

## Geothermobarometry in pelitic schists: A rapidly evolving field\*

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### ABSTRACT

The study of pelitic rocks for the purpose of deciphering pressure-temperature ( $P$ - $T$ ) information is an important area for collaboration between mineralogists and petrologists. Accurate geothermobarometry is especially important for studies of pressure-temperature-time paths of terranes during tectonism and for studies of the movement of metamorphic fluids. During the past decade, new developments have included thermodynamic data bases, sophisticated crystal structure determinations and associated site assignments, and analyses for  $\text{Fe}^{3+}$  and light elements (especially H and Li) for many minerals within a petrogenetic context. It is now necessary to apply these new findings to geothermobarometry in several important ways: (1) The stoichiometric basis for hydrous minerals should be revised in light of highly variable H and variable  $\text{Fe}^{3+}$ , which can now be estimated with considerable accuracy as a function of grade or mineral assemblage. (2) Mole fraction (activity) models should be based on the best crystal chemical considerations. For some minerals, H may be omitted from the model if all the substitutions involving H are coupled substitutions. (3) Thermodynamic data should be based on careful analysis of all available experiments and secondary comparison with natural assemblages. (4) The possibility of nonideal solid solution should be considered, as ideality is merely a special case of nonideality. It is better to estimate binary interaction parameters than to assume that they are zero. However, it is difficult to determine ternary interaction parameters. In such cases, little error is likely to result from assuming that strictly ternary interaction parameters are zero, while evaluating all the binary terms. Our understanding of garnet and biotite solutions has improved, and the garnet-biotite geothermometer has undergone numerous refinements, but additional information on these minerals and improvements in the garnet-biotite thermometer are still necessary.

As the  $P$  and  $T$  determinations become more precise, we can better evaluate  $X_{\text{H}_2\text{O}}$ ,  $X_{\text{CO}_2}$ , and  $X_{\text{CH}_4}$  in the fluid phase. In all probability, patterns will be discovered in the compositions of pelitic metamorphic fluids, especially when graphite is present. The hematite-ilmenite solid solution system is potentially useful for determining  $f_{\text{O}_2}$ , once the solvus is better understood. In graphitic rocks at known  $P$  and  $T$ , knowledge of  $f_{\text{O}_2}$  from coexisting hemoilmenite and rutile or hemoilmenite and magnetite enables one to determine the mole fraction of all fluid species.

Careful application of the present state of knowledge, combined with modest improvements, should allow accuracy approaching  $\pm 250$  bars and  $\pm 25$  °C in rocks formed at low to moderate pressures. It is very important to continue to revise thermochemical data, activity models, Margules parameters, and stoichiometric information, and it is equally important for petrologists and tectonicists to make use of these revisions as they become available.

### INTRODUCTION

In recent years, we have become concerned about the simplified view taken by some petrologists and tectonicists regarding quantitative estimation of the pressure and temperature of formation of metamorphic rocks. There are many possible sources of error in this procedure, and,

if we are not continually watching for them and correcting them wherever possible, we will not get the best precision, especially in the  $P$ - $T$  range outside of the range of calibration. This is an ideal area for collaboration between mineralogists and petrologists. Mineralogists provide valuable information on mineral structure and site assignments, and petrologists apply the results to activity models. Both mineralogists and petrologists are making important contributions to careful, complete chemical analysis of common metamorphic minerals.

Interesting work is being done on pressure-tempera-

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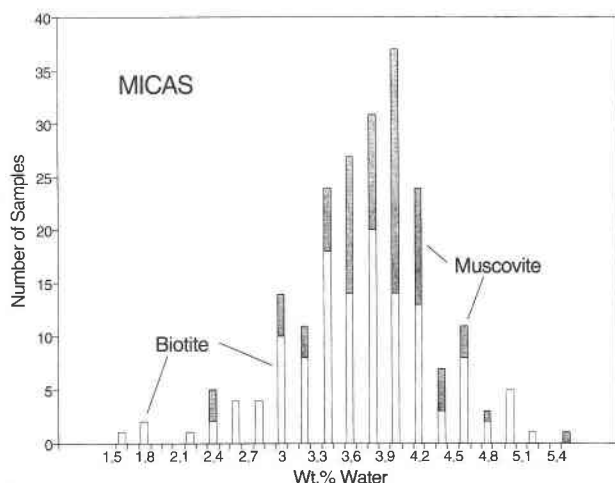


Fig. 1. Histogram of  $H_2O$  content of all muscovite and biotite samples analyzed by M.D. Dyar. After Dyar et al. (1993), reprinted with the kind permission of Pergamon Press.

ture-time paths (e.g., Spear and Selverstone, 1983) and on fluid composition and movement in metamorphic terranes (e.g., Ferry and Dipple, 1991). There are also significant controversies over how much  $P$ - $T$  information one can learn from zoned minerals (e.g., Frost and Tracy, 1991) and how much fluid actually passed through the rocks (e.g., Gray et al., 1991). The quality of the results of many of these studies may well be only as good as the quality of the geothermobarometry used. Only when significant improvements are made to the accuracy of  $P$ - $T$  determination will we possibly be able to answer these questions. That alone is an important justification for continuing our efforts to improve geothermobarometry.

To illustrate the seriousness of the problem, we compare two recent studies involving geothermobarometry in pelitic rocks. In Acadian M3 in Maine and in the Delamerian of South Australia, near Adelaide, isobaric thermal metamorphism produces assemblages containing staurolite + andalusite followed by sillimanite at higher grade. In both areas the appearance of sillimanite corresponds approximately to the disappearance of both andalusite and staurolite. In both areas, cordierite is locally present, probably because of an earlier, lower- $P$  subevent, a local decrease in  $P$ , or a difference in bulk composition. All petrologic evidence indicates that these two localities have enjoyed about the same  $P$ - $T$  conditions. Average metamorphic conditions for the staurolite-bearing rocks deduced by Holdaway et al. (1988) for Maine M3 are  $P = 3.1$  kbar,  $T = 531$  °C; conditions deduced by Dymoke and Sandiford (1992) for the Delamerian near Adelaide are  $P = 4.5$  kbar,  $T = 594$  °C, corresponding to an apparent  $P$  difference of 1.4 kbar or a depth difference of nearly 5 km. Whereas petrologists who work in rocks at higher  $P$  and  $T$  might not consider these to be serious differences, we believe it should be possible to obtain much greater accuracy in low- to moderate- $P$  rocks than is implied by this comparison. It is worth noting that the

$P$  difference between these two estimates is 45% of the lower value.

Here we review the process of  $P$ ,  $T$ , and  $X_{H_2O}$  estimation, focusing on five important areas: (1) determination of mineral stoichiometry, (2) mineral mole fraction (activity) models, using the mixing-on-sites model, (3) non-ideality in mineral solid solutions, (4) derivation and use of thermodynamic data, and (5) fluid composition and its use to test results. If petrologists carefully consider what is known in each of these areas and continue to heed developments as they became available, we will converge on a consistent  $P$ - $T$ - $X_{H_2O}$  grid for all metamorphic terranes and grades. In our analysis, we will focus on medium-grade pelitic metamorphism, but some of what we have to say is equally applicable to other grades or bulk compositions. The major silicate minerals we will be discussing are muscovite, biotite, garnet, staurolite, cordierite, aluminum silicates, and chlorite; the Fe-Ti oxides ilmenite, hematite, magnetite, and rutile, as well as graphite, will also come up for discussion. We will consider mainly the dominant mineral end-members and will not be considering sulfide equilibria. The effects of sulfide on  $X_{H_2O}$  in medium-grade reduced pelites can be ignored if the sulfide is pyrrhotite and not pyrite (Shi, 1992).

#### MINERAL STOICHIOMETRY

Extensive and, commonly, exclusive use of the electron microprobe for mineral analysis has left us short on important data for many minerals, especially hydrous ones. In many studies, mineral chemistry is based on microprobe data alone. The resultant shortcomings include a lack of data for  $Fe^{3+}/(Fe^{2+} + Fe^{3+})$  and a lack of light-element analyses, such as H, Li, B, and Be, on minerals as diverse as micas, chlorite, staurolite, garnet, and tourmaline. In this list all may contain significant amounts of  $Fe^{3+}$ , all but garnet have variable H, biotite and staurolite may have significant Li, and tourmaline has variable B (Dyar et al., 1992, 1993; Holdaway et al., 1986a, 1986b; Dutrow et al., 1986). The assumption of ideal or zero content of light elements and zero  $Fe^{3+}$  may have produced inaccurate stoichiometry, and it has precluded the possibility of several important substitutions that are coupled with those of major elements. Depending on the mineral, the H content of hydrous minerals may be a function of metamorphic grade, of mineral assemblage, or both. With light-element and  $Fe^{3+}$  analytical data for representative minerals, we can make appropriate corrections to the stoichiometric basis. Here we summarize what we know about  $Fe^{3+}/(Fe^{2+} + Fe^{3+})$  and light elements, how they affect stoichiometry, and possible site assignments for  $Fe^{3+}$ .

#### Muscovite

Muscovite suffers from two compositional problems. (1) Preliminary Mössbauer study (M. D. Dyar, unpublished data) shows that half to two-thirds of the Fe in muscovite is  $Fe^{3+}$ . Except for highly oxidized, low-grade, or high- $P$  rocks, this effect can be ignored because it has

**TABLE 1.** H<sub>2</sub>O content of Maine pelitic micas as a function of grade\*

Zone	Muscovite			Biotite		
	No.	Average (%)	$\sigma$	No.	Average (%)	$\sigma$
Garnet	8	3.54	0.86	16	4.52	0.30
Staurolite	10	3.78	0.39	10	4.16	0.47
Sillimanite	26	4.06	0.35	29	3.83	0.35
Ksp-Sil-Mus	4	3.84	0.20	5	3.21	0.30
All	48	3.90	0.49	60	4.02	0.51

\* Data of Dyar et al. (1993 and unpublished data).

a trivial effect on stoichiometry and activity. (2) Dyar et al. (1993 and unpublished data) have determined the H<sub>2</sub>O content of 48 pelitic muscovite samples from Maine that show a range from 2.5 to 4.8% H<sub>2</sub>O. Data for all the biotite and muscovite samples they have analyzed are summarized in Figure 1; the two minerals have similar ranges of H<sub>2</sub>O content. There is a general positive relationship between H<sub>2</sub>O content and grade for muscovite, with a slight decrease at the highest grade (Table 1). Note however, that most pelitic muscovite has less than the stoichiometric value of 4.5% H<sub>2</sub>O. This is also important because it may affect the nature of ionic substitutions in muscovite. For a muscovite in the potassium feldspar-sillimanite-muscovite zone, estimating 3.8% H<sub>2</sub>O from the results of Dyar et al. (1993 and unpublished data) has a small effect on the stoichiometry (Table 2). For a microprobe analysis, with O substituting for OH<sup>-</sup>, the O basis becomes 11.15 instead of 11, slightly increasing the total cationic content. The H<sup>+</sup> deficiency may compensate for excess charge in the octahedral layer over that necessary to charge balance the tetrahedral layer. F contents of muscovite are low and insufficient to explain the H<sup>+</sup> variations (Dyar et al., 1993 and unpublished data). Correcting for H and Fe<sup>3+</sup> increases activity slightly (Table 2).

**Biotite**

Metamorphic biotite has three problems associated with composition. (1) All pelitic biotite that grew under reduced conditions with graphite and ilmenite has about 12% of Fe as Fe<sup>3+</sup>, as shown by wet-chemical and Mössbauer studies. Guidotti and Dyar (1991) interpreted the Mössbauer spectra on reduced pelitic biotite from Maine to indicate on average 8% of the Fe as <sup>44</sup>Fe<sup>3+</sup> and 4% as <sup>60</sup>Fe<sup>3+</sup>. Both the amount and the site assignments for Fe<sup>3+</sup> in these pelitic biotite samples (Dyar, 1990) have been questioned by Rancourt et al. (1992) in a study of biotite of different composition and origin. However, Dyar (1993) pointed out that detection of <sup>44</sup>Fe<sup>3+</sup> requires random orientation in micas, <sup>44</sup>Fe<sup>3+</sup> has often been identified in biotite and other phyllosilicates, and the Fe<sub>tot</sub><sup>3+</sup> has been confirmed by many independent wet-chemical studies, such as that of Williams and Grambling (1990). Guidotti's (1984) review of chemistry of pelitic biotite also showed substantial Fe<sup>3+</sup>. (2) A few biotite samples contain quan-

**TABLE 2.** Stoichiometry of micas, specimen 143\*

Ion	Muscovite**		Biotite†	
	No correction	H, Fe <sup>3+</sup> corrected	No correction	H, Fe <sup>3+</sup> corrected
<sup>117</sup> Si	3.034	3.076	2.666	2.696
<sup>117</sup> Al	0.966	0.924	1.334	1.201
<sup>117</sup> Fe <sup>3+</sup>	0.000	0.000	0.000	0.103
<sup>131</sup> Al	1.866	1.947	0.390	0.542
<sup>131</sup> Ti	0.038	0.039	0.173	0.175
<sup>131</sup> Fe <sup>2+</sup>	0.060	0.031	1.277	1.136
<sup>131</sup> Fe <sup>3+</sup>	0.000	0.030	0.000	0.052
<sup>131</sup> Mg	0.055	0.056	0.952	0.963
<sup>131</sup> Mn	0.001	0.001	0.011	0.011
<sup>131</sup> □	0.980	0.896	0.197	0.121
<sup>131</sup> K	0.917	0.930	0.971	0.982
<sup>131</sup> Na	0.064	0.065	0.018	0.018
OH	2.000	1.666	2.000	1.602
Mole fraction‡	0.781	0.785	0.066	0.044

\* Holdaway et al. (1988). F neglected.

\*\* Assumes all <sup>131</sup>Al is on M2, all <sup>131</sup>□ is on M1; for corrected values, half of Fe is Fe<sup>3+</sup>.

† Assuming disorder of all species on M1 and M2, Guidotti and Dyar (1991) Fe<sup>3+</sup>.

‡ See Table 4 for mole fraction models. Biotite mole fractions are for annite.

tatively significant amounts of Li, as shown by Dutrow et al. (1986) and Dyar et al. (1992 and unpublished data). This effect can commonly be ignored but may be the cause of P-T discrepancies in individual specimens. (3) According to the work of Dyar et al. (1993 and unpublished data) on 60 specimens, pelitic biotite ranges between 2.9 and 5.2% in H<sub>2</sub>O, whereas the ideal value is 4%. As with muscovite, that affects the nature of ionic substitutions. Biotite shows a negative relationship between H<sub>2</sub>O content and grade (Table 1). For a biotite sample in the potassium feldspar-sillimanite-muscovite zone, Dyar's average H<sub>2</sub>O content of 3.2% increases the O basis to 11.2, increases the content of cations, and reduces the vacancy content of the octahedral sites (Table 2). The deficiency of H in many pelitic biotite samples cannot be explained by F (Dyar et al., 1992 and unpublished data) but may compensate for increased charge of Fe<sup>3+</sup>, Al, and Ti in the octahedral sites above that balanced by tetrahedral substitution (Dyar et al., 1993). In this case, note that making corrections for H and Fe<sup>3+</sup> reduces activity substantially, mainly because of the effect of Fe<sup>3+</sup>.

**Staurolite**

Work on staurolite shows that determination of staurolite stoichiometry suffers from the same problems as biotite. (1) Staurolite that grew under reducing conditions contains on average 3.5% of the Fe as Fe<sup>3+</sup> (Dyar et al., 1991; Holdaway et al., 1991), probably in the <sup>44</sup>Fe (T2) sites. (2) Most staurolite contains Li (Dutrow et al., 1986), and in the absence of a Li analysis or evidence of high Li, it is best to assume the average value of 0.2 Li ions to avoid systematic errors (Holdaway et al., 1991). Better yet, representative specimens from a terrane should be analyzed for Li with the ion microprobe or proton-in-

**TABLE 3.** Stoichiometry of natural staurolite samples at extremes of H content\*

Ion	3-3	71-62T
<sup>(M1)</sup> Al	7.70	7.70
<sup>(M1)</sup> R <sup>2+</sup>	0.30	0.30
<sup>(M2)</sup> Al	7.79	7.79
<sup>(M2)</sup> (R <sup>2+</sup> , Ti)	0.21	0.21
<sup>(M3)</sup> Al	1.87	1.59
<sup>(M3)</sup> (R <sup>2+</sup> , □)	0.13	0.41
<sup>(M4)</sup> Fe <sup>2+</sup>	0.02	0.51
<sup>(M4)</sup> (Zn, Li, □)	1.98	1.49
<sup>(T1)</sup> Si	7.63	7.59
<sup>(T1)</sup> Al	0.37	0.41
<sup>(T2)</sup> Fe <sup>2+</sup>	3.01	2.18
<sup>(T2)</sup> (R <sup>2+</sup> , R <sup>3+</sup> , Li, □)**	0.99	1.92
H	2.68	4.56
Si + Al - 1/3Li + 2/3Ti + Fe <sup>3+</sup>	25.53	25.38

\* Analytical data from Holdaway et al. (1986b) and Dyar et al. (1991), site assignments from a model based on Hawthorne et al. (1993a) and Holdaway et al. (1991), modified by Holdaway et al. (in preparation).

\*\* Excluding Fe<sup>2+</sup>.

duced  $\gamma$  emission. (3) Staurolite has variable H<sub>2</sub>O content. That which occurs with biotite or garnet has about 3 H<sup>+</sup> pfu, whereas that which occurs with aluminum silicate and no biotite or garnet has about 4 H<sup>+</sup> pfu (Holdaway et al., 1986a; Dyar et al., 1991). This observation can be used to determine the stoichiometry of staurolite that occurs with quartz in the absence of a H<sub>2</sub>O analysis, but in our opinion it is better to take advantage of the constancy of Si + Al and normalize the stoichiometry to Si + Al - 1/3Li + 2/3Ti + Fe<sup>3+</sup> = 25.55 (Holdaway et al., 1991; Table 3, this report). This approach preserves the constancy of Si and Al while correcting for the minor substitutions in natural staurolite that involve Si and Al. With this approach, subtraction of the total cation charge from 96 estimates H<sup>+</sup> within about 1 pfu. Either of these approaches is significantly better than the previously used method of assuming either 2 or 4 H pfu.

Comprehensive crystal structure studies by Hawthorne et al. (1993a, 1993b, 1993c) enable one to apportion the ions of a staurolite analysis into all the sites (Table 3). These two Fe-rich staurolite samples represent extremes of the known range of H content. Note that the Fe content of the T2 site is considerably less in the high-H staurolite because of the vacancy content of about one ion. This approach of assigning ions to their proper sites using crystal structure determinations as a model considerably improves the quality of stoichiometry and the resulting mole fraction calculations for stoichiometric staurolite end-members.

### Chlorite

We only wish to mention chlorite briefly. The work of Dyar and Guidotti (1992) showed that the stoichiometry of chlorite in pelites is affected by two main variables: (1) Chlorite contains Fe<sup>3+</sup> (about 11% of Fe). (2) Average H<sub>2</sub>O content is 10% compared with the ideal value of 12%. These observations should be taken into account when determining chlorite stoichiometry and activity.

### MOLE FRACTION MODELS

The proper choice of a mole fraction (activity) model is crucial for all subsequent calculations. The best possible choice of models is always a problem, and it is important to be as correct as possible. Also, petrologists should accept the fact that as our understanding of crystal structure, site assignments, and composition improves, we must continue to allow activity models to evolve. A number of important points are as follows: (1) It is better to make an incorrect decision on disorder or even site assignment than to make an error that renders the activity model inconsistent. For example, both the mole fraction basis of an ion and its exponent must be the same number. The equation for mole fraction must fit the model. (2) Care should be taken to avoid accounting for two substitutions when the ions are individually coupled by charge balance constraints. In staurolite, H substitution is always coupled to other major substitutions. (3) If a given model was necessary for retrieval of thermodynamic data, then that model, if reasonable, should also be used for geothermobarometry. (4) Any mineral that has two or more independent sites also has the potential for site interaction energies. When we ignore this possibility, we are assuming these energies are zero. Even if mixing on the independent sites is ideal, this cross-site interaction can have an effect on the mole fraction calculation. (5) In most cases, it is not yet possible to test alternative mole fraction models, although more such efforts should be attempted. With these points in mind, we present possible models for some of the common minerals (Table 4).

Activity models for micas are still very much open to question; the ones presented here are simply reasonable approximations. We assume octahedral sites in biotite are disordered. This is supported by the lack of contrary X-ray diffraction evidence and the fact that, at metamorphic *T*, disorder is even more likely than at room *T*. We assume <sup>(4)</sup>Al avoidance in micas, as advocated by Circone and Navrotsky (1992), and make the simplifying assumption that alternate tetrahedral sites are occupied by Si and show no solid solution. We suggest that the remaining two tetrahedral sites, occupied by one Al and one Si in end-member micas, and by Al, Si, and possibly Fe<sup>3+</sup> in natural micas, should be incorporated into the mole fraction model. Ackermann et al. (1993) presented spectroscopic evidence that OH<sup>-</sup> replaces some apical <sup>(4)</sup>O<sup>2-</sup> in synthetic germanium muscovite. This observation and compositional data suggest that at least some <sup>(4)</sup>Al is charge compensated by adjacent OH<sup>-</sup> replacing O<sup>2-</sup>. The <sup>(4)</sup>Al in micas is probably not charge coupled to octahedral substitutions on an ion by ion basis. However, Essene (1989) suggested that the tetrahedral sites should be omitted from mica models. The 12-fold site vacancies in many micas might be occupied by some form of H (e.g., Miller et al., 1991). H<sup>+</sup> deficiency in the OH<sup>-</sup> positions is almost certainly H<sup>+</sup> vacancies rather than OH<sup>-</sup> vacancies and is probably coupled to cation charge in

TABLE 4. Possible mole fraction models for some pelitic minerals in the FASH system

End-member	Composition	Activity model*
Muscovite	$KAl_2Si_3AlO_{10}(OH)_2$	$4 \cdot^{[A]}X_K \cdot^{[M2]}X_{Al}^2 \cdot^{[M1]}X_{Cl} \cdot^{[T]}X_{Al} \cdot^{[T]}X_{Si} \cdot X_{OH}^{w**}$
Annite	$KFe_3Si_3AlO_{10}(OH)_2$	$4 \cdot^{[A]}X_K \cdot^{[M]}X_{Fe}^3 \cdot^{[M]}X_{Al} \cdot^{[T]}X_{Si} \cdot X_{OH}^{w**}$
Almandine	$Fe_3Al_2Si_3O_{12}$	$^{[8]}X_{Fe}^3 \cdot^{[6]}X_{Al}^2 \cdot^{[4]}X_{Si}^3$
2H staurolite	$H_2Fe_2Al_2Al_8Si_6O_{48}$	$^{[T2]}X_{Fe}^2 \cdot^{[M4]}X_{Al}^4 \cdot^{[M1]}X_{Si}^3 \cdot^{[M2]}X_{Al}^8 \cdot^{[M3]}X_{Al}^2 \cdot^{[T1]}X_{Si}^6 \dagger$
6H staurolite	$H_6Al_4Fe_2Al_8Si_6O_{48}$	$^{[M4]}X_{Fe}^2 \cdot^{[M1]}X_{Al}^8 \cdot^{[M2]}X_{Al}^8 \cdot^{[M3]}X_{Al}^2 \cdot^{[T1]}X_{Si}^6 \dagger$
0H cordierite	$Fe_2Al_4Si_5O_{18} \cdot 0H_2O$	$^{[6]}X_{Fe}^2 \cdot (1 - X_{H_2O})$
2H cordierite	$Fe_2Al_4Si_5O_{18} \cdot 1H_2O$	$^{[6]}X_{Fe}^2 \cdot X_{H_2O}$

\* All Fe refers to Fe<sup>2+</sup>, except where noted.

\*\* For mica models, <sup>[T]Al</sup> avoidance is assumed, <sup>[T]X<sub>Si</sub></sup> = (Si - 2)/2, <sup>[T]X<sub>Al</sub></sup> = <sup>[T]Al</sup>/2, X<sub>OH</sub><sup>w</sup> = (OH/w)<sup>w</sup>, where w = OH + F. Essene (1989) suggested that the tetrahedral mica factors should be omitted. Circone and Navrotsky (1992) suggested <sup>[M]Al</sup> is mixed on a single site in phlogopite-eastonite.

† For staurolite models, <sup>[T2]X<sub>Fe</sub></sup> = <sup>([T2]Fe/n)</sup>, where n = <sup>[T2](Fe + Mg + Zn + Mn + Li + Al + Fe<sup>3+</sup>)</sup>.

octahedral layers above that of the Tschermak substitution (Dyar et al., 1993).

The staurolite mole fraction models and end-member formulas (Table 4) result in significant part from the efforts of Hawthorne et al. (1993a, 1993b, 1993c). The first three positions in the formula are coupled as demonstrated by their work. The best way to model a 2H staurolite end-member is with the mole fraction of vacancy on M4 (formerly U), with an additional correction for dilution of <sup>[4]Fe<sup>2+</sup></sup> by other ions on T2, and the best way to model a 6H staurolite end-member is with the mole fraction of <sup>[6]Fe<sup>2+</sup></sup> on M4. Even simple FASH staurolite samples resulting from experimental studies contain nonstoichiometric amounts of Fe<sup>2+</sup>-H<sup>+</sup> solid solution (Holdaway et al., 1993).

For cordierite, there has been a problem concerning the correct H<sub>2</sub>O content for the fully hydrous end-member. Carey and Navrotsky (1992) have shown that the cordierite-hydrous cordierite solid solution fits an ideal one-site model (Table 4).

These suggestions should make it clear that mole fraction models for many of these minerals will continue to evolve as additional information comes to light.

NONIDEALITY IN MINERALS

There is a tendency for petrologists to believe that many minerals may be modeled as ideal solid solutions, when in fact this is commonly not the case. In our view, ideality is merely a special case of nonideality, and some degree of nonideality is common in most solid solutions. When one sees indications of a solvus or irregular partitioning of major ions between mineral pairs, it is likely that there is nonideality. In our opinion, when there are no experimental data, it is better to estimate the nonideality from natural data than to assume ideality. A petrochemical analysis by Guidotti et al. (in preparation) may provide for the best muscovite-paragonite solvus information and shows clearly that the solvus is affected by phengite content; the Margules parameters for the 12-fold site in muscovite should be corrected for the new muscovite-paragonite data and for the effect of phengite component. Bhattacharya et al. (1988) showed that Fe-Mg mixing in cordierite is nonideal with computations based on natural

cordierite with garnet using the Ganguly and Saxena (1984) garnet mixing model. Much of this nonideality disappears if more recent garnet mixing and cordierite hydration data are incorporated into the approach. Fe-Mg end-members of biotite may also show some nonideality, which is not yet well understood. Hoisch (1991) has shown from natural occurrences that Ti and Al substitutions in biotite are nonideal solid solutions, and Circone and Navrotsky (1992) have confirmed Hoisch's conclusion for phlogopite-eastonite. Examples of probable nonideality between major end-members that have commonly been overlooked include iron-magnesium staurolite and hematite-ilmenite.

Even though there is some question regarding the strict applicability of the Margules approach, it seems to be useful in most cases, and it is far better than assuming ideality. There appear to be several inconsistencies in the literature regarding the nature of Margules equations for multicomponent systems. Mukhopadhyay et al. (1993) have derived all the equations for an excess parameter such as G<sup>XS</sup> and for RT ln γ in symmetrical and asymmetrical n-component systems from first principles using a Taylor series expansion. From a strictly mathematical standpoint, if the constituent binaries in a ternary system are symmetrical, there are no ternary interaction parameters. Both Helffrich and Wood (1989) and Mukhopadhyay et al. (1993) showed that, for a ternary asymmetric solution, if it becomes necessary to assume that ternary interaction parameters are zero for want of better information, we must be careful to use formulations that include all of the binary interactions. For an asymmetric regular ternary solution, G<sup>XS</sup> is given by

$$G^{XS} = X_1X_2(X_2W_{12} + X_1W_{21}) + X_1X_3(X_3W_{13} + X_1W_{31}) + X_2X_3(X_3W_{23} + X_2W_{32}) + X_1X_2X_3C_{123}$$

where

$$C_{123} = 1/2(W_{12} + W_{21} + W_{13} + W_{31} + W_{23} + W_{32}) - W_{123}.$$

It is far better to assume W<sub>123</sub> = 0 than to assume C<sub>123</sub> = 0 because C<sub>123</sub> is significantly based on the binary param-

**TABLE 5.** Recommended Margules parameters for garnet, per three cations

Interaction	$W_i$ (kJ)	$W_s$ (J/K)	$W_v$ (J/bar)*	Source**
Mg-Fe	6350	0	0.020	1
Fe-Mg	2080	0	-0.030	1
Mg-Ca	15000	39	0.177	2
Ca-Mg	56520	2.1	0.050	2
Fe-Ca	7770	0	0.099	3
Ca-Fe	-3270	0	0.064	3
Mg-Mn	0	0	0?	4, 5
Fe-Mn	0	0	0?	4, 6
Ca-Mn	0	0	0	3, 4
Mg-Fe-Ca	0?	0?	0.182	*

\* Values determined by statistical analysis of synthetic garnet molar volumes using data from Haselton and Newton (1980), Gelger et al. (1987), Wood (1988), Koziol and Newton (1989), and Koziol (1990).

\*\* Sources for  $W_i$ , and  $W_s$ : 1 = Hackler and Wood (1989); 2 = Wood (1988); 3 = Koziol (1990); 4 = Berman (1990); 5 = Wood (1991); and 6 = O'Neill et al. (1989).

eters. Comparison shows that although the equations of various authors appear to be quite different, most are the same and are, with few exceptions, correct.

The garnets represent an example of a four-component system that has been extensively studied for the past decade. The data used are from both experimental and natural occurrences. We have carefully reviewed the available results and arrived at what is probably the best overall set of Margules parameters for determining  $G^{xs}$  and  $V^{xs}$  (Table 5). One of the problems that arises in this type of analysis is the failure to adequately account for error in the data. This is important, as sometimes errors are greater in magnitude than the mean parameter because (1) experimental data were collected without proper design in the statistical sense, and (2) the number of data points is not statistically large enough to put tight constraints on the amounts of the errors. As a result, in some instances more complicated expressions have been advocated than are warranted by the data.

### EXCHANGE GEOTHERMOMETERS

Exchange geothermometers are especially useful for medium-grade pelites because they have low sensitivity to  $P$  and no sensitivity to  $X_{H_2O}$ . However, at granulite grade they are easily reset and may have serious difficulties. Although it still has some problems, the garnet-biotite geothermometer, corrected for at least garnet non-ideality, is by far the best exchange geothermometer. Ferry and Spear (1978) emphasized the kinds of rocks best suited and the error limitations of the method. For best results, graphite-bearing rocks should be used, and  $Fe^{3+}$  in both minerals should be accounted for, as done by Williams and Grambling (1990). Where garnet is present in medium-grade pelites, garnet-biotite geothermometry approaches an error of  $\pm 25$  °C under reducing conditions and a high biotite/garnet volume ratio. At high grades, or under conditions of resetting during cooling, accuracy is considerably worse. In appropriate rocks,  $T$  based on garnet-biotite geothermometry is probably more accurate

than most  $T$  based on more sophisticated thermodynamic data bases. This is because the thermometry is little affected by other intensive variables, and nonideality is corrected.

### GEOBAROMETERS

Several geobarometers have met with considerable success (Table 6). Most have the advantage of being reactions that involve no fluid component, which means that  $P$  may be estimated independently of  $X_{H_2O}$ . Almandine + muscovite + biotite + aluminum silicate has potential because it involves only major components, but it suffers from low  $\Delta V$  and  $\Delta S$  (Essene, 1989). Almandine + cordierite + sillimanite also has potential, mainly for high-grade rocks, but does involve  $H_2O$ . Ultimately, both  $P$  and  $T$  can be determined with this assemblage, providing something is known about  $X_{H_2O}$ . We are in the process of revising this geobarometer. The presence of garnet in all of these geobarometers emphasizes the importance of resolving garnet Margules parameters and the problem of obtaining  $P$  from garnet-absent pelites. Even with significant improvements in thermodynamic data, mole fraction models, and Margules parameters, some of these geobarometers may never be more accurate than  $\pm 0.5$  kbar.

### THERMODYNAMIC DATA AND DATA BASES

The most important single aspect of geothermobarometry is the quality of the thermodynamic data on which  $P$ - $T$  results are based. These data come from a combination of three sources: (1) calorimetric data, (2) experimental data, and (3) natural occurrences. Ideally, we would like to have agreement between these sources, but that is not common. The following cautions should be noted for deriving thermodynamic data: (1) Calorimetric enthalpy ( $H$ ) data derived from solution calorimetry tend to have errors larger than what can be obtained from the analysis of good experimental data. On the other hand, calorimetric entropy ( $S$ ), specific heat ( $C_p$ ), and X-ray diffraction molar volume ( $V$ ) data are likely to be more precise than  $H$ . (2) Methods of experimental studies should be checked carefully to be sure that the experiments represent true reversals of stable alternative assemblages and that experimental starting materials and products have been characterized as well as possible. (3) Each reversal should be independently judged, and conditions should be extended away from equilibrium to the limit of experimental error. We have found this to be especially important with the aluminum silicates, as seen below. (4) Comparison with natural assemblages should be a secondary process and should be done with extreme caution. (5) If natural assemblages are to be used for calibration, corrections should be made for mineral composition,  $Fe^{3+}$ , and fluid composition, where appropriate. The presence of graphite reduces the  $X_{H_2O}$  in fluid to 90% or less, depending on  $P$ - $T$  conditions. It is even possible that fluid in micaceous pelitic schists escapes more rapidly than in quartzites, and so  $P_{tot}$  in micaceous rocks would be slight-

TABLE 6. Some geobarometers for pelitic rocks\*

Geobarometer (from high- to low- <i>P</i> )	Reference	Comment
Almandine-rutile-ilmenite-aluminum silicate	Bohlen et al. (1983)	very good
Almandine-grossular-rutile-ilmenite-anorthite	Bohlen and Liotta (1986)	very good
Grossular-anorthite-aluminum silicate	Newton and Haselton (1981)**	very good
Pyrope-grossular-muscovite-anorthite-phlogopite	Ghent and Stout (1981)†	good
Almandine-grossular-muscovite-anorthite-annite	Ghent and Stout (1981)†	good
Almandine-muscovite-annite-aluminum silicate	McMullin et al. (1991)	good
Almandine-cordierite-aluminum silicate-H <sub>2</sub> O	Holdaway and Lee (1977)	needs work

\* Listed by end-member components for use in quartz-bearing rocks.  
 \*\* Also Koziol and Newton (1988).  
 † Also Hoisch (1990).

ly lower than that in adjacent quartzites, as suggested by Holdaway and Goodge (1990).

There are a number of possible naturally occurring pelitic assemblages whose presence or absence should serve as a test of the quality of thermodynamic data bases, provided corrections are made for mineral and fluid composition. These include (1) biotite + andalusite + muscovite + quartz, a common assemblage that should not occur, according to calculations based on the published version of the Holland and Powell (1990) data base (see also Powell and Holland, 1990); (2) cordierite + staurolite + muscovite + quartz, which does not occur in nature except in apparent disequilibrium or perhaps when stabilized by high Zn or Li in staurolite; (3) cordierite + garnet + muscovite + quartz, which can only occur if the garnet is stabilized by high Mn; (4) chloritoid + sillimanite + quartz, which has a narrow stability range in graphite-free, Fe-Al-rich rocks over a range of  $f_{O_2}$ ; and (5) paragonite + sillimanite + quartz, which has a narrow stability range in Na-Al-rich rocks. A necessary but not sufficient test of a thermodynamic data base is whether these conditions are met.

A problem with thermodynamic data bases in general is that, by their mathematical nature, they are self-consistent. Therefore, they tend to produce self-consistency among various reactions in a rock or group of related rocks. This self-consistency does not necessarily mean that the data base is accurate. It may very well be displaced in *P* and *T* from the correct position or be inconsistent with *P* and *T* determined from other bulk compositions and reactions.

An advantage of data bases is that retrieving *H* and *S* of minerals from experiments and from natural occurrences tends to correct for disorder and nonidealities that may not be easily corrected with direct calorimetric measurements on stoichiometric end-members. Examples are end-member disorder, minor amounts of solid solution such as 12-fold-site H or vacancy in micas, and partial replacement of Si by Al in staurolite.

Many of the important pelitic reactions used in data bases depend critically on aluminum silicate and, to some extent, on cordierite equilibria. Using studies since 1966, Holdaway and Mukhopadhyay (1993) have carefully evaluated all experimental work on aluminum silicates. If each reversal is judged independently, all the accept-

able reversals and half-reversals are totally consistent for each of the three phase boundaries (e.g., Fig. 2) and consistent with a triple point at  $504 \pm 20$  °C,  $3.75 \pm 0.25$  kbar. We also evaluated all the available molar volume data; our best estimates are given in Table 7. Kyanite, with only two determinations, needs more carefully determined unit-cell data on low-Fe<sup>3+</sup> samples. Using these results and the calorimetric data of Robie and Hemingway (1984) and Hemingway et al. (1991), we have refined *H* and *S* (Table 7). These values are recommended for aluminum silicate thermodynamic data.

The iron cordierite stability results of Holdaway and Lee (1977), Weisbrod (1973), and Richardson (1968) have been criticized on theoretical grounds. We now realize that in our work, unstable hercynite in the synthesized cordierite and almandine favored growth of metastable

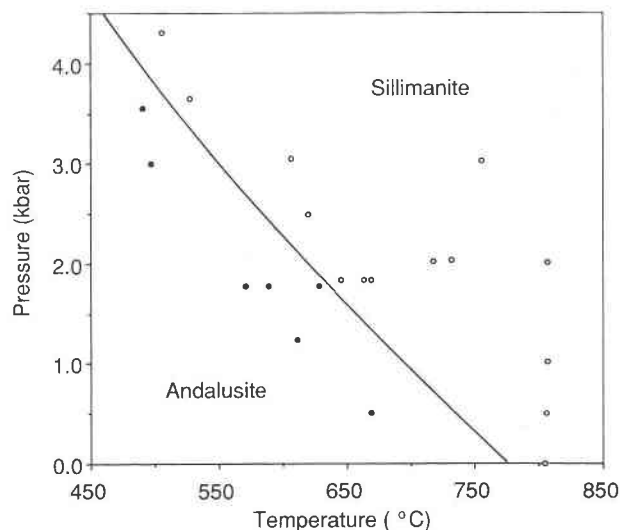


Fig. 2. Pressure-temperature phase diagram for the andalusite-sillimanite reaction showing all valid reversals and half-reversals adjusted to their error limits away from the phase boundary. Closed symbols = andalusite-stable half-reversals; open symbols = sillimanite-stable half-reversals. This boundary and similarly determined boundaries for kyanite + andalusite and kyanite + sillimanite are consistent with the thermochemical data given in Table 7. After Holdaway and Mukhopadhyay (1993).

**TABLE 7.** Thermodynamic data for aluminum silicates\*

Mineral	Molar volume (J/bar)	Entropy (J/mol-K)	Enthalpy (kJ/mol)
Kyanite	4.408(2)	82.86(50)	-2593.70(300)
Andalusite	5.146(2)	91.60(52)	-2589.66(300)
Sillimanite	4.984(2)	95.08(52)	-2586.37(300)

\* Holdaway and Mukhopadhyay (1993), based on analysis of experimental reversal data since 1966 and on calorimetric data of Robie and Hemingway (1984) and Hemingway et al. (1991).

cordierite, especially at lower  $T$ . Mukhopadhyay et al. (1991, in preparation) have recently redetermined this equilibrium (Fig. 3) and found it to have a positive slope. At 600 °C, equilibrium is 1.7 kbar lower than in previous determinations. This now will form the basis of a recalibrated cordierite-almandine-sillimanite geobarometer.

In a further effort to constrain thermodynamic data for pelitic minerals, we have retrieved thermodynamic data for 2H and 6H stoichiometric iron staurolite end-members from experimental reversal results. One major problem with staurolite is that neither natural nor synthetic staurolite is ever stoichiometric (Holdaway et al., 1991, 1993). Even simple FASH staurolite has solid solution on as many as six independent sites. Thermodynamic data reported previously have no real validity for the calculation of staurolite stability relations because they fail to take into account the  $\text{Fe}^{2+}$ - $\text{H}^+$  substitution (Hawthorne et al., 1993a), somewhat analogous to that of hydrogarnet. Our first step was to conduct multiple linear regressions on good quality unit-cell data of completely analyzed natural staurolite to estimate molar volumes for the two FASH end-members (Holdaway et al., 1993). Two models, one holding Si and Al constant at average values and using an eight-component ( $\text{Fe}^{2+}$ , Mg, Zn, Li, Mn, Ti,  $\text{Fe}^{3+}$ , □) fictive end-member approach (Fig. 4), and one using all ten elements (Si, Al,  $\text{Fe}^{2+}$ , Mg, Zn, Li, Mn, Ti,  $\text{Fe}^{3+}$ , H) agree and allow estimation of molar volumes for stoichiometric end-members:  $\text{H}_2\text{Fe}_2\text{Al}_8\text{Si}_8\text{O}_{48} = 44.61 \pm 0.03$  J/bar,  $\text{H}_6\text{Fe}_2\text{Al}_{18}\text{Si}_8\text{O}_{48} = 44.17 \pm 0.03$  J/bar. We have fitted experimental data in the FASH system to estimate thermodynamic data for 2H and 6H staurolite, allowing  $\text{H}^+$  content of staurolite to vary as a function of  $P$  and  $T$  (Fig. 5). The  $P$ - $T$  field of staurolite + quartz may be contoured on the basis of the  $\text{H}^+$  content of staurolite, depending on whether staurolite coexists with almandine or aluminum silicate. Points where these two sets of curves intersect for a given  $\text{H}^+$  content define the limits of staurolite + quartz stability. This approach does not explain the failure of agreement between experimental and natural staurolite  $P$ - $T$  estimates (e.g., Pigage and Greenwood, 1982; Holdaway et al., 1988). A future project will attempt to show whether or not staurolite T2 sites exhibit strongly nonideal behavior, as suggested by Mukhopadhyay et al. (1990).

There are four main thermodynamic data bases: (1) Helgeson et al. (1978), (2) Berman (1988, 1991) and Brown et al. (1988) (Ge0-Calc, most recently updated in Janu-

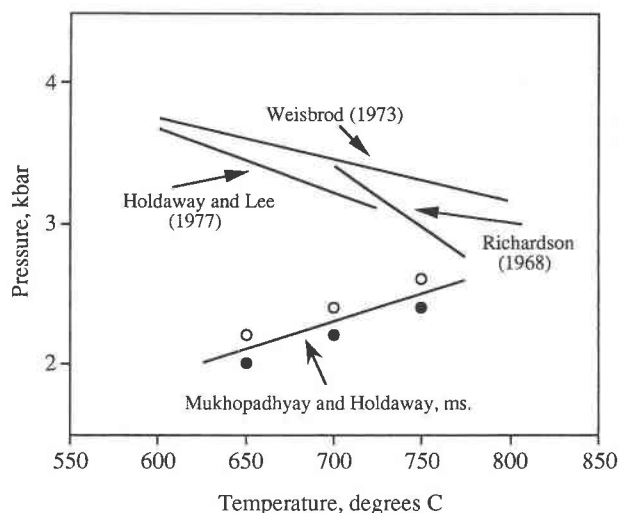


Fig. 3. Experimental iron cordierite stability diagram determined by Mukhopadhyay. Closed symbols = iron cordierite stable; open symbols = almandine, sillimanite, quartz, and  $\text{H}_2\text{O}$  stable. Previously determined iron cordierite phase boundaries are given for comparison. After Mukhopadhyay et al. (1991).

ary, 1992), (3) Spear and Cheney (1989), and (4) Powell and Holland (1988) and Holland and Powell (1990) (Thermocalc, most recently updated in September, 1992). Uncritical use of these data bases may lead to substantial errors for the following reasons: (1) Various reactions occurring in a single rock will tend to plot in a self-consistent fashion but may be incorrect because of systematic errors in the thermodynamic data. (2) Many  $P$ - $T$  slopes are positive, and so intersections may have large errors. (3)  $X_{\text{H}_2\text{O}}$  may have been different than that assumed, shifting dehydration curves to various extents. (4) Failure to properly account for nonideality may have produced errors. (5) Added weight may not have been given to the best-known reactions or thermodynamic data. We recommend extreme caution in using these data bases. The recently developed TWEEQU method (Berman, 1991), which draws a  $P$ - $T$  line for every possible end-member reaction occurring in a rock, can also be misleading if equal weight is given to each line and if the sole criterion for the quality of thermodynamic data is a tight cluster of intersections.

We have also observed that in some studies that apply data bases, not enough attention is paid to field relations, petrology, and geologic history. In such studies, the treatment of the geologic environment is so brief as to be misleading. Two examples from Maine illustrate our concern: A recent  $P$ - $T$  study of samples from an area near Augusta (Berman, 1991, p. 846) stated that the region suffered a single metamorphic event, when in fact papers on the area (Novak and Holdaway, 1981; Holdaway et al., 1982, 1988) demonstrated that there have been at least two events. The analysis shows that the high-grade rocks formed at higher  $P$  and appears to show that  $P$  increases with grade. The medium-grade metamorphic



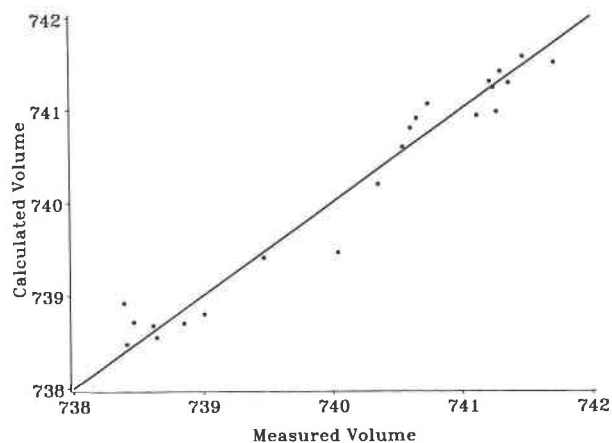


Fig. 4. Plot of measured vs. calculated molar volume for 22 staurolite specimens using a multiple linear regression model in which compositional variables are fictive end-members  $\text{Fe}^{2+}$ , Mg, Zn, Li, Mn, Ti,  $\text{Fe}^{3+}$ , and □. Si and Al are assumed to have average values. After Holdaway et al. (1993).

events (producing andalusite and sillimanite) are Acadian, and the high-grade metamorphism (locally producing kyanite) is late Paleozoic, and the region was more deeply buried at that time. In an analysis of rocks by Holdaway et al. (1988) in an area between Augusta and Rangeley (McMullin et al., 1991, p. 901), later plutonism and post-metamorphic folding are advocated as causes for  $P$  variation. In fact, the area suffered posttectonic metamorphism, and the observed sharp reentrants in isograds are the result of overlapping nonsynchronous adjacent granitic heat sources (Holdaway et al., 1982, 1988). All the metamorphism is synchronous with plutonic intrusion, and intrusion occurred over at least 75 m.y., during which time  $P$  increased significantly. In both of the cases cited above,  $P$  increased from north to south and with decreasing age of the metamorphism.

The application of a data base to only a very few specimens from an area is of concern to us. These specimens may not be representative in their degrees of equilibration, or they might represent limiting values of the  $P$  and  $T$  range or mineral compositions.

As an example of the kinds of problems that may occur, we use a contact metamorphic assemblage from western Maine at the north end of the Lexington batholith, studied by Dickerson and Holdaway (1989). The as-

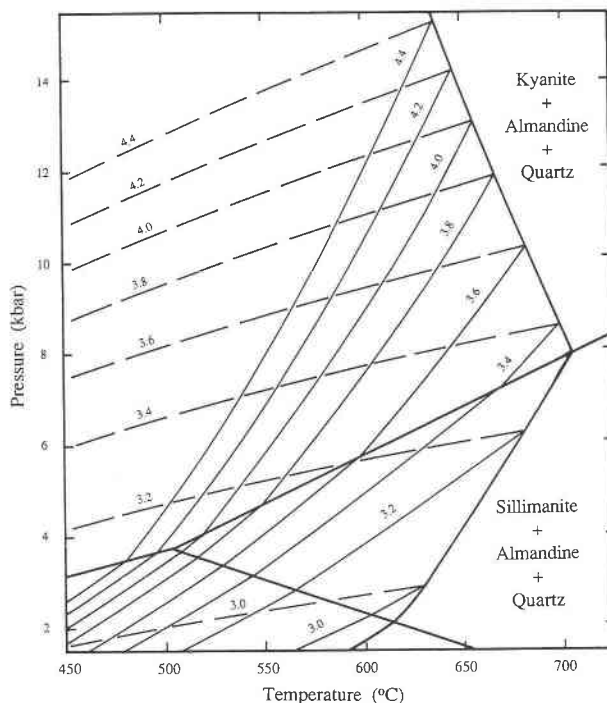


Fig. 5. Phase diagram for FASH staurolite with variable H from 2.8 to 4.4 coexisting with quartz. Heavy lines show aluminum silicate stability relations and the limit of staurolite-quartz stability. Solid contours show H content of staurolite coexisting with aluminum silicate, dashed contours show H content of staurolite coexisting with almandine. Limit of staurolite-quartz stability occurs where contours meet for a given H content. After Holdaway et al. (in preparation).

semblage, seen in several specimens, is andalusite + sillimanite + muscovite + potassium feldspar + cordierite + biotite + quartz + graphite, lying on Carmichael's (1978) bathograd. The first occurrence of sillimanite and the first occurrence of sillimanite + potassium feldspar consistently are found in the same place in the field. Dickerson and Holdaway (1989) estimated metamorphic conditions of 2.35 kbar, 600 °C, using three independent experimental  $P$ - $T$  reactions. One problem with this locality is the total absence of garnet, the result of low  $P$ . The Berman data base (1988, updated in 1992) gave similar  $P$ - $T$  conditions (Table 8). Berman's unpublished cordierite data do not account for  $\text{H}_2\text{O}$  and are provisional. His iron cordierite data are based on experimental results

TABLE 8. Estimates of  $P$ - $T$  conditions of formation for a rock from Maine\*

$P$ (kbar)	$T$ (°C)	Source	Details
2.35	600	Dickerson and Holdaway (1989)	three experimental reactions, activity-corrected
2.45	600	Berman (1988, updated 1992)	including iron cordierite, excluding magnesium cordierite
2.25	595	Berman (1988, updated 1992)	excluding all cordierite, aluminum silicate, muscovite only
3.00	635	Holland and Powell (1990, updated 1992)	including iron cordierite and magnesium cordierite

\* Mineral assemblage = andalusite + sillimanite + muscovite + potassium feldspar + cordierite + biotite + quartz + graphite. Locality = north lobe of Lexington batholith, Maine (Dickerson and Holdaway, 1989).

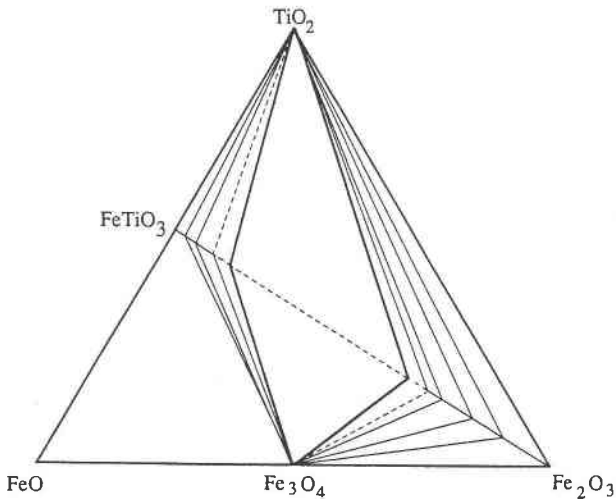


Fig. 6. FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> diagram showing possible hematite-ilmenite phase relations at about 600 °C. The dashed line is a schematic O<sub>2</sub> isobar.

of Mukhopadhyay et al. (1991) and can be expected to be most accurate close to the experimental  $P$ - $T$  conditions. The Holland and Powell data base (1990, updated in 1992) gave conditions at higher  $P$  and  $T$  (Table 8). Cordierite data in this data base account for H<sub>2</sub>O in cordierite but have not been adjusted to the new iron cordierite experimental results. In our opinion, the main problem with the Holland and Powell data base is that their thermodynamic data for aluminum silicate are not based on a careful analysis of all available experimental data (e.g., see Holdaway and Mukhopadhyay, 1993).

For the same assemblage in the Ballachulish aureole, Pattison (1992) deduced conditions of 3 kbar, 645 °C, using, in part, thermodynamic data for cordierite. Two differences between the Lexington and Ballachulish localities are that in most specimens the Ballachulish assemblage does not contain graphite and that in several specimens andalusite appears to have been stabilized by high Fe<sup>3+</sup>. Pattison assumed the fluid was pure H<sub>2</sub>O. We do not believe these conditions can be defended as a point on the andalusite-sillimanite  $P$ - $T$  boundary, as advocated by Pattison (1992).

In summary, much more careful work is needed before petrologists can depend on the use of thermodynamic data bases for  $P$  and  $T$  estimation. Eventually one should be able simply to use the data bases, with appropriate mole fraction models and corrections for nonideality, to evaluate  $P$  from the various geobarometers given in Table 6. Until that time, these data bases should not be used without careful critical examination of the results.

### FLUID COMPOSITION

In sulfide-absent medium-grade pelitic rocks, the predominant fluid species are H<sub>2</sub>O and CO<sub>2</sub>, and, where graphite is present, CH<sub>4</sub>, as well. Qualitative arguments to indicate the approximate composition of pelitic fluids in-

clude the following: (1) In many medium-grade pelitic terranes, coexisting thin metacarbonate units commonly exhibit minerals like grossular or epidote and sometimes contain no carbonate, indicating high  $X_{\text{H}_2\text{O}}$  even in the metacarbonate units. (2) Many metamorphic terranes have granitic heat sources, which are by nature H<sub>2</sub>O-rich. (3) The dominant prograde H<sub>2</sub>O-consuming mass-transfer reaction in most graphitic pelites is the reaction of H<sub>2</sub>O with graphite  $\text{C} + \text{H}_2\text{O} = \text{CO}_2 + \text{CH}_4$  and when this reaction, combined with simple dehydration reactions, controls fluid composition, it controls it near 80% H<sub>2</sub>O, 10% CO<sub>2</sub>, 10% CH<sub>4</sub>, and at  $f_{\text{O}_2}$  values near the QFM buffer, depending on  $P$  and  $T$ , as shown by Ohmoto and Kerrick (1977). (4) This observation is confirmed by the highly reducing nature of most graphitic schists, with no hematite component in the ilmenite. We can take advantage of this by assuming that the graphite + H<sub>2</sub>O equilibrium dominates, with either a closed system or one partially open to fluid movement, which allows  $X_{\text{CO}_2}$  to be equal to or somewhat greater than  $X_{\text{CH}_4}$ . Using this method, Holdaway et al. (1988) assumed  $X_{\text{CO}_2}$  was up to ten times  $X_{\text{CH}_4}$ . This approach enables us to estimate the composition of pelitic fluids in graphitic rocks. It will not work well if the graphitic rocks are at all oxidizing, with hematite component in the ilmenite, or if the pelites are deep and undergoing anatexis. The accuracy of the results also depends on the accuracy of the thermodynamic data and mixing models for fluids. Great strides have recently been made concerning thermodynamic data for fluids and fluid solutions, especially by Shi and Saxena (1992) and by Shi (1992). At present the above approach may be the best way to estimate fluid composition in appropriate pelites.

This approach can be strengthened by an accurate, independent determination of  $f_{\text{O}_2}$  because all fluid compositional variables in graphitic schists are uniquely determined by knowing  $P$ ,  $T$ , and  $f_{\text{O}_2}$ , and the assumption of subequal  $X_{\text{CO}_2}$  and  $X_{\text{CH}_4}$  becomes unnecessary. We are hoping to determine the hematite-ilmenite solvus experimentally. The schematic plot of Figure 6 incorporates what we know from petrologic observations at about 600 °C and illustrates that the system is nonideal and has a solvus. The dashed line is a schematic O<sub>2</sub> isobar, which shows that for a constant composition of ilmenite,  $f_{\text{O}_2}$  varies with the nature of the coexisting phase. Experimental determination of this system should enable one to determine  $f_{\text{O}_2}$  for the ilmenite + rutile equilibrium,  $2\text{Fe}_2\text{O}_3_{\text{ss in ilm}} + 4\text{TiO}_2 = 4\text{FeTiO}_3_{\text{ss}} + \text{O}_2$ , or the ilmenite + magnetite equilibrium,  $6\text{Fe}_2\text{O}_3_{\text{ss in ilm}} = 4\text{Fe}_3\text{O}_4 + \text{O}_2$ , in rocks, and to estimate a limited range of  $f_{\text{O}_2}$  for ilmenite-only assemblages by constraining  $f_{\text{O}_2}$  from the ilmenite + rutile and ilmenite + magnetite equilibria.

The alternative approach for determining fluid composition is to use geothermometers for  $T$  estimates, use fluid-absent geobarometers for  $P$  estimates, and, with the estimated  $T$  and  $P$ , use dehydration reactions to estimate  $X_{\text{H}_2\text{O}}$  from the compositions of coexisting phases. In some cases the results of such efforts indicate  $X_{\text{H}_2\text{O}}$  values far

from the predicted range of 70–90% in sulfide-absent graphitic pelites. That might be taken to indicate that such metamorphic rocks have a wide range of fluid compositions. We believe it commonly indicates a compounding of errors in  $T$ ,  $P$ , thermodynamic data, mole fraction model, and corrections for nonideality.

In our opinion, when we reach the point where various dehydration equilibria in graphitic schists independently and consistently give us reasonable values of  $X_{\text{H}_2\text{O}}$ , then we will be making real progress in geothermobarometry and homing in on the best thermodynamic data for all the minerals. Knowledge of fluid compositions can then serve as a check on the quality of the geothermobarometry and the thermodynamic data. At that stage, we will be able to say much more about the nature of fluids in pelitic rocks and perhaps test models for fluid behavior and movement.

### SUMMARY AND RECOMMENDATIONS

In summary, we recommend the following: (1) We should use all information available to determine the best possible stoichiometry and site assignments. (2) We should carefully think out mole fraction models and continue to experiment with and test them. (3) Nonideality should be evaluated whenever possible. (4) Thermodynamic data bases should be continually reevaluated, should be treated with some degree of skepticism, and should be applied with care. (5) Fluid reactions should be used to test and refine our methods. (6) Consistent with the times, we must be willing to accept change.

As we home in on the best activity models, values for thermodynamic data, and corrections for nonideality, it should be possible to approach accuracies of  $\pm 25^\circ\text{C}$ ,  $\pm 250$  bars, and  $\pm 10\%$   $X_{\text{H}_2\text{O}}$  in low- to medium- $P$  rocks.

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This work is dedicated to the memory of Patricia Piercy Holdaway, 1937–1991.

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