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On the  $\text{Al}_2\text{SiO}_5$  triple point and the natural occurrence  
of two  $\text{Al}_2\text{SiO}_5$  polymorphs under the same P-T conditions

by

Bruce S. Hemingway

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## Abstract

It is proposed that three regions of P-T space exist in which aqueous silica activity at or near equilibrium with quartz can stabilize two  $\text{Al}_2\text{SiO}_5$  polymorphs. Because the transformation of one  $\text{Al}_2\text{SiO}_5$  polymorph to another is controlled by dissolution/precipitation processes, kinetics will play an important role in the transformations. For geologic systems, the activity of aqueous silica rather than aqueous alumina is considered to be the critical factor in determining the  $\text{Al}_2\text{SiO}_5$  polymorph(s) that nucleate and grow. The disparate phase equilibrium results of Althaus (1967) for kyanite=sillimanite and of Richardson et al. (1969) for andalusite=sillimanite as compared to the results of Holdaway (1971) are viewed as representing metastable reaction boundaries in which the metastable polymorph, as defined by Holdaway (1971), has an aqueous silica activity near or equivalent to that of quartz. The results of the three studies and the data of Althaus (1967) for the breakdown of pyrophyllite + quartz are used to delineate the P-T fields where two coeval polymorphs may occur. The proposed P-T fields are consistent with the occurrence of andalusite in metamorphosed rocks of the Lepontine Alps, Switzerland, that otherwise demonstrate a decompression P-T-t path that remains within the kyanite stability field, without the need for pressure excursions. A similar argument is made for the formation of late stage fibrolite and andalusite in the Dalradian sequence of the Central Highlands of Scotland during decompression that remained within the kyanite stability field. A field for andalusite + peraluminous melt is shown.

## Introduction

Although most petrologists have used Holdaway's (1971) phase diagram for thermobarometric analysis of metamorphic rocks, considerable uncertainty regarding the phase equilibrium diagram exists and that affects interpretation of metamorphic processes. Despite the efforts in several recent studies (Bohlen et al., 1991, Hemingway et al., 1991, Kerrick, 1990, Holland and Powell, 1990, and Berman, 1988), an explanation for the cause of the variations in locations of the univariant equilibria and in the triple point for the  $\text{Al}_2\text{SiO}_5$  polymorphs (e.g., Althaus, 1967 and 1969, Richardson et al., 1969, Berman, 1988, and Holland and Powell, 1990) has not been adequately developed. In fact, two recent studies (Berman, 1988, and Holland and Powell, 1990) applying simultaneous computer analysis of extensive experimental data sets produced values for the  $\text{Al}_2\text{SiO}_5$  triple point and for the andalusite=sillimanite univariant equilibria that differ significantly. The present study will provide an explanation for the disparate experimental data for the three univariant equilibria and will show that simultaneous growth of two polymorphs can be expected at the same P-T conditions within restricted ranges of P and T.

## Discussion

The effective processes for the transformation of  $\text{Al}_2\text{SiO}_5$  polymorphs is solution/precipitation (e.g., Walther, 1986, and Schramke et al., 1987) which means that kinetics will play an important role. For most crustal and upper mantle processes, solid-solid transitions between minerals are unimportant because pressure changes of 100 kbars or more are typically required (Jeanloz, 1985).

Kerrick (1990, page 301) has noted that no experimental data exist on the kinetics of nucleation for the  $\text{Al}_2\text{SiO}_5$  polymorphs. While this is true, we may infer some kinetic information from early attempts to define the  $\text{Al}_2\text{SiO}_5$  phase diagram through synthesis studies. Figures 1 and 2 show the  $\text{Al}_2\text{SiO}_5$  triple point (9 kbar and 663 K) and reaction boundaries for the three polymorphs determined by Khitarov et al. (1963) from synthesis reactions using hydrous alumina-silica gel as a starting material. This study is consistent with other studies (e.g., Bell, 1963, Clark et al., 1957, and Hariya and Arima, 1975) that place the kyanite=sillimanite and andalusite=sillimanite synthesis reactions at a higher P at a given T than the generally accepted phase equilibrium reactions of Holdaway (1971), or the more recent studies cited in the Introduction. Commonly, the reactant materials used in the synthesis studies are poorly crystalline and highly reactive leading to high levels of aqueous silica and alumina during the experiment. The results presented by Khitarov et al. (1963) demonstrate that under the conditions of their experiment, andalusite nucleates and grows faster than kyanite and sillimanite at temperatures and pressures up to the curve located between 9 kbar and 663 K and 4.4 kbar and 865 K, and sillimanite nucleates and grows faster than kyanite up to the curve located between 9 kbar and 663 K and 15.4 kbar and 1150 K, with the exception of a synthesis field for mullite plus quartz located at higher temperatures and lower pressures than the curves located between 2 kbar and 880 K and 4.4 kbars and 865 K, and 4.4 kbars and 865 K and 4.6 kbars and 950 K (Figures 1 and 2).

The areas between the synthesis reaction boundaries and the equivalent equilibrium univariant reaction boundaries determined by Holdaway (1971) represent P-T space in which metastable growth of an  $\text{Al}_2\text{SiO}_5$  polymorph could be expected to occur under appropriate

conditions. It is the conclusion of this author that the metastable growth of sillimanite with respect to kyanite, of andalusite with respect to kyanite and sillimanite, and of mullite plus quartz with respect to andalusite and sillimanite is largely controlled by the activity of aqueous silica. This is an example of the Ostwald Step Rule (e.g., Hemingway, 1982, or Morse and Casey, 1988). If the activity of aqueous silica derived from reactant phases exceeds the activity of silica that would be in equilibrium with a metastable  $\text{Al}_2\text{SiO}_5$  polymorph, the solution is supersaturated with respect to that polymorph as well as the stable polymorph (assuming adequate aqueous alumina in the system) and the metastable polymorph may precipitate while the stable phase is not destabilized and may also grow.

The activity of aqueous alumina is not considered to be the controlling factor in natural systems because a large part of the alumina is often complexed in natural aqueous systems by alkali cations, particularly in reactions involving micas and feldspars, and may not be available to growing  $\text{Al}_2\text{SiO}_5$  polymorphs (e.g., Walther, 1986). However, this may not be true for solubility studies of the  $\text{Al}_2\text{SiO}_5$  polymorphs buffered by  $\text{Al}_2\text{O}_3$ . Hariya and Arima (1975) have shown that the addition of excess of either  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  (in gel form) over stoichiometric proportions slightly expands the synthesis field of sillimanite with respect to kyanite. Thus a similar effect is shown for the two chemical components at high P and T through the growth of sillimanite. But at lower P and T, Holdaway (1971) and Bowman (1975) have shown that aqueous silica has an effect not shown by aqueous alumina for the reaction andalusite=sillimanite. In these two studies, equilibrium was determined by observing the weight change of andalusite single crystals, which show growth to higher temperatures with higher silica activity (quartz buffer). Brown and Fyfe (1971) locate the kyanite=andalusite equilibria at higher T and lower P than Holdaway (1971) based upon the P-T conditions in which the activity of silica derived from solubility studies of kyanite and andalusite, each buffered by  $\text{Al}_2\text{O}_3$ , is equal. Control of the activity of aqueous alumina by  $\text{Al}_2\text{O}_3$  may suppress the equilibrium silica activity generated from the dissolution of the  $\text{Al}_2\text{SiO}_5$  polymorphs resulting in a shift of apparent equilibrium to higher T and lower P.

The most important conclusion that may be drawn from the forgoing analysis is that it is totally reasonable to find conditions of P and T under which two polymorphs will precipitate as coeval phases. This is possible because the activity of aqueous silica within rocks undergoing metamorphism will vary significantly since it will be controlled locally by the breakdown of reactant phases and the local precipitation of product phases, and by fluid pathways. For example, the activity of aqueous silica within a pelite can be expected to become less uniform as diagenesis and metamorphism progress, a consequence of changes in the distribution and size of pore space and because of the general coarsening of minerals.

Kyanite, andalusite, and sillimanite are stable with respect to quartz and corundum within the stability fields for the polymorphs derived by Holdaway (1971, also see Figure 1). Peterson and Newton (1990) have demonstrated this for kyanite at 1088 K and pressures from 6 to 10 kbar. Calorimetric data suggest that this is true throughout the P-T region (Peterson and Newton, 1990, and Hemingway et al., 1991). Therefore, the assemblage quartz plus corundum in stoichiometric proportions will yield a higher concentration of aqueous silica than an  $\text{Al}_2\text{SiO}_5$  polymorph within its stability field.

The activity of aqueous silica derived from two of the  $\text{Al}_2\text{SiO}_5$  polymorphs should be equivalent along the univariant curve representing equilibrium between the polymorphs, and that derived from the less stable polymorph will be higher than that for the stable polymorph on either side of the univariant reaction boundary (e.g., Brown and Fyfe, 1971). Thus there will

be a region in which the concentration of aqueous silica derived from quartz used as a reaction buffer (e.g., Althaus, 1969) or from a reacting phase (e.g., Chatterjee and Johannes, 1974) in natural systems will exceed the aqueous solubility of silica that would be derived from the less stable  $\text{Al}_2\text{SiO}_5$  phase. Within this region, the  $\text{Al}_2\text{SiO}_5$  polymorph with lower stability can precipitate, as can the stable  $\text{Al}_2\text{SiO}_5$  polymorph. The reaction boundary for kyanite=sillimanite (see Figure 2) derived by Althaus (1969) I believe represents the P-T conditions where the concentration of aqueous silica derived from quartz is comparable to that derived under the same conditions from metastable sillimanite. Althaus (1969) used samples of kyanite and sillimanite that were very finely ground. To this material was added finely ground quartz. During the experiments, Ostwald ripening would result in dissolution of finely ground material and precipitation of the phase that had the fastest precipitation kinetics. This process would result in the dissolution of fine grained kyanite, sillimanite, and quartz. The synthesis studies have shown that, under these conditions, sillimanite would likely have fast precipitation kinetics. I further believe that this is a geologically reasonable upper limit of the P-T region in which kyanite and metastable sillimanite (or fibrolite) may form as coeval phases (Figure 3). At higher pressures and temperatures, this region will be truncated by the synthesis boundary for kyanite=sillimanite (see Figures 1 and 3), that is, the nucleation and growth of kyanite finally becomes faster than that for metastable sillimanite. Similarly, at lower pressures and temperatures the region is truncated by the synthesis boundary for the reaction andalusite=sillimanite.

Support for the relative roles of aqueous silica and aqueous alumina is found in the 1.8 kbar results of Holdaway (1971) for sillimanite II = andalusite. Holdaway (1971) found a difference of about 115 K in the estimated temperature of equilibrium between sillimanite and andalusite depending upon whether quartz (1036 K) or corundum (921 K) was added to the starting materials. Because the same crystals of andalusite and powder of sillimanite were used, differences in the  $\text{Al}_2\text{SiO}_5$  phases can be ruled out. The major difference will arise from the aqueous silica or aqueous alumina differences that arise from quartz or corundum buffers. As noted above, Holdaway (1971) observed andalusite growth to higher temperatures when quartz was used as a buffer. The concentration of aqueous silica present in the runs equilibrated with quartz must be higher than those without quartz, or with an  $\text{Al}_2\text{O}_3$  buffer which, referring to the results of Brown and Fyfe (1971) discussed above, would imply a metastable equilibrium for andalusite. Similar differences are seen in the data of Bowman (1975).

A similar P-T region may be delineated in which coeval precipitation of andalusite and sillimanite is possible (Figure 3). The geologically practical upper limit for andalusite precipitation is derived from the experimental studies of Chatterjee and Johannes (1974), Chatterjee and Froese (1975), Evans (1965), and Khitarov et al. (1963). The reactions muscovite + quartz = sanidine + andalusite (or sillimanite) +  $\text{H}_2\text{O}$  were studied by Evans (1965) and Chatterjee and Johannes (1974). The latter results are consistent with the former and are shown in Figure 2. Chatterjee and Froese (1975) studied the reaction muscovite + albite + quartz = K-feldspar + sillimanite (or andalusite) +  $\text{H}_2\text{O}$ , the results of which are shown in Figure 2. The boundary between experimental conditions yielding andalusite or sillimanite as the stable phase (Figure 2) is roughly coincident with the mullite + quartz = sillimanite synthesis boundary reported by Khitarov et al. (1963) and at higher P and T than the equilibrium boundary of Holdaway (1971). The slope of the synthesis reaction boundary mullite + quartz = sillimanite chosen by Khitarov et al. (1963) is incorrect. Using data presented in Figure 4 of Khitarov et al. (1963), a reaction boundary consistent with the observations, but

with a decreasing slope (in pressure) can be constructed from 4.9 kbar and 845 K to 4.6 kbar and 973 K (Figure 3). This construction is more intuitively logical as it places a break-in slope for the andalusite=sillimanite synthesis curve near the boundary of the field of sillimanite stability as defined by the phase diagram of Holdaway (1971) and others cited in the Introduction (see Figure 3). This construction is reasonably consistent with the results presented by Chatterjee and Froese (1975) for the reaction  $\text{paragonite}_{ss} + \text{quartz} = \text{albite}_{ss} + \text{muscovite} + \text{kyanite (or andalusite)} + \text{H}_2\text{O}$ .

The P-T field where andalusite and sillimanite may coprecipitate (with the activity of silica near or equal to quartz) is most likely truncated by the andalusite=sillimanite reaction boundary determined by Richardson et al. (1969). Finely ground starting materials (3 to 5 % quartz in the andalusite) would lead to quick oversaturation of aqueous silica in the experiments of Richardson et al. (1969) and their reaction boundary possibly reflects the kinetic boundary where sillimanite grows faster than metastable andalusite. Similar results from experiments involving finely ground fibrolite support this choice (A. Nitkiewicz cited in Kerrick, 1990, p. 51). An interesting point can be made regarding the results of Heninger (1984, also discussed in Kerrick, 1990, p. 71). Heninger (1984) studied the andalusite = fibrolite equilibrium at 3 pressures. The reaction results reported for 3 kbar and 873 K are in good agreement with the results of Holdaway (1971) whereas those for 2 and 998 K, and 1 kbar and 1073 K are more consistent with the results reported by Richardson et al. (1969). Heninger (1984) was careful to exclude ultra-fine particles from the fibrolite powder used in the hydrothermal weight gain experiments with andalusite spheres. The fibrolite sample contained muscovite as an impurity. As can be seen from Figure 2, the 1 and 2 kbar measurements were made at temperatures above the stability field for muscovite, but the 3 kbar experiments were conducted with muscovite as a stable phase. The breakdown of muscovite in the 1 and 2 kbar experiments should lead to the formation of andalusite (see discussion above). These data also support the choice of an upper temperature-pressure reaction boundary for metastable andalusite = sillimanite.

The preceding discussion demonstrates that the stable  $\text{Al}_2\text{SiO}_5$  polymorph does not necessarily control the activity of aqueous silica in the muscovite and paragonite breakdown reactions. This has important ramifications for the methods by which thermodynamic properties are derived for phases from the reactions.

Reference to Figure 2 will show that the triple point and the andalusite = sillimanite reaction curve constructed by Holland and Powell (1990) are determined to a large extent by the experimental results of Chatterjee and Johannes (1974) and Chatterjee and Froese (1975) discussed above (also see Kerrick, 1990, p. 92-93). Kerrick (1990) has concluded that Holland and Powell (1990) are in error. I also believe that this selection is incorrect for reasons cited above, that is, the reaction curve represents conditions under which the activity of silica derived from the reactants is high enough to form metastable andalusite.

A P-T region in which andalusite and kyanite may form as coeval phases can be estimated from the experimental data of Althaus (1967) for the reaction  $\text{pyrophyllite} = \text{quartz} + \text{kyanite (or andalusite)} + \text{H}_2\text{O}$ . The reaction boundary of Althaus (1967) is shown in Figure 2. The inflection indicating the change from andalusite to kyanite as the "stable" polymorph is given by Althaus (1967) as about 6.1 kbar and 792 K, a value in good agreement with the synthesis reaction boundary for andalusite=kyanite given by Khitarov et al. (1963). This is not surprising since Althaus (1967) ground his starting materials "to very fine grain sizes" which would reduce the stability of these materials (increase the solubility) in line with the reactants used by Khitarov (1963). The synthesis boundary then should represent the reaction curve along which the

activity of silica derived from the reactants is equal to or exceeds the activity of silica derived from metastable andalusite. The practical limit of P-T space in which both andalusite and kyanite can form is most likely truncated by the pyrophyllite stability field (Figure 3) as defined by Althaus (1967).

### Geologic Implications

In his review of the  $\text{Al}_2\text{SiO}_5$  polymorphs, Kerrick (1990) identified several problems that remain unresolved. Some of these will be examined and interpreted based upon the model presented in this study.

Although the phase diagram deduced by Holdaway (1971) is commonly accepted and utilized by petrologists, an argument against the validity of the phase diagram has been the fact that there is not a stability field for andalusite + melt (Kerrick, 1990, p. 357) and there are several reports of andalusite in peraluminous granitoids (Kerrick, 1990, p. 354). Holdaway (1971) and others (e.g., Price, 1983, and Kerrick and Speer, 1988) have argued that such a stability field can be obtained from an expansion of the P-T field of melt as a consequence of increased levels of volatiles such as boron and fluorine. Zen (1988, p. 34) has argued that elevated levels of  $\text{B}_2\text{O}_3$  are unlikely in peraluminous melts although the common occurrence of tourmaline in peraluminous granitoids suggests the presence of some boron. Similarly, the presence of topaz suggests the presence of some fluorine. Alternatively, peraluminous melts should have an activity of silica at least equivalent to that necessary to precipitate quartz. Thus, the field in which andalusite could be expected to precipitate would be represented by the field shown in Figure 3 and would provide for a field of apparent stability for metastable andalusite + melt even in the absence of boron and fluorine in the melt.

Kerrick (1988) derived a thermobarometric decompression path for the Main Alpine metamorphism of the Lepontine Alps, Switzerland. He argued that andalusite formed from kyanite during the later stages of decompression. In his Figure 4, Kerrick (1988) shows a P-T trajectory for decompression of the host rocks that is totally within the field of stability for kyanite to preclude kyanite to andalusite conversion in the host rocks. However, he is forced to call upon "excursions" into the andalusite stability field to account for andalusite formation. The occurrence of andalusite is limited to segregations and Thompson (1976) suggested that this could be caused by differences in the amount of strain energy in kyanite in the segregations as compared to the host rock. Kerrick (1988) rejected this idea because andalusite occurred with undeformed kyanite and strongly bent kyanite was not altered. Wenk (1970) and Thompson (1976) have shown that andalusite is confined to the rocks at high elevations in the central Tessin region of the Lepontine Alps. Segregations that have no andalusite are suggested to have formed at higher pressure (greater depth) than those with andalusite. Kerrick (1988) has suggested that large amounts of aqueous fluids moved through fractures in the country rock during decompression. Keller (1968) has described the segregations and divided them into groups on the basis of mineralogy. The andalusite-bearing segregations contain kyanite + quartz + feldspar in addition to andalusite. Thus the silica activity during formation of the segregations had to be at least high enough for quartz precipitation. Therefore, I believe that the P-T trajectory proposed by Kerrick (1988) would simply pass through the field where kyanite + andalusite can coprecipitate (Figure 3). Kyanite would remain stable, and at higher silica activity andalusite could precipitate. No pressure "excursions" are necessary. Similar trajectories for rocks beginning at greater depth (greater pressure) would encounter a smaller

cross section of the field or miss the field, which would result in a decrease in andalusite with depth.

Kyanite and fibrolite are found in the Dalradian sequence of the Central Highlands of Scotland. Chinner (1966) concluded that fibrolite represented a "late overprint" following the main regional metamorphism. Wells (1979) used a numerical model to construct decompression paths for the Dalradian sequence. His model showed the P-T-t paths entirely within the kyanite stability field. He noted, however, that by increasing the rate of erosion his model would result in a decompression path that would pass through the sillimanite stability field and thus explain the sporadic occurrences of sillimanite. The problem with models that transect stability boundaries is that proof of a loss of stability must be found to justify the model. Here, kyanite should show signs of reaction where fibrolite has been precipitated, which is not observed. An alternative explanation may be seen in Figure 3. One of the extremes from Wells (1979) model shows the P-T-t path passing through the P-T regions in which sillimanite + kyanite, and andalusite + kyanite, would be stable under aqueous silica activity buffered by quartz. During decompression, it would appear to the author that local variations in permeability and silica activity could account for the sporadic occurrences of fibrolite and andalusite observed by Chinner (1966) as well as the apparent stability of kyanite.

### Conclusion

A proposal has been advanced to modify the phase diagram for the  $\text{Al}_2\text{SiO}_5$  polymorphs on the basis of a kinetic argument. The proposed modifications include P-T regions in which two  $\text{Al}_2\text{SiO}_5$  polymorphs may precipitate as coeval phases if the activity of aqueous silica is at or near that required for the precipitation of quartz. The argument is based upon experimental data designed to test other hypotheses. Thus the data are not adequate to provide an entirely quantitative definition of these P-T regions nor to rigorously test this proposal. The proposed fields do, however, provide a reasonable explanation for differing results from phase equilibrium studies and simpler and less contrived explanations for observed P-T-t paths of several natural rock systems. Further work will be necessary to evaluate the role of aqueous alumina in this system, as well as providing a better definition of the reaction boundaries controlled by aqueous silica. This process likely affects all mineral reactions involving minerals that exhibit polymorphism.

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### Figure Captions

Figure 1. The  $\text{Al}_2\text{SiO}_5$  triple point as defined by Hemingway et al. (1991) and which is close to that given by Holdaway (1971) is shown by the dashed curves. The synthesis boundaries for kyanite = sillimanite, andalusite = sillimanite, and andalusite or sillimanite = mullite + quartz from Khitarov et al. (1963) are shown as a dash-2 dot pattern. The synthesis boundary for kyanite = sillimanite from Kariya and Arima (1975) is shown by the solid curve. Parentheses indicate metastability.

Figure 2. The triple point of Hemingway et al. (1991) and the synthesis boundaries of Khitarov et al. (1963) are as shown in Figure 1. The triple point of Holland and Powell (1990) is shown by the solid curve. The triple point of Richardson et al. (1969) is shown by the dash-dot pattern. The triple point and boundary for the reaction pyrophyllite = kyanite or andalusite + quartz +  $\text{H}_2\text{O}$  from Althaus (1967) are shown by the dash-3 dot pattern. Data for the reaction muscovite + quartz = sillimanite (open square) or andalusite (open octagon) +  $\text{H}_2\text{O}$  is from Chatterjee and Johannes (1974). Data for the reactions paragonite + quartz = albite<sub>ss</sub> + muscovite + kyanite (filled triangle) or andalusite (open triangle) +  $\text{H}_2\text{O}$  and for the reaction muscovite<sub>ss</sub> + albite<sub>ss</sub> + quartz = K-feldspar<sub>ss</sub> + sillimanite (filled diamond) or andalusite (open diamond) +  $\text{H}_2\text{O}$  are from Chatterjee and Froese (1975). The arrows for the reaction andalusite → sillimanite are from Heninger (1984).

Figure 3. P-T regions in which two  $\text{Al}_2\text{SiO}_5$  polymorphs are stabilized by aqueous silica activity buffered by quartz (see text). The triple point and synthesis boundaries for sillimanite = kyanite and sillimanite = andalusite (see text) are as described in Figure 1. The data of Althaus (1967) are shown by the dash-3 dot pattern, and the data of Richardson et al. (1969) is shown by the dash-dot pattern; both portions of the results shown in Figure 2. The squares and the associated solid curve are the decompression path from Kerrick (1988) for the Lepontine Alps. The granodiorite solidus (water activity = 1) is from Manning and Pichavant (1983) and is shown by the long-short dash pattern. Wells (1979) model for post-metamorphic decompression of the Dalradian sequence of the Central Highlands of Scotland is shown by the long dash pattern.





