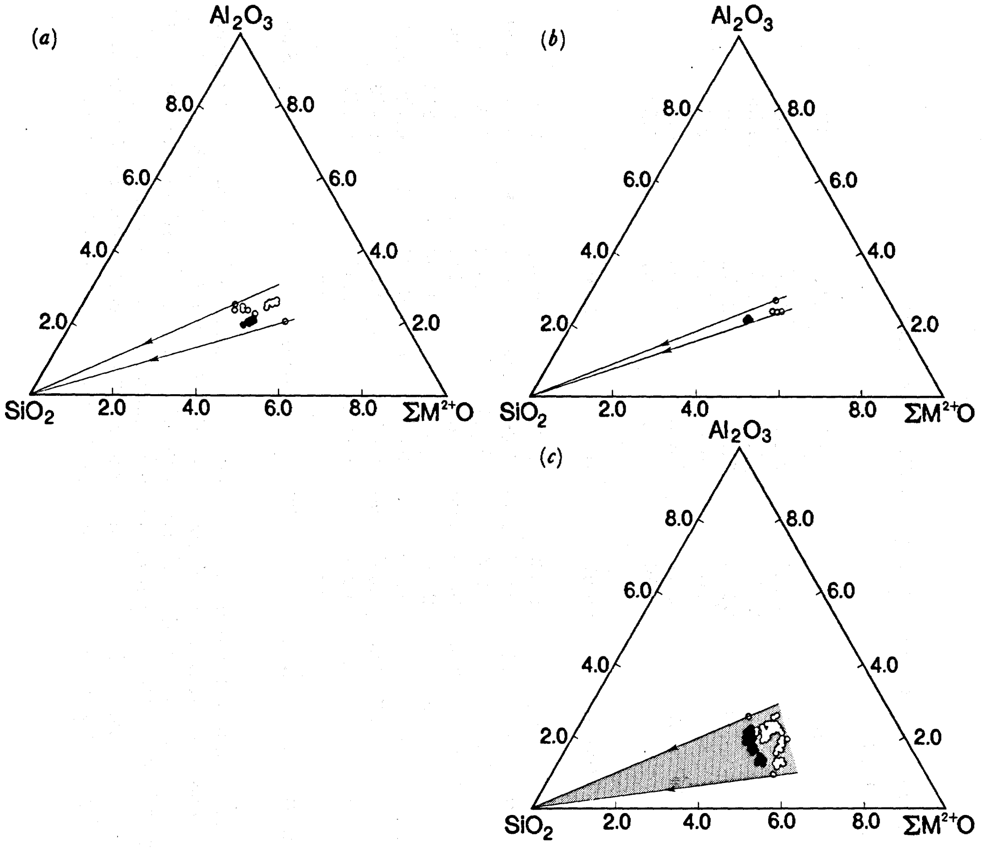


FIGURE 13. $M^{2+}O:Al_2O_3:SiO_2$ relations between chlorites (open circles) and almandine garnets (filled circles) in drill core from (*a*) Geco, Ontario, (*b*) Hemlo, Ontario, and (*c*) Mount Misery, Queensland.

is of course substantially caused by variation in proportions of divalent cations of different atomic mass, e.g. Fe^{2+} and Mg. Variation over the chlorite field also reflects this, together with variation in dioctahedral/trioctahedral nature and general deviation from stoichiometry.

Table 7 presents analyses of three chlorites and associated garnets from Geco and Hemlo (all from diamond drill core intersecting the relevant orebody). In the case of Geco (columns 1–3), column 1 sets out the analysis of a chlorite with its structural formula calculated on the basis of 14(O), column 2 gives an analysis of an immediately adjacent spot on the same grain, with the structural formula calculated on the basis of 12(O) (as for garnet) and column 3 sets out an analysis of a nearby manganiferous almandine garnet. For Hemlo, column 4 presents chlorite, column 5 an adjacent spot on the same grain with SiO_2 notionally substituted for an assumed 13 % H_2O of the chlorite, and the structural formula calculated on the basis of 12(O) as for garnet. Column 6 gives the chemical analysis and structural formula for a nearby almandine garnet. It may be seen that the structural formula for chlorite to which SiO_2 has been added and for adjacent garnet are, more or less inevitably, very similar. Column 7 shows a further chlorite from Hemlo, column 8 the same, brought to 100 % by notional dehydration and substitution of SiO_2 for H_2O, and calculation of the structural formula on the basis of 12(O). Column 9 shows an associated almandine for comparison. Columns 10–12 show similar data for chlorite, recalculated chlorite and an associated almandine from the Mount Misery deposit (Stanton 1982*b*).

Figure 13 and the various simple manipulations of table 7 show that through variation in

Table 7. Chlorite–almandine pairings from exhalative orebodies of Geco and Hemlo, Ontario, and Mount Misery, Queensland

	(1)		(2)		(3)		(4)		(5)		(6)		(7)		(8)		(9)		(10)		(11)		(12)	
SiO_2	31.08		31.95		35.29		25.84		39.62		37.12		24.06		39.77		37.32		24.85		38.44		38.06	
Al_2O_3	21.18		21.09		21.19		20.40		20.35		20.84		20.29		20.28		21.08		21.38		21.38		21.39	
FeO^a	15.68		15.45		28.20		26.54		25.71		32.61		28.39		28.63		32.98		24.72		24.72		33.60	
MnO	—		—		10.24		—		0.11		3.60		—		—		3.01		0.40		0.40		2.77	
MgO	17.54		17.30		3.32		13.25		13.00		2.45		11.40		11.32		3.01		15.05		15.05		4.08	
CaO	0.21		0.17		1.51		0.18		—		2.54		—		—		2.56		0.01		0.01		1.50	
K_2O	0.89		0.85		—		0.43		—		0.17		0.15		—		—		—		—		—	
total	86.59		86.81		99.75		86.64		98.79		99.33		84.29		100.00		99.97		86.41		100.00		101.40	
Si	3.116		2.727		2.861		2.761		3.044		3.011		2.679		3.055		2.983		2.935		2.996		3.00	
Al^{4+}	0.884	4.00	0.273	3.00	0.139	3.00	1.239	4.00	—	3.04	—	3.01	1.321	4.00	—	3.06	0.017	3.00	1.065	4.00	0.004	3.00	—	3.00
Al	1.618		1.848		1.885		1.329		1.843		1.992		1.341		1.837		1.969		0.917		1.902		1.99	
Fe^{3+}	n.d.		0.152	2.00	0.115	2.00	n.d.		0.157	2.00	0.008	2.00	n.d.		0.163	2.00	0.031	2.00	n.d.		0.112	2.01	—	1.99
Fe	1.315		0.950		1.797		2.371		1.495		2.208		2.644		1.758		2.173		2.442		1.450		2.216	
Mn	—	5.69	—		0.703		—	4.89	0.007		0.247		—	5.90	—		0.204		0.040	6.06	0.025	3.17	0.185	3.01
Mg	2.621		2.201	3.26	0.401	3.03	2.111		1.489	2.99	0.297	3.00	1.892		1.296	3.05	0.359	2.96	2.650		1.695		0.479	
Ca	0.023		0.015		0.131		0.021		—		0.220		—		—		0.220		0.004		0.001		0.127	
K	0.114		0.092		—		0.059		—		0.027		0.021		—		—		—		—		—	
total		9.69		8.26		8.03		8.89		8.03		8.01		9.90		8.11		7.96		10.06		8.18		8.00

Notes: n.d., not determined; ^{a} total iron as FeO.

Columns: (1) Chlorite, Geco stratiform Fe–Zn–Cu sulphide deposit, Manitowadge, Ontario. Structural formula calculated on basis of 14(O). (2) Chlorite of 1, reanalysed at adjacent spot and structural formula recalculated on basis of 12(O) as in almandine. (3) Almandine garnet, Geco orebody, from same drill core as chlorite. Structural formula on basis of 12(O). (4) Chlorite 1, Hemlo area, Ontario. Structural formula calculated on basis of 14(O). (5) Chlorite of 4, reanalysed at adjacent spot, with SiO_2 notionally substituted for 13% H_2O and recalculated on basis of 12(O). (6) Almandine garnet, Hemlo, from same drill core as chlorite. (7) Chlorite 2, Hemlo. Structural formula calculated on basis of 14(O). (8) Chlorite 2, Hemlo, with SiO_2 notionally substituted for H_2O and recalculated on basis of 12(O), as in almandine. (9) Almandine garnet, from same drill core as chlorite. (10) Chlorite from diamond drill core MD8, Mount Misery, Queensland (Stanton 1982*b*). (11) Same, with SiO_2 notionally substituted for H_2O and recalculated on the basis of 12(O), as in almandine. (12) Almandine garnet from MD8, Mount Misery.

Si/Al and in their dioctahedral/trioctahedral nature, some chlorites have compositions very reminiscent of those of Al^{3+} garnets. In some cases (e.g. chlorite 1–2, table 7) compositional similarities are so close that simple dehydration and solid–solid transformation could yield garnet. In other cases (e.g. chlorite 4–5, table 7) dehydration accompanied by the corresponding incorporation of finely dispersed chemical silica would yield a garnet composition.

Such chemical evidence – and there is an abundance of it – lends credence of a *constitutional* kind to an hypothesis that Al^{3+} garnet may derive directly from an aluminous chamositic precursor material.

In this general connection it may be significant that the inclusions within Al^{3+} garnets are, almost invariably, almost exclusively quartz. In some instances associated material is largely quartz, in which case a simple process of garnet growth and concomitant inclusion of matrix quartz provides a ready explanation. However, in other cases the matrix contains abundant muscovite, biotite and other minerals in addition to quartz – but the inclusions in garnet are, again, virtually exclusively quartz. Were this quartz the result of simple incorporation of matrix by a growing garnet, the appropriate proportions of muscovite, etc., might have been expected to appear among the inclusions too.

This opens the possibility that, at least in many instances, the quartz 'inclusions' do not result from the incorporation of matrix by a growing garnet crystal. In terms of the precursor mechanism, where the relevant chlorite contained *more* dispersed SiO_2 than was required for the formation of garnet, some of the excess SiO_2 segregated into rounded bodies as the chlorite transformed, and were simply trapped within the new crystal. In such cases the rounded shapes of the quartz bodies do not reflect corrosion; they result from the tendency towards attainment of minimum interfacial free energies along the quartz–garnet interfaces, and hence, in this case, the development of a spherical shape.

Thus, (1) where there is insufficient dispersed SiO_2 in the chlorite, the chlorite → garnet transformation will not take place; (2) where there is just sufficient SiO_2, chlorite → garnet with no or negligible segregation of quartz to form 'inclusions'; (3) where excess dispersed SiO_2 is present, the chlorite utilizes sufficient SiO_2 to transform to garnet, and the excess is expelled at grain boundaries and to segregate as rounded bodies within the garnet crystal – the characteristic and often abundant quartz 'inclusions' of many almandines.

Textural evidence. Derivation of garnet from chloritic materials – phyllosilicates – carries with it the possibility that phyllosilicate features such as pronounced cleavage, flaky habit, and cruciform and radiating aggregations might be preserved as pseudomorphs following the siliceous chlorite → garnet transformation.

Spectacular garnet textures that may be of such origin have been noted by Laajoki & Saikkonen (1977) in some of the Precambrian iron formations of Finland, and attributed by these authors to 'skeletal growth'. Two of their garnets are illustrated here (figures 14 and 15, plate 3, with kind permission) and show what may well be preservation of cleavages of earlier chlorite (especially figure 14), and chloritic flaky and radiating habits.

Just as these photographs of Finnish iron formation garnets were published, J. P. Vaughan and I noted apparently related structures in garnets from the Jollimont stratiform Pb–Zn prospect, near Cloncurry in northwest Queensland (Vaughan 1980; Stanton 1985; Vaughan & Stanton 1986). Following the suggestion (Stanton 1976) that some almandines of metapelitic rocks might result from solid–solid transformation of certain chamositic chlorites, evidence of pseudomorphed structures of this kind were deliberately being sought at the time. They were soon found, and some of the Jollimont garnet structures are shown in figures 16 and 17, plate 3. All gradations from what appear to be substantially and sharply preserved phyllosilicate structures, to garnets in which apparently only vestiges of such structures remain, may be found in a single thin section of core from Jollimont. Similar structures have now been found by the present author in garnets associated with the Hemlo and Bousquet gold orebodies of Ontario and Quebec respectively, and Duke (personal communication, 1986) has observed them in garnets from other Canadian occurrences.

Two further textural features may indicate that some almandines of regional metamorphic rocks derive from precursors.

1. In some cases single garnet crystals are elongate (flat), in the form of the bedding, an indication that the garnet developed with the bedding or that it is a pseudomorph of some other substance the earlier growth of which was influenced by the development of bedding.
2. Textures of garnets commonly vary in conformity with bedding. Such textural variations include:
    - (i) pronounced changes in garnet grainsize from one bed to the next;
    - (ii) changes from zoned to unzoned garnets from bed to bed;
    - (iii) changes in zone patterns from one bed to the next;
    - (iv) changes in density and pattern of inclusions – in some cases what might best be referred to as changes in degree of sieve-texturing – from one bed to the next.

The features of (2) – particularly those pertaining to zoning – seem to indicate that, from one bed to the next in each case concerned, the garnets did not grow under the same conditions. If they formed as postlithification, regional metamorphic entities, it seems hardly reasonable to propose that the garnets did not grow – as garnets – at the same time, and if they did grow at the same time it is difficult to propose that the physico-chemical conditions under which they grew varied from one bed to the next, i.e. over distances commonly of less than 1 mm. It seems not unreasonable to conclude from this that the garnet has grown by replacement of some specific material that could grow under slightly varying conditions; variation concomitant with the small changes in sedimentary/diagenetic environments as one bed deposited on top of another. One such material is chamosite.

There is thus both chemical and textural evidence indicating that some Al^{3+} garnets may be derived from particular chloritic precursors. In some cases the composition of the chlorites may be such that an essentially homogeneous, 'pure' chlorite simply dehydrates and transforms, *in situ*, to garnet. This may well be the origin of some of the Finnish and Queensland garnets of figures 14–17. In other cases a silica deficiency may be compensated for by finely dispersed chemical silica included within the body of the chlorite grain or flake. With dehydration and rise in temperature the silica is incorporated into the enclosing crystal structure as this undergoes a solid–solid transformation chlorite → garnet. The possibility of such a process is supported by the fact that, as noted above, by far the most common and abundant inclusion – often developing a sieve texture – in garnet is quartz.

It may be significant that in the chlorite–garnet pairings of figure 13 and table 7, most of the garnets contain notable Mn (percentage quantities), whereas the chlorites contain little or none. This is far from an unusual state of affairs. It is common for Al^{3+} garnets to contain conspicuous – sometimes abundant – Mn, and this is generally attributed to the garnet's

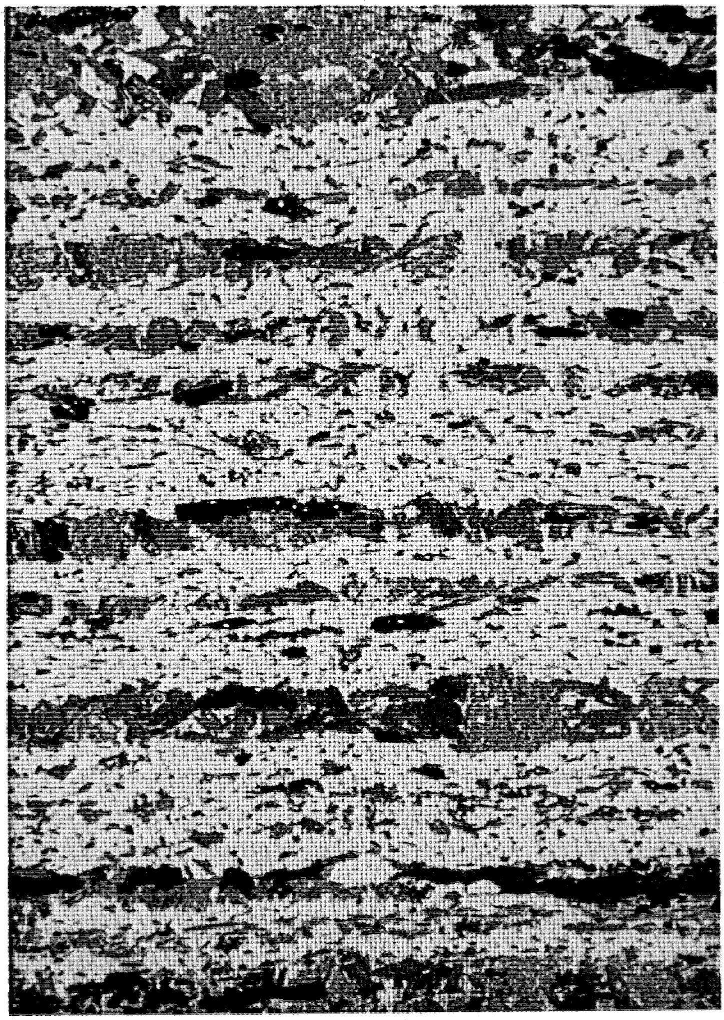


FIGURE 1. Sulphide–silicate assemblage from the regionally metamorphosed stratiform orebody of the Gorob Mine, South West Africa. Bedding is well preserved and biotite–staurolite–garnet–sulphide (chalcopyrite–sphalerite) assemblages are interbedded with quartz–feldspar dominated assemblages. The sulphides are regarded as sedimentary and hence in their present form to have derived directly from sedimentary precursors, as is the case with much of the quartz. The silicates on the other hand are generally assumed to have formed by a completely different process – metamorphic breakdown, diffusion and reaction. Plane polarized transmitted light. (Magn. × 22.)

11

12

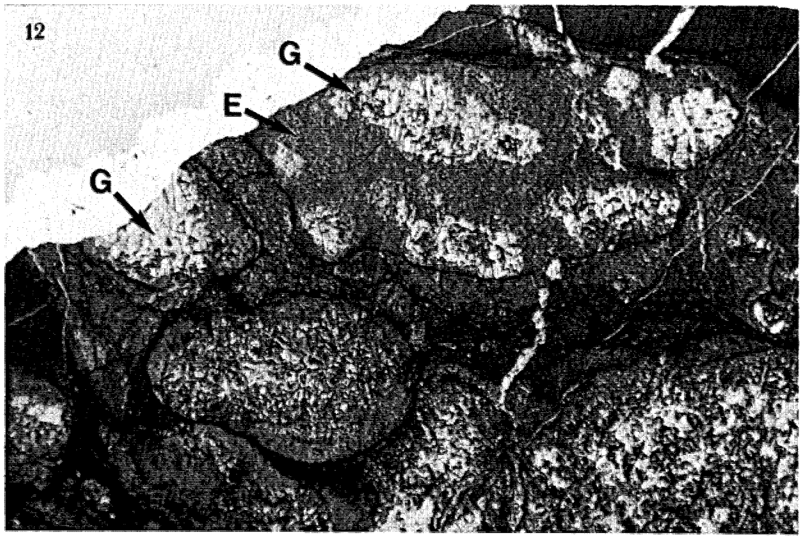
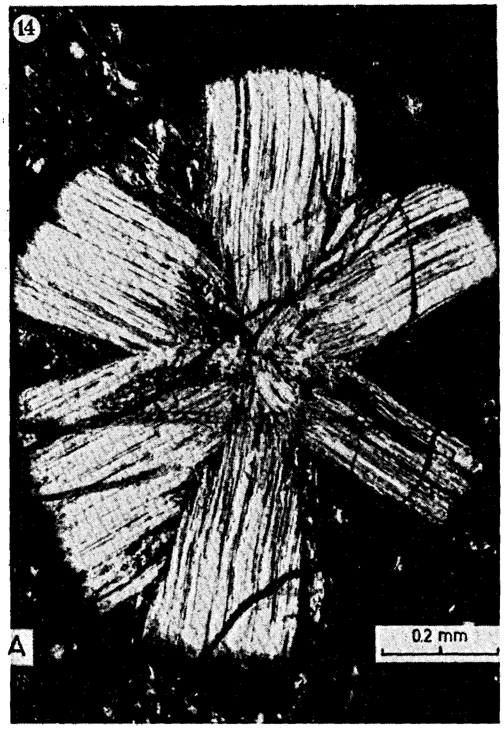


FIGURE 11. Calc-silicate and associated unmetamorphosed carbonaceous shaley–silty sediment in core from the Brindabella stratiform zinc sulphide bearing occurrence, southern New South Wales. The calc-silicate consists of what appear to be composite concretions of grandite garnet (light grey) and epidote (slightly darker grey). Ordinary light. (Magn. × 5.)

FIGURE 12. Right-hand portion of figure 11, rotated through 90° for convenience. Grandite (G) lighter grey; epidote (E) darker grey. Ordinary light. (Magn. × 10.)



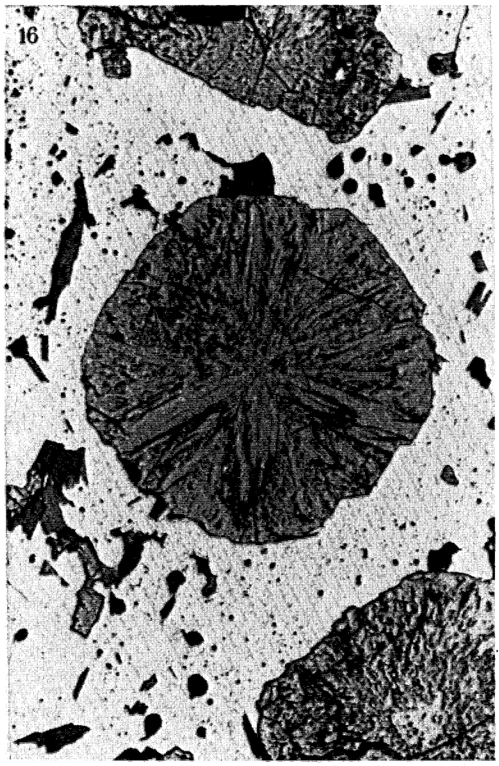


PLATE 3. For legend see overleaf.

DESCRIPTION OF PLATE 3

FIGURE 14. Spessatite garnet in iron-rich metapelites of Seppola, Finland (from Laajoki & Saikkonen 1977, with kind permission). Note apparent pseudomorphism of phyllosilicate cleavages and overall cross form. Scale as shown.

FIGURE 15. Spessatite garnet from the same locality as that of figure 12, but showing phyllosilicate-like platey shape (from Laajoki & Saikkonen 1977, with kind permission). Scale as shown.

FIGURE 16. Almandine garnet from the Jollimont sulphide-bearing metapelite, northwest Queensland, showing apparent relict phyllosilicate cleavage structure and radiating pattern; ordinary light. (Magn. × 10.) Photograph by J. P. Vaughan; see Vaughan & Stanton 1986.

FIGURE 17. Similar almandine from Jollimont, showing particularly well-developed radial structure in addition to apparent relict phyllosilicate cleavages; ordinary light. (Magn. × 10.) Photograph by J. P. Vaughan; see Vaughan & Stanton 1986.

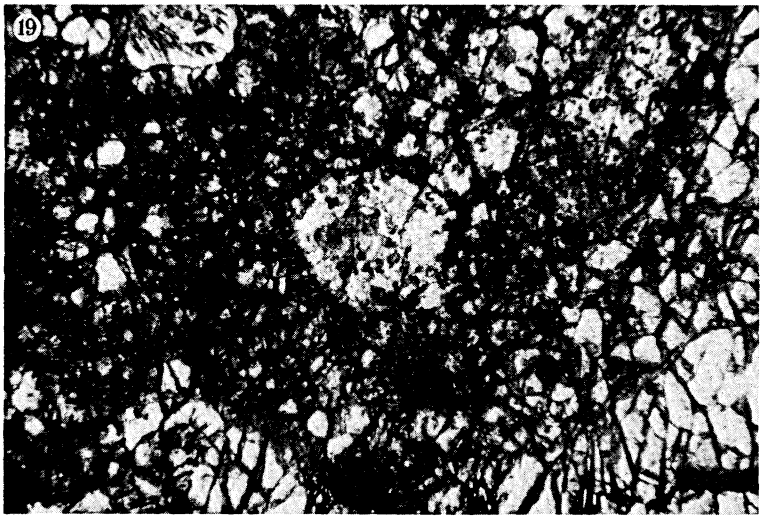


FIGURE 18. Grandite garnet (light areas, principally in upper half of photograph) with black opaque material of grandite-like composition identified here as a probable precursor to grandite. Note apparent abundant nucleation of fine grandite crystals through black material. Thin section of Ban Ban diamond drill core CD13, 69.3 m; ordinary light. (Magn. × 21.)

FIGURE 19. Material similar to that of figure 18, but at higher magnification and showing minor incorporation of dark material within the grandite crystals. Ordinary light. (Magn. × 76.)

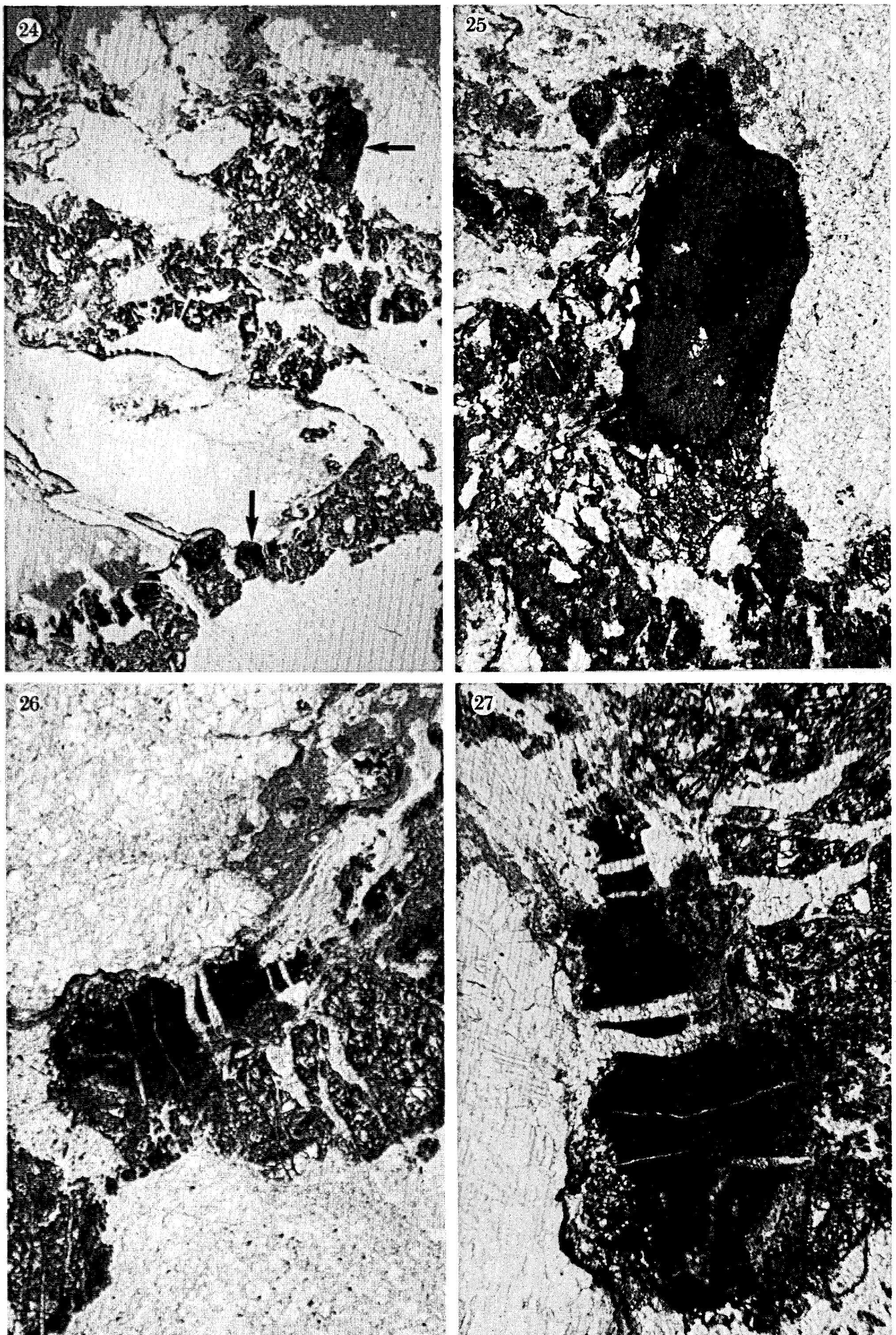


Plate 5. For description see opposite.

DESCRIPTION OF PLATE 5

FIGURE 24. Dark (near-black) areas of 'pyroxene precursor' (indicated by arrows) associated with grandite and grandite precursor (not quite such intense black) and carbonate (large areas of grey to white) in Brindabella diamond drill core DOW1. When viewed in whole core with the naked eye, this material appears to have undergone extensive soft-sediment deformation, and some pull-apart structure in a deformed bed of dark material may be discerned in the lower part of the photograph. Note also the unequilibrated grain boundaries of the abundant carbonate. Transmitted light. (Magn. × 3.5.)

FIGURE 25. Larger dark particle of upper right of figure 24, showing detail of lighter areas (13 analyses giving good diopside compositions) and associated, gradationally related, black material (19 analyses of less pure diopside). Average analyses of such material are given in columns 4 and 5, table 9). Transmitted light. (Magn. × 13.)

FIGURE 26. Enlargement of dark material of lower right centre of figure 24, showing pull-apart structure. Transmitted light. (Magn. × 5.7.)

FIGURE 27. Enlargement of upper extremity of black material of figures 24 and 26, rotated through approximately 90°, showing small irregular patches of just discernible translucency. Associated somewhat less dark material containing clear crystals occupying the right-hand side of this figure, and portions of figures 24, 25 and 26 is the postulated grandite precursor and contained grandite. Transmitted light. (Magn. × 20.)

㉚

㉛

㉜

㉝

PLATE 6. For description see opposite.

DESCRIPTION OF PLATE 6

FIGURE 30. Thin section of cordierite (white, upper left of photograph) and sudoitic chlorite (pale grey, trending NE–SW across central area of photograph) embedded in foliated but unaltered biotite and associated with clear, unaltered almandine (two subidiomorphic crystals near base). Arrows point to field of figure 31. Geco, Ontario, drill core DDH25–31, transmitted ordinary light. (Magn. × 16.)

FIGURE 31. Upper right of figure 30 (arrowed) at higher magnification, showing more clearly the slight colour difference between the cordierite and sudoitic chlorite, fresh unaltered condition of the associated biotite, and development of fine wispy sillimanite developed in all of cordierite, sudoitic chlorite and biotite. Ordinary, transmitted light. (Magn. × 40.)

FIGURE 32. Enlargement of cordierite towards upper left of figure 31 (see upper arrow, figure 31) showing detail of the development of sillimanite bundles in biotite and cordierite and the unaltered condition of the biotite flakes. The two very white grains to the upper left are carbonate. Transmitted ordinary light. (Magn. × 96.)

FIGURE 33. Enlargement of sudoitic chlorite of lower right of figure 31 (see lower arrow of figure 31) showing mode of occurrence of sillimanite in sudoitic chlorite analogous to that in cordierite, and analogous relations with unaltered biotite. Transmitted ordinary light. (Magn. × 96.)

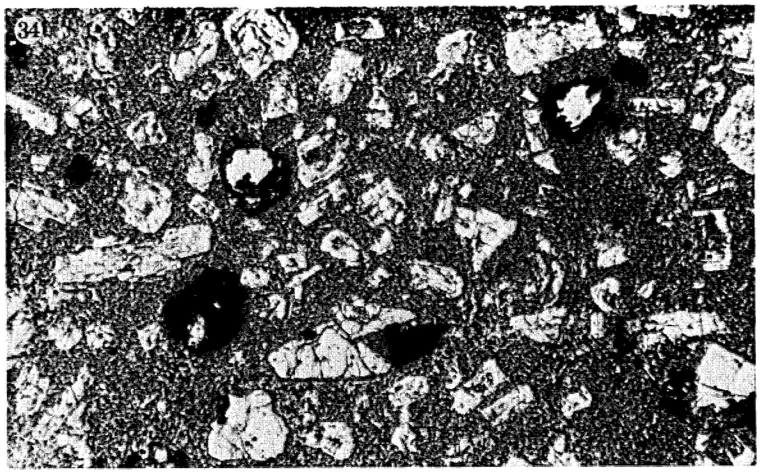


FIGURE 34. Thin section showing varying degrees of alteration of olivine (white, Fo60) to dark alteration product of table 11. Solomon Islands basaltic andesite, transmitted ordinary light. (Magn. × 25.)

FIGURE 35. Thin section showing advanced alteration of olivine (Fo68, white residue, centre of photograph) to dark alteration product (table 11) that may constitute a precursor to metamorphic amphibole in a variety of metabasites. White crystals to upper right and lower left are feldspar. Solomon Islands basaltic andesite, transmitted ordinary light. (Magn. × 25.)

DESCRIPTION OF PLATE 8

FIGURE 36. Thin section of quartz–chlorite–muscovite–biotite–almandine–staurolite–K-feldspar–sillimanite gneiss from diamond drill core intersecting the enclosing rocks of the Hemlo pyritic gold deposit, near Marathon, Ontario. Arrowed grains 1 and 2 show dark material, opaque at low magnification, associated with biotite, though many biotite grains are completely devoid of it. Transmitted plane polarized light. (Magn. × 10.)

FIGURE 37. Enlargement of grain 1 of figure 36, showing clear biotite at centre right of photograph of figure 36 merging into turbid dark material towards centre of photograph. Wispy sillimanite has developed round the margins of the dark material, particularly towards the top of the photograph. Transmitted plane polarized light. (Magn. × 50.)

FIGURES 38 AND 39. Composite grains analogous to those of figures 36 and 37 showing biotite (medium grey) and associated dark material which grades into fibrous sillimanite round its margins. Note the presence of other biotite grains showing no tendency to the development of the dark material. These are the two categories of biotites shown in figure 43. The light groundmass is quartz and K-feldspar, together with sieved staurolite. Transmitted plane polarized light. (Magn. × 50.)

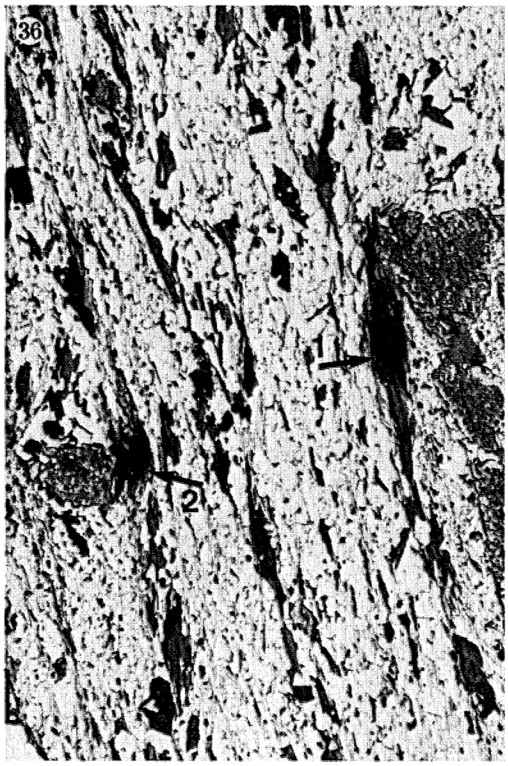


PLATE 8. For description see opposite.

particular propensity for gathering Mn from its (the garnet's) surroundings during metamorphism, and incorporating it in its structure. Chlorite, on the other hand, although certainly capable of accommodating Mn in its structure, does not seem to have the same strong tendency to do this.

There may, however, be another explanation for this contrast.

Millot (1970) has pointed out that in the experimental synthesis of manganiferous clays (including chamosite), the degree of crystallinity achieved is notably lower than that obtained with Fe, Zn, Ni, Co and other analogues. Apparently the amorphous product is more easily obtained, which Millot attributes to the reluctance of Mn^{2+} to develop 6-fold coordination – an obvious requirement for its incorporation in the octahedral layers of clays and chlorites. This might well be a factor influencing the transformation of chlorites to garnets, and particularly the early, low-temperature nucleation of high-Mn almandine, and spessartines. It may be that, owing to the instability of Mn^{2+} in 6-fold coordination in the chlorite structure, small domains within the latter develop with a high level of imperfection and remain in a poorly ordered, poorly stoichiometric state until, with moderate rise in temperature and pressure, atomic mobility increases to the point when Mn^{2+} goes from 6- to 8-fold coordination and a chlorite $\rightarrow$ garnet transformation is triggered. In this way the incorporation of small quantities of Mn 'impurity' in the chlorite would predispose it to transform to garnet. In such a case an impurity would not have a blocking effect, as is so often the case, but would constitute the basis of a triggering mechanism. Thus those chlorites of appropriate gross composition and containing significant Mn would tend to transform to garnet, those that lacked Mn would not. Hence the garnets contain conspicuous Mn – the chlorite remaining as chlorite does not. If this is so, the very strong tendency for the manganese of manganiferous garnet-bearing rocks to occur mainly in the garnet may not be caused by preferential capture and retention of manganese by the garnet during metamorphism as widely believed; rather it may be because of a predisposition of certain chlorites to transform to garnet because of the former's primary possession of small quantities of structurally destabilizing manganese (Stanton 1976).

(iii) *Grossular–andradite ('grandite') garnet*

The high incidence of calcium to the virtual exclusion of all other divalent ions in the grandite garnets precludes their derivation from phyllosilicates. The abundance of Fe^{3+} in the andradite component also militates against a phyllosilicate derivation in spite of the known existence of ferric chamosites. In an earlier contribution, the author (Stanton 1982) attempted to solve the problem of high calcium in some members of the almandine series by postulating diagenetic combinations of chemical–sedimentary ferrous chamosite, protopyroxenoid gel and SiO_2, or of early-formed prehnite with protopyroxenoid gel. It was also suggested that if the first of these combinations involved ferric rather than ferrous chamosite, grossular–andradite might be produced.

This kind of explanation derived from the fact that a variety of very fine materials, including pyroxene, epidote, a dark amorphous material of andradite-like composition, and prehnite, commonly occurred interstitially to and within aggregates of grandite garnet in some calc-silicate associated stratiform ores (Stanton 1982).

Although I remain of the opinion that early-developed authigenic/diagenetic combinations of this general kind may be important in principle, I no longer favour the detail of this earlier explanation. Prehnite, although certainly detected here and there by the electron microprobe in these materials, is generally not abundant, and the ferric component of all chamosites analysed has been very small.

The evidence now suggests that grandite garnets of stratiform ore environments may develop in two ways: (1) by direct nucleation and growth, as garnet, during sedimentation/diagenesis as noted in §3*a*vi; (2) by nucleation and growth as ordered domains within a complex, amorphous to microcrystalline, $Ca–Fe^{3+}–SiO_2$ rich sludge laid down during sedimentation. Concerning (2), the evidence is again both chemical and textural.

As shown in figures 18 and 19, plate 4, grandite garnets in stratiform ores of unmetamorphosed and low-grade terranes (e.g. Brindabella, New South Wales, and Ban Ban, Queensland) are frequently associated with a dark brown to black, microscopically irresolvable material that commonly occurs in much the same abundance as the garnet itself. This dark material constitutes (1) a dominant phase in which garnets appear to have nucleated and grown here and there, (2) an equal or less abundant accompaniment of the garnet forming an interstitial network to the latter, or (3) core, zonal or random inclusions in garnet.

Probe analysis shows the dark material to have a chemical composition highly reminiscent of the accompanying garnet, but more variable and 'impure', i.e. more complex in composition. Typical analyses of grandite and accompanying dark matter, and averages, are given in table 8. TiO_2 and, particularly, MnO and MgO tend to be higher in the dark matter

TABLE 8. ELECTRON MICROPROBE ANALYSES OF 'GRANDITE' GARNETS AND APPARENT PRECURSOR MATERIAL

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
SiO_2	35.05	35.11	36.74	34.72	34.07	34.77	34.96	35.96
TiO_2	0.93	0.95	0.51	nil	nil	nil	0.59	0.32
Al_2O_3	7.17	7.13	8.01	1.94	1.46	0.27	7.19	4.31
Fe_2O_3	n.d.	19.49	19.83	n.d.	29.85	31.34	20.85	24.14
FeO	18.37[a]	0.85	nil	26.76[a]	nil	nil	nil	nil
MnO	2.41	2.52	1.79	2.71	2.64	1.67	2.97	1.67
MgO	nil	0.10	nil	0.51	0.43	0.51	0.38	0.08
CaO	30.78	30.65	33.91	29.10	29.12	31.94	29.86	32.72
K_2O	nil	nil	nil	nil	nil	nil	nil	nil
Na_2O	nil	nil	nil	0.21	nil	nil	nil	nil
total	94.71	96.79	100.79	95.94	97.65	100.50	96.80	99.20
Si	3.126	2.963	2.966	3.212	2.950	2.943		
Ti	0.063	0.060	0.031	—	—	—		
Al	0.754	0.710	0.762	0.212	0.149	0.027		
Fe^{3+}	—	1.239	1.205	—	1.945	1.996		
Fe^{2+}	1.370	0.060	—	2.070	—	—		
Mn	0.182	0.180	0.122	0.212	0.194	0.120		
Mg	—	0.012	—	0.071	0.056	0.065		
Ca	2.941	2.774	2.933	2.885	2.709	2.896		
K	—	—	—	—	—	—		
Na	—	—	—	0.037	—	—		
total	8.436	8.000	8.020	8.700	8.003	8.047		

Notes: n.d., not determined; [a] total iron as FeO; all material from Ban Ban, S.E. Queensland.

Columns: (1) Dark precursor material A of Ban Ban drill core CD13 as analysed with notional structural formula calculated on the basis of 12(O). (2) Same, recalculated to total mols = 8. (3) Immediately adjacent clear grandite garnet crystal. (4) Dark precursor material B of Ban Ban drill core CD13, presented as for A. (5) Same, recalculated to total mols = 8. (6) Immediately adjacent clear grandite garnet crystal. (7) Average of 136 analyses of precursor material occurring in 13 sections representing a 14 m length of Ban Ban diamond drill core CD13, recalculated to total mols = 8. (8) Average of 208 analyses of clear grandite garnet crystals intimately associated with the precursor material of 7.

and CaO somewhat lower. Comparisons of MnO in the two entities as these occur in the Ban Ban and Brindabella skarns are given in figure 20, and CaO:$(Fe_2O_3+Al_2O_3)$:SiO_2 relations are depicted in figures 21*a* and 21*b* respectively. Calculation of 'structural formulae' on the basis of 12(O) (i.e. for comparison with the accompanying garnet) shows, as expected, a small but clear deficiency in CaO and a slight deficiency of SiO_2 with respect to the garnet (table 8). Totals for the dark matter are almost invariably lower than those for garnet (averages: 96.8 % and 99.2 % respectively) indicating the probable retention of bound H_2O in the former.

Comparison of the fields of figure 22, depicting CaO:$(Fe_2O_3+Al_2O_3)$:SiO_2 relations in garnet, dark matter and epidote of the Brindabella skarn, indicates that the low CaO/SiO_2 of the dark matter compared with the garnet may partly reflect an epidote component in the former. The molecule of grandite garnet is $3CaO(Fe^{3+},Al)_2O_33SiO_2$ and that of epidote $4CaO.3(Fe^{3+},Al)_2O_3.6SiO_2(OH)_2$, so that the CaO-deficiency might well result in part from subordinate proto-epidote in an ultrafine mixture. The somewhat diffuse nature of the field of the dark matter indicates, however, that its low CaO/SiO_2 is not entirely an 'epidote effect'.

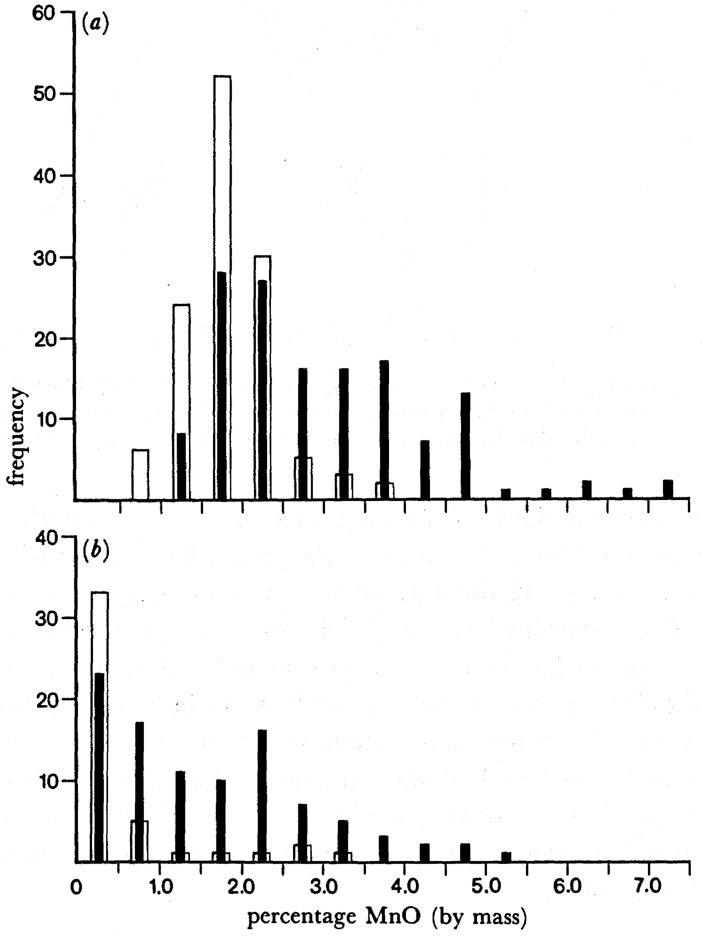


FIGURE 20. Frequency distributions of mass percentage MnO in grandite garnets (open bars) and closely associated black opaque materials (filled bars) (refer to figures 18 and 19) of (*a*) the Ban Ban CD13 and (*b*) Brindabella DOW1 diamond drill cores. Note that MnO has a marked tendency to be higher in the dark material. All analyses by electron microprobe.

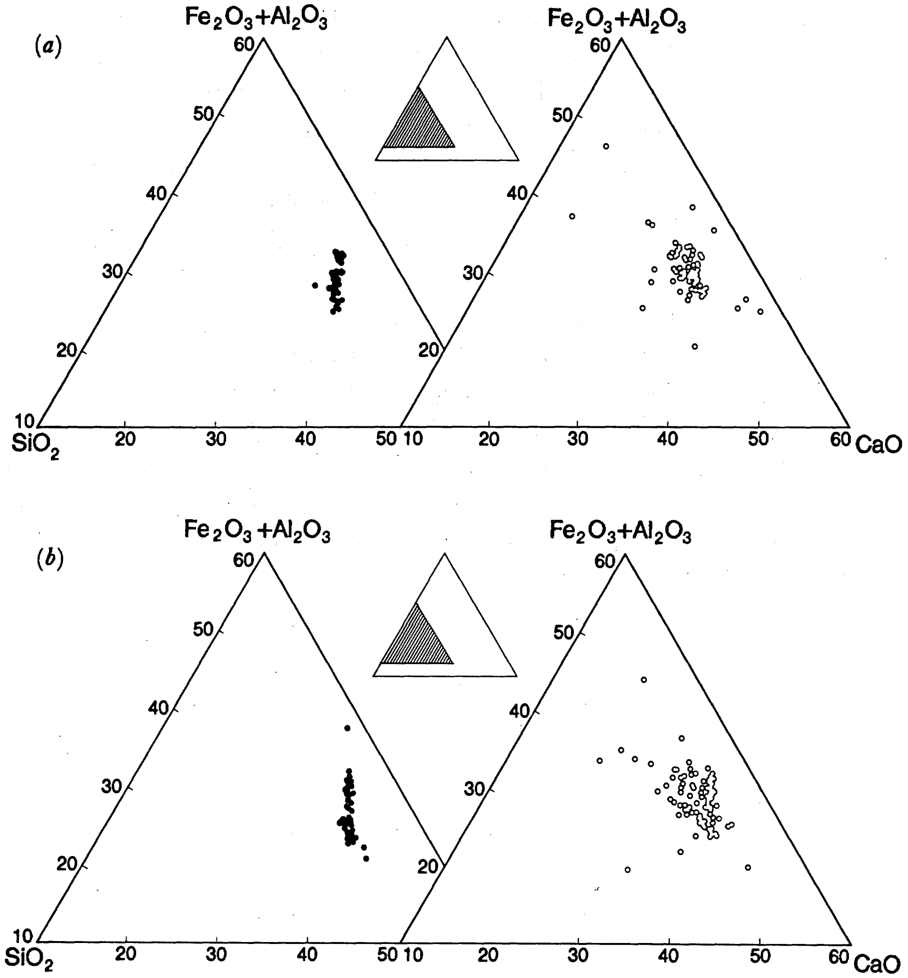


FIGURE 21. (*a*) CaO:($Fe_2O_3+Al_2O_3$):SiO_2 mass relations in grandite garnet crystals (filled circles) and associated dark material (open circles) from Ban Ban diamond drill core CD13. (*b*) Similar, in grandite garnet and associated dark material from Brindabella diamond drill core DOW1. All analyses by electron microprobe.

This general compositional similarity between garnet and associated dark matter, the more 'pure', i.e. simpler, more stoichiometric nature of the garnet relative to the dark matter, and the common incidence of garnet embedded within the latter, all suggest nucleation and growth of garnet as a process of metamorphic 'ordering' of a pre-existing, somewhat impure Ca:Fe:Al silicate precursor. In a manner loosely analogous to the nucleation and growth of strain-free metal grains within a deformed matrix, the garnet looks to have begun growth as random stoichiometric nuclei of simple composition, within an impure matrix of poor stoichiometry. Growth of the nuclei then proceeded at the expense of the matrix until concentration of impurity in the matrix precluded further garnet growth. By this stage the residue of matrix might constitute no more than an interstitial network to the garnet grains, or inclusions within polycrystalline garnet aggregates.

(iv) *Epidote*

The very close textural relations between garnet and epidote in the Brindabella skarn material (diagenetic concretions) of figures 11 and 12, and the incidence of very fine epidote

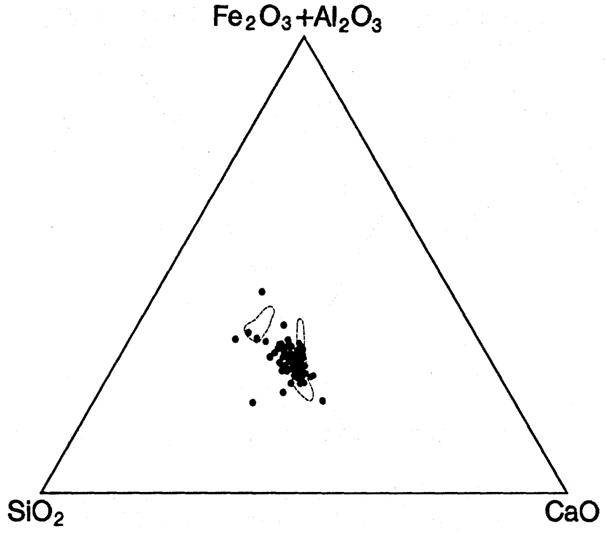


FIGURE 22. Comparison of CaO : $(Fe_2O_3+Al_2O_3)$: SiO_2 mass relations in the field of grandite garnets (elongated area enclosed by broken line to right), epidote (area enclosed by broken line to the left) and associated irresolvable dark material (filled circles) in the Brindabella diamond drill core DOW1 (compare with figure 21 *b*). All analyses by electron microprobe.

intimately associated with grandite garnet and dark matter in many of the Brindabella sections, indicates that the epidote here may have an origin very similar to that of the garnet, i.e. that it has formed directly, as epidote, as a diagenetic product, and by nucleation and growth in a Ca : Fe^{3+} : Al silicate matrix of low stoichiometry. Such a hypothesis is of course supported by the very substantial similarity of epidote and andradite compositions.

In an earlier contribution (Stanton 1982 *b*) on the Mount Misery stratiform skarn/sulphide deposit of northeast Queensland, the author noted that in several sections there occurred an extremely fine-grained brown to near-black material, in some cases apparently grading into very fine-grained epidote; the latter detected only by its muted, but none the less distinct, interference colours. Twenty areas of this material were analysed by the probe, giving Fe–Ca–Al–Si results generally reminiscent of epidote (1982 *b*, table 5). It was then suggested that the dark material might represent an early-formed dispersion of extremely fine mixed layer diaspore–goethite in similarly fine prehnite, which provided a precursor matrix for the nucleation and growth of epidote. The combination visualized was as follows.

$$\underset{\text{prehnite}}{2\,2CaO.Al_2O_3.3SiO_2.(OH)_2} + \underset{\text{diaspore}}{4AlO(OH)} + \underset{\text{goethite}}{4FeO(OH)} + 2H^+$$

$$\rightarrow \underset{\text{epidote}}{2\,2CaO.3(Al_{2.0},Fe^{3+}_{1.0})_2O_3.3SiO_2.(OH)} + 6H_2O$$

Figure 23 shows CaO–$(Fe_2O_3+Al_2O_3)$–SiO_2 relations in Mount Misery epidotes and associated dark matter. Clearly, these appear very similar in principle to those developed between grandite garnet and dark matter in the Brindabella and Ban Ban occurrences. As with the garnet, the epidote matrix material at Mount Misery also contains notably more MnO and TiO_2 than the well-crystallized epidote (see Stanton 1982 *b*, p. B54, table 5). It therefore appears that, in a manner analogous to that postulated for the Brindabella garnets, the epidote at Mount Misery nucleated and grew as stoichiometric, essentially 'pure' domains within a

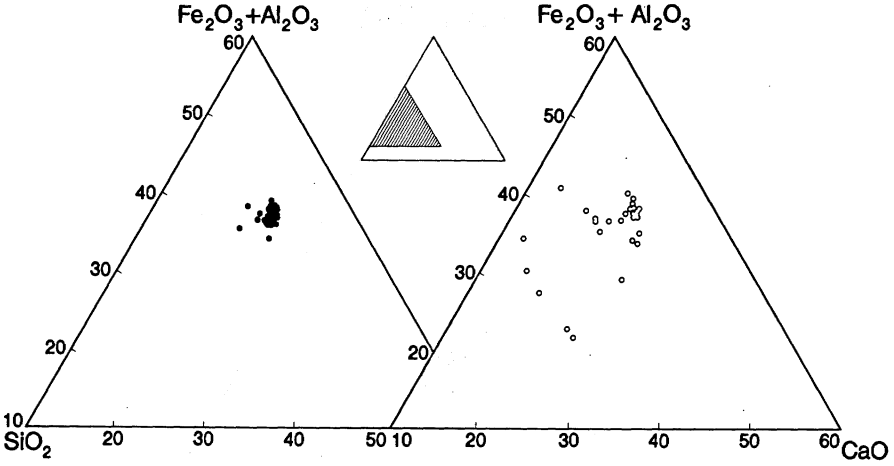


FIGURE 23. Comparison of $CaO:(Fe_2O_3+Al_2O_3):SiO_2$ mass relations in epidote crystals (filled circles) and associated irresolvable dark material (open circles) in the Mount Misery diamond drill core 77MD8 (see Stanton 1982*b*). All analyses by electron microprobe.

poorly ordered, 'impure' precursor matrix. Whether this was in fact a microcrystalline prehnite:diaspore:goethite mixture is not known, although the author now leans to the possibility that the original material was simply a poorly ordered sedimentary/diagenetic silicate: an early 'proto-epidote'.

Continued growth of the epidote has been inhibited, and finally stopped, by kinetic factors (the blocking action of components that would constitute a poor fit in the epidote crystal) so that small amounts of the original precursor material have been preserved.

(v) *Pyroxene*

Like the garnet of the garnet sandstones, hedenbergitic pyroxene occurs as almost monomineralic beds in the Mine Sequence at Broken Hill, New South Wales. As a result of the history of mining and the fact that these hedenbergitic units tend to occur in association with the stratigraphically lower ore lenses (towards the southern end of the field), the incidence of 'pure' hedenbergite units is not as widely known as that of garnet. However, the former are conspicuous where they occur, and appear as spectacular intersections in diamond drill core, particularly of A lode.

This raises questions analogous to those raised by the garnet sandstones concerning original composition of the beds: did these beds (up to a metre thick) have, by remarkable coincidence, multicomponent, 'bulk rock', compositions precisely appropriate for the almost exclusive formation of hedenbergite by metamorphic reactions, or was the development of hedenbergite pre-ordained by the existence of some single, specific sedimentary/diagenetic precursor material?

The latter would appear to be at least a strong possibility, and in the light of it it is not surprising that what appears to be a pyroxene precursor has duly appeared.

Here and there in diamond drill core from the Brindabella skarn there occur fine beds, nodules and irregular small patches 1–4 mm across of dark material which is substantially opaque in thin section (figure 24, plate 5). Small, ill-defined areas within the opaque material are just translucent, and show second-order interference colours between crossed nicols (figures 25, 26 and 27, plate 5). The nature of the opaque material cannot be determined by microscopical means, and identification of the subtranslucent material is uncertain.

However, analysis by electron probe immediately shows the subtranslucent areas to be composed of pyroxene yielding good structural formulae, and the opaque matter to be very close to pyroxene in composition with, again, good structural formulae in terms of this mineral (table 9, columns 1 and 2).

Table 9. Electron microprobe analyses of diopsidic pyroxene and associated dark opaque silicate material, Brindabella, New South Wales, diamond drill core DOW 1

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
n				19	13	80	7	60
SiO_2	49.88	53.84	54.42	49.77	54.49	50.87	54.80	54.51
TiO_2	nil	nil	nil	nil	nil	nil	nil	nil
Al_2O_3	3.28	1.82	1.78	3.61	0.37	2.43	1.24	0.62
Fe_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeO^a	2.29	1.94	1.06	2.43	1.10	1.95	1.40	1.21
MnO	0.35	0.49	nil	0.31	0.19	0.33	0.34	0.27
MgO	18.56	16.74	17.31	18.76	17.48	17.85	17.41	17.30
CaO	20.58	22.44	25.47	20.26	25.74	21.49	23.40	25.81
K_2O	0.60	nil	0.23	nil	nil	nil	nil	nil
Na_2O	nil	nil	—	nil	nil	nil	nil	nil
total	95.54	97.27	100.27	95.14	99.37	94.92	98.59	99.72
Si	1.900	1.995	1.966					
Ti	—	—	—					
Al	0.147	0.080	0.076					
Fe^{3+}	—	—	—					
Fe^{2+}	0.073	0.060	0.032					
Mn	0.011	0.015	—					
Mg	1.054	0.924	0.932					
Ca	0.840	0.891	0.986					
K	0.003	—	0.011					
Na	—	—	—					
total	4.028	3.965	4.003					

Notes: n.d., not determined; [a] total iron as FeO; n = number of analyses.

Columns: (1) Typical individual analysis of dark opaque. Structural formula calculated on the basis of 6(O). (2) Typical individual analysis of transitional (opaque → subtranslucent) material. Structural formula calculated on the basis of 6(O). (3) Typical individual analysis of associated subtranslucent material. Structural formula calculated on the basis of 6(O). (4) Average of 19 analyses of opaque silicate of single particle of figure 25. (5) Average of 13 analyses of translucent silicate of the single particle of figure 25. (6) Average of 80 analyses of opaque silicate of figure 24 and related sections. (7) Average of 7 analyses of material optically transitional between opaque and translucent silicates. (8) Average of 60 analyses of translucent silicate.

Careful inspection of analyses, however, reveals a number of small but probably significant differences in composition between the two materials. Results of 80 electron probe analyses of opaque, 60 of the subtranslucent material and 7 of what appeared under the microscope to be gradational, transition, zones between the two, are presented in table 9, and figure 28. Table 9, columns 1–3 give examples of individual analyses of opaque, transitional and subtranslucent materials; columns 4 and 5 give means of 19 opaque and 13 pyroxene analyses obtained entirely within the one small body shown in figures 24 and 25. Columns 6–8 give means for the complete sets of 80, 7 and 60 analyses of opaque, transitional and subtranslucent/translucent material respectively.

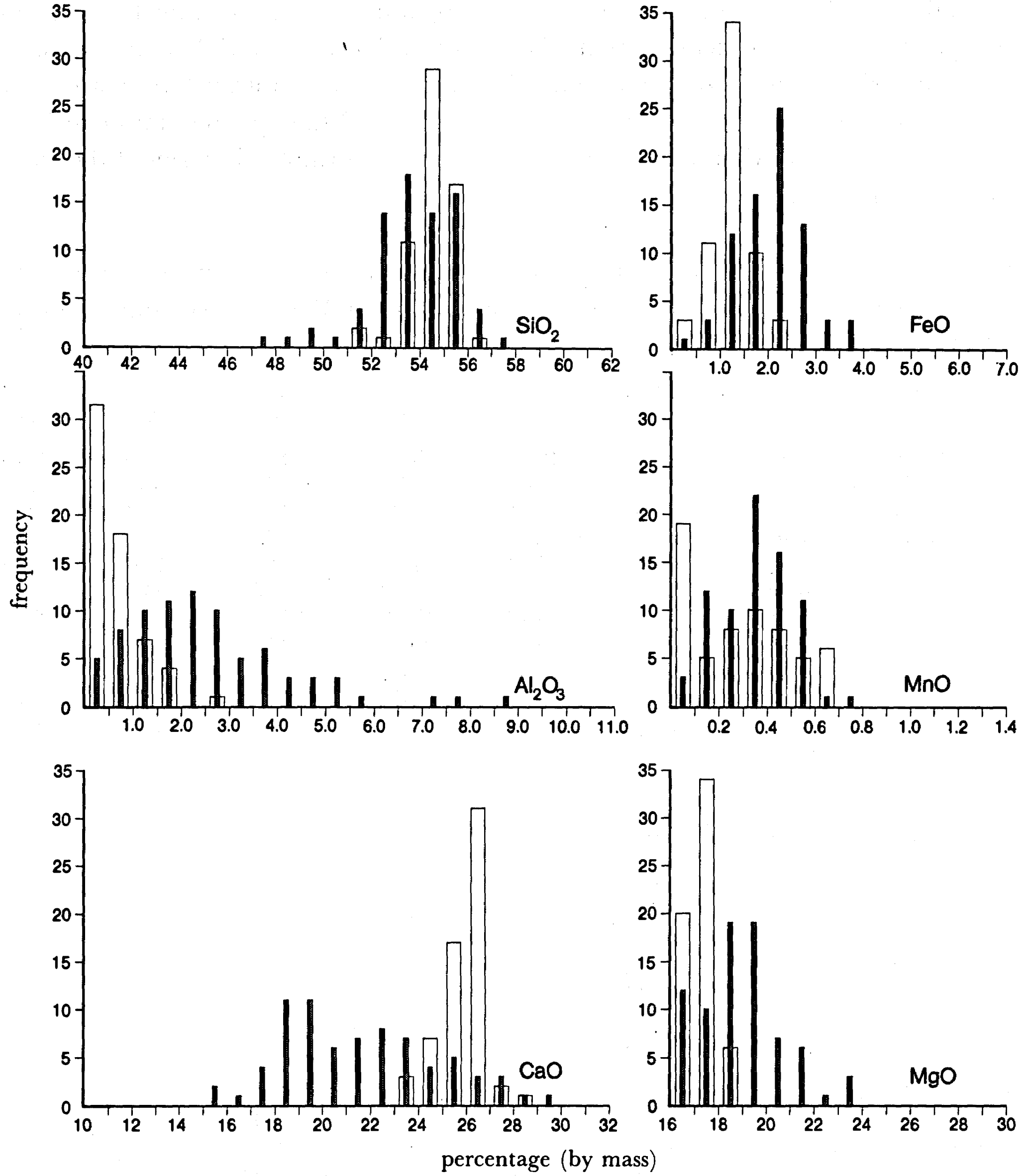


FIGURE 28. Frequency distributions of mass percent SiO_2, total iron as FeO, AlO_3, MnO, CaO and MgO in opaque material (filled bars, 80 analyses) and translucent pyroxene-like material (open bars, 60 analyses) in the Brindabella diamond drill core DOW1. All analyses are of material depicted in figures 24–27, and all are by electron microprobe.

The most distinct difference between opaque and subtranslucent materials lies in their Al_2O_3 contents. The opaque (mean $Al_2O_3 = 2.61\%$ on an anhydrous basis) contains over four times as much Al_2O_3 as the subtranslucent material (mean $Al_2O_3 = 0.62\%$). The opaque also contains slightly higher FeO, MnO and MgO, and somewhat lower SiO_2 and CaO than the subtranslucent material. Mean imputed H_2O for the opaque material is 4.62 %, although this varies widely for individual analyses as indicated by figure 28. (The accuracy of analysis, particularly in connection with the low totals, was constantly checked by repeated standardizing on associated well-developed clear crystals of grossular garnet.)

A further slight difference between the two materials was that the opaque gave persistently slightly high structural totals, whereas the subtranslucent patches gave totals consistently very close to 4.000 on the basis of six (O). The opaque almost invariably showed a low number of Si ions (generally *ca.* 1.7–1.9) and somewhat high ('Fe^{2+}' + Mn + Mg + Ca). All of this together suggests that a small but significant fraction of the total Fe may be present as Fe^{3+}.

As indicated by table 9, the subtranslucent material is a slightly aluminous diopside, with FeO and MnO present in only low amount. The opaque material is clearly very close to the diopside in composition, and may be identified as a hydrous, somewhat aluminous, slightly ferric analogue of the latter.

A conventional interpretation of these textural and compositional relationships that might be proposed is that the dark material represents an alteration product of the diopside, and that the subtranslucent patches are simply ill-defined unaltered residues of this pyroxene. This possibility seems most unlikely, however. Metamorphic pyroxene commonly develops as well-defined idiomorphic to subidiomorphic crystals and as polycrystalline aggregates exhibiting foam textures. Alteration might be expected to yield pseudomorphic preservation of such crystalline forms and/or textures, but there is no sign of this in the material examined. As shown in figure 24, this occurs chiefly as beds and nodules, and in some cases the former display pull-apart structures. It seems unlikely in the extreme that alteration of crystalline metamorphic pyroxenes could yield such features.

The impression gained from microscopical observation is, conversely, that the more crystalline, subtranslucent areas represent the somewhat patchy ordering of what was originally not-so-well ordered, entirely opaque, material. As already suggested in the case of grandite garnet and epidote, the process may have been crudely analogous to the nucleation and growth of strain-free metal grains in a matrix of deformed polycrystalline metal. In the present case, thermal activation accompanying initiation of the metamorphic process led to the nucleation of small points of perfectly ordered pyroxene within a matrix of poorly ordered 'proto-pyroxene' formed earlier by chemical sedimentation and/or authigenesis. As the continued development of the ordered state would be energetically favourable, growth from the nuclei – and the initiation of further nuclei – would proceed to completion or until blocked by some growth inhibitor. In this case it appears that completion of the transformation has indeed been blocked, so that evidence of the change from early-formed precursor to metamorphic pyroxene has been preserved. It appears – as in the case of the garnet and epidote already discussed – that the preserving influence has probably been kinetic: the presence of 'impurity', i.e. components such as Al and Fe^{3+} that could not be incorporated into the diopside structure in quantity, has partially inhibited transformation, leading to preservation of precursor material in association with its metamorphic daughter product.

(vi) *Cordierite*

In a recent contribution (Stanton 1984*a*) the author presented evidence indicating that some cordierites may arise directly – by incomplete dehydration and solid–solid transformation – from substantially dioctahedral, aluminous chlorites closely related to the sudoites of some Japanese kuroko ore environments.

These aluminous chlorites were detected as trace constituents in chlorite–muscovite–biotite–almandine–cordierite–anthophyllite–sillimanite–sulphide rocks encountered in diamond drill core DDH 25-31 drilled into the Geco orebody, Manitouwadge, Ontario from within the mine workings some 2500 ft beneath the present surface.

More recent reference to the work of Kramm (1980) indicates that the chlorites are closer in composition to carpholites than to sudoites, as indicated in table 10 and figure 29. It may be referred to by the provisional term 'sudoitic-carpholitic chlorite'.

Under the microscope the chlorite is pale creamy yellow and non-pleochroic. In isolated instances it has a pale but distinct pink tinge. It ranges from isotropic to just anisotropic, in the latter case exhibiting low-order greys and white. In polished section and reflected light it normally shows a good polish and prominent, characteristically smoothly curving grain boundaries.

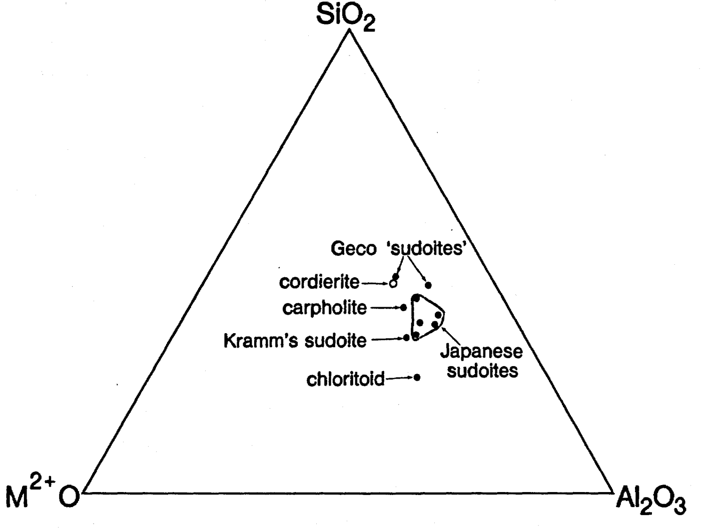


FIGURE 29. $M^{2+}O:Al_2O_3:SiO_2$ percent (by mass) relations in some sudoites, Geco 'sudoitic–carpholitic chlorites', and cordierite.

The principal association appears to be with biotite. The latter is normally fresh and unaltered, and free of the green ripidolitic chlorite commonly developed in biotites. The sudoitic–carpholitic chlorite occurs as irregular to lens-shaped bodies between closely packed plates of near massive biotite (figures 30–33, plate 6). Within this biotitic context it is often closely associated with staurolite and may form whole or partial envelopes about grains of the latter.

Most commonly the chlorite and cordierite occur separately, in adjacent foliae of the biotitic matrix. However, in isolated cases it occurs in contact with cordierite, with boundaries ranging from sharp to semigradational. In many instances the chlorite and associated (but separate) cordierite occur as adjacent, highly irregular foliae within a matrix of biotite rich in finely fibrous sillimanite. In these cases the forms of chlorite and cordierite appear completely analogous and both, like the enclosing biotite, are host to bundles of fine sillimanite fibres. The latter show no sign of sericitization or other retrogressive features.

Although a simple and easily-arrived-at interpretation of such textural and chemical similarities between these Geco sudoitic–carpholitic chlorites and cordierites is that the former may represent retrogression of the latter, the author has presented evidence to suggest (Stanton 1984*a*) that textural relationships and the general lack of retrogressive alteration in immediately associated minerals indicate the reverse – the derivation of cordierite from the chlorite – to be more likely. A process along the following general lines was suggested.

Table 10. Chemical and electron microprobe analyses of sudoite, capholite, ‘sudoitic chlorite’ and cordierite

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)
n									103	103	38	70	70	31		
SiO_2	35.63	39.01	35.67	32.55	34.03	37.09	37.12	43.75	42.71	48.09	49.44	39.76	45.84	48.36	46.86	43.60
TiO_2	nil	0.47	0.19	n.d.	nil	n.d.	n.d.	nil	nil	nil	nil	nil	nil	nil	0.12	0.11
Al_2O_3	34.87	32.15	37.41	34.87	37.07	30.82	30.67	29.39	28.23	31.79	33.21	32.54	37.52	32.96	30.58	28.45
Fe_2O_3	5.01	0.90	0.20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.69	0.64
FeO	0.43	0.10	0.09	3.39[a]	1.41[a]	3.45[a]	3.81[a]	3.99[a]	6.05[a]	6.81[a]	4.51[a]	8.28[a]	9.55[a]	9.18[a]	1.00	0.93
MnO	n.d.	n.d.	0.02	0.45	nil	8.42	9.28	nil	nil	nil	nil	nil	nil	nil	0.01	0.01
MgO	8.63	10.14	11.97	13.48	14.63	6.12	5.49	9.61	7.86	8.85	10.86	2.97	3.42	8.12	12.30	11.44
CaO	n.d.	n.d.	0.66	n.d.	0.07	n.d.	n.d.	nil	1.36	1.53	nil	1.79	2.06	nil	0.57	0.53
K_2O	0.46	1.52	0.43	n.d.	nil	n.d.	n.d.	nil	0.99	1.11	nil	0.40	0.46	nil	1.59	1.48
Na_2O	0.24	0.10	0.16	n.d.	nil	n.d.	n.d.	0.26	0.13	0.15	0.29	0.35	0.40	0.43	0.48	0.45
H_2O^+	14.15	14.15	13.30	15.26	12.79	14.10	13.63	13.00	12.67	1.69	1.69	13.91	0.75	0.75	6.49	13.00
H_2O^-			0.88													
total	99.42	98.44	100.98	100.00	100.00	100.00	100.00	100.00	100.02	100.02	100.00	100.00	100.00	100.00	100.69	100.64

Notes: n.d., not determined; [a] total iron as FeO; n = number of analyses; where totals = 100.00% exactly, total H_2O is imputed.

Columns: (1) Sudoite from the Honko orebody, Kamikita mine, Japan (Hayashi & Oinuma 1964). (2) Sudoite from the Daikokuzawa orebody, Furutobe mine, Japan (Tsukahara 1964). (3) Sudoite from the Uchinotai deposit, Kosaka mine, Japan (Tsuzuki & Honda 1975). (4) Sudoite from the Wippra Metamorphic Zone, Harz Mountains (Kramm 1980). (5) Sudoite from Mount Chalmers mine, Queensland (McLeod 1987). (6) Carpholite, Harz Mountains (Kramm 1980). (7) Carpholite, Harz Mountains (Kramm 1980). (8) Cordierite, Geco mine, Manitouwadge, Canada, recalculated from 1.69% to 13.00% H_2O (Stanton 1984). (9) Average of 103 electron probe analyses of ‘sudoitic chlorite’ from section A of DDH 25–31, Geco mine (Stanton 1984). (10) Same, recalculated to H_2O content of associated cordierite (1.69% total H_2O). (11) Average of 38 electron probe analyses of associated cordierite (see also (8) above). (12) Average of 70 electron probe analyses of ‘sudoitic chlorite’ of section B of DDH 25–31, Geco mine. (13) Same, recalculated to H_2O content of associated cordierite (0.75% total H_2O). (14) Average of 31 electron probe analyses of associated cordierite. (15) Highly hydrous cordierite, southern Norway (Beeson 1978). (16) Same, recalculated to approx. H_2O content of Geco suduoitic chlorite of analysis 9 (13.00% total H_2O). Compare with analysis 9 (Stanton 1984).

Initially a high-alumina clay–chlorite material was formed during deposition of the Geco sulphide-rich sediment, or by associated hydrothermal alteration closely following the event. Judging by the shapes and incidence of the aggregates of the present sudoitic–carpholitic chlorite and cordierite, the process may have been the alteration of rounded particles of volcanic glass. Such alteration led to the formation of an aluminous chloritic material of a range of composition and probably, in many cases, with some kaolinite admixture (cf. the young Japanese alteration assemblages of §3*d*). The compositional spectrum of the sudoitic–carpholitic material involved the approximate ranges: SiO_2, 37–44%; Al_2O_3, 27–34%; (MgO+FeO), 12–14%; Na_2O, 0–0.5%, giving a chlorite somewhat less dioctahedral than sudoite. In addition – and in terms of the present hypothesis, critically – some of the Geco material contained CaO in the 0–2.5% range, and K_2O from 0 to 1.5%, chiefly as interlayer cations.

The words 'led to the formation' of the above paragraph are chosen carefully. It cannot at present be known whether the generation of the above compositional range was purely a result of original deposition or whether it might reflect the diagenetic modification – towards some single, uniform, stable diagenetic product – of earlier depositional compositions. The latter is suspected to be the case and the structure to have progressed systematically during diagenesis towards the dioctahedral–trioctahedral sheet arrangement of an Mg–Fe-bearing aluminous–chlorite of sudoite–carpholite type. Such a progression also involved the progressive elimination of interlayer cations and, where Ca^{2+} and K^+ were rendered very low or absent, Si–Al–(Mg+Fe) relations converged on a chlorite composition very close to that of a hydrous analogue of cordierite. All of this proceeded under the open-system conditions of diagenesis.

With the close of diagenesis and the onset of metamorphism, those particles of chlorite that had achieved this condition underwent dehydration and isochemical, solid–solid transformation to cordierite. Those particles (a small minority), which had never achieved a 'pre-cordierite' condition, and whose transformation was thus inhibited by the locking effect of an original abundance of interlayer Ca^{2+} and K^+, remained substantially unaffected by metamorphism. These now appear, apparently anomalously, as rare patches of aluminous chlorite in an otherwise comparatively high-grade metamorphic assemblage. In this way they were analogous to the kaolinitic material, containing ultrafine residual biotite, so abundantly preserved in the Geco ore environment.

In some instances isolated grains of non-uniform composition, i.e. with an original non-uniform incidence of interlayer Ca^{2+} and K^+, were only partly converted to the 'proto-cordierite' condition during diagenesis and hence could only be partly transformed to cordierite during subsequent metamorphism. As a result such grains now remain composite, as illustrated in figures 13 and 14 of Stanton (1984*a*).

In this general connection the occurrence of conspicuous bundles of sillimanite needles in some of the Geco aluminous chlorites and associated cordierites (figures 31–33) may be significant. Probe analysis has shown that those chlorites containing such sillimanite are themselves notably aluminous (see Stanton 1984*a*, table 2, figures 7 and 10). This may indicate that some of the chlorites containing particularly high Al originally developed as mixed-layer clay–chlorites containing minor kaolinite–gibbsite interlayers, the latter being contemporary products of the exhalative régime. On metamorphism the kaolinite–gibbsite transformed to sillimanite (Stanton 1983, and see below), the aluminous chlorite to cordierite, and the result was the cordierite–sillimanite intergrowths now so abundantly preserved in the Geco material.

As mentioned previously (Stanton 1984*a*), it seems noteworthy that the development of all sudoites so far described in the literature has occurred in the environs of essentially unmetamorphosed exhalative ores. At the same time the incidence of localized concentrations of cordierite is commonly closely tied to the metamorphosed analogues of such ores. The Waite orebody of Noranda is an outstanding example, but the conspicuous association of metamorphosed exhalative Cu–Zn sulphide ores with the localized development of cordierite–orthoamphibole-bearing assemblages is worldwide.

The close chemical similarities and textural analogies between sudoitic chlorite and cordierite at Geco, and the fact that sudoite occurs in close association with unmetamorphosed exhalative ores, cordierite with their metamorphosed analogues, all combine to indicate the likelihood that *in this particular kind of environment* cordierite is derived directly from sudoitic–carpholitic chlorite.

There is of course no suggestion that all cordierite forms in this way. It is simply proposed that one mechanism – and it may be an important one – by which cordierite may form is by the not-quite-complete dehydration, and solid–solid transformation, of certain highly aluminous precursor chlorites of sudoite–carpholite type.

(vii) *Anthophyllitic amphibole*

In a recent detailed study of the younger (Pleistocene to Recent) basalts and andesites of the Solomon Islands (Stanton & Chappell 1989) it was noted that the olivines of some of the basalts and basaltic andesites were altered to a dark opaque material showing a tendency to phyllosilicate-like cleavage when viewed in polished section. This dark substance occurs only as an alteration product of olivine, most commonly – although not exclusively – of more fayalitic composition, i.e. Fo 60–75. Apart from this particular alteration product the parent rocks are fresh and essentially devoid of weathering effects, indicating that olivine alteration was probably of immediately post-solidification, pneumatolytic–hydrothermal kind.

This alteration product was initially analysed as a matter of little more than idle curiosity. The author was concerned with the electron microprobe analysis of the primary minerals of the rocks, and was searching particularly for the rather rare, more highly fayalitic olivine of the more felsic members of the basaltic suite. It was soon found that such olivine, rare even in primary form, commonly occurred as no more than minute residuals within the dark alteration product.

Initial microprobe analysis immediately indicated a dominantly Fe–Mg silicate with minor Al and approximately 12–14% imputed water. SiO_2 was significantly higher than that of chlorite and iddingsite, but, at the lower limit of its range, not dissimilar to that of a serpentine. When recalculated on an $H_2O = 2\%$ basis, the material revealed a range of compositions remarkably reminiscent of those of metamorphic amphiboles of the anthophyllite–(cummingtonite)–gedrite–grunerite groups.

Subsequent detailed investigation of some 60 grains within eight different Solomons basalts and basaltic andesites revealed a substantial range in composition of both parental olivine and daughter alteration product. Textural relations are shown in figures 34 and 35, plate 7. Representative analyses of the relevant olivines, their alteration product, and the latter recalculated to 98% (the notional total for amphibole, less structural water) on the basis of 24 (O, OH, F, Cl), are given in table 11.

The structural formulae computed on the basis of 2% 'H_2O' and 24 (O, OH, F, Cl) are clearly reminiscent of Fe–Mg–(Al) amphiboles. Totals are generally somewhat over 15, though

Table 11. Representative electron microprobe analyses of olivine and its alteration products in basaltic lavas of New Georgia, Solomon Islands

	(1)	(2)	(3)		(4)	(5)	(6)		(7)	(8)	(9)	
SiO_2	36.75	37.53	41.97		38.19	41.05	46.97		36.19	47.43	53.12	
Al_2O_3	—	11.58	12.74		0.11	6.99	7.85		0.15	4.48	5.02	
FeO[a]	27.90	32.59	36.04		22.19	20.38	23.04		30.78	19.03	21.31	
MnO	0.79	0.50	0.56		0.31	0.19	0.26		0.92	0.19	0.21	
MgO	33.87	5.07	5.52		39.04	16.85	19.28		31.18	15.52	17.38	
CaO	0.15	0.40	0.46		0.17	0.49	0.51		0.13	0.70	0.78	
K_2O	—	0.28	0.34		—	0.10	0.09		—	0.15	0.17	
Na_2O	—	0.22	0.17		—	—	—		—	—	—	
'H_2O'	—	11.83	2.00		—	13.95	2.00		—	12.50	2.00	
total	99.46	100.00	100.00		100.01	100.00	100.00		99.35	100.00	99.99	
mg. no.	68.39	21.71	21.44		75.82	59.58	59.86		64.36	59.24	58.80	
Si	0.992		6.870		0.993		7.199		0.993		7.978	
Al	—		1.130	8.00	—		0.801	8.00	—		0.022	8.00
Al	—		1.328		0.003		0.615		0.005		0.866	
Fe^{2+}	0.630		4.933		0.483		2.952		0.706		2.651	
Mn	0.018		0.078		0.007		0.033		0.021		0.040	
Mg	1.363		1.347	7.89	1.514		4.403	8.12	1.275		3.784	7.50
Ca	0.004		0.081		0.005		0.083		0.004		0.123	
K	—		0.071		—		0.015		—		0.032	
Na	—		0.055		—		—		—		—	
total	3.007		15.893		3.005		16.116		3.005		15.496	

[a] Total iron as FeO.

Columns: (1), (4) and (7) unaltered parent olivine crystals; structural formulae computed on the basis of 4(O). (2), (5) and (8) alteration products of (1), (4) and (7) respectively. (3), (6) and (9) alteration material of (2), (5) and (8), respectively, reanalysed on an adjacent spot, recalculated to 100% on the basis of $H_2O^+ = 2.0\%$, and structural formulae computed on the basis of 24(O, OH, Cl).

no allowance has been made for Fe_2O_3, some of which is undoubtedly present. High-SiO_2 material ($SiO_2 \approx 51–58\%$ on the basis of total = 98%) give Si above 8 and as high as 8.357. Low-SiO_2 material ($SiO_2 \approx 51–42\%$) give Si below 8 and as low as 6.530. In all cases where Si < 8 there is at least sufficient Al to bring the Z component to 8. The (X+Y) component (X is normally almost negligible, as Mg and Fe are overwhelmingly the dominant divalent ions) is generally somewhat above 7, so that structural totals (neglecting H_2O, Cl, F) are most commonly in the 15.5–16.0 range.

For the 60 analyses Al_2O_3 ranges from 2.23%, giving a composition reminiscent of a ferro anthophyllite–cummingtonite, to 12.62%. Table 12 compares one of the high-Al alteration grains with a ferrogedrite described by Eskola (1936) from Isopaa, Finland. The general compositional similarity is clear.

There appears no doubt, from the textural evidence, that the material in question has developed entirely at the expense of olivine. Among the group analysed this ranges from Fo = 56 to Fo = 88. In all cases alteration led to an increase in SiO_2 and CaO, decrease in FeO and MgO, and ingress of Al_2O_3 and K_2O. In most cases it was accompanied by little or no change in Mg number, although in several instances there was a sharp decrease, e.g. from 74 in the parent olivine to 52 in the alteration product. The very few instances of increase in Mg number detected involved minute change only. Thus Mg and Fe were subtracted essentially equally, or Mg removed somewhat preferentially. Increase in SiO_2 is partly complementary with decrease in (Mg+Fe) and partly caused by addition from outside the olivine grain.

TABLE 12. COMPARISON OF RECALCULATED OLIVINE ALTERATION PRODUCT WITH FERROGEDRITIC AMPHIBOLE

	(1)	(2)
SiO_2	43.83	43.70
TiO_2	—	0.55
Al_2O_3	10.57	10.88
Fe_2O_3	n.d.	3.52
FeO^a	24.50	26.53
MnO	0.44	0.24
MgO	17.53	11.48
CaO	1.04	0.54
K_2O	0.08	0.15
Na_2O	—	1.24
'H_2O'	2.00	1.36
total	99.99	100.19

numbers of ions on the basis of 24(O, OH, Cl)

	(1)		(2)	
Si	6.808	8.00	6.687	8.00
Al	1.192		1.313	
Al	0.743	8.23	0.649	7.65
Ti	—		0.063	
Fe^{3+}	—		0.404	
Fe^{2+}	3.183		3.396	
Mn	0.057		0.031	
Mg	4.059		2.618	
Ca	0.173		0.368	
K	0.017		0.030	
Na	—		0.088	
total	16.232		15.647	

Notes: n.d., not determined; ^{a} total iron as FeO.

Columns: (1) Olivine alteration product contained in Solomon Islands basalt, with 2% imputed H_2O^+ and structural formula computed on the basis of 24(O, OH, Cl). Note that the almost certain presence of some Fe_2O_3 (not determinable by electron probe) would reduce the total number of ions in the structural formula. (2) Ferrogedrite, Isopaa, Finland (Eskola 1936).

Increases in Al and Ca arise similarly, although Al must have derived almost entirely from an outside source.

It seems likely that this alteration product of the young Solomons basaltic lavas has arisen by late-stage reaction of the relevant olivines with adjacent, substantially glassy, still-hot groundmass, under the impetus of late-stage pneumatolytic–hydrothermal activity during cooling of the newly solidified lava. The range of compositions of the substance presumably reflects differences in composition of parent olivine and the adjacent glass, and the nature and physical condition of the pneumatolytic–hydrothermal agent.

The compositions of these olivine alteration products are so reminiscent of those of amphiboles commonly found in metamorphosed basaltic rocks of older terranes that it is tempting to suggest that in at least some cases such amphiboles derive more-or-less directly from such an early product of hydrothermal alteration of olivine. Minor compositional adjustment of the alteration phase, possibly during simple burial of the lavas in question, followed by dehydration and structural reordering during metamorphism (essentially a solid–solid transformation) would lead to the formation of amphibole, *in situ*, by isochemical metamorphism. The amphibole in such a case would not have formed as a result of metamorphic destabilizing of earlier minerals, diffusion and metamorphic reaction; it would have formed, quite simply, from a precursor.

(viii) *Sillimanite*

In a slightly earlier contribution based, like that on cordierite derivation, on observations of the mineralogy of the Geco ore environment, evidence indicating that some of the sillimanite there was derived directly from a kaolinitic precursor was presented (Stanton 1983). The incidence and relative abundances of K, Mg and Fe, and a common loose association with biotite, led the author to suggest that the process may have begun with deposition, during sedimentation, of detrital biotite that had previously undergone partial or complete weathering and concomitant degradation to kaolinite–gibbsite mixed layers. This degradation may have been accentuated during early diagenesis. With advancement of diagenesis and the onset of metamorphism, any remaining biotite was recrystallized and/or retextured, and the kaolinite–gibbsite mixed layers reordered into sillimanite fibres.

$$\underset{\text{kaolinite}}{Al_2O_3.2SiO_2.2H_2O} + \underset{\text{gibbsite}}{2Al(OH)_3} \rightarrow \underset{\text{sillimanite}}{2(Al_2O_3.SiO_2)} + 5H_2O$$

This, it was proposed, led to the common association of sillimanite and biotite and, in particular, to the well-known tendency for sillimanite to occur intergrown with biotite and parallel/sub-parallel to the latter's cleavages.

Observations on drill core material collected more recently from the newly discovered Hemlo pyritic gold deposit appear to confirm the biotite:kaolinite–sillimanite association and add weight to the possibility that sillimanite may develop from the kaolinitic products of biotite degradation.

Figures 36–39, plate 8, illustrate relationships as seen in a polished thin section of a gneiss from 484 m in Noranda drill hole no. NGG 20 W at Hemlo. Figure 36 shows a general view of the quartz–chlorite–muscovite–biotite–almandine–staurolite–K-feldspar–sillimanite assemblage. General examination of the photomicrograph shows biotite to be quite abundant. Closer scrutiny shows a substantial proportion of these biotite grains to grade into, or to be partly constituted of, much darker material. (This is not a pleochroic effect, involving several biotite grains at different orientations with respect to the polarizing prism.) Grains arrowed and numbered 1 and 2 are examples, and numerous others may be seen within the field of view. Figure 37 is a higher magnification of grain 1 (magn. ×50). The conspicuous cluster of staurolite grains to the right of grain 1 in figure 36 is clearly seen again in figure 37.

The latter photomicrograph illustrates well the relationships found between biotite and the dark material throughout the specimen. Towards the base of the photograph the grain, now seen to be composite, is clearly biotite. Proceeding upwards, this biotite grades into the dark brown to black material constituting the major part of the grain. Smaller grains of biotite towards the upper edge of the photograph behave similarly. The body of the darker material is somewhat inhomogeneous and mottled. Towards its edges, particularly around the upper portion of the clot, the latter exhibits a wispy, fibrous structure. This fibrous nature is shown more clearly in figures 38 and 39. The microscopical features of this dark material are therefore similar in principle to the dark clots found at Geco (Stanton 1983; fig. 2D, G, H and I) except that the Hemlo material now described shows close and gradational, and quite unequivocal, relationships with biotite. For the Geco material the tie between dark material and biotite was substantially deduced; at Hemlo it is now seen to be visually apparent as a common feature of the rock concerned.

Two hundred and eight electron microprobe analyses of dark material, biotite, and gradations between the two were carried out on the polished thin section represented by figures 36–39. Grain 1 was the most intensely studied and was the subject of 60 analyses: 12 other, similar dark patches appearing in the slide were subjected to somewhat less detailed analysis. In all there were 68 analyses of biotite and 140 of dark and gradational material. Results are presented in figures 40–42. These show various relationships between SiO_2, MgO, FeO, K_2O and Al_2O_3 in the range of materials from biotite, through a variety (on the basis of both colour and texture) of dark matter, to the wispy, fibrous patches of figures 36–39. It will be seen that in both figures 40 and 41 the points constitute a fairly well-ordered continuum from biotite to kaolinite and then to $Al_2O_3.SiO_2$ (sillimanite in this case). Figure 42 shows the frequency distribution of Al_2O_3% (by mass) as found in the sampling of this continuum. It must be emphasized that although the analytical points were chosen in as unbiased a way as could be done at the time, the points do indeed represent a sampling with its inevitable attendant error. However, figure 42 shows clearly that (1) all of the dark material has a higher Al_2O_3 content than the biotite from which it appears to derive; (2) the distribution peaks in the 30.00–34.99% Al_2O_3 range but has a substantial component (13% of the total) within the normal Al_2O_3 range for kaolinites (35–40%), and 41% of the total in and above the kaolinite range; and (3) maximum Al_2O_3 for the distribution is in the 60.00–64.99% range: the three analyses here are 60.65%, 61.06% and 60.68% Al_2O_3, essentially the normal alumina content of the Al_2SiO_5 polymorphs, in this case sillimanite.

Those Al_2O_3 values between *ca.* 18% and *ca.* 35% can be accounted for by progressive subtraction of K, Fe and Mg from biotite, and the well-known transformation to kaolinite. Al_2O_3 values above 40% can only be accounted for by the subtraction of SiO_2 and the additional formation of a non-silica-bearing Al compound such as gibbsite. Keeping in mind that the process is postulated as a pre-metamorphic, weathering effect, it appears likely that the decrease in SiO_2 with increase in Al_2O_3 above the kaolinite value is caused by progressive desilication and the development of a series of kaolinite–gibbsite mixed-layer materials (cf. Wilson 1966; Stanton 1983). If such gibbsite does develop as mixed layers within the kaolinite, metamorphism may lead to the structural ordering and union of the two to yield sillimanite in accordance with the hypothetical equation (given above).

Thus whereas in the earlier contribution on Geco (Stanton 1983) the suggestion that the dark aluminous material derived from biotite had a substantial element of surmise, the evidence now obtained on similar highly aluminous matter at Hemlo puts the matter virtually beyond doubt. The intimate textural relations between biotite and the high-alumina material, and the very well-developed chemical gradings from one to the other, clearly indicate that the aluminous matter is derived from the biotite. Textures, combined with gradational chemistries, indicate in turn that the very finely fibrous sillimanite is derived from the dark aluminous material.

It may immediately be asked (1) whether the formation of kaolinite and kaolinite–gibbsite might be a late retrograde rather than pre-metamorphic effect and (2) why it is that only some of the biotite grains are affected in this way, the majority apparently being quite devoid of kaolinite. As pointed out earlier (Stanton 1983), the fact that a large proportion of the flakes are not affected indicates that it is not a case of retrogression. If it were, why have not virtually

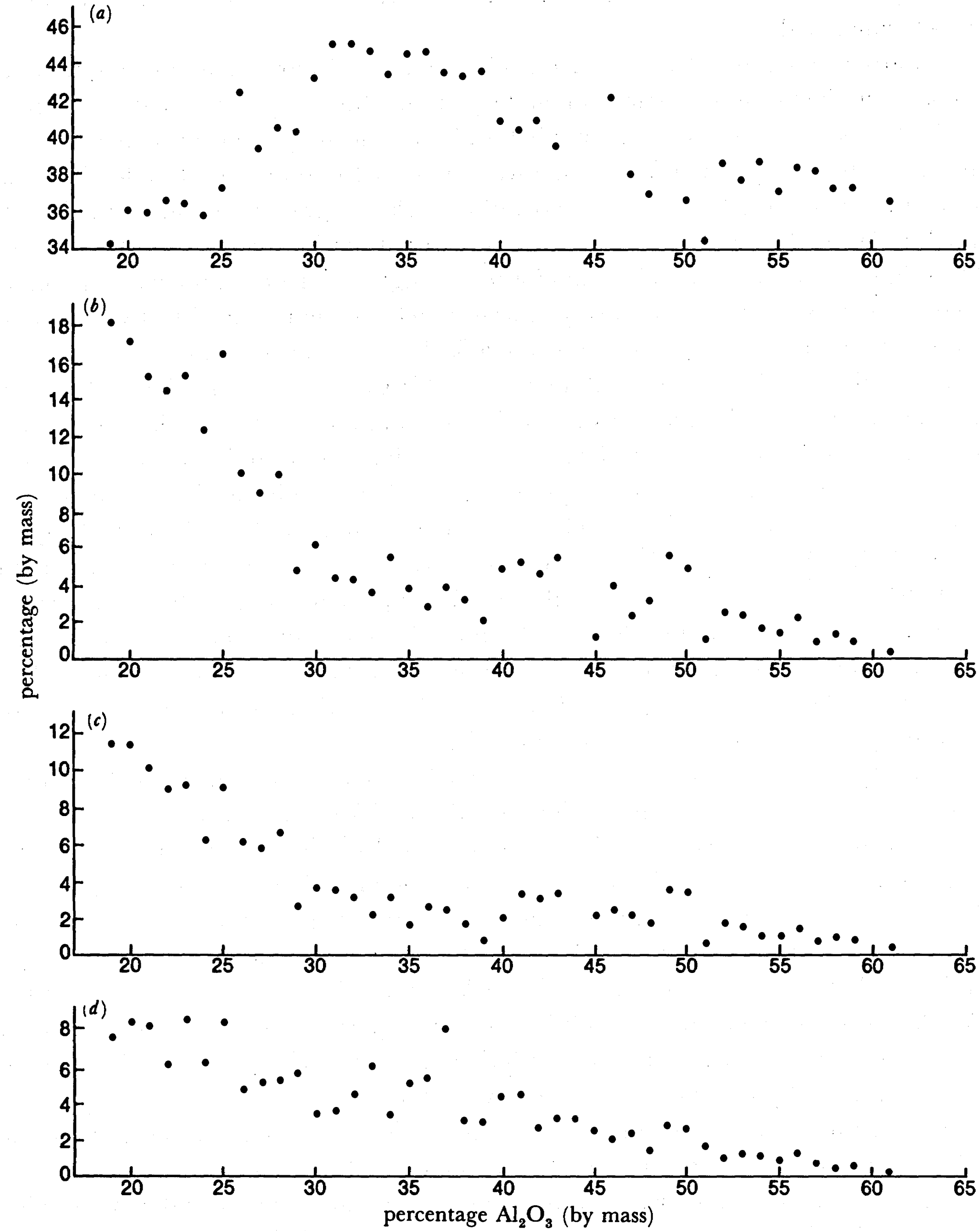


FIGURE 40. Variation in (*a*) SiO_2, (*b*) total iron as FeO, (*c*) MgO and (*d*) K_2O with systematic increase in Al_2O_3 from biotite (*ca.* 18% by mass, at the left-hand end of diagrams) to Al_2SiO_5 (*ca.* 61.7% by mass at the right-hand end) in the materials depicted in the biotite–composite grains of figures 36–39 from Hemlo. All analyses by electron microprobe: failure to obtain any analyses over 62% by mass Al_2O_3 may have been caused by the fineness of material relative to the diameter of the probe spot (*ca.* 1 μm).

all of the biotite grains undergone the transformation? It seems more likely that kaolinite/gibbsite formation reflects an earlier erosional/sedimentation/diagenetic degradation of detrital biotites that constituted components of the volcaniclastic sediments parental to the present Hemlo metapelite. If the biotites were of volcanic origin they may represent two histories. One set settled directly into the sea during volcanism and suffered no weathering. The

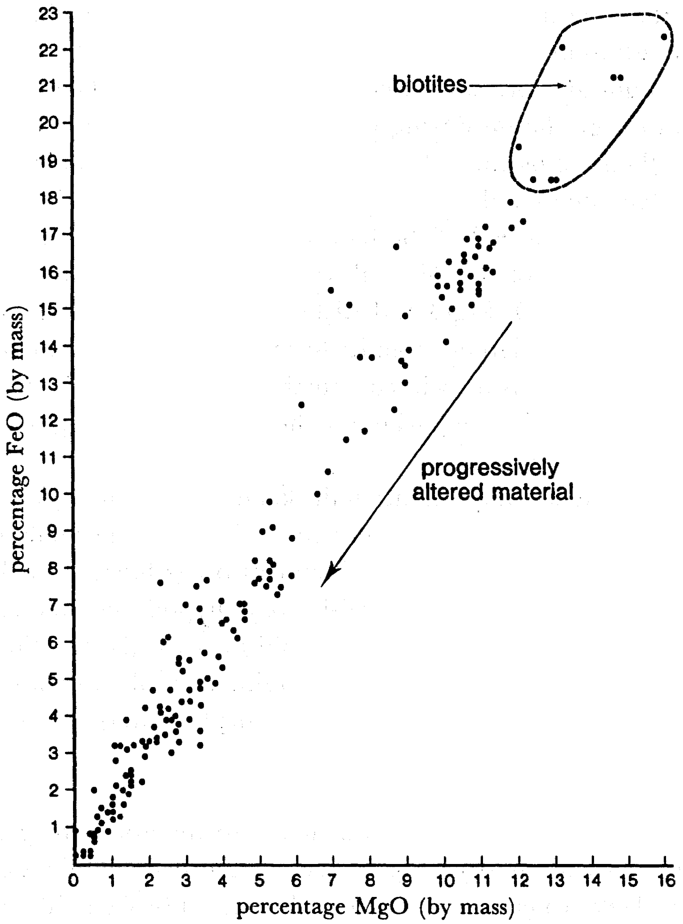


FIGURE 41. FeO/MgO relations in material of, and additional to, that depicted in figure 40. Retention of the ratios of the original biotite through the processes of presumed early degradation and later metamorphism is striking.

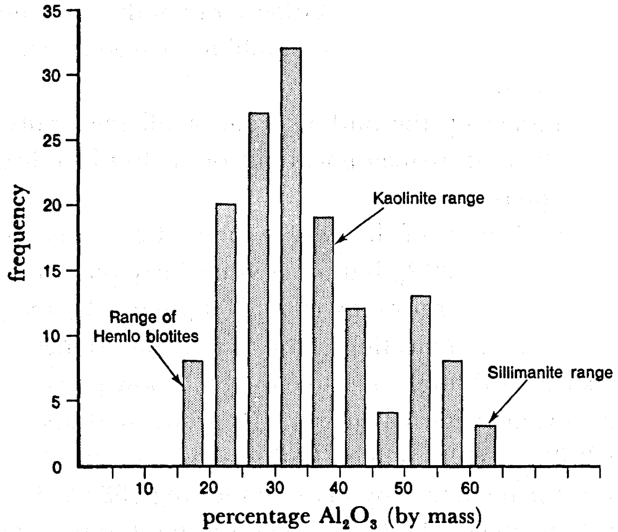


FIGURE 42. Frequency distribution of percentage (by mass) Al_2O_3 in 143 analysed biotites and (principally) their alteration and metamorphic daughter products of the materials of figures 36–41.

other was deposited on the cone and underwent at least minor weathering before later erosional transport to the sea. In addition to inducing gross degradation of the biotite, the weathering process may well have induced more subtle, cryptic changes to the flakes that also rendered them more susceptible to degradation during transport, sedimentation and diagenesis.

To examine this hypothesis 32 biotite flakes showing no evidence of kaolinite formation, and the apparently completely unaltered portions of 32 flakes that at their other extremity contained kaolinite (e.g. the lower end of the biotite of figure 37) were subjected to electron microprobe analysis. The results of the 64 analyses are shown in figure 43. The frequency distributions of values of K_2O, FeO, MgO and Al_2O_3 for the two categories of material show that the set of flakes exhibiting no sign of kaolinite formation is less variable in its composition than the set with which kaolinite is associated. Further, the flakes free of kaolinite average 2.37 % imputed water of crystallization, whereas the kaolinite-bearing set average 4.34 % H_2O, almost twice as much.

This apparent slight blurring of compositions of the kaolinite-bearing flakes, and their higher imputed structural H_2O, is interpreted as indicating (although the analysed areas appear completely fresh under the microscope) a subtle, incipient breakdown of the biotite crystals of this group. This appears to accord with the 'two-history' hypothesis: one category of grains never exposed to pre-sedimentation, pre-metamorphism weathering, the other variably degraded before sedimentation and metamorphism, leading to a subsequent role as a precursor to sillimanite and the familiar biotite–sillimanite metamorphic intergrowth.

(ix) *Spinel*

Earlier in this contribution (§2*a*) reference was made to the apparent preservation of the hydrous state in silica occurring as perfectly preserved fine beds within Lower Proterozoic pelitic rocks drilled since 1985 beneath sand cover to the west of Broken Hill, New South Wales (the Mundi Mundi Plain). In drill core available to the writer (I. R. Johnson, personal communication 1985), these rocks have the appearance of finely bedded, unmetamorphosed pelitic to slightly silty material, but when viewed in thin section under the microscope they are immediately seen to be quartz–muscovite–biotite–almandine–spinel assemblages in which bedding has been virtually perfectly preserved. Other cores of the same metasedimentary unit exhibit calcium-iron silicates, andalusite, minor sulphides, carbon, etc., all generally in the same finely bedded arrangement.

Throughout the core examined by the author occur small (generally less than 1.0 mm), dark, somewhat spongy specks that at magnifications of *ca.* 400 in reflected light appear as random intergrowths of two phases.

One of these, and the less reflective of the two, is the hydrous 'quartz' referred to above. Probe analysis indicates totals of 90–92 % but otherwise nearly pure SiO_2. Among the traces Zn however is prominent in the general range 500–5000 p.p.m. (by mass).

The other, somewhat more highly reflecting phase, is a zincian spinel (an iron-rich gahnite) which yields near-perfect structural totals but, like the SiO_2, low percentage totals (by mass). Compositional ranges and means determined from 10 probe analyses yielded: Al_2O_3, range 55.10–58.57, mean 56.36 %; FeO, range 12.68–16.62, mean 14.87 %; ZnO, range 19.54–25.12, mean 22.43 %; percentage (by mass) total range 93.62–100.78, mean 95.64 %; imputed H_2O, range 0–6.38, mean 4.46 %; structural total range 2.9959–3.0154, mean 3.0072.

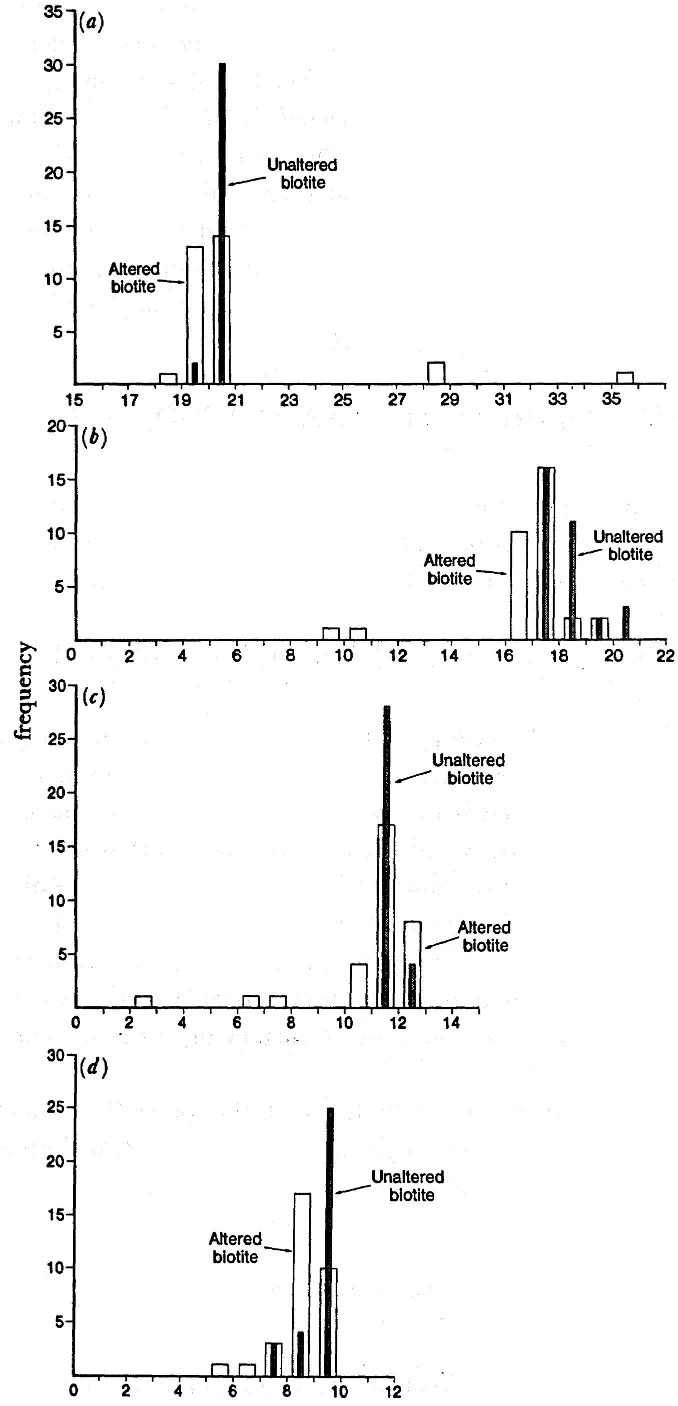


FIGURE 43. Frequency distributions of percentage (by mass) (*a*) Al_2O_3, (*b*) total iron as FeO, (*c*) MgO and (*d*) K_2O in 32 completely unaltered biotite flakes (filled bars) and in the apparently unaltered portions of 32 biotite flakes exhibiting alteration at their other extremity (open bars). The completely unaltered biotite shows a narrow, relatively sharply defined compositional range, whereas that of the incipiently altered material, although appearing completely fresh under the microscope, exhibits a slight broadening of compositional range, which is probably indicative of the very early stages of chemical breakdown. All analyses by electron microprobe.

This composite material appearing as somewhat spongy dark patches in transmitted light and as random two-phase aggregates in reflected light is therefore a silica (hydrous 'quartz', H_2O *ca.* 8–10%)–spinel (hydrous ferrous gahnite, H_2O *ca.* 4–5%) intergrowth. As far as can be judged at a magnification of 400 in reflected light, the two components occur in approximately equal proportions, with perhaps the quartz in slightly the greater abundance.

In his investigation of the petrology of the zinc lodes at the southern end of the Main Lode at Broken Hill, Segnit (1961) (see also §2*c*) pointed out that it is well known that argillaceous sediments will adsorb zinc oxide, sometimes in considerable amounts, and hence that it is likely that the zinc of the abundant gahnite at Broken Hill has been deposited with the original sediments. He postulated the following equation.

$$\underset{\text{kaolinite}}{Al_2Si_2O_6(OH)_2} + ZnO \rightarrow \underset{\text{gahnite}}{ZnAl_2O_4} + 2SiO_2 + H_2O.$$

Although accepting this as a possibility, I initially considered it more likely that, in a manner somewhat analogous to that first proposed for the combining of kaolinite with gibbsite to form sillimanite, Zn^{2+} (and Fe^{2+}) was adsorbed into sedimentary gibbsite to form the gahnite as follows.

$$\underset{\text{gibbsite}}{2Al(OH)_3} + (Zn,Fe^{2+}) + O^{2-} \rightarrow \underset{\text{gahnite}}{(Zn,Fe)O.Al_2O_3} + 3H_2O.$$

As for kaolinite + gibbsite → sillimanite, such a mechanism does not require the generation of quartz as a reaction product. However, the detection of the spongy hydrous intergrowths of gahnite and quartz in the recently discovered Mundi Mundi diamond drill core appears to support the mechanism proposed by Segnit. It is now proposed that this material represents a stage in the transformation of sedimentary kaolinite + adsorbed (ZnFe)O to ferriferous gahnite + quartz + water. The kaolinite may have been detrital, hydrothermal neoformed, or hydrothermal alteration, and the zinc and iron probably exhalative in origin. Combination may have taken place during diagenesis and/or metamorphism but, as evidenced by the still-hydrous nature of the two phases, the process has been 'caught' and preserved before completion.

In this case the material preserved is not, as in the preceding examples, an original precursor: it represents a stage in the regional metamorphic transformation of precursor material to final metamorphic daughter product.

(*b*) *Evidence from low-temperature experiments and industrial materials*

Simple precursors

The low-temperature aqueous experimental production of many of the substances involved in simple metamorphic grain growth, i.e. simple precursors, is commonplace. Most of the more important metallic sulphides are readily precipitated in the laboratory, as are a number of the iron and manganese oxides, and also carbonates, halides and sulphates of a variety of compositions. Among the silicates, the zeolites and clays are the most readily produced by precipitation and appropriate ageing, and the experimental formation of many of these by direct precipitation from aqueous solutions is now well-established.

In all of these cases the relevant compound, established both in its composition and crystal structure, is formed either at the moment of precipitation or after relatively brief ageing at close to room temperature. The role of later increase in temperature and pressure, either in the laboratory or during the natural processes of regional metamorphism, is simply that of inducing grain growth.

Complex precursors

Experimental production of complex precursors is, however, another matter: here we are concerned with the formation of materials that, by dehydration, change of valence states and modification of crystal structure undergo solid–solid transformation to a newly formed mineral. Three very simple examples of this kind of process have already been alluded to: (1) the formation of SiO_2 gel by addition of HCl to a solution of sodium metasilicate to form silica gel, which, with dehydration, transforms through one or more SiO_2 polymorphs to quartz; (2) formation of ZnS gel, which upon dehydration forms hexagonal ZnS (wurtzite or a variety of polytypes), which in turn inverts to the common cubic form, sphalerite; and (3) the reduction and transformation of goethite (FeO OH) to haematite (Fe_2O_3) and ultimately to magnetite ($FeO.Fe_2O_3$). All three of these examples of precursor formation are known in nature and are readily carried out in the laboratory.

Although there is little information on formation of more complex silicates by mechanisms such as these, some rudimentary evidence has been accumulating since about 1950. In that year, Sabatier (1950) prepared gels of forsterite and enstatite composition by mixing solutions of sodium metasilicate and magnesium chloride in the appropriate proportions (I have been able to repeat the enstatite experiment using $NaHSiO_3$ solution, but have been unable to produce a forsterite composition in this way). Barrer & Hinds (1950), Roy (1956), Luth & Ingamells (1965), Hamilton & Henderson (1968), Biggar & O'Hara (1969), Edgar (1973), Haaker & Ewing (1981) and others have produced a variety of gels, of various 'mineral' compositions, as starting materials of high T–P experiments on mineral stabilities and equilibria. For the latter purpose it is necessary to produce gels representing precise stoichiometric proportions together with homogeneity on an atomic scale, and such gels may be obtained on a semi-routine basis by mixing standardized aqueous solutions of metal nitrates, chlorides or hydroxides with a suitable source of silica such as stabilized silica sol, adding ethyl alcohol to ensure complete miscibility, and dialysing. Sabatier (1950) and the more recent investigators have converted the gels to their relevant crystalline analogues by high-temperature sintering. However, given that the gels in question are homogeneous on an atomic scale and have compositions corresponding precisely to the stoichiometric proportions of the elements in the relevant minerals, it seems inevitable that with appropriate ageing such gels would progressively dehydrate and, as amorphous solids, 'devitrify' to yield the ordered crystalline structure of the mineral concerned. Different conditions of such crystallization might, where this was possible, lead to the development of different polymorphs of a particular compound.

It has long been known that one of the products of the hydration and setting of Portland cement is isometric tricalcium aluminate hexahydrate, $3CaO.Al_2O_3.6H_2O$, i.e. hydrogarnet. Hydration of the glassy phase of the clinker yields materials of the general form $3CaO.(Al,Fe)_2O_3.nSiO_2(6-2m)H_2O$ where m ranges from 0 to 3 (cf. Carlson 1956).

Hydrothermal and X-ray studies of the system (Flint *et al.* 1941) have in fact shown that there is a complete solid solution series between the four compounds,

$$3CaO.Al_2O_3.6H_2O,$$

$$3CaO.Fe_2O_3.6H_2O,$$

$$3CaO.Al_2O_3.3SiO_2,$$

$$3CaO.Fe_2O_3.3SiO_2,$$

one member of which is the mineral plazolite, $3CaO.Al_2O_3.2SiO_2.2H_2O$.

Experiments by Flint & Wells (1941) on the possible hydration products of Portland cement indicated that the sulphate resistance of such cement could be increased by removing from it the $3CaO.Al_2O_3.6H_2O$, which is unstable in sulphate solutions (sodium sulphate solutions combine with it to give $3CaO.Al_2O_3.3CaSO_4.31.5H_2O$, causing expansion and disruption of the cement) by substitution of iron and silica and the consequent production of $3CaO.(Al,Fe)_2O_3.3SiO_2$, which is stable in sulphate solutions. This was induced industrially by 'steaming', or 'steam curing' the set cement, which caused free SiO_2 in the latter to substitute progressively for H_2O (and Fe^{3+} for Al) in the hydrogarnet, so increasing its resistance. That is, at relatively low temperatures Si and Fe^{3+} progressively replaced H_2O and Al in the hydrogarnet leading towards the development of minerals of the grossular–andradite series.

This suggests that in nature volcanic glasses of appropriate $CaO–(Al,Fe^{3+})_2O_3–3SiO_2$ proportions might well hydrate, as in the case of the synthetic glasses of cement clinker, to hydrogarnet and then, with burial and progressive silica uptake, convert to members of the grandite garnet series.

As well as deriving from the hydration of appropriate glasses, hydrogarnets may be produced in the laboratory by precipitation from aqueous solutions in a beaker under essentially room conditions. Ito & Frondel (1967) synthesized a range of microcrystalline garnets by the ageing of a series of gels precipitated at 85–105 °C at 1 atm† in NaOH solutions of pH 13.5. Several of Ito & Frondel's products showed substitution by SiO_2 of H_2O and an amorphous product of one experiment was identified as $3CaO.Fe_2O_3.3SiO_2.nH_2O$. Ito & Frondel alluded to the work of Peters (1965) on a natural andradite containing significant (OH) in its structure, and speculated that small amounts of (OH) might commonly be present in natural garnets, as had been suggested by Yoder (1950) for grossularite. Be this as it may, the work of Ito & Frondel has shown that hydrogarnet, with varying and significant substitution of SiO_2 for H_2O, is readily prepared by precipitation from solution in the laboratory at normal, surface, temperatures and pressures.

Grubb (1971) did a number of low-temperature experiments involving gels in connection with his studies in the Dales Gorge Member of the Brockman Iron Formation of Western Australia (see previous section on earlier suggestions concerning precursors). A series of mixed gels was prepared comprising various proportions of Si, Fe, Mg and Al as the chlorides, together with a 4% SiO_2 sol. After co-precipitation with 1 M NaOH, the gels were sealed in glass tubing and appropriate temperatures applied under the self-generated pressures. Experimental time ranged from three days to three years. Among the silicate mineral species produced in a series of experiments in the general range 150–250 °C (see Grubb 1971,

---

† 1 atm ≈ 10^5 Pa.

table 1, pp. 287–289) were crocidolite, riebeckite, greenalite, minnesotaite, talc, fayalite, kaolinite, nacrite and halloysite. Grubb noted, *inter alia*, the following points.

1. With appropriate gel composition a fibrous phase, almost amorphous to X-rays but with infrared absorbtion characteristics identical with those of crocidolite, can be synthesized at temperatures between 110–350 °C at 'low Eh'.
2. Incorporation of Al^{3+} in the mixed gel results in partial suppression of crocidolite growth in favour of greenalite. When Mg^{2+} is also added in small quantities riebeckite synthesis is favoured over that of crocidolite.
3. When Mg^{2+} is added to the appropriate gel system in any significant quantity greenalite becomes the predominant end-product.
4. In all gel runs carried out, greenalite is a conspicuous end-product. It forms as light greenish sheets that in time become rolled into fine, tubular, birefringent fibres.
5. Minnesotaite is frequently associated with greenalite at temperatures of only 150 °C, but in runs of three years' duration minnesotaite becomes the predominant phase.

Grubb's work was of considerable significance in showing that riebeckitic amphibole, greenalite, minnesotaite, talc and even fayalite could grow from gels at temperatures commonly achieved in, for example, the sea-floor hydrothermal environment, and that minnesotaite could develop directly from a greenalite precursor at 150 °C.

Following on from work by Reynolds (1929), Kastner & Waldbaum (1968), Martin (1969) and Kastner (1971), Flehmig (1977) synthesized K-feldspars, albites and plagioclases in the An_{20}–An_{38} range, at temperatures between 0 °C and 80 °C by means of hydroxide gels in aqueous solutions designed to simulate those of some natural environments. Optical and single-crystal X-ray investigation indicated the formation of monoclinic and triclinic K-feldspars, and low and intermediate albite. Degree of ordering and chemical composition of the relevant feldspars was related both to pH and salt concentration: the formation of albite was restricted to pH values above 8, the growth of K-feldspar to the pH range 5–10.

Flehmig considered that very small quantities of substances such as ferric hydroxide or amorphous aluminium silicate could provide sufficient gel medium for chemisorption, resultant concentration of the relevant ions, and the nucleation and growth of the feldspars. He noted, *inter alia*, that '...it is not necessary to operate with high alkali concentrations in the solution as has been done (e.g. Kastner 1971). Both the alkali and silica concentration of seawater is sufficient to enable any feldspar and quartz to form in conjunction with amorphous gel-like constituents even during the deposition of sediments' (1977, p. 8). A characteristic feature of Flehmig's gel-grown feldspars was the essentially allotriomorphic form of the large crystals and the development of polysynthetic twinning, the latter probably indicating rapid crystal growth following nucleation.

It is well established that one method of synthesizing wollastonite is through the precipitation of a gel and the formation of the hydrous analogue xonotlite ($6CaSiO_3.H_2O$), which, when heated, loses water of crystallization and inverts to wollastonite (see Deer *et al.* 1966). This experiment was repeated by the present author, using standardized $Ca(NO_3)_2$ and $NaHSiO_3$ solutions, precipitating in NaOH solution and ageing for six months, centrifuging, dialysing and heating at 108 °C for 4 h. The product yielded sharp peaks on the X-ray powder pattern, the latter being generally similar to, but not identical with, those of xonotlite. Analogous experiments, with ferrous and magnesium chlorides, were done to produce hydrated forms of $(CaMg)SiO_3$, $(Ca,Fe)SiO_3$, $(Fe,Mg)SiO_3$ and $MgSiO_3$. The hydrous 'diopside' and 'hedenbergite' compositions gave good X-ray patterns; those of hypersthene and enstatite remained substantially amorphous despite ageing for six months (all to be reported in detail elsewhere).

5. Summary statement on precursors

That at least some of the simple, non-silicate minerals of metamorphic rocks have developed directly from sedimentary/diagenetic precursors has been recognized and universally accepted for a long time. These include a wide variety of sulphides (particularly the iron sulphides), a range of Ca–Mg–Fe–Mn carbonates, the apatite of metamorphosed phosphatic beds, barite, and some of the iron and manganese oxide minerals. The formation of such minerals in pelitic sedimentary/diagenetic régimes is well-established, their experimental precipitation from aqueous solutions is no more than elementary chemistry, and their simple incorporation as components of regional metamorphic mineral assemblages is regarded as self-evident.

During the past 20 years a wide variety of clays and zeolites have been recognized as neoformed in both sedimentary and diagenetic milieux, and many of these hydrous aluminosilicates have been produced by precipitation from low-temperature aqueous solutions in the laboratory. Similarly the neoformation of chlorites and micas is now clearly recognized, and chlorites such as chamosite, and micas such as illite and glauconite, have been precipitated experimentally. Albitic plagioclase and K-feldspar are well known as diagenetic products, and they have now been produced experimentally from low-temperature aqueous solutions. Among the pyroxenoids the formation of a slightly hydrous 'wollastonite', xonotlite ($6CaSiO_3 H_2O$), by precipitation of a gel and its subsequent dehydration, is a standard method for producing synthetic wollastonite.

Although the direct incorporation of diagenetic quartz, albite and K-feldspar into metapelitic assemblages – 'diagenetic' silicates that convert directly to 'metamorphic' silicates in a manner completely analogous to the sulphides, oxides, carbonates, phosphates and so on – is now seen as self-evident, none the less silicates of the regional metamorphic milieu such as garnet, amphibole, pyroxene, staurolite, cordierite and the Al_2SiO_5 polymorphs have been regarded as a separate matter.

However, it has now been shown from the literature and in the foregoing that minerals such as chlorite, talc, pyrophyllite, muscovite, biotite, almandine and grandite garnet, amphiboles and pyroxenes have developed in rocks by chemical processes, without the influence of metamorphic temperatures and pressures. Chlorite, talc, muscovite, aluminous (almandine–spessartine) garnet, hydrogrossular, andradite and a variety of amphiboles and pyroxenes have now been found, as chemical products, in modern sediments and oozes. That is, what has long been known for the oxides, carbonates, sulphides, sulphates, phosphates and some quartz, albite and K-feldspar of metapelitic rocks – that they may arise directly from sedimentary/diagenetic *simple precursors* – is now being demonstrated for metamorphic silicates such as chlorite, mica, garnet, amphibole and pyroxene.

In addition, examination of some regionally metamorphosed pelitic rocks possessing a large chemical component has revealed what appears to be evidence for the development of a variety of metamorphic silicates from *complex precursors*. Such evidence lies in the juxtaposition of, or gradational textural and constitutional relations between, a given metamorphic mineral and a hydrous, perhaps poorly ordered material of generally similar composition. The latter are not recent weathering products, as most of the material studied is from diamond drill core, drilled deep below the present zone of weathering. Examples are the development of muscovite from illite, of aluminous garnet from siliceous, aluminous chlorites, of grandite garnet, epidote and diopsidic pyroxene by nucleation and growth in fine sedimentary precipitate of generally similar respective compositions, of cordierite from highly aluminous (sudoitic) chlorite, of anthophyllitic amphibole from a hydrothermal breakdown product of fayalitic olivine of basaltic lavas, and of sillimanite from kaolinite–gibbsite mixed layers resulting from the early weathering/hydrothermal degradation of biotite. It is thought that the preservation of small quantities of precursor material in each case is due largely to kinetic factors: for example, the presence of large interlayer cations, or the progressive concentration of 'impurities' around a new crystal nucleated and growing within a complex material, in each case leading to a blocking of transformation before this is quite completed.

The evidence seems to indicate that a given metamorphic silicate may arise from a simple or complex precursor or both, and that there may be more than one complex precursor capable of generating a particular metamorphic mineral. Examples are as follows.

(i) *Muscovite*. This may derive from a neoformed, simple precursor or by K-uptake and ordering of a complex illitic precursor.

(ii) Al^{3+} *garnet* (*almandine*, *spessartine*, *etc.*). Simple precursor in the form of fine authigenic crystals, or a complex precursor in the form of a siliceous, aluminous chlorite.

(iii) *Grandite garnet*. Simple precursor, or by nucleation and growth in a complex sedimentary material of 'near grandite' composition.

(iv) *Epidote*. No modern evidence of growth from a simple sedimentary/diagenetic precursor; some evidence provided by the Brindabella epidote–andradite concretions. Evidence of growth from a complex precursor in a manner similar to that for grandite garnet.

(v) *Pyroxene*. Both simple and complex (sedimentary) precursors.

(vi) *Amphibole*. Both simple and complex precursors, an example of the latter a hydrothermal alteration product of fayalitic olivine. *In situ* metamorphism would provide a direct route to anthophyllite in metabasalts; erosion, sedimentation and subsequent metamorphism would yield amphibole in metapelites.

(vii) *Cordierite*. Evidence only for a complex precursor: sudoitic (or carpholitic) chlorite.

(viii) *Feldspars*. K-feldspar, albite and other members of the plagioclase series, all probably derived from simple authigenic precursors, in turn developed both by neoformation and alteration of volcanic glass and other sedimented materials.

(ix) *Sillimanite*. No evidence for a simple precursor; derivation from mixed-layer kaolinite–gibbsite most likely. Other Al_2SiO_5 polymorphs may derive from related mixed-layer materials involving allophane, halloysite, nacrite, dickite with diaspore and boehmite.

(x) *Spinel*. Precursor developed by adsorbtion of divalent ions (i.e. Fe^{2+}, Zn^{2+}, Mn^{2+}) on kaolinite and other kandite clays, also possibly on aluminium hydroxides and oxyhydroxides. Magnetite series may develop by analogous adsorbtion on sedimentary goethitic precursors.

Doubt may be raised as to whether the relatively large numbers of precursors that would be required for the development of some of the more complex regional metamorphic rock types could form together and coexist through sedimentation and diagenesis. The development of a quartz–K-feldspar–muscovite–biotite–garnet (almandine)–sillimanite gneiss would for example require the development of an authigenic silica–K-feldspar–illite–glauconite–chamosite–(kaolinite–gibbsite) assemblage. All that can be said in reply at this stage is that many metamorphosed stratiform ores contain a number of mineral species, e.g. quartz–

pyrite–pyrrhotite–chalcopyrite–sphalerite–tetrahedrite–galena–arsenopyrite–calcite–barite, all of which are now accepted as self-evidently derived from separate but coexisting sedimentary/diagenetic precursors.

6. Digression on the possible significance of 'pure' chemical sediments in elucidating regional metamorphic processes

(a) *Detrital vis-à-vis chemical components in pelitic materials*

All fine-grained and hence pelitic sediments are mixtures of detrital and chemical components. For the most part it has been the detrital components (the clays and fine rock particles) that have received greatest emphasis in sedimentological–metamorphic studies and it is perhaps for this reason that the terms 'pelitic' and 'argillaceous' have become more or less synonymous in the minds of many investigators. They are not synonymous, however; the first refers to grain size, the second to composition. Whereas the argillaceous rocks consist largely of clays (argiles) and in consequence are usually highly aluminous as well as being fine-grained, the pelitic rocks are characterized only by their fine grain size and exhibit a very much larger range of composition. Indeed, the pelitic rocks constitute a very broad spectrum from essentially detrital (detrital clays and clay-type minerals, finely comminuted rock flour, organic detritus) to wholly chemical (chemically formed clays and related phyllosilicates, locally precipitated iron oxides, carbonates, sulphides, etc.). Between these 'detrital' and 'chemical' end-members the broad field of pelitic sediments embraces an almost infinite variety of proportions of 'detrital' and 'chemical' contributions.

Although the larger particles and, usually, portion of the matrix of such sediments are detrital, and the matrix a mixture of detrital and chemical, the precise identities of the matrix components are usually far from easy to perceive. (This is the case even with the use of the electron microscope: it may be impossible to tell whether a particular clay is detrital or neoformed.) When such a pelitic sediment is eventually metamorphosed the detrital and chemical identities of the matrix components – already obscure even in their primary state – become totally lost.

This has almost certainly been the case with most of the 'classical' metapelite occurrences. It is now suggested that such elimination of distinctions has played a critical role in obscuring the real nature of regional metamorphic mineral development.

(b) *The chemical component and its implications*

As, thus, metamorphic petrology of pelitic rocks has been dealing with a system of two 'components', detrital and chemical, without an accurate knowledge of the primary identities, abundances or dispositions of the two, it has not had any precise view of their relative contributions to the processes of regional metamorphic mineral development. Indeed, the potential relevance of the primary identities, chemical *vis-à-vis* detrital, of the sedimentary/diagenetic materials of pelitic rocks has been largely ignored by metamorphic petrologists. Their attention has been focused entirely on elemental constitution, i.e. 'bulk chemistry' of the parental fine-grained sediments and little or no relevance has been attributed to the siting of the elements, i.e. the structure of the crystal nuclei, concerned. However, it is now clear from the preceding discussion of precursors that the primary identities of the materials in which the various elements are sited at the cessation of diagenesis are likely to be of critical significance to the subsequent nucleation and growth of metamorphic minerals.

Perhaps, therefore, we should apply to our problem one of the simple techniques of mathematics – that of proceeding to a 'limiting case' (see, for example, Stanton & Williams 1978) – and concentrate attention on pelitic materials from which one of these components, either detrital or chemical, is entirely absent. In view of what at this point appears to be the particularly interesting nature of those fine-grained sediments in which the chemical component dominates, it may be appropriate to consider those pelites in which the chemical component exists to the virtual exclusion of detritus: that is, once again, the stratiform ores, their environments, and some of their exhalative associates.

The geologically, i.e. volumetrically, most important stratiform ores are the world's Proterozoic banded iron formations. We will revert to these a little later. Closely related to them, but also having several general features in common with the younger (chiefly Mesozoic) ironstones (James 1966) are the small banded iron formations of many stratiform metal sulphide ore occurrences already considered. James (1954) demonstrated with great elegance that mineralogical variation from haematite- to magnetite-, carbonate-, silicate- to sulphide-dominated mineralogies in the Proterozoic iron formations largely reflects the oxidation state of the original sedimentary environment; that these different but often gradationally related variations in mineralogy reflect large-scale basin-floor variation in oxygen activity and hence that the distinctive mineralogical zones of the iron formations represent chemical facies of sedimentation. James (1966) also pointed out that, as might have been expected, essentially similar zonation occurs in the ironstones, and that this similarly reflects original facies patterns of chemical sedimentation.

Such chemical facies changes, like all sedimentary facies variations, are developed both along and across bedding, the latter largely reflecting interdigitation at fluctuating facies boundaries.

The small iron formations associated with stratiform sulphide ores exhibit facies patterns similar to those of the iron formations and ironstones, and indeed in some notable cases, e.g. Gamsberg, Aggeneys and Pegmont, the metallic sulphide orebody constitutes, or is a part of, the sulphide facies of the iron formation concerned. Examples are numerous, and include the Gamsberg and related Aggeneys deposits of Namaqualand (Rozendaal 1978, 1980; Ryan *et al.* 1982; Moore 1983; Rozendaal & Stumpfl 1984), the Pegmont and associated deposits of Queensland (Stanton & Vaughan 1979; Vaughan & Stanton 1986), the BM and S deposits of New Brunswick (McAllister 1960; Bhatia 1981), Broken Hill, New South Wales (Richards 1966; Stanton 1972, 1976; Leyh & Larsen 1983), Geco, Ontario (Friesen *et al.* 1982), Mount Lyell†, Tasmania (Hendry 1981), and the Kelapa Kampit deposit of Billiton Island, Indonesia (R. S. H. Fardon, personal communication 1980). This group of deposits – no more than a small sampling of a vast number of iron formation-associated stratiform base metal orebodies – display the following features.

1. All are large deposits and in all cases associated iron formations are conspicuous and substantial.

2. In all instances the iron formations exhibit very well-preserved bedding in spite, in some cases, of apparently severe deformation of enclosing rocks, e.g. Broken Hill.

3. The deposits as a group span the full range of metamorphic 'grade'; Kelapa Kampit, essentially nil; Mount Lyell, chlorite/sericite; New Brunswick, biotite/almandine; Geco,

---

† The stratiform 'Prince Lyell' component of the Mount Lyell occurrence.

'amphibolite'; Aggeneys–Gamsberg and Pegmont, 'upper amphibolite'; Broken Hill, 'upper amphibolite to granulite'.

4. From Kelapa Kampit and Mount Lyell, in which chlorite is abundant, to Geco in which it is relatively minor to Broken Hill where overall it is minor (although locally abundant; Leyh & Larsen 1983), all of the iron formations contain primary chlorite in their silicate/sulphide facies.

5. In all cases the iron formations retain well-preserved facies patterns, involving all of oxide, silicate and sulphide facies. Carbonate is minor to absent and in some cases, e.g. the Broken Hill iron formations, there is no evidence of its existence at any time, indicating that the silicate facies are original, rather than products of carbonate–silica reactions.

6. Related to (5), the spatial distribution and distinctiveness of the two oxidation states of iron are commonly preserved through high-grade metamorphism. Richards (1963, 1966) referred to fine (less than 0.1 mm) interbedding of magnetite and haematite in the Broken Hill iron formations, and the fine preservation of bedding and chemical sedimentary facies relations between these two minerals in the iron formations of high-grade terranes is relatively commonplace.

7. Retention of these facies differences along strike, across beds and in small zones of interdigitation commonly manifests itself on a very fine scale. At Broken Hill, for example, where the iron formations have been subjected to upper amphibolite/granulite facies metamorphism, across-bedding variations in mineral assemblages and mineral chemistry have been maintained at a scale of around 0.1 mm (Stanton 1976; Stanton & Williams 1978).

8. The constitutions of the oxide facies (magnetite–(haematite)–quartz) and the sulphide facies (sulphide–silicate–(carbonate)) are essentially the same whatever the grade of metamorphism, are similar to those in banded iron formations unaffected by metamorphism, and conform with those that would be expected on the basis of low-temperature aqueous experimentation and the observation of modern environments such as the Red Sea deeps.

Thus, in these purely chemical metapelites, for which we know with a high degree of precision – from experiment, and from the observation of unmetamorphosed analogues – the general nature of original compositions and oxidation states, primary sedimentary/diagenetic features are preserved on the finest scale to the highest grades of metamorphism. Magnetite and haematite are intergrown and interbedded just as they are in the Red Sea oozes. Chlorites occur in positions appropriate to the silicate facies and retain 13% H_2O. Sulphides are interbedded with silicates and, in some cases, minor carbonate.

Clearly the whole sedimentary/diagenetic Eh/pH régime appears to have been preserved with quite exquisite precision. That is, these banded iron formations indicate incontrovertibly that not only have components such as Fe, Ca, P, Zn, Cu, Pb and Ba remained fixed in their original positions during metamorphism; the potential volatiles O_2, H_2O and CO_2 have also remained in place on scales of a fraction of a millimetre. We *know* the chemical compositions of iron formations in their primary state. Those that have undergone metamorphism to the highest grades exhibit precisely the same chemical features, including those as delicate as patterns of oxidation state, on the finest scale of bedding.

Thus these banded iron formations, essentially 100% chemical sediment, do provide the sort of vital clue it was suspected they might. They demonstrate, in some cases in the finest detail, that high-grade metamorphism has had no discernible effect on composition–space relationships that are known to have developed as primary sedimentary/diagenetic features.

These well-documented patterns of compositional variation in essentially purely chemical sediments therefore provide a clear-cut basis for discerning whether or not gross redistribution of elements has occurred during metamorphism, and, if so, the distances involved; estimations that it has never been possible to make where mixed detrital–chemical pelites, whose original compositional patterns were not known with the requisite precision, were involved.

Pelites consisting entirely of detrital matter might, in principle, be used in the same way although they, and compositional patterns developed within them, are probably not nearly so easy to discern as in chemical sediments. The latter, as suspected, do indeed appear to have very special significance in the quantitative estimation of elemental mobility during regional metamorphism, and hence, on a fine scale, in indicating the nature of regional metamorphic processes.

7. Some implications of the precursor principle

(a) *Regional metamorphic mineral zoning*

One of the most conspicuous features of regionally metamorphosed terranes is that variation in metamorphic mineral assemblages commonly displays a zonal arrangement. This ranges from the comparatively well-defined and systematic zoning of the Dalradian province of Scotland (Barrow 1893, 1912; Tilley 1924*b*; Kennedy 1948; and many others) to rather poorly defined, patchy arrangements found in many other regionally metamorphosed provinces. The relatively few areas of well-developed, conspicuous and apparently systematic metamorphic mineral zoning have been greatly emphasized in the literature, and those where zonation is less well-defined and not so systematic have received comparatively little. This has perhaps led to a somewhat exaggerated view of the incidence and development of regional metamorphic mineral zoning. Be this as it may, regional metamorphic mineral assemblages do vary, and they tend to do this in patterns. Much significance has been attributed to these patterns, which are generally regarded as manifestations of large-scale variations in temperature–pressure conditions of metamorphism, i.e. metamorphic grade.

(i) *Metamorphic zoning resulting from sedimentary/diagenetic zoning in iron formations*

The preservation of sedimentary facies patterns in the metamorphosed iron formations considered in the preceding section involves, *ipso facto*, the development of zoned arrangements of metamorphic mineral assemblages. The oxide facies yields a zone dominated by quartz–magnetite–(haematite) assemblages. The silicate facies yields a zone dominated by iron-rich silicates; a variety of assemblages involving quartz and such as iron-rich garnets, pyroxenes, amphiboles and, at lower silica levels, fayalitic olivines. The sulphide facies constitutes a zone normally dominated by pyrite and/or pyrrhotite, together with iron-rich silicates and, in some cases, sulphides of the non-ferrous metals.

Some sedimentary iron formations, e.g. the Marquette of U.S.A. and the Wabush of Canada, are of the order of tens of miles in length and hence of size sufficient to traverse several regional metamorphic grade zones. In such cases the possibility that the facies of iron formation might, in some extraordinary way, be regional metamorphic zone effects is perhaps arguable. Many iron formations, however, particularly those of many stratiform ore environments, are very much smaller. These are commonly only a few hundred feet or less in length, and are of minuscule size relative to the scale of any accompanying regional metamorphism. There can be no suggestion that regional metamorphic grade varied significantly through such minute volumes (volumes that are infinitesimally small, on a geological scale) and variation in metamorphic mineral assemblages must, as already indicated, stem directly from a primary sedimentary/diagenetic facies pattern.

Thus there is established, *for a strictly defined, fine-grained pelitic metasediment*, a type of regional metamorphic mineral zonation that is not the result of variation in metamorphic grade.

It might be said that such zoning in chemical pelites involves distinctly different classes of compounds – oxides, silicates and sulphides – as distinct from the zonation of silicates alone – chlorite, muscovite, garnet, staurolite, kyanite, sillimanite, etc. – in the classical occurrences of metamorphic zonation, and hence that the patterns of the chemical sediments are not relevant to the problem. Recently, however, an example of the zonation of silicate minerals within the silicate facies of a small sedimentary iron formation has been described. The small iron-rich metasedimentary unit of which the Pegmont Fe–Zn–Pb–Cu sulphide deposit forms a small part (Stanton & Vaughan 1979; Vaughan 1980; Vaughan & Stanton 1986) has been deposited in one of an extensive series of small Proterozoic basins in the Mary Kathleen Group of the 'Eastern Geosyncline' succession of northwest Queensland. The Pegmont basin has been transected by more than 30 diamond drill holes, a detailed study of which (see Vaughan & Stanton 1986) has demonstrated a clear sedimentary facies variation from an Fe-rich, Si and Al-poor basin centre to an Fe-poor, Si–Al-rich basin edge. Mn is a conspicuous, lesser component overall, and has a distribution relative to Fe reminiscent of that developed by diagenetic movement in modern lakes as deduced by Strakhov (1966). This overall chemical sedimentary facies change is now reflected by a basin-centre mineralogy dominated by fayalite:clinopyroxene, grading to a basin-slope assemblage dominated by clinopyroxene:amphibole:garnet, to a basin-edge assemblage of garnet–quartz–biotite, and eventually to quartz–feldspar–muscovite–(biotite–garnet–sillimanite), as depicted in figure 44.

The width of the Pegmont deposit is approximately 1400 m (maximum thickness *ca.* 8 m). Although minor quantities of sulphide and oxide appear in the different zones of the metapelites, the silicates constitute well over 90 % of the rocks in question. The clearly defined variation in relative abundances and mineral chemistry of these silicates demonstrates, again for a *strictly defined, fine-grained, pelitic metasediment*, that a regional metamorphic mineral zonation of silicate minerals alone may develop quite independently of any variation of metamorphic grade.

That variations in primary rock composition should lead to differences in derived metamorphic mineral assemblages has of course been recognized virtually throughout the history of metamorphic petrology, and has been treated in a more-or-less quantitative manner at least since the time of Eskola (1915). However, the potential significance of this in the development of systematic mineralogical zonation specifically within pelitic rocks does not seem to have been fully recognized. Barrow (1893) thought it possible to eliminate the effects of compositional variation, at least to a first approximation, by considering only the pelitic members of the Dalradian succession, a manoeuvre endorsed by Tilley (1924), Snelling (1957) and others, but questioned by Yoder (1955). Snelling (1957) presented 13 analyses of the Dalradian pelitic schists, carefully selected to represent the range of metamorphic zones in which the schists were involved. Of the chemical composition of the schists (1957, p. 301, table 1) he commented that 'their analyses are very similar...' (1957, p. 304). However, close examination of these analyses shows them to exhibit quite wide variation, as demonstrated in table 13, and attempts to demonstrate that the various mineral assemblages are compatible

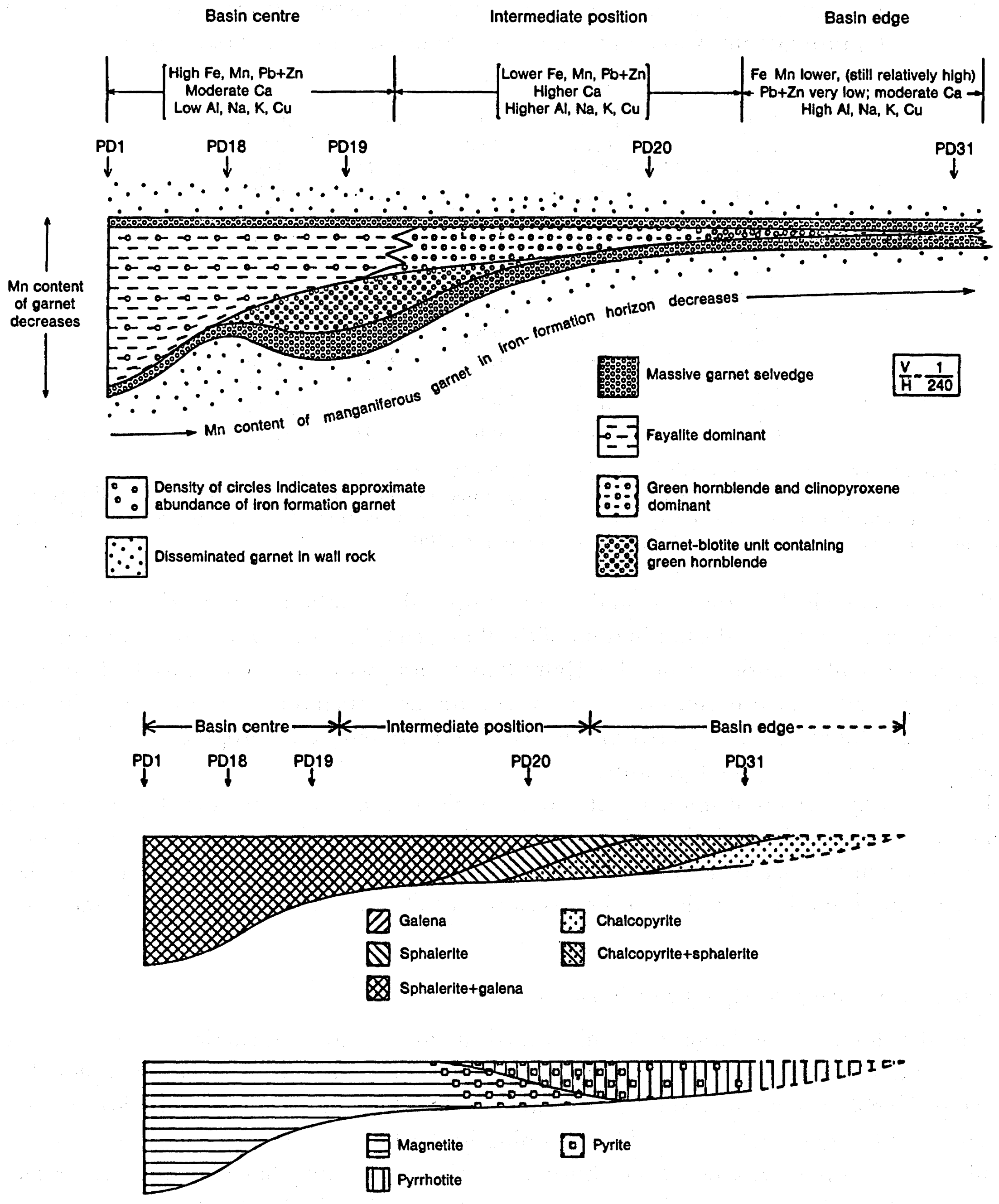


FIGURE 44. Cross sections of the Pegmont exhalative sulphide-bearing basin, showing (top) variation in metamorphic silicate assemblages, i.e. regional metamorphic mineral zoning, resulting from primary facies of chemical sedimentation. The latter is emphasized by the parallelism between the metamorphic silicate zoning and the sedimentary zoning of the associated exhalative sulphides. Maximum thickness of the unit (basin centre) is *ca.* 8.0 m, and maximum width of the basin is *ca.* 1400 m. PD1–PD31 indicate positions of principal drill holes (from Vaughan & Stanton 1986).

TABLE 13. RANGES OF MAJOR OXIDE VALUES OF REPRESENTATIVE METAPELITIC ROCKS OF THE BARROVIAN METAMORPHIC ZONES AS DETERMINED BY SNELLING (1957)

	(1)	(2)	(3)	(4)
SiO_2	43.36	62.17	18.81	30.26
TiO_2	0.18	2.53	2.35	92.89
Al_2O_3	18.55	33.29	14.74	44.28
Fe_2O_3	0.72	7.52	6.80	90.43
FeO	2.37	9.50	7.13	75.05
MnO	0.01[a]	0.20	0.19	95.00
MgO	1.12	3.92	2.80	71.43
CaO	0.20	2.38	2.18	91.60
K_2O	2.74	6.20	3.46	55.81
Na_2O	0.84	3.22	2.38	73.91
P_2O_5	0.01[a]	0.77	0.76	98.70
H_2O^+	2.39	5.40	3.01	55.74
H_2O^-	0.01	0.21	0.20	95.24
CO_2	0.01[a]	0.65	0.64	98.46

[a] Notional value of 0.01 applied where analysis indicates 'trace' or 'not detected'.

Columns: (1) lowest determination of Snelling's (1957) range of 13 Dalradian (Barrovian) metapelitic rocks; (2) highest determination of the 13 metapelites; (3) range of values (column 1 minus column 2); (4) range as percentage of highest value (column 3 divided by column 2 × 100).

with these chemical variations and with supposed variations in $P-T$ conditions are unconvincing, as a detailed examination of Snelling (1957) reveals. The author does not wish to place particular emphasis on the Dalradian zones (with which he has had negligible experience) and cites this simply as one of a number of metamorphic provinces in which currently accepted relations between chemistry, mineralogy, and proposed $P-T$ conditions seem to require some special pleading.

In view of the profound influence of zonal chemical variation on the development of zonal mineralogical variation within the minute – and without doubt isogradic – domain of the Pegmont chemical metapelites, it may be appropriate to consider a more substantial role for primary compositional variation in the development of mineralogical zonation in metapelitic terranes.

(ii) *Diagenetic zoning in evaporitic environments*

The development of large-scale mineralogical zoning by diagenetic processes is well-established. Diagenesis of saline lake sediments provides particularly good examples. Well-developed zeolite–analcite–K-feldspar zoning in the Pleistocene Big Sandy Formation of Arizona, and of glass–zeolite–K-feldspar zoning in the Pliocene sediments of Lake Tecopa in California (Sheppard & Gude 1968; Surdam & Sheppard 1978) have already been referred to (figures 45 and 46 respectively). The zonal pattern of the Big Sandy Formation is some 12 miles long, with individual zones up to *ca.* 1.8 miles wide. Surdam & Sheppard's (1978) description of the 'diagenetic mineral facies' (the term 'facies' being used in the sedimentary sense) is remarkably reminiscent of an account of metamorphic mineral zoning.

> Three diagenetic mineral facies are recognized in the tuffs of the Big Sandy Formation in Arizona. Tuffs nearest the margin of the formation [i.e. nearest the shore of the original saline lake] are characterized by zeolites other than analcime and are termed 'nonanalcimic zeolitic facies'. Tuffs in the central part of the lake basin are characterized by potassium feldspar and are termed the 'potassium feldspar facies'. Those tuffs between the nonanalcimic zeolite facies and the potassium feldspar facies are characterized by analcime and are called the 'analcime facies'....

> The boundaries between the facies are laterally gradational and difficult to recognize in the field. Fig. 7 [figure 45 of this present contribution] shows the diagenetic mineral facies for a composite of all the tuffaceous rocks in the Big Sandy Formation. This is the same pattern that is observed in individual tuff beds. The boundary between the nonanalcimic zeolite facies and the analcime facies was placed at the first appearance of analcime, and the boundary between the analcime facies and the potassium feldspar facies was placed at the first appearance of authigenic feldspar. (1978, pp. 153, 154.)

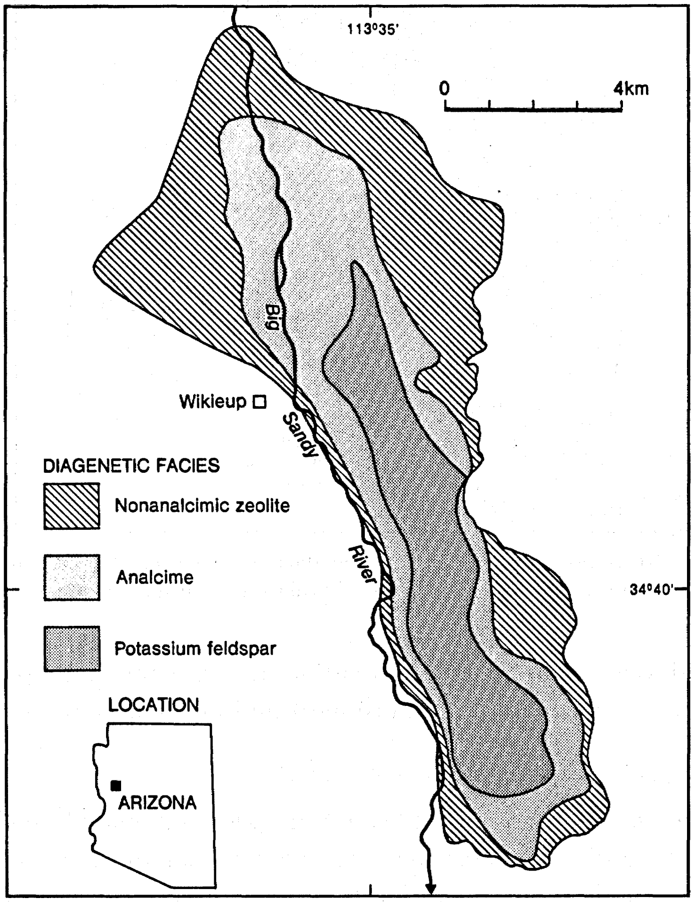


FIGURE 45. Diagenetic mineral zoning in the Pleistocene lake sediments of the Big Sandy Formation of Arizona (after Surdam & Sheppard 1978).

This description of relations between the diagenetic mineral zones is clearly couched in terms used by many metamorphic petrologists in describing relations between regional metamorphic mineral zones. Surdam & Sheppard go on to observe that 'the mineral facies in plan are elongated parallel to the depositional basin'. (1978, p. 154.)

Such saline lake deposits illustrate the potential for sedimentary/diagenetic zoning of zeolitic and feldspathic minerals. In a more or less analogous way Jeans (1978) has shown with considerable elegance the capacity of sedimentary/diagenetic processes to induce facies zoning of neoformed clays, chlorites and illites. Figure 47 (after Jeans 1978, fig. 91) illustrates the way in which interaction between restricted hypersaline water and normal seawater has led to the neoformation, in distinctive facies arrangement, of a range of clay–chlorite materials in the Keuper Marl. In this case the zonal (facies) distribution of the neoformed clays and

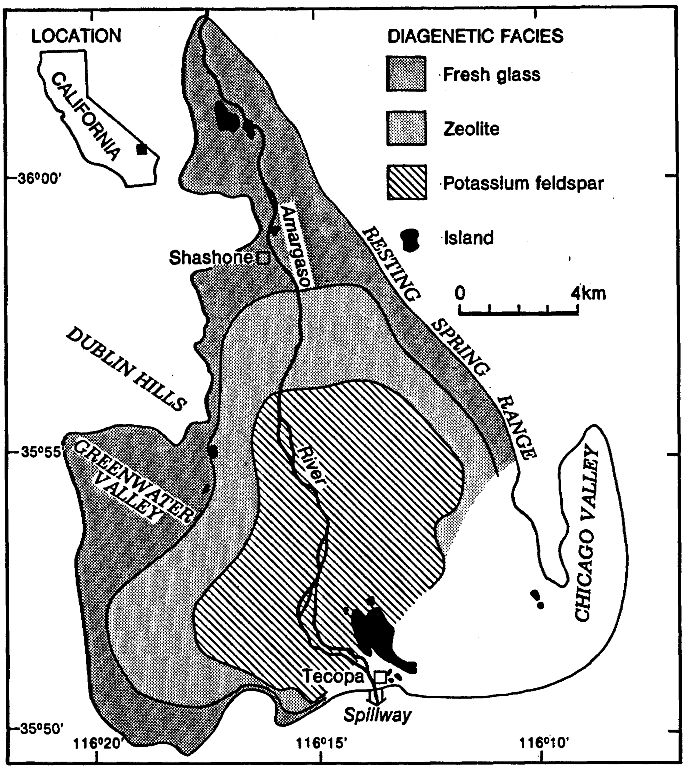


FIGURE 46. Distribution of preserved volcanic glass and zones of diagenetic minerals in the Pliocene sediments of Lake Tecopa, California (after Surdam & Sheppard 1978).

phyllosilicates has developed in systematic relationship with the facies patterns of carbonate and detrital materials (sandstones and mudstones) and of the accompanying evaporites.

(iii) *Sedimentary/diagenetic zoning in marine environments*

That different clays, chlorites, mixed-layer minerals and related zeolitic materials were capable of developing distinctive facies patterns, i.e. pre-metamorphic zonal distributions, in the sedimentary:diagenetic environment has been recognized for over 50 years. These involve both ancient and modern, and marine and non-marine, environments. Among the principal causes of such zoning are the varying interplay of different detrital and chemical sources, elutriation, differential adsorption and flocculation, ion exchange in clays and glassy materials, and neoformation under sedimentary/diagenetic conditions that vary systematically in space.

Galliher (1935), in considering the present-day development of glauconite by the marine degradation of detrital biotite, pointed out that in the sediments of Monterey Bay, California, biotite-rich sandy sediments laid down in near-shore zones were facies equivalents of glauconitic muds laid down further out in the bay.

Smoot (1960), working on the Chester Series of the Mississipian of Illinois, observed that the clay minerals of these sedimentary rocks were distributed in a regular pattern of essentially concentric zones that developed outwards from a delta on the open palaeoshelf. He considered this distribution of clay minerals to be essentially a depositional, rather than a diagenetic, feature: coarser kaolinite settled close in shore, whereas finer material remained suspended for

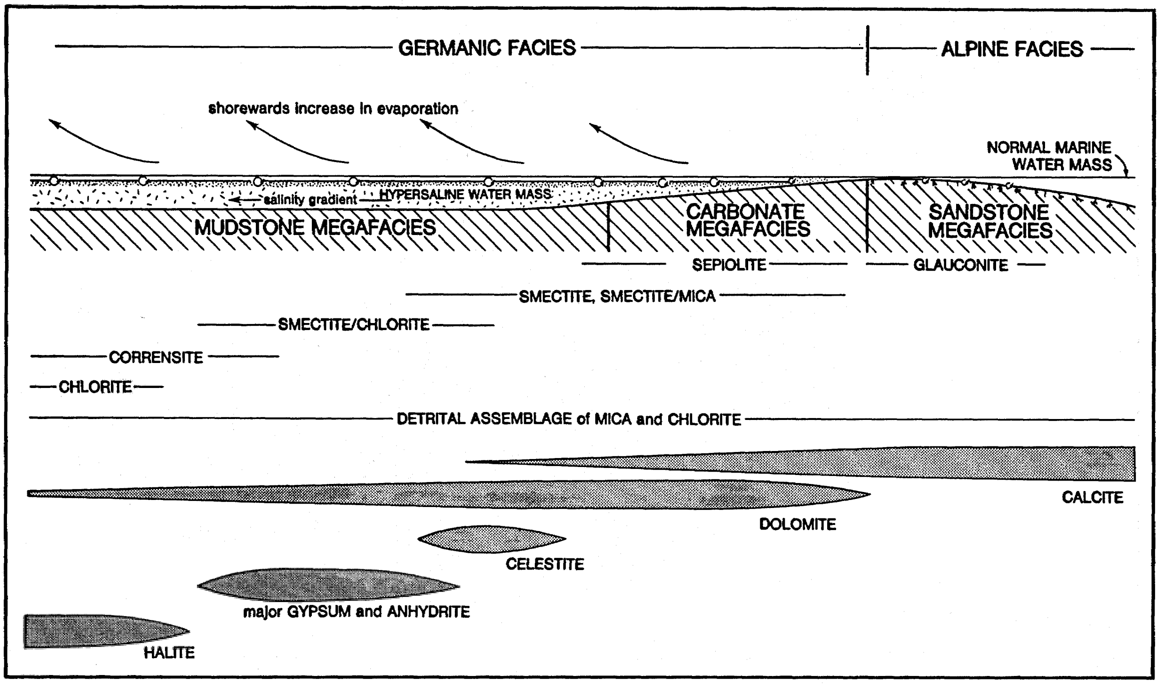


FIGURE 47. Distribution of clays and clay–chlorites in the Keuper Marl, and the model proposed for their origin by Jeans (after Jeans 1978).

some distance out to sea, thus adsorbing K^+ and being transformed to illite, which settled into the sediment further from shore.

Millot (1970 and several earlier works) and de Segonzac (1970) have both proposed that kaolinite, in tending to deposit as larger crystals closer to its continental source, may be a palaeogeographical indicator of old shorelines.

Griffen (1962), in studying clays being delivered to the present Gulf of Mexico, showed that a combination of current action and detrital clay particle size led to an ordered distribution of the different clay species, which in turn yielded a gradational facies pattern of clay minerals parallel to the coastline. Brockhamp (1942) and Hallam (1966) have noted that the Liassic chamositic ironstones of Germany and England respectively occur as a boundary facies between sandstones and shales, giving way laterally to sandstones on the shallower margin, and to silty shales towards deeper water. This led Brockhamp to propose that the ironstones developed as a near-shore facies, and to Hallam's suggesting that they were an accompaniment of pronounced delta formation, the chamosite-rich zones representing the pro-delta facies.

Ellison (1955) deduced a ferruginous facies, occurring near-shore between the palaeo-shoreline and carbonate reef facies, in the Middle Silurian sediments of eastern U.S.A. This ferruginous facies, the locus of the Clinton iron ores, constitutes a clear zonal development of iron-rich sediment containing abundant chamosite as well as the iron oxides. In a detailed study of this iron-rich facies, Shoen (1964) showed that all of chamosite, illite and chlorite were abundant as components of the silicate facies, the illite being detrital; chlorite, diagenetic; and the chamosite a primary, syngenetic precipitate, i.e. neoformed. Porrenga (1967), studying the development of iron-rich minerals in the modern sediments of the Niger delta, showed a clear

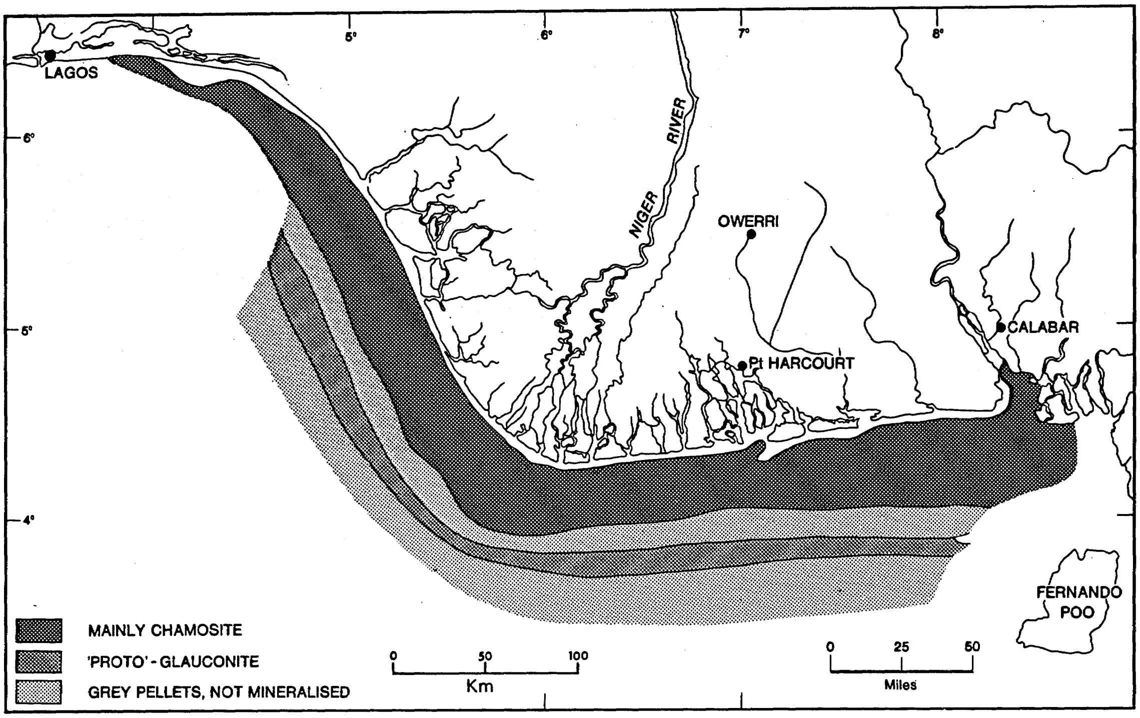


FIGURE 48. Sedimentry/diagenetic zoning of glauconite and chamosite (suggested precursors to biotite and almandine garnet respectively) and associated materials in the modern sediments of the Niger delta (after Porrenga 1967). Somewhat similar patterns might be expected in other major tropical deltas such as the Mouths of the Ganges, the Irrawaddy and the Mekong.

zoning of goethite, chamosite and glauconite parallel to the present shoreline (figure 48, after Porrenga 1967).

Also in the modern environment, Venkatarathnam & Ryan (1971) demonstrated a highly systematic zoning of chlorite, illite, smectite and kaolinite in the currently accumulating sediments of the eastern Mediterranean and Turovskii *et al.* (1981) have elucidated analogous zoning of hydromica, chlorite, 'chlorite mixed-layer', montmorillonite and kaolinite in the upper layer of the sediments of the Caspian Sea. Gibbs (1977), working on that part of the South American shelf receiving sediments from the Amazon River has demonstrated a clear zoning of clay minerals developed both along and across the shelf, which he attributes quite simply to sorting by size, i.e. elutriation processes in the shelf sea.

Jeans (1978), in the hybrid marine/evaporitic environment already alluded to (figure 47), recognized two principal clay assemblages.

1. A detrital assemblage of illite and lesser chlorite that occurred throughout the sediments investigated, and hence which did not exhibit any pattern of zoning.
2. A neoformed assemblage of Mg-rich clay minerals – sepiolite, smectite, chlorite and corrensite – each with a restricted (facies) distribution related to detrital, carbonate and evaporite mineral facies, the pattern as a whole having resulted from the transgression and regression of lighter, normal marine waters over heavier, highly saline Mg-rich waters of a restricted hypersaline environment.

Thus whatever the cause: variation in the nature and climate of the source; systematic differences in detrital particle size or susceptibility to flocculation; systematic variation in adsorption while suspended in the sea or following sedimentation; vagaries of neoformation, and patterns of sea-floor alteration and aggradation; variation in climate and water depth, and consequent differences in temperatures of sedimentation; marine transgression and regression; it is clear that the incidence of clay, mixed-layer clay and clay–chlorite–mica minerals in shelf and other relatively shallow marine and large-lake environments commonly acquires distinct zoned patterns in the sediments concerned. The details of these patterns are not entirely constant, and there is considerable overlap, but there does seem to be a widespread tendency for the sediments to develop broad facies patterns not only in the size and nature of their coarser components and in the nature and disposition of chemical materials such as carbonates and evaporites, but also, if less obviously, in the nature of the clay minerals that these sediments contain.

Little work seems to have been done on facies of clay and related mineral sedimentation on modern volcanic shelves, e.g. that of the northern side of Java. However, volcanic contributions – both detrital and chemical – may well modify and enhance features of clay mineral distribution. In areas of seaboard calc-alkaline volcanism and hydrothermal activity it is likely that kaolinite is joined by halloysite and one or more of gibbsite, diaspore and boehmite. Considerable hydrothermal iron is also added to the sediment, leading to the deposition of goethite, lepidocrocite, limonite and perhaps haematite in the near-shore oxide facies and, presumably, the generation of chamosite and glauconite in sedimentary facies approximating to those noted by Porrenga (1967). Uplift and reactivated erosion of senile hinterlands characterized by extensive laterite–bauxite would also lead to the gross contribution of ferriferous and aluminous material, and the addition of iron–aluminium hydroxide mixed-layers (e.g. the isostructural compounds goethite–diaspore), chamositic, glauconitic, and iron-rich chlorite, zones to the more common kaolinite–illite and smectite-rich clay mineral facies pattern.

(iv) *Possible influence of sedimentary/diagenetic zoning on regional metamorphic mineral zoning*

Thus with the superimposition of a substantial component of iron, and somewhat greater-than-usual amounts of aluminous matter, on what might be referred to as 'normal' patterns of clay mineral sedimentation, we may visualize the development of a clay and clay-type mineral zoning such as that shown in figure 49*a*.

It will now be recalled that all the minerals of this pattern have been proposed as precursor materials of the common regional metamorphic index minerals.

Figure 49*a* emphasizes the way in which such a facies pattern would lead to the development of zones variably transgressive to bedding, a feature of all sedimentary accumulations in which facies patterns have developed, and commonly sharply delineated by carbonate-rich facies. Figure 49*b*, *c* shows how such facies-based mineralogical zones would translate into regional metamorphic mineral zones on the basis of the precursor principle. For the pelitic rocks, on this basis, some regional metamorphic zones may reflect sedimentary/diagenetic facies, as the latter earlier manifested themselves in subtle variations in clay, mixed-layer clay, chlorite, clay–chlorite and clay–zeolite mineral assemblages.

It may be seen that under such circumstances a single stratum may encompass several zones (as noted by Barrow 1893 and Frey 1978), but that resulting metamorphic mineral zones may develop at a high angle to bedding and hence cut across later-developed fold structures. This may be further complicated by seaward migration of environments accompanying the

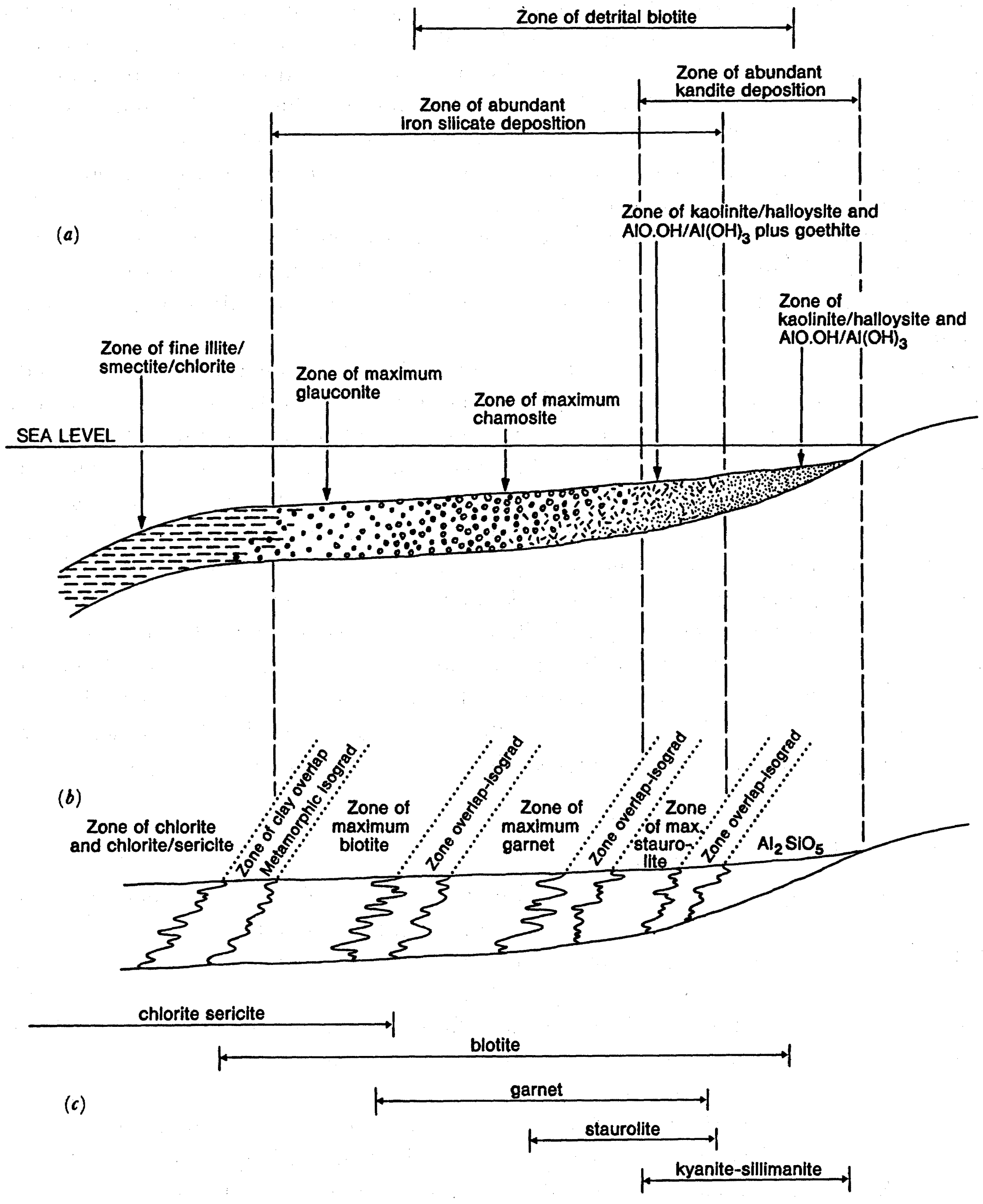


FIGURE 49. (*a*) Diagrammatic, idealized representation of a pattern of notably aluminium- and iron-rich clays and clay-type material that might develop in the warm waters of a tropical shelf to which seaboard calc-alkaline volcanic and hydrothermal activity were contributing. (*b*, *c*) Similarly idealized representation of metamorphic mineral zones that might result from isochemical regional metamorphism, with concomitant precursor → metamorphic mineral transformation, of the original pattern of detrital, sedimentary and diagenetic clays of (*a*). (Note that the original clay mineral facies boundaries and their derived metamorphic zones cut across bedding, and hence would be transgressive to later fold structures.) (After Stanton 1979, 1982*a*.)

development of large fans such as the Niger and Mississippi deltas (figure 50), cyclic migration of environments (figure 51) or regression and transgression of sedimentary facies patterns (figure 52). If (1) the different environments portrayed in these three figures involved clay mineral facies patterns; (2) as a result of progressive fan development, cyclicities, transgression and regression such facies patterns developed configurations such as those of figures 49–52; and (3) upon regional metamorphism, these clay mineral domains converted directly to metamorphic mineral zones, such zones would clearly exhibit discordant relations with bedding on both small and large scales.

The very simple situation portrayed in figure 49 may of course also be modified or even complicated by the development of off-shore banks and shallows, groups of islands and so on, which would have the general effect of inducing local facies reversals, the superimposition of local facies patterns surrounding banks on the broader pattern of the shelf as a whole, and so on. A variety of primary complications of this kind may be visualized, leading to corresponding complexities in subsequent derived metamorphic mineral zonation.

(v) *Regional vis-à-vis contact metamorphic mineral zoning patterns*

Whereas the mineralogical zoning developed in the Pegmont deposit, in many Proterozoic iron formations and in other chemical sediments exhibiting primary facies patterns can be

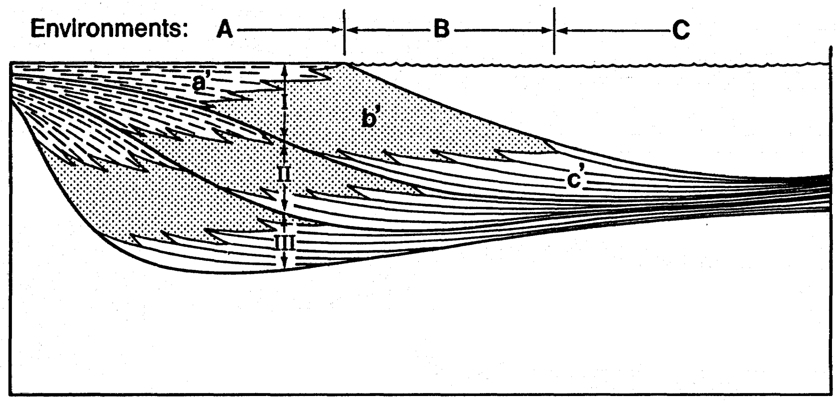


FIGURE 50. Diagrammatic cross section of a sedimentary fan illustrating the relation between environment (A, B, C), facies (a′, b′, c′), increments of sedimentation (I, II, III) and, finally, the relation of facies boundaries to bedding direction. If the facies shown here were also clay mineral facies, and if upon regional metamorphism the latter yielded a zonal arrangement of metamorphic mineral assemblages, the resulting metamorphic zones would dip across, i.e. in the opposite sense to, the bedding (after Busch 1971; Selley 1976).

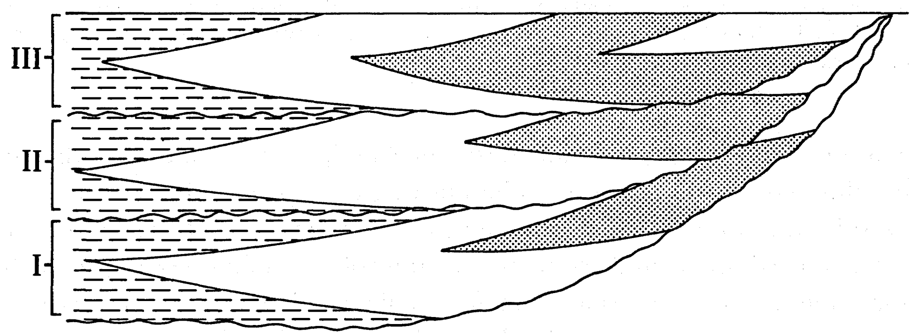


FIGURE 51. Diagrammatic cross section of portion of a sedimentary basin illustrating cyclicity (I, II, III) and lateral variation of cycle type within genetic increments of strata (after Selley 1976).

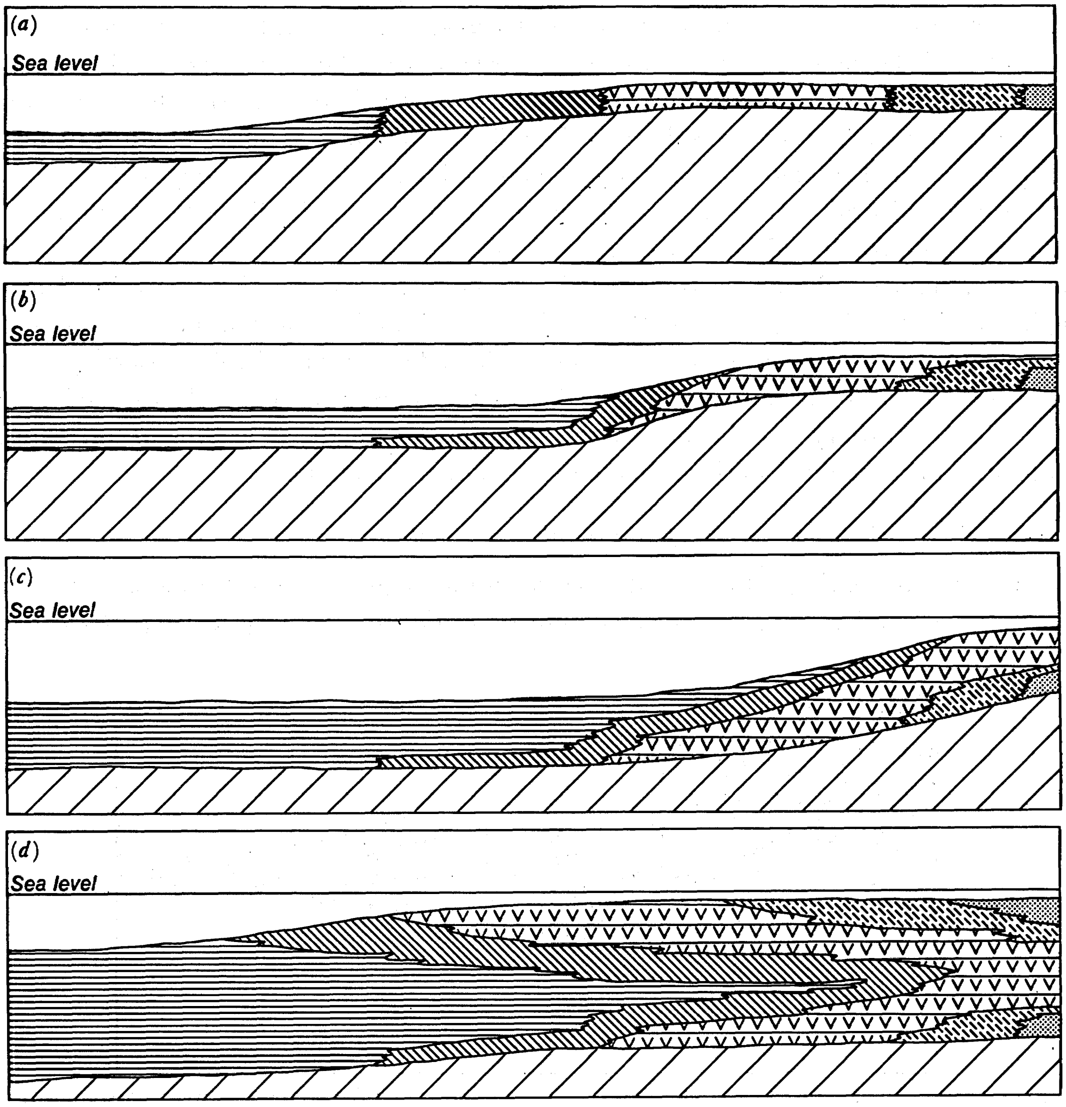


FIGURE 52. Diagrammatic cross section illustrating the effect of transgression and regression on the ultimate configuration of facies boundaries. If the facies patterns of this diagram and of figures 50 and 51 involved patterns of variation of clay minerals that later constituted precursors for the direct development of regional metamorphic minerals, the resultant metamorphic zones would have correspondingly complex configurations (adapted from Sheldon 1963; the sedimentary wedge has been thickened in (*a*) to increase the clarity of the legend). (*a*) Period of initial sedimentation of cycle and of maximum regression; (*b*) transgression; (*c*) period of maximum transgression; (*d*) period of maximum regression.

demonstrated to reflect original sedimentary/diagenetic zoning patterns, the inclusion of the common alumino-silicate minerals – the micas, garnet, staurolite and the Al_2SiO_5 polymorphs – within the ambit of such an interpretation immediately raises the question of analogies between regional and contact metamorphic zoning. Why, if such regional metamorphic mineral zonation has a sedimentary/diagenetic basis, is its pattern so similar to that of contact metamorphic zoning, clearly attributable to localized heating, metasomatism and reaction?

This is far too large and complex a question to be considered in detail here. Several salient points may however be enumerated.

1. Most granitoid/pelite contacts (for the world as a whole, perhaps 99% of such contacts) display little more than minor hornfelsing, and do not develop a well-defined pattern of mineralogical zoning. Those relatively few that do have attracted wide attention and become 'classic', and given a prominence and generality far beyond that merited by what is in reality a very limited incidence.

2. Some zonal arrangements around granitoids may represent sedimentary facies patterns, of the type already described, developed about marine volcanic centres now represented by the granitoid in question. A history of sub-volcanic intrusion might well lead to the contact metamorphism and 'baking in' of earlier circum-volcano facies patterns, particularly where the volcanism and associated pyroclastic and volcaniclastic debris was calc-alkaline, and the climate tropical (see §7*h*).

3. Among ore deposits of all types mineralogical zoning, including all of oxides, sulphides, sulphosalts, carbonates, silicates and others, is the rule rather than the exception. Zoning of oxide → copper sulphide → zinc–lead sulphides outward from granitoid contacts in Cornwall had been recognized by de la Beche by 1839 (see Dewey 1925) and this general type of pattern is not uncommon in contact metamorphic aureoles. However, lateral zoning of oxide → copper sulphide → zinc–lead sulphides is by no means uncommon as an exhalative:sedimentary feature in regionally metamorphosed stratiform orebodies. That is, much the same pattern of zoning is generated by contact metamorphic fissure filling and metasomatism on one hand, and by exhalative sedimentation followed by regional metamorphism on the other. Given the quite substantial variety of silicate zone patterns generated both by contact and regional metamorphism, it is not surprising that similarities between the two arise, even if only by chance.

A number of other considerations of this general kind present themselves and require careful analysis in any reevaluation of analogies between contact and regional metamorphic zoning.

(*b*) *Zonation of mineral chemistry*

We have been concerned to the present point with zoning of mineral *assemblages*. This, however, leads on to the possibility that zonation of metamorphic mineral *chemistry* may (at least in some cases) have a sedimentary:diagenetic ancestry.

Two relationships may provide examples: the increase in substitution of Al^{3+} for Si^{4+} in biotites, and the increase in $(FeO + MgO)/(MnO + CaO)$ in aluminous garnets, with increase in apparent regional metamorphic grade.

(i) *Aluminium in biotites*

On the basis of nine biotite samples from the range of Barrovian zones, Snelling (1957) noted a qualitative relationship between grade and the behaviour of Al in this mineral. He commented that it was 'of interest to note that the medium- and high-grade biotites have a higher alumina content and a lower silica content than the lower-grade biotite, suggesting that the degree of replacement of Si^{4+} by Al^{3+} in the Z group increases with increase in metamorphic grade.' (1957, pp. 302, 303.)

Rutherford (1973), on the basis of experimental results, indicated that higher Al increased the stability of biotite at higher temperatures and higher oxygen fugacities.

While the work of Rutherford does indeed indicate that Al in biotite may be temperature-dependent, it is interesting in the present context to consider the above deductions of Snelling (1957) in the light of a review of the nature and incidence of glauconite and chamosite in Phanerozoic sediments by Van Houten & Purucker (1984). These authors draw attention to the work of Sorokin *et al.* (1980) who report that glauconitic materials range from glauconitic mica (low-Al) in an open-sea facies to nearly pure smectite (high-Al) in a coastal facies in a very consistent way. Such a spatial (facies) control of glauconitic and chamositic materials is corroborated by observations on early Palaeozoic greensands of Baltoscandia (Berg-Madsen 1983) and late Cretaceous greensands of the Atlantic Coastal Plain (Owens & Sohl 1973). In both of these sequences low-Al glauconitic minerals appear to have developed in cool, deeper (750 m) water, whereas high-Al glauconitic minerals accumulated in cool, shallow water. Chamosite (see also Porrenga 1967) is also favoured by shallow-water conditions, but in warm seas. The high-Al mineral of Berg-Madsen (1983) is a low-Fe glauconitic mica, whereas the high-Al mineral of Owens & Sohl (1973) and Sorokin *et al.* (1980) is a glauconitic smectite. Van Houten & Purucker (1984) conclude that the formation of glauconitic materials is normally favoured by a cool climate or upwelling water, and that such materials contain a decreasing amount of aluminium seaward (1984, p. 233).

It has been suggested in preceding sections of the present contribution that (i) some regional metamorphic biotites are derived directly from glauconitic precursor materials and (ii) that, at least in some cases, increasing apparent regional metamorphic grade may reflect a progressive approach towards a shoreline, the kaolinite-rich near-shore facies constituting the parent materials for the Al_2SiO_5-bearing, 'high-grade' metamorphic zone.

If this is the case, the observations of Snelling (1957) on the increase in Al, and tetrahedral Al, of biotite with increasing apparent metamorphic grade in the Dalradian metapelites, and those of Van Houten & Purucker (1984) and others on the shoreward increase in Al in glauconitic materials, invite contemplation.

(ii) *Manganese in almandine garnet*

Miyashiro (1953), Engel & Engel (1960) and Sturt (1962) demonstrated a decrease in garnet Mn with increasing metamorphic grade in the Gosaisyo–Takanuki area of Japan, in the Adirondacks, and in the Dalradian of Scotland respectively. Lambert (1959) showed a decrease in Ca and an increase in (Fe + Mg) with increase in apparent regional metamorphic grade in the Morar district of NW Scotland and, combining this with information derived from analyses of Goldschmidt (1920) of garnets from the Stavangar area and by Barth (1936) on garnets from Dutchess County, New York, Sturt (1962) concluded that there was a systematic tendency for (Mn + Ca)/(Fe + Mg) in almandine-type garnets to decrease with increase in regional metamorphic grade. Although Sturt clearly recognized that this phenomenon might be affected by variation in the bulk composition of the host rocks (1962, p. 183) he considered the principal influence to be the decrease of garnet molar volume with increase in grade, and the concomitant progressive substitution of smaller ions (Fe, Mg) for larger ones (Mn^{2+}, Ca). He concluded that 'the ratio CaO + MnO:FeO + MnO in garnets of the pelitic schists may therefore be employed as a convenient and sensitive indicator of the metamorphic grade of the host-rock.' (1962, p. 183.)

It is now clear that Sturt's (1962) concern that (CaO + MnO):(FeO + MgO) relations might reflect bulk rock composition as well as metamorphic conditions was fully justified. The present author and his co-workers (Stanton 1976, 1982, 1987; Stanton & Roberts 1978; Stanton & Williams 1978) have shown that relatively huge variations in this ratio may occur over distances of a few millimetres – distances far too small to have sustained differences in regional metamorphic grade – and that such variations reflect primary constitutional differences related to bedding (cf. figures 2, 3, 5, 7 and 8).

The most spectacular small-scale variation of this kind occurs across bedding. However, it also occurs along bedding. In the two cases investigated in detail (Stanton & Roberts 1978, on Broken Hill; Stanton & Vaughan 1979, Vaughan & Stanton 1986, on Pegmont) the sediments had been laid down in small basins, and the Mn (and MnO + CaO) content of the garnets was found to increase systematically from the basin edge to basin centre (figure 53). That is:

(1) garnet compositions displayed zonal arrangements in space;

(2) the distances involved (*ca.* 1000 m at Pegmont; *ca.* 120 m at Broken Hill) were far too small to have sustained variations in regional metamorphic grade, and showed no independent evidence of having done so; and

(3) the 'zonal arrangements' of (1) corresponded with changing facies (microfacies) of sedimentation from the edges towards the centres of the smaller basins concerned.

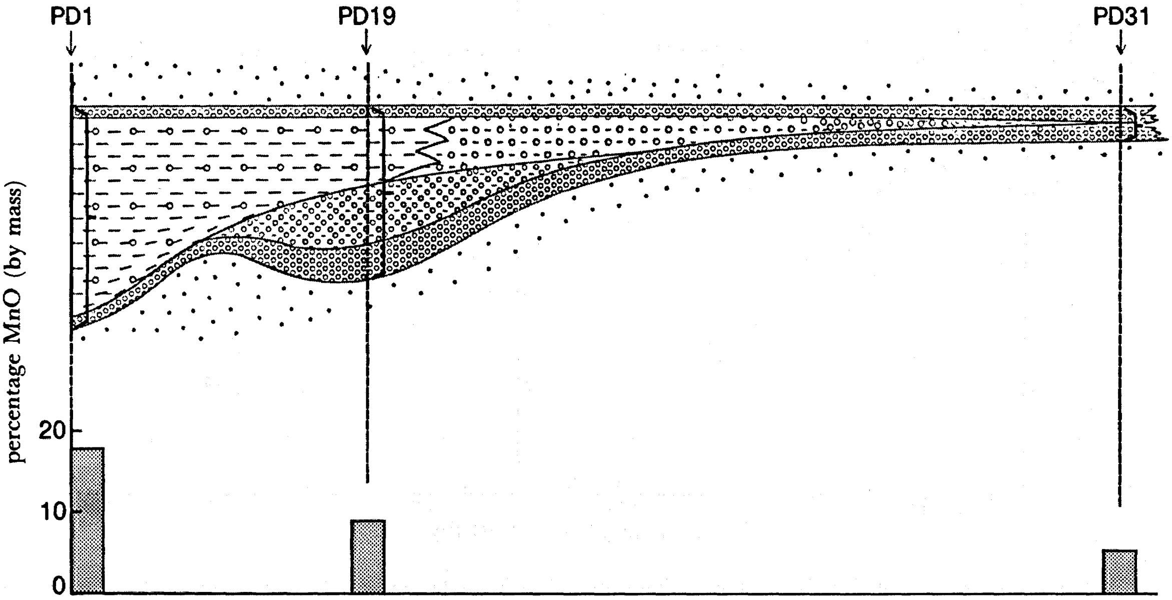


FIGURE 53. Mineralogical cross section of the Pegmont basin (cf. figure 44) showing average MnO content of almandine–spessatite garnets (filled bars along base of diagram) in the three diamond drill core intersections of the sulphide-bearing layer PD1, PD19 and PD31, representing basin centre, basin slope and basin edge respectively.

Figure 54 compares the diagrams of Miyashiro (1953), Engel & Engel (1960) and Sturt (1962), in which these authors relate MnO and (CaO + MnO) content of almandinic garnet to metamorphic grade, with diagrams showing facies and across-bedding variation in the small metapelitic ore and iron formation units at Pegmont and Broken Hill.

This indicates that present ideas concerning relations between garnet composition and regional metamorphic grade might be reexamined in the light of the precursor principle. It

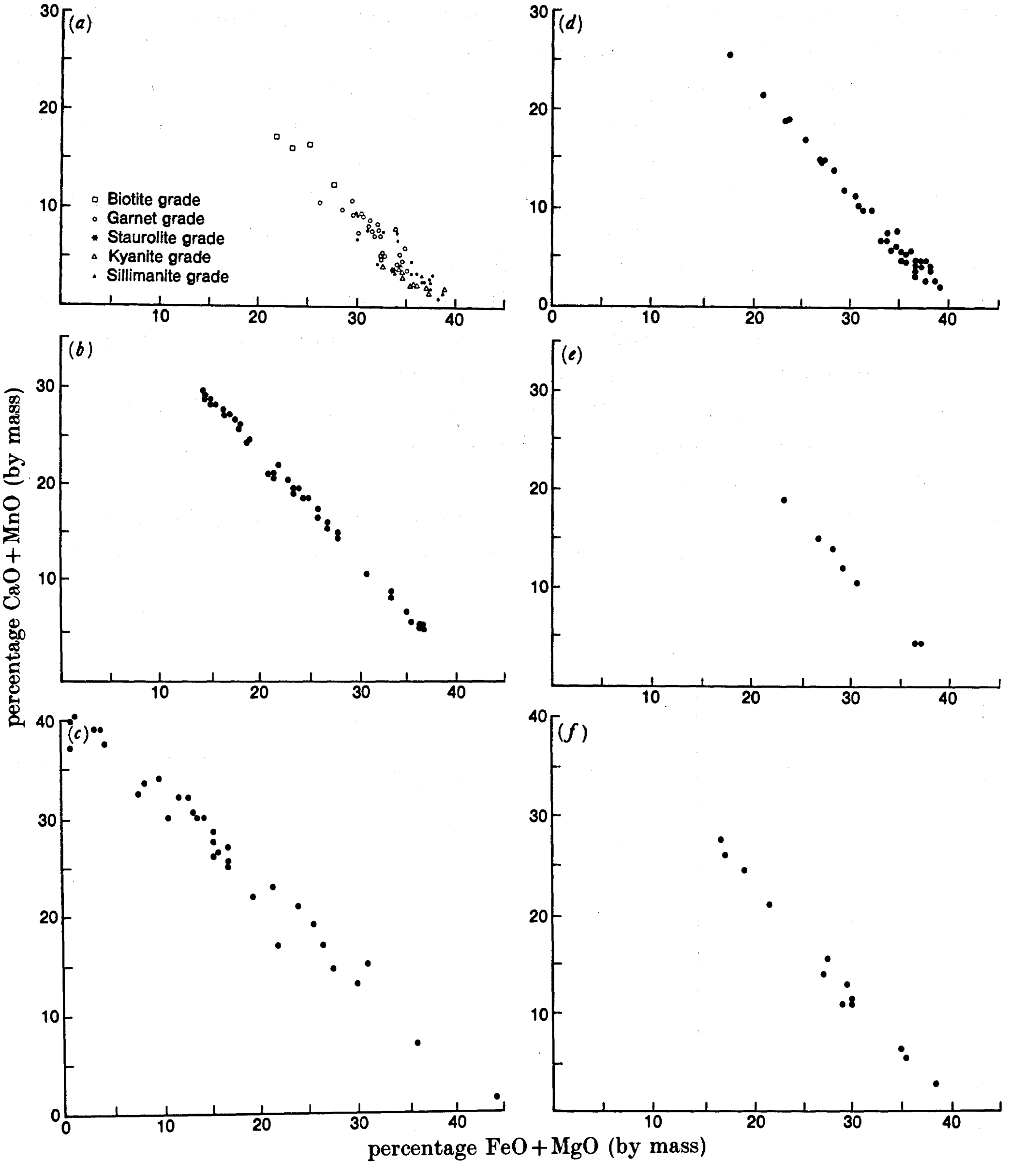


FIGURE 54. Comparison of Sturt's composite diagram indicating relationships between garnet (CaO+MnO):(FeO+MgO) in pelitic schists, with (CaO+MnO):(FeO+MgO) in garnets of exhalative localities too small to have sustained differences in metamorphic grade. (*a*) the diagram of Sturt, incorporating the results of numerous investigators (see Sturt 1962); (*b*) range of garnet compositions in the 10 m length of diamond drill intersection PD1 through the Pegmont unit and its immediate envelope; (*c*) range of garnet compositions in drill core intersecting the Gams Iron Formation of Gamsberg (Rozendaal 1982); (*d*) range of garnet compositions in an interval of 120 m along bedding in A-lode, Broken Hill, New South Wales (Zinc Corporation diamond drill hole nos. 404, 544 and 648, drilled underground at approximately 700 m); (*e*) range of garnet compositions across bedding in A-lode, Broken Hill, as represented by the single drill core intersection DD 1159; (*f*) range of garnet compositions across bedding in a small banded iron formation at Broken Hill as represented by the single 60 cm intersection of diamond drill core DD MMA-1A.

has been demonstrated by the above investigators that almandinic MnO (and CaO + MnO) commonly decrease with what appears to be increase in metamorphic grade. It is a corollary of the precursor principle that at least in some cases an apparent increase in grade may reflect nearer-shore sedimentation and diagenesis. As noted above, detailed investigation of garnet compositions in the two small, regionally metamorphosed, sedimentary basins of Broken Hill and Pegmont has demonstrated that garnet MnO and CaO decrease from basin-centre to basin-edge. Finally observations on modern marine sediments show manganese to be more abundant in those deposited in deeper water.

Thus although variation in the MnO and CaO contents of garnet may well be related to variation in regional metamorphic grade in some major metamorphic terranes, the above indicates that there may be others where it is related to large scale, primary facies patterns in which the original pelitic sediments were involved.

(*c*) *Grain size*

There is a strong tendency for at least some of the lithological units of high-grade terranes to exhibit a relatively large grain size. Not surprisingly this has been attributed to enhanced grain growth stemming from the higher temperatures concomitant with the higher grades of regional metamorphism.

Although it is unquestionably true that grain boundary migration and hence grain growth are promoted by rise in temperature, any assumption that temperature is the only influence in the development of a particular grain size is much too simple. Other factors that may be of importance are numbers of phases, grain boundary inhibitors and preferred orientations (see Stanton 1972*a*).

Numbers of phases

Wherever regional metamorphism has induced coarse grain size, it is noteworthy that the lithologies concerned are, mineralogically, relatively simple.

This effect is illustrated well by highly metamorphosed stratiform sulphide bodies, such as those of Broken Hill, New South Wales, and some of the units of their surrounds. Within the ore lenses of Broken Hill there occur considerable volumes of material, e.g. galena, sphalerite, pyrrhotite, bustamite, rhodonite, garnet, feldspar, which are almost monomineralic, i.e. 'single phase', in constitution and which exhibit individual grain sizes of the order of several centimetres. Among the more spectacular of these are coarse lenses of almost pure galena in which individual grains may be 7–10 cm in largest dimension, grain boundaries smoothly curved and of low curvature, and triple junctions close to 120°. Similar coarse grain sizes and grain boundary configurations are found in the other common sulphides, silicates, etc., where these occur as substantially single-phase aggregates.

Among the more prominent, substantially 'two-phase', aggregates of the conformable ore lenses at Broken Hill are those of sphalerite–galena and feldspar–quartz. The latter constitute much of the 'ore pegmatite' of the lodes: stratiform feldspar–quartz layers exhibiting coarse grain size, common graphic fabric, and the general appearance of igneous pegmatites. Like the associated conformable sphalerite–galena layers, however, these pegmatites appear to result from *in situ* coarsening, in this case, of K- and Na-rich feldspar and associated quartz. Although both of these pairings, and analogous, less common ones, develop grain sizes of the order of a centimetre or so they generally do not attain the extreme coarseness of grain exhibited by some of the essentially single-phase aggregates. (In this connection it should be noted that the incidence of *grain* boundaries *vis-à-vis phase* boundaries depends on the proportions of the phases as well as their number. For example, in a random two-phase aggregate a maximum ratio of phase boundary area to grain boundary area will occur when the proportions of the phases are 1:1. Any departure from this will decrease the ratio, assuming the preservation of randomness.)

Increasing mineralogical complexity brings a general decrease in mean grain size and, within the Broken Hill ore environment as a whole, the more complex silicate lithologies are relatively fine-grained, i.e. exhibit grain diameters less than 0.1 cm.

This general feature, i.e. an inverse relationship between grain size and number of phases, is common in all metamorphosed stratiform ore environments. It is a conspicuous and commonly noticed phenomenon in these situations, where economic pressures demand especially critical observation, but there can be no doubt that it pertains in regionally metamorphosed milieux generally.

The reason for such an inverse relationship is elementary and a simple consequence of the principles of grain growth. Within any polycrystalline aggregate, grain growth is a consequence of grain boundary movement, which proceeds towards the centre of curvature of the grain boundary and hence leads to the elimination of smaller grains and a corresponding enlargement of larger grains. Such movement is thermally activated and proceeds until equilibrium for a given temperature is approached.

With the exception of the formation of duplex twins, such grain boundary movement can occur only when like meets like, i.e. where, for example, two grains of galena, or of feldspar, meet. Apart from the duplex twinning mentioned above, no movement occurs where unlike meet, i.e. along *phase* boundaries, such as those between galena–sphalerite or feldspar–quartz.

It follows that the fewer the major phases in a polycrystalline aggregate, the more commonly like meets like in *grain-* (as distinct from phase-) boundaries, and the greater the opportunity for grain growth. Thus single-phase aggregates may provide a medium for extensive boundary migration and consequent growth, a phenomenon readily demonstrated by experiment, in which, at appropriate temperatures, aggregates consisting of thousands of grains may be converted to a single grain.

Conversely the more numerous the phases in a polycrystalline aggregate, the less commonly like meets like, the lesser the opportunity for grain boundary migration, and hence the lesser the amount of grain growth.

Grain boundary inhibitors

This is closely related to the foregoing. Small particles of a very minor phase – original 'impurities', minor products of exsolution that have found their way to grain boundaries, and so on – may occur along grain boundaries and at triple junctions in the major phase. For the reasons given above these may lock the major-phase grain boundaries in which they occur, so preventing grain boundary migration and inhibiting grain growth. In this way the grain growth in an otherwise overwhelmingly dominant major phase (perhaps 98 % of the rock) may be almost completely inhibited and lead to the retention of a relatively fine primary grain size. This appears to be well illustrated by the relatively fine-grained garnet sandstones (garnet quartzites) and cherty quartzites of the high-grade metamorphic terrane of Broken Hill.

Preferred orientations

Whereas grain boundary migration and consequent grain growth is dominantly thermally induced (some grain boundary changes are strain induced) the principal driving force for movement is the degree of misfit along the grain boundary; the higher the angle of misfit the higher the energy of the interface and hence the higher the driving force for boundary movement, reduction of degree of misfit and thus reduction of grain-boundary free energy.

Any factor that lessens or minimizes angles of misfit inevitably lessens the free energy of the interface and hence the tendency for that interface, the grain boundary, to move. One such factor is preferred orientation.

In the detrital sedimentary context, granular minerals such as quartz, feldspar, pyroxene, amphibole, and oxides such as magnetite, have a strong tendency to equidimensional shape and to settling into random (crystallographic) orientation with respect to each other. The phyllosilicates and clays, on the other hand, tend to flaky shape parallel to their basal cleavage, and to settle with basal planes near-parallel and hence with a substantial degree of preferred orientation. They may also develop preferred orientations during diagenetic growth: following its initial observation by Valeton (1958), Harder (1980) noted that 'newly formed glauconites in natural sediments show uniform optical orientation.' (1980, p. 221.)

The granular grains will therefore have a higher mean angle of misfit than the flaky grains. There will thus be a larger mean driving force for grain boundary movement in the granular aggregates and hence, all other things being equal, a greater degree of grain growth in the granular, compared with the flaky, aggregates.

It is thus apparent that there are several factors in addition to temperature that influence the final grain size of a sediment undergoing regional metamorphism. The most important of these are the numbers and proportions of phases, minor-phase grain boundary inhibitors, and preferred orientations. Thus for a given temperature it might be expected that a well-washed, one- or two-phase, granular sediment would attain a significantly greater equilibrium grain size than a poorly washed, six-phase sediment containing a large proportion of platy minerals.

This is a good first-order approximation to what is observed in the field. How does it accord with the suggested tie between regional metamorphic mineral zonations and pre-existing sedimentary facies patterns, and the proposition that increase in 'metamorphic grade' may in some cases reflect shallowing facies of sedimentation?

At first sight the correlation appears good. In, for example, a near-shore non-carbonate environment receiving a significant felsic–intermediate volcaniclastic component, the sediment might be expected to be a moderately winnowed quartzo-feldspathic silty one with, as its principal clay component, kaolinite (see previous section on zoning). With its small number of components such a sediment would have a relatively high capacity for grain growth and, if an appropriate temperature were reached, kaolinite and kaolinite–gibbsite mixed layers would convert to one or more of the Al_2SiO_5 polymorphs. Minor amounts of illite would yield subordinate muscovite. The result would be a relatively coarse-grained feldspar–quartz–sillimanite–(muscovite) assemblage – a 'quartzo-feldspathic sillimanite gneiss'.

At the other end of the palaeogeographical spectrum, i.e. towards the shelf-edge, the sediments would be finer and genuinely pelitic as compared with the nearer-shore silts. They would be products of extensive elutriation, and little winnowed. Their mineral assemblage would include the very finest fractions of quartzo-feldspathic detritus, illite and smectitic clays, chlorites, and perhaps glauconitic material and a variety of other authigenic products. They would thus consist of a large number of components and of these the major proportion would be clays, chlorites and related phyllosilicates, all of which have a pronounced platy form and which would settle and accumulate with a high degree of preferred orientation. Such features encompass all of the principal factors in the inhibition of grain boundary migration. Very little grain growth could occur and the final metapelitic rock, a chlorite–sericite–quartz schist, would have a grain size not very different from that of the original sediment.

An intrinsic part of any consideration of grain size is the development of porphyritic structure. This has been examined by many investigators and is a problem to which there almost certainly is no single, simple answer. Some possible mechanisms, which may operate under a variety of circumstances, are the following.

1. The simple transformation of large particles, e.g. chamosite ooliths and particles occurring in fine pelitic material, yielding garnet porphyroblasts set in a finer groundmass.
2. Transformation of concretions and related products developed by post-sedimentation and diagenetic processes, a derivation that would account for many 'spotty' porphyroblasts, and porphyroblasts that straddle bedding planes.
3. Transformation and grain growth of relatively pure patches of fine-grained diagenetic materials. Prelithification movement of such patches before or during transformation might well lead to the formation of 'rolled' grains, e.g. garnet, containing inclusions of matrix with oriented textures.
4. Random nucleation and grain growth in a slightly inhomogeneous matrix, e.g. nucleation and growth of garnet in slightly more siliceous domains of a chlorite matrix. This might account for the growth of very large porphyroblasts in fine-grained matrices.
5. Post-diagenetic and metamorphic inhibition-dependent and orientation-dependent grain growth ('secondary grain growth' or 'coarsening' in the metallurgical sense; cf. Stanton 1972*a*, p. 299). These processes would readily account for porphyroblasts of a given mineral in a matrix of its own kind, e.g. quartz porphyroblasts in cherty and other quartz-rich metapelites, sphalerite porphyroblasts in massive zinc ores, and would, again, account for porphyroblasts that straddle bedding planes. Such mechanisms, combined with appropriate processes of annealing, could provide an explanation for many cases of porphyroblasts developed during, and after, tectonic deformation.

A brief consideration of this kind shows that, as in the case of mineral assemblages, there are likely to be a number of factors other than temperature and pressure influencing metamorphic grain growth and ultimate grain size in metasedimentary rocks. As with sedimentary/diagenetic precursors and their daughter metamorphic minerals, grain size may, in addition to the simple and well-recognized results of elutriation, have a subtle but fundamental sedimentary facies tie.

(*d*) *Regional metamorphic grade*

Nothing that has been said in this contribution has been intended to suggest that prograde metamorphism – and in some areas, polymetamorphism – is not a response to increased temperature and pressure within the prism of material involved. That such metamorphism is indeed a P–T–X response (particularly a temperature–composition response) on a regional scale has been taken by the present author as self-evident, and as established beyond question.

What has been emphasized more strongly than in the past, however, is that development of new metamorphic minerals may result not so much from the 'bulk chemistry' of the parent pelitic material, as from the crystal structures and chemical compositions of the innumerable individual particles of which it is composed.

If (i) regional metamorphism is substantially a response of these pre-existing crystalline particles to rise in temperature, (ii) the different crystal structures respond at different temperatures and (iii) such temperatures vary in space and time, it may be expected that the various relevant metamorphic daughter products will develop in ordered patterns in space and time. That is, regional metamorphism may proceed to different 'grades' that may reveal themselves by the areal distribution of different mineral assemblages and paragenetic sequences.

At first sight this may appear to be exactly the current conventional view of regional metamorphic grade and mineral zonation. This, however, is not the case, and the principle involved may be seen through a hypothetical reexamination of the Barrovian of southeastern Scotland.

These zones are currently regarded (and have been so regarded for almost 100 years) as reflecting the progressively changing response of a pelitic rock of essentially uniform bulk chemical composition (see, however, the earlier reference (pp. 608 and 610) to Snelling's (1957) analyses) to a rise in temperature that itself exhibited an ordered increase in space. Thus the mineralogical zonation from SSE to NNW of chlorite- to sillimanite-bearing assemblages is interpreted as indicating a general increase in regional metamorphic temperatures in a NNW direction. However, on the basis of the precursor hypothesis metamorphic temperatures may not have been significantly different overall; they may simply have been sufficiently high to convert all members of a group of precursor materials, arranged in zones of premetamorphic origin, to their respective daughter products (see figure 49).

The words 'sufficiently high' have been chosen deliberately. It would be very surprising indeed if all precursors converted to their relevant metamorphic daughter products at similar temperatures. There can be little doubt that the various transformations (where transformation, as distinct from simple grain growth, has been the mechanism involved) would take place at different temperatures, and the range might well be considerable. If this were the case different grades of metamorphism would be marked by the temperatures of precursor transformations rather than temperatures of intermineral reactions as currently visualized.

Clearly the interplay between zonal sedimentary/diagenetic patterns of precursor occurrence on one hand, and different temperatures (and pressures) of transformation of these precursors on the other, may well be complex. It is likely that neoformed chlorite will assume a high degree of crystallinity, and illite transform to muscovite, at lower temperatures than siliceous chlorites might transform to almandine, or kaolinite–gibbsite mixed layers re-order to sillimanite. However, the place of other potential transformations in terms of the 'standard' pattern of regional metamorphic zonation (chlorite–biotite–garnet–kyanite–sillimanite) is quite unknown at this stage. Indeed, temperatures of any particular transformation may be influenced substantially by kinetic factors, as already suggested in the cases of sillimanite and cordierite (Stanton 1983, 1984*a* and this paper) and this, together with the palaeogeographical factors already referred to, might induce reversals and other deviations from 'normal' zoning patterns.

(*e*) *Metamorphic equilibrium: connotations of mineral chemistry of 'coexisting phases'*

It has long been known that certain coexisting metamorphic mineral pairs, e.g. garnet–biotite (Frost 1962), may exhibit systematic compositional relationships. Variation in such compositional ties has been ascribed to the attainment of chemical equilibrium under different metamorphic P–T conditions, and compositions (both major and trace element) of coexisting species have been used extensively as indicators of metamorphic P–T and P–T paths. The application of these techniques has, however, met with mixed success. When numbers of samples are used, crossed tie lines are common, and when more than one kind of coexisting pair is investigated correspondence of results is sometimes poor.

This has led to the suspicion in some cases that although the systematics of compositional variation in a given pair of minerals may indeed reflect a chemical equilibrium of some kind, the process that induced that equilibrium may not have been metamorphic.

In their investigation of the phyllosilicates and associated minerals of the group of Palaeozoic stratiform sulphide deposits already referred to §3*a*(v), McLeod & Stanton (1984) proposed that the phyllosilicate minerals in question had formed through the *in situ* modification of authigenic clays that had earlier precipitated, as neoformed entities, from the original ore solutions. McLeod & Stanton noted the following.

1. Two distinct phyllosilicate assemblages occurred as part of the bedded, syngenetic ore assemblages: (i) chlorite + talc ± phlogopite–biotite and (ii) chlorite + muscovite.
2. The chemistry of the chlorites, with respect to tetrahedral site substitutions, was related to the type of coexisting phyllosilicate. Siliceous chlorites occurred with talc and more aluminous chlorites with muscovite.
3. Chlorites coexisting with sphalerite were generally enriched in magnesium when compared with chlorites of chalcopyrite-bearing material from the same deposit.
4. The Mg number of chlorite systematically decreased as the mole percentage of FeS of accompanying sphalerite increased.
5. Where carbonates coexisted with chlorites, $Mg/(Mg+Fe)$ members of the two species exhibited systematic relationships.

The great abundance of chlorite and sericite–muscovite in the deposits studied, including their frequent occurrence as virtually monomineralic units in intimate association with sulphide-rich beds, themselves chemical sediments, and the substantial short-range variation of chemical composition of these minerals in conformity with bedding indicated to the writers that they had been neoformed: that is, that they, or immediate precursors to them, had precipitated directly from the ore solutions on mixing with seawater. Although present in lesser quantities, the biotite–phlogopite and talc showed similar bedded arrangements, variation in composition in accordance with bedding and associated bedded sulphides, and intimate intergrowth with the latter, and were therefore also identified as neoformed.

This being the case, McLeod & Stanton concluded that the detailed compositional features of the four minerals, and particularly the systematic co-variation in compositions developed in coexisting pairs or groups, stemmed from low-temperature equilibria prevailing during sea-floor exhalation, sedimentation and subsequent diagenesis. Specifically, the following are noted.

1. High aluminium concentrations in solution and low pH are favourable for the incorporation of Al in sixfold coordination, thereby favouring the formation of muscovite and

aluminous chlorite in the exhalative sedimentary régime. Higher pH on the other hand would favour the deposition of a more siliceous chlorite, talc and trioctahedral mica (biotite–phlogopite) in association with the bedded sulphides. Concomitant variation in the fugacity of sulphur (see (3) below) would influence the Mg:Fe ratios of the phyllosilicates neoformed with the sulphides.

2. Observation and experimental studies by Drever (1971*a*), Sholkovitz (1973) and Bischoff *et al.* (1975) have shown that the cation exchange capacity of clay minerals is enhanced under anoxic marine conditions, i.e. at lower Eh, resulting in an increase in magnesium in the clays and a related depletion of pore water magnesium. Any iron displaced from the clay minerals during this process reacts with any available reduced sulphur species to form pyrite. Drever (1971*b*) further concluded that a reaction of this type would be controlled by the Eh rather than being dependent on either pH or dissolved silica concentration. Thus the Eh of the environment, together with the availability of reduced sulphur to extract iron from the clays or to remove iron adsorbed on clay mineral surfaces may be important controlling mechanisms of the Mg content of the clays constituting precursors to later phyllosilicates.

3. In addition to the effects noted above, a high activity of reduced sulphur in the exhalative sedimentary environment results in an assemblage of highly magnesian chlorite; ankerite or dolomite; low-iron sphalerite; and abundant pyrite. A lower sulphur activity in the depositional environment produces less magnesian chlorite, together with siderite if the amount of available dissolved carbonate is sufficiently high. Under these conditions the sphalerite tends to a higher iron content and the iron sulphide fraction to include pyrrhotite.

Thus a number of features of the systematics of mineral association and mineral chemistry that might at first sight have been attributed to equilibria attained during low-grade metamorphism have, on close investigation, been deduced to derive from the much earlier influences of low-temperature–low-pressure aqueous equilibria developed during original exhalative sedimentation and diagenesis.

An analogous principle may hold for other mineral pairs and groups, e.g. garnet–biotite.

It has long been apparent that garnet and biotite coexist as major components of metapelitic rocks through a wide range of metamorphic grades. The two minerals have several important cations in common (especially Fe, Mg and Mn) and both have a wide range of composition. The pair were therefore an early choice for attempts to use the partitioning of common elements between coexisting minerals as geothermometers, and notable investigations were carried out by Ramberg (1952), Miyashiro (1953, 1956), Kretz (1959), Frost (1962) and Albee (1965). More recent contributions have been those of Saxena (1969), Goldman & Albee (1977) and Ferry & Spear (1978).

However, as first pointed out by Phinney (1963), if the compositions of members of coexisting biotite and garnet pairs from a single area are plotted on phase diagrams they all too commonly display a discouraging number of intersecting tie lines, indicating that in such cases equilibrium has not been attained. A variety of explanations, such as variation in bulk rock composition, metamorphic mineral assemblage and oxygen fugacity, have been proposed to account for this and hence to demonstrate that disequilibrium is only apparent: that equilibrium has in fact been attained and that short-range fluctuations in partition coefficients are simply caused by cryptic short-range variation in certain physicochemical conditions at the time of metamorphism.

I have, however, recently tested this by examining a quartz–muscovite–biotite–almandine–

spinel assemblage, in which sharply defined sedimentary bedding is well-preserved, from the Broken Hill district, New South Wales. Two adjacent beds contained similar mineral assemblages, but differed in their proportions of these minerals. One was dominated by quartz and garnet, its neighbour by biotite and garnet. At a chosen point the boundary between the beds was defined by a large flake of fresh biotite lying with its cleavage and larger dimension (in section) along and parallel to the bedding and separating, and in contact with, two garnets lying on opposing sides of this bedding boundary. Results of electron microprobe analysis of the three coexisting mineral grains are given in table 14.

TABLE 14. COMPOSITIONS OF TWO GARNETS IN CONTACT WITH A SINGLE, COMMON BIOTITE FLAKE IN LOWER PROTEROZOIC METAPELITE, MUNDI MUNDI PLAIN, NEAR BROKEN HILL, NEW SOUTH WALES

	(1)	(2)	(3)	(4)
SiO_2	37.58	37.94	34.95	37.81
TiO_2	0.29	0.18	2.38	0.23
Al_2O_3	21.31	21.40	19.51	21.27
FeO	20.59	30.04	24.83	31.20
MnO	15.49	6.05	0.30	3.79
MgO	0.83	1.58	5.56	1.68
CaO	3.81	3.07	<0.08	2.92
K_2O	<0.06	<0.06	9.18	<0.06
Na_2O	0.34	0.37	0.48	0.47
total	100.24	100.63	97.19	99.37
Si	3.0217	3.0272	5.3539	3.0455
Ti	0.0174	0.0111	0.2741	0.0141
Al	2.0192	2.0122	3.5229	2.0196
Fe^{2+}	1.3847	2.0047	3.1816	2.1020
Mn	1.0546	0.4090	0.0380	0.2589
Mg	0.0989	0.1880	1.2717	0.2017
Ca	0.3281	0.2626	—	0.2524
K	—	—	1.7945	—
Na	0.0533	0.0576	0.1422	0.0727
total	7.9779	7.9804	15.5789	7.9669

Columns: (1) garnet 1, bed 1, core (zoning not optically apparent); (2) same, rim (zoning not optically apparent); (3) biotite, bed 2, at interface of beds 1 and 2; (4) garnet 2, unzoned, bed 2.

Garnets 1 (analyses 1 and 2) and 2 (analysis 4) both in contact with biotite of analysis 3, but on opposite sides of the flake. Garnet structural formulae calculated on the basis of 12(O); biotite on the basis of 22(O). Analyses by electron microprobe.

The material appears to be entirely prograde and forms part of a high-grade metamorphic terrane. The assemblage is one in which the observer might normally assume that attainment of metamorphic equilibrium, but the chemical evidence certainly does not support such an assumption.

In his experimental investigation of the formation of glauconite and chamosite, Harder (1980) noted that in the natural marine environment, under particular early diagenetic conditions, glauconite probably develops at the interface between reducing and oxidizing zones in the muddy sediments. However, whether glauconite or chamosite develops in this milieu appears to depend on the silica content of the pore waters: in the course of his experiments Harder demonstrated that with silica in solution slightly on the high side glauconite and quartz form, with very slightly lower silica in solution, chamosite forms. Oscillation of glauconite and chamosite development may therefore be attained by a slight oscillation of the amount of silica (a few parts per million) in solution.

If, as proposed, the almandines and biotites of many metapelites are derived from chamositic and glauconitic precursors respectively, Harder's results may assume particular significance in the present case. If, in the appropriate sedimentary/diagenetic milieu, slight oscillations in the activity of silica in solution lead to the closely associated formation of chamosite and glauconite, subsequent regional metamorphism would – in terms of the precursor principle – induce the development of correspondingly closely associated almandine and biotite. Any systematic variations in sedimentary/diagenetic uptake of Fe^{2+}, Mg and Mn by the chamosite and glauconite – results of low-temperature aqueous equilibria prevailing during sedimentation and diagenesis – would be directly inherited by the metamorphic daughter products, the almandine and biotite. Thus any systematic partitioning of Fe^{2+}, Mg and Mn (distribution coefficients) now observed in coexisting almandine and biotite would reflect not a regional metamorphic, but an earlier sedimentary/diagenetic, equilibrium.

For the Broken Hill material (table 14), the biotite and garnet 2 occur in the same bed and their precursors were presumably formed just on either side of a silica oscillation and close to a sedimentary/diagenetic equilibrium. Garnet 1, although touching the bedding plane and in clear contact with the biotite in question, is a constituent of a separate bed and thus, presumably, is a product of a different sedimentary chemical régime. This latter, thin, quartz–garnet rich bed, which also contains abundant zincian spinel, is thought to be substantially exhalative in nature and that the high MnO of its garnet is a manifestation of this.

(*f*) *Alternative identities of some metamorphic intergrowths*

The starting materials for the development of metamorphic minerals in pelitic rocks are generally considered to be the products of more-or-less complete weathering – clay and clay–chlorite particles – together with extremely fine rock and mineral flour.

In some cases, however, weathering may have been incomplete, yielding composite grains of weathering product containing residual domains of primary material. In other instances clays formed by weathering may adsorb ions, e.g. K^+, from solution, leading to partial conversion, i.e. aggradation, to another clay or phyllosilicate. In yet other cases fine detritus may include particles that had undergone partial hydrothermal alteration long before weathering and erosion released them for transport and sedimentation. Clearly the range of possible variations of primary material : hydrothermal alteration product(s) : weathering product(s) : aggradation product(s) is wide.

In the context of the precursor mechanism of metamorphic mineral formation it is not difficult to visualize the later conversion of some of these complex (two or more phase) particles to metamorphic intergrowths. Possible pre-metamorphism identities of some commonly observed metamorphic intergrowths are as follows.

(i) *Biotite–chlorite*

This is a widely occurring intergrowth, usually attributed to retrograde metamorphism. However, chlorite is a prominent hydrothermal alteration product of biotite, and rapid erosion and sedimentation of, for example, granitic material containing partly chloritized biotite, would yield material which, with metamorphic reordering, could well yield some of the biotite–chlorite intergrowths now attributed to retrogression.

Recently, Eggleton & Banfield (1985) have shown that a granitic biotite from southeastern Australia has altered to chlorite (65%), epidote (10%) and sphene (10%) through a hydrothermal (330–340 °C) reaction in which two layers of biotite have become one layer of chlorite. They noted *inter alia*, that the tetrahedral sheet of the biotite was inherited intact by the chlorite, whereas the octahedral sheet had undergone element redistribution, principally loss of Ti and gain of Al. The overall hydrothermal reaction conserves Mg in the chlorite and Ti–Fe–Al within the pseudomorphing chlorite–epidote–sphene assemblage.

The undisrupted inheritance of the tetrahedral sheet of the biotite by the chlorite yields a true crystallographic 'intergrowth'. Regional metamorphism of such an intergrowth would probably involve little other than a slight ordering, or 'sharpening', of the biotite–chlorite structures, and the inheritance, by the developing prograde metamorphic assemblage, of a pre-existing duplex structure. Not only would the latter not be retrograde, it would pre-date the prograde event.

Small flatly lensoidal bodies of epidote, K-feldspar, albite or quartz occur variously in metamorphic biotites and are commonly seen in thin sections. Some of these may well have their origins in earlier, pre-erosion/pre-sedimentation hydrothermal alteration of the biotite of felsic igneous rocks.

(ii) *Biotite–sillimanite*

As already indicated in the section on precursors and the possible derivation of some sillimanite from kaolinite–gibbsite mixed layers, the biotite–sillimanite intergrowth is a common and striking one which has been commented upon by numerous authors (see, for example, Watson 1948; Tozer 1955; Chinner 1961; Stanton 1983).

Kato (1965), Wilson (1966) and others have shown that biotite weathers, under a range of conditions from moist temperate to moist tropical, to a variety of aluminous products, most importantly to mixed-layer kaolinite–gibbsite. The kaolinite and gibbsite develop as interlayers parallel to the basal stacking of the biotite. The new materials nucleate and grow at least partly from hydroxy-aluminium complexes contributed from outside the biotite, and are deposited in the cleavages as these expand during weathering. In at least some cases, growth of the new materials is epitaxial, so that the kaolinite–gibbsite mixed layers develop with a crystallographic orientation related to the crystal structure of the host biotite.

Once again, therefore, as for biotite–chlorite, host and alteration product maintain a crystal structure relationship. In the context of the precursor mechanism, metamorphism would resharpen the structure of the biotite, and transform the kaolinite–gibbsite to sillimanite in accordance with the equation given earlier.

(iii) *Sillimanite–sericite*

Many sillimanite schists and gneisses diagnosed as having undergone retrograde metamorphism display patches of fibrous sillimanite peppered with very fine particles of sericite. All proportions of sillimanite and sericite may occur and in some cases the latter dominates. The intergrowth is usually interpreted as resulting from hydration and K^+ adsorbtion by the sillimanite during retrograde metamorphism, with resultant greater or lesser replacement by sericite.

However, one of the best-known diagenetic aggradation processes is that of kaolinite, via K-fixation, to illite. This may be complete, or partial only. On the basis of the precursors discussed earlier, regional metamorphism of appropriate intensity would convert kaolinite (or kaolinite–gibbsite mixed layers), to sillimanite, illite to sericite. Thus what is conventionally interpreted as retrograde metamorphic degradation of sillimanite to sericite may in fact represent the contemporaneous prograde transformation of kaolinite:gibbsite–illite to sillimanite–sericite.

(iv) *Almandine–quartz*

As already noted, almandine commonly contains rounded 'inclusions' of quartz that may be so abundant as to give rise to sieve textures. In many instances these inclusions are exclusively quartz in spite of the fact that the groundmass to the garnet porphyroblasts contains, in addition to quartz, abundant biotite, muscovite and other minerals.

This pronounced difference in mineralogical proportions as between groundmass and inclusions indicates that the quartz occurring within the garnet does not simply represent groundmass incorporated as the latter grew. As indicated earlier the quartz may represent the segregation of SiO_2, earlier present in the siliceous chlorite precursor, in excess of that required for the transformation to almandine. The generally rounded form of the segregation would then reflect interfacial free energy requirements rather than random replacement.

Although any such suggestion is speculative at this stage, analogous mechanisms may be involved in the development of quartz inclusions and sieving in such minerals as staurolite and kyanite in many metamorphic rocks.

(*g*) *The identity of some 'retrograde' materials*

As indicated above, some minerals, e.g. sericite in sillimanite, currently identified as retrograde entities may in fact be prograde products. However, what may be a much more important category of materials misidentified as retrograde products is that of untransformed and, particularly, partially transformed, precursors.

Chlorite closely associated with almandine is usually interpreted as a retrograde product of the latter. On the contrary, as we have seen, the garnet may be a prograde product of the chlorite. The highly aluminous dark areas associated with some of the biotites at Hemlo and Geco are, at first sight, easy to attribute to retrogressive metamorphism. However, closer scrutiny of the evidence indicates that the aluminous matter is probably a pre-sedimentation to diagenetic breakdown product of biotite, and that it has undergone partial prograde transformation to sillimanite. The dark material associated with diopsidic clinopyroxene at Brindabella might be uncritically ascribed to retrograde metamorphism of the latter, but more detailed examination of form and composition indicates that the diopside has arisen as a prograde daughter-product of the dark material. The dark kaolinitic clots associated with some of the sillimanite at Geco (Stanton 1983) could, at first sight, be identified readily as a retrograde product of the sillimanite. Consideration of form and textural relations indicates otherwise, however, and there can be little doubt that the sillimanite has developed from the kaolinitic material.

Many other examples of such superficially ambiguous relations may be adduced. Clearly the principle is important. Many mineralogical relationships uncritically interpreted as retrograde effects may really represent incomplete prograde transformation from precursor material to metamorphic mineral. This is an aspect of regional metamorphism that requires much further, very careful, investigation.

(*h*) *Application of regional metamorphic mineral assemblages to the elucidation of primary environments*

As already noted, the common preservation of small-scale constitutional patterns in chemical sediments of 'high-grade' metamorphic terranes indicates that although regional metamorphism has induced mineralogical changes, it has not caused chemical modification on anything other than a very fine scale – of the order of a fraction of a millimetre. In the oxide facies of some iron formations, as observed earlier, even the finest patterns of bed-to-bed variation in oxidation state appear to have been preserved. That is, present metamorphic minerals may be extremely faithful consequences – and, hence, reflections – of the sedimentary/diagenetic/alteration precursor materials from which they were derived. Where these materials were partly or wholly formed during, and as a result of, these processes of sedimentation, diagenesis and/or alteration, they must represent not only the materials involved in these processes, but also the processes themselves and the conditions under which these took place. Thus the coexistence of bedded magnetite and pyrite in a metamorphosed iron formation has clear semi-quantitative connotations concerning Eh–pH conditions of the relevant chemical sedimentation. Analogous indications follow from the incidence of regionally metamorphosed sedimentary/diagenetic K-feldspar (see Flehmig 1977), the various iron silicates, and many other mineral compounds that may be formed in the relatively low *T–P* aqueous environment.

Such a conclusion raises interesting possibilities for greatly increased application of regional metamorphic mineralogy. In part it may provide a natural extension of sedimentology and hence a means for analysing metapelitic and associated rocks whose original features may at first sight appear to have been obliterated – or at least modified almost beyond recognition – by metamorphism. The premise may be examined in a very simple way.

The presence of abundant carbonate in highly metamorphosed sedimentary sequences – such as those of the Grenville of North America – is accepted as indicating carbonate sedimentation and hence the former presence of a 'carbonate' sedimentary environment. In some instances stromatolitic remnants are preserved and an algal reefal environment is deduced accordingly. Similarly the presence of abundant evaporitic minerals as observed in the Grenville is immediately assumed to indicate the primary deposition of such as gypsum, anhydrite and associated salts in arid lake, lagoonal, sabkha or related arid lacustrine or near-shore environments. The association of carbonates and evaporites within the high-grade metamorphic environment of the Grenville assemblage (and analogous terranes in other parts of the world) is seen as having clear sedimentological connotations: these are clearly perceived and unhesitatingly accepted in spite of the very high-grade metamorphic silicate assemblages present in the closely associated metapelitic rocks. The presence of well-bedded quartz–magnetite units in these terranes is unquestionably seen as indicating iron–silica sedimentation under oxidizing conditions. The occurrence of iron sulphide and associated graphitic beds is – in spite of the presence of sillimanite, staurolite, cordierite, garnet and other 'high-grade' silicates in the immediately enclosing metapelites – taken as clear evidence of sedimentation under reducing conditions, probably with a biological component. In each case it is accepted that, despite the high grades of metamorphism the rocks have undergone, the minerals concerned – calcite, dolomite, gypsum, anhydrite, magnetite, quartz, pyrite, pyrrhotite, graphite – have arisen *in situ* from precursors, that the latter were products of a particular sedimentary environment the solid products of which are preserved *in situ*, and that the new 'metamorphic' carbonate, sulphate, oxide, sulphide and carbon *constitute indicators of those sedimentary environments.*

If the metamorphic silicates are also derived from precursors, and if these precursors are, like the carbonate, oxides, sulphides, etc., products of sedimentary/diagenetic processes, perhaps these silicates, too, might constitute indicators of the environments in which they formed.

That they might is of course indicated by simple analogy. However, there is other geological evidence indicating the validity of the principle.

It is now established that many exhalative–sedimentary orebodies are underlain by hydrothermal feeder-pipes through which the materials of the ores were originally contributed to the sea-floor (the 'black smokers' of the modern ocean floor are currently being supplied through analogous, modern, feeder pipes and fissures). Numerous feeder-pipes, many of them as old as the Archaean, have now been recognized, and many remain in well-preserved state. In most cases the hydrothermal solutions have altered the rocks enclosing the pipe to clays, chlorites and other aluminous materials. Subsequent metamorphism has converted these highly localized, highly aluminous products of hydrothermal alteration to similarly localized, highly aluminous metamorphic assemblages including the Al_2SiO_5 polymorphs, cordierite, staurolite and garnet. In some cases (e.g. Mattabi, Ontario; Big Bell, Western Australia) these assemblages are quite different from, and out of keeping with, those of the metapelitic components of the surrounding terrane, in which no more than greenschist grade metamorphism may be indicated. That is, the present, highly localized metamorphic assemblages of the old feeder pipes indicate a former *hydrothermal alteration environment*: the metamorphic minerals are immediate derivatives of precursors that were products of a particular geological environment, and the metamorphic minerals are therefore now indicators of that environment.

This returns us to environments of sedimentation and, in part, to the earlier remarks concerning metamorphic zoning.

As noted earlier (see, for example, Smoot 1960; Millot 1970; Sudo & Shimoda 1978), of the clays, kaolinite tends to deposit along, and close to, shorelines. Relative primary concentration of kaolinite, kaolinite–gibbsite and related mixed-layer clays in this way should, with metamorphism, yield a sillimanite-bearing zone within the finer metasedimentary units. Do some regional metamorphic sillimanite zones thus reflect earlier near-shore facies of sedimentation? Chamosite shows its major development in the warm waters of tropical shelves. Harder (1978) has postulated that at least some chamosites are nucleated on laterite particles incorporated in shelf sediments. Could broad zones of abundant almandine thus indicate sedimentation of iron-rich material of tropical soils contributed to the warm waters of the adjacent shelves? Some glauconites are derived from the degradation of biotite (Galliher 1935, and many later authors) and it appears (Burst 1958) that biotite could derive from glauconite by appropriate aggradation and structural ordering. Glauconite tends to form in the sediments of the cooler waters of the deeper shelf (see Porrenga 1967), and thus we might expect its proposed daughter product, biotite, to appear in metamorphosed terranes in a palaeogeographical position somewhat seaward of almandine. I (Stanton 1979, 1982) have earlier suggested that some of the more prominent regional metamorphic mineral zonations may be reflections of volcanic shelf sedimentation (including concomitant hydrothermal contribution of copious quantities of iron and aluminium) under tropical conditions.

Other authors have proposed a connection between metamorphic mineralogy and palaeogeography and palaeoclimate. Dunn (1929), in considering the origin of concentrations of kyanite, sillimanite and corundum in some of the highly aluminous metamorphic rocks of northern India, commented: 'They may have been lenticular masses of highly aluminous clays deposited in small pools, or they may have been small areas of bauxitic clays derived from the alteration *in situ* of surrounding more siliceous clays' (1929, p. 244). He thought that 'the curious frequent occurrence of kyanite-rock at the borders of hornblende-schist...' might represent 'the metamorphic product of the aluminous clay which resulted from a prior alteration of a lava flow at its upper and lower surfaces' (1929, p. 249). Dunn clearly suspected that the highly aluminous metamorphic assemblages, and their dispositions, resulted from, and were indicators of, the Archaean landforms and climate of the area. In an analogous way Serdyuchenko (1975) considered that many scapolite-bearing metasedimentary rocks represented metamorphosed evaporite-bearing sediments. He noted that such metasediments commonly alternated with magnetite, which he thought represented ironstones originally interbedded with the evaporites.

Thus the incidence of metamorphic minerals, and assemblages of these, in pelitic and related metasediments may provide indicators of palaeosedimentology, palaeogeography, palaeoclimate, and palaeoprovenance of the sediments concerned. It may indicate the broader incidence of sea-floor hydrothermal activity that caused the more localized deposition of ore deposits, and it may reveal features of sea-floor hydrothermal alteration and of subsea-floor hydrothermal diagenesis. It may also indicate the nature and conditions of hydrothermal and weathering alteration of lavas (particularly those of andesitic and more basic composition) and of pyroclastic rocks. If many regional metamorphic silicate minerals have direct, lineal, derivation from precursor materials, and if the environments and conditions of formation of those precursors is known, those metamorphic silicates may – like certain metamorphic non-silicates – become powerful tools in palaeoenvironmental analysis.

8. Conclusion

In 1962 C. F. Davidson, in opposing the suggestion that some stratiform ore deposits might be derived by weathering and erosion of metalliferous land surfaces and subsequent chemical sedimentation, went on also to discount the possibility that such orebodies might be products of exhalative sedimentation. He said:

> If the landward derivation of the ore metals is denied, there remains only the possibility, within the range of syngenetic concepts, that they entered as volcanic or hydrothermal exhalations through the sea floor. Here again there is postulated a phenomenon quite unparalleled in actualistic experience, although submarine volcanic eruptions are common enough. As a rule, not even slight concentrations of polymetals accompany volcaniclastic sediments intercalated with marine strata. (1962, p. 269.)

In 1976 H. J. F. Winkler defined the onset of metamorphism as follows. 'Metamorphism has begun and diagenesis has ended when a mineral assemblage is formed which cannot originate in a sedimentary environment' (1976, p. 11).

By 1963 the first indications of the hot brines of the Red Sea floor had been detected, and by early 1965 it had been shown that these were actively discharging from submarine hot springs, and depositing sedimentary concentrations of iron, copper and zinc sulphides. From

1979 to the present, observation from submersibles of sea-floor exhalative discharge and concomitant sulphide sedimentation has become almost commonplace.

The doubts of Davidson – and many of his contemporaries – have thus been swept aside. Stratiform sulphide concentrations in pelitic and associated sediments can form as sediments themselves, and hence in many instances are not products of metasomatic reactions and replacement as was the earlier, and overwhelmingly, prevailing view. They are, in such cases, derived from sedimentary precursors.

As noted earlier (§3*c*i), Donnelly & Nalli (1973) reported, *inter alia,* the authigenic development of aluminous garnet (spessartine-rich) and K-feldspar in modern Caribbean sediments, and in 1974 Kempe & Easton (see §3*c*ii) described the large-scale incidence of grandite garnet in semi-lithified micarb chalk of the floor of the southwest Indian Ocean. In 1983, Zierenberg & Shanks (§3*c*iii) reported the authigenic development of andradite garnet, pyroxene and amphibole in the very Red Sea oozes that, some 17 years earlier, had provided evidence of the large-scale sedimentary formation of base metal sulphides.

Might it be that the present state of understanding of regional metamorphic silicate formation has analogies with our understanding of regionally metamorphosed stratiform sulphide ores when Davidson wrote in 1962?

It has been the principal purpose of the present contribution to propose that among the fine-grained sedimentary rocks those of essentially purely chemical origin may have a vital role to play in the elucidation of regional metamorphic processes. Among the more prominent rock assemblages of this kind are the banded iron formations, exhalative–sedimentary base metal sulphide and gold ores, and a range of exhalative sediments ('exhalites') that commonly accompany such ores. Most studies of the regional metamorphism of pelitic rocks have been concerned with fine-grained mixtures of detrital and chemical materials the proportions of which are unknown, and that do not exhibit clearly defined primary compositional patterns against which the effects of increasing intensities of metamorphism can be measured. Many of the purely chemical sedimentary accumulations, on the other hand, do exhibit quite clear-cut primary patterns of compositional variation. Their commonly sharply defined chemical stratification, and well-developed facies of chemical sedimentation, are well known and documented in completely unmetamorphosed terranes, and can therefore be used as 'markers' against which any changes accompanying increase in metamorphic intensity may be measured with considerable precision.

Examination of these patterns in some 'high-grade' metamorphic terranes indicates that while metamorphism has induced mineralogical changes, it has not caused chemical modification on anything other than a very fine scale, of the order of a fraction of a millimetre. This leads virtually inevitably to the deduction that in such cases those materials now found in any given small domain of a metamorphic rock must derive directly from the materials constituting that domain immediately before metamorphism, and hence that many of the commonly occurring regional metamorphic silicate minerals may, like their associated metamorphosed oxides, carbonates, sulphides, and metamorphosed authigenic quartz and feldspars, arise directly from precursors rather than through a progressive series of mineral reactions. The metamorphic milieu of principal concern in the present contribution has been that of the pelitic rocks, and rocks with a pelitic component, in which the precursors are mainly of chemical sedimentary/diagenetic origin. Other precursors may be derived from volcanic rocks, in which case they are probably mostly of late-stage hydrothermal alteration origin. Yet others may be produced by weathering processes and soil formation, and some well-known metamorphic intergrowths may result from the metamorphism of partly weathered primary minerals that have been eroded, transported, and incorporated in pelitic sediments.

If the regional metamorphic silicates do develop principally by transformation and grain growth, the problem of the elusive metamorphic reaction in the natural milieu is resolved. The preservation of what appear to be disequilibrium concentration gradients and mineral assemblages follows naturally if materials formed at low T–P simply undergo early water loss followed by *in situ* solid–solid transformation at higher T–P. There is no destabilizing of large chemical domains ('bulk chemistries') leading to extensive diffusion, no widespread reaction tending to new equilibria among minerals that develop as groups in accordance with the requirements of the Phase Rule. Yoder's somewhat puzzled speculation that some metamorphic rocks might attain their mineral assemblages directly rather than through a series of mineral reactions – and hence without passing through each successive grade – appears to be answered. The common lack of evidence that 'high-grade' zones have passed through all the mineral assemblages of the 'lower-grade' zones – an inevitable corollary of the 'progressive' nature of Barrovian metamorphism – seems accounted for. The real metamorphic grade indicators are then not the hypothetical intermineral reactions we now postulate, but the relevant precursor transformations. This being the case, it is solid–solid (and, in some cases, gel–solid) transformations, grain boundary movement and processes of annealing, rather than chemical reactions, to which the laws of thermodynamics are to be applied.

It would be going too far to maintain that there was no such thing as a regional metamorphic mineral reaction, or that regional metamorphic equilibrium was never attained. What the author has proposed is not that such phenomena never occur, but that they do not have anything like the dominating importance in regional metamorphism that is currently assumed: that the role of metamorphic reactions in generating the bulk of regional metamorphic mineral matter is probably, quite contrary to present belief, almost vanishingly small. Present considerations indicate that reaction and equilibrium adjustments substantially cease with the closure of pore spaces and cessation of diagenesis in sediments, and with the cessation of alteration in volcanic and other already lithified rocks. As is the case with the oxides (including quartz), carbonates, sulphides, authigenic feldspars, etc., by far the dominant processes of metamorphic silicate mineral development from that point on are the ordering of sedimentary/diagenetic gels and poorly ordered crystal structures, transformation of precursors, and grain growth. The mineral textures so developed may then go through many modifications – a wide variety of histories of repeated deformation and annealing – wherever they are subjected to polyphase metamorphism.

It must be made clear that in emphasizing the probable importance of precursors in influencing the nature, association and distribution of regional metamorphic minerals, the author certainly does not dismiss the concept of regional metamorphic grade. Any impression that he does would be quite incorrect.

Although it is proposed that the silicates and associated minerals arise from precursors rather than through reactions in the currently accepted sense, a rise in T–P conditions (i.e. the regional metamorphic process) is a requirement for the growth, transformation and further growth of precursor parent to metamorphic daughter product. Accepting that such a rise in T–P conditions must be involved, it is self-evident that these are likely to vary in space and time: that is, variation in regional metamorphic conditions in space and time is virtually inevitable and hence there must be a corresponding likelihood of variation in grade.

It is often the case that, where two hypotheses at first sight appear to differ, more careful analysis shows each to contain an element of truth. Sometimes it transpires that both are correct, and that the relevant ideas complement each other in such a way as to constitute a more complete theory. This may well be the case in the present instance.

It has already been suggested (Stanton 1979, 1982*a*, *b*, and earlier in this contribution) that perhaps the best precursor, and derived regional metamorphic, zoning may be developed in the sediments and pyroclastic materials of volcanic shelves of tropical regions. The volcanic segment of the régime would contribute highly reactive glass and related volcanic material, including a hydrothermal component, to the accumulating pile, and the tropical environment, with its warm shelf waters, would be conducive not only to the contribution of abundant products of tropical weathering but also to the development of such sedimentary/diagenetic materials as chamosite and glauconite.

Such volcanic shelves are usually disposed more or less parallel to an associated volcanic arc structure, which may be related to a continental coast or to a linear or arcuate volcanic island chain, e.g. the north flanks of Java and Sumatra.

That is, as we proceed from the outer, complex and fine-grained shelf sediments through glauconitic, chamositic to nearer-shore coarser grained, kaolinitic sediments we move progressively closer to the line or arc of volcanoes, and hence towards the zone of highest heat flow. The whole underlying control is tectonic: the development of the volcanic arc leads to the development of the associated parallel shelf; the contour lines of heat flow are parallel to the shelf and volcanic spine (figure 55), heat flow increasing towards the latter; and the facies pattern in the shelf sediments, including the cryptic pattern of clay–phyllosilicate–zeolite mineralogy, develops parallel to the shoreline, to the zone of the volcanic spine, and hence to the heat flow isotherms. If glass and other labile volcanic fragments tend to settle and accumulate in accordance with particular elements of the prevailing sedimentary facies pattern, exothermic processes of devitrification and crystal structure transformation would provide a source of indigenous heat (see Saull (1955) and below) that also bore a parallel relation with the volcanic isotherms and the patterns of precursor distribution. The overall thermal and precursor patterns are thus essentially parallel, complementing each other in the final development of metamorphic mineral zones. The same principle would of course apply where a linear volcanic edifice was bilaterally more or less symmetrical, and possessed a shelf on both sides – the paired metamorphic belts of Miyashiro (1961, 1965, 1973). In the light of the assemblages developed in the Green River Formation and in many other saline lake deposits, a similar principle might also apply in the metamorphism of the sedimentary accumulations of large saline lakes developed in continental volcanic rift valleys in arid regions.

All of this begins to indicate that at least the first major episode of regional metamorphism affecting a geological province is essentially an indigenous phenomenon: that certain materials have a primary nature and association through which they are pre-ordained to metamorphose themselves.

The germ of such an idea is by no means new. In 1857 James Hall speculated that the cause of metamorphism 'must have existed within the material itself; [so] that the entire change was due to motion or fermentation and pressure...'. Some 98 years later Saull noted:

> Data on heats of reaction indicate that metamorphic chemical changes may in certain cases develop temperature rises of several hundred degrees centigrade. From this evidence, and from geological reasoning, it appears that metamorphism may be fundamentally a spontaneous exothermic

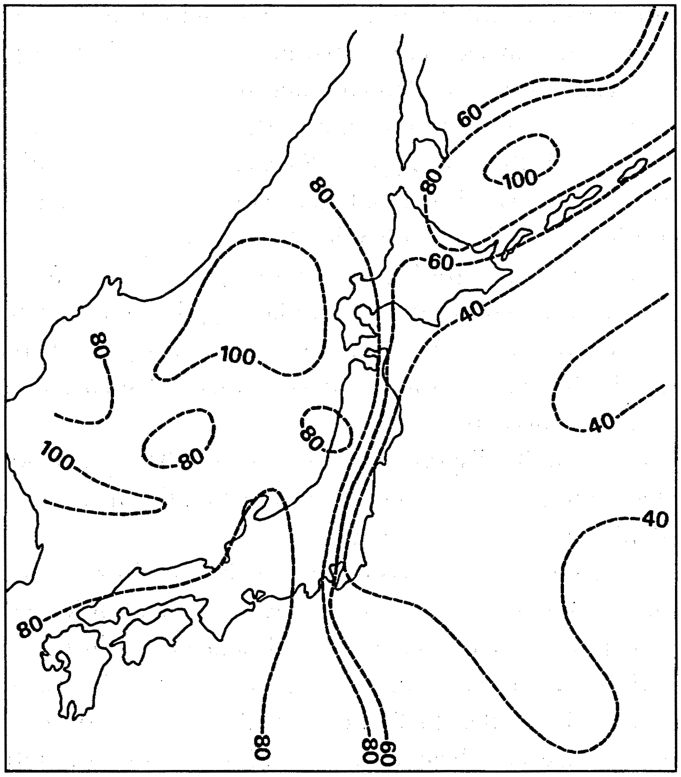


FIGURE 55. Pattern of heat flow around the northeast Japan volcanic arcs (in milliwatts per square metre (microcalories per square centimetre per second)). Heat flow contours projecting to the south of the Japan arc are following the Izu–Bonin arc, and to the northeast, the Kurile arc. (After Miyashiro 1973.)

chemical process, the initiation and general character of which depend upon kinetic factors. (1955, p. 86).

The transformation of poorly ordered precursors (including volcanic glass) to well-ordered diagenetic and metamorphic crystal structures are also exothermic phenomena, so if 'heats of transformation' be substituted for Saull's 'heats of reaction', there is still the potential for the generation of substantial indigenous heat. Thus through the existence of precursors, and the heat generated by the transformation of these, the materials and part of the heat required for the metamorphic process are provided *in situ*. In the case of sediments and volcanic matter associated with volcanic arcs and eugeosynclines, further heat is supplied by the well-patterned volcanic heat flow. Therefore by virtue of their primary nature, and the nature of the environment and association in which their primary accumulation took place, these rocks are, as noted above, pre-ordained to virtually metamorphose themselves. The path of such autometamorphism is thus substantially predestined, and its extent depends on the extent to which heat of transformation plus volcanic heat flow is sufficient to transform the various precursor materials that are present. Such transformations will doubtless take place at a variety of temperature–pressure conditions, i.e. grades of regional metamorphism and, as noted earlier, some of the materials currently loosely diagnosed as products of retrograde metamorphism may in fact be residues of precursors remaining after an aborted prograde metamorphism.

If all this is the case, application of the precursor principle should greatly extend the purview of regional metamorphic petrology. In addition to providing information on the physical conditions of the metamorphic process itself, regional metamorphic mineral assemblages may yield many insights into processes and conditions of earlier weathering and alteration, sediment transport and deposition, sedimentary environments and processes – including those of sea-floor hydrothermal activity – of sedimentation and diagenesis, and into many questions of ancient palaeogeography and palaeoclimate. There is much scope for further searching for possible precursor materials in a variety of rocks (especially among some of those somewhat obscure materials currently loosely dismissed as retrograde products) and modern sediments (especially those of the volcanic–sedimentary milieu). In the latter case materials obtained from oil drilling on calc-alkaline volcanic shelves such as the northern flank of Java may provide opportunities for testing the possible role of sedimentation and diagenesis in influencing regional metamorphic mineral zoning. There appears to be considerable scope for the extension of clay and mixed-layer clay–chlorite–zeolite mineral synthesis in low T–P laboratory experiment, and for the investigation of the product so obtained, at metamorphic temperatures and pressures. The experimental investigation of annealing and grain growth in natural and synthetic sulphides, as materials much more tractable in the laboratory than silicates, may lead to improved assessment of metamorphic textures and hence better interpretation of deformation histories (see, for example, Stanton & Willey 1970, 1971).

What may be termed the Barrovian approach has dominated the field of regional metamorphic petrology for almost 100 years, and it has constituted a remarkably useful working hypothesis for the investigation of regional metamorphic phenomena. However, during the past few years – and particularly since the beginning of the widespread use of the electron probe microanalyser – its detailed application has become increasingly complex and difficult and, many would say, less satisfactory. Although I hasten to acknowledge the great usefulness and resilience of the hypothesis, the data now presented seem to indicate that the time has come for its re-evaluation.

This contribution draws together the threads of work and thought extending over some 30 years and inevitably, during such a long period, many have helped.

First and foremost I acknowledge the perceptiveness and foresight of Haddon King, and thank him for his kindly, gentle, constant help and encouragement during a period of over 40 years. For their contributions in many discussions and for their help I also thank my old students S. M. Richards, I. R. Johnson, H. K. Herbert, R. L. McLeod, J. P. Vaughan, A. N. Yeates and T. F. McConachy, my industrial colleagues D. H. Mackenzie, N. Herriman, M. D. Muir and B. W. Hawkins (C.R.A.); R. Woodall and P. J. MacGeehan (Western Mining Corporation); R. T. Russell (Broken Hill South and Newmont); J. H. Hill (Preussag) and academic colleagues N. C. N. Stephenson and S. W. Richardson of New England and Oxford respectively. Although none of these people can be held responsible for any of my indiscretions, all have been most helpful in a variety of ways.

For financial assistance and other material help I thank the Australian Mineral Industries Research Association and its member companies who have supported me, the Broken Hill Mining Managers' Association, the Australian Research Grants Committee, the British Council and the University of New England Research Grants Committee. For periods as a guest, during which I was given access to extensive facilities and assistance, at Oxford and the Australian National Universities, I thank Professor E. A. Vincent of the Oxford Department of Geology and Mineralogy and Professors A. E. Ringwood and Kurt Lambeck of the ANU Research School of Earth Sciences.

I am greatly indebted to N. G. Ware (ANU) and C. T. Fagg (Oxford) for their assistance in my extensive use of their electron microprobe facilities; to J. S. Cook (New England) and the late R. Holland (Oxford) for their skilful preparation of material; to M. J. Roach who drew all of the diagrams; to Miss S. J. Dawson who carried out all microphotography; and Mesdames C. J. Kendall, H. M. Roan, F. Kershaw and S. Kelly who gave much effort and care to the typing of text and tables.

REFERENCES

Albee, A. L. 1965 *J. Geol.* **73**, 155–164.

Arggarwal, P. K. & Nesbitt, B. E. 1984 *Econ. Geol.* **79**, 815–825.

Atherton, M. P. 1965 In *Controls of metamorphism* (ed. W. S. Pitcher & G. W. Flynn), pp. 169–202. Edinburgh: Oliver & Boyd.

Banno, S. 1964 *J. Fac. Sci. Tokyo Univ.* **15**, 203–319.

Barrer, R. M. & Hinds, L. 1950 *Nature, Lond.* **166**, 562.

Barrow, G. 1893 *Q. Jl geol. Soc. Lond.* **49**, 330–356.

Barrow, G. 1912 *Proc. Geol. Ass.* **33**, 274–290.

Bath, T. W. 1936 *Bull. geol. Soc. Am.* **47**, 775–850.

Beeson, R. 1978 *Contr. Miner. Petr.* **66**, 5–14.

Benson, W. N. 1913 *Proc. Linn. Soc. N.S.W.* **38**, 490–517.

Benson, W. N. 1918 *Proc. Linn. Soc. N.S.W.* **43**, 593–599.

Berg-Madsen, V. 1983 *J. sedim. Petrol.* **53**, 875–893.

Berge, J. W. 1966 *Publications from The Mineralogical-Geological Instn of the Univ. of Uppsala*, vol. 63. (24 pages.)

Bhatia, D. M. S. 1981 Paper presented to AMIE Ann. Mtng, Chicago, 1981; *Preprint* no. 80–1. (11 pages.)

Biggar, G. M. & O'Hara, M. J. 1969 *Mineralog. Mag.* **37**, 198–205.

Bird, D. K., Schiffman, P., Elders, W. A., Williams, A. E. & McDowell, S. D. 1984 *Econ. Geol.* **79**, 671–695.

Bischoff, J. L., Clancy, J. J. & Booth, J. S. 1975 *Geochim cosmochim. Acta* **39**, 559–568.

Blake, R. L. 1965 *Am. Miner.* **50**, 148–169.

Blatt, H., Middleton, G. V. & Murray, R. C. 1980 *Origin of sedimentary rocks*, 2nd edn. Englewood Cliffs, New Jersey: Prentice-Hall.

Bliskovskii, V. Z. 1968 *Trudy̆ Fersman Mineral. Museum. U.S.S.R. Acad. Sci.* **18**, 24–40.

Brindley, J. C. 1954 *Sci. Proc. R. Dubl. Soc.* (N.S.) **26**, 245–262.

Brockhamp, B. 1942 *Arch. LagerstättForsch.* **75**, 181.

Buddington, A. F. 1966 *Econ. Geol.* **61**, 484–510.

Burst, J. F. 1958 *Am. Miner.* **43**, 481–497.

Busch, D. A. 1971 *Bull. Am. Ass. Petrol. Geol.* **55**, 1137–1154.

Carlson, E. T. 1956 *J. Res. U.S. natn Bur. Stand.* **56**, 327–335.

Carmichael, D. M. 1969 *Contr. Miner. Petr.* **20**, 244–267.

Cavarretta, G., Gianelli, G. & Puxeddu, M. 1982 *Econ. Geol.* **77**, 1071–1084.

Charnock, H. 1964 *Nature, Lond.* **203**, 591.

Chenhall, B. E. 1976 *J. geol. Soc. Aust.* **23**, 235–242.

Chinner, G. A. 1961 *J. Petr.* **2**, 312–323.

Cilliers, J. J. Le R. & Genis, J. H. 1964 In *The geology of some ore deposits in southern Africa* (ed. S. H. Haughton), vol. 2, pp. 543–570. Geol. Soc. S. Africa.

Cliff, R. A., Jones, G., Choi, W. C. & Lee, T. J. 1985 *Contr. Miner. Petr.* **90**, 346–352.

Coetzee, C. B. 1960 The geology of the Orange Free State goldfield. *Mem. geol. Surv. S. Afr.* **49**.

Coetzee, C. B. 1976 *Mineral Res. Republ. S. Afr.* 5th edn, Handbook no. 7, pp. 427–429.

Cook, H. E., Zemmels, I. & Matti, J. C. 1974 In *Initial reports of the Deep Sea Drilling Project* (ed. T. A. Davies *et al.*), vol. 26, pp. 573–592. Washington, D.C.: U.S. Government Printing Office.

Coombs, D. S., Kawachi, Y., Houghton, B. F., Hyden, G., Pringle, I. J. & Williams, J. G. 1977 *Contr. Miner. Petr.* **63**, 229–246.

Costa, U. R., Barnett, R. L. & Kerrich, R. 1983 *Econ. Geol.* **78**, 1144–1203.

Davidson, C. F. 1962 *Econ. Geol.* **57**, 265–274.

de Segonzac, G. D. 1970 *Sedimentology* **15**, 283–346.

Deer, W. A., Howie, R. A. & Zussman, J. 1966 *An introduction to the rock forming minerals*. London: Longman.

Dewey, H. 1925 *Proc. Geol. Ass.* **36**, 107–134.

Donnelly, T. W. & Nalli, G. 1973 In *Initial reports of the Deep Sea Drilling Project* (ed. N. T. Edgar *et al.*), vol. 15, pp. 929–961. Washington, D.C.: U.S. Government Printing Office.

Drever, J. 1971*a* *Science, Wash.* **172**, 1334–1336.

Drever, J. 1971*b* *J. sedim. Petr.* **41**, 982–994.
Duggan, M. B. 1986 *Mineralog. Mag.* **50**, 657–665.
Dunn, J. A. 1929 *Mem. geol. Surv. India*, vol. 52. (272 pages.) Calcutta: Government of India.
Easton, A. J., Hamilton, D., Kempe, D. R. C. & Sheppard, S. M. F. 1977 *Phil. Trans. R. Soc. Lond.* A **286**, 253–271.
Easton, A. J., Joslin, I. E., Kempe, D. R. C. & Hancock, J. M. 1982 *Mar. Geol.* **48**, M1–6.
Edgar, A. D. 1973 *Experimental petrology*. Oxford: Clarendon Press.
Eggleton, R. A. & Banfield, J. F. 1985 *Am. Miner.* **70**, 902–910.
Ellison, S. P. 1955 In *Econ. Geol. 50th Anniv. Vol.*, pp. 867–884.
Emmons, W. H. & Laney, F. B. 1911 *U.S. geol. Surv. Bull.* **470**C, 151–172.
Emmons, W. H. & Laney, F. B. 1926 *U.S. geol. Surv. prof. Pap.* **139**. (114 pages.)
Engel, A. E. J. & Engel, C. G. 1960 *Bull. geol. Soc. Am.* **71**, 1–58.
Enlows, H. E. & Oles, K. F. 1966 *Bull. Am. Ass. Petrol. Geol.* **50**, 1918–1926.
Eskola, P. 1915 *Bull. Comm. Finl.* **44**, 109–145.
Eskola, P. & Kervinen, T. 1936 *Bull. Commn. géol. Finl.* **115**, 475.
Eugster, H. P. 1969 *Contr. Miner. Petr.* **22**, 1–31.
Ferry, J. M. & Spear, F. S. 1978 *Contr. Miner. Petr.* **66**, 113–117.
Flehmig, W. 1977 *Contr. Miner. Petr.* **65**, 1–9.
Flint, E. P., McMurdie, H. F. & Wells, L. S. 1941 *J. Res. U.S. natn Bur. Stand.* **26**, 14–33.
Flint, E. P. & Wells, L. S. 1941 *J. Res. U.S. natn Bur. Stand.* **27**, 171–180.
Frey, M. 1978 *J. Petr.* **19**, 93–135.
Friesen, R. G., Pierce, G. A. & Weeks, R. M. 1982 Geology of Geco base metal deposit. In *Precambrian sulphide deposits: J. S. Robinson memorial volume* (ed. R. W. Hutchinson, C. D. Spence & J. M. Franklin), *Spec. Pap. geol. Ass. Can.* no. 25, pp. 343–363: Waterloo, Ontario: Geological Association of Canada.
Frost, M. J. 1962 *Geol. Mag.* **99**, 427–438.
Fujii, N., Togashi, Y. & Igarashi, T. 1976 An outline of kaolin, pyrophyllite and sericite deposits in Japan. *Geol. Surv. Japan.* (25 pages.)
Gair, J. E. & Vokes, F. M. 1984 *Econ. Geol.* **79**, 1425–1427.
Galliher, E. W. 1935 *Bull Am. Ass. Petrol. Geol.* **19**, 1569–1601.
Gibbs, R. J. 1977 *J. sedim. Petr.* **47**, 237–243.
Goldman, D. S. & Albee, A. L. 1977 *Am. J. Sci.* **277**, 750–761.
Goldschmidt, V. M. 1921 *Skr. norske Vidensk-Akad.* K **1**, 10.
Griffen, G. M. 1962 *Bull. geol. Soc. Am.* **73**, 737–768.
Grubb, P. L. C. 1971 *Econ. Geol.* **66**, 281–292.
Haaker, R. F. & Ewing, R. C. 1981 *J. Am. ceram. Soc.* **64**, C-149.
Hackett, J. P. & Bischoff, J. L. 1973 *Econ. Geol.* **68**, 553–564.
Hallam, A. 1966 *Nature, Lond.* **290**, 1306–1309.
Hamilton, D. L. & Henderson, C. M. B. 1968 *Mineralog. Mag.* **36**, 832–838.
Harder, E. C. 1980 *Clays Clay Miner.* **26**, 65–72.
Harder, E. C. 1978 *Clays Clay Miner.* **28**, 217–222.
Harker, A. 1893 *J. Geol.* **1**, 574–578.
Harker, A. 1950 *Metamorphism*, 3rd edn. London: Methuen & Co. Ltd.
Harker, A. & Marr, J. E. 1893 *Q. Jl geol. Soc. Lond.* **49**, 359–371.
Hay, R. L. 1978 In *Natural zeolites: occurrence, properties, use* (ed. L. B. Sand & F. A. Mumpton), pp. 135–144. Oxford: Pergamon Press.
Hayashi, H. & Oinuma, K. 1964 *Clay Sci.* **2**, 22–30.
Hekinian, R. 1971 *Bull. geol. Soc. Am.* **82**, 659–682.
Hendry, D. A. F. 1981 *Econ. Geol.* **76**, 285–303.
Herbert, H. K. 1981 Ph.D. thesis, Univ. of New England.
Hunziker, J. C., Frey, M., Clauer, N., Dallmeyer, R. D., Friedrichsen, H., Flehmig, W., Hochstrasser, K., Roggwiler, P. & Schwander, H. 1986 *Contr. Miner. Petr.* **92**, 157–180.
Iijima, A. 1974 In *Geology of Kuroko deposits* (ed. S. Ishihara, K. Kanehira, A. Saski, T. Sato & Y. Shimazaki), Soc. Mining Geologists of Japan, Mining Geology Spec. Iss. no. 6, pp. 267–289.
Iijima, A. 1978 In *Natural zeolites: occurrence, properties, use* (ed. L. B. Sand & F. A. Mumpton), pp. 175–198. Oxford: Pergamon Press.
Isokangas, P. 1978 In *Mineral deposits of Europe* (ed. S. H. U. Bowie, A. Kvalheim & H. W. Haslam), vol. 1 (*Northwest Europe*), pp. 39–90. London: The Institution of Mining and Metallurgy, The Mineralogical Society & Bartholomew Press.
Ito, J. & Frondel, C. 1967 *Am. Miner.* **52**, 1105–1109.
James, H. L. 1954 *Econ. Geol.* **49**, 235–293.
James, H. L. 1966 *U.S. geol. Surv. prof. Pap.* **440**-W. (61 pages.)
Jeans, C. V. 1978 *Phil. Trans. R. Soc. Lond.* A **289**, 549–639.
Jolly, W. T. 1970 *Contr. Miner. Petr.* **27**, 204–224.

Jolly, W. T. 1974 *Can. Mineral.* **12**, 499–508.

Kastner, M. 1971 *Am. Miner.* **56**, 1403–1441.

Kastner, M. & Waldbaum, D. R. 1968 *Am. Miner.* **53**, 1579–1602.

Kato, Y. 1965 *Soil Sci. Plant Nutr.* **11**, 30–40.

Kempe, D. R. C. & Easton, A. J. 1974 In *Initial reports of the Deep Sea Drilling Project* (ed. T. A. Davies *et al.*), vol. 26, pp. 593–601. Washington: U.S. Government Printer.

Kennan, P. S. 1972 *Geol. Mag.* **109**, 165–170.

Kennedy, W. Q. 1948 *Geol. Mag.* **85**, 229–235.

Kinosaki, Y. 1963 *Geol. Rep. Hiroshima Univ.* **12**, 35.

Klein, C. 1974 *Can. Mineral.* **12**, 475–498.

Kramm, U. 1980 *Neues Jb. Miner. Abh.* **138**, 1–13.

Kretz, R. 1959 *J. Geol.* **67**, 371–402.

Kwak, T. A. P. 1974 *Contr. Miner. Petr.* **44**, 57–80.

Klein, C. & Fink, R. P. 1976 *Econ. Geol.* **71**, 453–487.

Korsch, R. J. 1977 *J. geol. Soc. Aust.* **25**, 339–355.

Laajoki, K. & Saikkonen, R. 1977 *Bull. geol. Surv. Finl.* **293**. (137 pages.)

Lambert, R. St. J. 1959 *Trans. R. Soc. Edinb.* **63**, 553–588.

Leitch, E. C. 1975 *J. geol. Soc. Aust.* **22**, 413–422.

Leitch, E. C. & Cawood, P. A. 1980 *Sedim. Geol.* **25**, 5–22.

Leyh, W. R. & Larsen, D. F. 1983 In *Broken Hill conference, 1983*, pp. 133–156. Melbourne: Australasian Institute of Mining & Metallurgy.

Lonsdale, P. F., Bischoff, J. L., Burns, V. M., Kastner, M. & Sweeney, R. E. 1980 *Earth planet. Sci. Lett.* **49**, 8–20.

Luth, W. C. & Ingamells, C. O. 1965 *Am. Miner.* **50**, 255–258.

McAllister, A. L. 1960 *Trans. Can. Inst. Min. Metall.* **63**, 50–60.

McDowell, S. D. 1983 *Am. Miner.* **68**, 1146–1159.

McDowell, S. D. & Elders, W. A. 1980 *Contr. Miner. Petr.* **74**, 293–310.

McLeod, R. L. 1987 *Trans. Instn Min. Metall.* B **96**, 117–127.

McLeod, R. L. & Stanton, R. L. 1984 *Econ. Geol.* **79**, 1–22.

Martin, R. F. 1969 *Contr. Miner. Petr.* **23**, 323–339.

Matsumoto, K. 1968 *Geol. Rep. Hiroshima Univ.* **6**, 25.

Millot, G. 1970 *Geology of clays* (English transl. W. R. Farrand & H. Paquet). London: Chapman & Hall.

Milton, C. 1971 In *Contributions to geology: Trona issue* (ed. R. B. Parker & L. E. Mannion), pp. 47–63. University of Wyoming, Laramie, Wyoming.

Miyashiro, A. 1953 *Geochim. cosmochim. Acta* **4**, 179–208.

Miyashiro, A. 1956 *J. geol. Soc. Japan* **62**, 700–702.

Miyashiro, A. 1965 *Metamorphism and metamorphic belts.* Tokyo: Iwanami Shoten. (English transl. 1973. London: George Allen and Unwin.)

Moore, J. M. 1983 Paper presented to AIME Ann. Mtng, Atlanta, 1983; *preprint* no. 83-12. (4 pages.)

Morey, G. B., Papike, J. J., Smith, R. W. & Weiblen, P. W. 1972 *Mem. geol. Soc. Am.* **135**, 225–264.

Muffler, L. P. J. & White, D. E. 1969 *Bull. geol. Soc. Am.* **80**, 157–182.

Nesbitt, B. E. & Kelly, W. C. 1980 *Econ. Geol.* **75**, 1010–1021.

Nesbitt, B. E. & Essene, E. J. 1980 *Eos, Wash.* **61**, 391.

Owens, J. P. & Sohl, N. F. 1973 *Bull. geol. Soc. Am.* **84**, 2811–2838.

Phinney, W. C. 1963 *J. Petr.* **4**, 90–130.

Porrenga, D. H. 1967 *Mar. Geol.* **5**, 495–501.

Pottorf, R. J. & Barnes, H. L. 1978 *Geol. Soc. Am.* Abstracts with Programs **10**, 473.

Ramberg, H. 1952 *The origin of metamorphic and metasomatic rocks.* University of Chicago Press.

Reynolds, D. L. 1929 *Geol. Mag.* **66**, 390–399.

Richards, S. M. 1963 Ph.D. thesis, Univ. of New England.

Richards, S. M. 1966 *Econ. Geol.* **61**, 72–96; 257–274.

Roy, R. 1956 *J. Am. ceram. Soc.* **39**, 145–146.

Rozendaal, A. 1978 *Geol. Soc. S. Afr. Spec. Publn* **4**, 235–265.

Rozendaal, A. 1980 In *Proc. 5th Quadrennial IAGOD Symp.*, pp. 620–633. Stuttgart: E. Schweizerbart'sche Verlagsbuchhandlung (Nägele u. Obermiller).

Rozendaal, A. & Stumpfl, E. F. 1984 *Trans. Instn Min. Metall.* B **93**, 161–175.

Rutherford, M. J. 1973 *J. Petr.* **14**, 159–180.

Ryan, P. J., Lawrence, A. L., Lipson, R. D., Moore, J. M., Paterson, A., Stedman, D. P. & van Zyl, D. 1982 University of the Witwatersrand Economic Geology Research Unit, Information Circular no. 160, p. 33.

Sabatier, G. 1950 *C.r. hebd. Séanc. Acad. Sci., Pa* **280**, 1662–1664.

Saxena, S. K. 1969 *Contr. Miner. Petr.* **22**, 259–267.

Schiffman, P., Elders, W. A., Williams, A. E., McDowell, S. D. & Bird, D. K. 1984 *Geology* **12**, 12–15.

Schoen, R. 1964 *J. sedim. Petr.* **34**, 855–863.

Sholkovitz, E. 1973 *Geochim. cosmochim. Acta* **37**, 2043–2073.

Segnit, E. R. 1961 *Australas. Instn Min. Metall.* **199**, 87–112.
Shelley, R. C. 1976 *An introduction to sedimentology*. London: Academic Press.
Sheldon, R. P. 1963 *U.S. geol. Surv. prof. Pap.* no. 313-B, p. 159.
Sheppard, R. A. & Gude, A. J. 1968 *U.S. geol. Surv. prof. Pap.* no. 597, p. 38.
Sheppard, R. A. 1973 *U.S. geol. Surv. prof. Paper* no. 830.
Smith, R. E. 1969 *J. Petr.* **10**, 144–163.
Smoot, T. W. 1960 *Illinois State geol. Surv.* **293**, 1–19.
Snelling, N. J. 1957 *Geol. Mag.* **94**, 297–304.
Spear, F. S., Selverstone, J., Hickmott, D., Crowley, P. & Hodges, K. V. 1984 *Geology* **12**, 87–90.
Sorokin, V. I., Vlasov, V. V., Varfolomeeva, E. K. & Urasin, M. A. 1980 *Lithol. Miner. Res.* **14**, 690–693.
Stanton, R. L. 1972*a* *Ore Petrology*. New York: McGraw-Hill.
Stanton, R. L. 1972*b* *Econ. Geol.* **67**, 1128–1145.
Stanton, R. L. 1976 *Trans. Instn Min. Metall.* B **85**, 118–131.
Stanton, R. L. 1979 Text of the Charles F. Davidson Memorial Lecture, University of St Andrews, 22nd November 1979, unpublished, p. 48.
Stanton, R. L. 1982*a* *Proc. Australas. Instn Min. Metall.* **282**, 11–32.
Stanton, R. L. 1982*b* *Trans. Instn Min. Metall.* B **91**, 47–71; 72–80.
Stanton, R. L. 1983 *Econ. Geol.* **78**, 422–437.
Stanton, R. L. 1984*a* *Econ. Geol.* **79**, 1245–1264.
Stanton, R. L. 1984*b* *Econ. Geol.* **79**, 1428–1441.
Stanton, R. L. 1985 Stratiform ores and geological process. *J. Proc. R. Soc. N.S.W.* **118**, 77–100.
Stanton, R. L. 1987 *Trans. Instn Min. Metall.* B **96**, 37–57.
Stanton, R. L. 1988 In *Edwin Sherbon Hills – Pathways in Geology. Edwin Hills Memorial Vol.* (ed. R. W. Le Maitre). Melbourne: Blackwell.
Stanton, R. L. & Chappel, B. W. 1989 (In preparation.)
Stanton, R. L. & Roberts, W. P. H. 1978 *J. de Mineralogia Recife* 7 (Djalma Guimaraes Vol.), pp. 143–154.
Stanton, R. L. & Vaughan, J. P. 1979 *Proc. Australas. Instn Min. Metall.* **270**, 25–38.
Stanton, R. L. & Wiley, H. G. 1970 *Econ. Geol.* **65**, 182–194.
Stanton, R. L. & Wiley, H. G. 1971 *Econ. Geol.* **66**, 1232–1238.
Stanton, R. L. & Williams, K. L. 1978 *J. Petr.* **19**, 514–529.
Steinmann, G. 1927 *C.r. XVIme Congr. Geol. Int., 1926*, II, pp. 637–667.
Strakhov, N. M. 1966 *Int. Geol. Rev.* **8**, 1172–1196.
Sturt, B. A. 1962 *J. Petr.* **3**, 181–191.
Sudo, T., Hayashi, H. & Yokoura, H. 1957 *Clay miner.* **3**, 258–263.
Sudo, T. & Shimoda, S. 1978 *Clays and clay minerals of Japan*. Oxford: Elsevier.
Surdam, R. C. & Sheppard, R. A. 1978 In *Natural zeolites: occurrence, properties, use* (ed. L. B. Sand & F. A. Mumpton), pp. 145–174. Oxford: Pergamon Press.
Swallow, J. C. & Crease, J. 1965 *Nature, Lond.* **205**, 165, 166.
Tilley, C. E. 1924*a* *Geol. Mag.* **61**, 167–171.
Tilley, C. E. 1924*b* *Q. Jl geol. Soc. Lond.* **81**, 100–110.
Tozer, C. F. 1955 *Geol. Mag.* **92**, 310–320.
Tsukahara, N. 1964 *Clay Sci.* **2**, 56–75.
Tsuzuki, Y. & Honda, S. 1975 *Abstr. Ann. Mtg Miner. Soc. Jap.*, p. 92.
Tulloch, A. J. 1979 *Contr. Miner. Petr.* **69**, 105–117.
Turner, F. J. 1968 *Metamorphic petrology*. New York: McGraw-Hill.
Turovskii, D. S., Kheirov, M. B. & Rateev, M. A. 1981 *Lit. i Pol. Isk.* **16**, 6–17. (Transl. Consultants Bureau, New York.) New York: Plenum Publishing.
Valeton, I. 1958 *Mitt. Geol. StInst. Hamb.* **27**, 88–131.
Valliant, R. I. & Barnett, R. L. 1981 *Can. J. Earth Sci.* **19**, 992–1010.
Van Houten, F. B. & Purucker, M. E. 1984 *Earth Sci. Rev.* **20**, 211–243.
Vaughan, J. P. 1980 Ph.D. thesis, Univ. of New England.
Vaughan, J. P. & Stanton, R. L. 1986 *Trans. Instn Min. Metall.* B **95**, 94–121.
Venkatarathnam, K. & Ryan, W. B. F. 1971 *Mar. Geol.* **11**, 261–282.
Vernon, R. H. 1978 *Lithos* **11**, 283–289.
Voll, G. 1959 *Lpool Manchr geol. J.* **2**, 503–567.
Watson, J. 1948 *Geol. Mag.* **85**, 149–162.
Weiss, H. M., Noltner, T. & Stoffers, P. 1980 *Neues Jb. Miner. Abh.* **139**, 239–253.
Wickham, S. M. & Taylor, H. P. 1986 *Terra Cogn.* **6**, 209.
Williams, G. H. 1890 *U.S. Geol. Surv. Bull.* **62**.
Wilson, M. J. 1966 *Mineralog. Mag.* **35**, 1080–1093.
Winkler, H. G. F. 1976 *Petrogenesis of metamorphic rocks*, 4th edn. New York: Springer-Verlag.
Wolfbauer, C. A. 1971 In *Contributions to geology: Trona issue* (ed. R. B. Parker & L. E. Mannion), pp. 3–8. University of Wyoming, Laramie, Wyoming.
Yakovleva, M. Ye. 1970 *Dokl. Akad. Nauk SSSR* **191**, 1134–1137.

Yoder, H. S. 1952 *Am. J. Sci.* Bowen Vol., pp. 569–627.
Yoder, H. S. 1955 In *Geol. Soc. Am. Spec. Paper* **62**, 505–524.
Yoder, H. S. 1957 Annual report of the Director of the Geophysical Laboratory. Papers from the Geophysical Laboratory, Carnegie Institution of Washington, vol. 1277, pp. 232–237.
Yudin, N. I. & Plotnikova, L. Y. 1983 *Lit. i Pol. Isk.* **2**, 65–70. (English transl. by Plenum Publishing Corp., pp. 172–176.)
Zierenberg, R. A. & Shanks, W. C. 1983 *Econ. Geol.* **78**, 57–72.

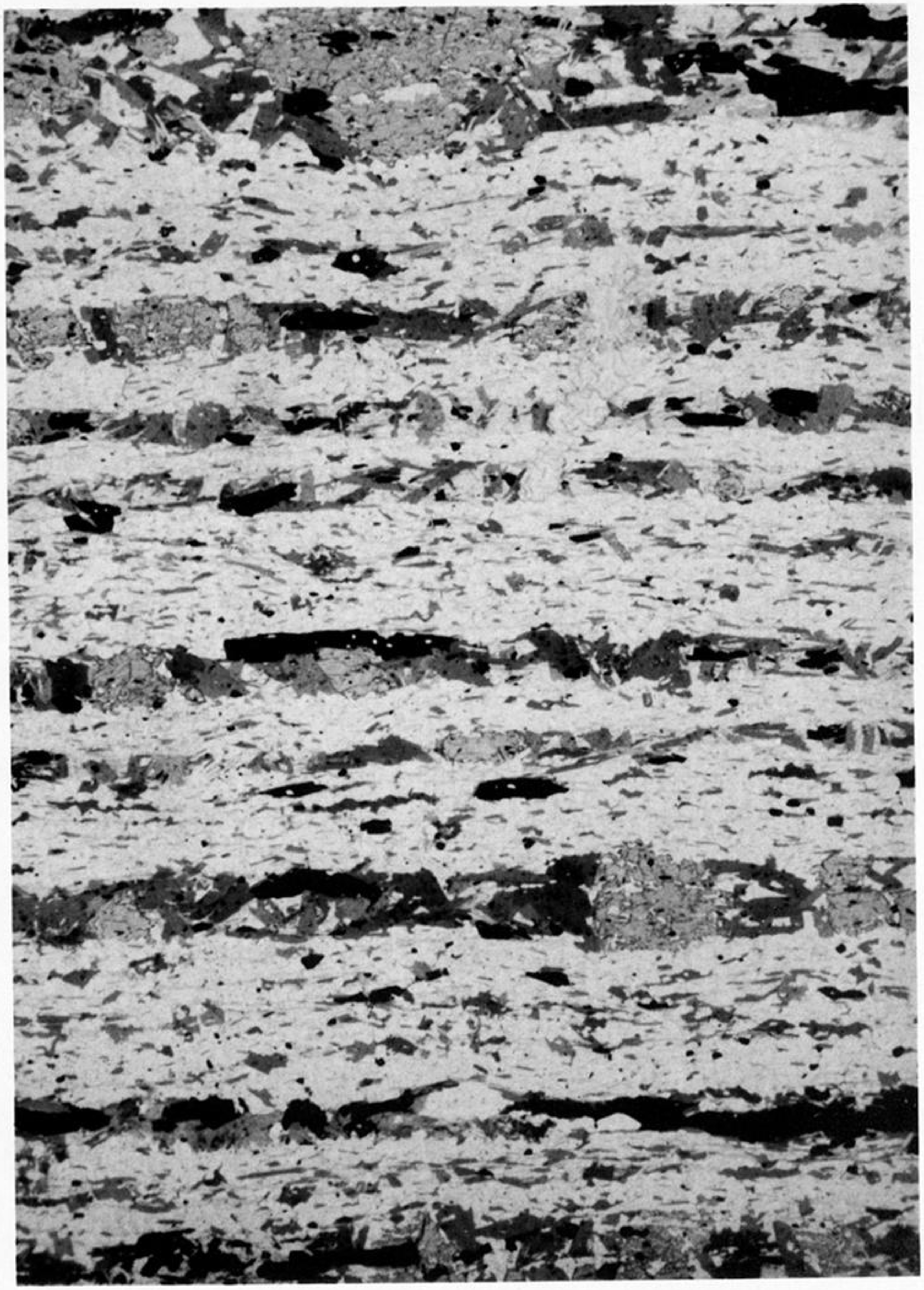


FIGURE 1. Sulphide–silicate assemblage from the regionally metamorphosed stratiform orebody of the Gorob Mine, South West Africa. Bedding is well preserved and biotite–staurolite–garnet–sulphide (chalcopyrite–sphalerite) assemblages are interbedded with quartz–feldspar dominated assemblages. The sulphides are regarded as sedimentary and hence in their present form to have derived directly from sedimentary precursors, as is the case with much of the quartz. The silicates on the other hand are generally assumed to have formed by a completely different process – metamorphic breakdown, diffusion and reaction. Plane polarized transmitted light. (Magn. × 22.)

FIGURE 11. Calc-silicate and associated unmetamorphosed carbonaceous shaley–silty sediment in core from the Brindabella stratiform zinc sulphide bearing occurrence, southern New South Wales. The calc-silicate consists of what appear to be composite concretions of grandite garnet (light grey) and epidote (slightly darker grey). Ordinary light. (Magn. ×5.)

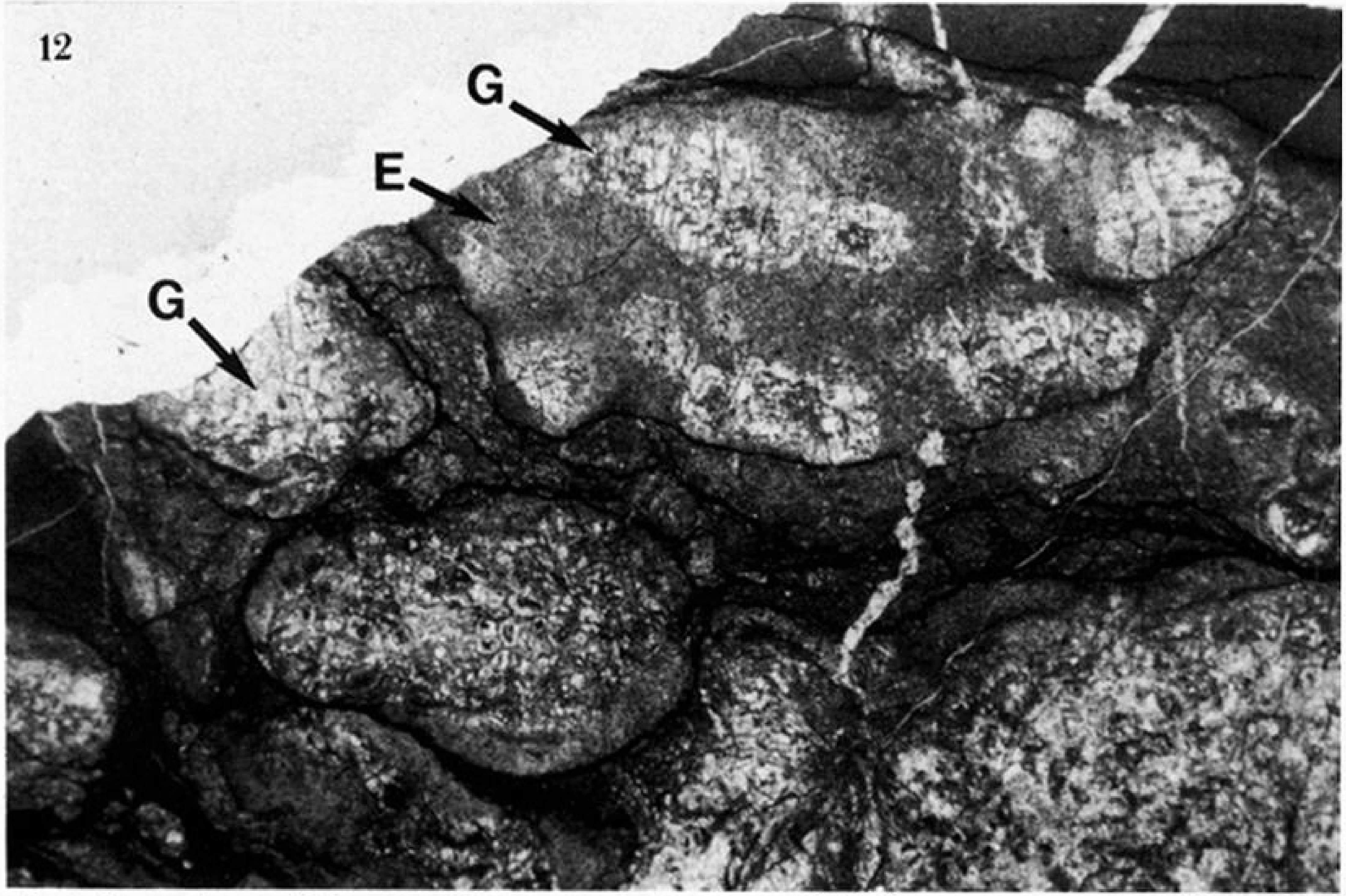


FIGURE 12. Right-hand portion of figure 11, rotated through 90° for convenience. Grandite (G) lighter grey; epidote (E) darker grey. Ordinary light. (Magn. ×10.)

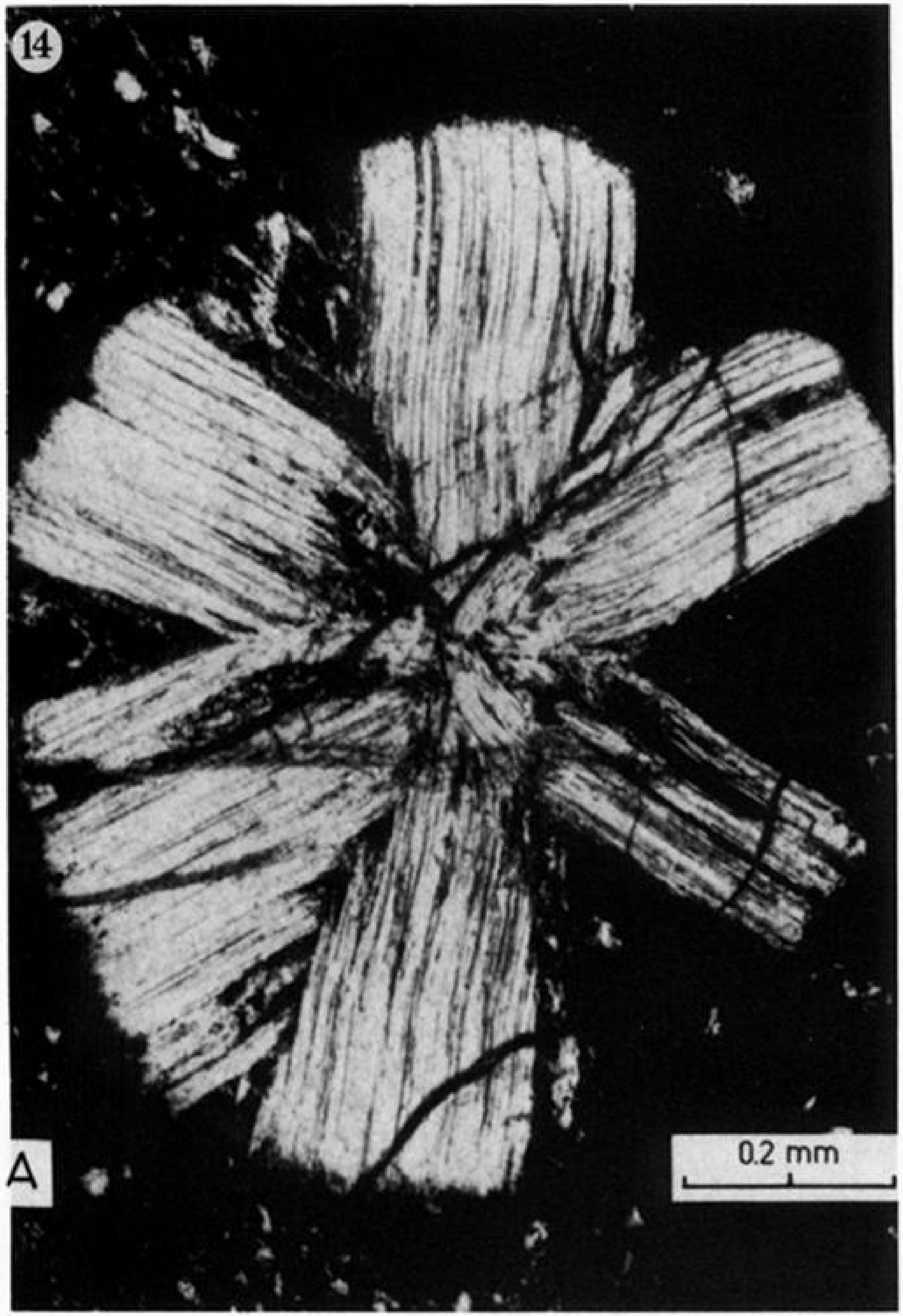


FIGURE 14. Spessatite garnet in iron-rich metapelites of Seppola, Finland (from Laajoki & Saikkonen 1977, with kind permission). Note apparent pseudomorphism of phyllosilicate cleavages and overall cross form. Scale as shown.

FIGURE 15. Spessatite garnet from the same locality as that of figure 12, but showing phyllosilicate-like platey shape (from Laajoki & Saikkonen 1977, with kind permission). Scale as shown.

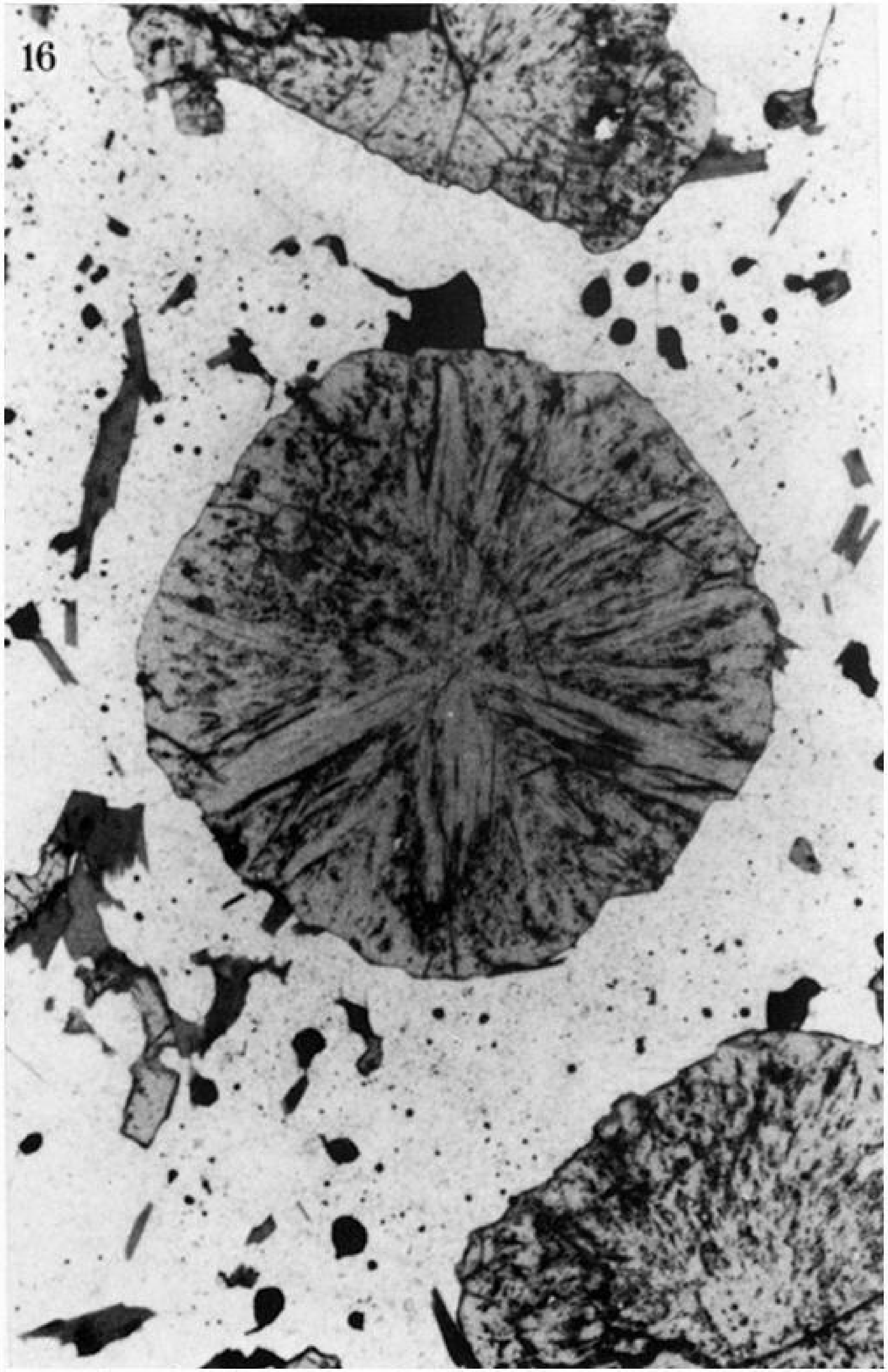


FIGURE 16. Almandine garnet from the Jollimont sulphide-bearing metapelite, northwest Queensland, showing apparent relict phyllosilicate cleavage structure and radiating pattern; ordinary light. (Magn. × 10.) Photograph by J. P. Vaughan; see Vaughan & Stanton 1986.

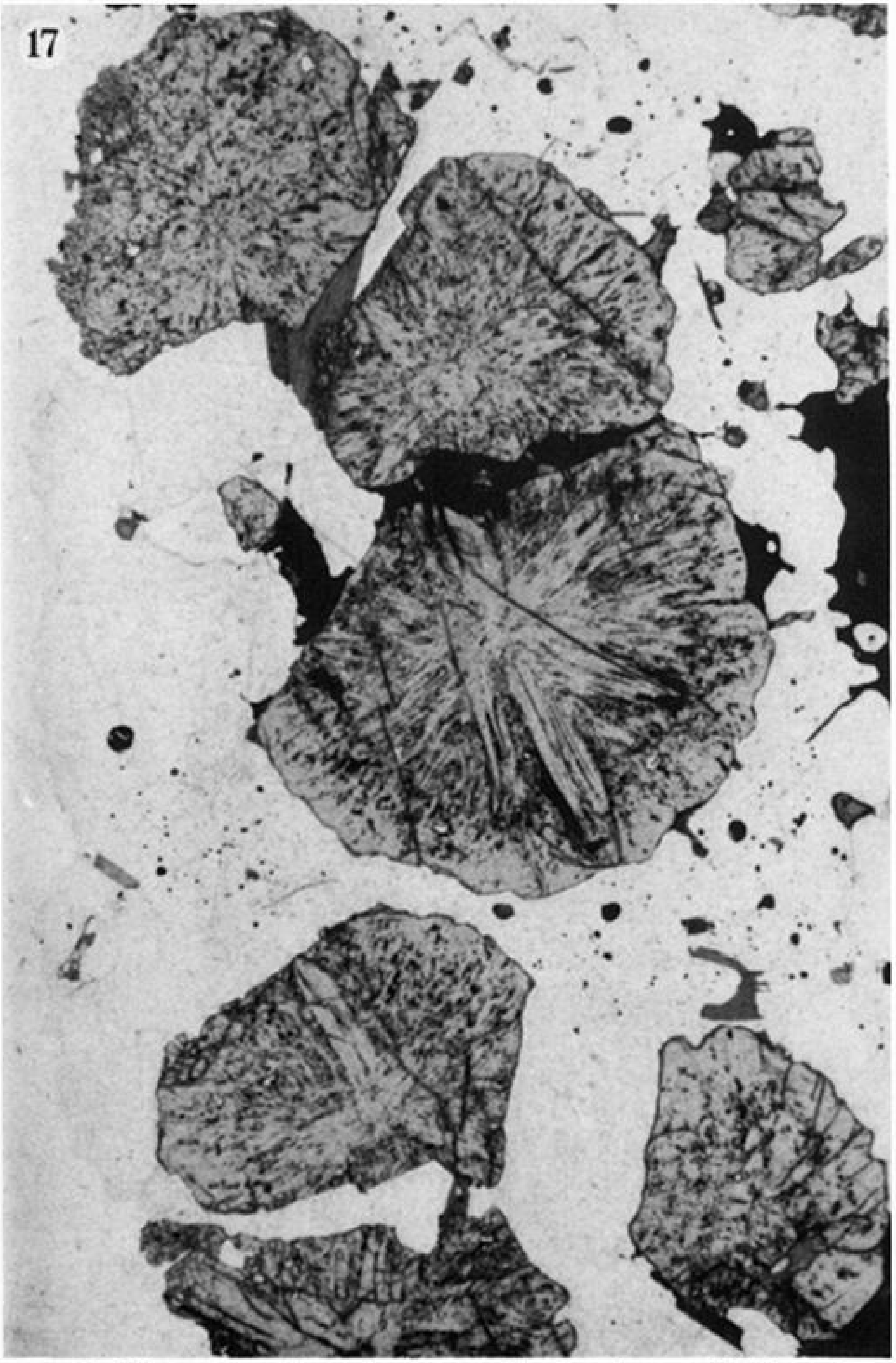


FIGURE 17. Similar almandine from Jollimont, showing particularly well-developed radial structure in addition to apparent relict phyllosilicate cleavages; ordinary light. (Magn. × 10.) Photograph by J. P. Vaughan; see Vaughan & Stanton 1986.

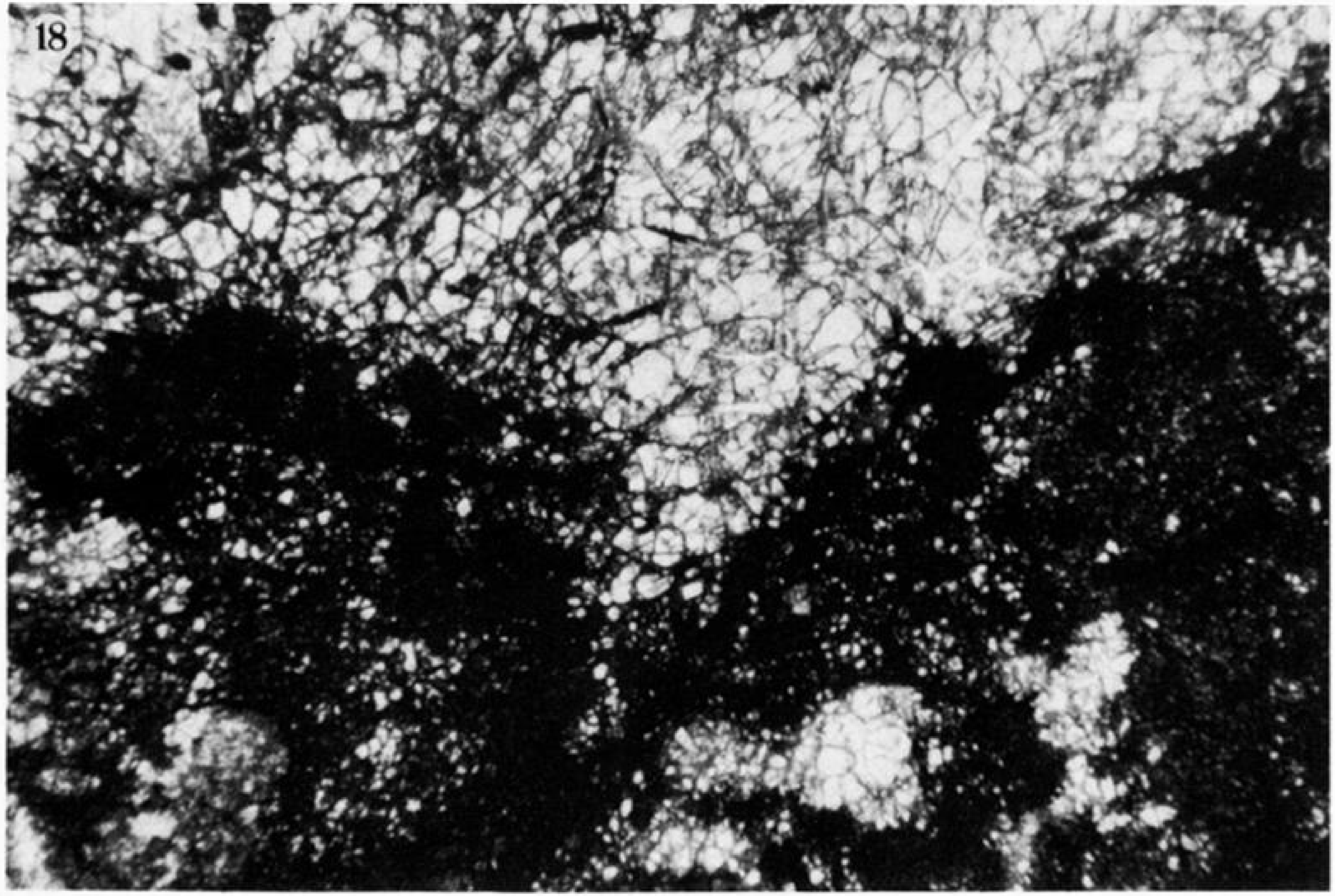

18

FIGURE 18. Grandite garnet (light areas, principally in upper half of photograph) with black opaque material of grandite-like composition identified here as a probable precursor to grandite. Note apparent abundant nucleation of fine grandite crystals through black material. Thin section of Ban Ban diamond drill core CD13, 69.3 m; ordinary light. (Magn. ×21.)

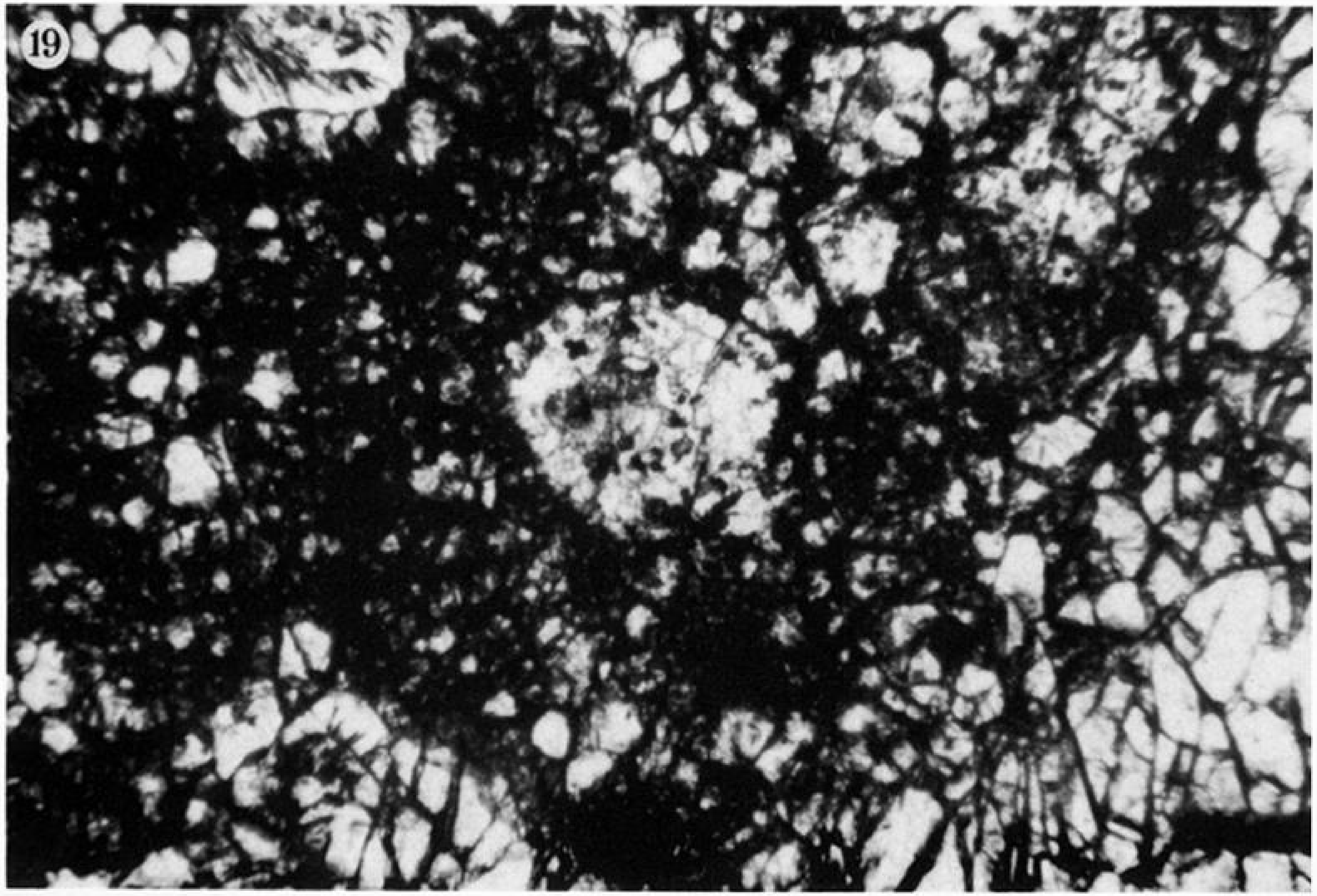


FIGURE 19. Material similar to that of figure 18, but at higher magnification and showing minor incorporation of dark material within the grandite crystals. Ordinary light. (Magn. ×76.)

Figure 24. Dark (near-black) areas of 'pyroxene precursor' (indicated by arrows) associated with grandite and grandite precursor (not quite such intense black) and carbonate (large areas of grey to white) in Brindabella diamond drill core DOW1. When viewed in whole core with the naked eye, this material appears to have undergone extensive soft-sediment deformation, and some pull-apart structure in a deformed bed of dark material may be discerned in the lower part of the photograph. Note also the unequilibrated grain boundaries of the abundant carbonate. Transmitted light. (Magn. ×3.5.)

FIGURE 25. Larger dark particle of upper right of figure 24, showing detail of lighter areas (13 analyses giving good diopside compositions) and associated, gradationally related, black material (19 analyses of less pure diopside). Average analyses of such material are given in columns 4 and 5, table 9). Transmitted light. (Magn. × 13.)

26

Figure 26. Enlargement of dark material of lower right centre of figure 24, showing pull-apart structure. Transmitted light. (Magn. ×5.7.)

FIGURE 27. Enlargement of upper extremity of black material of figures 24 and 26, rotated through approximately 90°, showing small irregular patches of just discernible translucency. Associated somewhat less dark material containing clear crystals occupying the right-hand side of this figure, and portions of figures 24, 25 and 26 is the postulated grandite precursor and contained grandite. Transmitted light. (Magn. ×20.)

FIGURE 30. Thin section of cordierite (white, upper left of photograph) and sudoitic chlorite (pale grey, trending NE–SW across central area of photograph) embedded in foliated but unaltered biotite and associated with clear, unaltered almandine (two subidiomorphic crystals near base). Arrows point to field of figure 31. Geco, Ontario, drill core DDH25–31, transmitted ordinary light. (Magn. ×16.)

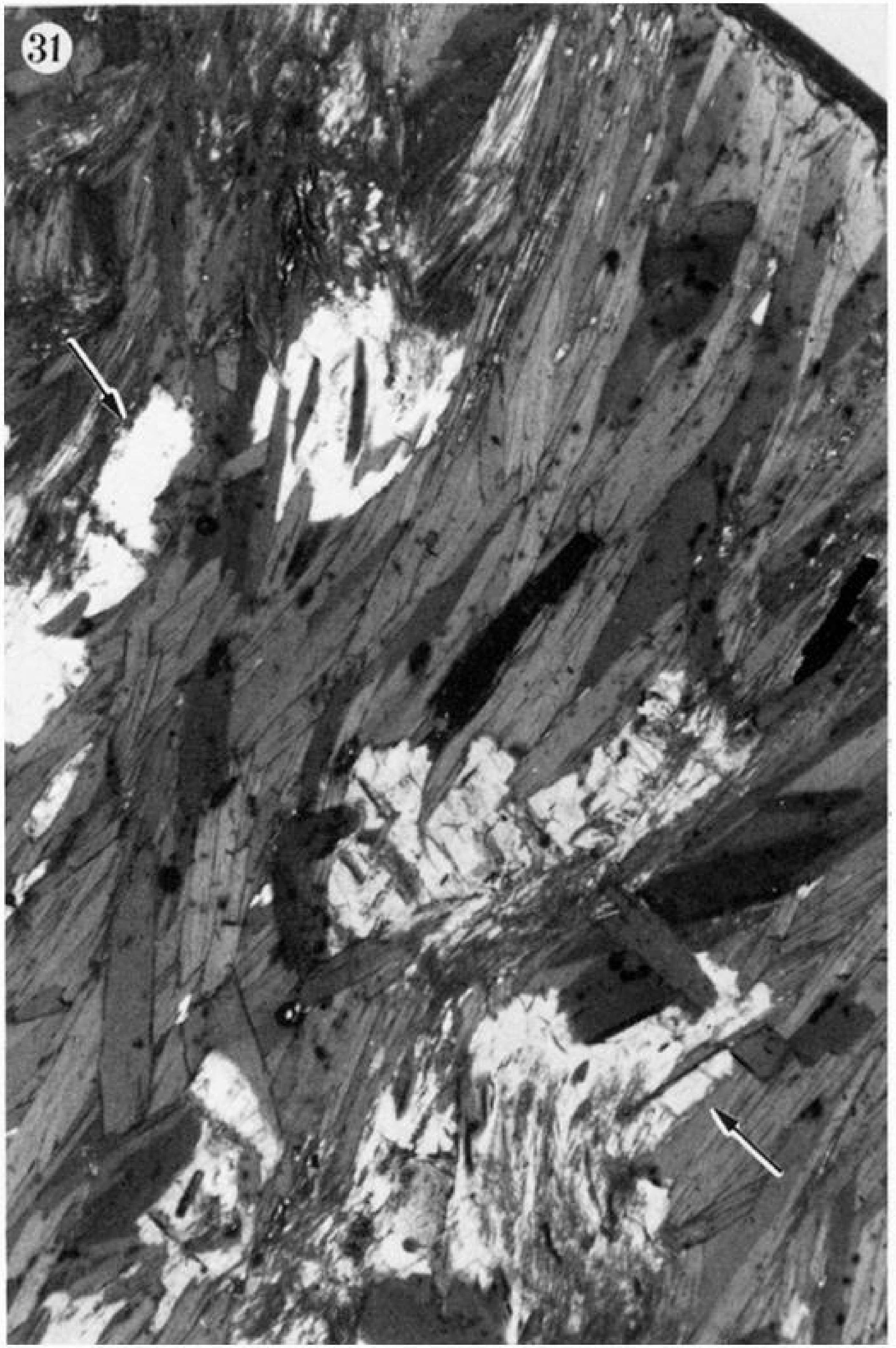


FIGURE 31. Upper right of figure 30 (arrowed) at higher magnification, showing more clearly the slight colour difference between the cordierite and sudoitic chlorite, fresh unaltered condition of the associated biotite, and development of fine wispy sillimanite developed in all of cordierite, sudoitic chlorite and biotite. Ordinary, transmitted light. (Magn. ×40.)

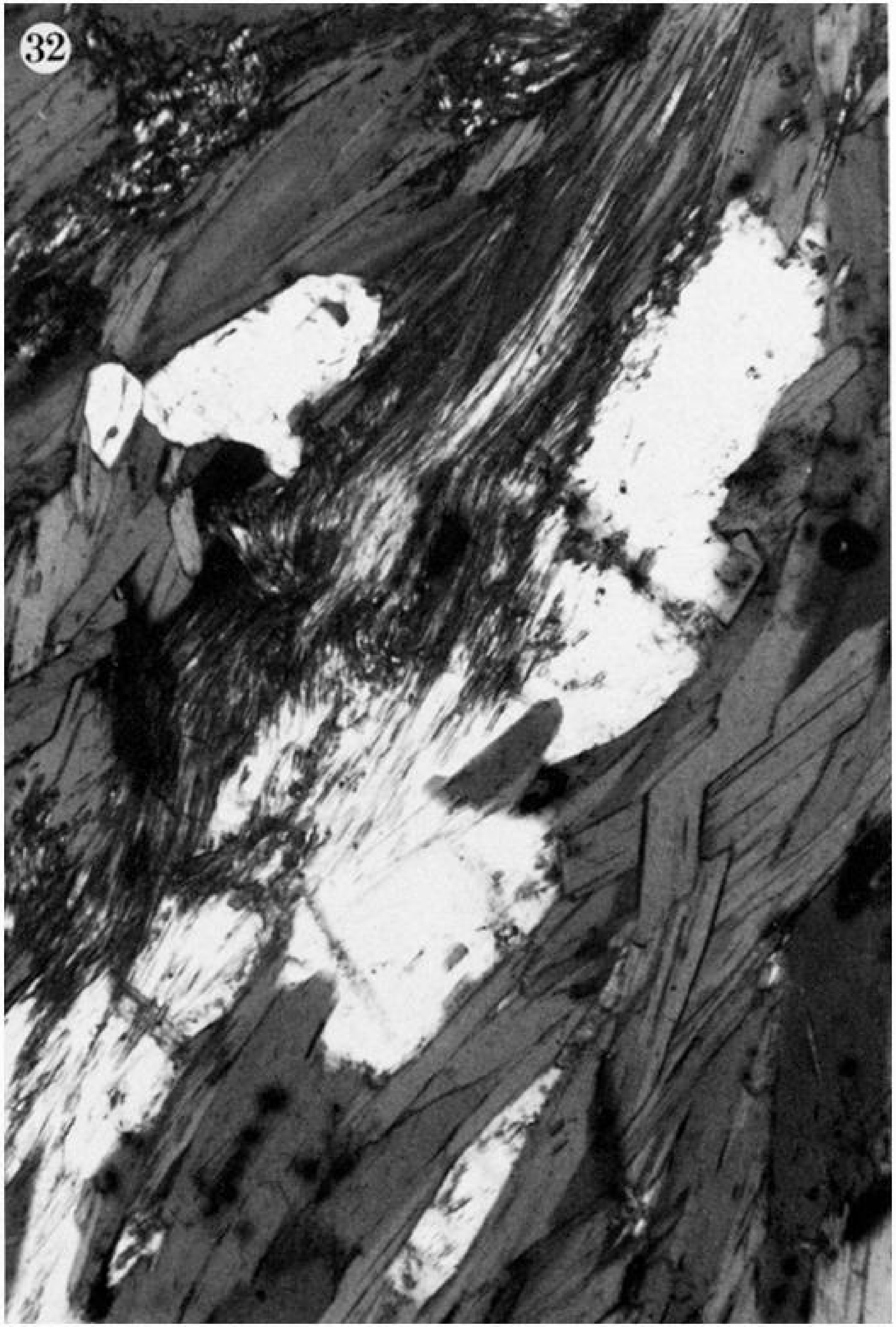


Figure 32. Enlargement of cordierite towards upper left of figure 31 (see upper arrow, figure 31) showing detail of the development of sillimanite bundles in biotite and cordierite and the unaltered condition of the biotite flakes. The two very white grains to the upper left are carbonate. Transmitted ordinary light. (Magn. ×96.)

Figure 33. Enlargement of sudoitic chlorite of lower right of figure 31 (see lower arrow of figure 31) showing mode of occurrence of sillimanite in sudoitic chlorite analogous to that in cordierite, and analogous relations with unaltered biotite. Transmitted ordinary light. (Magn. ×96.)

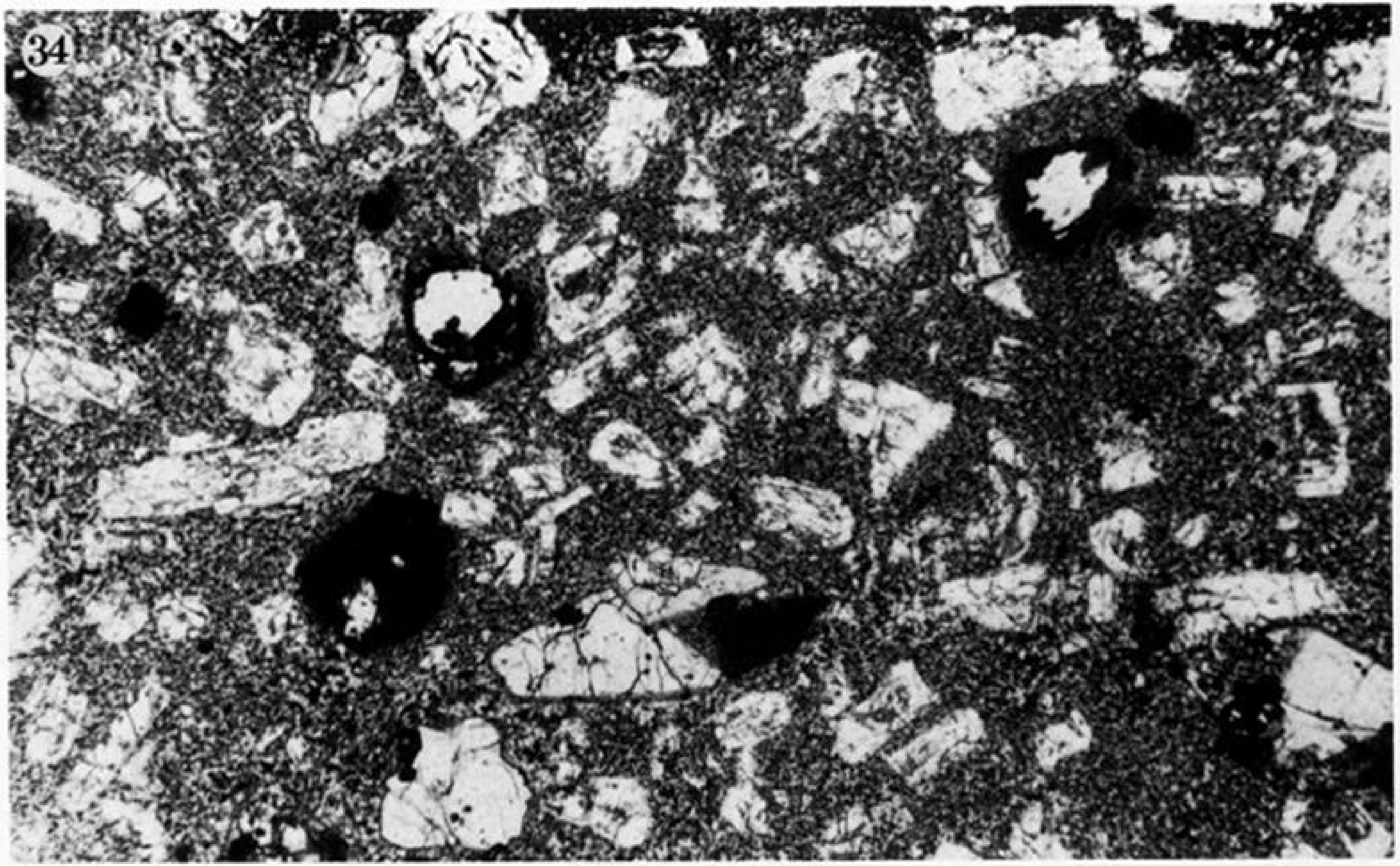


FIGURE 34. Thin section showing varying degrees of alteration of olivine (white, Fo60) to dark alteration product of table 11. Solomon Islands basaltic andesite, transmitted ordinary light. (Magn. ×25.)

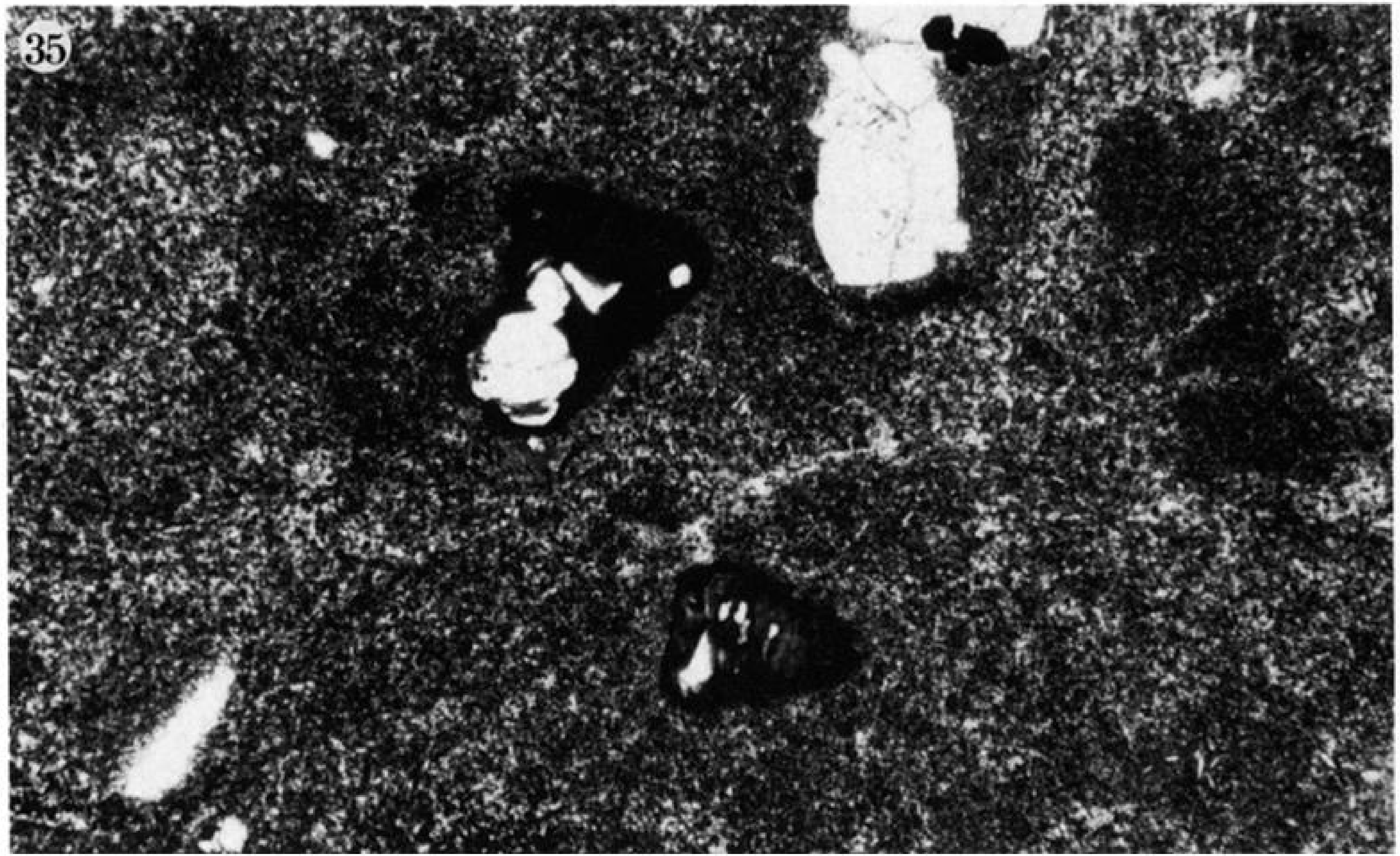


FIGURE 35. Thin section showing advanced alteration of olivine (Fo68, white residue, centre of photograph) to dark alteration product (table 11) that may constitute a precursor to metamorphic amphibole in a variety of metabasites. White crystals to upper right and lower left are feldspar. Solomon Islands basaltic andesite, transmitted ordinary light. (Magn. ×25.)

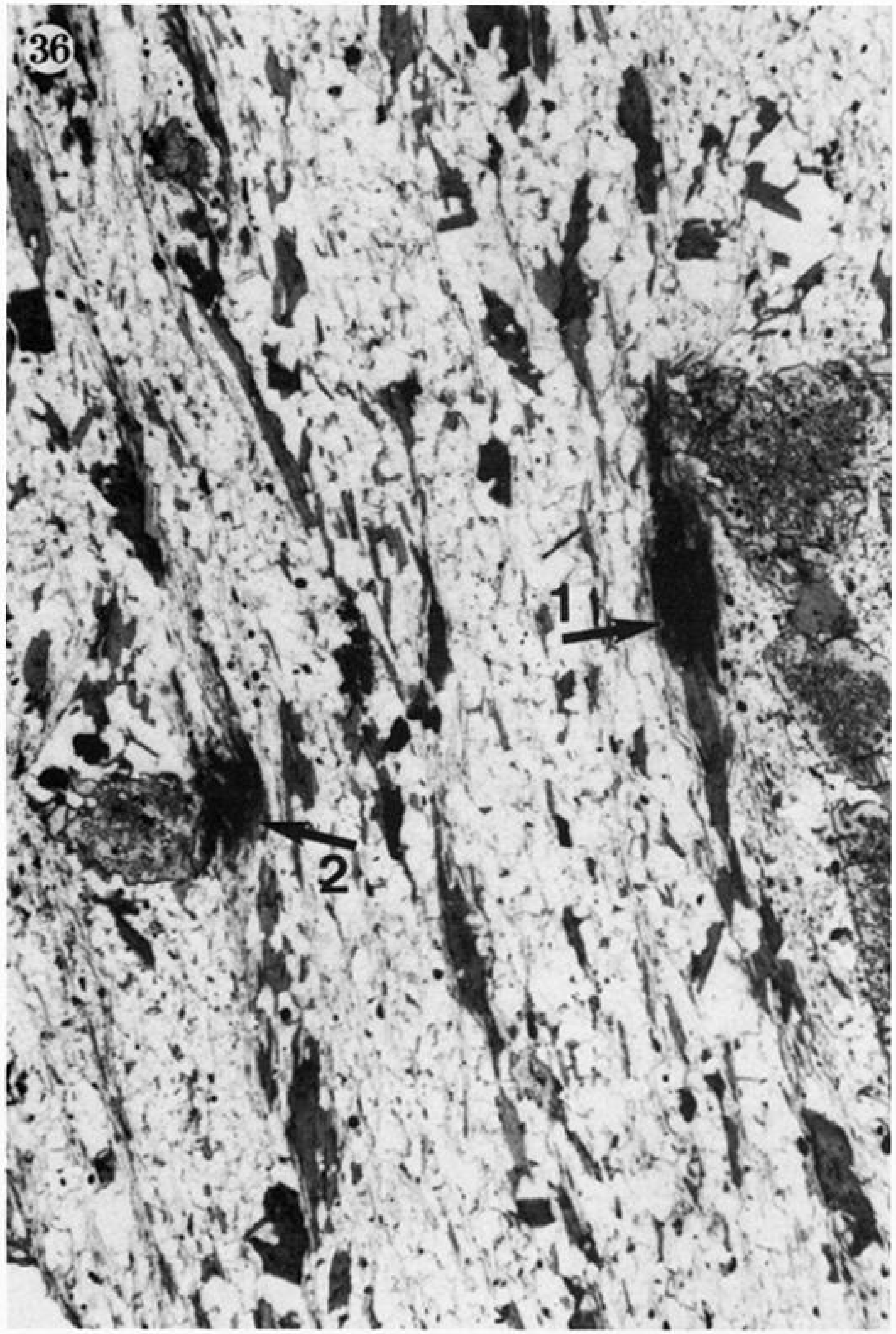
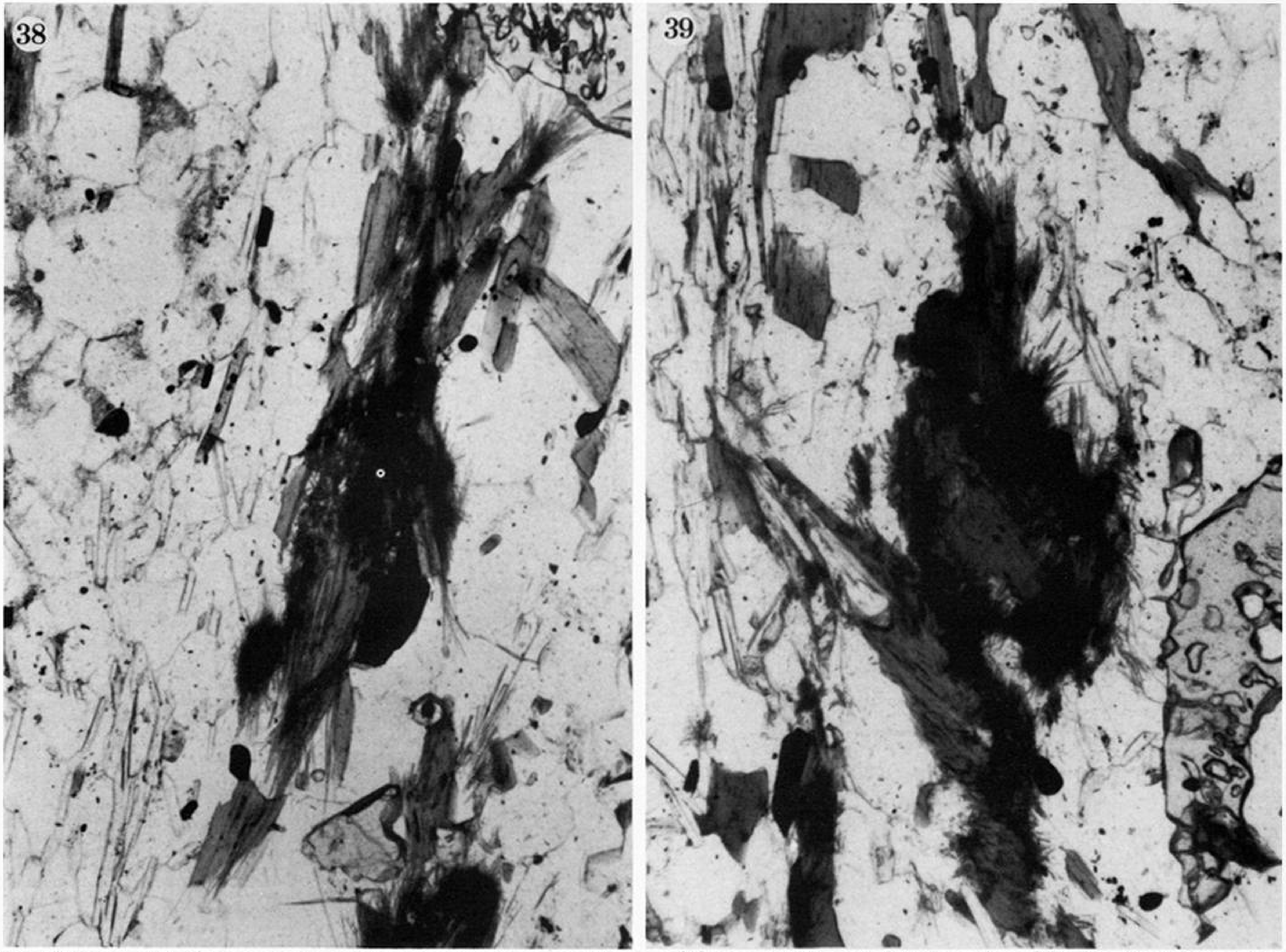


FIGURE 36. Thin section of quartz–chlorite–muscovite–biotite–almandine–staurolite–K-feldspar–sillimanite gneiss from diamond drill core intersecting the enclosing rocks of the Hemlo pyritic gold deposit, near Marathon, Ontario. Arrowed grains 1 and 2 show dark material, opaque at low magnification, associated with biotite, though many biotite grains are completely devoid of it. Transmitted plane polarized light. (Magn. ×10.)

FIGURE 37. Enlargement of grain 1 of figure 36, showing clear biotite at centre right of photograph of figure 36 merging into turbid dark material towards centre of photograph. Wispy sillimanite has developed round the margins of the dark material, particularly towards the top of the photograph. Transmitted plane polarized light. (Magn. ×50.)



FIGURES 38 AND 39. Composite grains analogous to those of figures 36 and 37 showing biotite (medium grey) and associated dark material which grades into fibrous sillimanite round its margins. Note the presence of other biotite grains showing no tendency to the development of the dark material. These are the two categories of biotites shown in figure 43. The light groundmass is quartz and K-feldspar, together with sieved staurolite. Transmitted plane polarized light. (Magn. ×50.)