[AMERICAN JOURNAL OF SCIENCE, VOL. 277, MAY, 1977, P. 585-593]

THE ENTHALPY CHANGE OF THE ANDALUSITE-SILLIMANITE REACTION AND THE Al_2SiO_5 DIAGRAM

P. A. M. ANDERSON*, R. C. NEWTON**, and O. J. KLEPPA**

ABSTRACT. The enthalpy of solution of natural andalusite has been measured in a melt of composition $2PbO \cdot B_2O_3$ at 973 ± 1 K. The corrected value of 7.55 ± 0.20 kcal/gfw (average of two samples) and the results for two natural sillimanite samples published by Anderson and Kleppa (1969) yield $\Delta H^\circ_{\text{and}\rightarrow\text{sill}}$ at 973 K = 0.67 ± 0.23 kcal/gfw and a calculated dP/dT slope of −12 ± 4 bars K^{-1} at 973 K. This result can be compared with the dP/dT slopes of −13.7 bars K^{-1} of Holdaway's (1971) diagram, −25.2 bars K^{-1} of Richardson, Gilbert, and Bell (1969), and −67.4 bars K^{-1} of Althaus 1967. The diagram of Brown and Fyfe (1971) shows a triple point at 2000 bars and 460°C and a dP/dT slope of about −6 bars K^{-1} which is closer to the present results but outside our limit of uncertainty.

The agreement with the Holdaway slope cannot be considered fortuitous, especially in view of the fact that from it Holdaway correctly predicted the magnitude of the sillimanite disordering enthalpy, later verified by calorimetric measurements (Navrotsky, Newton, and Kleppa, 1973). Thus, his diagram is the only one that is in agreement with all the thermochemical data. The experimental evidence of Richardson, Gilbert, and Bell (1969) and Chatterjee and Johannes (1974) in favor of a higher-temperature andalusite-sillimanite boundary can be explained as due to the difficulty of synthesizing well-ordered sillimanite in a reversal reaction from andalusite. This leads to a wide region of uncertainty and a false high-temperature impression of andalusite stability.

INTRODUCTION

Current use of the Al_2SiO_5 diagrams.—Since Holdaway (1971) published his experimental Al_2SiO_5 phase diagram to challenge the earlier one of Richardson, Gilbert, and Bell (1969), most petrologists have accepted one or the other as a focal point in discussions of metamorphic parageneses. The Richardson, Gilbert, and Bell (1969) diagram shows a triple point among the polymorphs andalusite, sillimanite, and kyanite at 5.5 kb and 622°C and seems to be cited more frequently (for example, Miyashiro, 1972; Loomis, 1972; Dallmeyer, 1974) than the Holdaway diagram (for example, Kerrick, 1972; Chatterjee, 1973; Abraham and Schreyer, 1975), which shows a triple point at 3.8 kb and 500°C. Some authors impartially present both versions in their petrogenetic grids (Purtscheller, Hoernes, and Brown, 1972), and some adopt compromise diagrams with triple points in between the two published locations (Froese and Gasparini, 1975). A few authors (for example, Scharbert and Kurat, 1974) cite the diagram of Althaus (1967) which shows a triple point at 7 kb and 650°C.

Some authors give reasons for their preference of one diagram over the others. Thus, Froese and Gasparini (1975) think that a lower pressure of the triple point than given by Richardson, Gilbert, and Bell, but a higher triple point temperature than given by Holdaway to be compatible with their field data in central Manitoba. Thompson (1974) cites the occurrence of andalusite-bearing pegmatites as evidence for a higher-temperature andalusite field of stability than shown by Holdaway (1971).

* Ontario Science Center, Toronto, Ontario, Canada
** Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637

Ganguly (1969) thought that his experimentally-determined field of stability of chloritoid should overlap into the field of sillimanite, which is impossible with the Richardson, Gilbert, and Bell diagram. Atherton, Naggar, and Pitcher (1975) prefer a low-pressure triple-point to explain the widespread development of kyanite in the relatively shallow contact aureoles of the Donegal granites and favor the Brown and Fyfe (1971) diagram for this reason. The diagrams are compared in figure 1.

Experimental Al_2SiO_5 diagram determination.—There is general agreement on the P-T locations of the kyanite-sillimanite and kyanite-andalusite reaction boundaries. The hydrothermal determinations of Newton (1966a, 1966b) and of Richardson, Gilbert, and Bell (1969) over a limited temperature range (about 700°-850°C) under well-determined pressure conditions, combined with thermodynamic data, are in agreement. The pressure of the kyanite-sillimanite boundary is near 9 kb at 750°C, and the dP/dT slope is about 20 bars K^{-1}. Althaus (1967) gives a much higher pressure at 750°, but his hydrothermal determination is rendered suspect by the drastic grinding of his starting mineral mix (Newton, 1969). The pressure of the kyanite-andalusite boundary is about 6.5 kb at 750°C (metastable in sillimanite field), and the dP/dT slope is about 11 bars K^{-1}.

The equilibrium position of the much more sluggish andalusite-sillimanite reaction is partially determined by the intersection of the kyanite-sillimanite and the kyanite-andalusite boundaries. This intersec-

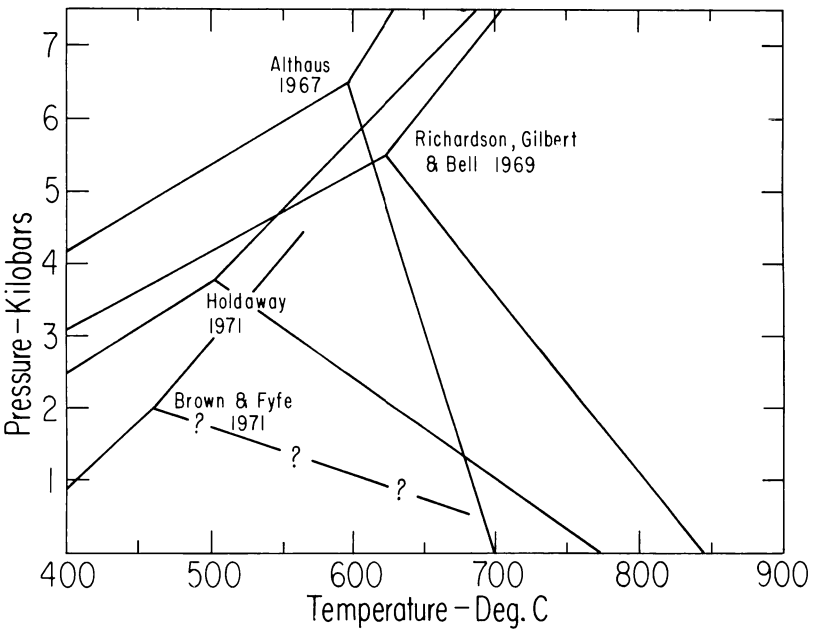

Fig. 1. Experimental Al_2SiO_5 diagram according to Richardson, Gilbert, and Bell (1969), Holdaway (1971), Althaus (1967), and Brown and Fyfe (1971).

tion is so oblique, however, that a large polygon of error in the triple-point location results from small uncertainties in the locations of the two kyanite reactions. For instance, Newton's (1966b) polygon of error extends from the Richardson, Gilbert, and Bell (1969) triple-point nearly to the Brown and Fyfe (1971) triple-point. The Althaus (1967) triple-point falls outside the mutually-embracing error polygons of the others.

An additional uncertainty lies in the entropy change of the andalusite-sillimanite transition. This quantity is so small that non-third law entropies, such as would result from tetrahedral Al-Si disorder of sillimanite (Anderson and Kleppa, 1969; Zen, 1969), could greatly influence the dP/dT slope. The third-law entropies (Pankratz and Kelley, 1974) together with the very accurate high-temperature volume data available for the Al_2SiO_5 minerals (Skinner, Clark, and Appleman, 1961) give such a flat dP/dT slope (about -5 bars K^{-1} that any andalusite-sillimanite boundary would have to be drawn through a very low-pressure triple point in order to be compatible with the 1-atm intercept of about 775°C given by the cryolite solubility studies of sillimanite and andalusite by Weill (1966). However, only a few percent of Al-Si disorder in sillimanite would allow a considerably steepened dP/dT slope.

Thus, additional independent experimental evidence on the andalusite-sillimanite boundary is essential. Richardson, Gilbert, and Bell (1969) used the method of very long hydrothermal runs, as much as 120 days in duration, on mixes of natural andalusite and sillimanite with periodic interruptions to grind vigorously the reactants in order to reduce kinetic barriers to the reaction. They secured apparent reversals (that is, growth of one mineral at the expense of the other, as determined by relative intensities of X-ray powder diffraction peaks). Their brackets indicated a dP/dT slope of about 25 bars/°C, much steeper than predicted by the third law entropies. Holdaway (1971) used the sensitive method of weight gain or loss of a polished single crystal of natural andalusite immersed in water and a powder of natural sillimanite and held at various pressure and temperature conditions for times of up to one month. He observed a curious behavior in the weight loss or gain of some sillimanite samples with time. In shorter runs the andalusite crystals showed weight gains, indicative of stability, under P, T conditions compatible with the Richardson, Gilbert, and Bell diagram. Longer runs at the same conditions, however, caused eventual net weight losses, which would indicate a lower temperature limit of stability of andalusite in the pressure range 2 to 4 kb. Holdaway attributed this to the presence of a less-stable, ultra-fine-grained sillimanite component, fibrolite, which was present in his natural starting material and also present in the Richardson, Gilbert, and Bell starting material. According to Holdaway, the andalusite grew in some runs at the expense of fibrolite, until the fibrolite was all consumed and then began to decline relative to the more stable coarse-grained sillimanite. He attributed the higher-temperature stability limit found by Richardson, Gilbert, and Bell mainly to the presence of faster-reacting but less stable fibrolite in their samples but implied that a non-equili-

brium amount of Al-Si disorder of their natural starting material under the run conditions could explain some of the difference.

Thermodynamic considerations.—The dP/dT slope of the andalusite-sillimanite reaction found by Holdaway (1971) in his crystal weighing experiments is about −14 bars K^{-1}, that is, somewhat too steep to be compatible with the third law entropy and volume data. Holdaway applied the idea of temperature-dependent Al,Si tetrahedral disorder in sillimanite to gain an increased sillimanite entropy. He used a simple site exchange mixing theory which has had considerable success in explaining the disordering of synthetic spinels (Navrotsky and Kleppa, 1968). Consider the exchange reaction of Al and Si on tetrahedral sites:

$$Al_{Al} + Si_{Si} \rightleftharpoons Al_{Si} + Si_{Al}$$

where Al_{Al} denotes aluminum on the "right" (that is, perfectly ordered) tetrahedral site, and Al_{Si} denotes Al transferred to a site occupied exclusively by Si in the ideally ordered crystal. If X is the mol fraction of Al_{Si}, then:

$$K(T) = \frac{X^2}{(1-X)^2} \cong \exp - \frac{\Delta H^{int}}{RT}$$

where ΔH^{int} is the interchange enthalpy; that is, the enthalpy of transfer of one mol of Al from the "right" sites to the "wrong" sites in an infinite quantity of ideally ordered sillimanite. Holdaway assumed ΔH^{int} independent of X over a moderate range of disorder. The additional (configurational) entropy of sillimanite is $-2R\{X\ln X + (1-X)\ln(1-X)\}$. The dP/dT slope of the andalusite-sillimanite boundary thus fixes X and ΔH^{int}. Holdaway derived a value of +14.7 kcal/mol for ΔH^{int} from his experimental boundary.

Simultaneously and independently, Greenwood (1972) brought forth a temperature-dependent disordering theory of sillimanite which involves a cooperative aspect to the disorder (Bragg and Williams, 1934); that is, ΔH^{int} decreases to zero as disorder becomes more complete, and essentially complete disorder sets in catastrophically as a critical temperature is approached. The theories of Greenwood and Holdaway are convergent in the low temperature range when X is small. From simple considerations having to do with the possible uncertainty in the triple point location, inferred from experiment and field occurrences, Greenwood showed that the enthalpy of exchange at low X, which is comparable to Holdaway's ΔH^{int}, should be between 10 and 20 kcal per mol. His preferred value was 16 kcal, compared to Holdaway's 14.7. At temperatures up to about 800° the theories of Greenwood and Holdaway predict very similar amounts of disorder, but above 800° Greenwood predicts increasingly larger amounts of disorder, going to completion at about 1700°C.

Navrotsky, Newton, and Kleppa (1973) measured the heats of solution of heat-treated natural sillimanite. At temperatures in the range 1400° to 1600°C they found substantial decreases in the heats of solution, as compared to the untreated starting material, which could only be

explained by cation disorder. Heat-treatment at lower temperatures yielded no thermal effects, undoubtedly because of the limited extent and the slowness of the disordering reaction. Application of Holdaway's theory to the results betwen 1400° and 1550°C leads to a ΔH^{int} of 16 kcal per mol, in striking agreement with his derived value. Above 1550°, the additional disordering was greater than could be explained by the simple theory, with a sudden approach near 1700°C to the value predicted by Greenwood. This result may be interpreted to constitute a thermodynamic endorsement of Holdaway's diagram.

The subtleties of the above thermodynamic evaluation seem not to have become generally influential among metamorphic petrologists, as evidenced by their relatively infrequent citation of the Holdaway diagram. Another more direct piece of evidence would seem to be needed. Recently, we have realized that the enthalpy of the andalusite to sillimanite transition is a critical discriminant among the published Al_2SiO_5 diagrams. The Brown and Fyfe (1971) diagram would demand a ΔH of about 0.35 kcal/gfw, the Holdaway configuration predicts a value of about 0.80 kcal; the Richardson, Gilbert, and Bell diagram calls for 1.35 kcal; and the Althaus diagram implies about 3.6 kcal. It is well within the capability of the high temperature oxide melt solution calorimeter (Kleppa, 1972) to discriminate narrowly within this large spread of values. The calorimetric results will be directly applicable in that the calorimeter temperature of 700°C is in the middle of the andalusite-sillimanite equilibrium interval. A pressure correction for at most a few kb to the measured enthalpy difference at 1 atm will be small. Although early work with the oxide melt solution calorimeter by Holm and Kleppa (1966) yielded thermochemical data that have proved somewhat inaccurate, the ability of the calorimetric method to yield precise results on aluminum silicates now has been amply demonstrated (Anderson and Kleppa, 1969; Navrotsky, Newton, and Kleppa, 1973). In this paper we present new measurements of the enthalpy of solution of andalusite. These are combined with the sillimanite data of Anderson and Kleppa (1969) to give ΔH for the andalusite to sillimanite transition.

EXPERIMENTAL METHODS AND RESULTS

In the work reported here we made use of two different samples of andalusite from Brazil. One sample, which we shall designate Andalusite I, consisted of faceted gemstones obtained from the late D. R. Waldbaum. He noted on the material "Probably from Minas Novas." This sample was analyzed by the grating spectrograph and found to contain about 0.5 wt percent Fe and 0.1 percent Ti.

The second sample, Andalusite II, was purchased as "M423-50, 10 carat vial of andalusite" from Grieger's Inc., Pasadena, Calif.; 14 vials were bought. This material was labeled "Andalusite-Brazil" and represented reject material (too small, cracks, inclusions) from lapidary supplies. The best of this material was hand-picked, ground, and separated into 150 to 200, 200 to 250, and 250 to 325 mesh batches by sieving. Any

batch in which any impurities (either as separate grains or as inclusions) were detected was then settled in diiodomethane. The batch was accepted only if the impurities, as judged by microscopic examination, were $<<$ 1 percent. This material was pleochroic in green (pale) and brown-red (strong). Although obtained from two different sources the samples appeared to be very similar.

In the calorimeter we used samples sized in the range 150 to 400 mesh of Andalusite I and in the range 150 to 325 mesh of Andalusite II. One sample of andalusite was heated in air for 5 days at 700°C and showed no perceptible change of any sort on the bases of X-ray and microscopic examination. The X-ray diffractograms of both I and II showed only andalusite.

Andalusite I: A total of 10 calorimetric measurements were carried out on I in 1968 and gave the following enthalpies of solution: 7.23, 7.61, (6.79), 7.74, 7.39, (6.62), 7.47, 7.56, 7.84, 7.68 kcal gfw^{-1}. Rejecting the two outliers, we have a mean of 7.57 kcal gfw^{-1} with a standard deviation of $\pm$ 0.19 kcal gfw^{-1}.

Andalusite II: A total of 24 separate measurements were carried out during May-June 1969, with the following results: 7.34, 7.70, 7.55, 7.26, 7.50, 8.06, 7.85, 7.81, 7.67, 7.92, 7.70, 7.39, 7.88, 7.76, 7.60, 7.71, 7.39, 7.38, 7.82, 7.54, 7.44, 7.79, 7.41, 7.51 kcal gfw^{-1}. The mean is 7.62 $\pm$ 0.21 kcal gfw^{-1}.

The calorimetric results confirm that the two samples are very similar in character; we shall adopt 7.60 kcal gfw^{-1} as the mean value of the two enthalpies of solution at 700 $\pm$ 1°C.

In our preliminary calorimetric work we made use of a small sample of andalusite supposedly from Oreville, S. D. This sample showed an enthalpy of solution of 7.22 $\pm$ 0.11 kcal gfw^{-1}. However, a more careful check of the sample showed it contained impurities at a level that produced foreign lines in the X-ray diffraction pattern. Hence, this result has been disregarded.

Although only Andalusite I was analyzed spectrographically, we shall assume that the impurity content in the two samples was comparable; only the iron impurity needs to concern us here. If iron is present as Fe_2O_3, which seems likely, we estimate that the 0.5 percent Fe content provides a positive increment in the observed enthalpy of solution of about 0.05 kcal, based on the enthalpy of solution of Fe_2O_3 of 17.44 kcal/gfw measured in this laboratory (Shearer, ms). Hence, our best value for the enthalpy of solution of pure, iron-free andalusite is 7.55 kcal gfw^{-1} with an estimated maximum uncertainty of $\pm$ 0.20 kcal gfw^{-1}. By comparing this result with the enthalpies of solution of α–Al_2O_3 (7.88 $\pm$ 0.24 kcal gfw^{-1}) and SiO_2 (-1.04 ± 0.07 kcal gfw^{-1}) given in Shearer and Kleppa (1973), we may now also obtain the standard enthalpy of formation of andalusite from the component oxides at 700°C, $\Delta H_f^\circ = -0.71$ kcal gfw^{-1}. The estimated uncertainty in this result is $\pm$ 0.30 kcal (or better).

DISCUSSION

The heat of solution of andalusite given above may be compared quite directly with that of sillimanite given in Anderson and Kleppa (1969). Their average of two samples was 6.88 ± 0.11 kcal/gfw. Thus the $\Delta H°$ (973 K) of the andalusite to sillimanite transition may be taken as 0.67 ± 0.23 kcal/gfw.

At 973 K the molar volume change is −2.20 cm^3/mol, using the volume and thermal expansion data of Skinner, Clark, and Appleman (1961). Holdaway accepted a temperature of 775°C as the 1 atm intercept of the andalusite sillimanite boundary, based on the cryolite solubility measurements of Weill (1966). Over the temperature range 700° to 850°C the change in ΔH is trivial. Hence the calculated dP/dT slope at 775°C is -12 ± 4 bar K^{-1}. If the Richardson, Gilbert, and Bell intercept of 840°C is accepted, the calculated slope becomes -11.4 ± 4 bar K^{-1}.

Holdaway's slope, alone among those put forth, is consistent with the thermochemical data. The dP/dT slope of the Richardson, Gilbert, and Bell diagram would call for a ΔH of about 1.35 kcal/gfw and that of Althaus (1967) about 3.6 kcal/gfw. These heats of reaction are quite beyond the limits of allowable values. The Brown and Fyfe diagram calls for a ΔH of about 0.35 kcal/gfw which is closer than the others to the measured value of 0.67 kcal but just outside the estimated error limits.

The thermodynamic consistence of Holdaway's diagram separates it in terms of credibility from the others. No less important than the accurately predicted ΔH of the andalusite-sillimanite reaction is the correct magnitude of disordering enthalpy and degree of disorder of sillimanite that it predicts. Holdaway's Al-Si disorder theory, confirmed by calorimetry, leads to a plausible explanation of the experimental results of Richardson, Gilbert, and Bell (1969) on the andalusite-sillimanite boundary. They interrupted their long hydrothermal runs at intervals to give the charges 15 to 30 min of mortar grinding. While this would have been insufficient to produce marked X-ray line broadening due to ultracomminution of most of the sample, there must have been some amount of degradation. The ultrafine or strained portion of a charge could have inverted to andalusite at a temperature well above the stability limit of well ordered sillimanite, simply because it is probably impossible to grow anything approaching a well-ordered sillimanite in quantities large enough to produce an increase in X-ray peak heights in feasible runtimes. This phenomenon might well explain the results of Chatterjee and Johannes (1974) on the hydrothermal muscovite plus quartz reaction to sanidine and sillimanite or andalusite. Their temperature region of no reaction is noticeably larger using the (natural) sillimanite than with andalusite, and the implied interpretation is greater stability of andalusite in a temperature range above the Holdaway andalusite stability limit. The probable explanation is again the difficulty of synthesizing a maximally stable ordered sillimanite in amounts large enough to be detected as an increase by their X-ray peak-height method.

ACKNOWLEDGMENTS

The spectrographic analysis was carried out by Miss M. C. Bachelder. The calorimetric work was supported by a grant from the Army Research Office-Durham to O. J. Kleppa. Our work also benefitted from the support of Materials Research at the University of Chicago provided by ARPA and NSF-MRL.

REFERENCES

Abraham, K., and Schreyer, W., 1975, Minerals of the viridine hornfels from Darmstadt, Germany: Contr. Mineralogy Petrology, v. 49, p. 1-20.

Althaus, Egon, 1967, The triple point andalusite-sillimanite-kyanite: Contr. Mineralogy Petrology, v. 16, p. 29-44.

Anderson, P. A. M., and Kleppa, P. J., 1969, The thermochemistry of the kyanite-sillimanite equilibrium: Am. Jour. Sci., v. 267, p. 285-290.

Atherton, M. P., Naggar, M. H., and Pitcher, W. S., 1975, Kyanite in some thermal aureoles: Am. Jour. Sci., v. 275, p. 432-443.

Bragg, W. L., and Williams, E. J., 1934, The effect of thermal agitation on atomic arrangement in alloys: Royal Soc. London Proc., v. 145A, p. 699-730.

Brown, G. C., and Fyfe, W. S., 1971, Kyanite-andalusite equilibrium: Contr. Mineralogy Petrology, v. 33, p. 227-231.

Chatterjee, N. D., 1973, Low-temperature compatibility relations of the assemblage quartz-paragonite and the thermodynamic status of the phase rectorite: Contr. Mineralogy Petrology, v. 42, p. 259-271.

Chatterjee, N. D, and Johannes, W., 1974, Thermal stability and standard thermodynamic properties of synthetic $2M_1$–muscovite, $KAl_2[AlSi_3O_{10}(OH)_2]$: Contr. Mineralogy Petrology, v. 48, p. 89-114.

Dallmeyer, R. D., 1974, Eclogite inclusions in an alpine peridotite sill, Georgia-North Carolina: their chemistry and petrogenetic evolution: Am. Jour. Sci., v. 274, p. 356-377.

Froese, E., and Gasparini, E., 1975, Metamorphic zones in the Snow Lake area, Manitoba: Canadian Mineralogists, v. 13, p. 162-167.

Ganguly, J'bamitra, 1969, Chloritoid stability and related parageneses: theory, experiments and applications: Am. Jour. Sci., v. 17, p. 910-944.

Greenwood, H. J., 1972, Al^{IV}–Si^{IV} disorder in sillimanite and its effect on phase relations of the aluminum silicate minerals: Geol. Soc. America Mem. 132, p. 553-571.

Holdaway, M. J., 1971, Stability of andalusite and the aluminum silicate phase diagram: Am. Jour. Sci., v. 271, p. 91-131.

Holm, J. L., and Kleppa, O. J., 1966, The thermodynamic properties of the aluminum silicates: Am. Mineralogist, v. 51, p. 1608-1622.

Kerrick, D. M., 1972, Experimental determination of muscovite + quartz stability with P_{H_2O} P_{total}: Am. Jour. Sci., v. 272, p. 946-958.

Kleppa, O. J., 1972, Oxide melt solution calorimetry: Colloques Internat., Centre Natl. Recherche Sci., no. 201-Thermochemie, p. 119-127.

Loomis, T. P., 1972, Coexisting aluminum silicate phases in contact metamorphic aureoles: Am. Jour. Sci., v. 272, p. 629-656.

Miyashiro, A., 1972, Metamorphism and related magmatism in plate tectonics: Am. Jour. Sci., v. 272, p. 629-656.

Navrotsky, A., and Kleppa, O. J., 1968, The thermodynamics of cation distribution in simple spinels: Jour. Inorg. Nuclear Chemistry, v. 29, p. 2201-2214.

Navrotsky, A., Newton, R. C., and Kleppa, O. J., 1973, Sillimanite-disordering enthalpy by calorimetry: Geochim. et Cosmochim. Acta, v. 37, p. 2497-2508.

Newton, R. C., 1966a, Kyanite-sillimanite equilibrium at 750°C: Science, v. 151, p. 1222-1225.

———— 1966b, Kyanite-andalusite equilibrium from 700° to 800°C: Science, v. 153, p. 170-172.

———— 1969, Some high-pressure hydrothermal experiments on severely ground kyanite and sillimanite: Am. Jour. Sci., v. 267, p. 278-284.

Pankratz, L. B. and Kelley, K. K., 1964, High temperature heat contents and entropies of andalusite kyanite and sillimanite: U.S. Bur. Mines Rept. Inv., v. 6370, 7 p.

Purtscheller, F., Hoernes, S., and Brown, G. G., 1972, An example of occurrence and breakdown of paragonite: Contr. Mineralogy Petrology, v. 35, p. 34-42.

Richardson, S. W., Gilbert, M. C., and Bell. P. M., 1969, Experimental determination of kyanite-andalusite and andalusite-sillimanite equilibria: the aluminum silicate triple point: Am. Jour. Sci., v. 267, p. 259-272.

Scharbert, H. G., and Kurat, G., 1974, Distribution of some elements between coexisting ferromagnesian minerals in Moldanubian granulate facies rocks, Lower Austria, Austria: Tscher. Min. Pet. Mitt., v. 21, p. 110-134.

Shearer, J. A., ms, 1973, Thermochemistry of the garnets and some related compounds: Ph.D. thesis, Dept. Chemistry, Univ. Chicago.

Shearer, J. A., and Kleppa, O. J., 1973, The enthalpies of formation of $MgAl_2O_4$, $MgSiO_3$, Mg_2SiO_4 and Al_2SiO_5 by oxide melt solution calorimetry: Jour. Inorg. Nuclear Chemistry, v. 35, p. 1073-1078.

Skinner, B. J., Clark, S. P. Jr., and Appleman, D. E., 1961, Molar volumes and thermal expansion of andalusite, kyanite and sillimanite: Am. Jour. Sci., v. 259, p. 651-668.

Thompson, A. B., 1974, Calculation of muscovite-paragonite-alkali feldspar phase relations: Contr. Mineralogy Petrology, v. 44, p. 173-194.

Weill, D. F., 1966 Stability relations in the Al_2O_3–SiO_2 system calculated from solubilities in the Al_2O_3–SiO_2–Na_3AlF_6 system: Geochim. et Cosmochim. Acta, v. 30, p. 223-237.

Zen, E.-A., 1969, The stability relations of the polymorphs of aluminum silicate: a survey and some comments: Am. Jour. Sci., v. 267, p. 297-309.