# Stability of Andalusite and Sillimanite and the Al<sub>2</sub>SiO<sub>5</sub> Triple Point: Constraints from the Ballachulish Aureole, Scotland<sup>1</sup>

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#### ABSTRACT

Andalusite (And) and sillimanite (Sil) occur in well-defined zones in the Ballachulish aureole. In most of the aureole's sillimanite-bearing rocks, sillimanite grain diameters range from  $\leq 2 \,\mu$ m to  $\geq 10 \,\mu$ m. The boundary between prograde andalusite and prograde sillimanite is constrained to a zone of max. 30 m width upgrade of the muscovite + quartz = andalusite + K-feldspar + H<sub>2</sub>O reaction isograd. This boundary is interpreted to correspond to the And=Sil equilibrium. The common occurrence of andalusite well upgrade of the first occurrence of sillimanite is ascribed to sluggish kinetics of the polymorphic inversion. The *P*-*T* position of the And=Sil equilibrium in the aureole is estimated as  $645 \pm 20^{\circ}$ C and  $3.0 \pm 0.4$  kbar, based on a combination of (1) location of the Ms + Qtz = And + Kfs + H<sub>2</sub>O reaction, corrected for non-end member fluid and mineral compositions, and (2) independent pressure estimates obtained from equilibria in metapelites, marbles, calcsilcates, and granitoids, all in excellent agreement. The effects of grain size and minor element content of andalusite and sillimanite on the equilibrium appear negligible. From this *P*-*T* constraint, the And=Sil equilibrium was extrapolated, using entropy and volume data, to intersect the overlapping uncertainty envelopes for the Ky=And and Ky=Sil equilibria, giving an estimate of the triple point of 4.5 ± 0.5 kbar, 550 ± 35°C, midway between Richardson's and Holdaway's determinations, and satisfying the petrological criteria used to support either.

#### Introduction

The location in P-T space of the andalusitesillimanite equilibrium remains a contentious issue in petrology (Holdaway 1971; Greenwood 1972; Day and Kumin 1980; Salje 1986; Newton 1987; Kerrick 1990). The location of the equilibrium is of paramount importance in defining baric series in metamorphosed pelitic rocks (e.g., Carmichael 1978; Harte and Hudson 1979), because its intersection at high angles with the kyanite(Ky) = sillimanite(Sil) and kyanite = andalusite(And) equilibria provides an important constraint on the location of the Al<sub>2</sub>SiO<sub>5</sub> triple point. However, the free energy difference between and alusite and sillimanite is so small that unambiguous experimental determination of the boundary has remained elusive. Some might argue that, because subtle energetic effects in either or both of the polymorphs may significantly perturb the equilibrium, attempts to constrain the equilibrium are fruitless. However, the fact that and alusite and sillimanite zones from

<sup>1</sup> Manuscript received March 18, 1991; accepted March 3, 1992.

different low-pressure baric series in nature show consistent patterns with respect to other isograds (e.g., Pattison and Tracy 1991) argues for a reasonably well-defined boundary, if not a unique one.

Unfortunately, substantially conflicting experimental determinations (Richardson et al. 1969; Holdaway 1971) and a controversial study by Salje (1986) have resulted in considerable latitude in the positioning of the equilibrium. Minor changes in the free energy of either of the polymorphs, which can cause a significant displacement of And = Sil, may have no significant effect on the position of other equilibria with higher free-energy changes (e.g., Richardson et al. 1969; Holland and Powell 1985; Berman 1988). In principle, it is possible to calculate the position of the And = Sil equilibrium and the Al<sub>2</sub>SiO<sub>5</sub> triple point from the location of the Ky = And and Ky = Sil equilibria (e.g., Newton 1966b; Bohlen et al. 1991). Because the And = Kyand Ky=Sil equilibria have similar slopes, however, even minor uncertainties in their location result in substantial uncertainty in the calculated And=Sil equilibrium and triple point (e.g., New-

<sup>[</sup>Journal of Geology, 1992, volume 100, p. 423-446] © 1992 by The University of Chicago. All rights reserved. 0022-1376/92/10004-005\$1.00

ton 1966b; Kerrick 1990, his fig. 3.46); thus, precise determination of the And = Sil equilibrium may be beyond the resolution of existing thermodynamic data.

This paper suggests that the And = Sil equilibrium may require a calibration based on natural data, because only in nature may the time scales be sufficient for the subtle energetic differences between the polymorphs to manifest themselves. Provided here is an estimate of the P-T location of the And = Sil equilibrium based on its occurrence in the Ballachulish thermal aureole, Scotland (Voll et al. 1991). A distinction is made between the occurrence of the andalusite-sillimanite polymorphic inversion and the stability fields of the two polymorphs. Prograde sillimanite first occurs at or immediately upgrade of the muscovite + quartz =andalusite + K-feldspar + H<sub>2</sub>O reaction isograd. Because the P-T location of the Ms + Qtz breakdown reaction is relatively uncontroversial and is not significantly displaced due to solid solution in the phases in the aureole, an estimate of a point on the And = Sil equilibrium can be made, provided a precise pressure estimate can be made. The equilibrium is then extrapolated using entropy and volume data (Hemingway et al. 1991) to provide an estimate for the location of the Al<sub>2</sub>SiO<sub>5</sub> triple point.

## Previous Determinations of the Andalusite-Sillimanite Equilibrium

**Phase Equilibrium Experiments.** Several experimental calibrations of the And = Sil equilibrium have been published (see review in Kerrick 1990). The two most widely cited are those of Holdaway (1971) and Richardson, Gilbert and Bell (1969), hereafter referred to as "H" and "R." These differ by about 150°C, with the R curve at higher temperature. Most subsequent placements of the equilibrium lie between the H and R curves (Kerrick 1990). Day and Kumin (1980), in a thermodynamic analysis of the R and H data, concluded that an uncontroversial choice between the two could not be made.

Of the two studies, Holdaway's (1971) experiments are generally favored (e.g., Robie and Hemingway 1984). Richardson et al.'s results are questioned because of the presence of fibrolite (Fib; fine-grained sillimanite) mixed in with the sillimanite starting material (Holdaway 1971), and/or the grain size diminution of sillimanite due to intense grinding of Richardson et al.'s run materials (Newton 1969; Kerrick 1990). Because of the small entropy change of the And = Sil reaction (ca. 3-4 J/K-mol, using the thermodynamic data of Hemingway et al. 1991), slight differences in the free energy of the two polymorphs can have a large effect on the temperature of the equilibrium. For example, a 0.1 KJ/mol increase in the free energy of sillimanite results in an up-temperature displacement of the curve at 3 kbar of about 30°C. Fibrolite is thought to have a higher free energy than coarse-grained sillimanite, principally because of the non-negligible contribution of grain boundary energy arising from its very fine grain size (Holdaway 1971; Kerrick 1990; Hemingway et al. 1991). Thus, the position of the Richardson et al. And = Sil(Fib) equilibrium at higher temperatures than the Holdaway And=Sil determination appears to be explained by the higher free energy of fibrolite relative to coarse sillimanite (figure 1a). Nevertheless, some aspects of the Holdaway (1971) And = Sil experiments have also been questioned (see critique in Kerrick 1990).

**Calorimetry.** Heat of solution measurements were made by Topor et al. (1989) on andalusite, coarse sillimanite, and fibrolite. Unfortunately, the uncertainties on derived enthalpies for the phases  $(\pm 0.7-0.9 \text{ KJ})$  are too large to improve the existing constraints on the And = Sil equilibrium. Topor et al.'s results suggested that fibrolite has a higher enthalpy than coarse sillimanite, although the differences were within experimental uncertainty.

Salje (1986) measured heat capacities of natural andalusite, coarse sillimanite, and fibrolite to obtain standard entropies and combined these data with available volume data and the 1 atm bracket of Weill (1966) to calculate a range of And=Sil curves for different types of sillimanite. He concluded that there is a continuous And = Sil reaction interval, with the lower temperature boundary applicable to coarse defect-free sillimanite and the higher temperature boundary (almost 300°C higher at 3 kbar!) appropriate for defect-richer fibrolitic sillimanite. In contrast, Kerrick (1986) found no evidence for energetically significant variations in defect density of natural sillimanite and fibrolite. Kerrick (1990) and Hemingway et al. (1991) have questioned some of the theoretical and experimental aspects of Salje's study.

Nevertheless, Salje's study has been used by some (e.g., Powell and Holland 1990) to argue for "considerable flexibility" in the position of the And = Sil boundary. However, the consistency in distribution of And and Sil in relation to other mineral reactions in a large number of low-pressure







Figure 1. Two schematic isobaric G-T diagrams showing possible relations between andalusite, sillimanite and fibrolite. (a) Equilibrium. Fibrolite is assumed to have a higher free energy than coarse-grained sillimanite, primarily due to non-negligible grain boundary energy arising from its fine grain size. Consequently, the (metastable) And = Fib equilibrium lies at higher temperatures than the And = Sil equilibrium. (b) Kinetic overstep. Paths A and B represent possible paths followed during heating of a natural andalusite-bearing metamorphic rock. Path A represents the metastable persistence of andalusite into the sillimanite stability field due to sluggish kinetics of the polymorphic inversion. At some temperature above the And = Sil equilibrium, the kinetic barriers are overcome and sillimanite grows directly from andalusite. Path B represents the formation of fibrolite from a devolatilization reaction involving matrix minerals other than andalusite: due to more favorable kinetics, fibrolite may form even when at the same temperature and alusite remains effectively inert. As temperature increases, fibrolite recrystallizes to the more stable coarse-grained sillimanite.

metapelitic sequences, representing a wide range of grain sizes and heating rates (Pattison and Tracy 1991), argues for a considerably more discrete transition than suggested by figure 3 of Salje (1986).

Distribution of Andalusite, Sillimanite, and Fibrolite in Nature. In contrast to laboratory-based studies, which indicate that the And = Fib equilibrium occurs at higher temperatures than the And=Sil equilibrium, evidence from natural low-pressure metapelitic sequences suggests that, upgrade of the andalusite zone, fibrolite generally occurs at lower grade than coarse sillimanite (e.g., Pitcher and Read 1959; Naggar and Atherton 1970; Speer 1982; Berg and Docka 1983; Kerrick 1987; Vernon 1987; Kerrick and Woodsworth 1989; Pattison and Tracy 1991). As grade increases, most textural relationships suggest that coarse-grained sillimanite has replaced fibrolite (Chinner 1961; Naggar and Atherton 1970; Vernon 1987). These observations suggest that, even though fibrolite has a higher free energy and is therefore less stable than sillimanite (figure 1a), its formation in many rocks appears to be kinetically favored over coarse sillimanite. The higher free energy of the fine-grained fibrolite crystals probably explains the tendency for fibrolite to recrystallize to the coarser-grained, more stable sillimanite as grade increases (Vernon 1987; see figure 1*b*).

**Extrapolation from Laboratory to Nature.** Extrapolation of laboratory results on the And = Sil equilibrium to natural occurrences of the two polymorphs is complicated by differences between the minerals used in the runs and those found in nature. These include grain size, minor element content (Grambling and Williams 1985; Kerrick and Speer 1988), non-stoichiometry, defect density, and order-disorder, although as argued by Kerrick (1986; 1990) and Hemingway et al. (1991), the last three may generally be negligible.

Because of the small free energy change of the And = Sil reaction, kinetic effects may also be important. The difference in time scales between laboratory experiments, ca.  $10^{-1}$  yr, and natural contact or regional metamorphic events, ca.  $10^{5}-10^{7}$  yr, is 6–8 orders of magnitude. Given the ubiquitous evidence for disequilibrium coexistence of the two polymorphs in nature, the numerous subtle but possibly significant energetic effects that could influence experimental determinations (Kerrick 1990), and the relatively short experimental run times possible, it may be overly optimistic to expect that the And = Sil equilibrium can be satisfactorily (e.g., to better than  $\pm 30^{\circ}$ C) and *unambiguously* bracketed in experimental studies.

Calibration by the Use of Natural Parageneses. Given the above considerations, natural parageneses provide an important means of constraining the And=Sil equilibrium. Schuiling (1957) and Hietanen (1967) estimated the position of the And = Sil equilibrium and the  $Al_2SiO_5$  triple point from natural parageneses and existing phase equilibrium data; Schuiling's estimates are close to the H determinations, whilst Hietanen's estimates are close to the R determinations. Greenwood (1976) expressed a preference for Holdaway's experiments, but ultimately turned to natural parageneses for his estimate of the And = Sil P-T boundary, which he placed between the H and R curves, closer to the R curve. Vernon (1982, p. 78), in his study of low-pressure metapelitic sequences in the Wongwibinda area, SE Australia, noted that the H and R curves are both controversial, and favored an intermediate curve which "appears to fit the Wongwibinda [petrological] observations and interpretations best." Holland and Powell (1985, p. 350), who place the And = Sil boundary midway between the H and R curves, "prefer to exclude [experimental data on And = Sil altogether, rather than make the invidious choice of which experimental study to incorporate"; the estimated position and uncertainty of their boundary "adequately reflect our petrological prejudices." Kerrick (1990, p. 106), in concluding his chapter on the phase equilibria of the  $Al_2SiO_5$  polymorphs, stated that "it is ironic that this chapter concludes by turning to fieldoriented studies."

#### **Distinction between Fibrolite and Sillimanite**

Considerable importance has been attached to the distinction between fibrolite and coarse-grained sillimanite in natural rocks (Kerrick 1987, 1990). Kerrick and Speer (1988) proposed the following arbitrary distinction between sillimanite and fibrolite based on thickness of prisms measured normal to the *c*-axis: grain diameters <10  $\mu$ m represent fibrolite, whereas grain diameters >10  $\mu$ m represent sillimanite.

A different criterion is proposed here, based on a grain size that causes a significant displacement of the And = (Sil,Fib) equilibrium. A grain boundary energy increment of 100 J/mol results in an uptemperature displacement of the And = (Fib,Sil) boundary of about 30°C, comparable to uncertainties in experimentally determined devolatilization reactions (see diagrams in Berman 1988) and somewhat better than uncertainties in common geothermometers (e.g., Grt-Bt, Ferry and Spear 1978). A molar grain boundary energy of 100 J/mol corre-

sponds to a grain diameter of 1–3 μm, according to the grain boundary energy models of Kerrick (1990). Kerrick's preferred grain boundary energy estimate of 1000 ergs/cm<sup>2</sup> corresponds to a grain diameter of about 2 µm, which is proposed here as the grain size distinction between fibrolite (finer) and sillimanite (coarser). An alternative boundary might be the grain size at which grain boundary energy begins to increase asymptotically, namely ca. 0.5  $\mu$ m (figure 7.5 of Kerrick 1990); however, this corresponds to grain boundary energies of 200-600 J/mol, which cause excessive displacements of And = (Fib,Sil) of  $60-180^{\circ}$ C. Optically, prisms of 2 µm can be identified as discrete crystals at 500x, in contrast to the hair-like crystals in fibrolite aggregates that cannot be distinguished individually.

Many rocks contain sillimanite/fibrolite aggregates in which there is a continuum of grain sizes that span the 2  $\mu$ m boundary (e.g., figure 2); in such cases, "sillimanite + fibrolite" may be an appropriate description. In the author's experience, most rocks that *appear* to contain only fibrolite, have sillimanite grain diameters typically ranging from <0.5  $\mu$ m to >10  $\mu$ m.

In the Ballachulish aureole, most of the sillimanite has grain diameters  $<10 \ \mu m$  but  $>2 \ \mu m$ (table 1 and figures 5–10). It typically occurs in discrete crystals and crystal aggregates, less commonly in mats and felts characteristic of fibrolite. Using the proposed grain size criterion above, most of the sillimanite at Ballachulish is best described as fine-grained sillimanite.

## Petrography of Andalusite and Sillimanite at Ballachulish

The Ballachulish Igneous Complex and Aureole. The Ballachulish Igneous Complex and aureole have been the focus of a multidisciplinary study on equilibrium and kinetic aspects of contact metamorphism (Voll et al. 1991). The igneous complex is a  $412 \pm 28$  Ma,  $4 \times 7$  km<sup>2</sup> composite, calcalkaline pluton emplaced in Dalradian metasediments (Weiss and Troll 1989; Pattison and Voll 1991). The pluton consists of a monzodioritequartz diorite envelope intruded by a central granite (figure 3). The emplacement temperatures of the envelope and the later granite were ca.  $1100^{\circ}$ C and 900–850°C, respectively (Weiss and Troll 1989).

Metapelitic mineral assemblage zones in the contact aureole, in order of increasing grade, include (1) Chl  $\pm$  Bt  $\pm$  Grt (regional grade protolith), (2) Crd + Bt + Chl, (3) Crd + Bt, (4) Crd + Kfs or



**Figure 2.** Photomicrograph of fibrolitic sillimanite in a dense mat of hair-like crystals replacing biotite (from Mt. Roberts Formation, south of Castlegar, B.C.). Most crystal diameters are  $<0.5 \mu$ m, with the largest about 6  $\mu$ m (upper right of photo). Using the proposed 2  $\mu$ m fibrolite/sillimanite criterion, the Al<sub>2</sub>SiO<sub>5</sub> in this sample would be described as fibrolite + sillimanite.

Crd + And, (5) Kfs +  $Al_2SiO_5$ , (6) anatectic migmatite, and (7) Bt + Grt + Crd  $\pm$  Opx anatectic migmatite (Pattison and Harte 1985, 1988, 1991). Mineral abbreviations follow Kretz (1983). Figures 3 and 4 show the distribution of inferred reaction isograds between the different pelitic mineral zones. Mineral assemblages and mineral chemical trends are described in Pattison (1987) and Pattison and Harte (1991).

Construction and calibration of a petrogenetic grid for the metapelitic reactions is described in Pattison and Harte (1985, 1991) and Pattison (1989), respectively. Temperatures increased from ca. 550°C in the Crd + Chl + Bt zone to 750–800°C at the igneous contact (Pattison 1989); these estimates agree well with estimates from equilibria in interbedded metacarbonates (Masch and Heuss-Assbichler 1991; Pattison 1991). Contact temperatures and temperature-distance profiles for different parts of the aureole are closely reproduced using the thermal models of Buntebarth (1991). The duration of the contact metamorphic event (temperatures raised above 500°C) was  $10^5-10^6$  m.y. (Buntebarth 1991).

**Distribution and Textures of**  $Al_2SiO_5$  *Minerals.* The distribution of andalusite and sillimanite in the aureole is illustrated in figures 3 and 4. Figure 4 is a blow-up of an area on the northeast flank of the complex where extensive sampling was conducted. Textures of andalusite and sillimanite are illustrated in figures 5–10 and in figures 8.9–8.14 of Pattison and Harte (1991). Changes with grade of modal Sil/(And + Sil) and thickness of sillimanite prisms are listed in table 1; because of the difficulty of making precise modal estimates, modal ranges are given. Much of the ensuing discussion is concerned with andalusite and sillimanite relations on the northeast flank.

Andalusite. The lowest-grade occurrence of  $Al_2SiO_5$  minerals is andalusite in the assemblage Ms + Crd + And + Bt + Qtz, but this assemblage is relatively uncommon and is restricted to the graphitic Ballachulish Slate in the southeast part of the aureole (Zone IV, assemblage IVa, of Pattison and Harte 1991). The majority of rocks in Zone IV, including all rocks on the northeast flank of the aureole (figure 4), contain the  $Al_2SiO_5$ -absent subassemblage Ms + Bt + Qtz + Crd + Kfs (fig-



**Figure 3.** Simplified geology of the Ballachulish Igneous Complex and contact aureole, showing the prograde metapelitic reaction sequence and the distribution of andalusite (open diamonds), sillimanite (filled diamonds) and andalusite + sillimanite (half-filled diamonds). For clarity, only the major quartzite units and main pelitic units have been shown. A more complete stratigraphy is found in Bailey and Maufe (1960) and Pattison and Voll (1991). Geology of the igneous complex is from Weiss and Troll (1989) and contact metamorphic zones are from Pattison and Harte (1985, 1991).



Figure 4. Geology of the syncline, NE flank of the igneous complex. Solid circles = Ms + Qtz + Bt + Crd +Kfs. L = limestone and calcsilicate. Other symbols the same as in figure 3. The dotted line is a smoothed estimate of the igneous contact used to obtain the distances in table 1.

ure 3). In the graphitic Ms + Crd + And + Bt + Qtz assemblage, and alusite typically forms ca. 0.5 mm subhedral crystals, normally with inclusion-packed cores and ragged to sharp edges (figure 5). And alusite crystals may be as long as 10 mm. Textural, modal and chemical data suggest that and alusite formed by the model reaction Ms + Crd = And + Bt + Qtz + H<sub>2</sub>O (Pattison and Harte 1985, 1991).

In the  $Al_2SiO_5$  + K-feldspar zone (Zone V of Pattison and Harte 1991), there is an abrupt modal increase in andalusite, and sillimanite first appears. On the northeast flank of the complex, andalusite comprises 95–100% of the Al<sub>2</sub>SiO<sub>5</sub> through a zone between 500 and 300 m from the igneous contact (equivalent to 200 m upgrade of the Ms + Qtz-breakdown), and even at higher grades it is volumetrically the dominant Al<sub>2</sub>SiO<sub>5</sub> polymorph (table 1). Andalusite texturally appears to be in equilibrium with the other minerals in the rock, based on comparable grain size, low energy-type grain-grain contacts, and a variety of spatial associations with other minerals. It forms in two main habits: (1) anhedral, skeletal crystals and mosaic crystal aggregates, typically surrounded by K-feldspar and biotite (figures 6 and 7); and (2) euhedral prisms, sometimes intergrown with quartz and surrounded by K-feldspar (figures 8 and 9, and fig. 8.10 of Pattison and Harte 1991). Rare samples contain crystals with pink pleochroic cores that give an anomalous gray-blue birefringence (figures 8 and 9); the pleochroism is due to elevated  $Fe^{3+}$  (see below).

The abrupt increase in modal and alusite and de-

		Distance within Igneous	Sil/	Thickness of sillimanite prisms (µm)		
Specimen <sup>a</sup>	Assemblage <sup>b</sup>	$(\pm 20 \text{ m})$ upgrade of Ms + Qtz = And + Kfs + H <sub>2</sub> O	$(\pm 40 m)$ from contact	(And + Sil) (vol %)	Avg.	Range
D25a	Ms	30	470	1–5	4–6	.5–18
D515	Qtz	80	430	<1	2-4	.5-14
D391	Ms + Crn	100	410	<1	2-4	.5–6
D663	Crn	130	370	1-5	3-5	.5–14
D37	Crn	180	340	<1	3-5	.5-8
D516	Cm	180	370	1-5	6-8	2 - 28
D63b	Crn	200	310	20-30	9-11	2-32
D678	Qtz	270	270	30-40	9-11	2 - 21
D676	Ċm	290	250	5-10	10-12	2 - 40
D608	Crn			100	12–14	2–46

 Table 1.
 Specimens Containing Andalusite and Sillimanite

<sup>a</sup> For specimen locations, see figure 4.

<sup>b</sup> All assemblages contain And, Sil, Crd, Bt, Kfs, Pl, Ilm.



**Figure 5.** Photomicrograph of andalusite in a matrix of muscovite, biotite, quartz, albite, graphite and cordierite, ca. 150 m downgrade of the Ms +  $Qtz = And + Kfs + H_2O$  isograd, southeast flank of aureole. Due to the abundance of fine graphite, diffuse cordierite poikiloblasts are not distinguishable in the photo. Diameter of andalusite crystal in center of photo is about 380  $\mu$ m.

crease in modal muscovite is due to the model reaction Ms + Qtz = And + Kfs + H<sub>2</sub>O (Pattison and Harte 1985, 1991). This reaction marks the first appearance of andalusite in rocks, which at lower grade, contain the common Zone IV assemblage Ms + Crd + Bt + Qtz + Kfs, including all rocks from the northeast flank of the aureole (Figures 3 and 4). Figure 4 shows the thin section control on the isograd on the northeast flank.

Sillimanite. Sillimanite is present in most andalusite-bearing samples above the Ms + Qtz breakdown isograd (figures 3 and 4). On the northeast flank, sillimanite first occurs at most 30 m closer to the contact than the first occurrence of And + Kfs (figure 4). In a given sample, there is invariably a range of sillimanite grain sizes (table 1). With increasing grade, sillimanite modal abundance and grain size generally increases. Through a zone about 200 m above the first occurrence of sillimanite, grain diameters straddle the proposed 2  $\mu$ m fibrolite/sillimanite boundary, although the average grain size is always above 2  $\mu$ m. Within 300 m of the igneous contact, modal sillimanite exceeds 5% of total Al<sub>2</sub>SiO<sub>5</sub> and all grain diameters exceed 2  $\mu$ m. In one sample from a screen within the igneous complex, sillimanite is the only Al<sub>2</sub>SiO<sub>5</sub> polymorph present.

Sillimanite occurs in a range of textures. The most common is as discrete prismatic crystals and crystal aggregates in cordierite poikiloblasts (figures 6 and 7). In the matrix, sillimanite typically occurs in radiating sprays of crystals around ilmenite, tourmaline, zircon, and less commonly andalusite crystals (figures 7–9 and figures 8.10–8.11 of Pattison and Harte 1991), most likely having used these minerals as nucleating substrates. In most rocks, the matrix sillimanite occurs adjacent to cordierite crystals. At higher grades, it occurs both in discrete crystals and crystal aggregates (figure 10). In all rocks, sillimanite clearly formed later than andalusite.

The widespread development of sillimanite upgrade of the Ms + Qtz breakdown isograd, and its increase in grain size and modal abundance with grade, suggest that it formed during prograde contact metamorphism (Pattison and Harte 1991). There is no evidence for the textural association of fibrolite and biotite described by Kerrick (1987) in



**Figure 6.** Photomicrograph of andalusite and sillimanite in D516 (figure 4), ca. 370 m from the igneous contact, 180 m above the Ms +  $Qtz = And + Kfs + H_2O$  isograd. Andalusite (right side of photo) occurs in skeletal, anhedral crystals intergrown with K-feldspar and some biotite. Sillimanite occurs in elongate prisms within cordierite (average crystal diameter 6–8 µm). These textures are similar to those in sample D25a, one of the lowest-grade occurrences of sillimanite in the aureole (see figure 8.10 of Pattison and Harte 1991).

the Ardara aureole, N. Ireland, which he interpreted as a retrograde feature caused by late fluid movement away from the igneous complex. At Ballachulish, petrological and stable-isotopic data indicate that there was no significant fluid movement either away or toward the igneous complex during contact metamorphism (Pattison and Harte 1988, 1991; Hoernes et al. 1991; Harte et al. 1991).

Sillimanite-Forming Reactions. Although and alusite and sillimanite occur together in most  $Al_2SiO_5$ -bearing rocks right up to the contact, there is, with one exception, no evidence for the *reaction* of andalusite to sillimanite. For example, figure 10 shows a rock within 250 m of the contact containing a sillimanite-rich sublayer in which euhedral andalusite prisms show no evidence of reaction. The preservation of such angular, euhedral andalusite crystals argues against even minor dissolution. Moreover, several rocks upgrade of the first occurrence of sillimanite contain andalusite with no sillimanite (figures 3 and 4). Apparent andalusite inertness in rocks containing fibrolite and/ or sillimanite has been noted by many other workers (e.g., Pitcher and Read 1959, 1963; Naggar and

Atherton 1970; Kerrick 1987; Vernon 1987; Kerrick and Woodsworth 1989). A noteworthy example of the capacity for andalusite to persist well into the sillimanite stability field is provided by Speer (1982) in his study of the Kiglapait aureole, in which rocks containing andalusite and sillimanite occur at the same grade as rocks containing granulite-facies garnet + orthopyroxene + cordierite assemblages.

Sillimanite at Ballachulish must therefore have formed by reaction(s) involving matrix minerals other than andalusite. Its formation at or slightly above the Ms + Qtz = And + Kfs isograd is consequently problematic, because andalusite (and Kfeldspar) clearly proliferated due to the breakdown of Ms + Qtz. Three possibilities are listed: (1) Modally minor, refractory (phengitic or F-rich?) muscovite may have reacted with quartz upgrade of the main Ms + Qtz breakdown to produce the small amount of sillimanite. (2) Reactions involving cordierite, K-feldspar, quartz and exchange components in biotite, such as (Fe,Mg)Si = 2Al (Tschermak exchange) (e.g., Thompson 1982; Pattison 1987) and 3(Fe,Mg) = 2Al (dioctahedral = tri-



**Figure 7.** Photomicrograph of sillimanite prisms nucleating on, but not replacing, a skeletal, anhedral andalusite crystal contained within cordierite (sample D516). Diameter of thickest sillimanite crystal is 18 μm.

octahedral exchange) (e.g., Grover et al. 1992) may have produced sillimanite upgrade of the Ms + Qtz = And + Kfs isograd. Two examples out of many possible reactions are:

 $(Fe,Mg)_{2}Al_{4}Si_{5}O_{18} + SiO_{2} = 4 Al_{2}SiO_{5}$ cordierite quartz sillimanite + 2 (Fe,Mg)SiAl\_{-2}

 $3 (Fe,Mg)_2Al_4Si_5O_{18} = 8 Al_2SiO_5$ cordierite sillimanite

+ 7 SiO<sub>2</sub> + 2 (Fe,Mg)<sub>3</sub>Al<sub>-2</sub> quartz dioct.-trioct. exchange in Bt

tschermak exchange in Bt

(3) Sillimanite may have formed from reactions involving inclusions in cordierite. Downgrade of the And + Kfs isograd in Ms + Crd + Bt + Qtz + Kfs assemblages, cordierite poikiloblasts are typically packed with inclusions of muscovite, quartz, biotite, and K-feldspar (Pattison and Harte 1985, 1991). If muscovite and quartz inclusions were partially or wholly isolated physically within cordierite poikiloblasts, they may have been preserved to slightly higher grade than the Ms + Qtz = And + Kfs + H<sub>2</sub>O reaction isograd, eventually reacting to form Sil + Kfs instead of And + Kfs. Alternately, muscovite inclusions may have reacted with their cordierite host to form sillimanite by the Fe-Mg continuous reaction Ms + Crd = Sil + Bt + Kfs + $H_2O$ . Reactions involving inclusions in cordierite account for the combination of subordinate modal sillimanite, its growth later than andalusite, and its conspicuous spatial association with cordierite. The Ms + Crd reaction would additionally account for the observed modal decrease in muscovite inclusions in cordierite upgrade of the Ms + Qtz breakdown isograd.

Equilibrium and Kinetic Aspects of Andalusite and Sillimanite at Ballachulish. Andalusite-bearing, sillimanite-absent assemblages are relatively common upgrade of the first occurrence of sillimanite in the aureole. In only one sample (D2 in figure 3) is andalusite directly replaced at its margins by coarse (>20  $\mu$ m) sillimanite, a texture suggestive of the polymorphic inversion. However, in other nearby andalusite-bearing samples, including many closer to the contact, sillimanite is absent (figure 3). These observations strongly suggest that kinetic barriers inhibited the progress of the polymorphic inversion reaction, even though *P-T* conditions were evidently within the sillimanite stability field.

Regarding the And = Sil *equilibrium*, evidence is preserved of voluminous nucleation and growth of



**Figure 8.** Photomicrograph of andalusite and sillimanite in D515 (figure 4), ca. 430 m from the igneous contact, 80 m above the Ms +  $Qtz = And + Kfs + H_2O$  isograd. Euhedral andalusite prisms (left side of photo) are surrounded by an envelope of K-feldspar. Fine grained sillimanite (average crystal diameter 2–4  $\mu$ m) and fibrolite nucleate on small andalusite crystals (center and bottom right of photo) and on ilmenite crystals (center bottom of photo).



**Figure 9.** Same as figure 8, crossed nicols. Cores of andalusite prisms have anomalous blue-gray birefringence, due to  $Fe_2O_3$  contents as high as 4 wt %. Diffuse gray poikiloblastic crystal at bottom is cordierite.



**Figure 10.** Photomicrograph of andalusite and sillimanite in D678, ca. 270 m from the igneous contact, 270 m above the Ms + Qtz = And + Kfs + H<sub>2</sub>O isograd. Abundant prisms of fine-grained sillimanite (average crystal diameter 9–11  $\mu$ m) occur in the same sublayer as euhedral andalusite prisms showing no sign of reaction to sillimanite.

and alusite at the Ms + Qtz breakdown isograd and subordinate nucleation and growth of sillimanite at most 30 m above the isograd. Both minerals are interpreted to have formed during prograde contact metamorphism, with sillimanite having formed after and alusite but apparently not from and alusite. If one makes the common assumption that andalusite (+ K-feldspar) nucleated and grew in its stability field by reaction of unstable matrix minerals (Ms + Qtz  $\pm$  Crd  $\pm$  Bt), it follows that nucleation and growth of sillimanite from reaction of the same range of matrix minerals probably occurred in the sillimanite stability field. Kerrick et al. (1991), in a critique of the first draft of this paper, suggested that and alusite (and K-feldspar) produced from the Ms + Qtz breakdown reaction might have grown metastably in the sillimanite stability field, owing to the presence of pre-existing andalusite crystals which facilitated the nucleation and growth of andalusite rather than sillimanite. This suggestion is untenable in the majority of rocks, including all those discussed in detail in this paper, because the lowest grade development of andalusite occurs at the Ms + Qtz = And+ Kfs +  $H_2O$  reaction isograd.

Therefore, the boundary between rocks in the

andalusite stability field and rocks in the sillimanite stability field appears to be tightly constrained to a zone between the Ms + Qtz = And + Kfs isograd (represented by the first appearance of And + Kfs) and 30 m above the isograd where sillimanite first occurs. The virtual absence of evidence for the direct replacement of andalusite by sillimanite may therefore have no bearing on the equilibrium stability fields of the two polymorphs, because this process may have been inhibited by the sluggish kinetics of the polymorphic inversion.

These observations carry significant implications for the interpretation of andalusite/sillimanite relations in other low-pressure settings. For example, if an aureole shows andalusite being replaced directly by sillimanite, it is likely that the And = Sil *equilibrium* lies at lower grade (e.g., figure 1b). This study therefore contrasts with Kerrick (1987) and Kerrick and Woodsworth (1989), who argued that the equilibrium boundary between andalusite and sillimanite is where andalusite is replaced by coarse sillimanite, and that lower-grade occurrences of fibrolite (fine-grained sillimanite?) in andalusite-bearing rocks represented metastable growth in the andalusite field.

It is significant that, in the lowest-grade occur-

rences of sillimanite (e.g., D25a, figure 4), grain diameters range from  $<0.5 \ \mu m$  (fibrolite) to 18  $\mu m$ (sillimanite) (table 1). There is therefore no evidence for displacement of the And=Sil equilibrium due to grain size variation of sillimanite. This suggests that, at least at Ballachulish, fibrolite growth was a kinetically controlled phenomenon nevertheless indicative of sillimanite stability.

# **Mineral Chemistry**

Chemical analyses of andalusite and sillimanite from five rocks are listed in table 2. Analyses were performed by E. Zaleski on the ARL SEMQ electron microprobe at The University of Calgary, using procedures described by Nicholls and Stout (1988). Natural Brazilian andalusite was used as a standard for Al and Si, and natural almandine garnet was used as a standard for Fe.

Cores and rims of andalusite were analyzed. In the andalusite of D515 (figures 8 and 9), the pink pleochroic, anomalously birefringent cores gave up to 4 wt % Fe<sub>2</sub>O<sub>3</sub> (table 2); according to the survey of Kerrick (1990), this is the highest Fe-content for an Al<sub>2</sub>SiO<sub>5</sub> polymorph yet reported. This rock contains ilmenite and pyrite, and so is not anomalously oxidized, unlike the hematite-bearing host rocks to the Fe-rich andalusites of Grambling and Williams (1985).

Andalusite rims typically contain 1.5–2 times the Fe-content of sillimanite, similar to the findings of Okrusch and Evans (1970). Judging by the consistency of this ratio in both Fe-rich samples (e.g., D515) and Fe-poor samples (e.g., D25a), sillimanite appears to have equilibrated chemically with the andalusite rims, even though there is no evidence for andalusite having reacted to form sillimanite.

The equilibrium constant between andalusite rims and sillimanite,  $K_D = X_{Al_2SiO_5}^{Sil}/X_{Al_2SiO_5}^{And}$ , was calculated assuming  $X_{Al_2SiO_5} = (1 - MAlSiO_5)$ , where *M* is the sum of all cations other than Al and Si, assuming a total of 5 oxygens (Kerrick and Speer 1988).  $K_D$ (And-Sil) ranges from 1.003 to 1.021 (table 2) and shows no apparent pattern with grade (table 1). This suggests that, in contrast to Kerrick and Speer (1988), differing bulk composition of the rocks was more important in controlling the Fecontents of the polymorphs than evolution along a  $T-X_{MAlSiO_5}$  loop.

It is notable that the compositions of andalusite and sillimanite in the lowest-grade sillimanitebearing rocks (e.g., D427 and D25a, tables 1 and 2; figures 3 and 4) are closest to end member  $Al_2SiO_5$ . This suggests that the *P*-*T* location of the inferred And = Sil equilibrium in the aureole was not significantly affected by minor elements.

# Pressure-Temperature Location of the Andalusite-Sillimanite Equilibrium at Ballachulish

The *P*-*T* location of the And = Sil equilibrium can be estimated by locating the position of the Ms +  $Qtz = And + Kfs + H_2O$  reaction, corrected for impurities, and providing a pressure estimate.

Location of  $Ms + Qtz = And + Kfs + H_2O$  for Pure End Members. The reaction Ms + Qtz = And +

 Table 2.
 Andalusite and Sillimanite Analyses

Sample: Al silicate	D25a And	D25a Sil	D63b And-C	D63b And-R	D63b Sil	D427 And-C	D427 And-R	D515 And-C	D515 And-R	D515 Sil	D516 And-C	D516 And-R	D516 Sil
SiO <sub>2</sub>	37.05	35.51	36.78	37.13	36.82	37.02	36.84	36.45	36.40	37.05	36.64	36.40	36.20
TiO	.03	.03	.07	.06	.02	.11	.05	.18	.05	nd	.04	.08	.01
Al <sub>2</sub> O <sub>3</sub>	62.86	63.80	61.78	62.05	61.92	61.94	62.66	58.73	60.78	61.43	61.75	61.56	61.81
Fe <sub>2</sub> O <sub>3</sub>	.21	.10	.87	.74	.40	.29	.21	3.99	1.96	1.04	1.57	1.49	1.00
MnO	nd	.01	.01	.01	.01	.01	nd	nd	nd	nd	nd	.01	nd
MgO	.06	.03	.07	.07	.08	.05	.02	.10	.04	.02	.04	.03	.02
Total	100.21	99.48	99.58	100.06	99.25	99.42	99.78	99.45	99.23	99.54	100.04	99.57	99.04
Si	.998	.965	.999	1.003	1.007	1.005	.997	1.003	.997	1.007	.994	.992	.990
Ti	.001	.001	.001	.001	.000	.002	.001	.004	.001	nd	.001	.002	.000
Al	1.996	2.043	1.979	1.977	1.986	1.983	1.998	1.906	1.962	1.968	1.974	1.977	1.992
Fe <sup>3+</sup>	.004	.002	.018	.015	.008	.006	.004	.083	.040	.021	.032	.031	.021
Mn	nd	.000	.000	.000	.000	.000	nd	nd	nd	nd	nd	.000	nd
Mg	.002	.001	.003	.003	.003	.002	.001	.004	.002	.001	.002	.001	.001
Total	3.001	3.012	3.000	2.999	2.999	2.998	3.001	3.000	3.002	2.997	3.003	3.003	3.004
XMAISIO	.007	.004	.022	.019	.011	.010	.006	.090	.043	.022	.035	.034	.022
X <sub>Al2SiO5</sub>	.993	.996	.978	.981	.989	.990	.994	.910	.957	.978	.965	.966	.978
	$K_D =$	1.003		$K_D =$	1.008				$K_D =$	1.021		$K_D =$	1.012

Note. C = core; R = rim; nd = not detected.

Kfs +  $H_2O$  for pure end members has been located by five independent experimental determinations (Evans 1965; Althaus et al. 1970; Kerrick 1972; Chatterjee and Johannes 1974; Schramke et al. 1987). Allowing for quoted experimental uncertainties, these constrain the curve to a very tight interval of about 10°C between 1 and 4 kbar (see figure 39c of Berman 1988). At 3 kbar, the equilibrium lies at 645 ± 10°C.

Mineral Activities. Muscovite from three samples containing the model univariant sub-assemblage Ms + Kfs +  $Al_2SiO_5$  + Qtz (Pattison 1985, 1987) has the average composition  $K_{0.88}$  $Na_{0.07}Fe_{0.07}Mg_{0.08}Ti_{0.03}Al_{2.78}Si_{3.07}O_{10}(OH)_2$ , assuming complete OH-occupancy of the hydroxyl site. Ideal on-sites mixing models of Powell (1978) and Powell and Holland (1990) for muscovite give  $a_{\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2^{\text{Ms}}}$  of 0.75 and 0.82, respectively. Multiplying by the activity coefficient for KAl<sub>3</sub>Si<sub>3</sub>- $O_{10}(OH)_2$  in paragonite-muscovite solution (1.01; Chatterjee and Froese 1975) gives activities of 0.76 and 0.83, respectively. These activities may be lowered somewhat by departures from full OHoccupancy, such as by  $F^-$ ,  $Cl^-$  and  $O^{2-}$  which were not analyzed.

K-feldspar has the average composition  $K_{0.79}$ Na<sub>0.20</sub>(Ba + Ca)<sub>0.01</sub>Al<sub>1.01</sub>Si<sub>2.99</sub>. The activity coefficient for KAlSi<sub>3</sub>O<sub>8</sub> in K-feldspar-albite solution (Waldbaum and Thompson 1969) is 1.03, giving  $a_{\text{KAlSi}3O_8}^{\text{Kfs}}$  of 0.82. The  $a_{\text{Al}_2\text{Si}O_8}^{\text{And}}$  is 0.99 (ideal mixing; table 2).

The average compositions of biotite and cordierite in the model univariant assemblage are, respectively,  $K_{0.88}Na_{0.02}Fe_{1.39}Mg_{0.86}Mn_{0.01}Al_{1.76}Ti_{0.15}Si_{2.68}O_{10}(OH_{1.88}F_{0.12})$ , neglecting  $Cl^-$  and  $O^{2-}$ , which were not determined, and  $K_{0.03}Na_{0.02}Fe_{1.00}Mg_{0.99}Mn_{0.02}Al_{3.99}Si_{4.97}$ , neglecting  $H_2O$  and  $CO_2$ , which were not determined.

Water Activity. Harte et al. (1991) presented several arguments that fluid pressure equalled rock pressure during times of reaction in the Ballachulish aureole: (1) dehydration-reaction isograds in metapelites are sharp rather than diffuse; (2) the zonal sequence and spacing of metapelitic assemblages and inferred reactions between them can be rationalized by experimentally based petrogenetic grids for which  $P_{\text{rock}} = P_{\text{fluid}} = P_{\text{H2O}}$ ; (3) pressure and temperature estimates from anhydrous equilibria, metapelitic dehydration equilibria, and metacarbonate  $H_2O-CO_2$  mixed volatile equilibria are in excellent agreement (±20°C, ±0.2 kbar, Pattison 1991); (4) a range of textures in metacarbonate lithologies (calcite veining, strings of reaction products at reaction sites) demonstrate a hydraulic fracturing mechanism for fluid escape, indicating that fluid pressures during periods of reaction must have equalled and transiently exceeded rock pressure (Masch and Heuss-Assbichler 1991); (5) profound textural and mineralogical transformations from slates and phyllites outside the aureole to massive hornfelses in the aureole make it unlikely that fractures open to lower pressures could remain open throughout times of reaction dehydration; (6) petrologic and stable-isotopic data indicate minimal fluid flow either toward or away from the aureole during contact metamorphism (Hoernes et al. 1991; Harte et al. 1991), in contrast to shallow level intrusions in which fluid circulation systems were established (e.g., Taylor and Forester 1979). This suggests that open cracks required for fluid flow were not present at Ballachulish, other than transiently to allow water produced from dehydration reactions to escape.

The three samples containing the sub-assemblage Ms + And + Kfs + Qtz appear to be graphite-free (optical determination) and are not interbedded with carbonate-bearing layers, so that dilution of the hydrous fluid by C-bearing fluid species is thought to have been minor. This interpretation is strengthened by the contrast in mineral assemblages, mineral compositions, and isograd locations between graphitic and non-graphitic pelites, which Pattison (1989) demonstrated could be explained by the significant presence of C-bearing fluid species in the graphitic pelites, but not in the graphite-absent pelites. Solutes such as Si, K, Na, and Al may have been present in the fluid, but probably in negligible quantities: based on the modeling and experiments of Burnham and Nekvasil (1986), these would amount to about 1.6 wt % dissolved quartz + feldspar at 3 kbar and 650°C, which amounts to a mole fraction (moles solutes/moles water + solutes) <0.005. Thus,  $a_{\rm H2O}$  (variable *P*-*T* standard state) at the Ms + Qtz breakdown isograd is considered to have been unity, with a conservative lower limit of 0.95.

Taking the above activities, the equilibrium constant  $K = [a_{Al_2SiO_5^{And}} * a_{KAlSi_3O_8^{Kfs}} * a_{H_2O^{Vap}}]/[a_{KAl_3Si_3O_{10}|OH|_2^{Ms}} * a_{SiO_2^{Qtz}}]$  ranges between 0.93 and 1.07, depending on the muscovite activity model and water activity. Using the thermodynamic data of Berman (1988), this causes a displacement of the end member curve of  $-7^{\circ}$  to  $+7^{\circ}$ C.

**Pressure Estimates.** Several independent estimates of pressure in the Ballachulish aureole have been made (Pattison 1991), all of which show a high degree of consistency (figure 11). These are discussed individually below.

*Metapelite Equilibria.* Isopleths of Mg/Fe + Mg (Crd) in any of the KFMASH divariant reactions



Figure 11. Pressure estimates for contact metamorphism in the Ballachulish aureole (see text for explanation of methods). Solid dots connected to inward facing triangles are pressure estimates with uncertainties. Unconnected inward facing triangles give pressure ranges only. RGB 69—intersection of Ms + Qtz = And + Kfs+  $H_2O$  with the And=Sil curve of Richardson et al. (1969). H 71—the same for the And = Sil curve of Holdaway (1971). Methods: 1—metapelitic petrogenetic grid estimate of Pattison (1989). 2-metapelite estimate from grid of Holdaway and Lee (1977). 3-metapelite estimate from GeO-Calc (Berman et al. 1987; Berman 1988, 1989 update). 4—isobaric invariant point Fo + Diop + Tr + Cc + Dol, Masch and Heuss-Assbichler (1991). 5-isobaric univariant curve (11), unconstrained X<sub>CO2</sub>, Masch and Heuss-Assbichler (1991). 6-8-Grt - Opx - Pl -Qtz barometry estimates, calibrations of Bohlen et al. (1983), Moecher et al. (1988) and Perkins and Chipera (1985; Fe-calibration). 9-projections of Alb - Kfs -Otz components of granitoids into haplogranite system of Tuttle and Bowen (1958) (Weiss and Troll 1991).

that intersect the degenerate model univariant reaction Ms +  $Qtz = Al_2SiO_5 + Kfs + H_2O$  provide a pressure estimate of metamorphism at the Ms + Qtz breakdown reaction (e.g., figure 7, Holdaway and Lee 1977). Taking the measured Mg/Fe + Mg (Crd) value of 0.50 for the model univariant assemblage Ms + Qtz + And(Sil) + Kfs + Crd + Bt at Ballachulish (Pattison 1987; Pattison and Harte 1991), Holdaway and Lee's calibrated grid gives  $2.9 \pm 0.4$  kbar for  $a_{\rm H2O} = 1.0$ .

Pattison (1989) calibrated a petrogenetic grid from experimental data involving the phases Ms, Chl, Bt, Qtz, Crd, Kfs, And, Sil, Ky, and Crn, corrected for impurities in the natural minerals at Ballachulish. Using the Holdaway and Lee method to contour the Fe-Mg divariant reactions in Mg/Mg + Fe(Crd), he obtained an estimate of  $3.1 \pm 0.5$ kbar.

Other published data sets give a range of estimates. Using GeO-Calc software (Berman and Perkins 1987] and the thermodynamic data set of Berman (1988, updated in 1989), all possible equilibria involving the phases Ms – Bt – Qtz – hydrous Crd - Kfs - And - H<sub>2</sub>O were calculated for the mineral compositions listed above, giving a *P-T* estimate of  $3.8 \pm 0.4$  kbar and  $660 \pm 10^{\circ}$ C (quoted uncertainty due to spread of calculated equilibria only). This P-T estimate for the andalusite-bearing assemblage lies well into the sillimanite stability fields of Berman (1988) and Holdaway (1971). Using the calibrated grid of Spear and Cheney (1989), one obtains a pressure estimate using the isopleth method of about 3 kbar, comparable to estimates using the Holdaway and Lee (1977) and Pattison (1989) grids. In the petrogenetic grid of Powell and Holland (1990),  $Bt + Al_2SiO_5$  is not stable below about 5 kbar unless Fe<sup>3+</sup> is preferentially added to biotite, and even then Bt + Sil is not stable below about 4.4 kbar, and Bt + And + Kfs has no stability field.

The accuracy of these estimates depends on the accuracy of the experimental data used to derive the thermodynamic data. Experimental data relevant to the equilibria used in the above calculations are illustrated in figure 3 of Pattison (1989). Of particular importance is the P-T location of the reaction Fe-Bt + Sil + Qtz = Fe-Crd + Kfs +  $H_2O_1$ , which represents the low-pressure Fe-end member boundary of the Fe-Mg continuous reaction Bt + Sil + Qtz = Crd + Kfs +  $H_2O$ . Judging by figure 2 of Holdaway and Lee (1977), this reaction appears to be tightly constrained. However, recalibration by Mukhopadhyay et al. (1991) of a related reaction in Holdaway and Lee's (1977) study, Fe-Crd = Fe-Grt + Sil + Qtz, suggests that Fe-Crd stability relative to Fe-Grt + Sil + Qtz is restricted to lower pressures by 0.5-1.0 kbar compared to Holdaway and Lee. If the Fe-end member reaction Fe-Bt + Sil + Qtz = Fe-Crd + Kfs +  $H_2O$  also occurs at lower pressures than reported in

Holdaway and Lee, then pressure estimates from grids using the Holdaway and Lee data (e.g., Holdaway and Lee 1977; Pattison 1989) may require downward revision. For example, if the Fe-end member reaction is lowered by 0.5 kbar, with no change in *P*-*T* position of the Mg-end member reaction, pressure estimates would be lowered by about 0.25 kbar for Mg/(Mg+Fe)(Crd) = 0.5.

Metacarbonate Equilibria. Masch and Heuss-Assbichler (1991) mapped isograds in siliceous carbonates and impure limestones in the aureole. They obtained pressure estimates by combining detailed calcite-dolomite thermometry with the  $P-T-X_{CO_2}$  position of selected isograd reactions. Of their four selected reactions, only two give reasonably precise pressure estimates (their numbering): isobaric univariant reaction (11) Diop + Dol = Fo+ Cc +  $CO_{2'}$  and isobaric invariant assemblage (III) Fo + Tr + Diop + Cc + Dol. Whole rock analyses (Mg/(Mg + Fe) = 0.95-0.97) and mineral analyses (Mg/(Mg + Fe) = 0.95-0.99) show that the minerals are closely represented by the system CaO – MgO – SiO<sub>2</sub> –  $H_2O$  – CO<sub>2</sub> (Heuss-Assbichler 1987). *P-T-X*<sub>CO<sub>2</sub></sub> positions of the reactions used by Masch and Heuss-Assbichler (1991) for pressure estimates are based on the experimental data and derived thermodynamic data of Gottschalk (1990).

Their best pressure estimate,  $2.8 \pm 0.4$  kbar, comes from the intersection of a calcite-dolomite temperature of 620°C with the P-T trace of the isobaric invariant point (III). The quoted uncertainty is due to experimental uncertainty in the location of the *P*-*T* trace of the invariant point. In figure 11, the uncertainty has been expanded to  $\pm 0.5$  kbar to take account of uncertainty in the thermometry and slight deviation from end member mineral compositions. For isobaric univariant reaction (11), along which  $X_{CO_2}$  is unconstrained between values of 0.45 and 1.0, a pressure range of 2.6-3.8 kbar is calculated for a calcite-dolomite temperature of 640°C. If temperatures are underestimated due to resetting of the calcite-dolomite geothermometer and/or fractionation of minor amounts of Fe, the inferred pressures are minima, owing to the positive *P*-*T* slope of both equilibria.

Geobarometry of High-Grade Assemblages. Garnet-cordierite-orthopyroxene-plagioclase-quartz geothermobarometry was applied to high-grade metapelitic hornfelses in the aureole by Pattison (1989). Calibrations of the Grt - Opx - Pl - Qtz barometer based on the Fe-end member systems (Bohlen et al. 1983; Perkins and Chipera 1985; Moecher et al. 1988) are preferred over those based on the Mg-end member systems (Newton and Perkins 1982; Perkins and Chipera 1985), because the garnet and orthopyroxene at Ballachulish are Ferich. Pressures for the Bohlen et al., Perkins and Chipera (Fe-system), and Moecher et al. calibrations are 3.2, 2.7, and 3.7 kbar, respectively. Estimates of uncertainty of the calibrations are reported as ca.  $\pm 0.5$  kbar (Bohlen et al. 1983), ca.  $\pm 0.5-1.0$  kbar (Perkins and Chipera 1985), and better than  $\pm 1.0$  kbar (Moecher et al. 1988). Cordierite-bearing equilibria are not included here because of the unknown H<sub>2</sub>O<sup>-</sup> and CO<sub>2</sub>-contents of cordierite and their thermodynamic effects; nevertheless, pressure estimates from cordieritebearing equilibria are in excellent agreement with the Grt – Opx – Pl – Qtz results (Pattison 1989).

**Compositions of Late Granites.** Weiss and Troll (1991) projected CIPW-normative albite-orthoclase-quartz components of granitoid samples from the Ballachulish Igneous Complex into the Alb – Kfs – Qtz ternary of Tuttle and Bowen (1958). The samples plotted along the  $P_{\rm H_{2O}} = 3$  kbar thermal valley, with late crystallizing leucogranites plotting on or near the 3 kbar thermal minimum. From these data, Weiss and Troll (1991) estimated a pressure of 2.5–3.0 kbar. A minimum uncertainty of 0.5 kbar is added to account for the effect of other components in the natural granitoids, giving a range of 2.0–3.5 kbar.

Summary of Pressure Estimates. The agreement between independent pressure estimates is excellent (figure 11). With the exception of the metapelite estimate using the data of Berman (1988, 1989 update), a range of 2.6–3.4 kbar satisfies the uncertainty brackets of all methods. The excellent agreement between pressures calculated from anhydrous Grt – Opx – Pl – Qtz barometry and from the metapelitic and metacarbonate devolatilization equilibria supports the contention that  $P_{\rm fluid}$ was close to  $P_{\rm rock}$  during times of reaction in the aureole.

Taking an average of 3.0 kbar for the Pattison (1989) and Holdaway and Lee (1977) metapelite estimates, 2.8 kbar for the calcsilicate isobaric invariant assemblage estimate, and 3.2 kbar for the average of the Grt – Opx – Pl – Qtz geobarometry estimates, a best estimate pressure of 3.0 kbar is obtained. For comparison, intersection of the Ms + Qtz = And + Kfs + H<sub>2</sub>O reaction with the H and R And = Sil curves give pressures of 2.1 and 4.1 kbar, respectively.

Location of the And = Sil Boundary at Ballachulish. The rhombohedral box in figure 12 is the combined uncertainty of the And = Sil equilibrium position in the aureole. For 3 kbar the position of the Ms +  $Qtz = And + Kfs + H_2O$  reaction for pure end Journal of Geology



**Figure 12.** Compilation of experimental data on Ky = And, Ky = Sil, and And = Sil. Uncertainties of  $\pm 20^{\circ}C$ have been arbitrarily applied to the Ky = And and Ky = Sil equilibria (Kerrick 1990). Slopes of the Ky = Sil and Ky = And equilibria are estimated from Hemingway et al. (1991). The rhombohedral box is the uncertainty in position of the And=Sil equilibrium from this study. The solid diamond within the stippled box represents the estimated position of the triple point with its uncertainty, obtained by extrapolating the And = Sil equilibrium from this study using entropy and volume data from Hemingway et al. (1991). The small solid dots and accompanying dotted lines are the triple points and And=Sil curves of Holdaway (1971; H), Richardson et al. (1969; R), and Bohlen et al. (1991; B), respectively. Data of Kerrick and Heninger (1984) are reported in Kerrick (1990).

member mineral compositions is taken as  $645 \pm 10^{\circ}$ C (see figure 39c of Berman 1988). This assumes that sanidine was the stable K-feldspar at the time of reaction, even though the K-feldspar in the rocks now is orthoclase (Kroll et al. 1991). Uncertainty in the equilibrium constant, due to non-end member mineral and fluid compositions, adds  $\pm 5^{\circ}$ C.

The 30 m interval between the first appearance of And + Kfs and first appearance of sillimanite corresponds to a temperature interval of 10°C. This estimate is based on the thermal modeling of Buntebarth (1991), and the 100 m distance between the Ms = Crn + Kfs + H<sub>2</sub>O isograd and the Ms + Qtz = And + Kfs + H<sub>2</sub>O isograd, the temperature separation of which is 30°C (Chatterjee and Johannes 1974). The net result is a possible temperature range of 625°-665°C at 3 kbar for the andalusitesillimanite equilibrium. This temperature uncertainty is extended along the Ms + Qtz = And + Kfs + H<sub>2</sub>O reaction between 2.6 and 3.4 kbar to give the rhombohedral box in figure 12.

Kinetic Effects. Implicit in the above treatment is that there was no significant kinetic overstep of the Ms + Qtz = And + Kfs +  $H_2O$  reaction in the aureole. Walther and Wood (1984) argued that in regional and contact metamorphism, overstepping of devolatilization reactions is not expected to be more than a few degrees. In contrast, modeling of Lasaga (1986) suggested that overstepping could be significant (e.g., tens of degrees, depending on several variables). Field evidence Ballachulish suggests minimal overstepping. Pattison (1991) noted that the sequence, spacing, and mineral chemical trends of devolatilization reaction isograds in interbedded metapelites and metacarbonates is consistent with those of the experimentally determined reactions. If overstepping had been important, then its extent must have been approximately uniform throughout the aureole and in all rock types, even though the rate of heating in the inner part of the aureole was much faster than at the margins of the aureole (Buntebarth 1991), and the different reaction isograds involved a wide range of reactant and product assemblages, fluid compositions, and grain sizes. Nevertheless. if overstepping was significant, the above constraint on the And = Sil equilibrium is a minimum.

#### Extrapolation to the Al<sub>2</sub>SiO<sub>5</sub> Triple Point

Figure 12 is a compilation of experimental constraints on the And=Sil, Ky=And, and Ky=Sil equilibria. Following Kerrick (1990, fig. 3.46), uncertainties of  $\pm 20^{\circ}$ C were applied to the Ky= And and Ky=Sil equilibria. Slopes for these two reactions are 11.5 and 20.7 bar/°C, respectively, using the entropy and volume data reported in Hemingway et al. (1991). Although in theory the And=Sil boundary and triple point can be constrained from the intersection of the Ky=And and Ky=Sil equilibria, the intersection of the uncertainty bands of the two equilibria results in a large region of uncertainty for the triple point (ca. 2 kbar, 130°C). Bohlen et al.'s (1991) extremely small uncertainty in the location of the triple point using this method,  $4.2 \pm 0.3$  kbar and  $520 \pm 30^{\circ}$ C, depends on the validity of their 600°C reversal bracket of Ky = Sil, in particular sillimanite growth at 6 kbar (figure 12).

Using entropy and volume data from Hemingway et al. (1991), the And = Sil constraint from Ballachulish was extrapolated (slope = -16.0 bar/ °C) to intersect the uncertainty box formed by the intersection of Ky = And and Ky = Sil equilibria. The high angle of intersection of the And = Sil equilibrium with the other two equilibria gives an improved constraint on the position of the triple point: 4.5 kbar and 550°C, with an uncertainty represented by the stippled diagonally shaped box in figure 12. Uncertainty in the slope of the And = Sil equilibrium between the constraint from Ballachulish and the estimated triple point results in a small (<±0.2 kbar) added uncertainty to the stippled area in figure 12.

Comparison with Other Determinations of And=Sil and the Triple Point. The And = Sil curve and triple point derived here are for essentially pure (>99%  $Al_2SiO_5$ ) and alusite and sillimanite (see "Mineral chemistry"). They lie midway between the H and R determinations, and are similar to the estimates of Froese and Gasparrini (1975), Greenwood (1976), and Holland and Powell (1985).

Based on the data at Ballachulish, the R curve must be too high because there is abundant evidence for nucleation and growth of prograde sillimanite at least 50°C below the R And = Sil equilibrium. Pattison (1989) suggested that the H curve was still a possibility if one allowed for substantial kinetic overstep of the And = Sil reaction. This view is now rejected because of the evidence for voluminous nucleation and growth of prograde andalusite at the Ms + Qtz = And + Kfs + H<sub>2</sub>O reaction isograd, indicating andalusite stability at least 50°C above the H And = Sil curve.

The triple point of Bohlen et al. (1991),  $4.2 \pm 0.3$ kbar and  $520 \pm 30^{\circ}$ C, lies in the lower *P*-*T* portion of the stippled region in figure 12. Bohlen et al.'s And = Sil curve was constrained by the andalusite weight loss experiments of Kerrick and Heninger (1984), illustrated in Kerrick (1990, his figure 3.26). Kerrick and Heninger's 1 kbar and 2 kbar data for sillimanite stability are in good agreement with the preferred location of And = Sil of this study, but the 3 kbar, 600°C constraint on sillimanite stability is only marginally in agreement (figure 12). For the 3 kbar experiments, none of the andalusite weight losses considered diagnostic of sillimanite stability exceeded about 20  $\mu$ g, a weight loss which Kerrick (1990) regarded as being on the margin of reliability. Further experiments at higher temperatures showing greater andalusite weight losses might provide a less ambiguous indication of sillimanite stability.

# **Comparison with Phase Equilibrium Constraints**

When evaluated against petrological constraints used to support either Richardson et al. (1969) or Holdaway's (1971) determinations the P-T positions of the And = Sil equilibrium and triple point proposed here appear to satisfy all these criteria.

Stability of Chloritoid + Sillimanite. The apparently stable coexistence of sillimanite and chloritoid has, to the author's knowledge, been reported only three times (Holdaway 1978; Grambling 1981; Milton 1986). Based on the independent, mutually consistent experiments of Hoschek (1967), Richardson (1968), and Rao and Johannes (1979), the reaction Fe - Ctd + Al<sub>2</sub>SiO<sub>5</sub> = Fe - St + $Qtz + H_2O$  lies at least 50°C below the R triple point (figure 13), which has been used as evidence in favor of the H triple point (e.g., Grambling 1981). The Richardson and Rao and Johannes experiments were conducted at the QFM  $f_{O_2}$  buffer, whereas Hoschek's experiments were unbuffered. Ganguly (1969) estimated that there was an  $f_{\Omega_2}$ -dependent reaction interval of about 30°C between conditions at the QFM and HM buffers (figure 13).

Numerous examples of And + Ctd and Ky + Ctd suggest that the extreme rarity of Sil + Ctd is not due to bulk compositional effects, but rather to a very restricted P-T stability field. Using the H triple point, the region of possible stability is a rather large triangular region ranging from about 500°C, 3.8 kbar, to about 570°C, 2.5-4.8 kbar. The position of the triple point proposed in this study, even without allowance for experimental uncertainties, allows a small stability field for Fe - Ctd+ Sil under oxidizing, high- $a_{H_{2O}}$  conditions, similar to the conditions inferred in the studies of Holdaway (1978) and Grambling (1981). Substitution of Mg into staurolite and chloritoid results in a small up-temperature displacement of the equilibrium (Holdaway 1978), expanding the P-T range of the assemblage. In contrast to Grambling (1981) and Milton (1986), it is argued here that the extreme rarity of Ctd + Sil, rather than supporting Holdaway's (1971) triple point, supports a higher P-T triple point that results in a smaller stability field for this subassemblage.

Stability of Paragonite + Sillimanite. The occurrence of the subassemblage paragonite + silliman-



**Figure 13.** Comparison of the And = Sil curve and  $Al_2$ -SiO<sub>5</sub> triple point of this study with selected phase equilibrium constraints. Experimental brackets for the reaction Fe-Ctd +  $Al_2SiO_5 = Fe-St + Qtz + H_2O$  are from the following sources: RJ, QFM-Rao and Johannes (1979), QFM buffer; Ho-Hoschek (1967), unbuffered; R, QFM-Richardson (1968), QFM buffer; G-Ganguly (1969), estimate in position of the reaction for  $f_{O_2}$  conditions at the HM buffer. The inflection in the reaction across the Ky = And boundary reaction is based on the data of Holland and Powell (1990). Brackets for the Kfs + Ab + Qtz +  $H_2O$  = L granite solidus curve (TB) are from Tuttle and Bowen (1958). Solidus curves for variable F and B<sub>2</sub>O<sub>3</sub> contents in the melt are from Pichavant and Manning (1984). The reaction Parag + Qtz = Ab + $Al_2SiO_5 + H_2O$  is from Chatterjee (1972).

ite was used by Grambling (1984) to argue against the R triple point and in favor of the H triple point (figure 13). With the higher P-T triple point proposed here, there is still a significant stability field for this subassemblage.

Stability of Muscovite + Andalusite + Biotite. In contrast to the extreme rarity of the subassemblages Ctd + Sil and Parag + Sil, the subassemblage Ms + Bt + And is very common in lowpressure regional and contact metamorphic metapelites (Pattison and Tracy 1991). Using the contracted andalusite stability field of Holdaway (1971), Ms + And + Bt stability is restricted to Fe-rich bulk compositions only and pressures less than about 2 kbar, using the grids of Holdaway and Lee (1977), Pattison (1989), Spear and Cheney (1989) and a grid constructed from the data of Berman (1988, 1989 update). With the enlarged andalusite field proposed here, however, a less restricted Ms + Bt + And field is created in the above grids (e.g., figure 4, Pattison 1989), which may be more consistent with the widespread development of this subassemblage.

Andalusite-Bearing Granites and Migmatites. One central argument in support of the Richardson et al. (1969) And = Sil boundary is the occurrence of andalusite-bearing granites (e.g., Brammall and Harwood 1932; Hills 1938; Exley and Stone 1966; Haslam 1971; Clarke et al. 1976; Clarke 1981; MacDonald and Clarke 1985) and anatectic migmatites (e.g., Pattison and Harte 1988; Vernon and Collins 1988; Vernon et al. 1990). In contrast to the H And = Sil curve, which allows no stability field for andalusite + granite melt, the And = Sil boundary proposed here allows a significant And + Melt stability field below about 3 kbar (figure 13).

Holdaway (1971) and Kerrick and Speer (1988), based on the occurrence of topaz and/or tourmaline in late phases of peraluminous granitoid suites, suggested that the water-saturated solidus of natural andalusite-bearing granites and migmatites might be lowered by solution of F and B in the melt, such that it intersects the Holdaway (1971) andalusite field. However, as emphasized by Pichavant and Manning (1984), tourmaline- and topazenriched bodies in which such an effect might be important typically represent late and volumetrically minor phases of granitoid masses. In the classic occurrences of andalusite-bearing granite in the South Mountain, Musquodoboit and New Ross batholiths, Nova Scotia, and alusite occurs in intermediate phases of the bodies (Clarke et al. 1976; MacKenzie and Clarke 1985; Clarke written comm. 1991).

To create a significant andalusite + melt + vapor stability field using the Holdaway (1971) andalusite field and the haplogranite solidus of Tuttle and Bowen (1958), melt must contain about 4 wt % F or 2 wt %  $B_2O_3$  (figure 4 of Pichavant and Manning 1984; figure 13). These melt concentrations correspond to concentrations in the coexisting fluid of 0.4–0.8 wt % F (fractionation factor of Hards 1976) and 6 wt %  $B_2O_3$  (fractionation factor of Pichavant 1981). Pichavant and Manning (1984) and Zen (1988) argued that  $B_2O_3$  contents of peraluminous granitoids are unlikely to exceed 1 wt %, which would result in a lowering of the solidus due to  $B_2O_3$  of <30°C (figure 13). Relative to the

solidus of Tuttle and Bowen (1958), however, this down-temperature displacement would be partially compensated by an up-temperature displacement due to the presence in natural granitoids of intermediate plagioclase rather than pure albite, which raises the solidus by  $10-20^{\circ}$ C (Johannes 1978). Thus, if there is a stability field for And + Melt + Vapor due to B<sub>2</sub>O<sub>3</sub> solubility, using the Holdaway (1971) andalusite field, it is likely to be restricted to pressures of ca. 1.5 kbar or less.

Munoz and Ludington (1974) showed that a sensitive indicator of fluorine concentration in a fluid is the composition of coexisting biotite. Based on their hydrothermal experiments at 2 kbar and 627°C, biotite with an F/(F + OH) ratio of about 0.45 coexists with a hydrous vapor phase with a  $f_{\rm HF}/(f_{\rm HF} + f_{\rm H2O})$  ratio of only 0.0022. Thus, vaporsaturated melts containing 2-4 wt % F should be accompanied by very F-rich biotite. In the andalusite-bearing phases of the South Mountain Batholith, there is no evidence for unusually elevated F- or B-contents: tourmaline is sporadic and minor, F-bearing accessory phases are absent, and biotite has low concentrations of fluorine (F/F + OH < 0.15; L. Richard and D. B. Clarke, written comm. 1991). Thus, significant lowering of the solidus by F is unlikely in these granites.

The andalusite-bearing anatectic migmatites of Pattison and Harte (1988) and Vernon and Collins (1988) are both inferred to have formed by vaporsaturated melting at pressures of about 3 kbar. In both studies, andalusite was interpreted to have formed down-grade of the migmatite boundary. However, Vernon and Collins provided evidence for regrowth of andalusite rims on refractory unmelted andalusite crystals, which they ascribed to crystallization from a peraluminous vapor-saturated melt. Consequently, an And + melt + vapor stability field is required. F contents of biotite are very low, and tourmaline is only present sporadically, suggesting negligible lowering of the solidus (Vernon et al. 1990).

It is possible that the above discussion places undue emphasis on the simple coexistence of andalusite with vapor-saturated melt. If andalusite crystallized at higher temperatures on the liquidus (Abbott and Clarke 1979; Clarke 1981), possibly from a vapor-undersaturated melt, the andalusite stability field must be large enough to intersect not only the vapor-saturated solidus but also the liquidus. Existing experimental data (e.g., Le Breton and Thompson 1988) suggest minimum temperatures for crystallization of Al<sub>2</sub>SiO<sub>5</sub> on the vapor-undersaturated liquidus of 700°C. This may be a further argument against the contracted andalusite stability field of Holdaway (1971) and in support of a higher And = Sil boundary, such as proposed here.

## ACKNOWLEDGMENTS

E. Zaleski did the microprobe work on andalusite and sillimanite. D. B. Clarke and L. Richard provided advice on peraluminous granites in Nova Scotia, in addition to some unpublished analyses of biotite from andalusite-bearing phases of the South Mountain Batholith. Discussions with D. M. Carmichael were very helpful. Detailed reviews by K. L. Currie, D. M. Kerrick, and R. H. Vernon led to improvements in the manuscript. The research was supported by NSERC operating grant no. 0037233.

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