

# Instability of Al<sub>2</sub>SiO<sub>5</sub> “triple-point” assemblages in muscovite+biotite+quartz-bearing metapelites, with implications

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## ABSTRACT

This paper uses constraints from experiments, thermodynamic modeling, and natural mineral assemblages to argue that Al<sub>2</sub>SiO<sub>5</sub> “triple-point” assemblages, in which all three Al<sub>2</sub>SiO<sub>5</sub> minerals are in stable equilibrium, are not possible in common muscovite(Ms)+biotite(Bt)+quartz(Qtz)-bearing metapelitic rocks because the reactions that first introduce an Al<sub>2</sub>SiO<sub>5</sub> mineral to these bulk compositions occur at higher temperature than the triple point. Less-common, highly aluminous bulk compositions may develop Al<sub>2</sub>SiO<sub>5</sub> minerals at temperatures below the triple point such that stable triple-point assemblages are theoretically possible. The “invisibility” of the triple-point to common Ms+Bt+Qtz-bearing metapelites calls into question most metapelitic triple-point localities reported in the literature, and carries implications for the topology of the metapelitic petrogenetic grid, the bathozone/bathograd scheme of Carmichael (1978), and the possibility of prograde kyanite → andalusite → sillimanite sequences. Re-examination of reported triple-point localities suggests that in most if not all cases, the Al<sub>2</sub>SiO<sub>5</sub> minerals grew at different times in the metamorphic history of the rock.

## INTRODUCTION

The triple point involving the Al<sub>2</sub>SiO<sub>5</sub> polymorphs—kyanite, andalusite, and sillimanite—is arguably the most important invariant point in metamorphic petrology. Despite some remaining debate, most agree that it is located in *P-T* space somewhere in the interval between 3.8 kbar, 500 °C (Holdaway 1971; Holdaway and Mukhopadhyay 1993) and 4.5 kbar, 550 °C (Pattison 1992; Pattison et al. 2002) (see also Kerrick 1990 and Bohlen et al. 1991). These conditions are conveniently in a part of *P-T* space traversed by many crustal metamorphic sequences, so that immediate inferences about *P-T* conditions can be made based on the occurrence of one or more of the polymorphs.

One of the most common rock types that develops Al<sub>2</sub>SiO<sub>5</sub> minerals is pelite (metamorphosed mudstone, siltstone, or wacke). There has been great interest in possible metapelitic “triple-point assemblages,” those containing all three Al<sub>2</sub>SiO<sub>5</sub> minerals in stable equilibrium, because they potentially represent valuable fixed *P-T* reference assemblages for calibration of thermobarometers (e.g., Hodges and Spear 1982), stable isotope fractionations, and a range of other geochemical parameters.

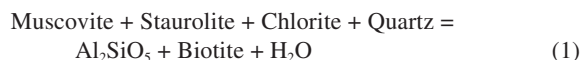
This paper argues that except under exceptional circumstances, such triple-point assemblages cannot represent a stable association in common metapelitic rocks. Common metapelitic rocks are defined as those containing muscovite+biotite+quartz and which have bulk compositions that plot below the garnet-chlorite tie-line on the AFM projection from muscovite, quartz, and water (Fig. 1). The arguments presented are purely phase-equilibrium arguments that, if correct, make moot the related

debates about the “unlikelihood” of metapelites forming at exactly the conditions of the triple point, or how different nucleation and growth kinetics of the polymorphs make their simultaneous growth unlikely. Implications of the “invisibility” of the triple point to common metapelitic compositions are discussed with respect to the metapelitic petrogenetic grid, the bathograd scheme of Carmichael (1978), and the possibility of prograde kyanite → andalusite → sillimanite sequences.

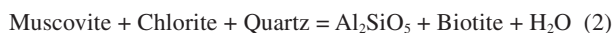
## THEORETICAL CONSIDERATIONS

Whether Al<sub>2</sub>SiO<sub>5</sub> triple-point assemblages are possible as a stable association in Ms+Bt+Qtz-bearing metapelites (abbreviations of Kretz 1983) boils down to a simple question: do reactions that introduce an Al<sub>2</sub>SiO<sub>5</sub> mineral to these bulk compositions occur at higher or lower temperature than the triple point (Fig. 2)? In the ensuing discussion of reactions, interested readers may wish to refer to Figures 32–33 and 36–39 of Pattison and Tracy (1991).

The lowest temperature reaction that introduces coexisting Al<sub>2</sub>SiO<sub>5</sub>+Bt to metapelites is the model K<sub>2</sub>O-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (KFMASH) univariant reaction:

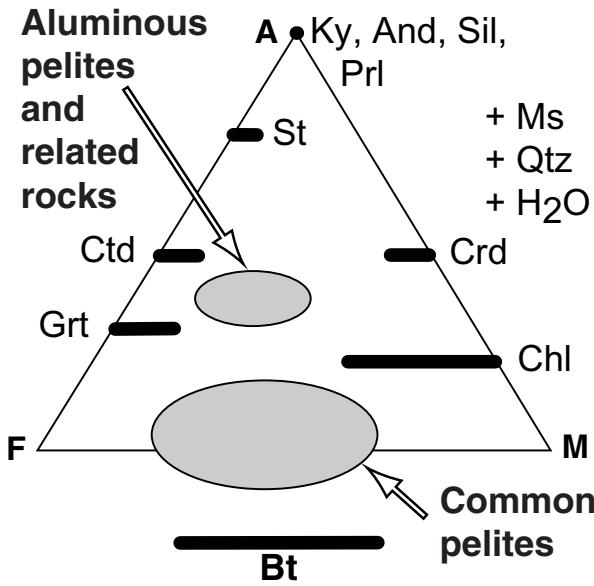


(Thompson and Norton 1968; reaction 2 of Pattison and Tracy 1991). In rocks lacking staurolite, the relevant reaction is the model KFMASH divariant reaction:



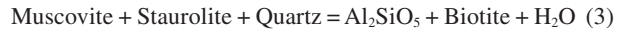
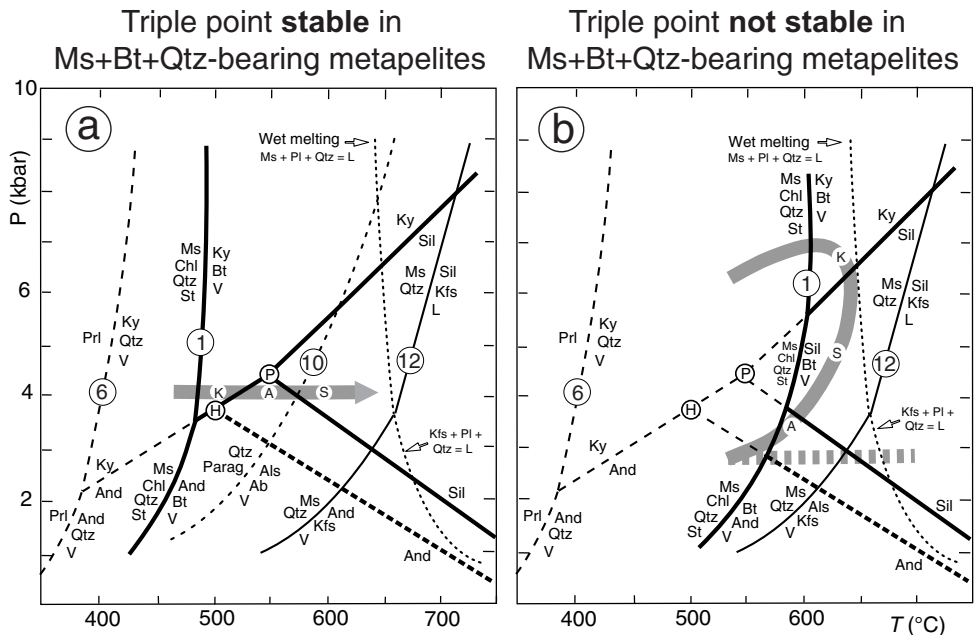
(reaction 9 of Pattison and Tracy 1991) whereas in rocks lacking chlorite, the relevant reaction is the model KFMASH divariant reaction:

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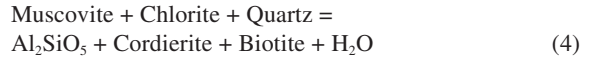


**FIGURE 1.** AFM diagram projected from muscovite, quartz, and water showing schematically the plotting positions of common biotite-bearing pelites (below the Grt-Chl tie line) and less-common aluminous pelites and other related aluminous rock types (above the Grt-Chl tie line). See also Figure 10-3 of Spear (1993). A = Al<sub>2</sub>O<sub>3</sub>-3K<sub>2</sub>O; F = FeO, M = MgO.

**FIGURE 2.** Illustration of how the location of reaction 1 with respect to the Al<sub>2</sub>SiO<sub>5</sub> triple-point determines whether or not stable triple-point assemblages are possible in common Ms+Bt+Qtz-bearing metapelites. Reaction numbering is the same as in the text. (a) Reaction 1 occurs down-temperature of the triple point, permitting a stable triple-point assemblage in Ms+Bt+Qtz-bearing metapelites. The isobaric *P-T* path shows how kyanite-andalusite-sillimanite sequences would be possible in these rocks. (b) Reaction 1 occurs up-temperature of the triple-point, such that a stable triple-point assemblage is not possible in Ms+Bt+Qtz-bearing metapelites. The looping *P-T* path shows how all three Al<sub>2</sub>SiO<sub>5</sub> minerals could develop in a given rock even though no point on the *P-T* path may have been close to triple point *P-T* conditions. The dashed part of the *P-T* path represents contact metamorphic effects due to intrusions. H = triple point and A = Sil curve of Holdaway (1971). P = triple point and And = Sil curve of Pattison (1992).

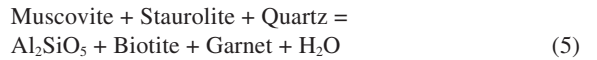


(reaction 14 of Pattison and Tracy 1991). At low pressure and/or in magnesian compositions, the lowest-temperature reaction that introduces coexisting Al<sub>2</sub>SiO<sub>5</sub>+Bt to metapelites is the model KFMASH univariant reaction:



(reaction 1 of Pattison and Tracy 1991).

At a given pressure, reaction 1 of this paper occurs at a lower temperature than any of reactions 2, 3, and 4 (e.g., Figs. 1 and 2 of Thompson 1976; Figs. 36–39 of Pattison and Tracy 1991), and at a lower temperature than the important staurolite-consuming, Al<sub>2</sub>SiO<sub>5</sub>-forming KFMASH univariant reaction:



(Thompson and Norton 1968; reaction 4 of Pattison and Tracy 1991). Even though reaction 5 accounts for the first development of Al<sub>2</sub>SiO<sub>5</sub> minerals in many metapelites (Carmichael 1978), reaction 1 is the key one to investigate by virtue of occurring at the lowest temperature and is consequently the focus of much of the paper.

Previous studies are split over whether reaction 1 occurs up-temperature or down-temperature of the triple point. The metapelitic petrogenetic grids of Hess (1969), Kepezhinskias and Khlestov (1977), Carmichael (1978, 1990 in Davidson et al. 1990), Harte and Hudson (1979), and Froese (1997) show reaction 1 down-temperature of the triple point, whereas the grids of Hoschek (1969), Thompson (1976), Korikovskii (1979), Spear and Cheney (1989), Powell and Holland (1990),

Pattison and Tracy (1991), and Xu et al. (1994) show reaction 1 up-temperature of the triple point (cf., Fig. 2a vs. 2b).

### $\text{Al}_2\text{SiO}_5$ MINERALS IN LESS-COMMON ALUMINOUS BULK COMPOSITIONS

Less common but nevertheless widely reported aluminous pelites, quartzites, and altered felsic volcanics have compositions that plot above the garnet-chlorite tie-line in AFM projection (Fig. 1).  $\text{Al}_2\text{SiO}_5$  minerals may be introduced to these rocks by reactions other than those listed above, some of which occur at temperatures below the triple point. In aluminous rocks that contain pyrophyllite, the lowest-temperature occurrence of an  $\text{Al}_2\text{SiO}_5$  mineral is by the reaction:



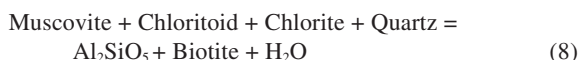
This reaction occurs at about 400 °C (Chatterjee et al. 1984) (Fig. 2), well below the triple point, potentially introducing an  $\text{Al}_2\text{SiO}_5$  mineral at greenschist-facies conditions and thus allowing the possibility of stable triple-point assemblages at higher grades.

Other possible reactions involve chloritoid (itself commonly a reaction product of pyrophyllite + chlorite, Spear 1993). The reaction:

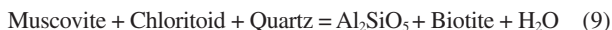


has been inferred from  $\text{Cld}+\text{Chl}+\text{Ky}$  and  $\text{Cld}+\text{Chl}+\text{And}$  assemblages in several field studies (e.g., Fox 1975; Mengel and Rivers 1994), consistent with predictions from thermodynamic modeling (e.g., Reche et al. 1998; Spear et al. 2001) that place reaction 7 down-temperature of the triple point. Such assemblages in theory could evolve with rising temperature to develop a stable triple-point assemblage. A key point with respect to the bulk compositions that “see” reactions 7 and 8 is that biotite is not part of the  $\text{Al}_2\text{SiO}_5$ -bearing mineral assemblages and does not appear until reactions such as 1–5 are encountered at higher grade.

Two reactions involving chloritoid that have been proposed to account for  $\text{Al}_2\text{SiO}_5$ +biotite-bearing assemblages are the KFMASH univariant reaction:



(Thompson and Norton 1968; Okuyama-Kusunose 1994) and the KFMASH divariant reaction



(Thompson and Norton 1968). Field-based studies (Okuyama-Kusunose 1994) and thermodynamic modelling (Spear et al. 2001) suggest that reactions 9 and 10 are restricted in  $P$ - $T$  space to the andalusite field up-temperature of reaction 1.

In rocks that contain sufficient Na to develop paragonite, the reaction:



may develop an  $\text{Al}_2\text{SiO}_5$  mineral (Guidotti 1968, 1984). Reaction 6 occurs up-temperature of the triple point (Chatterjee 1972; Grambling 1984) (see Fig. 2a).

### EXPERIMENTAL AND THERMODYNAMIC CONSTRAINTS

There are no direct experiments on reaction 1. However, Hoschek (1969) investigated reaction 3 as well as the following reaction:



(see Fig. 3a), both of which are divariant in KFMASH. Reaction 3 is the chlorite-absent divariant reaction that emanates from univariant reaction 1, whereas reaction 11 is the  $\text{Al}_2\text{SiO}_5$ -absent divariant reaction that emanates from reaction 1. From Schreinemakers' rules, the locus of intersections of isopleths of  $\text{Mg}/(\text{Mg} + \text{Fe})$  in divariant reactions 3 and 11 exactly defines the location of univariant reaction 1. Reaction 1 must therefore lie between the experimental constraints on reactions 3 and 11, as shown in Figure 3a.

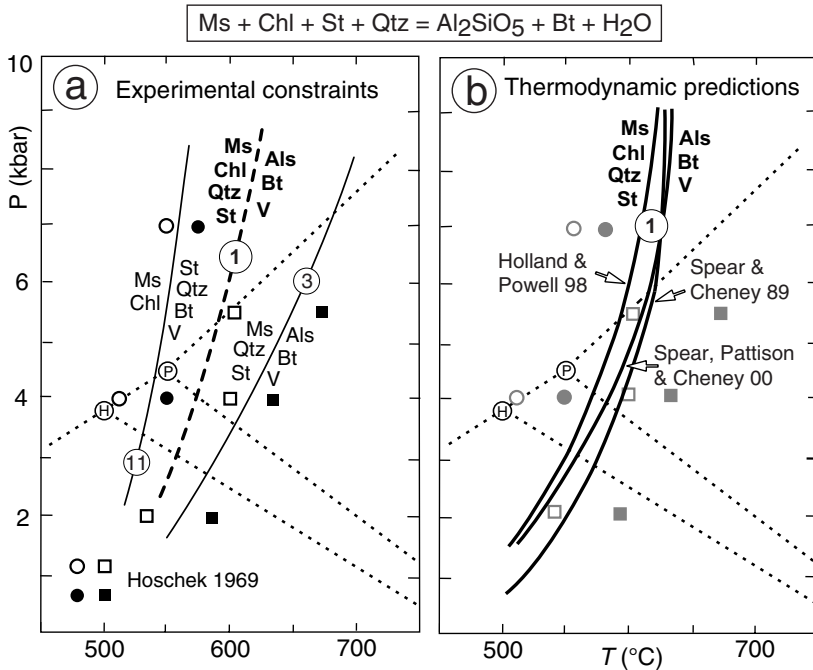
Predicted positions of reaction 1 using the internally consistent thermodynamic databases of Spear and Cheney (1989) and Spear, Pattison and Cheney (2000 unpubl.; reported in Pattison et al. 2002), themselves based on the databases of Berman (1988), and Holland and Powell (1998) satisfy the experimental constraints (Fig. 3b). Because the above thermodynamic databases did not use the experiments of Hoschek as input to their data extraction routines, they represent an independent line of evidence. The experimental and thermodynamic constraints indicate that reaction 1 lies up-temperature of the triple point, whichever location of the triple point is preferred.

### NATURAL CONSTRAINTS

Given the uncertainties in thermodynamic modeling of metapelitic phase equilibria, especially those at low pressure, natural constraints are essential (Pattison and Tracy 1991; Pattison et al. 1999, 2002). The critical difference between the topologies in Figures 2a and 2b is that reaction 1 traverses the andalusite, sillimanite, and kyanite fields if it lies up-temperature of the triple point, but only the andalusite and kyanite fields if it lies down-temperature of the triple point.

A simple test is whether there are well-documented natural localities where sillimanite is produced from reaction 1. Reaction 1 is expected to be relatively uncommon in natural settings, especially at higher pressure, because chlorite is a reactant in the production of garnet and staurolite at lower grade than reaction 1, so that there may be none left by the time the rocks have reached the conditions of reaction 1. Nevertheless, there are some well-studied localities where this reaction has been inferred (e.g., Carmichael 1970; Lang and Rice 1985; Mengel and Rivers 1994; Mezger et al. 2001), including two in which sillimanite is the  $\text{Al}_2\text{SiO}_5$  mineral produced.

The first example is in the classic metamorphic terrain of West Central Maine, where Guidotti (1974) mapped in detail a sillimanite isograd that he interpreted was due to reaction 1. Figure 2b of Guidotti (1974) shows a decrease in modal chlorite and a concomitant increase in modal sillimanite through a



**FIGURE 3.** Experimental constraints (a) and thermodynamic constraints (b) on reaction 1, with the  $\text{Al}_2\text{SiO}_5$  phase boundaries for reference. The reaction positions in (a) are sketched in by eye. The Spear, Pattison, and Cheney (2000, unpublished) data base is discussed in Pattison et al. (2002). H = triple point and And = Sil curve of Holdaway (1971). P = triple point and And = Sil curves of Pattison (1992).

narrow transition zone between the Upper Staurolite Zone (sillimanite-absent) and Lower Sillimanite Zone (chlorite-absent). Accompanying these changes is a weak modal increase of biotite and weak modal decrease of garnet across the transition zone. He interpreted the transition zone to be the reaction zone for reaction 1, broadened by the influence of minor elements and perhaps variations in water activity.

The second example is in the File Lake–Snow Lake belt of Manitoba, described by Froese and Gasparrini (1975), Bailes and McRitchie (1978), and Gordon et al. (1991). They used field mapping, petrography, and mass-balance analysis to argue that the sillimanite-biotite isograd was due to reaction 1. The appearance and increase in sillimanite coincides with a decrease in modal chlorite, muscovite, and staurolite (Bailes and McRitchie 1978; Gordon et al. 1991). The analysis of Gordon et al. included the effect of non-KFMASH elements Mn, Ca, and Ti, resulting in the additional possible involvement of garnet as a reactant and plagioclase a product in reaction 1, with the role of ilmenite uncertain.

The participation of garnet in both settings is potentially problematic, as its involvement raises the question whether reaction 5 equally well represents the sillimanite-forming reaction (e.g., Carmichael 1978). In this scenario, the observed chlorite in the rocks would represent a late alteration mineral. In both studies, garnet was inferred either modally (Guidotti 1974) or chemically (Gordon et al. 1991) to be a reactant in the sillimanite-producing reaction, whereas garnet is a product in reaction 5. The modal and textural data in both localities indicates that as sillimanite increases up-temperature, chlorite decreases. On this basis, reaction 1 seems to account for the observations better, although garnet clearly appears to have participated to some degree in the natural multi-component

reaction.

In summary, the evidence from nature seems to support the experimental and thermodynamic evidence that reaction 1 occurs up-temperature of the triple point. If so, stable triple-point assemblages should not be possible in common  $\text{Ms}+\text{Bt}+\text{Qtz}$ -bearing metapelites. As noted earlier, these arguments may not apply to the less common highly aluminous rock compositions in which  $\text{Al}_2\text{SiO}_5$ -producing reactions are possible at lower temperatures than the triple point.

#### EVALUATION OF REPORTED TRIPLE-POINT LOCALITIES

Despite the above considerations, there are several triple-point localities that are well known in the literature. These include the Boehls Butte area, Idaho (Hietanen 1956), Mt. Moosilauke area, New Hampshire (Rumble 1973; Hodges and Spear 1982), and several areas in north-central New Mexico (Holdaway 1978; Grambling 1981; Grambling and Williams 1985).

The Boehls Butte area is the type locality for the “Idahoan” facies series of Heitanen (1967). It was based on the widespread occurrence of all three  $\text{Al}_2\text{SiO}_5$  polymorphs in  $\text{Ms}+\text{Bt}+\text{Qtz}$ -bearing pelitic schists, which Heitanen (1956) took to indicate  $P$ - $T$  conditions near the triple point (although she recognized that andalusite was the latest to form of the three  $\text{Al}_2\text{SiO}_5$  minerals). More recent investigations (Carey et al. 1992; Grover et al. 1992) showed that the area experienced a long and complex metamorphic history in which different  $\text{Al}_2\text{SiO}_5$  minerals grew at different times along a  $P$ - $T$  path that at no time was near the conditions of the triple point (Fig. 11 of Grover et al. 1992). The occurrence of all three  $\text{Al}_2\text{SiO}_5$  minerals in individual rocks was interpreted to be due to metastable persistence of early formed regional kyanite and sillimanite in rocks that later developed andalusite (see the schematic  $P$ - $T$  path in Fig. 2b).

The Mt. Moosilauke area was used by Hodges and Spear (1982) to calibrate geothermobarometers in Ms+Bt+Qtz-bearing metapelites based on the assumption that the rocks experienced  $P$ - $T$  conditions at or slightly below those of the triple point. It lies along the trace of the regional triple-point isobar of Thompson and Norton (1968). Although all three  $\text{Al}_2\text{SiO}_5$  minerals were not found in individual samples, andalusite and sillimanite occur in Ms+Bt+Qtz-bearing pelitic schists in the Mt. Moosilauke septum, whereas kyanite occurs in aluminous quartzites 5 km to the west in the vicinity of Black Mountain (Rumble 1973). More recent work (Florence et al. 1993; Spear 2000, personal communication) suggests that the Mt. Moosilauke area is part of a nappe structure in which the lower-pressure And-Sil rocks are separated from the intermediate-pressure Ky rocks by a thrust fault, compromising the assumption of triple-point conditions at Mt. Moosilauke.

Perhaps the best known triple-point region includes the Rio Mora, Picuris, Tusas, and especially Truchas uplifts in north-central New Mexico (Holdaway 1978; Grambling 1981; Grambling and Williams 1985; Holdaway and Goodge 1990). Mineral assemblages containing all three  $\text{Al}_2\text{SiO}_5$  minerals are found in each uplift. Many of the triple-point rocks are common Ms+Bt+Qtz-bearing pelitic schists containing combinations of garnet, staurolite, cordierite, and chlorite, but there is additionally a considerable volume of variably aluminous and manganeseiferous quartzite and schist that commonly contain combinations of the  $\text{Al}_2\text{SiO}_5$  minerals.

The above authors mapped out the distribution of the  $\text{Al}_2\text{SiO}_5$  minerals and performed phase-equilibrium calculations assuming that the rocks experienced a single metamorphic event at or very near triple-point  $P$ - $T$  conditions. More recent work by Daniel et al. (1992) and Williams and Karlstrom (1996) suggests that most if not all of the  $\text{Al}_2\text{SiO}_5$ -bearing rocks were involved in looping clockwise (decompressional)  $P$ - $T$  paths traversing, in order, the kyanite, sillimanite, and andalusite fields (Fig. 2 of Williams and Karlstrom 1996, similar to the  $P$ - $T$  path shown schematically in Fig. 2b of this paper). Kyanite and subsequent sillimanite, commonly aligned with the regional foliation and lineation, are overgrown by andalusite, which overprints the foliation (Daniel et al. 1992). The emplacement of abundant plutons during the decompressional stage of the regional metamorphic episode may account for much of the late andalusite. The central point is that the  $\text{Al}_2\text{SiO}_5$  minerals in these rocks do not appear to have formed at the same time and hence cannot be regarded as stable triple-point parageneses, notwithstanding the possibility that parts of the looping  $P$ - $T$  paths may have passed near the triple point as suggested by Williams and Karlstrom (1996). Whether the associated aluminous quartzites, in which  $\text{Al}_2\text{SiO}_5$  minerals may have formed at temperatures below the triple-point by pyrophyllite breakdown, preserve stable triple-point assemblages remains an open question, although Larson and Sharp (2000) have argued on isotopic grounds that the  $\text{Al}_2\text{SiO}_5$  minerals in these rocks were not in equilibrium.

In summary, the purported triple-point localities in the literature appear to be the result of one or more of the following: sequential growth of the  $\text{Al}_2\text{SiO}_5$  minerals along  $P$ - $T$  paths that may or may not have been near triple-point conditions; tec-

tonic juxtaposition; or polymetamorphism. Consequently, these occurrences do not contradict the experimental, thermodynamic, and other natural evidence indicating that triple-point assemblages are not stable in common Ms+Bt+Qtz-bearing metapelites.

#### CONDITIONS REQUIRED FOR STABLE METAPELITIC TRIPLE-POINT ASSEMBLAGES

It is interesting to examine what conditions would be required for stable triple-point assemblages to be possible in Ms+Bt+Qtz-bearing metapelites. Focusing again on reaction 1, the question is what would be required to either suppress reaction 1 to temperatures below the triple point, or expand the stability field of andalusite to exceed the temperature of reaction 1.

Regarding suppression of reaction 1, there are few minor element effects that expand the stability of  $\text{Al}_2\text{SiO}_5$ +Bt.  $\text{Fe}^{3+}$  and Ti, once thought to expand the stability field of  $\text{Al}_2\text{SiO}_5$ +Bt significantly (Powell and Holland 1990), have been shown by White et al. (2000) to have a negligible (<10 °C) effect on reaction 1 unless in unusually high concentration. Indeed, the most likely minor element effects involve staurolite (e.g., Zn, Mn) and would tend to displace reaction 1 to higher rather than lower temperatures.

This leaves reduced  $a_{\text{H}_2\text{O}}$  as the most likely way to suppress reaction 1. Reaction 1 was displaced for reduced  $a_{\text{H}_2\text{O}}$  using the Gibbs method (Spear 1988, 1990) until it coincided with the triple point. The minimum temperature difference involves the Holland and Powell (1998) reaction 1 curve and the Pattison (1992) triple point (ca. 30 °C), whereas the maximum difference involves the Spear and Cheney (1989, 2000 in Pattison et al. 2002) reaction 1 curve and the Holdaway (1971) triple point (ca. 90 °C) (Fig. 3b). The resulting values of  $a_{\text{H}_2\text{O}}$  range between 0.78 and 0.43. These values are significantly lower than  $a_{\text{H}_2\text{O}}$  in C-O-H fluids in equilibrium with graphite or in C-O-H-S fluids in equilibrium with graphite, pyrrhotite, and pyrite at triple-point conditions (ca. 0.96 and 0.90, respectively, Connolly and Cesare 1993), i.e., lower than can be produced internally in dehydrating metapelites. Reduction of  $a_{\text{H}_2\text{O}}$  of the magnitude calculated above would require infiltration of low  $a_{\text{H}_2\text{O}}$  fluids into the dehydrating metapelites and dilution of the nearly pure water being produced in the pores of rock by reaction 1, *throughout the time of reaction*. This scenario seems unlikely in most reacting metapelitic rock volumes.

Regarding expansion of the stability field of andalusite, Grambling and Williams (1985) argued that elevated Mn and Fe contents of andalusite in some samples from north-central New Mexico could displace the triple-point up-temperature and up-pressure by up to 40 °C and 0.9 kbar, potentially reconciling the occurrence of purported stable triple-point assemblages with geothermobarometry constraints presented in their paper (and perhaps with the phase-equilibrium constraints presented in this paper). They displaced the  $\text{Al}_2\text{SiO}_5$  phase boundaries by calculating the equilibrium constant between pairs of coexisting  $\text{Al}_2\text{SiO}_5$  minerals. Using the andalusite-sillimanite equilibrium as an example, the equilibrium constant,  $K_D = X_{\text{Al}_2\text{SiO}_5}^{\text{Sill}}/X_{\text{Al}_2\text{SiO}_5}^{\text{And}}$ , was calculated assuming  $X_{\text{Al}_2\text{SiO}_5} = (1 - M/\text{AlSiO}_5)$ , where M is the sum of all cations other than Al and

Si assuming a 5 oxygen atom formula unit.

Using the same combinations of triple point and position of reaction 1 as before,  $K_D$  between andalusite and sillimanite must range between 1.04–1.11 to expand the andalusite stability field to reach reaction 1, whereas the highest recorded  $K_D$  in Ms + Bt + Qtz-bearing metapelites is 1.023 (Kerrick and Speer 1988; Pattison 1992). The highest of the  $K_D$  values reported in the study of Grambling and Williams (averaging 1.039) came from unusually manganiferous and aluminous metasedimentary layers. In addition, their calculations were based on the equilibrium co-existence of the  $\text{Al}_2\text{SiO}_5$  minerals, a conclusion that may or may not be valid (see above discussion). In summary, it seems that only under exceptional and to date unreported circumstances will a combination of minor-element effects and reduced water activity permit stable triple point assemblages in Ms + Bt + Qtz-bearing metapelites.

### IMPLICATIONS FOR THE INTERPRETATION OF METAPELITIC MINERAL ASSEMBLAGES

#### Metapelitic petrogenetic grid

The conclusion that reaction 1 occurs at higher temperature than the triple point carries obvious implications for the topology of the metapelitic petrogenetic grid. The results of the present study are consistent with petrogenetic grids calculated with the thermodynamic data sets of Spear and Cheney (1989), Spear et al. (2000; reported in Pattison et al. 2002), and Holland and Powell (1998) (Fig. 3b), but contrast with some other well-known grids that place reaction 1 below the triple point (see earlier discussion). The absolute location of the triple point in  $P$ - $T$  space is still debated. Arguments for and against the Holdaway (1971) and Pattison (1992) placements are discussed in Pattison (1992), Holdaway and Mukhopadhyay (1993), and Pattison et al. (2002).

#### The bathozone/bathograd scheme of Carmichael (1978) and the “triple-point isobar”

Carmichael (1978) devised a series of six metamorphic bathozones (depth zones) separated by pressure-dependent, temperature-independent bathograds based on common mineral assemblages in amphibolite-facies metapelites. The bathograds of Carmichael correspond to intersections of univariant reactions in the model pelitic system NaKFMASH, as shown in Figure 4a (the prefix “C” in front of the numbered bathozones stands for Carmichael). In addition to the phase boundaries among kyanite, andalusite, and sillimanite, the key univariant dehydration reactions in the scheme of Carmichael are reaction 5 ( $\text{Ms} + \text{St} + \text{Qtz} = \text{Al}_2\text{SiO}_5 + \text{Grt} + \text{Bt} + \text{H}_2\text{O}$ ) and:



The occurrence of reaction 1 up-temperature of the triple point leads to a proposed modified scheme shown in Figure 4b (the prefix “P” in front of the numbered bathozones stands for Pattison). The bathozone numbering in Figure 4b is designed to retain as much as possible of the original Carmichael system as well as to accommodate the low-pressure facies series of Pattison and Tracy (1991) (see further discussion below).

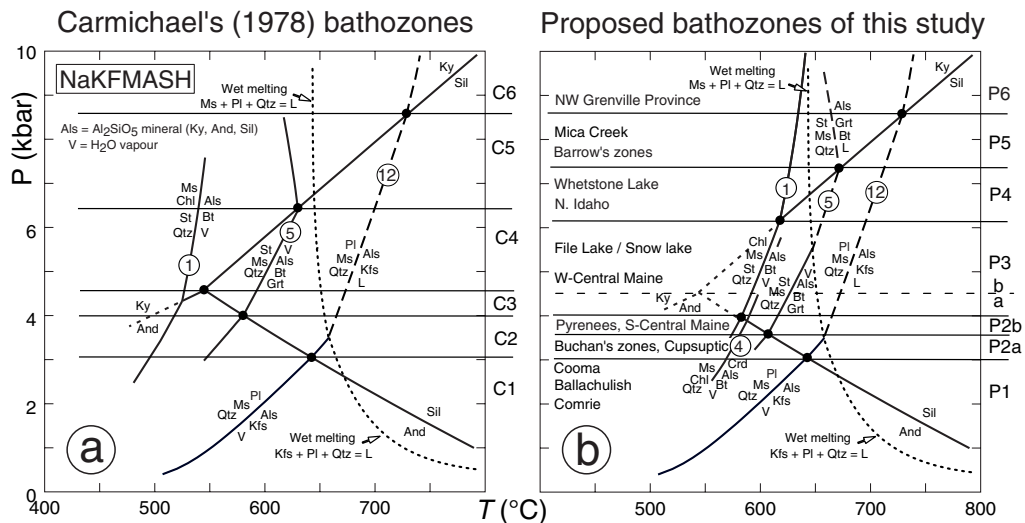
The absolute position of the reactions constraining the bathozones in Figure 4b is less important than the overall topology of the diagram. Some well-known metamorphic sequences from the literature have been placed in Figure 4b.

In the Carmichael scheme in Figure 4a, bathograd C3/C4 corresponds to the triple-point isobar. However, because the first occurrence of  $\text{Al}_2\text{SiO}_5$  minerals in biotite-bearing metapelites (reaction 1) occurs up-temperature of the triple-point, the triple-point bathograd is “invisible” to these compositions. In the scheme proposed in this paper (Fig. 4b), with its emphasis on common Ms+Bt+Qtz-bearing metapelites, the triple-point isobar is dashed. Only if metapelitic rock packages contain especially aluminous rocks, in which  $\text{Al}_2\text{SiO}_5$  minerals may develop at temperatures below the triple point, could bathozone P3 in Figure 4b be split into lower-pressure (a) and higher-pressure (b) sub-zones based on the triple-point bathograd.

These considerations do not invalidate the utility of the triple point for first-order evaluation of the  $P$ - $T$  conditions of Ms+Bt+Qtz-bearing metapelites, nor do they call into question the regional significance the “triple-point isobar” mapped by Thompson and Norton (1968) in new England, and by Carmichael (1978) in the Scottish Highlands and the Bergell Alps. However, they do loosen the restrictions implied in the Carmichael scheme in Figure 4a. In Figure 4b, the presence of kyanite in Ms+Bt+Qtz-bearing metapelites indicates pressures above bathograd P3/P4 (intersection of reaction 1 with  $\text{Ky} = \text{Sil}$ , ca. 6 kbar), whereas the presence of andalusite in Ms+Bt+Qtz-bearing metapelites indicates pressures below bathograd P2b/P3 (intersection of reaction 1 with  $\text{And} = \text{Sil}$ , ca. 4 kbar), with the triple-point isobar residing in between within bathozone P3. Thus the triple-point isobar can never be more than approximately located in the field based on assemblages in Ms+Bt+Qtz-bearing metapelites. Tightly defined triple-point isobar localities deserve careful scrutiny (see earlier section).

For metapelitic rocks in which chlorite is consumed before reaction 1 is reached, bathozones P2b to P4 will be indistinguishable because reaction 1, on which the P2b/P3 and P3/P4 bathograds are based, involves chlorite as a reactant. Consumption of chlorite prior to the onset of reaction 1 is expected to be more common at high pressure than low pressure because it is involved in garnet formation and garnet is increasingly stabilized as pressure rises. Indeed, Carmichael’s emphasis on reaction 5 as a key dehydration reaction in his bathozone/bathograd scheme was based on his observation that most staurolite-bearing metapelitic rocks do not contain chlorite.

With respect to the low-pressure metapelitic facies series scheme of Pattison and Tracy (1991), their facies series 1, 3, and 4 correspond to bathozones P1, P3, and P4 of Figure 4b. However, their facies series 2a and 2b do not coincide with bathozones P2a and P2b. The Pattison-Tracy facies series are based on generally higher-pressure staurolite-bearing (2b) vs. generally lower pressure cordierite-bearing (2a) assemblages in Ms+Bt+Qtz-bearing metapelites in the andalusite field (see also Table 1 of Pattison et al. 1999). The P2a/P2b bathograd (same as the C2/C3 bathograd of Carmichael: intersection of reaction 5 with  $\text{And} = \text{Sil}$ ) lies within facies series 2b of Pattison



**FIGURE 4.** Comparison of the bathograd/bathozone scheme of Carmichael (1978) (a) with the proposed scheme of this paper (b). The reaction positions in (b) are from Spear, Pattison, and Cheney (2000, unpublished, reported in Pattison et al. 2002), but the absolute position of the reactions is less important than the overall topology of the diagram. For ease of comparison, only one triple point is shown (Pattison 1992), even though in the scheme of Carmichael the Holdaway (1971) triple point was used. In (a), the positions of reactions 1 and 5 have been arbitrarily displaced down-temperature to more closely match the appearance of the Carmichael (1978) scheme. The dashed parts of reaction 5 and 12 are where these reactions cross the wet solidus (curving dotted line) and become dehydration melting reactions. In (b), the triple-point isobar is shown as a dashed line and divides bathozone P3 into higher-pressure (a) and lower-pressure (b) subzones (see text for discussion). References to the bathozone P1, P2a, and P2b localities are given in Pattison and Tracy (1991) and Pattison et al. (1999). References to the West-Central Maine, File Lake/Snow Lake and Whetstone Lake areas are given in the text of this paper. N. Idaho = Lang and Rice (1935); Barrow's Zones = Barrow (1893), Tilley (1925), Atherton (1977), Yardley (1989); Mica Creek = ghent et al. (1982); NW Grenville = Rivers (1983).

and Tracy. Complications in the use of this bathograd are discussed in Pattison and Tracy (1991, p. 141–142 and 157–159). Although reactions involving cordierite are not formally part of the bathograd scheme of Carmichael (1978) or indeed the one in Figure 4b, reaction 4 ( $Ms + Chl + Qtz = Crd + Al_2SiO_5 + Bt + H_2O$ ) has been added to Figure 4b to account for the observation that cordierite±andalusite-t  $Ms + Bt + Qtz$ -bearing assemblages become dominant in bathozones P1 and P2a at low pressure (Pattison and Tracy 1991).

#### Kyanite-andalusite-sillimanite prograde sequences and the problem of kyanite in thermal aureoles

The presence of kyanite in  $Ms+Bt+Qtz$ -bearing metapelites in low-pressure, andalusite-sillimanite type aureoles and regional settings has been a source of considerable controversy (Loomis 1972; Atherton et al. 1975; Pattison and Tracy 1991, p. 147, 160). An isobaric or gently sloping metamorphic field gradient at a pressure below the triple point traverses the stability fields of all three  $Al_2SiO_5$  minerals, in theory allowing a prograde sequence involving sequential growth of kyanite, andalusite and sillimanite (Fig. 2a). In a discussion of kyanite-bearing andalusite-sillimanite type aureoles worldwide, with special emphasis on the Donegal aureoles (Naggar and Atherton 1970; Pitcher and Berger 1972), Atherton et al. (1975) inferred such a  $P$ - $T$  path and  $Al_2SiO_5$  mineral growth history. Grambling (1981, p. 709) inferred a similar prograde path to explain some kyanite-andalusite rocks from the Truchas uplift, New Mexico.

This interpretation is not viable for  $Ms+Bt+Qtz$ -bearing metapelites because kyanite does not form at pressures below the triple point in these compositions (Fig. 2b). An alternative explanation for such rocks is that the kyanite-bearing rocks formed during an earlier higher-pressure metamorphism and were variably overprinted at lower pressure by andalusite and perhaps sillimanite. On the other hand, prograde kyanite-andalusite-sillimanite sequences reflecting a single metamorphic event may be possible in aluminous bulk compositions that develop  $Al_2SiO_5$  minerals down-temperature of the triple point.

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#### REFERENCES CITED

- Atherton, M.P. (1977). The metamorphism of the Dalradian rocks of Scotland. *Scottish Journal of Geology*, 13, 331–370.  
 Atherton, M.P., Naggar, M.H., and Pitcher, W.S. (1975) Kyanite in some thermal aureoles. *American Journal of Science*, 275, 432–443.  
 Bailes, A.H. and McRitchie, W.D. (1978) The transition from low to high grade metamorphism in the Kiseynew sedimentary gneiss belt, Manitoba. In J.A. Fraser and W.W. Heywood, Eds., *Metamorphism in the Canadian Shield*. Geological Survey of Canada Paper, 78–10, 155–179.  
 Barrow, G. (1893) On an intrusion of muscovite biotite gneiss in the SE Highlands of Scotland and its accompanying metamorphism. *Quarterly Journal of the Geological Society of London*, 49, 330–358.

- Berman, R.G. (1988) Internally-consistent thermodynamic data for minerals in the system Na<sub>2</sub>O-K<sub>2</sub>O-CaO-MgO-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-TiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub>. *Journal of Petrology*, 29, 445–522.
- Bohlen S.R., Montana, A.L., and Kerrick, D.M. (1991). Precise determinations of the equilibria kyanite = sillimanite and kyanite = andalusite, and a revised triple point for Al<sub>2</sub>SiO<sub>5</sub> polymorphs. *American Mineralogist*, 76, 677–680.
- Carey, J.W., Rice, J.M., and Grover, T.W. (1992) Petrology of aluminous schist in the Boehls Butte region of Northern Idaho: Geologic history and aluminum-silicate phase relations. *American Journal of Science*, 292, 455–473.
- Carmichael, D.M. (1970) Intersecting isograds in the Whetstone Lake area, Ontario. *Journal of Petrology*, 11, 147–181.
- (1978) Metamorphic bathozones and bathograds: A measure of the depth of post metamorphic uplift and erosion on the regional scale. *American Journal of Science*, 278, 769–797.
- Carmichael, D.M., Moore, J.M., and Skippen, G.B. (1978) Isograds around the Hastings metamorphic "low". In A.L. Currie and W.O. Mackasey, Eds., Toronto '78 Field trips guidebook, 325–346. Geological Association of Canada—Geological Association of America combined meeting.
- Chatterjee, N.D. (1972) The upper stability limit of the assemblage paragonite + quartz and its natural occurrences. *Contributions to Mineralogy and Petrology*, 34, 288–303.
- Chatterjee, N.D., Johannes, W., and Leistner, H. (1984) The system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O: new phase equilibria data, some calculated phase relations, and their petrological applications. *Contributions to Mineralogy and Petrology*, 88, 1–13.
- Connolly, J.A.D. and Cesare, B. (1993) C-O-H-S fluid compositions and oxygen fugacity in graphitic metapelites. *Journal of Metamorphic Geology*, 11, 379–388.
- Daniel, C.G., Thompson, A.G., and Grambling, J.A. (1992) Decompressional metamorphic P-T paths from kyanite-sillimanite-andalusite bearing rocks in North-Central New Mexico. *Geological Society of America Annual Meeting—Abstracts with Program*, 24, A264.
- Davidson, A., Carmichael, D.M., and Pattison, D.R.M. (1990). Metamorphism and geodynamics of the Southwestern Grenville Province, Ontario. Field Trip no. 1, International Geological Correlation Program, Projects 235–304: 'Metamorphic Styles in Young and Ancient Orogenic Belts' meeting. Department of Geology and Geophysics, University of Calgary, Alberta.
- Florence, F.P., Spear, F.S., and Kohn, M.J. (1993) P-T paths from northwestern New Hampshire: Metamorphic evidence for stacking in a thrust/nappe complex. *American Journal of Science*, 293, 939–979.
- Fox, J.S. (1975) Three dimensional isograds from the Lukmanier Pass, Switzerland, and their tectonic significance. *Geological Magazine*, 112, 547–626.
- Froese, E. (1997). Metamorphism in the Weldon Bay-Syme Lake area, Manitoba. In: Current Research. Geological Survey of Canada Paper, 1997-E, 35–44.
- Froese, E. and Gasparrini, E. (1975) Metamorphic zones in the Snow Lake area, Manitoba. *Canadian Mineralogist*, 13, 162–167.
- Ghent, E.D., Knitter, C.C., Raeside, R.P. and Stout, M.Z. (1982) Geothermometry and geobarometry of pelitic rocks, upper kyanite and sillimanite zones, Mica Creek area, British Columbia. *Canadian Mineralogist*, 20, 295–305.
- Gordon, T.M., Ghent, E.D., and Stout, M.Z. (1991) Algebraic analysis of the biotite-sillimanite isograd in the File Lake area, Manitoba. *Canadian Mineralogist*, 29, 673–686.
- Grambling, J.A. (1981) Kyanite, andalusite, sillimanite, and related mineral assemblages in the Truchas Peaks region, New Mexico. *American Mineralogist*, 66, 702–722.
- (1984) Coexisting paragonite and quartz in sillimanitic rocks from New Mexico. *American Mineralogist*, 69, 79–87.
- Grambling, J.A. and Williams, M.L. (1985) The effect of Fe<sup>3+</sup> and Mn<sup>3+</sup> on aluminum silicate phase relations in north-central New Mexico, U.S.A. *Journal of Petrology*, 26, 324–354.
- Grover, T.W., Rice, J.M., and Carey, J.W. (1992) Petrology of aluminous schist in the Boehls Butte region of Northern Idaho: Phase equilibria and P-T evolution. *American Journal of Science*, 292, 474–507.
- Guidotti, C.V. (1968) On the relative scarcity of paragonite. *American Mineralogist*, 53, 963–974.
- (1974) Transition from staurolite to sillimanite zone, Rangeley Quadrangle, Maine. *Geological Society of America Bulletin*, 85, 475–490.
- (1984). Micas in metamorphic rocks. In S.W. Bailey, Ed., *Micas*, 13, 357–468. Mineralogical Society of America, Reviews in Mineralogy, Washington, D.C.
- Harte, B. and Hudson, N.F.C. (1979) Pelite facies series and the temperatures and pressures of Dalradian metamorphism in E Scotland. In A.L. Harris, C.H. Holland, and B.E. Leake, Eds., *The Caledonides of the British Isles-Reviewed*. Geological Society of London Special Publication, 8, 323–336.
- Hess, P.C. (1969) The metamorphic paragenesis of cordierite in pelitic rocks. *Contributions to Mineralogy and Petrology*, 24, 191–207.
- Heitonen, A. (1956) Kyanite, andalusite and sillimanite in the schist in Boehls Butte quadrangle, Idaho. *American Mineralogist*, 41, 1–27.
- (1967) On the facies series in various types of metamorphism. *Journal of Geology*, 75, 187–214.
- Hodges, K.V. and Spear, F.S. (1982) Geothermometry, geobarometry and the Al<sub>2</sub>SiO<sub>5</sub> triple point at Mt. Moosilauke, New Hampshire. *American Mineralogist*, 67, 1118–1134.
- Holdaway, M.J. (1971) Stability of andalusite and the aluminum silicate phase diagram. *American Journal of Science*, 271, 97–131.
- (1978) Significance of chloritoid-bearing and staurolite-bearing rocks in the Picuris Range, New Mexico. *Geological Society of America Bulletin*, 89, 1404–1414.
- Holdaway, M.J. and Goode, J.W. (1990) Rock pressure vs. fluid pressure as a controlling influence on mineral stability: An example from New Mexico. *American Mineralogist*, 75, 1043–1058.
- Holdaway, M.J. and Mukhopadhyay, B. (1993) A re-evaluation of the stability relations of andalusite: thermochemical data and phase diagram for the aluminum silicates. *American Mineralogist*, 78, 298–315.
- Holland, T.J.B. and Powell, R. (1998) An internally consistent thermodynamic data set for phases of petrological interest. *Journal of Metamorphic Geology*, 16, 309–344.
- Hoschek, G. (1969) The stability of staurolite and chloritoid, and their significance in the metamorphism of pelitic rocks. *Contributions to Mineralogy and Petrology*, 22, 208–232.
- Kepezhinskas, K.B. and Khlestov, V.V. (1977) The petrogenetic grid and subfacies for middle temperature metapelites. *Journal of Petrology*, 18, 114–143.
- Kerrick, D.M. (1990) The Al<sub>2</sub>SiO<sub>5</sub> polymorphs. *Mineralogical Society of America, Reviews in Mineralogy*, 22, 406 p.
- Kerrick, D.M. and Speer, J.A. (1988) The role of minor element solid solution on the andalusite-sillimanite equilibrium in metapelites and peraluminous granulites. *American Journal of Science*, 288, 152–192.
- Korikovskii, S.P. (1979) Metamorphic facies of metapelites. Nauka Press, Moscow.
- Kretz, R. (1983) Symbols for rock-forming minerals. *American Mineralogist*, 68, 277–279.
- Lang, H.M. and Rice, J.M. (1985) Regression modelling of metamorphic reactions in metapelites, Snow Peak, Northern Idaho. *Journal of Petrology*, 26, 857–887.
- Larson, T. and Sharp, Z. (2000) Isotopic disequilibrium in the classic triple-point localities of New Mexico. *Geological Society of America Annual Meeting Abstracts Volume*, 32, A297–298.
- Loomis, T.P. (1972). Coexisting aluminum silicate phases in contact metamorphic aureoles. *American Journal of Science*, 272, 933–945.
- Mengel, F. and Rivers, T. (1994) Metamorphism of pelitic rocks in the Paleoproterozoic Ramah Group, Saglek area, Northern Labrador: Mineral reactions, P-T conditions and influence of bulk composition. *Canadian Mineralogist*, 32, 781–801.
- Mezger, J.E., Chacko, T., and Erdmer, P. (2001) Metamorphism at a late Mesozoic accretionary margin: a study from the Coast Belt of the North American Cordillera. *Journal of Metamorphic Geology*, 19, 121–138.
- Naggar, M.H. and Atherton, M.P. (1970) The composition and metamorphic history of some aluminium silicate-bearing rocks from the aureoles of the Donegal Granites. *Journal of Petrology*, 11, 549–589.
- Okuyama-Kusunose, Y. (1994) Phase relations in andalusite-sillimanite Fe-rich metapelites: Tono contact metamorphic aureole, northeast Japan. *Journal of Metamorphic Geology*, 12, 153–168.
- Pattison, D.R.M. (1992) Stability of andalusite and sillimanite and the Al<sub>2</sub>SiO<sub>5</sub> triple point: Constraints from the Ballachulish aureole, Scotland. *Journal of Geology*, 100, 423–446.
- Pattison, D.R.M. and Tracy, R.J. (1991) Phase equilibria and thermobarometry of metapelites. In: D.M. Kerrick, Ed., *Contact metamorphism*, 26, 105–206. Mineralogical Society of America, Reviews in Mineralogy, Washington, D.C.
- Pattison, D.R.M., Spear, F.S., and Cheney, J.T. (1999) Polymetamorphic origin of muscovite + cordierite + staurolite + biotite assemblages: implications for the metapelitic petrogenetic grid and for P-T paths. *Journal of Metamorphic Geology*, 17, 685–703.
- Pattison, D.R.M., Spear, F.S., DeBuhr, C.L., Cheney, J.T., and Guidotti, C.V. (2002) Thermodynamic modelling of the reaction Muscovite + Cordierite → Al<sub>2</sub>SiO<sub>5</sub> + Biotite + Quartz + H<sub>2</sub>O: constraints from natural assemblages and implication for the metapelitic petrogenetic grid. *Journal of Metamorphic Geology*, in press.
- Pitcher, W.S. and Berger, A.R. (1972) *The geology of Donegal: A study of granite emplacement*. Wiley, New York.
- Powell, R. and Holland, T. (1990) Calculated mineral equilibria in the pelitic system, KFMASH (K<sub>2</sub>O-FeO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O). *American Mineralogist*, 75, 367–380.
- Reche, J., Martinez, F.J., Arboleya, M.L., Dietsch, C., and Briggs, W.D. (1998) Evolution of a kyanite-bearing belt within a HT-LP orogen: the case of the NW Variscan Iberia. *Journal of Metamorphic Geology*, 16, 379–394.
- Rivers, T. (1983) Progressive metamorphism of pelitic and quartzofeldspathic rocks in the Grenville Province of western Labrador: tectonic implications of bathozone 6 assemblages. *Canadian Journal of Earth Sciences*, 20, 1791–1804.
- Rumble, D. (1973) Andalusite, kyanite and sillimanite from the Mount Moosilauke region, New Hampshire. *Geological Society of America Bulletin*, 84, 2423–



- 2430.
- Spear, F.S. (1988) The Gibbs method and Duhem's theorem: The quantitative relationships among P, T, chemical potential, phase composition and reaction progress in igneous and metamorphic systems. *Contributions to Mineralogy and Petrology*, 99, 249–256.
- (1990) Petrologic determination of metamorphic pressure-temperature-time paths. In F.S. Spear and S.M. Peacock, S.M. Metamorphic pressure-temperature-time paths, p. 1–55. 28th International Geological Conference—Short Course in Geology, 7, Washington, D.C.
- (1993) Metamorphic phase equilibria and pressure-temperature-time paths. Mineralogical Society of America Monograph, 1, 799 p.
- Spear, F.S. and Cheney, J.T. (1989) A petrogenetic grid for pelitic schists in the system  $SiO_2-Al_2O_3-FeO-MgO-K_2O-H_2O$ . *Contributions to Mineralogy and Petrology*, 101, 149–164.
- Spear, F.S., Pyle, J. M., and Storm, L. (2001) Thermodynamic modeling of mineral reactions: An introduction to Program Gibbs. Northeastern Geological Society of America Short Course 504, March 12, 2001, Burlington, Vermont.
- Thompson, A.B. (1976) Mineral reactions in pelitic rocks: I. Prediction of P-T-X(Fe-Mg) phase relations. II. Calculation of some P-T-X(Fe-Mg) phase relations. *American Journal of Science*, 276, 401–424, 425–454.
- Thompson, J.B. and Norton, S.A. (1968) Paleozoic regional metamorphism in New England and adjacent areas. In: E. Zen, W.S. White, J.B. Hadley and J.B. Thompson, J.B., Eds., *Studies of Appalachian Geology—Northern and Maritime*: New York. John Wiley and Sons, 319–327.
- Tilley, C.E. (1925) Metamorphic zones in the southern Highlands of Scotland. *Quarterly Journal of the Geological Society of London*, 81, 100–112.
- White, R.W., Powell, R.J., Holland, T.J.B., and Worley, B.A. (2000) The effect of  $TiO_2$  and  $Fe_2O_3$  on metapelitic assemblages at greenschist and amphibolite conditions: mineral equilibria calculations in the system  $K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O-TiO_2-Fe_2O_3$ . *Journal of Metamorphic Geology*, 18, 497–512.
- Williams, M.L. and Karlstrom, K.E. (1996) Looping P-T paths and high-T, low-P middle crustal metamorphism: Proterozoic evolution of the southwestern United States. *Geology*, 24, 1119–1122.
- Xu, G., Will, T.M., and Powell, R. (1994) A calculated petrogenetic grid for the system  $K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O$ , with particular reference to contact-metamorphosed pelites. *Journal of Metamorphic Geology*, 12, 99–119.
- Yardley, B.W.D. (1989) *An introduction to metamorphic petrology*, 248 p. Longman Scientific, Harlow, England.

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