

## Margarite stability and compatibility relations in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ as a pressure-temperature indicator

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### Abstract

Margarite is a common rock-forming dioctahedral mica, found in many low- to medium-grade metamorphic rocks. To facilitate petrogenetic interpretation of various observed assemblages involving margarite, a complete elucidation of its compatibility relations in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  is a necessary first step.

Applying the methods of experimental and theoretical phase equilibria, the phase relations of margarite in the above system have been deciphered. It is found that the commonly observed assemblage margarite + quartz is stable to a maximum  $P_{\text{H}_2\text{O}}$  of 8.6 kbar, within a temperature range of 300 to 560°C. This explains why quartz + margarite is restricted in nature to low- and medium-grade crustal metamorphic rocks.

At  $P_{\text{H}_2\text{O}}$  in excess of 7 to 8.6 kbar, the assemblage quartz + margarite gives way to the high-pressure assemblage zoisite + kyanite. This is in agreement with the repeatedly reported zoisite + kyanite assemblage from many greenschist to amphibolite facies eclogites. Furthermore, if  $a_{\text{H}_2\text{O}}$  in the equilibrium fluid is reduced to 0.7 due to the presence of other inert gas species, zoisite + kyanite will be stabilized to as low a  $P_{\text{total}}$  as 6.1 kbar. The assemblage quartz + margarite may, therefore, be regarded as an indicator of low- to moderate-pressure regimes of rock metamorphism.

### Introduction

The application of X-ray diffractometry and electron-probe microanalysis to petrologic studies indicates that margarite is a wide-spread rock-forming mineral. During the last five years, numerous margarite occurrences have been reported from a wide variety of low- to medium-grade metamorphic rocks (Sagon, 1970; Jones, 1971; Frey and Niggli, 1972; Ackermann and Morteani, 1973; Chinner, 1974; Höck, 1974; Fox, 1975; Guidotti and Cheney, 1976). In many cases, margarite occurs in assemblages with other dioctahedral micas like phengitic muscovite and/or paragonite. Electron-probe microanalyses of coexisting micas indicate that margarite usually contains significant amounts of paragonite, but practically no muscovite in crystalline solution. Interpretation of margarite-bearing rocks would, therefore, require data on the phase relations of margarite-paragonite crystalline solution in complex natural rock-systems. As a first step toward this end, the present effort aims at delineating the stability and compatibility relations of margarite in the model sys-

tem  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ . Owing to very slow reaction rates in phase equilibria experiments involving margarite, theoretical methods have been extensively used.

### Previous work

Phase relations in the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  have been investigated by a large number of researchers (Newton and Kennedy, 1963; Newton, 1966; Hays, 1966; Boettcher, 1970; Liou, 1971; and others). Boettcher (1970) summarized the subsolidus and liquidus relations in this system at temperatures above 580°C, while Liou (1971) worked out the phase relations below 400°C. The phase margarite has not been considered in these studies.

Since then, margarite phase relations within the system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  have been studied experimentally by several workers (Velde, 1971; Chatterjee, 1974; Storre and Nitsch, 1974). Using pure synthetic phases, Velde (1971) and Chatterjee (1974) determined the equilibrium decomposition of margarite to anorthite + corundum +  $\text{H}_2\text{O}$ . On the other

hand, Storre and Nitsch (1974), using a natural margarite containing substantial amounts of paragonite and some ephesite end-member in crystalline solution, determined the upper thermal compatibility limit of quartz + margarite. Furthermore, in an abstract, Wall and Essene (1972) presented the results of a theoretical study of subsolidus phase relations in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ . Based on the then available *preliminary* experimental results on the thermal decomposition of margarite, Wall and Essene (1972) concluded that the assemblage margarite + quartz should be stable below 10 kbar  $P_{\text{H}_2\text{O}}$  over a narrow temperature range of approximately 70°C.

### Theoretical background

The approach followed in the present study involves obtaining internally consistent thermochemical data for all phases relevant to margarite compatibility relations in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  (Fig. 1), and calculating the phase relations. In doing so, it appeared easier to start at the upper thermal stability limit of margarite and to pursue the phase relations to lower temperatures.

For the purpose of thermodynamic treatment of dehydration equilibria involving pure solids and essentially pure  $\text{H}_2\text{O}$  fluid, the standard and reference states have to be specified. The standard state of the condensed phases is defined as the pure solid at 1 bar pressure and given temperature  $T$  (°K), that of  $\text{H}_2\text{O}$  fluid is pure  $\text{H}_2\text{O}$  gas at a fugacity of 1 bar and stated

temperature. Under these conditions, the non-ideal  $\text{H}_2\text{O}$  gas will have the same Gibbs energy as a hypothetical ideal  $\text{H}_2\text{O}$  gas at 1 bar pressure and given temperature. The reference states for standard molar enthalpy of formation  $H_{f,T}^0$ , standard molar entropy of formation  $S_{f,T}^0$ , and standard molar Gibbs energy of formation  $G_{f,T}^0$  are the constituent elements in their stable form and standard state of 1 bar and given temperature  $T$  (°K). In these notations, the superscript "0" refers to 1 bar standard state, while the subscript "T" denotes the specified temperature  $T$  (°K), and finally, the subscript "f" indicates formation from the elements, *i.e.* the reference state.

In dealing with simple dehydration equilibria to moderate pressures and temperatures, the following assumptions have been found to be permissible (Fisher and Zen, 1971; Chatterjee, 1975):

- (1) The fluid in equilibrium with the condensed phases is essentially pure  $\text{H}_2\text{O}$ .
- (2)  $\Delta V_s$ , the volume change due to the solids involved in an equilibrium, is not a function of pressure or temperature; *i.e.*  $(\partial \Delta V_s / \partial T)_P = 0$  and  $(\partial \Delta V_s / \partial P)_T = 0$ . Thus,  $\Delta V_s = \Delta V_{298.15,s}^0$ .
- (3)  $(\partial \Delta H_s^0 / \partial T)_P = 0 = T(\partial \Delta S_{f,s}^0 / \partial T)_P$ . In other words,  $\Delta H_s^0$ , the standard enthalpy of reaction due to the solids and  $\Delta S_{f,s}^0$ , the change in standard entropy of formation due to the solids are independent of temperature. Thus  $\Delta H_{f,s}^0 = \Delta H_{298.15,s}^0$  and  $\Delta S_{f,T,s}^0 = \Delta S_{f,298.15,s}^0$ . Furthermore, through the choice of standard state at 1 bar,  $\Delta H_s^0$  and  $\Delta S_{f,s}^0$  are also independent of pressure. Given these assumptions, for a reaction of the type



where  $a$  moles of the condensed phase A dehydrates to  $b$  moles of another condensed phase B plus  $n$  moles of  $\text{H}_2\text{O}$  fluid, it can be demonstrated that (Chatterjee, 1975)

$$\begin{aligned} \Delta G_T^P &= \Delta H_{298.15,s}^0 \\ &- T\Delta S_{f,298.15,s}^0 + \Delta V_{298.15,s}^0 (P - 1) \\ &+ nG_{f,T,\text{H}_2\text{O}}^0 + nRT \ln f_{\text{H}_2\text{O}} \end{aligned} \quad (2)$$

where  $\Delta G_T^P$  denotes the Gibbs energy change of the reaction at a given  $P$  and  $T$ , and  $f_{\text{H}_2\text{O}}$  refers to the fugacity of  $\text{H}_2\text{O}$  at the same  $P$  and  $T$ . Recalling that at equilibrium  $\Delta G_T^P$  equals zero, equation (2) can be rearranged to

$$\begin{aligned} \Delta V_{298.15,s}^0 (P - 1) + nG_{f,T,\text{H}_2\text{O}}^0 + \\ nRT \ln f_{\text{H}_2\text{O}}^* = -\Delta H_{298.15,s}^0 \\ + T\Delta S_{f,298.15,s}^0 \end{aligned} \quad (3)$$

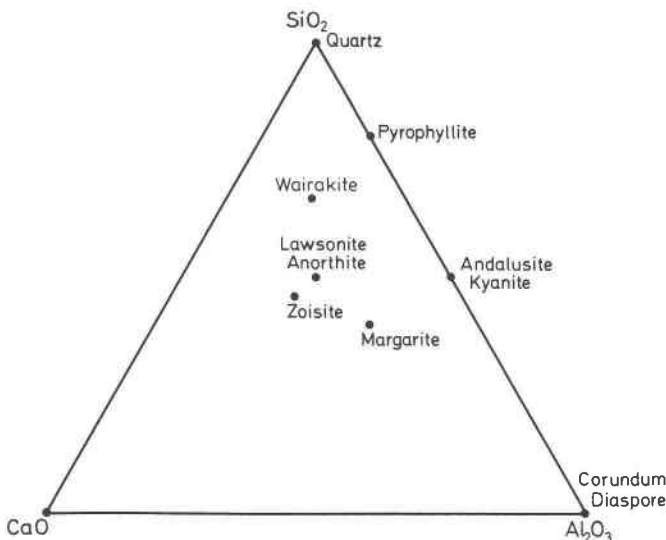


FIG. 1. Crystalline phases in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  pertinent to the compatibility relations of margarite, projected from the  $\text{H}_2\text{O}$  apex of the quaternary system onto the anhydrous base of the tetrahedron.

A plot of the left-hand side of equation (3) against  $T$  ( $^{\circ}\text{K}$ ) yields a straight line with a slope of  $\Delta S_{f,298.15,s}^0$ , its intercept at  $0^{\circ}\text{K}$  is  $-\Delta H_{298.15,s}^0$ . If  $S_{f,298.15}^0$  and  $H_{f,298.15}^0$  of the phase B in equation (1) are known, we can evaluate  $S_{f,298.15}^0$  and  $H_{f,298.15}^0$  of the unknown phase A, and vice versa.

Calculation of univariant equilibria in a  $P_{\text{total}}(=P_{\text{H}_2\text{O}})$ - $T$  plane involves solving equation (2) for  $P_{\text{total}}(=P_{\text{H}_2\text{O}})$  at any given  $T$ , setting  $\Delta G_T^P = 0$ . If, however, the  $\text{H}_2\text{O}$  gas in equilibrium with the mineral phases is diluted by other inert gas species, the phase relations can be displayed on a  $P_{\text{total}}$  vs.  $T$  projection for arbitrarily chosen values of  $a_{\text{H}_2\text{O}}$ . At any given  $P$  and  $T$ ,  $a_{\text{H}_2\text{O}} \equiv f_{\text{H}_2\text{O}}/f_{\text{H}_2\text{O}}^*$ , i.e. water activity is the ratio of fugacity of  $\text{H}_2\text{O}$  in the gas mixture,  $f_{\text{H}_2\text{O}}$ , to the fugacity of pure  $\text{H}_2\text{O}$ ,  $f_{\text{H}_2\text{O}}^*$ . To obtain the desired phase relations in a  $P_{\text{total}}-T-a_{\text{H}_2\text{O}}$  space, the equation (2) is modified to

$$\begin{aligned} \Delta G_T^P = & \Delta H_{298.15,s}^0 - T\Delta S_{f,298.15,s}^0 \\ & + \Delta V_{298.15,s}^0 (P - 1) + nG_{f,T,\text{H}_2\text{O}}^0 \\ & + nRT \ln f_{\text{H}_2\text{O}}^* + nRT \ln a_{\text{H}_2\text{O}} \end{aligned} \quad (4)$$

Again, at equilibrium  $\Delta G_T^P = 0$ ; the equation (4) is solved for  $P_{\text{total}}$  at given  $T$  and  $a_{\text{H}_2\text{O}}$ .

## Results

### An internally consistent set of thermodynamic data

Basically, there are two sources of thermodynamic data: (1) direct calorimetric, electrochemical, and spectroscopic measurements and (2) those extracted from phase equilibria studies. If sufficient care is taken in experimental work, the latter source yields data of a quality comparable to those obtained from calorimetric measurements (cf. Fisher and Zen, 1971, p. 313; Chatterjee, 1975, p. 54). The present study is based on data combined from both of these sources.

Obtaining a set of internally consistent thermochemical data by direct calorimetry is often beset with difficulties. As Zen (1969) pointed out for the first time, use of inconsistent calorimetric reference sources of aluminum led to a discrepancy of about 7 kcal between the tabulated (Robie and Waldbaum, 1968) standard enthalpies of formation,  $H_{f,298.15}^0$ , of kaolinite on the one hand, and  $\text{Al}_2\text{SiO}_5$

TABLE 1. Standard thermodynamic parameters of the condensed phases

Phase	Composition	$H_{f,298.15}^0$ (cal/mole)	$S_{f,298.15}^0$ (cal/ $^{\circ}\text{K}$ -mole)	$G_{f,298.15}^0$ (cal/mole)	$V_{298.15}^0$ (cal/bar)	References
Gibbsite	$\text{Al}(\text{OH})_3$	-309325	-110.326	-276431	0.76377	(see text)
Andalusite	$\text{Al}_2\text{O}(\text{SiO}_4)$	-619390	-118.250	-584134	1.2316	1
Anorthite	$\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$	-1015190 <sup>a</sup>	-180.024	-961516 <sup>a</sup>	2.4089	1
Corundum	$\text{Al}_2\text{O}_3$	-400400	-74.854	-378082	0.61126	1
Diaspore	$\text{AlO}(\text{OH})$	-239569	-64.254	-220412	0.42447	2
Kaolinite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$	-985355 <sup>a</sup>	-256.908	-908758 <sup>a</sup>	2.3786	1
Kyanite	$\text{Al}_2\text{O}(\text{SiO}_4)$	-620118	-120.152	-584295	1.0538	3
Lawsonite	$\text{CaAl}_2(\text{OH})_2(\text{Si}_2\text{O}_7) \cdot \text{H}_2\text{O}$	-1167205 <sup>a</sup>	-283.096	-1082800 <sup>a</sup>	2.4216	1
Margarite	$\text{CaAl}_2(\text{Al}_2\text{Si}_2\text{O}_{10})(\text{OH})_2$	-1496078	-308.205	-1404186	3.0984	4
Pyrophyllite	$\text{Al}_2(\text{Si}_4\text{O}_{10})(\text{OH})_2$	-1348797	-300.128	-1259314	3.0505 <sup>b</sup>	5
Quartz	$\text{SiO}_2$	-217650	-43.616	-204646	0.54226	1
Sillimanite	$\text{Al}_2\text{O}(\text{SiO}_4)$	-617860	-116.779	-583042	1.1926	3
Wairakite	$\text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 2\text{H}_2\text{O}$	-1581579	-333.175	-1482243	4.558	6
Zoisite	$\text{Ca}_2\text{Al}_3\text{O}(\text{SiO}_4/\text{Si}_2\text{O}_7)(\text{OH})$	-1657225	-319.087	-1562089	3.2436	7

a. Adjusted to new Al reference source (see text); b. Taylor and Bell (1970).

References: 1. Robie and Waldbaum (1968); 2. Extracted from experimental data by Haas (1972); 3. Adjusted to experimental data (Richardson et al, 1969); 4. Extracted from experimental data by Chatterjee (1974); 5. Extracted from experimental data "PAQW" by Haas and Holdaway (1973); 6. Extracted from experimental data by Liou (1970b); 7. Extracted from preliminary experimental data by Chatterjee and Frentrup (unpublished), combined with those by Newton and Kennedy (1963).



binning the andalusite data linearly with  $\Delta G_T^0$  of andalusite  $\rightleftharpoons$  kyanite and kyanite  $\rightleftharpoons$  sillimanite phase transitions (Richardson *et al.*, 1969).

Additional phases, for which the standard thermodynamic data were extracted from phase equilibria studies, include diaspore, margarite, pyrophyllite, zoisite, and wairakite (Table 1). The format of calculation used for data retrieval has been outlined in the last section. The phase equilibria considered involved one "unknown" solid phase and one or more "known" solids. In each case except zoisite, direct calorimetric data were available for the "known" phases. For zoisite, the "known" phases included grossular, for which thermodynamic data had to be extracted utilizing  $P$ - $T$  data for the equilibrium 2 grossular = 3 wollastonite + 1 gehlenite + 1 anor-

thite (Huckenholz *et al.*, 1975). The uncertainty in the derived thermodynamic data of zoisite is thus considered larger than that of the other phases.

In this way one of the many theoretically possible sets of internally consistent thermodynamic data has been derived (Table 1). These data have been used to calculate margarite phase relations. It should be remembered, however, that the individual uncertainties in  $G_{7,298.15}^0$  of the phases range between 0.5 to 3.0 kcal/mole, the consequences of which will be discussed later.

#### Calculated phase diagrams

Using the thermodynamic data of the condensed phases given above (Table 1) and those of  $H_2O$  from

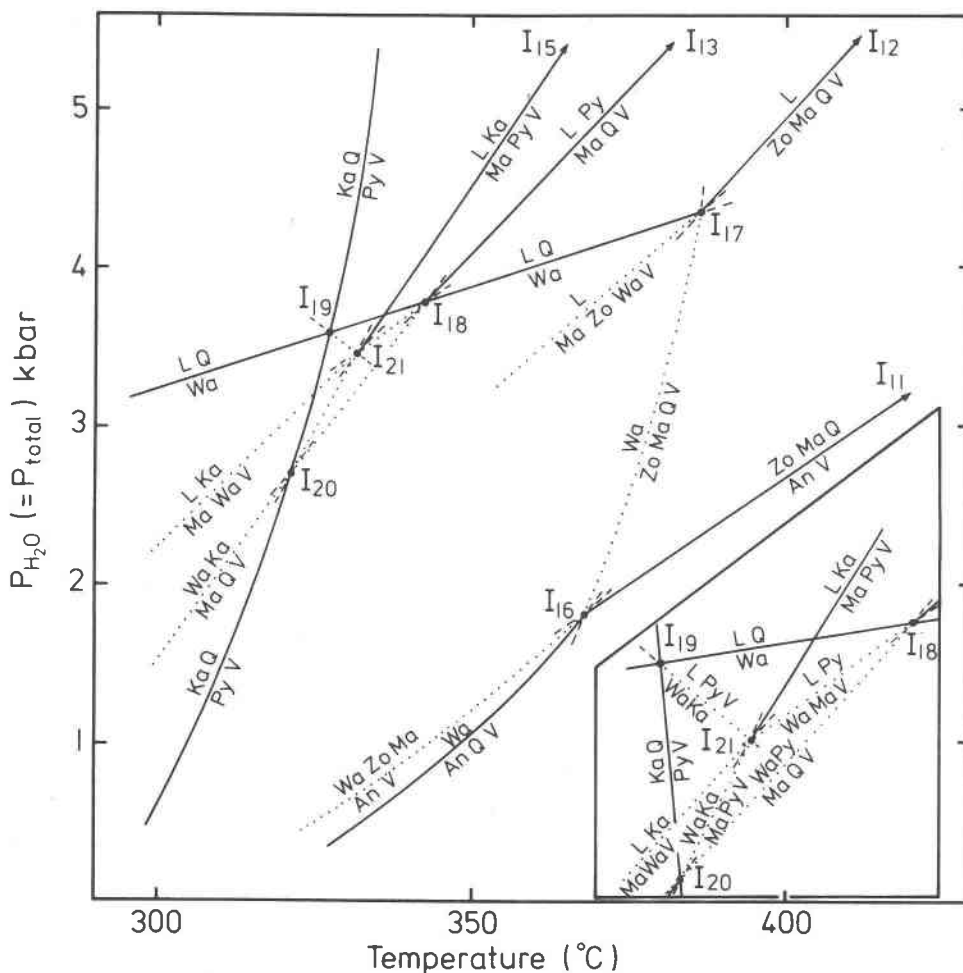


FIG. 3. Margarite-wairakite phase relations in the system  $CaO-Al_2O_3-SiO_2-H_2O$ . Univariant curves in solid black are either calculated or experimentally determined, those shown as dotted lines are conjectural.

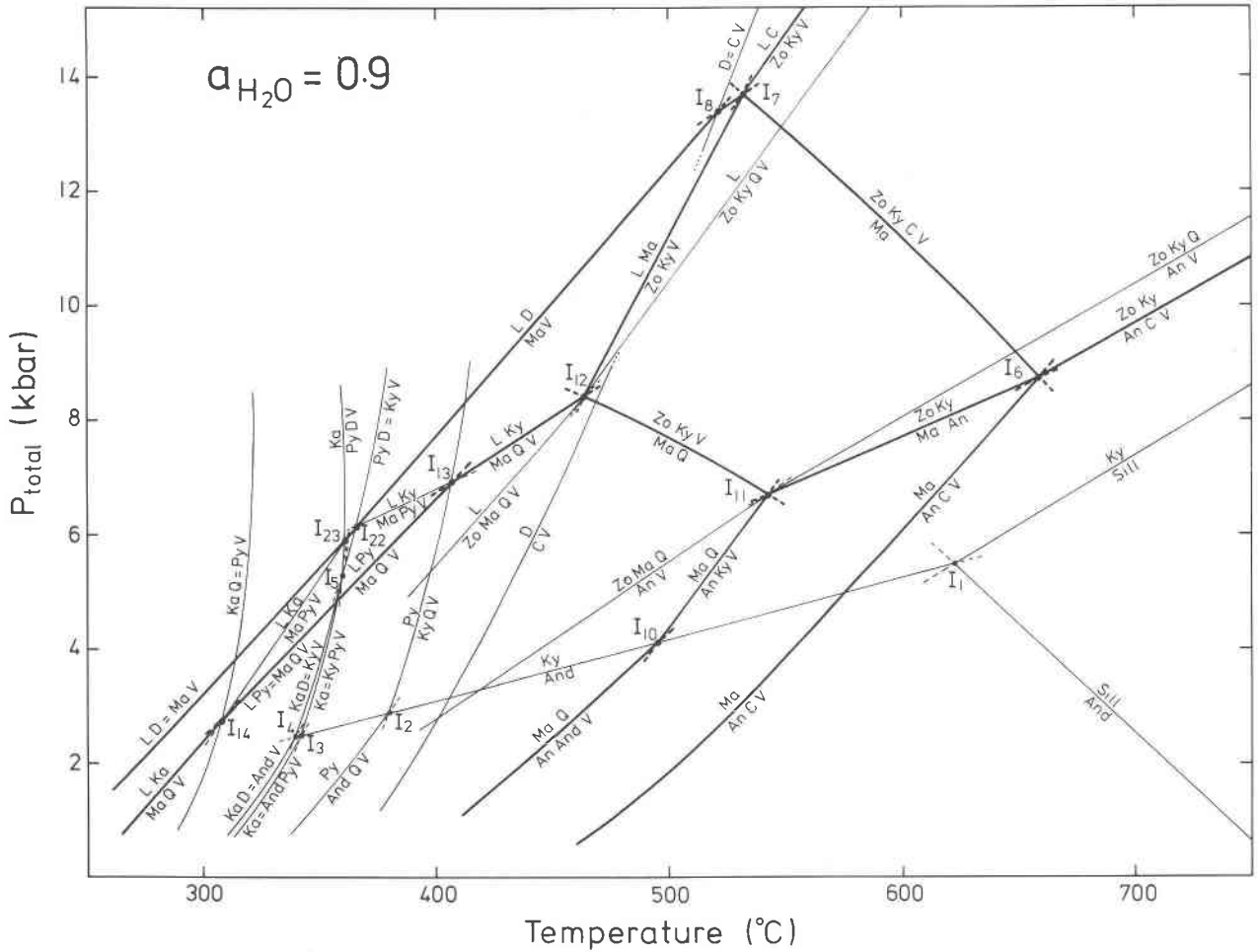


FIG. 4. Margarite phase relations in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  shown on a  $P_{\text{total}}$  vs.  $T^\circ\text{C}$  projection for  $a_{\text{H}_2\text{O}} = 0.9$ . The stability field of margarite and those of the assemblages quartz + margarite and zoisite + kyanite indicated with bold lines.

Robie and Waldbaum (1968),<sup>1</sup> coupled with water fugacity data from Burnham *et al.* (1969), the phase relations of margarite in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  have been computed. The results are reproduced in Figure 2 in a  $P_{\text{H}_2\text{O}} (= P_{\text{total}})$  vs.  $T$  projection. It is seen that the phase margarite is stable to a maximum  $P_{\text{H}_2\text{O}}$  of 14 kbar. By contrast, the assemblage quartz + margarite—reported from many metamorphic rocks—is stable only up to 8.6 kbar  $P_{\text{H}_2\text{O}}$ . With respect to temperature, the assemblage margarite + quartz is stable between 300 and 560°C, agreeing with its reported occurrences in low- to medium-grade metamorphic rocks.

One feature of the phase relations, not indicated in

<sup>1</sup> The values of the Gibbs energy of formation of  $\text{H}_2\text{O}$ , tabulated by Robie and Waldbaum (1968), are valid for the 1 atmosphere standard state. Following Fisher and Zen (1971), these values were adjusted for the 1 bar standard state chosen in this study.

Figure 2, warrants comment. At the low-temperature/low-pressure end of this diagram, the phase wairakite will enter into compatibility relation with other phases of the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ . This will further complicate the phase relations in the  $P_{\text{H}_2\text{O}}-T$  range of 2 to 4 kbar and 300 to 400°C. Attempts to calculate these equilibria on the basis of the thermodynamic data of wairakite (Table 1), extracted from Liou's (1970b)<sup>2</sup> study of the equilibrium wairakite = anorthite + 2 quartz + 2  $\text{H}_2\text{O}$ , yielded erratic results. A careful scrutiny of Liou's data showed that one of the basic assumptions made in this study— $(\partial\Delta H_s^\circ/\partial T)_P = 0 = T(\partial\Delta S_s^\circ/\partial T)_P$ —

<sup>2</sup> In corresponding with Liou (personal communication, 1975), it was brought out that the published data on the wairakite = anorthite + 2 quartz + 2  $\text{H}_2\text{O}$  (Liou, 1970a, p. 259) equilibrium were slightly misquoted, besides being incomplete. The present study is based on Liou's original run data (Liou, 1970b).

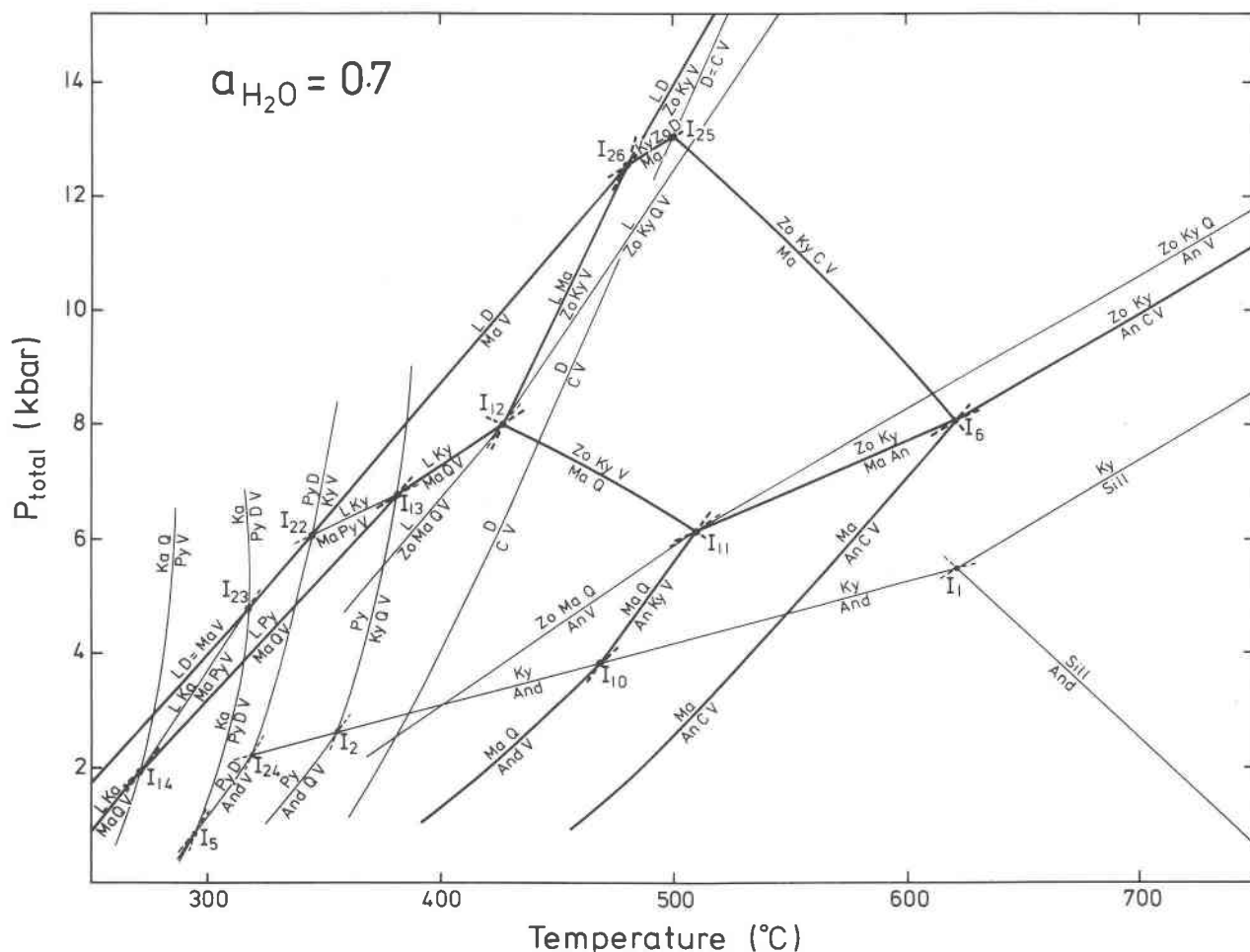


FIG. 5. Margarite phase relations in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  displayed on a  $P_{\text{total}}$  vs.  $T$  projection for a constant  $a_{\text{H}_2\text{O}}$  equalling 0.7.

does not hold in this case.<sup>3</sup> The reason for this kind of behavior may be sought in the presence of zeolitic water in the structure of wairakite.

Fortunately, this problem could be essentially overcome by directly combining experimental data on the equilibria wairakite = anorthite + 2 quartz +  $\text{H}_2\text{O}$  (Liou, 1970b) on the one hand, and lawsonite + 2 quartz = wairakite (Liou, 1971) on the other, with the calculated equilibrium curves of Figure 2. The resulting phase relations are indicated in Figure 3. It should be noted that the  $P_{\text{H}_2\text{O}}-T$  positions of the invariant points  $I_{16}$  through  $I_{19}$  can be determined accurately, while that of  $I_{20}$  is conjectural. A direct consequence of these phase relations is that the in-

variant point  $I_{14}$  of Figure 2 will become metastable with respect to the stable equilibria of Figure 3.

Having thus completed the study of margarite phase relations in the  $P_{\text{H}_2\text{O}} (= P_{\text{total}})$  vs.  $T$  plane, we shall turn to the problem of uncertainties in the thermodynamic data of each individual phase. As pointed out earlier, uncertainties in  $G_{7,298.15}^0$  of the order of 0.5 to 3.0 kcal/mole have to be tolerated for most of these phases. It is obvious that consideration of such uncertainties will inevitably lead to mutually contradictory phase relations. However, we shall see presently that the phase relations obtained in this study agree excellently with field data on margarite-bearing natural rocks. This lends credence to these results, and justifies the thermodynamic approach.<sup>4</sup>

<sup>3</sup> The standard thermodynamic data of wairakite listed in Table 1 were obtained by assuming that  $\Delta S_f^\circ$  and  $\Delta H_f^\circ$  are independent of temperature. It is not surprising that calculations based on these numbers gave no meaningful results.

<sup>4</sup> Following the methods of linear programming outlined by Gordon (1973), a "better" set of thermodynamic data with smaller uncertainties will eventually result. Once such data are available, it will be possible to refine the phase relations presented in this study.

In nature, the fluid phase coexisting with the solids during the process of equilibration will seldom, if ever, be pure  $H_2O$ . Since we are restricting ourselves to the system  $CaO-Al_2O_3-SiO_2-H_2O$ , we have to assume all other fluids to be inert. Consequently, we shall now deal with margarite phase relations in a  $P_{total}-T-a_{H_2O}$  space. The equilibria will be shown by projecting the phase relations onto a  $P_{total}$  vs.  $T$  plane, keeping  $a_{H_2O}$  constant at some arbitrarily chosen value. Figure 4 displays the margarite phase relations on a  $P_{total}$  vs.  $T$  projection for a constant  $a_{H_2O}$  equalling 0.9. Comparison with phase relations obtained for  $P_{total}(=P_{H_2O})$  vs.  $T$  plane reveals two important changes. First, the stability fields of margarite and that of the assemblage quartz + margarite are shifted to somewhat lower temperatures and pressures. Secondly, the invariant point  $I_5$ , located outside the margarite stability field for  $P_{H_2O} = P_{total}$  conditions, has now entered the margarite field. As a result, two new invariant points  $I_{22}$  and  $I_{23}$  are generated at the expense of  $I_9$  and  $I_{15}$  (cf. Fig. 2).

Figure 5 indicates the phase relations of margarite on a  $P_{total}$  vs.  $T$  diagram for a constant  $a_{H_2O}$  equalling 0.7. Again, the stability field of margarite and that of the assemblage quartz + margarite have moved further to lower temperatures and pressures. Moreover, the invariant point  $I_5$  is now located at a very low pressure within the stability field of the assemblage quartz + margarite; this has resulted in the generation of the new invariant point  $I_{24}$  to the exclusion of the former  $I_3$  and  $I_4$ . Additional changes in the compatibility relations include the incoming of  $I_{25}$  and  $I_{26}$  at the expense of  $I_7$  and  $I_8$  (cf. Figs. 2 and 4).

### Geological application

Within the system  $CaO-Al_2O_3-SiO_2-H_2O$ , the following assemblages have been reported from margarite-bearing metamorphic rocks of various localities:

- (1) quartz + margarite-bearing assemblages
  - (a) margarite-quartz
  - (b) margarite-quartz-kaolinite (Sagon, 1970; Jones, 1971)
  - (c) margarite-quartz-pyrophyllite (Sagon, 1970)
  - (d) margarite-zoisite-quartz (Höck, 1974)
  - (e) margarite-clinozoisite-quartz (Frey and Niggli, 1972; Chinner, 1974)
  - (f) margarite-kyanite-quartz (Fox, 1975)
- (2) quartz-free margarite-bearing assemblages
  - (a) margarite-diaspore (Deer *et al.*, 1962)
  - (b) margarite-corundum (Deer *et al.*, 1962)
  - (c) margarite-kyanite-corundum (Schuiling, 1973, personal communication)

(d) margarite-clinozoisite (rim on epidote)-kyanite (Ackermann and Morteani, 1973).

Comparison with the calculated margarite phase relations (Fig. 2) shows that there is excellent agreement between the theoretically predicted and observed mineral assemblages. Indeed, each one of the assemblages reported from natural rocks thus far has a distinct  $P_{H_2O}-T$  range of stability. In a general way, it can be said that if  $P_{H_2O}$  equals  $P_{total}$ , the assemblage margarite + quartz is stable from about 300° to 560°C. This explains the common occurrence of quartz + margarite in low- to medium-grade metamorphic rocks.

The fluids equilibrated with the mineral phases in nature will, however, hardly ever be pure  $H_2O$ . Presence of other gas species like  $CO_2$ ,  $CH_4$ ,  $H_2$ ,  $H_2S$  *etc.* will reduce the activity of  $H_2O$  in metamorphic fluids. Decreasing  $a_{H_2O}$  will lead to gradual shift of the stability fields of margarite, quartz + margarite, zoisite + kyanite *etc.* to successively lower temperatures and pressures, as indicated in Figure 6. In other words, with decreasing  $a_{H_2O}$  the zoisite + kyanite stability field will expand at the cost of the stability field of the assemblage quartz + margarite. Therefore, margarite + quartz will be restricted to low- to medium-pressure regimes of rock metamorphism. At higher total pressures, one would expect the assemblage zoisite + kyanite, rather than quartz + margarite. This is compatible with many reported occurrences of the assemblage zoisite + kyanite from greenschist to amphibolite facies eclogitic rocks (Mottana *et al.*, 1968; Miller, 1970; Heritsch, 1973). A detailed study of zoisite-kyanite-bearing eclogites from the Tauern area, coupled with independent temperature determination by oxygen isotope thermometry, led Abraham *et al.* (1974) to the conclusion that these eclogites must have equilibrated around 500 to 550°C at a minimum pressure of 6 kbar, whereby "the fluid pressure nearly equaled total pressure." Comparison with Figure 6 indicates that if such rocks were indeed to have equilibrated at a  $P_{total}$  of 6 kbar, the  $a_{H_2O}$  in the fluid phase must have been  $\leq 0.7$ .<sup>5</sup>

<sup>5</sup> Abraham *et al.* (1974) observed the assemblage talc + kyanite in some of their zoisite + kyanite-bearing eclogites. If  $P_{H_2O}$  were equal to  $P_{total}$ , at a temperature of 550°C the assemblage talc + kyanite would indicate a  $P_{H_2O} \geq 14$  kbar, according to experimental data by Schreyer and Seifert (1969). Indeed, naturally occurring talc-kyanite rocks have been repeatedly interpreted to have formed under a  $P_{H_2O}$  in excess of 10 kbar (Vrána and Barr, 1972; Schreyer, 1973). At least for those rocks, in which talc + kyanite assemblage is associated with the assemblage zoisite + kyanite, the postulate of extremely high  $P_{H_2O}$  of the order of 10 to 15 kbar (Chinner and Dixon, 1973) has to be reconsidered in the light of the present study.



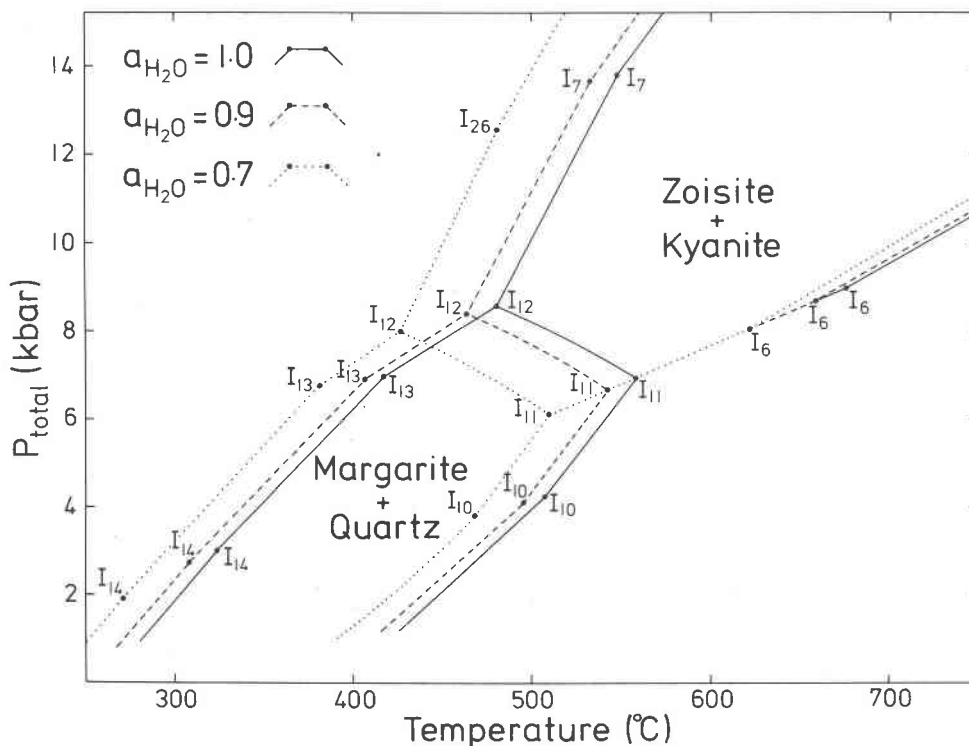


FIG. 6. A synoptic  $P_{\text{total}}$  vs.  $T^{\circ}\text{C}$  diagram showing shifting stability fields of the assemblages quartz + margarite and zoisite + kyanite as a function of  $a_{\text{H}_2\text{O}}$ . The individual univariant curve, not labelled here, can be identified by comparison with Figs. 2, 4, and 5. Note that the univariant curve joining the invariant points  $I_6$  and  $I_{11}$  pertains to the fluid-absent equilibrium zoisite + kyanite = margarite + anorthite; as such, it is independent of  $a_{\text{H}_2\text{O}}$ .

As pointed out earlier, natural margarites—especially in garnet- and staurolite-kyanite-grade pelitic rocks—often contain significant amounts of paragonite in crystalline solution. In absence of data on the margarite-paragonite crystalline solution, one might get some insight into the problem by considering the compatibility relations of the mica *end-members* margarite and paragonite in quartz-staurolite-kyanite-bearing rocks. Figure 7 summarizes the relevant phase equilibria data. It is seen that the assemblage margarite + quartz + staurolite + kyanite has a very small stability field compared with that of the assemblage paragonite + quartz + kyanite + staurolite. This is again in agreement with field observations: whereas paragonite + quartz + kyanite + staurolite is a common assemblage, margarite + quartz + kyanite + staurolite (Fox, 1975) is a rare one. However, by analogy with muscovite-paragonite phase relations (Chatterjee and Froese, 1975), it will be expected that the thermal compatibility limit of the assemblage margarite + quartz will be shifted toward higher temperature if some paragonite end-member is held in crystalline

solution in margarite. This will increase the  $P_{\text{H}_2\text{O}} - T$  range of stability of the assemblage margarite crystalline solution + quartz + kyanite + staurolite to some extent. As Storre and Nitsch (1974) have already indicated, experimental investigations with a margarite crystalline solution containing substantial amounts of paragonite (and some ephesite) end-member clearly demonstrate this trend.

#### Conclusions and implications

The phase relations of margarite in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  provide an excellent temperature-pressure indicator for margarite-bearing crustal metamorphic rocks. Specifically, the common metamorphic mineral assemblage quartz + margarite is stable between  $300^{\circ}$  and  $560^{\circ}\text{C}$  up to a maximum  $P_{\text{H}_2\text{O}}$  of 8.6 kbar. If the activity of  $\text{H}_2\text{O}$  in the equilibrium fluid is reduced because of the presence of inert gas species, the stability field of margarite + quartz will be shifted to yet lower temperatures and pressures. This effect will be countered to some extent by the incorporation of paragonite end-member in crystalline solution in margarite. However, little or no

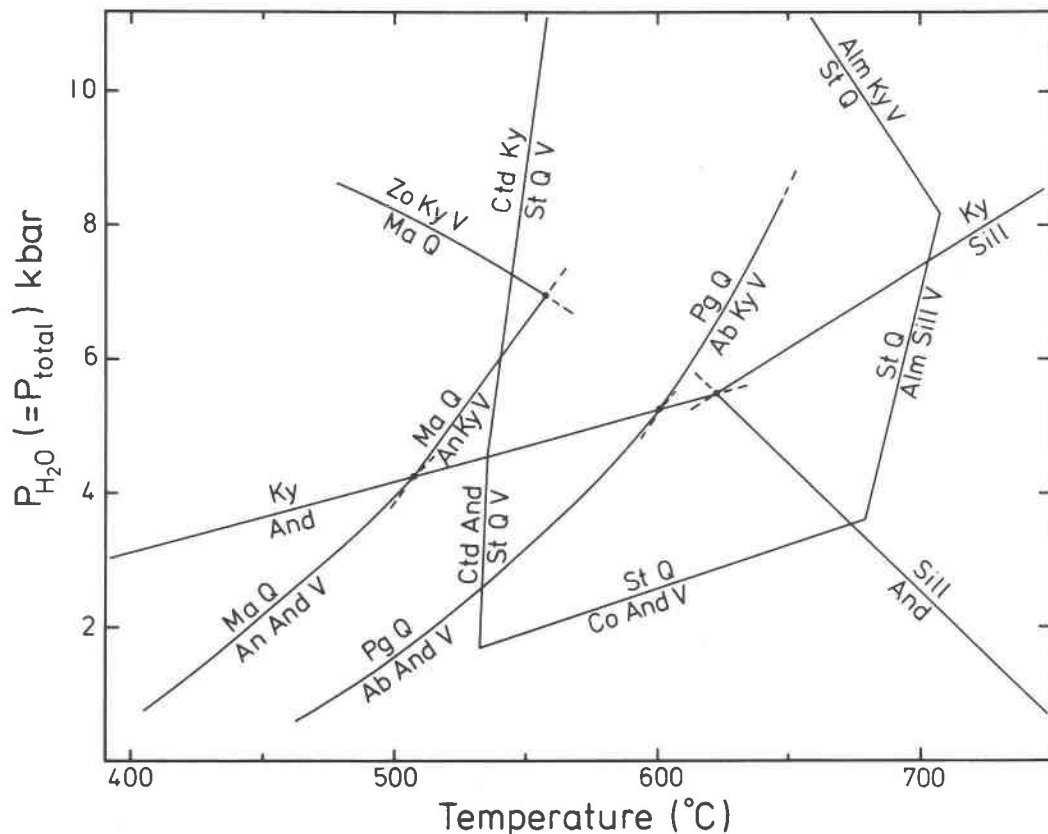


FIG. 7. A composite  $P_{\text{H}_2\text{O}} (= P_{\text{total}})$  vs.  $T^\circ\text{C}$  diagram showing the upper thermal stability limits of the assemblages margarite + quartz (this study) and paragonite + quartz (Chatterjee, 1972). Additionally indicated are the  $\text{Al}_2\text{SiO}_5$  phase relations (Richardson *et al.*, 1969) as well as the stability relations of the assemblage quartz + Fe-stauroilite, valid for oxygen fugacities around the middle of the magnetite field (Ganguly, 1972).

information is available at present on the thermodynamic mixing properties of the binary margarite-paragonite crystalline solution. Such data are indispensable for a quantitative prediction of the behavior of margarite crystalline solution commonly encountered in metamorphic rocks.

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