

The stability of anthophyllite—A reevaluation based on new experimental data

JOSEPH V. CHERNOSKY, JR.¹

U.S. Geological Survey, Reston, Virginia 22092

Abstract

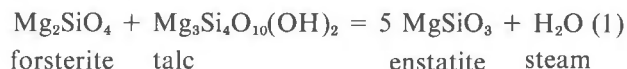
The univariant reactions (1) $Ta + Fo = 5En + Stm$ and (2) $Ta = 3En + Qtz + Stm$ have been experimentally reversed at $P_{H_2O} = P_{total}$. Smooth curves drawn between the brackets pass through the coordinates 0.5 kbar, 617°C; 1 kbar, 638°C; 2 kbar, 662°C; 3 kbar, 679°C; 4 kbar, 696°C for reaction (1); and 0.5 kbar, 660°C; 1 kbar, 697°C; 2 kbar, 738°C, for reaction (2). The positions of the curves are probably within 5°C of the stated values. Intersections of reactions (1) and (2) with the reversed reactions (3) $9Ta + 4Fo = 5Ant + 4Stm$ and (4) $Ant = 7En + Qtz + Stm$, respectively, generate two invariant points. The reaction (7) $Ant = Ta + 4En$ is common to both invariant points and together with reactions (3) and (4) serves to bound the stability field of anthophyllite. Reactions (2) and (4) intersect at $P_{H_2O} = 5$ kbar, and their positions are consistent with the P - T diagram proposed by Greenwood. However, the slope of reaction (1) is less positive than the slope of reaction (3), and this is inconsistent with Greenwood's proposed P - T diagram. If reaction (1) is accurately positioned, the conflict can be resolved in one of two ways. Reaction (3) can be rotated until its slope is less positive than the slope of reaction (1), or the P - T diagram can be inverted. The first alternative is most plausible. If Greenwood's proposed P - T diagram is correct, the data presented here limit the stability of pure Mg-anthophyllite with respect to the assemblage $Ta + En$ to a maximum pressure of about 5 kbar P_{H_2O} .

Introduction

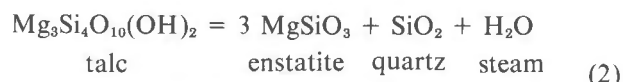
Because of the potential value of anthophyllite as an indicator of metamorphic grade in magnesium silicate (–carbonate) assemblages, considerable effort has been expended to determine its stability field (Bowen and Tuttle, 1949; Yoder, 1952; Fyfe, 1962; Greenwood, 1963) and to obtain its thermodynamic constants (Greenwood, 1963 and 1971; Mel'nik and Onoprienko, 1969; and Zen, 1971). Based on a hydrothermal investigation of phase equilibria in the system MgO – SiO_2 – H_2O , Bowen and Tuttle (1949) concluded that anthophyllite does not have a true stability field. After conducting experiments using natural anthophyllite as a starting material, Fyfe (1962) suggested that Bowen and Tuttle were not able to determine a stability field for anthophyllite because it was a very difficult phase to nucleate. Greenwood (1963) supported Fyfe's conclusion by experi-

mentally determining that anthophyllite did have a true stability field.

During the course of the present study, the reactions



and



were bracketed, with reversed experiments, at P_{H_2O} below 4 kbar in order to define more closely the maximum pressure to which anthophyllite is stable. The reader is referred to Table 1 for compositions of phases and balanced reactions considered in this paper. The preliminary results of the experimental work have been reported (Chernosky, 1974).²

¹ Present address: Department of Geological Sciences, University of Maine, Orono, Maine 04473

² Note that reactions (1), (3) on one hand and (2), (4) on the other have been accidentally reversed in an earlier statement (Chernosky, 1974) of the problem.

TABLE 1. Abbreviations and compositions of phases and balanced reactions

Anthophyllite	Ant	$Mg_7Si_8O_{22}(OH)_2$
Enstatite	En	$MgSiO_3$
Forsterite	Fo	Mg_2SiO_4
Quartz	Qtz	SiO_2
Steam	Stm	H_2O
Talc	Ta	$Mg_3Si_4O_{10}(OH)_2$

1. $Ta + Fo = 5En + Stm$
2. $Ta = 3En + Qtz + Stm$
3. $9Ta + 4Fo = 5Ant + 4Stm$
4. $Ant = 7En + Qtz + Stm$
5. $Ant + Fo = 9En + Stm$
6. $7Ta = 3Ant + 4Qtz + 4Stm$
7. $Ant = Ta + 4En$

Experimental methods

Starting material

Mixtures with bulk compositions corresponding to $MgO \cdot SiO_2$, $2MgO \cdot SiO_2$, and $3MgO \cdot 4SiO_2$ were prepared by weighting and mixing requisite proportions of MgO (Fisher, lot 787699) and SiO_2 glass (Corning lump cullet 7940, lot 62221). MgO and SiO_2 glass were fired at 1000°C for two hours to drive off adsorbed water. Forsterite, talc, and enstatite were synthesized hydrothermally from the mixes; examination of the synthetic phases with a petrographic microscope and by X-ray diffraction revealed them to be entirely crystalline, with less than 0.5 percent impurities, which will be described in a later section.

Synthetic talc, enstatite, forsterite, and natural quartz mixed in the appropriate proportions with an excess of distilled, deionized water were used as the starting materials for the bracketing experiments. The high-temperature assemblage constituted 69 weight percent (excluding H_2O) of the starting material for the reaction $Ta = 3En + Qtz + Stm$ and 38 weight percent (excluding H_2O) of the starting material for the reaction $Ta + Fo = 5En + Stm$.

Procedure

All experiments reported in this paper were conducted in horizontally mounted, cold-seal hydrothermal vessels (Tuttle, 1949). The reaction $Ta = 3En + Qtz + Stm$ was bracketed at the United States Geological Survey; the reaction $Ta + Fo = 5En + Stm$ was bracketed at the Massachusetts Institute of Technology. Details concerning the procedure for calibrating the hydrothermal apparatus are described

by Chernosky (1973). Temperatures were controlled to within $\pm 2^\circ C$ for the duration of each experiment and are judged to be accurate to within $\pm 5^\circ C$ of the stated value. Pressures were measured with 16 inch, factory-calibrated Bourdon-tube gauges and are believed accurate to ± 2 percent of the stated value.

Unit-cell parameters for synthetic phases were calculated by refining powder patterns obtained with an 11.46 cm Debye-Scherrer camera and $CuK\alpha$ radiation. BaF_2 ($a = 6.1971 \pm 0.0002 \text{ \AA}$) and silicon (Johnson Matthey Lot Number S3354, $a = 5.43067 \pm 0.00018 \text{ \AA}$, Huebner and Papike, 1970) were used as internal standards. Silicon and BaF_2 were standardized against gem diamond ($a = 3.56703$, Robie *et al.*, 1966). Sufficient high-angle forsterite reflections were present to permit a film shrinkage correction without recourse to an internal standard. Least squares unit cell refinements were performed with a computer program written by Appleman and Evans (1973).

The products of each experiment were examined with a petrographic microscope and by X-ray powder diffraction. Because reaction rates at temperatures near the equilibrium curves were sluggish, complete reaction was generally not obtained. Judgement as to which assemblage is stable at a given pressure and temperature was based on an examination of the X-ray diffractometer trace over the interval 5° to $36^\circ 2\theta$ ($CuK\alpha$ radiation). In order to ascertain the range of intensities which could be obtained from a given reflection within a particular sample, ten smear mounts of the same aliquot (~ 20 milligrams) of each starting material were successively prepared and X-rayed. The variation in intensities for a given reflection was remarkably small. Based on observation of these diffraction patterns, a reaction was considered reversed if a 30 percent change in the intensities of X-ray reflections relative to those of the starting material could be observed after the completion of an experiment.

Results

Phase characterization

Enstatite ($MgSiO_3$) was synthesized hydrothermally in experiments of 5 to 7 days duration at $815^\circ C$, $P_{H_2O} = 1$ kbar. Synthetic enstatite typically crystallized as fine-grained prismatic crystals which were free of inclusions. The synthetic crystals exhibit parallel extinction, and their powder pattern corresponds to that of enstatite from the Bishopville meteorite (ASTM powder pattern 7-216), suggesting that

the synthetic product is orthorhombic enstatite. The unit-cell parameters for synthetic enstatite are given in Table 2.

Forsterite (Mg_2SiO_4) was synthesized hydrothermally in experiments of 5 to 10 days duration at $810^\circ C$, $P_{H_2O} = 1$ kbar. The synthetic product typically crystallized as small prismatic or rounded crystals and contained tiny inclusions which were interpreted as entrapped fluid. The powder pattern and unit-cell parameters (Table 2) compare favorably with those published for synthetic forsterite (Fisher and Medaris, 1969).

Talc [$Mg_3Si_4O_{10}(OH)_2$] was synthesized hydrothermally in experiments of 5 to 10 days duration at $680^\circ C$, $P_{H_2O} = 2$ kbar. Synthetic talc typically crystallized as aggregates of very fine-grained plates. The synthetic product contained less than 0.5 percent forsterite as an impurity. The unit-cell parameters of synthetic talc are given in Table 2.

The natural quartz (SiO_2) used in the bracketing experiments is from Minas Gerais, Brazil. The carefully-cleaned quartz is from a lot obtained by J. S. Huebner from E. Roedder. Unit-cell parameters are given in Table 2.

The reaction $Ta + Fo = 5En + Stm$

The critical experiments which bracket the position of the univariant curve for the reaction (1) $Ta + Fo$

TABLE 2. Unit cell parameters of natural quartz and synthetic talc, enstatite, and forsterite

	Quartz*	Talc	Enstatite	Forsterite
a	4.9124(1)	5.27(4)	18.19(3)	4.769(2)
b	—	9.15(2)	8.763(7)	10.210(15)
c	5.4052(2)	18.66(10)	5.18(2)	5.987(8)
V	112.960(6)	885(8)	825(3)	291.4(4)
β	—	$100^\circ 27'$	—	—
N	13	9	12	31
S	silicon	BaF ₂	BaF ₂	—

Figures in parentheses represent the standard deviation in terms of least units cited for the value to their immediate left; these were calculated by the program used to refine the parameters and represent precision only.

Abbreviations: S = X-ray standard; N = number of reflections used in refinement. Cell parameters are expressed in angstroms.

*Determined by J. S. Huebner and K. Shaw.

= $5En + Stm$ are summarized in Table 3. The reaction is plotted in Figure 1, where it is compared to the curve obtained by Bowen and Tuttle (1949) and two reversed experiments obtained by Greenwood (1963). The bracketing data are consistent with Greenwood's reversals; however, the equilibrium curve lies at a temperature $20^\circ C$ (at $P_{H_2O} = 1$ kbar) lower than the curve determined by Bowen and Tuttle, which is

TABLE 3. Experiments bracketing the reaction $Ta + Fo = 5En + Stm$

Experiment number	P_{H_2O} (bars)	T ($^\circ C$)	Duration (hours)	Comments
17	500	600	3912	Ta(+) Fo(+) En(-)
16	500	621	3910	Ta(-) Fo(-) En(+)
15	500	635	3910	Ta(-) Fo(-) En(+)
14	1000	620	2064	Ta(+) Fo(+) En(-)
8	1000	637	3910	Ta(+) Fo(+) En(-)
7	1000	657	1053	Ta(-) Fo(-) En(+)
2	2000	603	188	Ta(+) Fo(+) En(-)
1	2000	640	142	Ta(+) Fo(+) En(-)
6	2000	663	3908	Ta(-) Fo(-) En(+)
3	2000	677	1968	Ta(-) Fo(-) En(+)
4	2000	689	1968	Ta(-) Fo(-) En(+)
18	3000	662	2794	Ta(+) Fo(+) En(-)
12	3000	692	696	Ta(-) Fo(-) En(+)
13	3000	703	696	Ta(-) Fo(-) En(+)
11	4000	686	762	Ta(+) Fo(+) En(-)
9	4000	706	762	Ta(-) Fo(-) En(+)
10	4000	722	762	Ta(-) Fo(-) En(+)

Growth or diminution of a phase is indicated by a (+) or (-) respectively. All assemblages include steam.

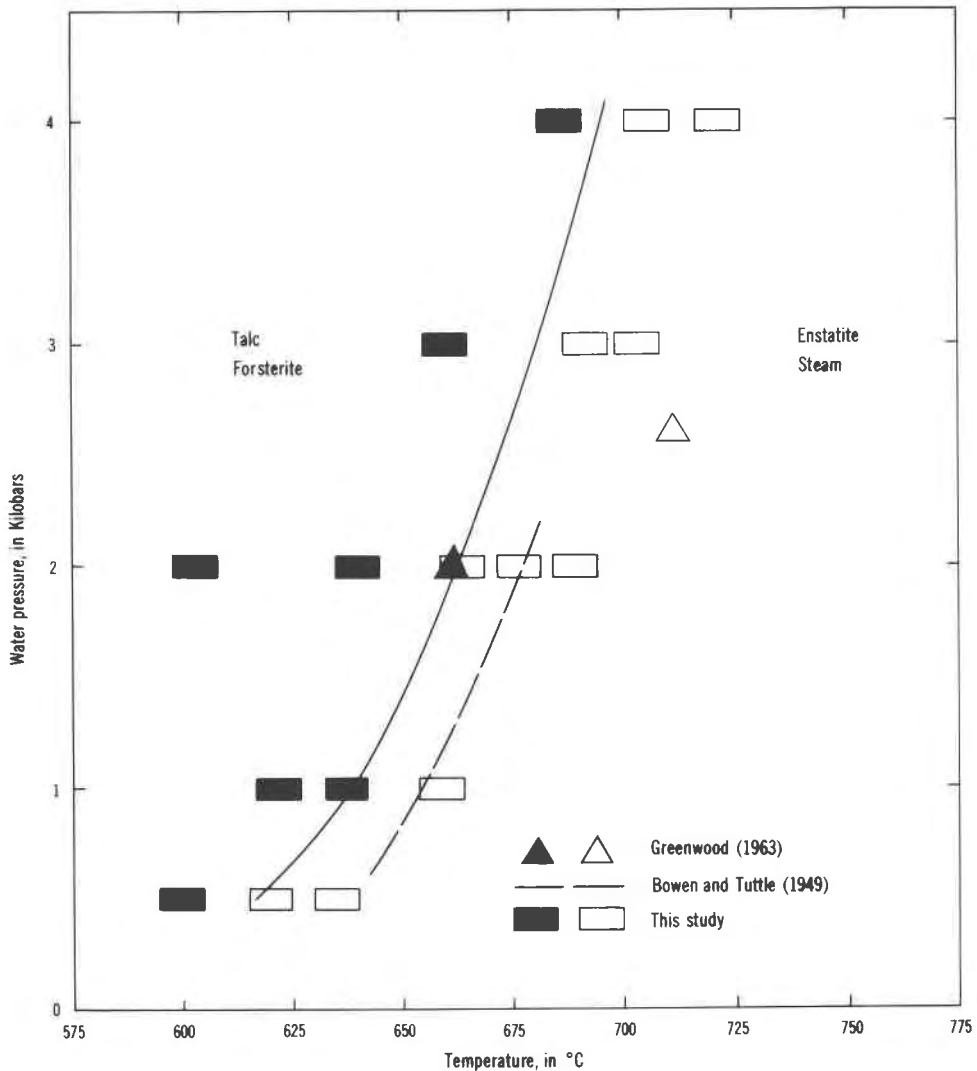


FIG. 1. Dehydration curve for the reaction $Ta + Fo = 5En + Stm$. Solid symbols represent growth of the high-temperature assemblage; open symbols represent growth of the low-temperature assemblage. Rectangles and solid line represent data obtained during this study. Size of rectangles represents uncertainty in pressure and temperature. Triangles represent reversals obtained by Greenwood (1963); dashed curve is from Bowen and Tuttle (1949).

based on synthesis rather than on reversed experiments.

The reaction $Ta = 3En + Qtz + Stm$

The critical experiments which delineate the position of the univariant equilibrium curve for the reaction (2) $Ta = 3En + Qtz + Stm$ are summarized in Table 4 and plotted in Figure 2. Reaction rates near the equilibrium curve were sluggish, especially at low pressure, where experiments of 659 hours (Table 4, experiment 38) and 699 hours (Table 4, experiment

33) duration did not result in any detectable reaction. The solid curve shown on Figure 2 was drawn so as to be consistent with the brackets obtained in this study³ and with Skippen's 2 kbar bracket. Even though Skippen's experiments were performed under Ni-

³ The P - T coordinates of experiments shown in Fig. 2 were chosen for the purpose of testing Chayes' (1968) idea of probabilistic location of univariant curves by random selection of P - T values of experiments. The result of that test will be reported elsewhere.

TABLE 4. Experiments bracketing the reaction $Tc = 3En + Qtz + Stm$

Experiment number	P_{H_2O} (bars)	T (°C)	Duration (hours)	Comments
5	133	691	220	Ta(-) En(+) Qtz(+)
40	500	648	4896	Ta(+) En(-) Qtz(-)
38	500	659	1968	no detectable reaction
35	500	672	672	Ta(-) En(+) Qtz(+)
37	500	681	1968	Ta(-) En(+) Qtz(+)
4	533	783	143	Ta(-) En(+) Qtz(+)
14	598	646	336	Ta(+) En(-) Qtz(-)
1	666	717	740	Ta(-) En(+) Qtz(+)
7	867	684	796	Ta(+) En(-) Qtz(-)
13	979	660	144	Ta(+) En(-) Qtz(-)
32	1000	680	618	Ta(+) En(-) Qtz(-)
33	1000	699	618	no detectable reaction
12	1000	721	623	Ta(-) En(+) Qtz(+)
9	1200	718	526	Ta(-) En(+) Qtz(+)
15	1420	635	166	Ta(+) En(-) Qtz(-)
3	1466	766	144	Ta(-) En(+) Qtz(+)
10	1669	695	166	Ta(+) En(-) Qtz(-)
30	1800	729	2136	Ta(+) En(-) Qtz(-) Ant(+)
6	1803	717	552	Ta(+) En(-) Qtz(-)
2	1866	675	215	Ta(+) En(-) Qtz(-)
11	1925	679	200	Ta(+) En(-) Qtz(-)
41	2000	744	1080	Ta(-) En(+) Qtz(+) Ant(+)
39	2000	761	1080	Ta(-) En(+) Qtz(+) Ant(+)

Growth or diminution of a phase is indicated by a (+) or (-) respectively. All assemblages include steam.

NiO buffer conditions, his reversals are very close to the ones obtained in this study because the activity of H_2O in his experiments was greater than 0.998.

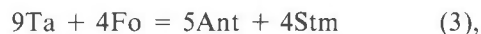
The curve obtained by Bowen and Tuttle (1949) (Fig. 2) lies at a temperature $100^\circ C$ (at $P_{H_2O} = 1$ kbar) above the equilibrium curve determined in the present study, because Bowen and Tuttle's curve is based on synthesis rather than on reversed experiments. The reversed brackets obtained in the present study are consistent with Greenwood's bracket at $P_{H_2O} = 2$ kbar.

Discussion

Anthophyllite stability

Six invariant points involving the phases talc, forsterite, quartz, anthophyllite, enstatite, and steam are possible in the ternary system $MgO-SiO_2-H_2O$. The closed net depicting the chemographic relations of the phases in this multisystem is shown in Figure 3; the area within which anthophyllite is stable is

shaded. Of the six possible invariant points, only two, [Qtz] and [Fo], are likely to be stable, because the others imply that quartz and forsterite can coexist in equilibrium. The univariant scheme about these two invariant points is depicted in Figure 4, which shows both possible enantiomorphic forms of the phase diagram. Figure 4a shows anthophyllite as a low-pressure phase relative to enstatite + talc; this version is preferred by Greenwood (1963). Figure 4b depicts anthophyllite as a high-pressure phase relative to enstatite + talc. The stability field of anthophyllite (shown by shading) is bounded by the following two reactions which have been experimentally bracketed by Greenwood (1963):



The slopes of reactions (3) and (4) were extrapolated by Greenwood to a pressure of about 20 kbar where they intersect two other reactions involving anthophyllite (Fig. 4a): $Ant + Fo = 9En + Stm$ (5),

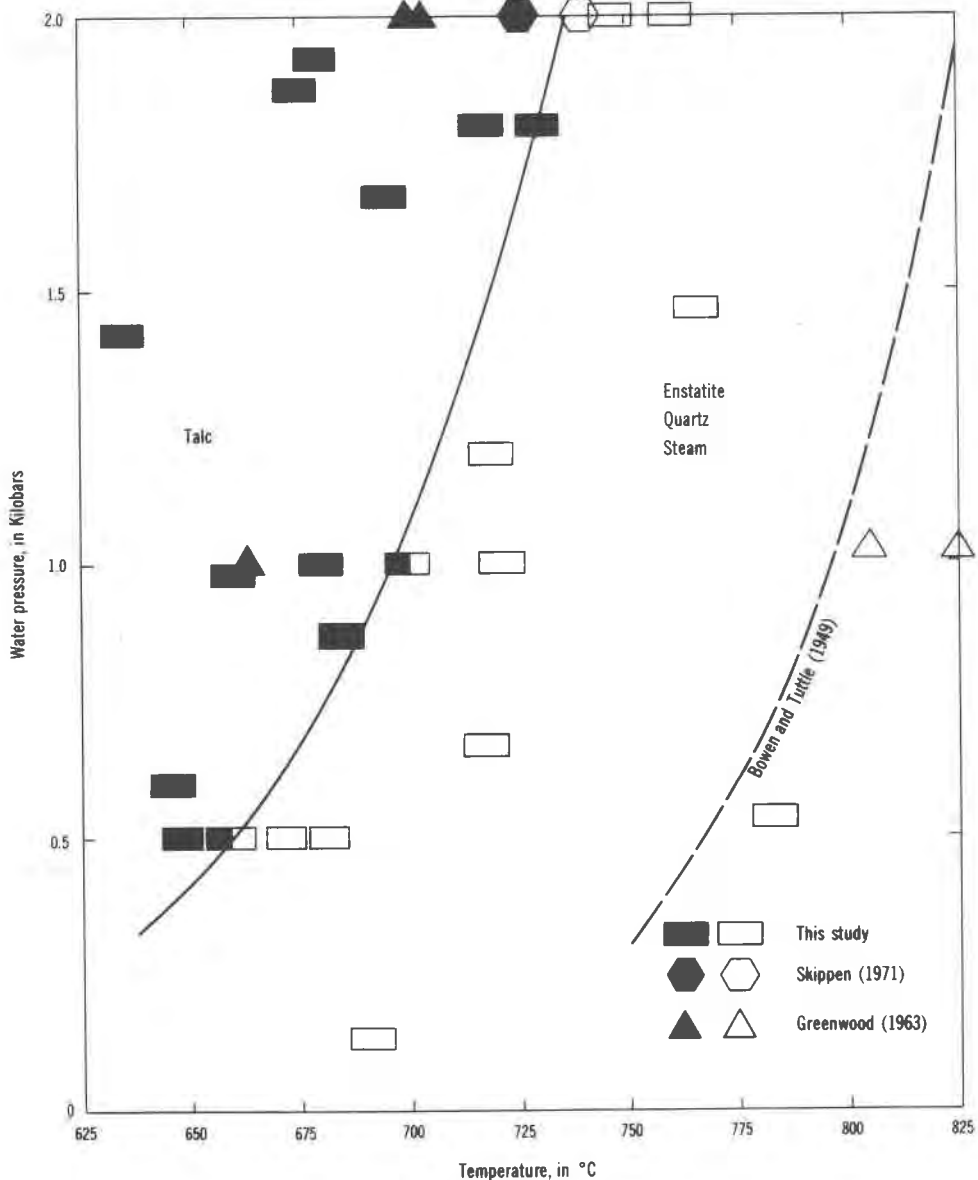


FIG. 2. Dehydration curve for the reaction $Ta = 3En + Qtz + Stm$. Solid symbols represent growth of talc, open symbols represent growth of the high-temperature assemblage, and half-filled symbol represents "no reaction." Rectangles and solid curve represent data obtained during this study; size of rectangles represent reversals obtained by Greenwood (1963), hexagons represent reversals obtained by Skippin (1971), and dashed curve is from Bowen and Tuttle (1949).

and $7Ta = 3Ant + 4Qtz + 4Stm$ (6). The invariant points generated by the intersection of these reactions are connected by the reaction $Ant = Ta + 4En$ (7) which, according to Greenwood, bounds the maximum pressure to which anthophyllite is stable. Reactions (1) and (2) were bracketed during this study in order to locate the [Qtz] and [Fo] invariant points

more accurately in pressure-temperature space.

The experimental data obtained in the present study are plotted together with Greenwood's data on a $\log f_{H_2O} - 1/T$ diagram (Fig. 5). If the activities of the solid phases are unity and if steam is the only volatile species involved in the reactions, van't Hoff's equation reduces to:

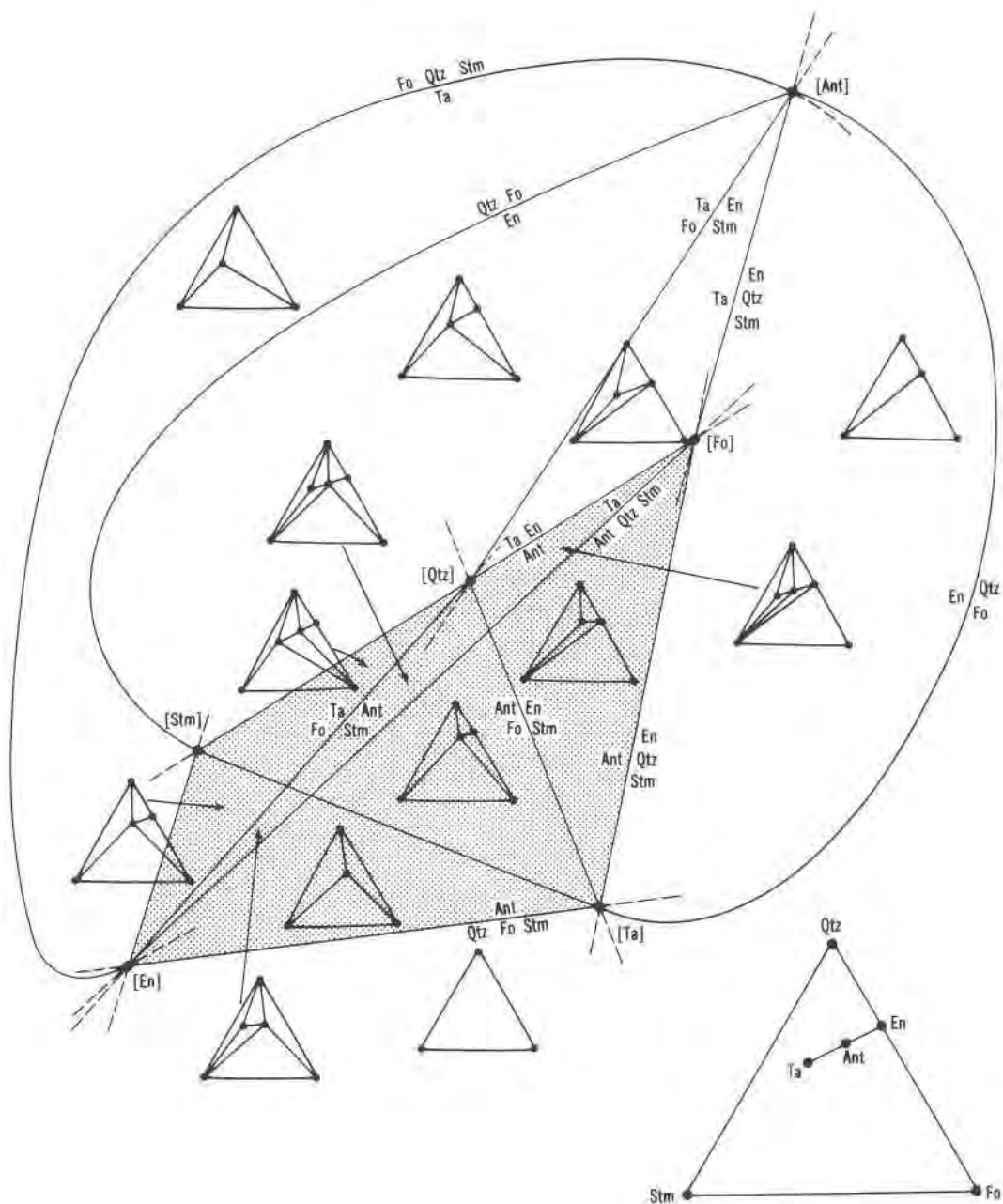


FIG. 3. Closed net for the ternary multisystem MgO-SiO₂-H₂O involving the phases anthophyllite, enstatite, forsterite, quartz, steam, and talc. Anthophyllite can only be a stable phase within the shaded region. Compositional relations within the compatibility diagrams are distorted for illustration purposes.

$$\left(\frac{\partial \log f_{\text{H}_2\text{O}}}{\partial 1/T} \right)_{P_s} = - \frac{(\Delta H)_{P_s}}{2.303 R}$$

where $f_{\text{H}_2\text{O}}$ is the fugacity of H₂O, P_s is the pressure on the solid phases, ΔH is the enthalpy of reaction, and R is the gas constant. Orville and Greenwood (1965)

have shown that a dehydration boundary will plot as a straight line on a $\log f_{\text{H}_2\text{O}}-1/T$ diagram if ΔH at constant P_s is constant. All data points have been replotted as they would have appeared if the experiments had been performed at the same constant total pressure (2000 bars). The correction term applied to the fugacity (Eugster and Wones, 1962) is

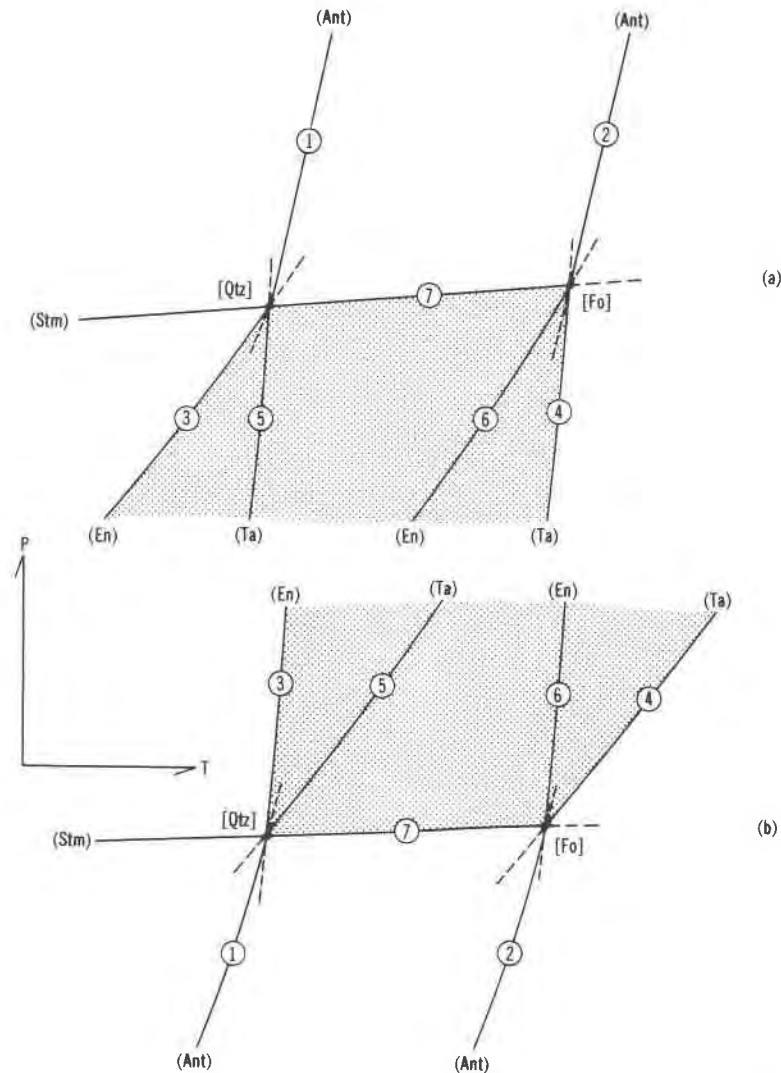


FIG. 4. Details of the phase relations in the multisystem of Fig. 3; only the stable invariant points are included. The stability field for anthophyllite is shaded. Fig. 4a is the version preferred by Greenwood (1963); Fig. 4b is the enantiomorphic form of Fig. 4a. Equilibria numbered as in text; compatibility relations are shown in Fig. 3.

$$\Delta \log f_{\text{H}_2\text{O}} = - \frac{\Delta V_s (P - P_{\text{exp}})}{2.303RT}$$

where P is the pressure to which the points are being moved (2000 bars) and P_{exp} is the experimentally-determined pressure.

Figure 6a is an attempt to combine the equilibrium curves obtained for the reactions (1) and (2) (this study) with curves for reactions (3) and (4) and several reversed experiments for reactions (5) and (6) obtained by Greenwood (1963). The experimentally located positions for reactions (2) and (4) about the [Fo] invariant point are consistent with the

univariant scheme depicted on Figure 4a. Because the brackets for reaction (4) are broad (see Fig. 5), the equilibrium boundary may be rotated considerably in P - T space; consequently, the resolution for locating the [Fo] invariant point is not good. Figure 6a suggests that the intersection of reactions (2) and (4) should occur near a pressure of 5200 bars rather than at 20 kbar as suggested by Greenwood. The experimentally located positions for reactions (1) and (3) (Fig. 6a) are inconsistent with the univariant scheme depicted on Figure 4a. The stable portion of reaction (3) must lie between reaction (7) and the metastable extension of reaction (1) (see Fig. 6a, dashed curve).

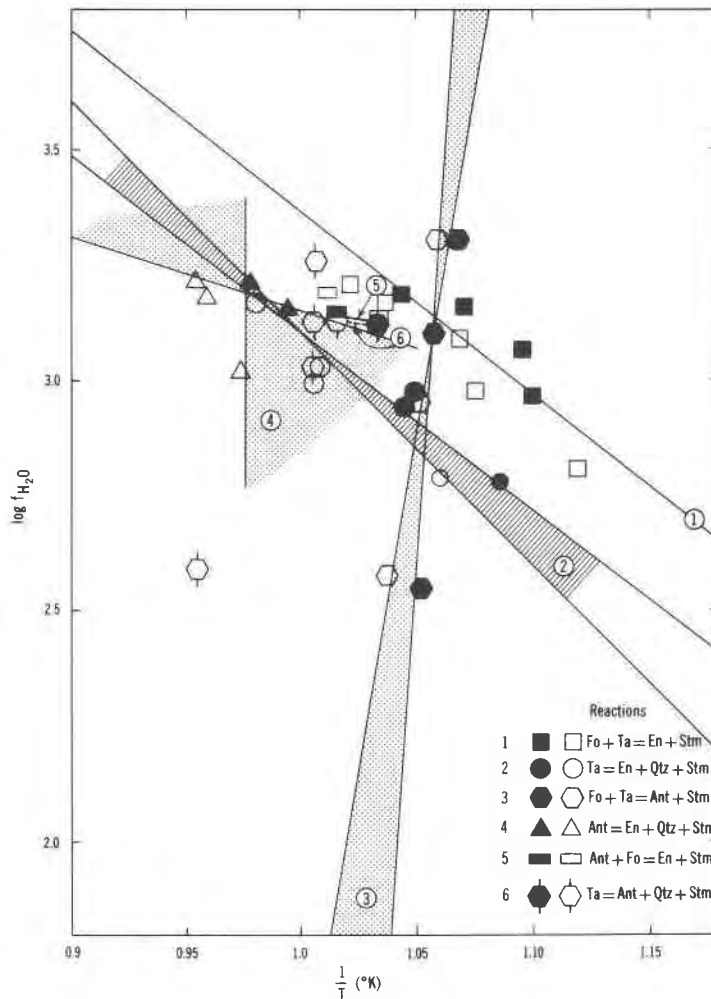


FIG. 5. Log $f_{\text{H}_2\text{O}}-1/T$ plot of experimental data available for reactions (1)–(6) (equilibria numbered as in text). All data points corrected to $P_{\text{total}} \approx P_{\text{H}_2\text{O}} = 2000$ bars. Data points for reactions (1) and (2) are contained in Tables 3 and 4; data points for reactions (3)–(6) are from Greenwood (1963).

Figure 6a clearly illustrates that reaction (3) has much too steep a slope. The inconsistency cannot be remedied by rotating the reactions within the experimentally-determined brackets.

Chernosky (1974) suggested that the inconsistency could be resolved by inverting Greenwood's proposed chemography (Figs. 4b and 6b), *i.e.* by considering that anthophyllite rather than talc + enstatite is stable at high pressures. This solution seems implausible in light of four lengthy low-pressure experiments (Table 4, experiments 30, 39 and 41; Table 3, experiment 3) during which anthophyllite nucleated and grew from a starting material which initially contained talc + enstatite + quartz or forsterite. These four experiments suggest that anthophyllite is more

stable than the assemblage talc + enstatite at $P_{\text{H}_2\text{O}} \leq 2$ kbar, which is consistent with the negative volume change (-0.23 J bar^{-1}) for reaction (7), $\text{Ant} = 4\text{En} + \text{Ta}$, at 298 K, 1 bar.

A second way to resolve the inconsistency is to concede that the bracketing data for at least one of the reactions (1) or (3) are incorrect. Because of the difficulty of synthesizing anthophyllite, Greenwood (1963) used starting materials which contained talc + anthophyllite + clinoenstatite + cristobalite + quartz or forsterite to reverse reaction (3). The use of clinoenstatite + cristobalite instead of enstatite + quartz could make a great difference in the position and slope of reaction (3). Clearly, additional experimental work is needed to resolve the inconsistency

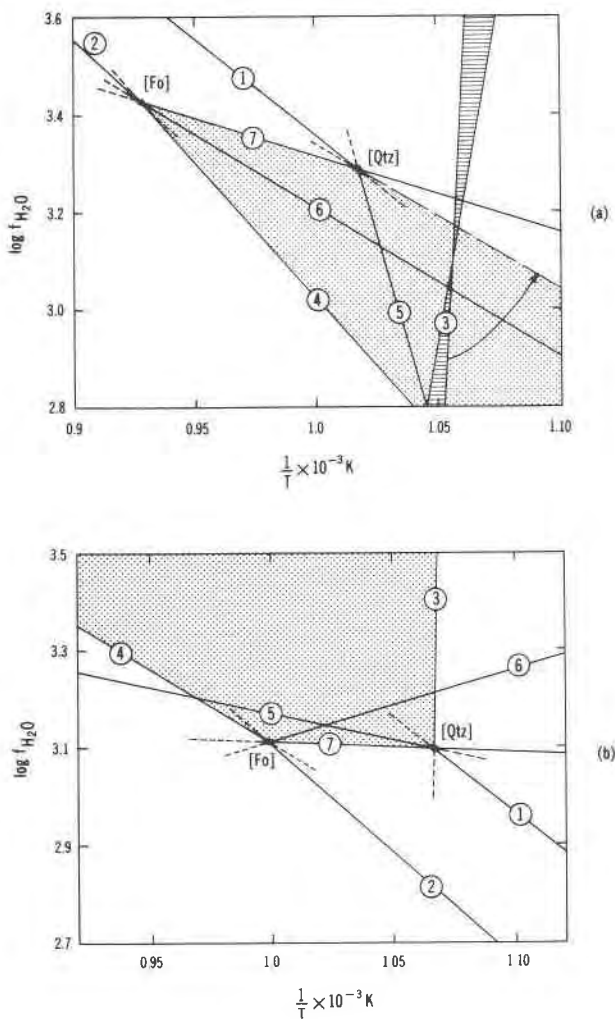


FIG. 6. $\log f_{H_2O} - 1/T$ plots showing two possible ways to combine Greenwood's experimental data with the data of this study. Equilibria numbered as in the text. Figs. 6a and 6b correspond to Figs. 4a and 4b, respectively. The slope of reaction (3) (Greenwood, 1963) is inconsistent with the topology of Fig. 6a; to resolve the discrepancy, reaction (3) must be rotated to the position shown by the arrow.

and to locate unambiguously the [Fo] and [Qtz] invariant points in pressure-temperature space.

Geological application

If the [Qtz] and [Fo] invariant points occur at low pressure and if anthophyllite is stable at low pressure relative to talc + enstatite, as is suggested by the results of this study, the presence or absence of anthophyllite might be a useful indicator of the pressure and temperature of recrystallization of magnesium silicate (-carbonate) assemblages. The presence of anthophyllite would suggest recrystallization within a

restricted range of P - T conditions, whereas the presence of talc + enstatite would indicate recrystallization at relatively higher pressure (> 5 kbar). Several occurrences of apparently stable talc + enstatite in regional-metamorphic rocks of the Central Alps (Evans and Trommsdorff, 1974) support the inference that the reaction $\text{Ant} = \text{Ta} + 4\text{En}$ occurs at pressures lower than those suggested by Greenwood (1963).

Caution should be exercised in applying the experimental results to natural rocks. The experiments were conducted at $P_{H_2O} = P_{\text{total}}$ (i.e., $a_{H_2O} \approx 1$); however, if the aqueous fluid phase in nature contained CO_2 (as was the case in rocks studied by Evans and Trommsdorff, 1974) then $a_{H_2O} < 1$ and the equilibrium boundaries would be shifted to lower temperature. Furthermore, the synthetic phases did not contain iron or aluminum in solid solution. The experimental work of Hinricksen (see Ernst, 1968, p. 43) shows that the thermal stability of anthophyllite decreases by approximately 100°C with 60 percent of the magnesium replaced by iron. Based on microprobe analyses of enstatite ($X_{\text{Mg}} = 0.900$), talc ($X_{\text{Mg}} = 0.973 \pm 0.002$), and anthophyllite ($X_{\text{Mg}} = 0.88 \pm 0.01$), Evans and Trommsdorff (1974) calculate that the reaction $\text{Ant} = \text{Ta} + 4\text{En}$ (7) occurs at a lower pressure or a higher temperature in the iron-free system by an amount given by $\Delta T = RT/\Delta S \ln K \approx 200 \pm 95^\circ\text{C}$. They emphasize that "the magnitude of the compositional effect is so great" that the topology shown in Figure 4 could be "a function of the composition of the system alone."

Acknowledgments

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