

PRESIDENTIAL ADDRESS

Patterns of mineral occurrence in metamorphic rocks

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ABSTRACT

Patterns in the occurrence of minerals in metamorphic rocks suggest additional opportunities for investigating chemical and physical processes during metamorphism. Three such patterns are reviewed. First, trace minerals in metamorphic rocks commonly occur with regular distributions indicating their participation in prograde reactions that can be mapped as isograds. Examples include the distribution of allanite and monazite in pelitic rocks and of zircon and baddeleyite in siliceous dolomites. Recognition of these isograds points to the potential for developing a chronology of specific chemical reactions during metamorphism and for defining the *P-T* conditions of those reactions. Second, the mineralogical products of retrograde metamorphism in many cases occur in distinctive associations that are consistent with partial mineral-fluid equilibrium. Examples include the distribution of retrograde calcite, quartz, and tremolite in siliceous limestones and of retrograde tremolite, dolomite, brucite, and serpentine in siliceous dolomites from contact aureoles. Among other things, application of partial equilibrium to retrograde metamorphic rocks leads to constraints on the amount and direction of fluid flow in contact aureoles as they cool. Third, pseudomorphs are typically absent from prograde metamorphic rocks but are common in retrograde metamorphic rocks. The distribution may be explained by the effect of “force of crystallization.” The pattern of occurrence of pseudomorphs thus suggests novel phenomena during metamorphism that develop from an interplay between chemical and mechanical processes.

INTRODUCTION

Recognition of distinctive patterns in the occurrence of minerals in rocks has a long and distinguished history in the development of petrology. The foundation of modern metamorphic petrology specifically can in large part be traced to the natural grouping of minerals in metamorphosed mafic igneous rocks discovered independently in pioneering studies by Goldschmidt and Eskola. These patterns, in turn, led to the concept of metamorphic facies. Almost eighty years ago Eskola (1922) had already identified the diagnostic mineral occurrences of the pyroxene hornfels, sanidinite, greenschist, amphibolite, and eclogite facies and anticipated those of the blueschist facies. Furthermore, he deduced that each occurrence represented equilibrium within a characteristic region of *P-T* space and assigned each facies to its correct relative position on a *P-T* diagram. The notion of facies later led naturally to the concept of a petrogenetic grid (Bowen 1940) and to the active fields of mineral thermometry and mineral barometry.

The patterns of mineral occurrence observed by Goldschmidt and Eskola, of course, are hardly the only ones recognized in metamorphic rocks. This paper points out additional patterns in the occurrence of (1) trace minerals in contact and regional

metamorphic terrains, (2) retrograde minerals in contact aureoles, and (3) pseudomorphs in prograde and retrograde metamorphic rocks. These patterns are common in metamorphic terrains worldwide. Each pattern suggests new opportunities for investigating the process of metamorphism. It is certain that many other patterns of mineral occurrence in metamorphic rocks remain to be discovered, and that the recognition of such patterns will continue to play a fundamental role in advancing our understanding of chemical and physical phenomena in Earth's crust.

TRACE MINERALS IN PROGRADE METAMORPHIC ROCKS

Casually defined, trace minerals are both relatively small (typically several 10s of mm in diameter or less) and occur in small abundance (typically 10^{-4} to 10^{-6} % by volume). Because of their small size and abundance, trace minerals are usually invisible or unidentifiable with optical microscopy. If they have a distinctive mean atomic number, however, trace minerals can be readily located with back-scattered electron (BSE) imaging and identified with energy-dispersive X-ray spectrometry (EDS). Table 1, although not a complete catalog, lists some of the more common trace minerals I have encountered imaging thin sections of contact and regional metamorphic rocks over the last decade with BSEs. Even this partial list demonstrates

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both that many mineral groups are represented and that some minerals like geikielite and baddeleyite, normally considered exotics, are surprisingly common at least in certain types of metamorphic rocks. Although the occurrence and importance of trace minerals in metamorphic rocks is widely appreciated, there have been relatively few investigations of the petrology of trace minerals. At the first level of study, understanding their petrology begins with identifying common patterns in their occurrence in a variety of metamorphic terrains. Two examples of pairs of trace minerals in Table 1 that exhibit systematic and petrologically significant patterns in their occurrence are (a) monazite (Mnz) and allanite (Aln), and (b) zircon (Zrn) and baddeleyite (Bad). [These and all other abbreviations for minerals follow Kretz (1983).]

Monazite and allanite

Distribution. Allanite and Mnz are almost ubiquitous trace minerals in pelitic schists and hornfelses, but their distribution is neither random nor uniform. Nevertheless, there is little agreement whether Mnz develops as a low-grade metamorphic mineral (Franz et al. 1996; Heinrich et al. 1997), a medium-grade metamorphic mineral (Smith and Barreiro 1990; Bingen et al. 1996), or is detrital (Suzuki and Adachi 1994; Suzuki et al. 1994). These questions were addressed by examining the occurrence of Mnz and Aln in more than 100 samples of pelitic rocks from three metamorphic environments: a contact aureole in central Maine, a low-*P* Buchan regional metamorphic terrain in south-central Maine, and a medium-*P* Barrovian regional metamorphic terrain in east-central Vermont (Ferry 1994; Symmes and Ferry 1995; Wing and Ferry 1999; Wing et al. 1999).

Results for the contact aureole (Fig. 1) are representative of the minerals' distribution in all three terrains. Metamorphism occurred with the emplacement of the Devonian Onawa granodiorite at $P \approx 3000$ bars and T up to ≈ 650 °C (Symmes and Ferry 1995). At the lowest grades of metamorphism, all pelites contain Mnz that is distinctive both for its patchy chemical zoning (chiefly in ThO_2 content) and its irregular habit. This type of Mnz from the area in south-central Maine must be detrital because its isotopic age, measured with the ion microprobe, can be older than the stratigraphic age of the host formation. The detrital Mnz grains have isotopic age and texture reset to varying degrees by the later metamorphic event. Monazites at the lowest grade of metamorphism in the Onawa aureole are likely detrital as well, although a diagenetic, authigenic, or very low-grade metamorphic origin cannot be discounted with certainty. With increasing grade, the detrital Mnz disappears and the rare-earth elements in the rock are sited in Aln, which appears as euhedral metamorphic porphyroblasts. The Mnz \rightleftharpoons Aln transition can be mapped as an isograd, and it coincides exactly in the regional metamorphic terrains with the biotite (Bt) isograd [contact aureoles lack a distinct Bt isograd; Bt first appears with the development of andalusite (And) or cordierite]. The Mnz \rightleftharpoons Aln and Bt-forming reactions are almost certainly the same during regional metamorphism, with Mnz, rutile (Rt), muscovite, and carbonate as mineral reactants and with Aln, Bt, apatite, ilmenite, and anorthite component of plagioclase as products (Ferry 1984, 1994). Quartz (Qtz) and

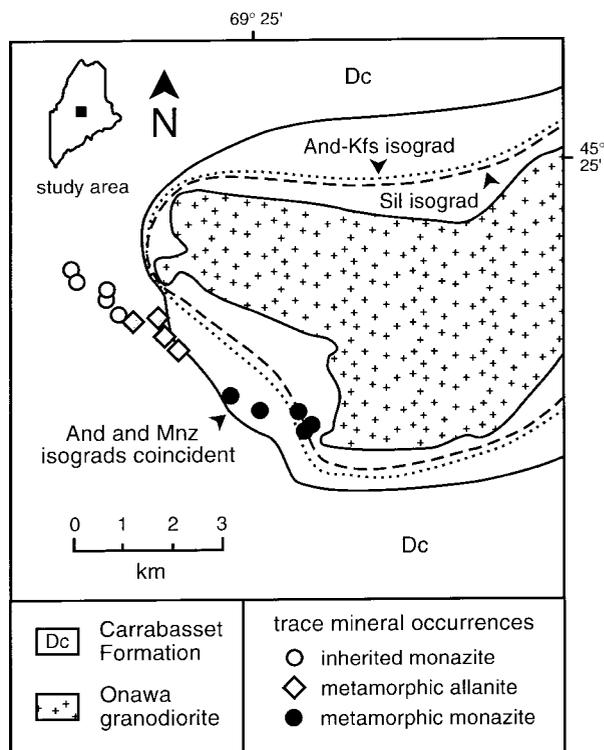


FIGURE 1. Geologic sketch map of the western half of the Onawa contact aureole, Maine, showing location of the isograd based on formation of prograde monazite (Mnz) from allanite in pelitic rocks (from Symmes and Ferry; Wing and Ferry 1999; Wing et al. 1999). Symbols are sample localities that constrain the position of the isograd. Conventional isograds are based on the formation of prograde andalusite (And), andalusite + potassium feldspar (And-Kfs), and sillimanite (Sil).

TABLE 1. Selected common trace minerals in metamorphic rocks

oxides: baddeleyite, geikielite, perovskite, qandalite, rutile, uraninite, zirkelite
phosphates: apatite, monazite, xenotime
silicates: allanite, axinite, thorite, zircon
sulfates: anhydrite, celestite
sulfides: arsenopyrite, chalcopyrite, galena, glaucodot, pentlandite, sphalerite

chlorite may be either reactants or products. With still further increase in grade, Aln disappears and is replaced by metamorphic Mnz that occurs as rounded, chemically unzoned grains. The Aln \rightleftharpoons Mnz transition can also be mapped as an isograd, and it coincides exactly with the isograd based on the first appearance of an Al_2SiO_5 mineral [And in the contact aureole and Buchan terrain and kyanite (Ky) in the Barrovian terrain]. The nature of the Aln \rightleftharpoons Mnz reaction and its relation to the And- and Ky-forming reactions is under investigation. There are two exceptions to this pattern of occurrence of Mnz and Aln. Detrital Mnz is stabilized in a few samples from the garnet zone of the regional terrains with lower than average whole-rock Al and/or Ca contents. Metamorphic Aln is stabilized in some samples from the And and Ky zones of the regional terrains with higher than average Al and/or Ca contents. The ob-

served pattern of occurrence in the three terrains explains why previous studies have variously described Mnz as a detrital mineral, as a metamorphic mineral that develops at low grades, and as a metamorphic mineral that develops at medium grades.

Significance of the distribution. The mapped Mnz \pm Aln and Aln \pm Mnz isograds demonstrate that trace minerals are not necessarily inert during metamorphism, but may be active participants in prograde mineral reactions. In fact, the coincidence between the Aln-Mnz isograds and the Bt, Ky, and And isograds is most simply understood in terms of the trace minerals' participation in the prograde Bt-, Ky-, and And-forming reactions. Because a number of trace minerals can be dated isotopically, especially Mnz (Parrish 1990; Smith and Barreiro 1990; Robinson et al. 1992; Harrison et al. 1995; Williams 1996; Hawkins and Bowring 1997), the participation of trace minerals in metamorphic reactions has important bearing on attempts to determine the age(s) of metamorphism. The precision of isotopic dates under favorable circumstances may be approximately ± 1 Ma while the duration of regional metamorphism is on the order of several tens of Ma. An understanding of the petrology of trace minerals therefore holds the promise not just of dating an episode of metamorphism but of developing a chronology of specific chemical processes during metamorphism. Isotopic ages for metamorphic Mnz in the Ky or And zones, for example, specifically date the formation of the Aln \pm Mnz isograd. Moreover, because of the coincidence between the Aln \pm Mnz and Ky or And isograds, isotopic Mnz ages date the formation of the Ky or And isograds as well. Thus, by understanding the petrology of trace minerals in metamorphic rocks, a chronology of metamorphism based on dating trace minerals can be placed in a broadly meaningful petrologic context. The potential for Mnz to date an And or Ky isograd, in particular, will most likely be realized by analyzing chemically unzoned Mnz from the And or Ky zones of terrains that have a relatively simple metamorphic history. Measured ages of Mnz and other trace minerals from polymetamorphic terrains will inevitably be much more difficult to interpret (e.g., Robinson et al. 1992).

Results of the first attempt to date Mnz with the specific aim of determining the age of formation of And and Ky isograds are summarized in Table 2. Procedures, whose details are the subject of a separate paper, are described by Harrison et al.

(1995). Briefly, U, Th, and Pb were sputtered from Mnz grains in thin section using the Cameca ims 1270 ion microprobe in the Department of Earth and Space Sciences at UCLA. Ratios of the isotopes of U, Th, and Pb were measured and then converted to a ^{232}Th - ^{208}Pb age using a natural well-characterized Mnz as a standard. Because the uncertainty in the measured ages is greater than the duration of contact metamorphism, the ages of Mnz from the And and sillimanite (Sil) zones of contact aureoles test the prediction that they date the age of the And isograd. Specifically, if these monazites formed during metamorphism, their isotopic age should match the crystallization age of the associated pluton. In two contact aureoles (the Onawa aureole, Maine, and the Mt. Morrison pendant, California) measured Mnz ages from And- or Sil-bearing pelitic hornfels match published U-Pb ages of zircons from the associated plutons within error of measurement. Considering the size of the analyzed Mnz grains (30–40 μm), the maximum peak metamorphic T in the regional terrains (550 $^{\circ}\text{C}$), and the diffusion rate of Pb in Mnz (Smith and Giletti 1997; Cherniak et al. 2000), measured Mnz ages in Table 2 are crystallization ages rather than cooling ages unless cooling rates were slower than 10 $^{\circ}\text{C}/\text{Ma}$. The absence of any decrease in measured ages with increasing grade of metamorphism in the regional terrains is a further qualitative argument that the dates reported in Table 2 are not cooling ages. Both the lack of correlation between measured Mnz age and grade of metamorphism and the agreement between Mnz ages in the contact aureoles and the crystallization ages of associated plutons therefore validate interpreting the dates for Mnz from the And, Ky, and Sil zones of the regional metamorphic terrains in Table 2 as the age of formation of the And and Ky isograds. The broader implications of the measured dates to the history of Acadian regional metamorphism in northern New England, particularly the relation between Mnz ages and the range of other ages for the areas in Maine and Vermont listed in Table 2, will be discussed in another publication.

Although results in Table 2 for Mnz are encouraging, the utilization of trace minerals to define a precise chronology of specific, petrologically meaningful, chemical processes during regional metamorphism will only be fully realized both after further development of other trace minerals as radiometric dating tools and after further investigations of their metamorphic

TABLE 2. Pb-Th ages of monazite from pelitic rocks and related radiometric dates

Location	Monazite age (Ma)*	Related radiometric dates (Ma)
Onawa aureole, Maine	405 \pm 2	405, Pb-U age of zircon from associated pluton†
Mt. Morrison pendant, California	89.6 \pm 1.5	89, Pb-U age of zircon from associated pluton‡
Buchan terrain, south-central Maine	364 \pm 1	360-394, whole-rock Rb-Sr age of nearby plutons§ 352-362, Ar-Ar age of hornblende from nearby plutons 367-371, Pb-U age of zircon and monazite from nearby pegmatite dikes#
Barrovian terrain, east-central Vermont	354 \pm 1	350-397, Ar-Ar age of hornblende from metvolcanics**

* Samples from the andalusite, kyanite, or sillimanite zones only. Ages determined at the UCLA ion microprobe facility following procedures described by Harrison et al. (1995). Reported value is the weighted mean of all measurements; uncertainty is twice the standard error of the weighted mean.

† Bradley et al. (1996).

‡ Stern et al. (1981).

§ Dallmeyer and vanBreenan (1981); Dallmeyer et al. (1982).

|| Dallmeyer (1979); Dallmeyer et al. (1982).

Osberg et al. (1995).

** Spear and Harrison (1989).

petrology. Possible candidates for this exercise include Aln and xenotime in pelites, sphene in metaigneous rocks, and baddeleyite, thorite, and uraninite in siliceous carbonate rocks.

Zircon and baddeleyite

Distribution. Zircon and baddeleyite (ZrO_2) are very common trace minerals in contact metamorphosed siliceous dolomites, and their distribution, like that of Mnz and Aln in pelites, is neither random nor uniform. Their pattern of occurrence in the Ballachulish aureole, Scotland (Fig. 2), is like that observed in other contact metamorphic terrains worldwide, including: the Beinn an Dubhaich aureole, Scotland (Ferry and Rumble 1997); the Silver Star aureole, Montana (Ferry and Rumble 1997); and the Monzoni and Predazzo aureoles, Italy (Ferry 1998). At relatively low grades of metamorphism, siliceous dolomites contain Zrn (likely of detrital origin) but not Bad. With increasing grade of metamorphism, Zrn disappears from Qtz-free rocks and Bad simultaneously appears. (Zircon is stable in Qtz-bearing rocks up to and through conditions of partial melting.) The transition from Zrn-bearing to Bad-bearing marbles can be mapped as an isograd (Fig. 2) that lies at a higher grade than the forsterite (Fo) isograd but at grades lower than the periclase (Per) isograd. The principal minerals in marbles at the Bad isograd are dolomite (Dol), calcite (Cal), and Fo. The likely mineral-fluid reaction at the isograd therefore is:

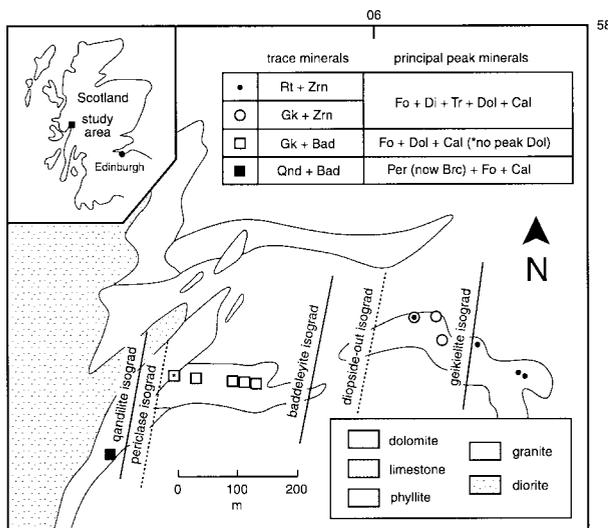
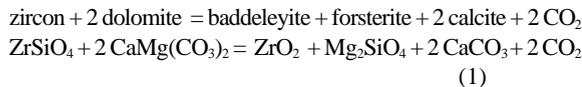


FIGURE 2. Geologic sketch map of the northeast corner of the Ballachulish contact aureole, Scotland, showing locations of isograds based on formation of prograde trace minerals geikielite (Gk), baddeleyite (Bad), and qandilite (Qnd) in siliceous dolomites (from Ferry 1996a). Symbols are sample localities that constrain the positions of the isograds. Rt = rutile; Zrn = zircon; Fo = forsterite; Di = diopside; Tr = tremolite; Dol = dolomite; Cal = calcite; Per = periclase; Brc = brucite. Numbers outside border refer to National Grid Reference System.

Significance of the distribution. The mapped Bad isograd, as well as isograds based on the first appearance of geikielite and qandilite in dolomitic marbles of the Ballachulish aureole (Fig. 2), reinforce the conclusion that trace minerals are not inert during metamorphism but actively participate in prograde mineral reactions involving both trace and principal minerals. The T - X_{CO_2} conditions of peak metamorphism in the Ballachulish aureole at the Bad isograd can be estimated in two independent ways (Fig. 3): (a) from a curve computed from the equilibrium based on Reaction 1, and (b) from T based on calcite-dolomite thermometry and X_{CO_2} based on carbonate-silicate equilibria in the dolomites other than Reaction 1. [Figure 3 and all other phase diagrams were calculated using the data of Berman (1988, updated 1990) and the equation of state for CO_2 - H_2O fluid taken from Kerrick and Jacobs (1981).] The excellent agreement between the two estimates suggests not only that trace minerals participate in prograde reactions, but also that trace minerals closely approach local equilibrium during metamorphism with each other and with the principal minerals in the rock. The evidence for local equilibrium, in turn, highlights the opportunity for trace minerals to serve not just as a record of the age of specific chemical processes during metamorphism but to serve additionally as a record of the physi-

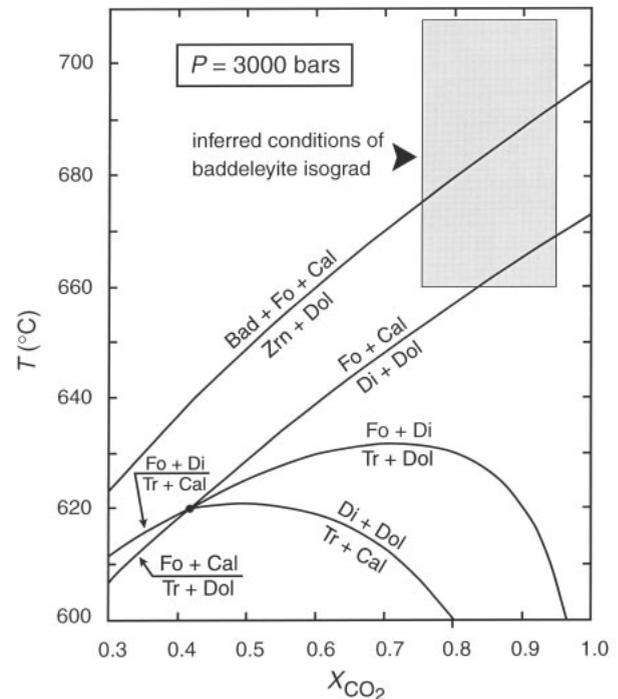


FIGURE 3. T - X_{CO_2} diagram illustrating selected phase equilibria among diopside (Di), dolomite (Dol), forsterite (Fo), calcite (Cal), tremolite (Tr), zircon (Zrn), baddeleyite (Bad), and CO_2 - H_2O fluid at 3000 bars. Pressure is appropriate to contact metamorphism in the Ballachulish aureole, Scotland. All minerals assumed pure substances. Conditions of the Bad isograd predicted by the Zrn-Dol-Bad-Fo-Cal equilibrium are consistent with conditions independently inferred from Cal-Dol thermometry and the Di-Dol-Fo-Cal equilibrium (shaded rectangle).

cal P - T - X_{CO_2} conditions of those processes, a point that has not escaped the attention of others (e.g., Graz and Heinrich 1997). In order for the potential of trace minerals to record quantitatively the physical conditions of prograde mineral reactions to be fully realized, however, better thermodynamic data for a variety of trace minerals will be needed. The capacity for refractory trace minerals such as Zrn and Bad to record the P - T - X_{CO_2} conditions of peak metamorphism will be particularly important in the study of rocks severely affected by retrograde metamorphism in which the principal prograde minerals are entirely replaced by retrograde minerals.

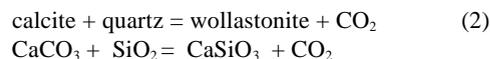
THE MINERALOGY OF RETROGRADE METAMORPHISM

The mineralogy of retrograde metamorphic rocks in itself is a second example of how systematic patterns of mineral occurrence suggest additional opportunities for a further understanding of metamorphism. It is doubtful that any metamorphic terrain worldwide is devoid of at least some mineralogical effects of retrograde metamorphism, and, in the extreme, some samples from some terrains are composed almost entirely of retrograde minerals. Nevertheless, there has been relatively little study of the chemical processes of retrograde metamorphism. For example, retrograde metamorphism is nowhere discussed by Spear (1993) in his treatise on metamorphism, and the subject is mentioned on just three pages in the textbooks by Yardley (1989) and by Bucher and Frey (1994). The lack of attention paid to retrograde metamorphic minerals is unfortunate because they represent a record of processes that occur in metamorphic terrains as they cool that are just as important as processes that occur as terrains heat. One factor that may explain the relatively small effort devoted to the study of retrograde metamorphism is the lack of consensus on a conceptual model to work with. I propose such a model, partial mineral-fluid equilibrium. Partial equilibrium, in the sense introduced to the study of metamorphism more than three decades ago by Helgeson (1967), considers that fluid and product minerals are in equilibrium during a mineral-fluid reaction. Reaction eventually leads to a state where fluid and mineral products are also in equilibrium with mineral reactants. This final state in which fluid, mineral reactants, and mineral products are in local equilibrium is the one assumed for retrograde metamorphism. There may be other minerals in the system, however, that do not participate in the reaction and that are never in equilibrium either with fluid or with mineral products and reactants. In the following sections, evidence is first presented for partial equilibrium in the distribution of retrograde minerals in metamorphic rocks. Next, two applications of partial mineral-fluid equilibrium are reviewed that lead to a better understanding of chemical and physical processes in cooling contact aureoles.

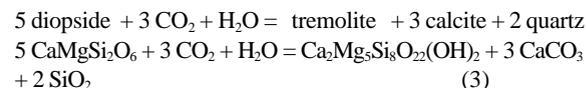
Distribution of retrograde metamorphic minerals

Contact metamorphosed siliceous limestones. Siliceous limestones in pendants of the Sierra Nevada batholith, eastern California, usually contained one of two different mineral assemblages during the peak of high-grade metamorphism. The first is abundant wollastonite (Wo) and minor grossular (Grs) with Cal or Qtz but not both, and the second is Cal + Qtz + anorthite (An) without Wo (e.g., Ferry et al. 1998). Both as-

semblages contained diopside (Di), potassium feldspar (Kfs), titanite (Ttn), and a variety of accessory minerals as well. The two mineral assemblages can be interbedded, even in the same outcrop, and are principally related by the infiltration-driven prograde reaction:



Even where they are interbedded in the same outcrop, the two assemblages developed different retrograde minerals when they reacted with fluids as the pendants cooled. Wollastonite reacted with CO_2 -bearing fluids by the reverse of Reaction 2 to form retrograde Cal + Qtz, often occurring as a direct replacement of Wo (Fig. 4). Diopside, Kfs, Grs, and Ttn in the Wo-bearing rocks, however, remain completely fresh and devoid of retrograde mineralogical alteration. Diopside in the Wo-free rocks, on the other hand, almost always is partially altered to retrograde tremolite (Tr) according to the reaction:



(Fig. 5). Potassium feldspar, An, and Ttn remain unaltered in Wo-free rocks. Rocks with Wo at the peak of metamorphism always contain retrograde Cal + Qtz but never retrograde Tr. Rocks without Wo at the peak of metamorphism, however, almost always contain retrograde Tr. The antipathy of Wo and Tr in calc-silicate rocks from the eastern Sierra Nevada is striking enough that it was noticed by geologists conducting basic mapping in the region more than 35 years ago (e.g., Rinehart and Ross 1964). This systematic pattern to the occurrence of retrograde minerals in siliceous limestones is observed in other contact aureoles worldwide [e.g., Balluchulish aureole (Ferry 1996b)].

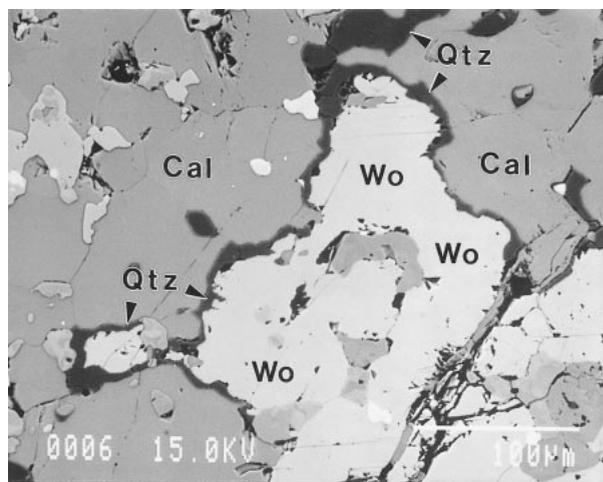


FIGURE 4. Backscattered electron (BSE) image of continuous rim of quartz (Qtz) around wollastonite (Wo) in a matrix of calcite (Cal) illustrating incipient progress of retrograde Reaction 2 (in reverse) in siliceous limestone from the Ritter Range pendant, California. Sample 2O of Ferry et al. (1998). Long dimension of photo is 0.36 mm.

A simple explanation for the distribution of the retrograde minerals is phase equilibrium (Fig. 6). If there was partial mineral-fluid equilibrium in the contact metamorphic terrains as they cooled, the composition of retrograde $\text{CO}_2\text{-H}_2\text{O}$ fluids in Wo-bearing rocks would have been buffered along the Wo-Cal-Qtz reaction curve. At $T < 555^\circ\text{C}$, fluid composition would lie at the edge of the vertically ruled area of Figure 6. Mineral-fluid equilibrium during retrograde metamorphism then explains the preservation of fresh Di, Kfs, Grs, and Ttn in the Wo-bearing rocks, and the lack of retrograde Tr, An, Rt, and phlogopite (Phl). In the absence of Wo, however, retrograde fluids could have taken on the higher values of X_{CO_2} of a fluid that would react with Di to form Tr by Reaction 3 as T decreased. The composition of retrograde fluids in Wo-free rocks then would have been buffered along the Di-Tr-Cal-Qtz reaction curve, and confined to the edge of the horizontally ruled area of Figure 6. Mineral-fluid equilibrium during retrograde metamorphism then explains the preservation of fresh An, Kfs and Ttn, and the absence of retrograde Grs, Wo, Rt, and Phl in Wo-free rocks. In the case of siliceous limestones, it appears that all principal minerals were in local equilibrium with fluid, not just those that participated in retrograde mineral-fluid reactions (Fig. 6).

Contact metamorphosed siliceous dolomites. Most siliceous dolomites in the Ballachulish contact aureole, Scotland, contained one of two different mineral assemblages at the peak of high-grade metamorphism. The first is Per + Fo + Cal, and the second is Dol + Fo + Cal (Ferry 1996b). Both assemblages contained Bad and a variety of accessory minerals as well (Fig. 2). The two mineral assemblages can be closely associated spatially and are related by the prograde infiltration-driven reaction:

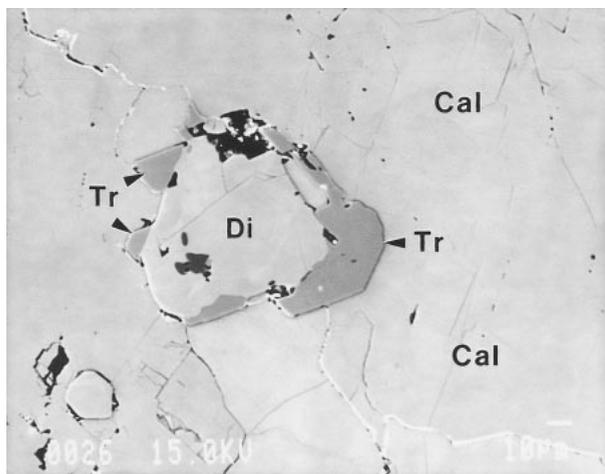
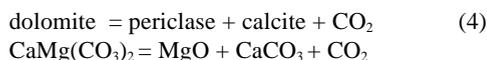
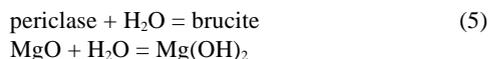


FIGURE 5. BSE image of subhedral tremolite (Tr) crystals developed at the margin of diopside (Di) in contact with calcite (Cal), illustrating incipient progress of retrograde reaction 3 in siliceous limestone from the Ritter Range pendant, California. Sample 4H of Ferry et al. (1998). Long dimension of photo is 0.22 mm.

Even where they are separated by a few m, the two assemblages developed different retrograde minerals when they reacted with fluids as the aureole cooled. In rocks that contained Per, Per first reacted with $\text{CO}_2\text{-H}_2\text{O}$ fluids to form retrograde brucite (Brc), according to:



Brucite then reacted with Cal and fluid to form retrograde Dol by:

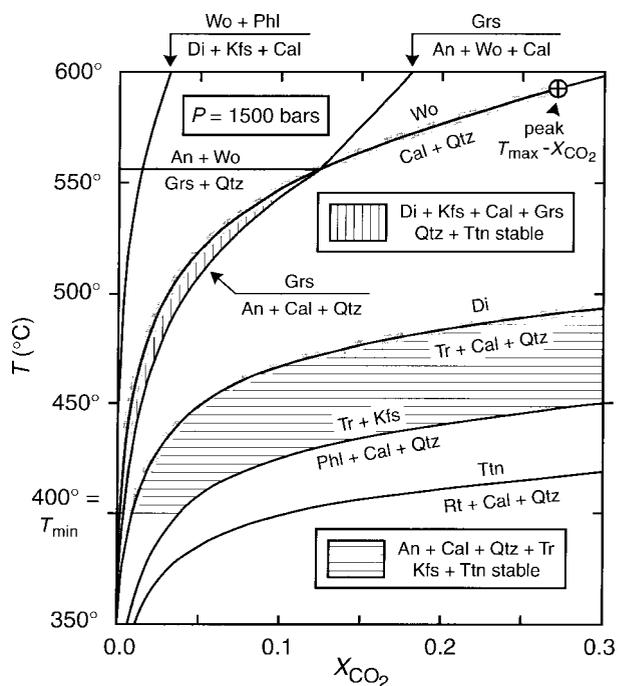
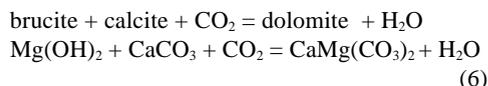
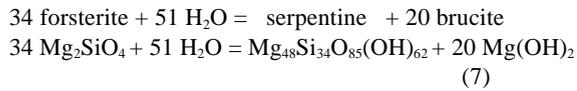


FIGURE 6. $T\text{-}X_{\text{CO}_2}$ diagram illustrating selected phase equilibria among tremolite (Tr), calcite (Cal), quartz (Qtz), diopside (Di), wollastonite (Wo), phlogopite (Phl), potassium feldspar (Kfs), grossular (Grs), anorthite (An), rutile (Rt), titanite (Ttn), and $\text{CO}_2\text{-H}_2\text{O}$ fluid at 1500 bars. Pressure is appropriate to contact metamorphism of pendants in the eastern Sierra Nevada, California. All minerals assumed pure substances. Shaded solid and shaded dashed curves illustrate the inferred $T\text{-}X_{\text{CO}_2}$ evolution of Wo-bearing and Wo-free siliceous limestones, respectively, during cooling of the pendants and retrograde mineral-fluid reaction. The observed retrograde mineral assemblage in Wo-bearing siliceous limestones is stable at equilibrium in the vertically ruled area; the observed retrograde mineral assemblage in Wo-free rocks is stable in the horizontally ruled area. If local mineral-fluid equilibrium was attained, therefore, the two shaded curves explain the different retrograde mineral assemblages developed in Wo-bearing and Wo-free rocks.

(Fig. 7). Forsterite is altered to retrograde Brc + Srp by:



(Fig. 8). A second set of retrograde mineral-fluid reactions, on the other hand, is observed in siliceous dolomites that contained Dol + Fo + Cal without Per at the peak of metamorphism. The least commonly preserved involves the replacement of Fo by retrograde Tr:

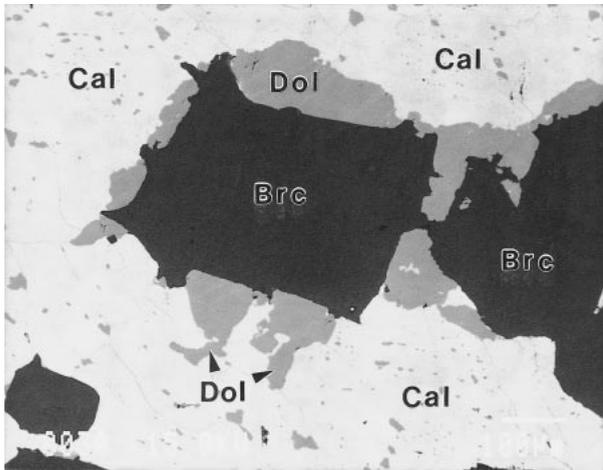
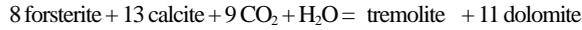
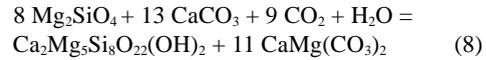
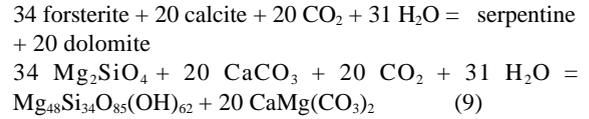


FIGURE 7. BSE image of nearly continuous rim of dolomite (Dol) grains around brucite (Brc) pseudomorph after periclase in a matrix of calcite (Cal), illustrating completion of retrograde Reaction 5 and incipient progress of retrograde Reaction 6 in siliceous dolomite. Sample S1Q of Ferry and Rumble (1997). Long dimension of photo is 0.89 mm.



(Fig. 9). More commonly Fo is either replaced by retrograde Srp + Dol according to:



(Fig. 10) or by retrograde Srp + Brc according to Reaction 7. Rocks with Per at the peak of metamorphism always contain

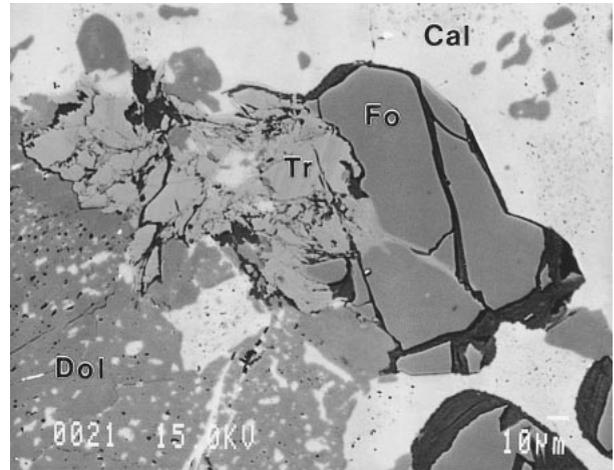


FIGURE 9. BSE image of partial replacement of forsterite (Fo) by tremolite (Tr) in a matrix of calcite (Cal) and dolomite (Dol), illustrating progress of retrograde Reaction 8 in siliceous dolomite from the Ballachulish aureole, Scotland. Sample 1A of Ferry (1996b). Long dimension of photo is 0.26 mm.

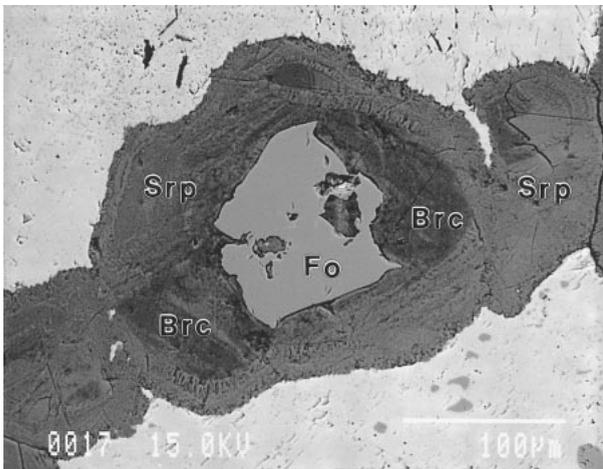


FIGURE 8. BSE image of direct replacement of forsterite (Fo) by an intergrowth of serpentine (Srp) and brucite (Brc), illustrating progress of retrograde Reaction 7 in siliceous dolomite from the Ballachulish aureole, Scotland. Sample 8C of Ferry (1996b). Long dimension of photo is 0.38 mm.

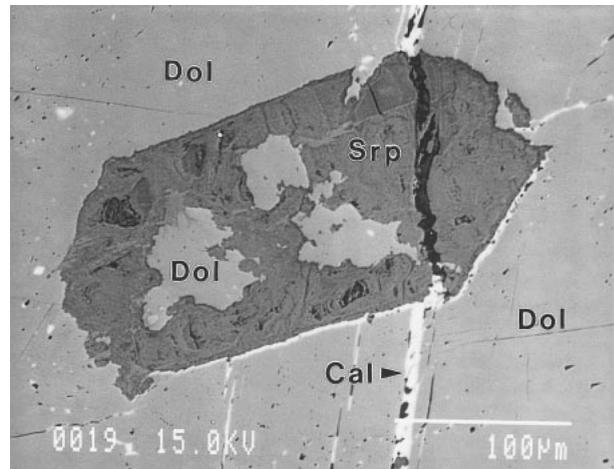


FIGURE 10. BSE image of pseudomorphic replacement of forsterite (Fo) by an intergrowth of serpentine (Srp) and dolomite (Dol), illustrating completion of retrograde Reaction 9 in siliceous dolomite from the Ballachulish aureole, Scotland. Brightest mineral is calcite (Cal). Sample 8B of Ferry (1996b). Long dimension of photo is 0.32 mm.

retrograde Brc but never retrograde Tr. Rocks without Per at the peak of metamorphism, however, almost always contain retrograde Tr but never Brc except where intergrown with Srp as a replacement of Fo. This systematic pattern to the occurrence of retrograde minerals in siliceous dolomites is observed in other contact metamorphic terrains worldwide [e.g., Beinn an Dubhaich aureole, Scotland (Ferry and Rumble 1997); Silver Star aureole, Montana (Ferry and Rumble 1997); Ritter Range pendant, California (Ferry et al. 1998); Monzoni and Predazzo aureoles, Italy (Ferry 1998)].

A simple explanation for the distribution of the retrograde minerals is phase equilibrium (Fig. 11). If there was partial mineral-fluid equilibrium in the contact metamorphic aureoles as they cooled, the composition of retrograde $\text{CO}_2\text{-H}_2\text{O}$ fluids in the initially Per-bearing rocks would have been buffered along the Brc-Cal-Dol curve once Per was hydrated to Brc by Reaction 5. Retrograde fluids in the initially Per-bearing rocks would have had CO_2 -contents too low for either Tr + Dol or Srp + Dol to be stable, and neither pair of minerals would have developed in these rocks during retrograde metamorphism. In the absence of Per and Brc, however, retrograde fluids could have taken on the higher values of X_{CO_2} of fluid in the stability fields of Tr + Dol and Srp + Dol explaining the alteration of Fo to both Tr + Dol and Srp + Dol by retrograde Reactions 8 and 9. The composition of retrograde fluids in Per-free rocks then would have been buffered along the Fo-Cal-Tr-Dol and Fo-Cal-Srp-Dol curves. Equilibrium further explains the alteration of Fo to Srp + Brc in both rocks that contained Per at the peak of metamorphism and those that did not. The Brc-Cal-Dol and Fo-Cal-Srp-Dol curves in Figure 11a meet at an invariant point at $T \approx 395^\circ\text{C}$ and $X_{\text{CO}_2} \approx 0.0002$ (Fig. 11b). Buffering of the composition of retrograde fluids by mineral-fluid equilibria in initially Per-bearing rocks by Reaction 6 and of fluids in initially Per-free dolomites by Reaction 9 as the rocks cooled would have inevitably led to the same $T\text{-}X_{\text{CO}_2}$ conditions at the invariant point. Forsterite then would have reacted with fluid to produce Srp + Brc by Reaction 7 in both rock types. The distribution of retrograde Brc, Dol, Srp, and Tr in contact metamorphosed siliceous dolomites appears consistent with a close approach to equilibrium among carbonates, silicates, hydroxides, and fluid during retrograde metamorphism. Equilibrium with the oxides geikielite (Gk) and Bad, however, is another matter in Per-free rocks.

If the composition of fluid coexisting with Per-bearing marbles was buffered along the Brc-Cal-Dol reaction curve in Figure 11 as the rocks cooled, Bad would have been stable throughout their retrograde metamorphism. The prediction is confirmed by the observation of fresh, euhedral Bad grains in all samples of Per-bearing marbles. On the other hand, if fluid composition during retrograde metamorphism of Per-free rocks was buffered along the Fo-Cal-Tr-Dol and Fo-Cal-Srp-Dol curves, Rt + Zrn + Dol rather than Gk + Bad + Fo + Cal should have been stable at mineral-fluid equilibrium from ≈ 620 to $\approx 495^\circ\text{C}$ (Figs. 3 and 11; Fig. 4 of Ferry 1996a). Below $\approx 495^\circ\text{C}$ both Zrn and Rt would then react with Fo and fluid to form retrograde Bad, Gk, and Srp. Periclase-free rocks, however, contain completely fresh, euhedral grains of Gk and Bad and are devoid of Rt and Zrn. The size, shape, and occurrence of Bad grains in

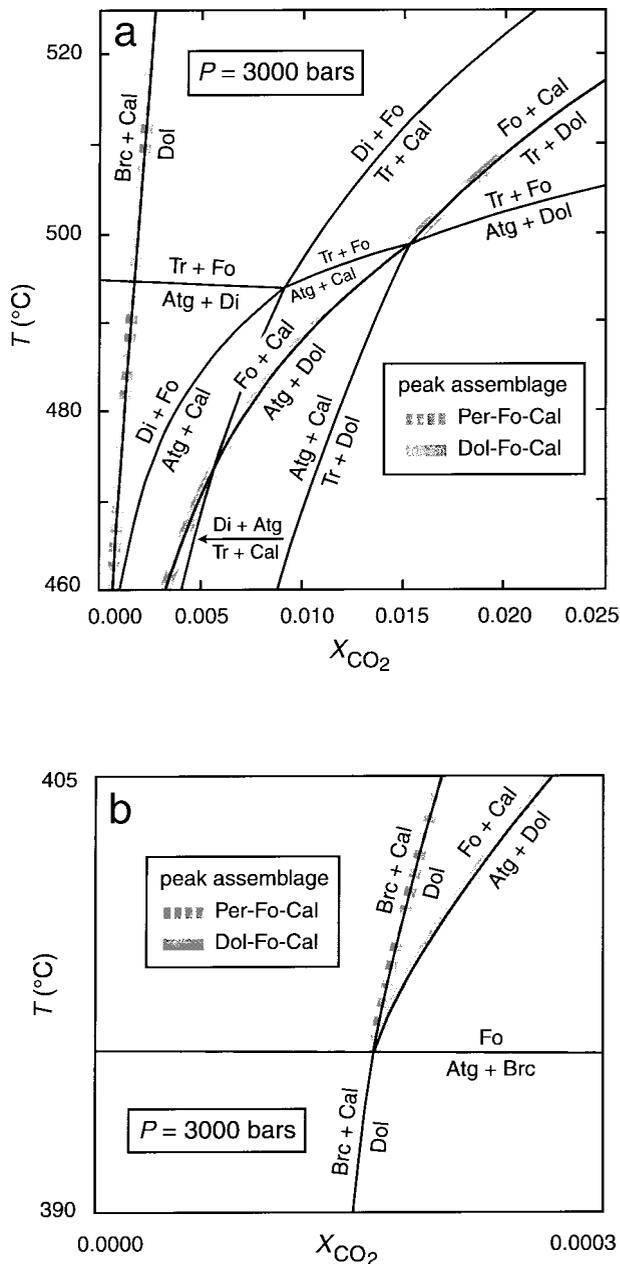


FIGURE 11. $T\text{-}X_{\text{CO}_2}$ diagram illustrating selected phase equilibria among dolomite (Dol), brucite (Brc), calcite (Cal), serpentine, diopside (Di), tremolite (Tr), forsterite (Fo), and $\text{CO}_2\text{-H}_2\text{O}$ fluid at 3000 bars. Antigorite (Atg) taken as the thermodynamic model for serpentine. Pressure is appropriate to contact metamorphism in the Ballachulish aureole, Scotland. All minerals assumed pure substances. Shaded dashed and shaded solid curves illustrate the $T\text{-}X_{\text{CO}_2}$ evolution of initially periclase-bearing and periclase-free siliceous dolomites, respectively, during cooling of the aureole and retrograde mineral-fluid reaction. If partial mineral-fluid equilibrium was attained, the two shaded curves explain the different retrograde mineral assemblages developed in initially periclase-bearing and periclase-free rocks as well as the replacement of Fo by serpentine + Brc in both rock types. (a) $T = 460\text{--}525^\circ\text{C}$, $X_{\text{CO}_2} = 0\text{--}0.025$. (b) $T = 390\text{--}405^\circ\text{C}$, $X_{\text{CO}_2} = 0\text{--}0.0003$.

the Per-free rocks are identical to those in the Per-bearing rocks. There is no textural evidence that Gk and Bad in Per-free rocks first reacted to Rt and Zrn during high- T retrograde metamorphism and then later reappeared at the expense of the retrograde Rt and Zrn. Instead, the Gk and Bad in Per-free marbles almost certainly are refractory relicts from the peak of contact metamorphism. Geikielite and Bad therefore must have been out of equilibrium with fluid and the other minerals while the Ballachulish aureole cooled between peak T and ~ 495 °C. The Per-free siliceous dolomites thus are an example of a system that attained only partial equilibrium during retrograde metamorphism.

Applications of partial mineral-fluid equilibrium to retrograde metamorphism

Further work is needed to assess how common the evidence is for partial mineral-fluid equilibrium during retrograde metamorphism. In addition, it is unclear which minerals commonly attain mineral-fluid equilibrium in a metamorphic rock as it cools and which do not. For example, relatively reactive minerals in pelitic rocks like mica, chlorite, quartz, and feldspar might be expected to attain equilibrium with fluid during retrograde metamorphism while refractory minerals like garnet and Al-silicates might not. Nevertheless it seems that partial equilibrium is attained or closely approached in at least some instances. Exploration of two applications of partial mineral-fluid equilibrium to the characterization of the chemical and physical processes of retrograde metamorphism therefore appears justified.

Direction of fluid flow during contact metamorphism.

The debate over whether the direction of fluid flow during prograde contact metamorphism is typically in the direction of increasing T , toward the pluton, or in the direction of decreasing T , upward or away from the pluton has been sustained for more than a decade (Labotka et al. 1988; Ferry and Dipple 1992; Nabelek and Labotka 1993; Hanson 1995a, 1995b; Ferry 1995). At the center of the debate is the interpretation of the common and widespread occurrence of both reactants and products of decarbonation-dehydration reactions in contact metamorphosed siliceous carbonate rocks (e.g., Rice 1976a, 1976b; Suzuki 1977; Masch and Heuss-Assbichler 1991; Holness 1992). If the reactions were driven by fluid flow along a metamorphic T -gradient, the occurrences of reactants and products define the direction of fluid flow relative to the T -gradient at the reaction site by:

$$q = \xi / A = \frac{\xi [v_{\text{CO}_2} - X_{\text{CO}_2} (v_{\text{CO}_2} + v_{\text{H}_2\text{O}})]}{\left(\frac{\partial X_{\text{CO}_2}}{\partial T}\right)_P \left(\frac{\partial T}{\partial z}\right) + \left(\frac{\partial X_{\text{CO}_2}}{\partial P}\right)_T \left(\frac{\partial P}{\partial z}\right)} \quad (10)$$

where q is the molar time-integrated fluid flux; x is progress of the reaction (positive for decarbonation and/or dehydration; negative for carbonation and/or hydration); n_{CO_2} and $n_{\text{H}_2\text{O}}$ are the stoichiometric coefficients of CO_2 and H_2O in the reaction; $(\partial X_{\text{CO}_2}/\partial T)_P$ and $(\partial X_{\text{CO}_2}/\partial P)_T$ are the dependence of X_{CO_2} on T and P at the reaction site; $(\partial T/\partial z)$ and $(\partial P/\partial z)$ are the T - and P -gradients along the flow path, z , at the reaction site; and z is positive in the direction of fluid flow (Baumgartner and Ferry

1991). The algebraic sign of q is positive by definition. If partial mineral-fluid equilibrium is closely approached or attained at the reaction site, application of Equation 10 to the question of fluid flow direction is straightforward. The systematics of phase equilibria in siliceous carbonate rocks are such that $(\partial X_{\text{CO}_2}/\partial P)_T (\partial P/\partial z)$ is small relative to $(\partial X_{\text{CO}_2}/\partial T)_P (\partial T/\partial z)$ and can be neglected, and the terms $[n_{\text{CO}_2} - X_{\text{CO}_2} (n_{\text{CO}_2} + n_{\text{H}_2\text{O}})]$ and $(\partial X_{\text{CO}_2}/\partial T)_P$ agree in algebraic sign. The algebraic signs of x and $(\partial T/\partial z)$ therefore must agree as well. If the occurrences of reactants and products of a mineral-fluid reaction in a contact aureole are interpreted as an arrested prograde reaction, then reaction involved decarbonation and/or dehydration, x would have been positive, and $(\partial T/\partial z)$ positive as well. In this case fluid flow must have been in the direction of increasing T as the contact aureole heated. A consideration of partial equilibrium during retrograde metamorphism bears on the debate if the occurrences of reactants and products alternatively are interpreted as an arrested retrograde reaction (like the ones illustrated in Figs. 4–10). Reaction then would have involved carbonation and/or hydration, x would have been negative, and $(\partial T/\partial z)$ negative as well. In this second case, fluid flow must have been in the direction of decreasing T as the aureole cooled.

It is critical therefore in deciphering the direction of fluid flow in contact aureoles to determine whether occurrences of mineral products and reactants developed during prograde or retrograde metamorphism. Some occurrences of minerals in contact metamorphosed carbonate rocks that have been previously interpreted as prograde minerals may instead have developed during retrograde metamorphism, judging from textures like those illustrated in Figs. 4–10. For example, Tr in siliceous dolomites close to their contact with the Ballachulish igneous complex has been interpreted as the product of an overstepped prograde reaction (Heuss-Assbichler and Masch 1991). The development of Tr in these rocks by a retrograde carbonation-hydration reaction, however, seems more likely based on textures (Fig. 9). In cases where the occurrence of reactants and products of mineral-fluid reactions in carbonate rocks from a contact aureole is the result of retrograde reactions, the mineralogical evidence for metamorphic fluid flow would turn out to be one of retrograde flow in the direction of decreasing T . Careful examination of the textural relations among reactants and products of arrested mineral-fluid reactions in contact metamorphic terrains worldwide is needed to evaluate how general this circumstance may be.

The amount of fluid flow in contact aureoles as they cool.

The current interest in fluid flow during contact metamorphism can be traced to groundbreaking stable isotopic studies proving that heated meteoric water circulates through and around plutons after they are emplaced (e.g., reviews by Taylor 1974, 1977). Pioneering thermal and hydrologic models demonstrated that significant flow of hydrothermal/metamorphic fluids occurs around plutons as their host rocks cool (e.g., Norton and Knight 1977; Norton and Taylor 1979). Retrograde minerals constitute a mineralogical record of reactions between rocks and circulating hydrothermal/metamorphic fluids in cooling contact aureoles. This mineralogical record, in principle, can be quantitatively interpreted in terms of the amount of fluid flow during retrograde metamorphism through Equation 10. In prac-

tice, application of Equation 10 is greatly simplified by assuming partial equilibrium among reactants and products during retrograde mineral-fluid reactions. The terms X_{CO_2} , $(\partial X_{\text{CO}_2}/\partial T)_P$, and $(\partial X_{\text{CO}_2}/\partial P)_T$ may be evaluated from phase equilibria. Measurement of the progress of the retrograde reaction, combined with estimates of the T - and P -gradients along the flow path then lead to calculations of the amount of fluid flow as a time-integrated flux. Even with the assumption of partial equilibrium during retrograde metamorphism, however, application of Equation 10 is complicated by the strong temperature dependence of the A term in Equation 10 and continued mineral-fluid reaction over a significant temperature interval as a contact aureole cools. There are two possible solutions to the problem raised by mineral-fluid reaction over a large temperature interval. First, the A term in Equation 10 may be evaluated for the maximum T of retrograde metamorphism (T_{max} , the peak T of prograde metamorphism) and for the minimum likely T , T_{min} . Values of time-integrated flux, q , computed for T_{max} and T_{min} , then formally bracket the true value. Second, if there is continuous mineral-fluid reaction as rocks cool from T_{max} to T_{min} , and if fluid flux is assumed proportional to the cooling rate (i.e., $\partial q/\partial T = \text{constant}$), then Equation 10 is applied as:

$$\xi = q\bar{A} \quad (11)$$

where

$$\bar{A} = \frac{\int_{T_{\text{min}}}^{T_{\text{max}}} A(T)dT}{T_{\text{max}} - T_{\text{min}}} \quad (12)$$

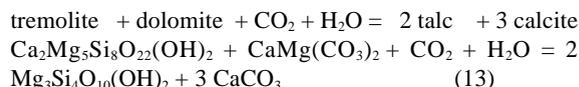
As an example, the development of retrograde Cal + Qtz in the sample of metamorphosed siliceous limestone illustrated in Figure 4 can be quantitatively interpreted in terms of time-integrated retrograde fluid flux using Equations 10–12 and assuming partial mineral-fluid equilibrium during progress of Reaction 2 (i.e., assuming fluid composition is buffered by the reverse of Reaction 2 along the thick solid shaded path in Fig. 6 between peak T and the minimum T \approx 400 °C). Measured progress of Reaction 2 in the sample is $-1.47 \cdot 10^{-3}$ mol/cm³; the estimated P during prograde and retrograde metamorphism was 1500 bars; T_{max} , the estimated peak T of prograde metamorphism, was 595 °C and T_{min} was estimated as 400 °C based on the general absence of retrograde clinozoisite in siliceous limestones from the area; $(\partial T/\partial z)$ was taken as -100 °/km; $(\partial P/\partial z)$ was taken as the lithostatic pressure gradient, -270 bars/km; $(\partial X_{\text{CO}_2}/\partial T)_P$, and $(\partial X_{\text{CO}_2}/\partial P)_T$ were computed from the Cal-Qtz-Wo-fluid equilibrium; and the values of n_{CO_2} and $n_{\text{H}_2\text{O}}$ are 1 and 0, respectively (Ferry et al. 1998). If all fluid flow and retrograde mineral reaction occurred at T_{max} , then $q = 230$ mol fluid/cm² rock; if all flow and reaction occurred at T_{min} , then $q = 27,000$ mol/cm². The true retrograde time-integrated fluid flux must lie between these two values. If fluid flow and reaction occurred continuously as the rock cooled from 595 to 400 °C and $(\partial q/\partial T)$ was constant, then $q = 1100$ mol/cm². The last value is consistent with time-integrated fluid fluxes for the cooling pendant independently predicted from a thermal-hydrologic

model for the area (Hanson et al. 1993; Ferry et al. 1998). Agreement between the two studies validates the assumption of partial equilibrium used in interpreting the mineralogical evidence for fluid flow and, more broadly, suggests that the concept of partial mineral-fluid equilibrium may find practical application in quantitatively characterizing other chemical and physical processes of retrograde metamorphism as well.

PSEUDOMORPHS IN METAMORPHIC ROCKS

Distribution of pseudomorphs in metamorphic rocks

Some of the most distinctive textural features of retrograde metamorphic rocks are pseudomorphs that develop by the direct replacement of a reactant in a mineral reaction by one or more of the mineral products with the outward preservation of the crystal shape of the reactant. Examples from contact metamorphosed siliceous dolomites include: replacement of individual crystals of Fo by an intergrowth of retrograde Srp + Dol according to Reaction 9 (Fig. 10); replacement of Fo by an intergrowth of retrograde Srp + Brc according to Reaction 7 (Fig. 8); replacement of Per by retrograde Brc by Reaction 5 (Fig. 7); and replacement of Tr by retrograde talc (Tlc) + Cal according to:



(Fig. 12). An example from contact metamorphosed siliceous limestones is the direct replacement of Wo by retrograde Qtz by the reverse of Reaction 2 (Fig. 4). Pseudomorphs are not limited to metamorphosed siliceous carbonate rocks. The term “pinite” refers to pseudomorphs formed by the common replacement of cordierite in pelitic rocks by an intergrowth of retrograde chlorite and muscovite (Ms). In many cases, retro-

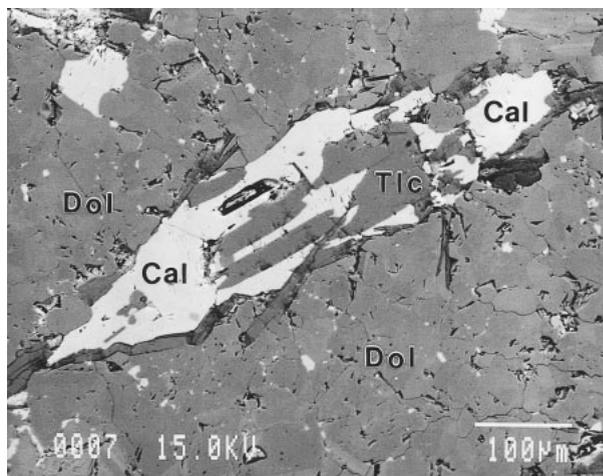


FIGURE 12. BSE image of talc (Tlc) + calcite (Cal) pseudomorph after tremolite in a matrix of dolomite (Dol), resulting from Reaction 13. Sample from the Reed Dolomite in the contact aureole of the Sage Hen Flat pluton, White Mountains, California. Long dimension of photo is 0.62 mm.

grade Ms forms pseudomorphs after prograde andalusite in pelitic hornfelses (Fig. 13).

In contrast, pseudomorphs are relatively uncommon in prograde metamorphic rocks. Their general absence led Carmichael (1969) to propose that prograde mineral reactions involved mechanisms other than the simple replacement of mineral reactants by mineral products. As a typical example, Carmichael specifically examined the prograde kyanite (Ky) to Sil transformation in pelitic schists. Sillimanite normally does not directly replace Ky with the formation of Sil pseudomorphs after Ky (although exceptions are not unknown). The mechanism preferred by Carmichael for the prograde Ky \rightleftharpoons Sil transformation involves simultaneous reactions at three different sites. At one site Ky + Qtz react to Ms. At a second site Ms + albite (Ab) react to Sil + Qtz + Bt. At the third site Bt reacts to Ab. The net mineralogical change is the transformation of Ky to Sil with Ms, Qtz, and Bt serving as catalysts in the overall reaction.

The distribution of pseudomorphs in metamorphic rocks therefore is neither random nor uniform. They are common in retrograde metamorphic rocks but uncommon in prograde metamorphic rocks. The distinctive distribution of pseudomorphs in metamorphic rocks is significant because it may be the record of a novel phenomenon that results from the coupling of a chemical process (mineral reaction) with a mechanical process (force of crystallization) during metamorphism.

Force of crystallization, mineral reactions, and the formation of pseudomorphs

Background and theory. Force of crystallization is the force exerted by a growing crystal against its surroundings if those surroundings have finite yield strength. Laboratory experiments demonstrating force of crystallization were first reported in the geological literature more than 80 years ago (Becker and Day 1916; Taber 1916). Experiments conducted 30 years later by

Correns (1949) showed that the force exerted by an alum crystal growing in an aqueous solution is linearly related to the degree of supersaturation of the solution (at low degrees of supersaturation). Force of crystallization is believed to be a significant natural phenomenon. Beginning more than 70 years ago, sedimentologists have attributed some textures of fractured and displaced quartz grains in carbonate-cemented clastic rocks to the effects of force of crystallization (Rothrock 1925; Dapples 1971; Buczynski and Chafetz 1987). Maliva and Siever (1988a) summarized numerous textural observations that they interpreted as empirical evidence for a role of force of crystallization in the silicification of calcitic fossils in sediments during diagenesis. The effects of force of crystallization are not limited to sedimentary rocks. Turner and Weiss (1965) and Carmichael (1987) proposed that the distinctive twinning exhibited by pseudomorphs of retrograde Brc after Per in marbles records force exerted by growing Brc against the host Cal.

Numerous thermodynamic models for force of crystallization with varying levels of detail have been proposed (Weyl 1959; DeBoer 1977; Maliva and Siever 1988a, 1988b; Dewers and Ortoleva 1990). There appears to be general agreement that the simplest one is at least approximately correct at low levels of non-uniform stress. Consider the planar surface of mineral phase A in a system at temperature T and uniform, isotropic pressure, P . Phase A has fixed composition represented by component i . If a stress, s_n , is applied normal to the surface, the activity of component i in phase A in the stressed state, $a_{i,A}^{\sigma_n,T}$ is:

$$a_{i,A}^{\sigma_n,T} \approx \exp(\Delta\sigma\bar{V}_A / RT) \tag{14}$$

where $Ds = s_n - P$ and \bar{V}_A is the molar volume of the mineral (DeBoer 1977, Eq. 7). Equation 14 is equivalent to the equation on p. 393 of Maliva and Siever (1988a) and to Equation 1 of Dewers and Ortoleva (1990). It is an approximation for ignoring strain energy in the crystal, considered negligible for small values of Ds . Molar Gibbs free energy of phase A in the stressed state, $\bar{G}_A^{\sigma_n,T}$, is related to molar Gibbs free energy in the unstressed state, $\bar{G}_A^{P,T}$, by:

$$\bar{G}_A^{\sigma_n,T} = \bar{G}_A^{P,T} + RT \ln a_{i,A}^{\sigma_n,T} \approx \bar{G}_A^{P,T} + \Delta\sigma\bar{V}_A. \tag{15}$$

Consider phases A and B, both pure substances with the same composition, in equilibrium across a planar interface at temperature T and isotropic pressure P . If stress, s_n , is applied across the interface, the molar Gibbs free energy of the reaction $A = B$ at the interface, $\Delta\bar{G}^{\sigma_n,T}$, is:

$$\Delta\bar{G}^{\sigma_n,T} = \bar{G}_B^{\sigma_n,T} - \bar{G}_A^{\sigma_n,T} \approx \Delta\sigma\Delta\bar{V} \tag{16}$$

where $\Delta\bar{V} = \bar{V}_B - \bar{V}_A$ is the molar volume of reaction. The result is supported the experimental data of Correns (1949) which empirically define a linear relation between degree of supersaturation ($\Delta\bar{G}^{\sigma_n,T}$) and weight displaced by a growing crystal (Ds) predicted from Equation 16.

Equation 16 identifies circumstances in which force of crystallization can drive the formation of pseudomorphs in rocks

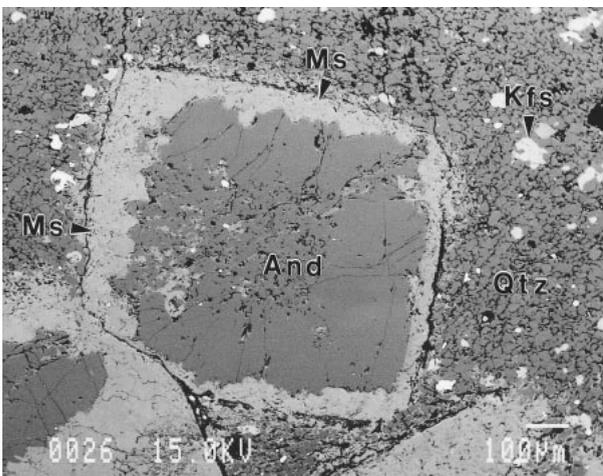


FIGURE 13. BSE image of partial pseudomorphic replacement of andalusite (And) by muscovite (Ms) in a matrix of quartz (Qtz) and potassium feldspar (Kfs). Pelitic hornfels from the Convict Lake Formation in the Mt. Morrison pendant, California. Long dimension of photo is 1.4 mm.

during the reaction $A = B$ and those in which it cannot. When phase B first nucleates at the A-B interface, force of crystallization produces $Ds > 0$. If $D\bar{V} < 0$, then $\Delta\bar{G}^{\sigma_n, T} < 0$ and the Gibbs free energy of the products will be less than that of the reactants. Force of crystallization makes the A-B interface a favorable site for the reaction. Phase B will directly replace phase A, and a pseudomorph will develop. On the other hand, if $D\bar{V} > 0$, then $\Delta\bar{G}^{\sigma_n, T} > 0$ and the Gibbs free energy of the products will be greater than that of the reactants. Force of crystallization makes the A-B interface an unfavorable site for the reaction. For phase B to nucleate and grow, it must find another more energetically favorable site in the rock. No pseudomorph of B after A then develops.

Application to pseudomorphs in metamorphic rocks.

Force of crystallization provides a simple explanation for the distribution of pseudomorphs in metamorphic rocks. Mineral reactions during retrograde metamorphism almost always involve carbonation and/or hydration and have relatively large, negative values of $D\bar{V}$. For example, Table 3 lists $D\bar{V}$ of Reactions 2, 5, 7, 9, and 13 involved in the formation of pseudomorphs illustrated in Figs. 4–13. Normalized to unit volume of reactants, they are in the range -13 to -58% . Force of crystallization therefore typically promotes the formation of pseudomorphs during retrograde metamorphism. In contrast, mineral reactions during prograde metamorphism usually involve decarbonation and/or dehydration and have relatively large, positive values of $D\bar{V}$ (values like those in Table 3 but with the opposite algebraic sign). Force of crystallization therefore discourages the formation of pseudomorphs during prograde metamorphism.

The role of force of crystallization in the formation of pseudomorphs can also be illustrated with a P - T diagram for a generic hydration-dehydration reaction (Fig. 14). Like almost all hydration-dehydration reactions at low to moderate P , the reaction curve everywhere has a positive slope. The reaction curve is approached during retrograde metamorphism from the high- T side with decreasing T . When phase A first nucleates on phase B, following reaction of B with H_2O , force of crystallization drives the A-B interface further into the stability field for A. The interface becomes a favorable place for the $B \rightleftharpoons A$ reaction to proceed. Phase A directly replaces phase B and a pseudomorph develops. In contrast, the reaction curve is approached during prograde metamorphism from the low- T side with increasing T . If phase B first nucleates on phase A, following reaction $A \rightleftharpoons B + H_2O$, force of crystallization drives

the A-B interface back into the stability field for A. The interface becomes an unfavorable place for the $A \rightleftharpoons B$ reaction to proceed. Phase B must nucleate and grow at some other, more energetically favorable, site in the rock, and no pseudomorph develops.

Force of crystallization therefore offers an explanation why the proposed reaction mechanisms of Carmichael (1969) appear to generally apply to prograde metamorphism of pelitic rocks. Figure 15 is a petrogenetic grid illustrating the principal metamorphic mineral reactions in pelites; the thick arrowed curves are generic P - T paths for prograde contact and Barrovian metamorphic terrains. With two exceptions, the P - T paths cross nothing but reaction curves with positive slopes. Force of crystallization inhibits the development of pseudomorphs over the entire normal prograde reaction history of pelites. Reaction mechanisms like those of Carmichael that involve mineral products nucleating and growing at sites in the rock removed from mineral reactants would be expected.

There are two exceptions to the generalization that prograde P - T paths cross only reaction curves with positive slopes on Figure 15. The first exception is five curves that involve pure

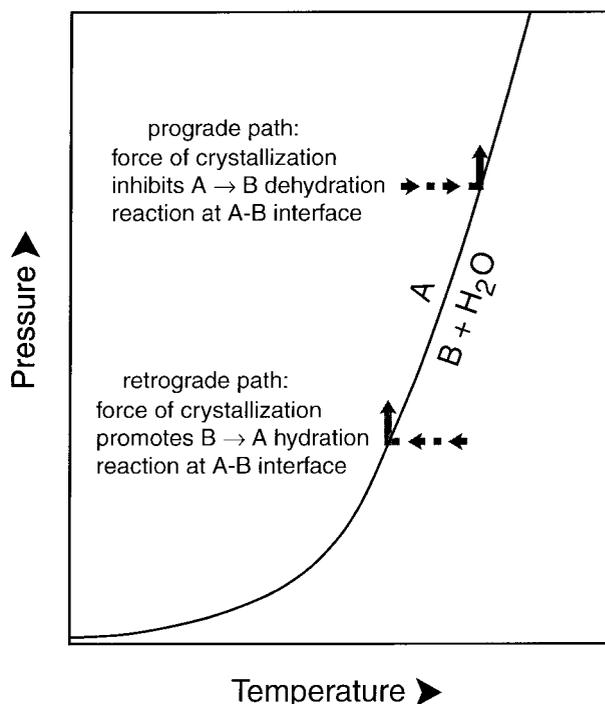


FIGURE 14. Schematic P - T diagram qualitatively illustrating the effect of force of crystallization on the generic hydration-dehydration reaction $A + H_2O = B$ (thick shaded paths with arrows). During prograde metamorphism, force of crystallization drives the A-B interface back into the stability field for A making the interface an unfavorable site for the $A \rightleftharpoons B$ reaction. No pseudomorph of B after A develops. During retrograde metamorphism, force of crystallization drives the A-B interface further into the stability field for A making the interface a favorable site for the $B \rightleftharpoons A$ reaction. Pseudomorph of A after B develops.

TABLE 3. Molar volume of selected pseudomorph-forming reactions*

No.	Reaction	T (°C)†	$D\bar{V}/V_{\ddagger}$
2	$Wo + CO_2 = Cal + Qtz$	550	-54.9%
5	$Per + H_2O = Brc$	600	-58.4%
7	$34 Fo + 51 H_2O = Atg + 20 Brc$	365	-18.4%
9	$34 Fo + 20 Cal + 20 CO_2 + 31 H_2O = Atg + 20 Dol$	450	-36.5%
13	$Tr + Dol + CO_2 + H_2O = 2 Tlc + 3 Cal$	400	-12.9%

* Reaction numbers refer to text. Values calculated from Berman (1988) and Kerrick and Jacobs (1981). Molar volumes of minerals taken at 1 bar and 25 °C. Molar volumes of CO_2 and H_2O taken at 1000 bars and T indicated in table.

† Appropriate T of reaction during contact metamorphism at 1000 bars.

‡ Molar volume of reaction referenced to unit volume of reactants.

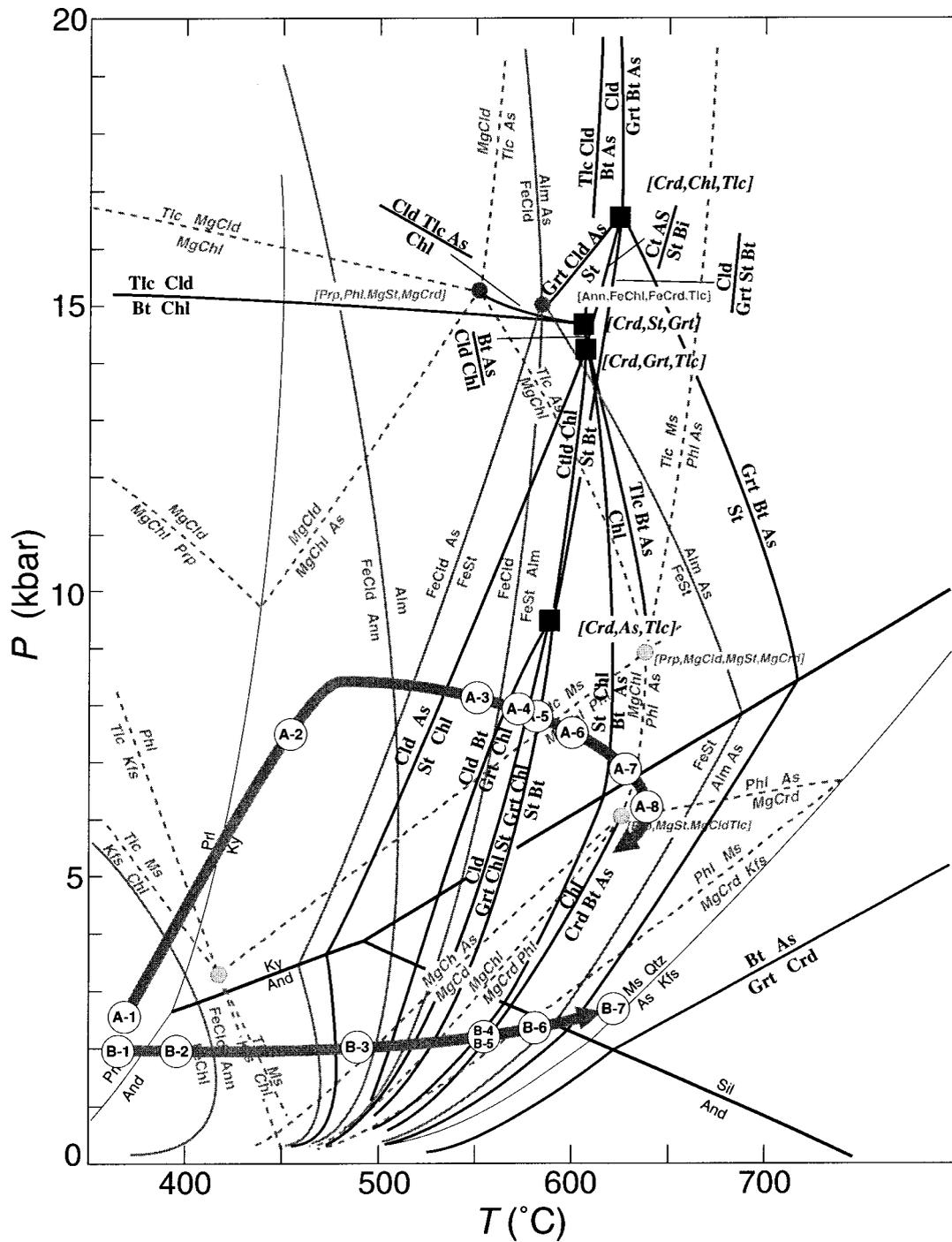


FIGURE 15. Petrogenetic grid illustrating common mineral reactions in pelitic rocks as a function of P and T (Fig. 10–19 of Spear 1993). Thick shaded curves represent generic prograde P - T paths for contact and Barrovian regional metamorphism. With two exceptions, the paths cross nothing but reaction curves with positive slopes. With reference to Figure 14, force of crystallization may explain the typical absence of the direct replacement of mineral reactants by mineral products during prograde metamorphism of pelitic rocks (Carmichael 1969). The two exceptions, the And-Sil curve and some reactions involving pure Mg or pure Fe phases, are discussed in the text.

Fe chloritoid or pure Mg talc. Reactions that involve these pure Mg or pure Fe phases only occur in rocks with unusual bulk composition, however, and are not relevant to most pelites in nature. The second exception is the And-Sil reaction, which is the one common prograde reaction in pelitic rocks characterized by a curve with negative slope on a P - T diagram. It is an exception that proves the rule (Fig. 16). The positive slope of the Ky-Sil reaction on Figure 16 is representative of prograde mineral reactions in pelites generally. If Sil nucleates on Ky with increasing T , force of crystallization drives the Ky-Sil interface back into the stability field for Ky, making the interface an unfavorable place for the reaction to proceed (path a, Fig. 16). Sillimanite therefore would be expected to nucleate and grow elsewhere in the rock as is normally observed, most notably by Carmichael (1969). On the other hand, if Sil nucleates on And, force of crystallization drives the And-Sil interface further into the stability field for Sil, making the interface a

favorable site for the reaction to progress (path b). Sillimanite therefore would be expected to replace And directly with the formation of a Sil pseudomorph after And. In harmony with this prediction, there are numerous reports of prograde Sil pseudomorphs after And (e.g., Rosenfeld 1969; Tracy and Robinson 1988; Spear et al. 1990; Kohn et al. 1997). Figure 16 predicts another, related exception to the absence of pseudomorphs during prograde metamorphism. The other exception develops along prograde P - T paths that involve increase in P at near constant T , such as path (c) in Figure 16 from the And to the Ky field. If Ky nucleates on And at the And-Ky reaction curve, force of crystallization drives the And-Ky interface further into the Ky stability field, making the interface a favorable place for the reaction and promoting the formation of a Ky pseudomorph after And. Kyanite pseudomorphs after And, in fact, have been reported from a metamorphic terrain where prograde metamorphism was driven by crustal loading at near constant T (Brown 1996). Force of crystallization therefore offers an explanation both for the general rule of an absence of pseudomorphs during prograde metamorphism of pelitic rocks as well as for some exceptions to that rule.

Discussion. The success of transport-limited kinetic models of prograde mineral reactions in explaining the textures of metamorphic rocks (e.g., Foster 1981, 1983; Dutrow et al. 1999) indicates that transport rather than force of crystallization may be a decisive factor in controlling the development of pseudomorphs during metamorphism in some circumstances. A thin intergranular volatile-rich film that acts as a fast-transport medium is a prerequisite both for the phenomenon of force of crystallization (Weyl 1959; DeBoer 1977) and for reaction mechanisms like those proposed by Carmichael (1969). Force of crystallization therefore is particularly unlikely to be important in the textural evolution of dry rocks resulting, for example, either from prior partial melting or from an earlier episode of granulite-facies metamorphism. "Dry" metamorphism then may explain some of the rare occurrences of Sil pseudomorphs after Ky. Only further work will determine the importance of force of crystallization as a control on the textures of metamorphic rocks relative to transport or other factors. In any case, regardless of its role, a consideration of force of crystallization as an explanation for the pattern of occurrence of pseudomorphs in metamorphic rocks is significant for prompting an appreciation of novel phenomena that may occur during metamorphism that arise from an interplay between chemical and mechanical processes.

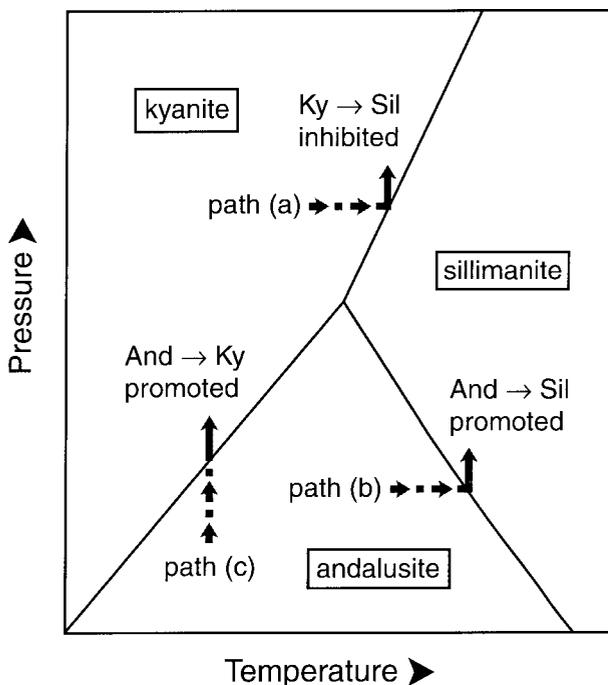


FIGURE 16. Schematic P - T diagram qualitatively illustrating phase equilibria among kyanite (Ky), sillimanite (Sil), and andalusite (And) and three possible paths of prograde metamorphism (shaded with arrows). During prograde metamorphism along path (a), force of crystallization makes the Ky-Sil interface an unfavorable site for the Ky \rightleftharpoons Sil reaction, explaining the typical absence of Sil pseudomorphs after Ky in progressively metamorphosed pelitic rocks. During prograde metamorphism along path (b), on the other hand, force of crystallization makes the And-Sil interface a favorable site for the And \rightleftharpoons Sil reaction, explaining numerous reports of prograde Sil pseudomorphs after And. During prograde metamorphism driven by an increase in P at nearly constant T (path c), force of crystallization makes the interface between Al_2SiO_5 polymorphs a favorable site for the denser polymorph to replace the less dense one. The denser polymorph then forms a pseudomorph after the less dense one.

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