Scapolite–plagioclase stability relations at high pressures and temperatures in the system $NaAlSi_3O_8–CaAl_2Si_2O_8–CaCO_3–CaSO_4$

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Abstract

Meionite ($3CaAl_2Si_2O_8 \cdot CaCO_3$ or $MeCO_3$) is stable only above 875°C; and sulfate meionite ($3CaAl_2Si_2O_8 \cdot CaSO_4$, or $MeSO_4$), also stable only at elevated temperatures, is favored by pressure. Isobaric, isothermal phase relations in the systems Ab–An–$CaCO_3$, Ab–An–$CaSO_4$, and Ab–An–½$CaCO_3$–½$CaSO_4$, are given at 15 kbar and from 1000° to 1300°C. Compositional tie-lines could not be reversed in the dry system, and although synthesis data are internally consistent, equilibrium is not assured. Na stabilizes scapolites to lower temperatures.

In addition to the end members $MeCO_3$, $MeSO_4$, and $Me(CO_3 \cdot SO_4)$, chlorine-free solid solutions containing substitutions of NaSi for CaAl up to approximately 50 percent in all three cases are stable over a range of *PT* conditions. Unit-cell data for the scapolite solid solutions are given.

The scapolite–plagioclase tie-lines are temperature-dependent; partitioning of Na and Ca between scapolite and plagioclase gives a provisional geothermometer. Non-ideality in the more sodic portions of the system apparently limits the usefulness to compositions with anorthite equivalents greater than 70 percent. Two granulite xenoliths from pipes in eastern Australia give temperatures of 875°–900°C, in agreement with other thermometers. These xenoliths must be fragments of the deep crust, unrelated to the volcanic pipes. An Archaean granulite from Western Australia gives a temperature of 890°. However, scapolites with *sodic* plagioclase from several terranes give impossible temperatures of 1200°–1300°C.

Introduction

The scapolite minerals are identified for the most part with metamorphic terranes, and Shaw (1960) has pointed out the wide range of occurrences in which they have been observed. Although it is apparent that they can be formed over a significant range of conditions, little consideration has been given to the scapolites as relatively deep-earth, or high-pressure minerals. Lovering and White (1964) studied the granulite inclusions in a number of the breccia- and basalt-filled igneous pipes in eastern Australia. Euhedral scapolite was described as a "primary phase" in the two assemblages commonly found—two-pyroxene granulites (orthopyroxene–clinopyroxene–plagioclase) and the garnet–clinopyroxene granulites (pyrope-rich garnet–pyroxene–plagioclase). Lovering and White also noted the scapolite reported as a "suggested secondary constituent" in garnet–clinopyroxene granulite inclusions in the Zarnitsa kimberlite pipe in Yakutia (Bobrievich and Sobolev, 1957), and on the basis of the Australian and Siberian observations suggested that scapolite may well be a significant constituent of the material making up the lower continental crust. Newton and Goldsmith (1975, 1976) also called attention to the presence of scapolite in granulites brought up by kimberlite diatremes and carbonate-rich pyroclastic volcanoes in Africa, described by Dawson (1964, 1968, 1971), Cox *et al.* (1973), and Verhoogen (1938), strengthening the view of Lovering and White.

The sulfur content of scapolites in metamorphic rocks in general was also considered by Lovering and White, and they suggested that sulfur-rich scapolites are characteristic and perhaps diagnostic of granulite-facies assemblages. The scapolites in the Australian pipes are very sulfur-rich, containing up to 72 percent S (or more) in the *R* (anionic, or C, S, F, and Cl) position. They also state from their data as well as from the literature, "... there appears to be a pro-

gressive increase in the possible sulfur content with increasing grade within the granulite facies." The concept of grade, although not clarified in the above, is usually thought of in terms of temperature rather than pressure. There is some evidence from scapolite analyses in the literature, however, that a high sulfur content may be associated with the deep-seated, or high-pressure occurrence (see also Knorring and Kennedy, 1958; Deer *et al.,* 1963, p. 326).

Scapolites are compositionally complex, with a variety of substitutions possible in the cation as well as the anion sites. Lovering and White were handicapped by the absence of data on the effect of pressure on the sulfur content. Indeed, based on the early structural determination of scapolite (Pauling, 1930), they presumed that the collapse or expansion of the adjacent strings of silica tetrahedra in the opposite sense can limit or favor the entrance of the largest of the anion groups, SO_4^{2-}. Thus an increase in sulfur content was expected with increased temperature as a result of this expansion, and it was presumed that increasing pressure would have the opposite effect. Their observations and conclusions are somewhat conflicting, however, for they also note that sulfur-rich scapolites do not occur in high-grade contact rocks, as would be expected by the above reasoning. Much of their interpretation is based on the possibility that S^{2-} replaces Cl^{-}. Chappell and White (1968) subsequently showed by X-ray spectroscopy, and Lovering and Widdowson (1968) by an electron microprobe determination, that the sulfur is coordinated as SO_4^{2-}.

The present study is an investigation at high temperatures and pressures of the sulfate and carbonate scapolites. Chlorine is not a major constituent in the scapolites of deep-seated rocks, and is not included as a component in this work.

Previous experimental work

The first reported syntheses of the pure end members marialite and meionite were by Eugster and Prostka (1960) and by Eugster *et al.* (1962). Marialite was synthesized dry from mixtures of Al_2O_3, $Na_2O \cdot 6SiO_2$, and NaCl at 1 bar between 700°C and 850°C. Seeding was necessary. Meionite was grown under CO_2 pressures between 1 and 4 bars, at temperatures between 850°C and 975°C, from SiO_2, Al_2O_3, and $CaCO_3$. There is some evidence that the meionite syntheses were metastable (see Orville, 1975, p. 1092). Aside from this, almost all of the work on synthetic scapolites has been carried out in the past several years. Orville (1975) investigated the system

$NaAlSi_3O_8$–$CaAl_2Si_2O_8$–$NaCl$–$CaCO_3$ at 4 kbar and 750°C, and showed that chlorine is not an essential constituent of the Ca-rich scapolites. At 750°C and 4 kbar, scapolite is stable relative to plagioclase plus calcite and NaCl over a rather wide range of bulk "equivalent An-content," although under these conditions the pure Ca end member (meionite) is not. Newton and Goldsmith (1975, 1976) synthesized and investigated the thermal behavior and stability of the end members meionite, or $MeCO_3(3CaAl_2Si_2O_8 \cdot CaCO_3)$, sulfate–meionite, or $MeSO_4$[1] $(3CaAl_2Si_2O_8 \cdot CaSO_4)$, and marialite, or $MaCl$ ($3NaAlSi_3O_8 \cdot NaCl$). $MeCO_3$ was shown to be stable with respect to anorthite and calcite only at temperatures greater than 800° (modified to slightly higher temperatures in the current study), in agreement with the deduction of Orville that the end-member meionite is unstable at 750°C and 4 kbar. Newton and Goldsmith (1976) also showed that $MeSO_4$ requires even higher temperatures for stability, and that the field of scapolite stability is increased with pressure; the $P–T$ curve of the reaction anorthite $+ CaSO_4 \rightleftarrows MeSO_4$ has a negative slope. In the present work a redetermination of the curve has produced a major shift in its position, increasing the size of the $MeSO_4$ stability field over that of the earlier determination. Marialite was also shown to have a high-temperature field of stability, although the position of the $P–T$ curve was not delineated.

The Ca-rich scapolites are remarkably refractory; the thermal breakdown curve of $MeCO_3$ in the pressure range 15–30 kbar approaches that of anorthite, and is in excess of 1400°C at 10 kbar. $MeSO_4$ is even more refractory; its melting curve is close to that of anorthite, and in fact exceeds it at pressures above 20 kbar. Scapolite should be formed by reactions of calcic plagioclase with $CaCO_3$, CO_2, or oxidized sulfur in the lower crust, and can probably precipitate as a primary igneous mineral from a carbonate- or sulfate-bearing basic or intermediate magma if the pressure is high enough.

We have also shown (Newton and Goldsmith, 1976) that marialite is stable relative to albite plus NaCl at temperatures at least as low as 800°C in the pressure range 8–15 kbar. This range of stability was not anticipated by Orville (1975), who worked at 750°C and 4 kbar. Our data, in conjunction with Orville's, indicated a boundary between 750°C and

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[1] Following Shaw (1960), we shall use the abreviation $MeCO_3$ for meionite, $MeSO_4$ for what we have heretofore called sulfate-meionite, and $MaCl$ for marialite.

800°C in the pressure range 0–8 kbar, with a steep dP/dT slope. The general appearance of the marialite stability diagram is probably much like that of meionite, with the scapolite on the high-temperature side of the reaction plagioclase + NaCl ⇌ scapolite. We have not pursued the end-member marialite relations further in this study, inasmuch as scapolites of deep-seated origin are Ca-rich and contain chlorine only in trace amounts.

Newton and Goldsmith (1976) also considered the upper pressure limits for the stability field of scapolites. Breakdown of Ca-scapolite to grossular, kyanite, quartz, and $CaCO_3$ and/or $CaSO_4$, and of Na-scapolite to jadeite, quartz, and NaCl at pressures not greatly above the stability limit of the equivalent feldspars is probable. This places a depth restriction on the scapolites; they are essentially limited to the crust or uppermost mantle. The $P–T$ conditions for stability combined with the compositional requirements would point to the lower crust as an ideal environment for Ca-rich scapolites; they are high-temperature high-grade minerals.

Goldsmith (1976) discussed some of the implications of the recent work on scapolites, including the Na–Ca distribution with temperature between coexisting scapolites and plagioclases, although no specific data were presented. These and associated data are given in full here, along with revised information on the stability of the end members $MeCO_3$ and $MeSO_4$.

Experimental methods and results

General methods

Most of the experimental runs were made with the 0.75″-diameter piston-cylinder apparatus, using NaCl, soft glass (Kimbal R6), or Pyrex solid-pressure media. The techniques were generally similar to those described by Newton and Goldsmith (1975, 1976) with a few important exceptions, *i.e.* the use of sealed capsules, instead of the unsealed capsules previously used,[2] and the use of H_2O to promote faster reaction rates in the case of the runs delineating the $P–T$ curves. Temperatures were controlled and monitored by W-W25Re and chromel–alumel thermocouples. The latter were used only below 1200°C.

Most of the runs were made with the "piston-out"

technique. With the NaCl pressure medium, the assembly was pressed cold to a pressure considerably below the final-desired nominal pressure. Heating to 800°–900°C brought the gauge pressure up to the final nominal pressure by the very large thermal expansion of NaCl. The large pressure increase due to heating was precalibrated, and insured that the piston was moving out of the chamber as the final run conditions were approached. Under these conditions the salt pressure medium is very weak, and the correction due to "friction" in the assembly is negligible at sample temperatures above 600°C (Johannes *et al.,* 1973; Mirwald *et al.,* 1975). The soft glass is much superior to Pyrex in transmitting pressure in the temperature range 800°–1100°C, as shown by studies on decarbonation equilibria done in this laboratory by H. T. Haselton using various pressure media. He found essentially no difference between soft glass and NaCl at 950°C. Accordingly, we have made no friction correction for the piston-out soft-glass runs.

The equilibrium $3An + CaSO_4 \rightleftharpoons MeSO_4$

Starting materials for determination of the stability of the $MeSO_4$ end-member scapolite were mixtures of scapolite, previously synthesized at high temperatures and pressures, and crystalline anorthite + $CaSO_4$.

We had previously observed (Newton and Goldsmith, 1976) that the sulfate-containing runs showed evidence of reaction with the platinum capsules, especially at the higher temperatures. In the new series of runs the presence of PtS was inferred from a gray coating on the platinum container, and positively identified in the X-ray diffractograms of some of the quenched charges. The reaction of sulfate with platinum, to produce PtS ($SO_4 + Pt \rightleftharpoons Pts + 2O_2$) was particularly troublesome in long runs in the unsealed tubes, because the loss of oxygen permitted the reaction to proceed. Alternatively, diffusion of hydrogen into the capsule might produce the reaction $Pt + CaSO_4 + 3H_2 \rightarrow Ca(OH)_2 + 2H_2O + PtS$, and the loss of H_2O from the open tube would also permit the reaction to proceed. With less sulfate available to produce scapolite, the region of apparent anorthite stability was enlarged. The direction of the reaction is determined by the *relative* amounts, estimated from diffractograms, of plagioclase + $CaSO_4$ as compared to scapolite in the run products, the starting material containing essentially equal amounts of products and reactants. The particular reactant-product proportions that were produced in the earlier runs to give apparent consistency in curve-

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[2] Although not so stated, the $MeSO_4$ runs in Newton and Goldsmith (1976) were made in tubes that were pinched shut, but not welded. Most of the tie-line (two-phase) and three-phase runs of the current study were also made in pinched but unsealed capsules.

pinning is a good example of the perversity of nature in experimental systems.

In the present redetermination, sealed capsules were used to retard formation of PtS and thus loss of sulfate. The capsules were dried for a few minutes at low red heat before sealing to remove any volatiles. The method proved effective—minor reaction with platinum and $CaSO_4$ depletion was observed in the run charges, but it was not enough to be a major problem.

Runs on dried charges with sealed Pt capsules showed that the true PT stability curve of $MeSO_4$ is shifted, relative to our previous determination, to much lower temperatures. Accordingly, it was necessary to introduce a small amount of H_2O to promote reactions in feasible run times. This was done by adding gypsum to the charge in about one-third the amount of the anhydrite. Both gold and platinum capsules were used, with identical results where comparisons were made. Reversal reactions produced by this technique proved to be quite swift; indeed, at run temperatures of 900° or above it was necessary to come to the run temperature as rapidly as possible in heating, to avoid reaction to anorthite + anhydrite on the way to the desired temperature.

Reversal runs obtained were for the most part definitive, as shown in Figure 1. Selected runs that delineate the fields and define the P–T curve are listed in Table 1. At pressures above 10 kbar and temperatures below 800°C zoisite appeared in the charges and effectively prevented further investigation. Failure of the glass pressure assemblies occurs in heating below 3 kbar. Thus we have a rather short experimental temperature and pressure range over which to

Fig. 1. The P–T curve for the reaction $3An + CaSO_4 \rightleftharpoons MeSO_4$. Dashed curve from Newton and Goldsmith (1976), see text for details.

define a dP/dT slope. The experimental slope value is -48 bars/°C.

The equilibrium $3An + CaCO_3 \leftrightarrows MeCO_3$

The P–T curve for the reaction $3An + CaCO_3 \leftrightarrows MeCO_3$ (Newton and Goldsmith, 1976) was based on dry determinations at only 2 pressures, 8 and 15 kbar. The 15 kbar determination was done with NaCl as the pressure medium, and we have no reason to doubt the results. The 8 kbar determination was done in Pyrex glass, and at these low temperatures, somewhat over 800°C, the hard glass is not as trustworthy. The "softening point" of Pyrex is given as 820°C (Corning Glass Works data), and in the particular assembly used, the glass sleeve was thick-walled (~0.120″). Thus the outer portion of the glass is significantly cooler, and the effective "friction" of the assembly probably rather high.

The new determinations were done in both NaCl and soft-glass media, and with both Au and Pt capsules, sealed. The location of the curve is such that a one-kilobar determination was possible in cold-seal pressure vessels. The one-kbar runs were made with oxalic acid $(H_2C_2O_4 + 2H_2O)$ added to the capsule, which upon decomposition during heating supplies an H_2O–CO_2 ratio of 3:1. The platinum capsule containing the charge plus the oxalic acid was buffered by placing it in an outer gold capsule filled with hematite and H_2O. A fairly large number of piston-cylinder runs were made (over 30) with a variety of techniques, including buffered capsules containing various mixtures of anhydrous oxalic acid, silver oxalate, and $CaCO_3$, all designed to avoid zoisite formation. It was ultimately found that at the lower pressures buffering was unnecessary, at least in the short run times, and that oxalic acid alone produced a hydrothermal environment in which anorthite and scapolite were stable relative to zoisite.

Table 1 contains only those runs that delineate the curve. Figure 2 shows the redetermined curve, with the earlier version (Newton and Goldsmith, 1976, Fig. 1, p. 342) shown as a dashed line. Within our limits of determination, it is sensibly vertical.

$CaAl_2Si_2O_8$–$NaAlSi_3O_8$–$CaSO_4$–$CaSO_3$ scapolites

Most of the syntheses of the present study were performed on intimately-homogenized mechanical mixtures of glasses of plagioclase composition and reagent-grade $CaCO_3$ or $CaSO_4$ or both. A smaller number of runs was made on mixtures of synthetic plagioclase and $CaCO_3$ or $CaSO_4$. The glasses were prepared by melting together reagent-grade $CaCO_3$,
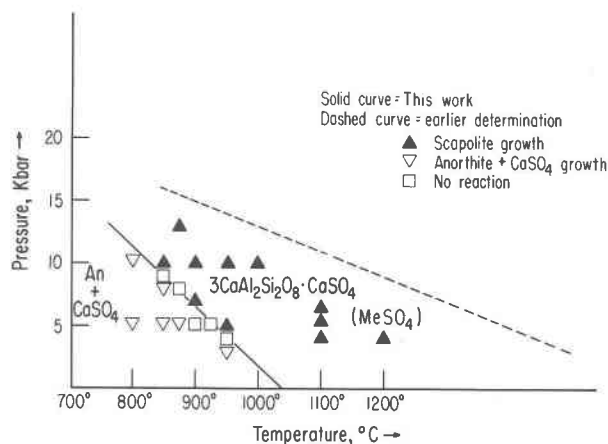
Table 1. Runs used to delineate meionite stability

Run No.	Starting Material[*]	P, kbar	T, °C	Time, hrs.	Results
	$MeSO_4$				
SC 244	Scap + An + $CaSO_4$ + gyps (Au)	10	800	2	An + $CaSO_4$ (no Scap)
SC 285a	Scap + An + $CaSO_4$ + gyps (Pt)	5	800	23	An + $CaSO_4$ (no Scap)
SC 285b	Scap + An + $CaSO_4$ + gyps (Au)	5	800	23	An + $CaSO_4$ (no Scap)
SC 283	Scap + An + $CaSO_4$ + gyps (Pt)	10	850	1	Slight Scap growth
SC 286	Scap + An + $CaSO_4$ + gyps (Au)	10	850	20	Scap growth
SC 292	Scap + An + $CaSO_4$ + gyps (Au)	9	850	4	No reaction
SC 291	Scap + An + $CaSO_4$ + gyps (Au)	8	850	6	An growth
SC 290	Scap + An + $CaSO_4$ + gyps (Au)	5	850	4.25	Strong An growth
SC 214b	Scap + An + $CaSO_4$ (dry) (Au)	13	875	504	Slight Scap growth, some Zo
SC 293	Scap + An + $CaSO_4$ + gyps (Au)	8	875	5	No reaction
SC 299	Scap + An + $CaSO_4$ + gyps (Au)	5	875	5	Strong An + $CaSO_4$ growth
SC 281	Scap + An + $CaSO_4$ + gyps (Pt)	10	900	0.5	Strong Scap growth
SC 282	Scap + An + $CaSO_4$ + gyps (Pt)	7	900	0.5	Scap growth
SC 289	Scap + An + $CaSO_4$ + gyps (Au)	5	900	3.5	No reaction
SC 298	Scap + An + $CaSO_4$ + gyps (Au)	5	900	7	No reaction
SC 297	Scap + An + $CaSO_4$ + gyps (Au)	5	925	5.25	No reaction
SC 280	Scap + An + $CaSO_4$ + gyps (Pt)	10	950	0.5	All Scap (no An)
SC 288	Scap + An + $CaSO_4$ + gyps (Au)	5	950	2.5	Strong Scap growth
SC 238	Scap + An + $CaSO_4$ (dry)	4	950	144	No reaction
SC 294	Scap + An + $CaSO_4$ + gyps (Au)	3	950	4.25	An + $CaSO_4$ (no Scap)
SC 279	Scap + An + $CaSO_4$ + gyps (Pt)	10	1000	0.5	All Scap
SC 276	Scap + An + $CaSO_4$ + gyps (Pt)	6.5	1100	0.25	Strong Scap growth
SC 277	Scap + An + $CaSO_4$ + gyps (Pt)	5.5	1100	0.25	Strong Scap growth
SC 220	Scap + An + $CaSO_4$ (dry) (Pt)	4	1100	139	Slight Scap growth
SC 215	Scap + An + $CaSO_4$ (dry) (Pt)	4	1200	44	Scap growth

Run No.	Starting Material	P, kbar	T, °C	Time, hrs.	Results
	$MeCO_3$				
SC 167	Scap + An + $CaCO_3$ (dry) (Pt)	15	850	504	An growth
SC 236	Scap + An + $CaCO_3$ + Ox + aOx (Au)	10	850	5	An growth
SC 226	Scap + An + $CaCO_3$ + aOx (Buffered)	8	850	28	Strong An growth
SC 306	Scap + An + $CaCO_3$ + Ox (Pt)	5	850	6	Strong An growth
SC 237	Scap + An + $CaCO_3$ + Ox (Buffered)	1	850	67	An growth
SC 227	Scap + An + $CaCO_3$ (dry) (Au)	18	875	433	Strong Scap growth (some Zo)
SC 171	Scap + An + $CaCO_3$ (dry) (Pt)	15	875	431	No reaction
SC 214a	Scap + An + $CaCO_3$ (dry) (Pt)	13	875	504	No reaction
SC 235a	Scap + An + $CaCO_3$ + aOx + AgOx (Pt)	10	875	5	Scap growth
SC 230	Scap + An + $CaCO_3$ + aOx (Buffered)	8	875	5.5	No reaction
SC 307	Scap + An + $CaCO_3$ + Ox (Pt)	5	875	5.5	No reaction
SC 239	Scap + An + $CaCO_3$ + Ox + AgOx (Buffered)	1	875	51	No reaction
SC 245	Scap + An + $CaCO_3$ + AgOx (Pt)	18	900	168	Very strong Scap growth
SC 86	Scap + An + $CaCO_3$ (dry) (Pt)	15	900	140	Scap growth
SC 234	Scap + An + $CaCO_3$ + aOx + AgOx (Pt)	10	900	5	Very strong Scap growth
SC 232	Scap + An + $CaCO_3$ + aOx (Buffered)	8	900	5.5	Scap growth
SC 305	Scap + An + $CaCO_3$ + Ox (Pt)	5	900	6	Very strong Scap growth
SC 308	Scap + An + $CaCO_3$ + Ox (Buffered)	1	900	47	Scap growth

* Scap = scapolite, An = anorthite, Zo = zoisite, Ox = oxalic acid, aOx = "anhydrous" oxalic acid ($H_2C_2O_4$), AgOx = silver oxalate, (Au) = gold capsule, (Pt) = platinum capsule.

Na_2CO_3, $Al(OH)_3$, and SiO_2 glass at temperatures 40–50° above the plagioclase liquidus. Compositions were $An_{0.33}$, $An_{0.40}$, $An_{0.50}$, $An_{0.65}$, $An_{0.70}$, and $An_{0.77}$ in mole fraction. A glass of composition $An_{0.833}$ prepared by N. L. Bowen (1913) for his classic work on the melting phenomena of the plagioclase feldspars was also used. A glass of pure anorthite composition prepared by J. F. Schairer was used for some of the syntheses of the end-member carbonate and sulfate

scapolites, and synthetic crystalline plagioclases also prepared by Schairer were used for some of the runs. The synthetic plagioclases used in other runs were crystallized with a molten lithium molybdate–vanadate flux by J. Ito. Their compositions are as noted in Tables 3–5.

Synthesis runs were basically of three kinds. The first series was to characterize the trends of the unit-cell constants of the scapolites with composition.
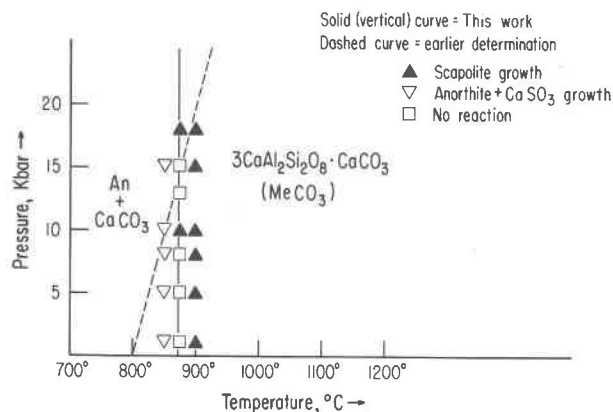
Fig. 2. The P–T curve for the reaction $3An + CaCO_4 \rightleftharpoons MeCO_3$. Dashed curve from Newton and Goldsmith (1976).

These runs used mixtures of scapolite compositions (three plagioclase plus one $CaCO_3$ or $CaSO_4$) or mixtures having an excess of either or both oxysalts (usually 1:1 plagioclase to oxysalt). The syntheses were done at 1200°C and 15 kbar pressure for 4–5 hours. The syntheses on theoretical composition commonly showed small amounts of residual plagioclase in the X-ray diffractograms, indicating incomplete homogenization and insufficient diffusion time. The syntheses on the one plagioclase to one oxysalt mixtures usually showed complete reaction to scapolite, as would be expected for greater mutual availability of the reactants. There was no observable difference in the unit-cell constants from runs which yielded residual plagioclase, however.

Unit-cell constants were determined by powder X-ray diffractometry of the charges with Cu$K\alpha$ radiation at $1/8°$ 2θ per minute with a $KBrO_3$ internal standard (Orville, 1963). Five to eight scapolite peaks in the range $23°$–$35°$ 2θ were used to compute the tetragonal unit-cell constants by a least-squares method.

The second type of synthesis runs was made to determine the limiting amount of Na in the scapolite at a given temperature and pressure. These "three-phase runs," so-called because they defined the compositions of scapolite coexisting with $CaCO_3$ or $CaSO_4$ and plagioclase, were made for the most part on the 1:1 plagioclase to oxysalt compositions. It is evident from the geometry of Figures 7 and 8 that, if the synthesis composition lies even a short distance in the three-phase field, an amount of plagioclase much larger than could be accounted for by residual unreacted plagioclase appears in the charge. This criterion provided fairly sensitive indications of the positions of the scapolite apices of the three-phase triangles in the synthesis diagrams. The penetration into a three-phase field is corroborated by an abrupt break in the trend of the unit-cell vs. composition curve (Figs. 1–3), indicating saturation of the Na-scapolite component. The compositions of the plagioclase apices of the three-phase triangles were determined geometrically from the limiting compositions in which no scapolite appeared in the syntheses.

The third kind of syntheses was tie-line runs to determine the compositions of coexisting scapolite and plagioclases within the two-phase field at a given temperature and pressure. These were made on compositions of six plagioclase plus one oxysalt, and all such runs used the glass-containing starting mixes. The compositions of the scapolites were determined from the trends of the a axes for the $CaCO_3$ and $CaSO_4$ scapolites. The scapolites in the two-phase syntheses were subjected to complete unit-cell refinements, in the same manner as for the first type of synthesis, in order to measure the a axes. The composition of the plagioclase coexisting with the scapolite in a tie-line run was fixed by the intercept on the base of the composition triangle of a straight line through the scapolite composition and bulk composition points.

All runs were performed in the piston-cylinder high-temperature apparatus with 0.75″-diameter chamber and Pyrex and talc high-pressure media. The samples, usually two per run, were encased in sealed or unsealed platinum jackets. Other techniques were as in the General Methods section. Run times varied from one to two hours at 1300° to as long as 3 weeks at 1000°C.

Most of the runs were at 15 kbar nominal pressure, and of the piston-in type (Johannes et al., 1971), with heating and pressing done in the following manner. First a locking pressure of about 8 kbar was applied. The sample was heated to about 600°C to soften the glass, and the assembly was pumped to the desired nominal pressure. The temperature was then brought to the final desired value. During the heating the glass relaxed greatly, requiring continuous instroke of the piston to maintain nominal pressure. Because of this it is certain that the sample pressure was less than the nominal pressure, perhaps by as much as 20 percent at the lowest temperatures. However, as will be shown, absolute pressure in the range 5 to 15 kbar does not have an appreciable effect on the phase relations or distribution of tie-lines, so that accurate pressure characterization is not essential. The nominal pressure of 15 kbar quoted here must be high, perhaps by a few kbar.

Platinum encapsulation of the charges was not completely satisfactory. The carbonate-bearing charges commonly came out light to dark gray, indicating some reduction of the carbonate to graphite. This occurs because hydrogen from dissociation of water from sources external to the capsule diffuses through the platinum and reacts with the charges. The sulfate-bearing charges showed some reaction with the platinum as described, especially in the longer high-temperature runs. In long high-temperature runs with abundant sulfate the capsules showed noticeable embrittlement. The depletion of sulfate or carbonate was not severe enough to alter the phase relations. In runs where residual plagioclase remained because of failure of reaction to scapolite, residual carbonate or sulfate was detectable also.

Temperatures of the present study were limited to the range 1000°–1300°C. At 1300°C there was some indication of melting in some of the more Na-rich compositions in the mixed $CaCO_3$–$CaSO_4$ system. An attempt to produce a series of equilibrations at 900°C in the carbonate and sulfate systems in runs of a month's duration yielded amounts of scapolite too small for reliable compositional determination.

A few attempts to "reverse" some of the phase relations on the tie lines were made, by establishing tie lines at higher temperatures and then attempting to change the tie-lines to a lower-temperature configuration. These attempts were completely unsuccessful. Apparently, once crystallization takes place between plagioclase-composition glass and carbonate or sulfate, further changes involving Al–Si interchange in dry systems are extremely slow (Goldsmith, 1952). Therefore, the diagrams presented here are synthesis diagrams only. Plausibility of the diagrams is defended on grounds other than clean-cut reversals.

Figures 3 to 5 show the trends of the a axes of scapolites from runs at 1200°C to determine the unit-cell constants as functions of composition. The runs and unit-cell constants are listed in Table 2. There is no obvious break in slopes such as reported in natural specimens by Ulbrich (1973). The scatter in the data for the runs of $\frac{1}{2}CaCO_3$–$\frac{1}{2}CaSO_4$ compositions is considerably greater than for the single oxysalt compositions. There may be several reasons for this. First, the variable depletion by reduction of carbonate and sulfate in the charges could change the sulfate to carbonate ratio. Second, the kinetics of reaction could be considerably different for the formation of sulfate and carbonate scapolites, which could bias the synthesis products towards carbonate- or sulfate-rich
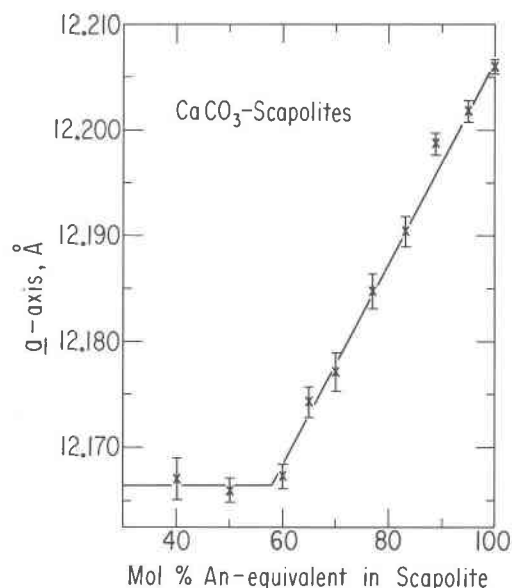

Fig. 3. a axes of $CaCO_3$–scapolite solid solutions as a function of equivalent An-content. All runs made at 1200°C.

compositions. In general, we have found the carbonate mixtures to react considerably faster than the sulfate mixtures. Finally, the mixing of the carbonate–sulfate materials involved an extra homogenization step, introducing the possibility of additional compositional deviation. As nearly as can be
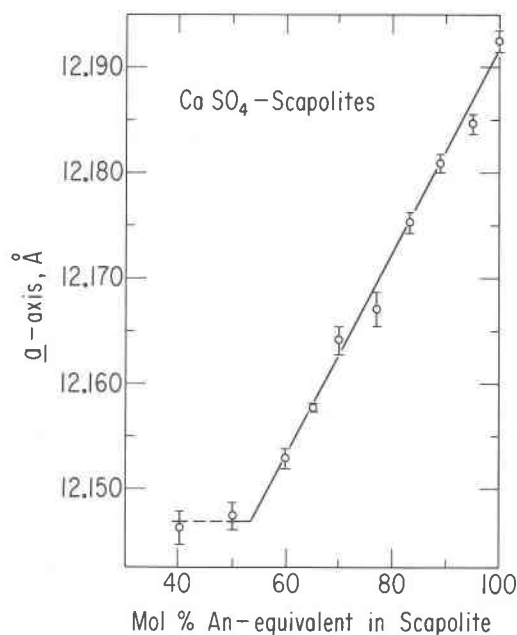

Fig. 4. a axes of $CaSO_4$–scapolite solid solutions as a function of equivalent An-content. All runs made at 1200°C.
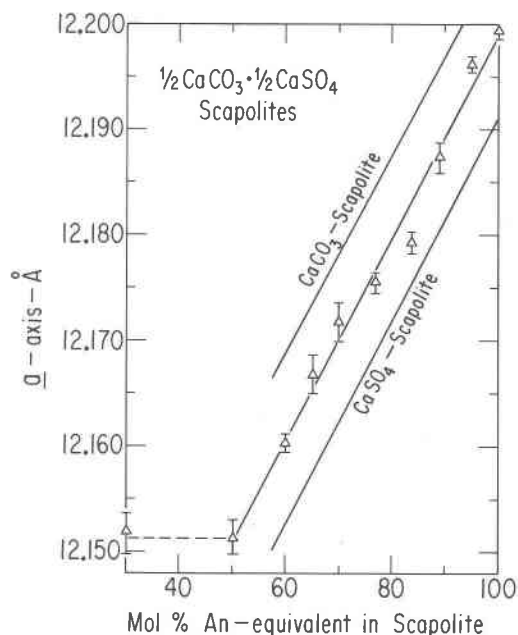
Fig. 5. *a* axes of ½CaCO₃–½CaSO₄ scapolite solid solutions as a function of equivalent An-content. The values for the CaCO₃- and CaSO₄–scapolites also shown. All runs made at 1200°C.

volume to determine the Na–Ca ratio. Also, there is the suggestion of a change of slope at about 70–75 percent "meionite" component.

The results of runs to determine the configurations of isobaric, isothermal phase triangles and the tie-lines are listed in Tables 3–5, and some of the data are shown in Figures 7 and 8. It is clear that there are systematic changes in slopes of the tie-lines with changes in temperature. This temperature dependence is shown still more emphatically in the "Roozeboom" diagrams of the data at "15" kbar (Figs. 9 and 10).

The solid-solution limits of the scapolites (scapolite apex of the 3-phase triangles) are not accurately determined at all the temperatures studied. However, at least from 1100 to 1300° the range of solid solutions is extended toward more sodic compositions with decreasing temperature. This may not be a simple unidirectional effect. It is apparent, however, that in the absence of Cl solid solutions with essentially one-half of the Ca replaced by Na are possible at the

told, the *a* axes for the ½–½ composition lie midway between the trends for the end members (Fig. 5).

In most of the determinations of the *a* axis, standard deviations were less than 0.002A. In Figures 3 and 4, the uncertainty of composition of the scapolite in a specific synthesis is taken to be ± 2 mole percent. This introduces an equal uncertainty in determination of the associated plagioclase compositions by the methods outlined above. The data scatter for the ½carbonate–½sulfate compositions precluded establishing the tie lines with the same confidence as in the pure sulfate and pure carbonate systems.

The abrupt cessation of the downward trends of the *a* axes with increasing sodium content in Figures 3–5 must be due to saturation of the scapolites with the 3(NaAlSi₃O₈) component at the conditions of the syntheses (1200°C, "15 kbar"). This provided a sensitive way to determine the scapolite apices of the three-phase triangles in the synthesis diagrams.

The trends of the unit-cell volumes are plotted in Figure 6. It is interesting that there is very little deviation in the molar volumes of the carbonate–sulfate scapolites at a given sodium content. The ½carbonate–½sulfate scapolites seem to have slightly smaller unit cells. If these trends are followed in natural scapolites, it may be possible to use the *a* axes to determine the carbonate–sulfate ratio and the cell

Table 2. Unit-cell constants of synthetic scapolites

Composition*	Run No.	$\underline{a}$, Å	$\underline{c}$, Å	v, Å³
		Carbonate Scapolites, 3(Ab,An)·CaCO₃		
An₁₀₀	SC 67	12.2060(7)	7.5899(7)	1130.79(13)
An₉₅	SC 96a	12.2019(11)	7.5874(22)	1129.67(30)
An₈₉	SC 149a	12.1988(10)	7.5767(10)	1127.50(18)
An₈₃.₃	SC 84a	12.1904(15)	7.5751(15)	1125.71(30)
An₇₇	SC 145b	12.1848(16)	7.5650(17)	1123.16(30)
An₇₀	SC 84b	12.1770(19)	7.5630(20)	1121.45(34)
An₆₅	SC 146b	12.1743(14)	7.5591(15)	1120.36(28)
An₆₀	SC 85a	12.1673(11)	7.5577(13)	1118.85(21)
An₅₀	SC 85b	12.1659(11)	7.5584(18)	1118.72(23)
An₄₀	SC 64a	12.1670(20)	-	
		Sulfate Scapolites, 3(Ab,An)·CaSO₄		
An₁₀₀	SC 95a	12.1925(10)	7.6045(19)	1130.47(26)
An₉₅	SC 96b	12.1846(9)	7.5958(13)	1127.71(20)
An₈₉	SC 74a	12.1809(9)	7.5945(17)	1126.82(23)
An₈₃.₃	SC 71b	12.1753(9)	7.5906(21)	1125.20(29)
An₇₇	SC 146a	12.1670(16)	7.5862(17)	1123.03(31)
An₇₀	SC 88a	12.1641(13)	7.5796(15)	1121.52(26)
An₆₅	SC 149b	12.1577(4)	7.5799(4)	1120.38(72)
An₆₀	SC 88b	12.1529(8)	7.5791(9)	1119.38(15)
An₅₀	SC 75a	12.1474(12)	7.5692(13)	1116.91(22)
An₄₀	SC 75b	12.1462(16)	7.5732(17)	1117.28(30)
		½ carbonate – ½ sulfate scapolites, 6(Ab,An)·CaCO₃·CaSO₄		
An₁₀₀	SC 95b	12.1995(9)	7.5928(9)	1130.01(17)
An₉₅	SC 97b	12.1963(7)	7.5903(8)	1129.05(14)
An₈₉	SC 91a	12.1874(14)	7.5834(14)	1126.38(26)
An₈₃.₃	SC 71a	12.1793(10)	7.5799(13)	1124.37(21)
An₇₇	SC 190a	12.1756(8)	7.5701(9)	1122.24(16)
An₇₀	SC 192a	12.1719(17)	7.5700(28)	1121.54(41)
An₆₅	SC 192b	12.1663(18)	7.5661(23)	1120.02(36)
An₆₀	SC 190b	12.1604(7)	7.5634(7)	1118.44(13)
An₅₀	SC 92a	12.1513(17)	7.5636(19)	1116.78(34)
An₃₀	SC 91b	12.1519(18)	7.5628(12)	1116.79(28)

* Equivalent An content, mol percent. All runs made at 1200°C.

temperatures of this study. At these temperatures we see no indication, nor does Ellis (1977), of the very limited compositional range of solid solutions near Me_{76} suggested by Orville (1975) and defined as a unique ("mizzonite") composition.

In an attempt to "reverse" the phase relations, a "15" kbar tie-line synthesis was made on the $6An_{77} \cdot CaCO_3$ composition at 1300°. This charge was then held for three weeks at 1100°C at the same pressure. According to Figures 7 and 9, there should have been a significant change in the composition of the scapolite if reequilibration to lower temperature had occurred. No significant change was found. In another reversal attempt, a synthesis was made in the three-phase triangle in the carbonate system at 1300°C. The temperature was lowered to 1100°C, and the charge was held for three weeks. The composition of the apical scapolite was found to correspond to that of a 1300°C determination, without subsequent change.

Apparently, the small driving forces available to reequilibrate plagioclase and scapolite composition over small ranges are not sufficient at 1100°C to overcome the large energy barrier involved in breaking Si–O and Al–O bonds and redistributing the Al and Si as well as the Na and Ca, as is necessary for compositional reequilibration. This is not surprising in view of the lack of success in trying to homogenize zoning and fine intergrowths in natural plagioclases at temperatures just under the solidus, particularly in the absence of H_2O (Goldsmith, 1952).

In spite of the failure to reverse the relations, the systematic sweep of the curves in Figures 9 and 10 indicates that temperature-dependent equilibrium exercises a large control over the phase relations. The greatest degree of equilibration is likely to be present in the highest-temperature runs (1300°C) and the least siliceous compositions, near the anorthite–meionite ends of the diagrams. The distribution of the experimental Roozeboom isotherms in the $CaCO_3$ system is quite consistent with a few experimental and observational data at temperatures much lower than those of the present study, as will be shown, which indicates that the temperature-dependence of the tie lines in the $CaCO_3$ system is now known with reasonable confidence, at least for plagioclase compositions greater than about An 70. The good results obtained on the end-member stability give hope that reversals of the tie-line equilibria may be obtainable in the low-temperature range with similar methods.

The tie-line synthesis data for the $\frac{1}{2}CaCO_3$–

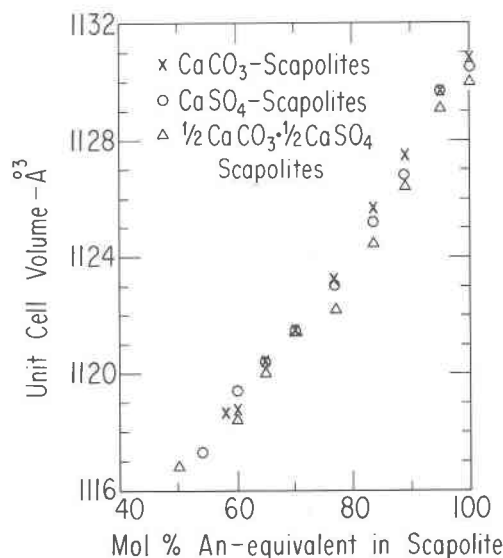Fig. 6. Unit-cell volume as a function of equivalent An-content for the $CaCO_3$, $CaSO_4$, and $\frac{1}{2}CaCO_3$–$\frac{1}{2}CaSO_4$ scapolites.

$\frac{1}{2}CaSO_4$–Ab–An system are much less regular than for either of the end members, probably for the same reasons that the unit-cell data for the mixed oxysalt compositions showed more scatter than those of the end members. Figures 11 and 12 show 1200° and 1000°C data, respectively, for the $\frac{1}{2}$–$\frac{1}{2}$ system at "15" kbar. Plotted for comparison are the smoothed curves for the $CaCO_3$ and $CaSO_4$ system from Figures 9 and 10. In spite of the experimental scatter, it is probable that sulfate to carbonate ratio can be accounted for at a given Na level by a proportional interpolation between the results for the end members.

The volume changes at 25°C in the reaction of plagioclase and oxysalt to scapolite are extremely small, less than one percent except for the very sulfate-rich compositions, for which the volume change approaches three percent (Newton and Goldsmith, 1976). For most compositions, the sign of change itself at high temperatures is uncertain. Therefore, pressure should have a negligible effect on the distribution of the tie lines. A special run (SC 187b) was made at 1000°C and a nominal 8 kbar on the $6An_{70} \cdot CaSO_4$ composition to search for a pressure effect where it should be maximal. The scapolite and plagioclase compositions (Table 4) indicate no detectable difference between 8 and 15 kbar nominal pressures. The tie-line configurations may therefore be assumed to be independent of pressure, even in those parts of the system which show maximal volume change.

Table 3. Runs in 3-phase and 2-phase (tie-line) areas, 15 kbar $CaCO_3$–scapolites, $3(Ab,An)\cdot CaCO_3$

Run No.	Composition[*]		Time, hrs.	Results[**]	Run No.	Composition	Time, hrs.	Results
				1300°C				**1100°C**
SC 101b	$3\ An_{50}\cdot cc$		3.5	3 phases. Scap is An_{67} (12.1735)	SC 109a	$3\ An_{60}\cdot cc$ (1300° for 2½ hr)	48	Me_{67} (12.1745) Reversal attempt. No success.
SC 103a	$3\ An_{42}\cdot cc$		3.25	Plag > Scap	SC 109b	$3\ An_{50}\cdot cc$ (1300° for 2½ hr)	48	Me_{62} (12.1705) Reversal dubious.
SC 122b	$3\ An_{40}^{*}\cdot cc$		4	No Scap	SC 108b	$3\ An_{50}\cdot cc$	24	Plag = Scap $(Me_{52}?)$
SC 103b	$3\ An_{33}\cdot cc$		3.25	No Scap	SC 130a	$3\ An_{33}\cdot cc$	120	No Scap
SC 89a	$3\ An_{30}^{*}\cdot cc$		1.5	No Scap	SC 130b	$3\ An_{30}\cdot cc$	120	No Scap
SC 89b	$3\ An_{25}^{*}\cdot cc$		1.5	No Scap	SC 59	Amelia Ab + cc	4	No Scap
SC 122a	$6\ An_{83.3}\cdot cc$	tie-line (2-phase) runs	4	Me_{89}, An_{78} (12.196)	SC 194b	$6\ An_{83.3}\cdot cc$	tie-line (2-phase) runs	116	Me_{83}, An_{83} (12.190)
SC 120b	$6\ An_{70}\cdot cc$		4.5	Me_{80}, An_{60} (12.1872)	SC 127b	$6\ An_{70}\cdot cc$	72	Me_{72}, An_{68} (12.180)
SC 188a	$6\ An_{60}\cdot cc$		1.5	Me_{72}, An_{48} (12.180)	SC 108a	$6\ An_{60}\cdot cc$	24	Me_{65}, An_{55} (12.1725)
				1200°C				**1000°C**
SC 77a	$3\ An_{60}^{*}\cdot cc$		22	Scap >> Plag	SC 142b	$3\ An_{60}\cdot cc$	312	Me_{60} (12.167)
SC 85a	$3\ An_{60}\cdot cc$		4	Me_{60}, tr. Plag	SC 133a	$6\ An_{50}\cdot cc$	312	Me_{57} + Plag (12.1647)
SC 60	$3\ An_{50}^{*}\cdot cc$		2.25	Scap > Plag	SC 141a	$3\ An_{50}\cdot cc$	312	Me_{54} (12.162)
SC 85b	$3\ An_{50}\cdot cc$		4	Me_{61} + Plag	SC 141b	$3\ An_{40}^{*}\cdot cc$	312	No Scap
SC 94a	$3\ An_{42}\cdot cc$		4	Plag > Scap	SC 134b	$3\ An_{40}\cdot cc$	312	Trace Scap
SC 64a	$3\ An_{40}^{*}\cdot cc$		3	Plag > Scap	SC 129a	$6\ An_{83.3}\cdot cc$	tie-line (2-phase) runs	312	Me_{79}, An_{87} (12.1857)
SC 90a	$3\ An_{33}^{*}\cdot cc$		3	No Scap	SC 129b	$6\ An_{70}\cdot cc$	312	Me_{71}, An_{69} (12.179)
SC 62	$3\ An_{30}^{*}\cdot cc$		2	Trace Scap?	SC 128b	$6\ An_{60}\cdot cc$	312	Me_{64}, An_{56} (12.1724)
SC 87a	$3\ An_{25}^{*}\cdot cc$		4	No Scap				
SC 64b	$3\ An_{20}\cdot cc$		2	No Scap				
SC 65a	$3\ An_{10}\cdot cc$		3	No Scap				
SC 195b	$6\ An_{83.3}\cdot cc$	tie-line (2-phase) runs	26	Me_{85}, An_{82} (12.192)				
SC 193a	$6\ An_{70}\cdot cc$		23.5	Me_{77}, An_{64} (12.184)				
SC 195a	$6\ An_{60}\cdot cc$		26	Me_{68}, An_{52} (12.176)				

* Asterisk over composition refers to crystalline starting material. $3\ An_{30}^{*}\cdot cc$ = 3 parts crystalline An_{30} + 1 part calcite. Otherwise glass. ** Number refers to $\underline{a}$-axis of scapolite.

Discussion

CaCO₃–scapolites

Orville (1975) and Ellis (1977) found experimentally that the meionite end-member scapolite in the system $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–$CaCO_3$ was unstable at 750°C at 4 kbar. Their results were based on the successive appearance of scapolite and disappearance of plagioclase in a system containing excess $CaCO_3$ as albite component was added to the system. A small amount of water was added to the system as a flux, and a small correction was made to the bulk compositions for consequent lime depletion to form grossular and corundum. Orville (1975) obtained compositions of An_{85} and Me_{68} in the more calcic of the three-phase triangles. The two-phase region scapolite–calcite was found to be very small, with the more sodic three-phase triangle having apical compositions of about Me_{66} and An_{40}. The more detailed data of Ellis (1977) show three-phase composition pairs of Me_{83} and An_{92}, and Me_{53} and An_{48}, respectively.

The work of Newton and Goldsmith (1976) and the redetermination reported here show that pure

meionite is unstable at all temperatures below 875°C, independent of pressure.

One natural three-phase assemblage involving Ca-rich scapolite, plagioclase, and calcite is known to the authors, communicated by A. B. Thompson. A high-grade calc-silicate rock from eastern Connecticut contains calcite, plagioclase (An_{95}), and equant granules of apparently primary scapolite (Me_{74}), in addition to clinopyroxene and amphibole. The temperature of the association was estimated by Thompson to be in the range 650°–700°C on the basis of several mineralogic indicators (personal communication). The compositions of the plagioclase and scapolite were measured with the electron microprobe at Harvard. The virtual absence of chlorine and sulfur was established with the University of Chicago microprobe.

Figure 13 shows the experimental Roozeboom isotherms for the $CaCO_3$ system and the additional points of Orville and Thompson. The total data exhibit a consistent temperature-dependence of the Na–Ca partitioning between scapolite and plagioclase, at least for anorthite equivalents greater than

70 percent. Figure 14 shows the data replotted in a more convenient form. Points from the smoothed set of isotherms are plotted as well as the actual data points. On this basis, a natural scapolite–plagioclase pair determines a temperature. A lower limit of useful plagioclase composition is about An_{70}. More sodic compositions are less reliable because of slower kinetics and nonideality of solid solutions. The plagioclase isocomposition lines of Figure 14 down to An_{70} can be essentially reproduced as straight lines in the temperature range 1300°–800°C and are given by an equation of the type:

$$(1) \qquad T = f_1\left(X\frac{Pl}{An}\right)X\frac{Sc}{Me} + f_2\left(X\frac{Pl}{An}\right)$$

where X_{An}^{Pl} denotes the mole fraction of $CaAl_2Si_2O_8$ in plagioclase and X_{Me}^{Sc} the mole fraction of $3CaAl_2Si_2O_8 \cdot CaCO_3$ in scapolite. Data for determi-

Table 4. Runs in 3-phase and 2-phase (tie-line) areas, 15 kbar $CaSO_4$–scapolites, $3(Ab,An)\cdot CaSO_4$

Run No.	Composition*		Time, hrs.	Results+
		1300°		
SC 105b	3 An$_{50}$*·cs		2.5	Me$_{56}$ >> Plag (12.1491)
SC 119b	6 An$_{50}$·cs		4.5	Me$_{56}$ (12.1496)
SC 121a	3 An$_{40}$·cs		4	Plag >> Scap
SC 107b	3 An$_{33}$·cs		3.25	No Scap
SC 121b	3 An$_{33}$·cs		4	No Scap
SC 116b	6 An$_{83.3}$·cs		5	Me$_{84}$, An$_{82}$ (12.1766)
SC 118a	6 An$_{83.3}$·cs	tie-line	5	Me$_{86}$, An$_{81}$ (12.1778)
SC 120a	6 An$_{70}$·cs	(2-phase)	4.5	Me$_{75}$, An$_{65}$ (12.1686)
SC 188b	6 An$_{60}$·cs	runs	2	Me$_{65}$, An$_{55}$ (12.158)
		1200°		
SC 87b	An$_{50}$·cs		4	Me$_{55}$ >> Plag (12.1484)
SC 75a	3 An$_{50}$*·cs		22	Almost all Scap
SC 75b	3 An$_{40}$*·cs		22	Me$_{54}$ > Plag (12.1465)
SC 90b	3 An$_{33}$·cs		3	Plag, trace Scap
SC 76a	3 An$_{30}$·cs		22.5	No Scap
SC 76b	3 An$_{20}$·cs		22.5	No Scap
SC 117a	6 An$_{83.3}$·cs	tie-line	4	Me$_{83}$, An$_{83}$ (12.1757)
SC 193b	6 An$_{70}$·cs	(2-phase)	22.5	Me$_{69}$, An$_{71}$ (12.1617)
SC 117b	6 An$_{60}$·cs	runs	4	Me$_{62}$, An$_{58}$ (12.1552)
		1100°		
SC 194b	6 An$_{83.3}$·cs	tie-line	120	Me$_{79}$, An$_{88}$ (12.1712)
SC 132a	6 An$_{70}$·cs	(2-phase)	96	Me$_{67}$, An$_{73}$ (12.1596)
SC 132b	6 An$_{60}$·cs	data (only)	96	Me$_{59}$, An$_{61}$ (12.1524)
		1000°		
SC 128a	6 An$_{83.3}$·cs	tie-line	312	Me$_{77}$, An$_{90}$ (12.1699)
SC 133b	6 An$_{70}$·cs	(2-phase)	312	Me$_{62}$, An$_{78}$ (12.1552)
SC 134a	6 An$_{60}$·cs	data (only)	312	Me$_{56}$, An$_{64}$ (12.1497)
		1000°, 8 kbar		
SC 187a	6 An$_{83.3}$·cs		216	Plag >> Me$_{76}$ (12.1705) (Prob. metastable)
SC 187b	6 An$_{70}$·cs		216	Me$_{62.5}$, An$_{77.5}$ (12.1554)

* Asterisk over composition refers to crystalline starting material. $3An_{30}$*·cs = 3 parts crystalline An_{30} + anhydrite. Otherwise glass. + Number = a-axis of scapolite.

Table 5. Runs in 3-phase and 2-phase (tie-line) areas, 15 kbar ½ carbonate–½ sulfate scapolites, $6(Ab,An)\cdot CaCO_3 \cdot CaSO_4$

Run No.	Composition*		Time, hrs.	Results*
		1200°		
SC 92a	6 An$_{50}$*·cc·cs		4	Plag > Me$_{50}$ (12.1515)
SC 93a	6 An$_{42}$·cc·cs		4	Scap > Plag
SC 91b	6 An$_{40}$*·cc·cs		3	Plag + Me$_{51}$ (12.153)
SC 92b	6 An$_{30}$*·cc·cs		4	Plag + some Scap
SC 94b	6 An$_{25}$·cc·cs		4	No Scap
SC 137b	12 An$_{83.3}$·cc·cs		4	Me$_{83}$, An$_{83}$ (12.182)
SC 138b	12 An$_{83.3}$·cc·cs	tie-line	24	Me$_{86}$, An$_{80}$ (12.185)
SC 140a	12 An$_{70}$·cc·cs	(2-phase)	6.5	Me$_{74}$, An$_{66}$ (12.174)
SC 154b	12 An$_{70}$·cc·cs	runs	6	Me$_{77}$, An$_{63}$ (12.177)
SC 140b	12 An$_{60}$·cc·cs		6.5	Me$_{65}$, An$_{55}$ (12.1648)
		1000°		
SC 142a	12 An$_{83.3}$·cc·cs	tie-line	312	Me$_{78}$, An$_{88}$ (12.1780)
SC 143a	12 An$_{70}$·cc·cs	(2-phase) runs	312	Me$_{67}$, An$_{73}$ (12.1674)
SC 143b	12 An$_{60}$·cc·cs	(only)	312	Me$_{58}$, An$_{62}$ (12.1593)

* See footnotes, Tables 3 and 4, for abbreviations.

nation of f_1 and f_2 from Figure 4 were fitted by a least-squares method to a quadratic expression:

$$(2) \qquad f = A + BX\frac{Pl}{An} + C\left(X\frac{Pl}{An}\right)^2$$

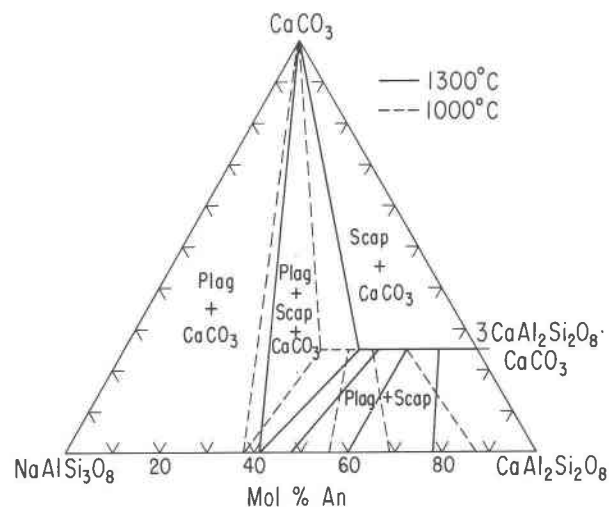The coefficients are given in Table 6. Equations 1 and 2 constitute a provisional scapolite–plagioclase ther-

Fig. 7. Isothermal, isobaric phase relations in the system $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–$CaCO_3$ at 1300°C and 1100°C, 15 kbar. Additional data at other temperatures relative to the 2-phase scapolite–plagioclase "tie-line" equilibria are plotted in the Rooze-boom diagram, Fig. 9.
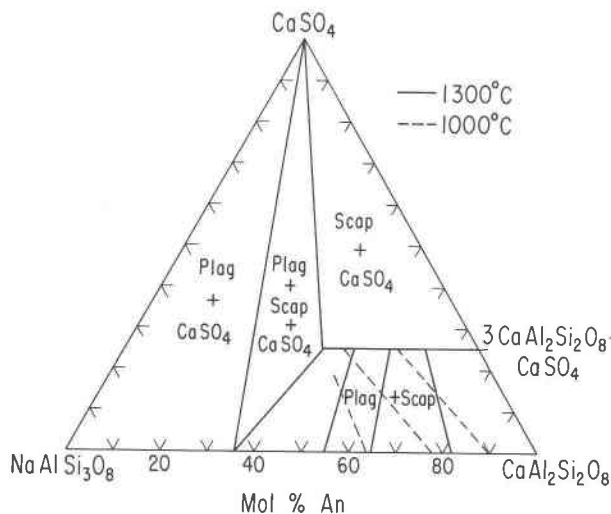
Fig. 8. Isothermal, isobaric phase relations in the system $NaAlSi_3O_8$–$CaAl_2Si_2O_8$–$CaSO_4$ at 1300°C, 15 kbar. "Tie-lines" at 1000°C also shown. Additional data at other temperatures relative to the 2-phase scapolite-plagioclase "tie-line" equilibria are plotted in the Roozeboom diagram, Fig. 10.

mometer, based on our synthesis data and the lower-temperature data of others.

Plagioclase and meionite activities are probably nearly ideal (equal to their mole fractions) in the Ca-rich range at temperatures above 700°C. Orville (1972) deduced a unit activity coefficient for anorthite component in plagioclase at 700°C and compositions greater than An_{50} from hydrothermal alkali-exchange experiments. The scapolite structure is a framework similar to that of the plagioclases (Papike, 1964; Lev-
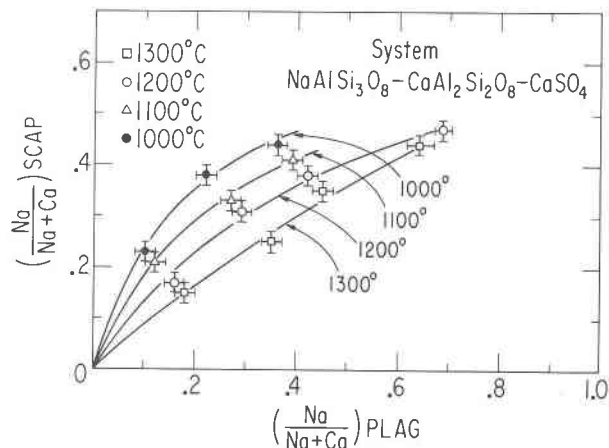
Fig. 10. Plot of the atomic ratio Na/(Na+Ca) in scapolite against the atomic ratio Na/(Na+Ca) in plagioclase (Roozeboom diagram) for the $CaSO_4$-scapolites, at 1000°, 1100°, 1200°, and 1300°C, at 15 kbar. Ratios independent of Ca in oxysalt. Brackets are ± 2 mole percent.

ien and Papike, 1976), with a very similar cation substitution scheme (Evans et al., 1969). Figure 15 is a plot of the logarithm of the activity ratio for reaction $An + 1/3CaCO_3 \rightleftharpoons 1/3MeCO_3$ vs. $1/T$ based on the ideality assumption. Data used are the experimental and natural composition pairs for Ca-rich three-phase triangles. Plotted also is the datum from our three-phase triangle at 1300°C, which involves a Na-rich feldspar and scapolite. However, the highest-temperature determination is most likely to represent
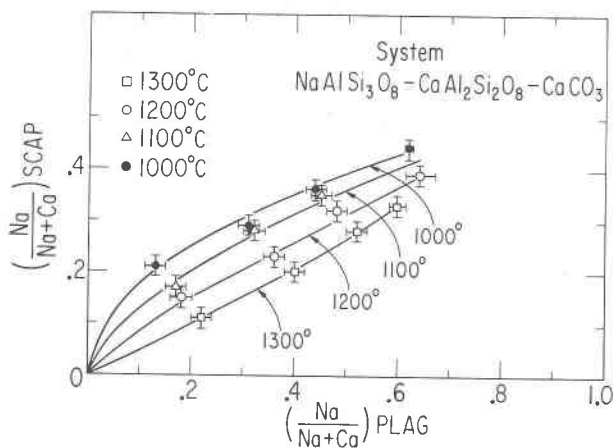
Fig. 9. Plot of the atomic ratio Na/(Na + Ca) in scapolite against the atomic ratio Na/(Na+Ca) in plagioclase (Roozeboom diagram) for the $CaCO_3$-scapolites, at 1000°, 1100°, 1200°, and 1300°C, at 15 kbar. Ratios independent of Ca in oxysalt. Brackets are ± 2 mole percent.
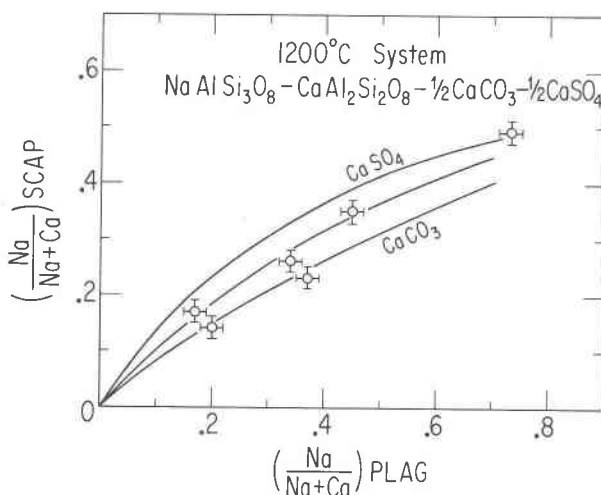
Fig. 11. Plot of the atomic ratio Na/(Na+Ca) in scapolite against the atomic ratio Na/(Na+Ca) in plagioclase (Roozeboom diagram) for the $1/2CaCO_3$–$1/2CaSO_4$ scapolites at 1200°C, 15 kbar. Appropriate curves for the $CaCO_3$- and $CaSO_4$-scapolites included for comparison. Ratios independent of Ca in oxysalt.
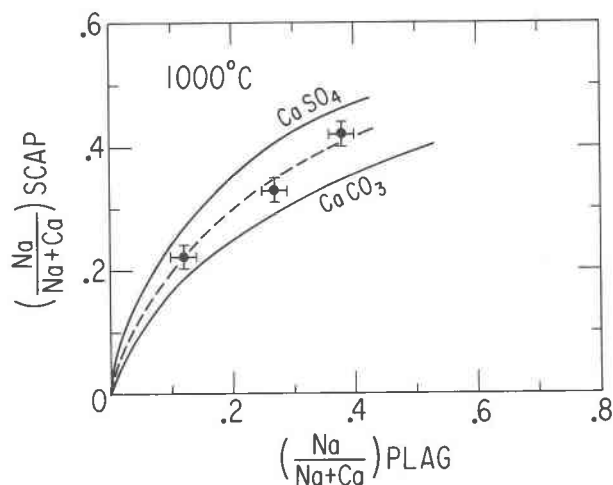
Fig. 12. Plot of the atomic ratio Na/(Na+Ca) in scapolite against the atomic ratio Na/(Na+Ca) in plagioclase (Roozeboom diagram) for the ½CaCO₃–½CaSO₄ scapolites at 1000°C, 15 kbar. Appropriate curves for the CaCO₃- and CaSO₄-scapolites included for comparison. Ratios independent of Ca in oxysalt.
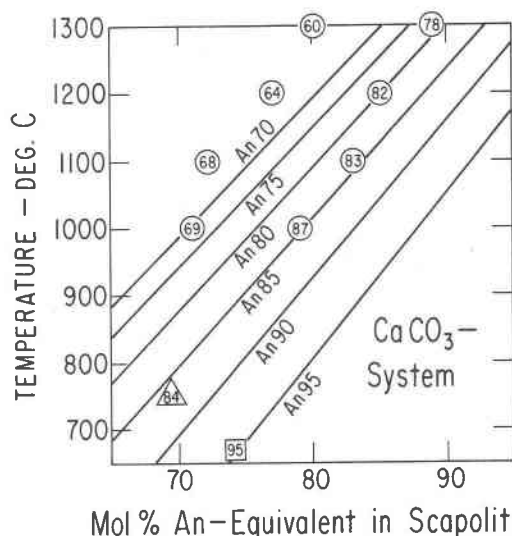

Mol % An–Equivalent in Scapolite

Fig. 14. Data from Roozeboom diagrams, Figs. 9 and 13, for CaCO₃-scapolites, replotted so that temperature can be directly from the plagioclase isopleths and An-equivalent of the scapolite. Points from the smoothed set of isotherms in Figs. 9 and 13 are indicated as circles, with An-content indicated. Triangle represents data of Orville (1975), square, data of A. B. Thompson (private communication).

equilibrium, and the activities of the components are most likely to be nearly ideal at the highest temperature, even for sodic compositions. This is supported for the plagioclase solid solution by the high-temperature syntheses of Windom and Boettcher (1976) on the grossular–quartz–albite system; they found an activity coefficient for $CaAl_2Si_2O_8$ of 1.2 at 1100° for plagioclases rich in albite. Orville (1972) found an activity coefficient of anorthite of 1.28 for Na-rich plagioclases at 700°C. The point for $\Delta G^0 = 0$ at 875°C which results from our work on the stability of

pure meionite relative to anorthite plus calcite is plotted also.

Figure 15 yields a value for ΔS^0 of 9.0 ± 0.5 cal/°C. An entropy change this large in favor of the scapolite explains its high-temperature stability. The high entropy of $MeCO_3$ undoubtedly results from (Si,Al) framework disorder and carbonate-group positional disorder. The maximum entropy resulting from such disorder can be estimated. Anorthite is well-ordered even at high temperatures, primarily because of the tendency for Al–O–Al bridges to be avoided, which results in a regular alternation of Al and Si throughout the structure (Goldsmith and Laves, 1955). "Aluminum avoidance" (Loewenstein,

Fig. 13. Roozeboom diagram, as in Fig. 9, of the CaCO₃-scapolites. Square represents data of A. B. Thompson (private communication). Triangle represents data of Orville (1975), see text.

Table 6. Data reduction coefficients for CaCO₃ and CaSO₄ systems

1) $T = f_1 (X_{An}^{Pl}) X_{Me}^{Sc} + f_2 (X_{An}^{Pl})$

2) $f = A + B X_{An}^{Pl} + C (X_{An}^{Pl})^2$

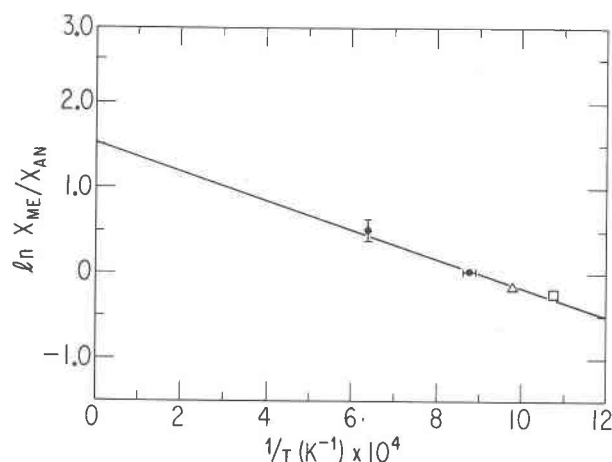|		A	B	C
CaCO₃ system	f_1	5179	-9023	6518
	f_2	-3968	10842	-8313
CaSO₄ system	f_1	1164	-413.4	1296
	f_2	-883.2	4626	-4531

Fig. 15. Logarithm of the activity ratio for the reaction An + $1/3CaCO_3 \rightleftharpoons 1/3MeCO_3$ vs. $1/T$ (see text). Point with horizontal error bars is from the $P-T$ curve for the reaction (Fig. 2), where $\Delta G^0 = 0$ at 875°; the point with vertical error bars from the three-phase triangle at 1300° (Fig. 7); the triangle from the data of Orville (1975); the square from the data of A. B. Thompson (private communication).

1954) cannot be strictly observed in the scapolite structures, however, because unlike the feldspars, scapolites contain 5-member tetrahedral rings positioned about the oxysalt-bearing structural cavities. In addition to this necessary but partial framework disorder, Lin and Burley (1973, 1974) give structural reasons why, as the Al content increases, so does Al/Si disorder, and a structural determination on the meionite from Monte Somma (93 percent Me) shows a very high degree of disorder. The maximum entropy for complete Al–Si disorder would be $12R\ln2 = 16.52$ cal/°C-gfw. An additional amount $R\ln4 = 2.76$ results from disorder of the triangular CO_3 groups about four possible structural positions (Levien and Papike, 1976), which brings the total to 19.3 cal/°C-gfw. This is more than enough to account for the observed entropy difference between the high- and low-temperature assemblages, even ignoring differ-

Table 7. Standard volume changes and entropy changes and dP/dT slopes of scapolite-forming reactions

	ΔV, cm^3	ΔS, cal/°C	dP/dT, bars/°C
1. 3An + Cc = MeCO$_3$	1.22	indeterminate	~ vertical
2. 3An + Cs = MeSO$_4$	-7.87	9.03	-48
3. 3Ab + NaCl = MaCl	1.76	*	*

* From Newton and Goldsmith (1976)

ences in heat capacities, which remain unknown at this time. The very steep dP/dT slope of the reaction $3CaAl_2Si_2O_8 + CaCO_3 \rightleftharpoons MeCO_3$ indicates that ΔV^0 is very small, surely less than 1 cm^3. The 25°C volume change is 1.2 cm^3 (see Table 7 for data on the scapolite reactions). Theoretically, the ratio of activity coefficients of meionite and anorthite, divided by an analogous ratio for the Na end-member components, should be constant along an isotherm. This may be tested with the 1300°C data, which are more likely to represent an equilibrium distribution than those at lower temperatures. The activity constant at the most Na-rich tie line, that of the three-phase triangle, is 3.02, assuming ideality of all components. The other three experimental tie lines yield 2.78, 2.68, and 2.28 with increasing Ca content. Although there seems to be a decrease with increasing Ca, the error limits, averaging about ± 0.6, are mutually embracing for all of the equilibrium constants. The mean value of 2.6 predicts a ΔG^0 at 1200°C of 5224 cal for the reaction of albite and calcite to the unstable end-member Na-scapolite, $3NaAlSi_3O_8 \cdot CaCO_3$.

At lower temperatures non-ideality affects the plagioclase solid-solution series, and may well be present in the carbonate scapolites also. This will especially affect phase relations involving scapolites and plagioclases of higher Na content. In particular, the onset of ordering within the scapolites, of the sort for which X-ray diffraction evidence was found by Lin and Burley (1974) in natural samples at about 50 percent meionite, would have an effect on the activity and equilibrium constant. Non-ideality in plagioclase and possibly in scapolite probably explains the relatively low-temperature occurrences of Na-rich plagioclase and relatively Ca-rich scapolite reported from a number of localities. These occurrences are apparently in violation of the regular temperature-dependence of the compositional tie-lines deduced in the present study, and will be discussed further below.

$CaSO_4$-scapolites

The experimental tie-lines and the plagioclase-scapolite distribution diagram are shown in Figures 8 and 10. The dependence of temperature and composition is given by an empirical equation derived from the present tie-line data, as for the $CaCO_3$-scapolite data. Table 6 lists the coefficients of the reduction equation for the $CaSO_4$ end member.

In general, the sulfate-scapolites require, at a given temperature, more Na for stabilization relative to plagioclase and oxysalt than do the $CaCO_3$-scapo-

lites. Non-ideality of the scapolites may be apparent in Figure 10 even at 1300°C.

Thermodynamic properties of the end-member $MeSO_4$ can be derived from the equilibrium data of Figure 1. The experimental slope of the stability boundary of −48 bars/°C, together with the 25°C ΔV^0 of −7.87 cm³, yields ΔS^0 = 9.03 cal/deg-mole. The consistency of this value with the other experimental work is demonstrated by making a plot, similar to that of Figure 15, of the logarithm of the activity ratio of scapolite to anorthite against $1/T$ in the $MeSO_4$ system, together with the temperature (1040° ± 40°) for which the end-member reaction is in equilibrium at one atmosphere. The equilibrium constant at 15 kbar and 1300°C has to be corrected for the non-negligible solid volume change. Although the possible error of this calculation is large, a line through the mid-points of the uncertainty limits yields a value of ΔS^0 very close to 9 cal/°C, in good agreement with that inferred from the slope of Figure 1. Figure 16, for the sulfate–scapolite system, is similar to Figure 14. Again, the isopleths can be expressed as straight lines for the plagioclase range An_{75}–An_{100}. The coefficients for equations 1 and 2 are given in Table 6.

$CaSO_4$-$CaCO_3$-scapolites

The mixed carbonate-sulfate scapolites are further stabilized by the entropy of mixing of carbonate and sulfate groups. There may also be a slight decrease of the unit-cell volume (Fig. 6) for a mixed scapolite. These features combine to stabilize scapolite relative to other phases at high temperatures and pressures. The available evidence from Figures 11 and 12 suggests that the Na–Ca partitioning between scapolite and plagioclase is roughly proportional between the sulfate and carbonate end members at a given temperature and Na content. Given this property, the empirical equations 1 and 2 can be used as a thermometer to deduce the crystallization temperatures of scapolites in the system $CaAl_2Si_2O_8$-$NaAlSi_3O_8$-$CaCO_3$-$CaSO_4$. The apparent crystallization temperatures for the $CaCO_3$ and $CaSO_4$ end members are found from the equations and the coefficients of Table 6. The temperature for the actual scapolite is then proportioned between these two extremes as the $CaCO_3$ to $CaCO_3$ + $CaSO_4$ ratio. In this calculation the anorthite content of the plagioclase must lie in the range An_{70}–An_{98}. The extent of the control data can be seen in Figures 14 and 16. An effective additional control, not apparent in Figures 14 and 16, is that the Roozeboom isotherms must
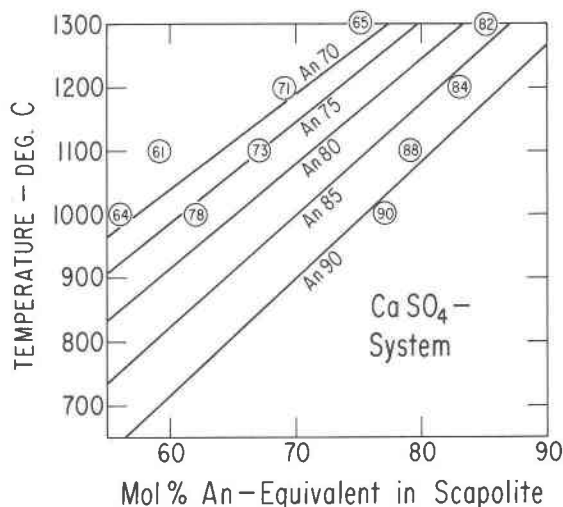

Fig. 16. Data from Roozeboom diagram, Fig. 10, for $CaSO_4$-scapolites, replotted so that temperature can be read directly from the plagioclase isopleths and An-equivalent of the scapolite. Points from the smoothed set of isotherms in Fig. 10 are indicated as circles, with An-content indicated.

project through the origin in pressure and temperature ranges where the end members are stable.

Geologic application

Calcic plagioclase approaching pure An is known to coexist with calcite in a number of metamorphic occurrences, and Figures 1 and 2 show that extreme metamorphic conditions would be required to stabilize end-member Ca-scapolites in the crust. The Nanga Parbat region of the northwest Himalayas (Misch, 1964) contains anorthite up to An_{98} in association with calcite, and the unusual association of anorthite and wollastonite is present in many of the rocks. Newton (1966) has determined the equilibrium grossular + quartz $\rightleftarrows$ anorthite + wollastonite, and the P–T curve is shown in Figure 17. The vertical line represents the equilibrium anorthite + calcite $\rightleftarrows$ $MeCO_3$. The region between the two curves represents the possible range of P and T for the Nanga Parbat rocks, or any rocks containing anorthite, wollastonite, and calcite. Misch (1964) states: "There can be no doubt that at Nanga Parbat total rock pressure was greater than 2 or 3 kilobars." If it is assumed that the pressure was 5 kbar ± 2 kbar, then at the lower pressure the temperature range would be from approximately 640° to 875°, and at 7 kbar from 800° to 875°C. This range is illustrated in Figure 17. The two curves meet at 875° and 9 kbar; at temperatures greater than this meionite will be formed, and at higher pressures grossular + quartz would be pro-
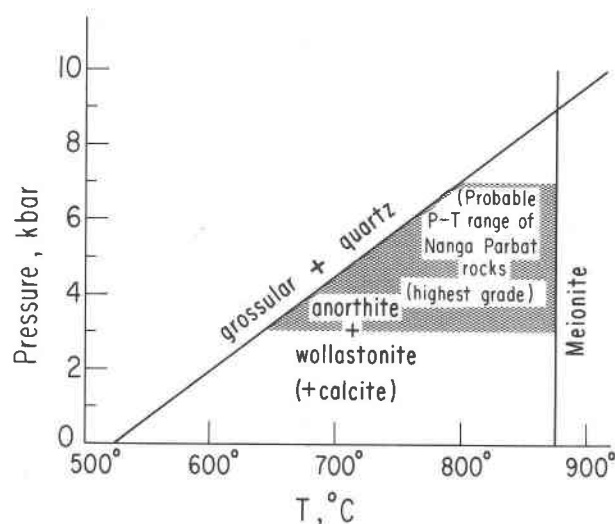
Fig. 17. Curves for the reactions grossular + quartz ⇌ anorthite + wollastonite, and for anorthite + calcite ⇌ meionite. The probable *P–T* range for the Nanga-Parbat rocks (Misch, 1964) is indicated by the shaded region.

duced. Other locations with anorthite and calcite (but not wollastonite) associations are in the Alps (An_{100}; Wenk, 1962), and in Maine, with An_{95} + calcite up to a scapolite isograd (Ferry, 1976, and personal communication).

The conditions for the stability of $MeSO_4$ are even more extreme, largely because of the pressure effect on the equilibrium. Although scapolite is generally a metamorphic mineral, the highly Ca-rich scapolites require such extreme conditions that if compositions approaching the pure end-members were to be produced in crustal rocks, even in the deep crust, they would probably be formed as primary magmatic minerals. All that would be required for direct crystallization from the melt would be an adequate amount of CO_2 or oxidizable sulfur. Millhollen (1974) has shown that a scapolite of the composition 2An + 1Ab + $CaCO_3$ is formed in the presence of liquid in a nepheline–syenite melt with a vapor rich in CO_2 and H_2O at pressures above 3 kbar.

Although scapolite with a compositional range considered in this paper is becoming known as a characteristic mineral of deep-seated granulite-facies terrains (Knorring and Kennedy, 1958), and may be an important if not ubiquitous component of much of the lower continental crust (Lovering and White, 1964), only a few samples have as yet been documented well enough to warrant an attempt at geothermometry on the basis of the present experimental work. We constrain these occurrences to those con-

taining Ca-rich plagioclase, because of factors such as the greater uncertainty as to experimental equilibrium in the Na-rich range, the very large dT/dX_{Na} dependence, the greater departure of the anorthite component of the plagioclase from ideality, and possibly also of the meionite component in the scapolite due to the onset of ordering. The major rock type which bears scapolite of the requisite type is a two-pyroxene basic granulite which probably crystallized under intermediate levels in the continental crust. Rocks of this type are found abundantly as xenoliths in the alkaline-basalt breccia pipes of Delegate, southeastern Australia (Lovering and White, 1964, 1969). The rocks contain major calcic plagioclase, orthopyroxene, and clinopyroxene, and as much as 5 percent meionite scapolite in some samples. Garnet is abundant in a few examples, probably formed by exsolution from pyroxene during slow cooling. A small amount of spinel occurs in some. The granoblastic "mosaic" textures of the specimens and the lack of zoning of the minerals attest to the suddenness of removal from a deep-seated site of long-term equilibration. The scapolite has altered rims, chiefly of fine-grained plagioclase with an An content essentially that of the unaltered scapolite. This texture must have resulted as the scapolite was removed from its stability field at depth either by the reduced pressure (the scapolite is sulfur-rich), lowered temperature, or both.

Rock R18 from Delegate contains scapolite of composition Me 72 and SO_4/CO_3 ratio of 0.60, according to the electron microprobe analyses of Lovering and White (1969). The associated plagioclase is An_{89}. Rock R804 has a plagioclase An_{90} with a scapolite of composition Me_{74} and a sulfate-to-carbonate ratio of 0.67. Figure 18 shows an isotherm on the Roozeboom diagram appropriate to a sulfate-to-carbonate ratio of 0.50, proportionally interpolated from the data for the end members, together with the points for Delegate rocks R804 and R18. It is clear that they were equilibrated at temperatures well below 1000°C and, from the distribution of the isotherms in Figs. 9 and 10, probably near 900°C.

A more quantitative estimate may be made from the empirical equations 1 and 2 and the coefficients of Table 6. For rock R18, the temperature indicated for a Me_{72}–An_{89} pair for the pure sulfate system would be 955°C and for the pure carbonate system 760°C. For a sulfate-to-carbonate ratio of 0.60, the interpolated temperature would be 877°C. Similarly, rock 804 yields 907°C. Complete wet-chemical analyses are given by Lovering and White (1969) for the two

pyroxenes of R18, which makes possible a comparison based on the semi-empirical two-pyroxene thermometer of Wood and Banno (1973). Their thermometer gives 951°C. Rock R804 contains a considerable amount of garnet, as reaction rims between pyroxene and plagioclase. Microprobe analyses of the garnet and the associated clinopyroxene yield a K_D^{Gt-cpx} for Fe and Mg of 2.62, which gives a temperature of 932°C by the experimental garnet–clinopyroxene thermometer of Råheim and Green (1974), assuming a pressure of 10 kbar.

The substantial agreement of the present scapolite–plagioclase estimate with the Råheim-Green estimate of rock 804 supports the interpretation of Lovering and White, and later Irving (1974), that the two-pyroxene granulites in the Delegate pipes are indeed accidental fragments taken from the deep crust by the passage of the alkali-basalt magma. Irving (1974) based his conclusion partly on experimental syntheses of the two-pyroxene–plagioclase assemblage, at high temperatures and elevated pressures, which indicated a subsolidus origin at pressures between 6 and 11 kbar, and partly on the preliminary Sr–Rb data of Compston and Lovering (1969), which suggested an age on the order of 1 billion years, which would make the fragments much older than the probable Mesozoic alkaline volcanism. The temperature estimates for rock 18 would be considered consistent, despite the 66°C difference between them, in view of the suggestion that the Wood-Banno two-pyroxene thermometer may give results which are sometimes as much as 50°C too high (Wood, 1975, p. 304).

High-grade granulites of Archaean age, some scapolite-bearing, are exposed in a long wedge adjacent to the Fraser Fault in Western Australia (Wilson, 1969). At one locality, scapolite makes up about 9 percent of a clinopyroxene–garnet–plagioclase-quartz rock (A. F. Wilson, personal communication, 1975). Electron microprobe analysis of the scapolite reduces to $Me_{73.7}$ with a sulfate to sulfate + carbonate ratio of 0.303 and negligible Cl. The associated plagioclase is An_{87}, and these data are also plotted on Figure 18. The scapolite–plagioclase temperature scale from the present experimental work gives 891°C for the equilibration. This may be compared with a temperature of 870° deduced from oxygen isotopes of the major minerals (Wilson, personal communication). The Fraser Fault Zone has an associated large positive gravity anomaly, which may indicate the presence of an up-tilted block exposing a former deep-crustal section in the manner postulated for the Ivrea Zone of the southern Alps (Mehnert, 1975).

A few examples are now known of Cl-free scapolite coexisting with a sodic plagioclase, which cannot be readily understood in terms of the present experimental work. Wilkinson (1974) reported scapolite-bearing garnet–granulite xenoliths from an alkaline basaltic pipe near Gloucester, New South Wales. The scapolite is Me_{65} with an $SO_4/CO_3 + SO_4$ ratio of 0.30. The associated plagioclase is An_{40}. The present experimental temperature scale, if applied literally to this occurrence, would give a temperature of between 1200° and 1300°C. However, the granulites are probably deep-crustal xenoliths which must have equilibrated at much lower temperatures. The presence of primary hornblende is a guarantee of temperatures below 1100° (Essene et al., 1970). Similarly, the sulfate-rich mizzonite of the Mampong, Ghana, granulite area (Knorring and Kennedy, 1958) is associated with an oligoclase. Such a pair would have not been interpretable in Figure 9 as a product of crustal metamorphism. It is not quite certain, however, that the scapolite and the oligoclase are an equilibrium pair, as the latter is found in cross-cutting, possibly late, veins. J. V. Smith (personal communication, 1975) has analyzed a very similar scapolite–plagioclase pair from the Sittampundi Complex, southern India. E. Essene (personal communication, 1975) reports a calc-silicate rock from the northwest
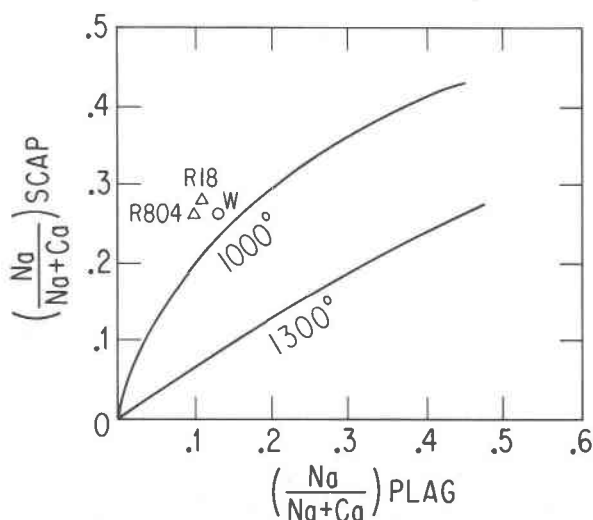

Fig. 18. The 1000° and 1300°C isotherms (Roozeboom diagram) appropriate for a sulfate/carbonate ratio of 0.50, proportionately interpolated from the data plotted in Fig. 9 and Fig. 10. Delegate rocks R804 and R18 (Lovering and White, 1969) are plotted as triangles, and the circle designated W represents the data on an Archaean granulite from Western Australia (Wilson, personal communication).

Adirondack granulite area which has a Cl-free mizzonite Me_{75} together with plagioclase An_{38} in apparent primary textural equilibrium. The estimated temperature is $600° \pm 50°C$. Our Figure 9, if applied directly, would give the absurd temperature of more than $1300°C$ for this rock.

It appears that the thermometer based on our experimental work does not yield reasonable temperatures for metamorphic scapolites coexisting with sodic plagioclases. Possible reasons for this failure may be: (1) The present synthesis work may not approach equilibrium in the high-Na range. The associated siliceous scapolites and plagioclases probably react much more sluggishly than more Ca-rich (and less siliceous) ones. (2) The plagioclase and scapolite components may exhibit strongly non-ideal behavior in this composition range at metamorphic temperatures. (3) Scapolite ordering may set in at lower temperature for compositions near Me_{60} (Lin and Burley, 1974), which could seriously affect the tie-line relations with plagioclase. (4) In some occurrences retrograde alteration might preferentially alter plagioclase by removal of Ca.

It is likely that reasons 1, 2, and 3 are all important in explaining the apparent paradox. The equilibrium isotherms in the sodic range may well focus together more closely than shown in Figures 9 and 10, in such a way that the low-temperature isotherms may even cross over the higher-temperature ones. If Cl-free scapolite in the lower-temperature range behaves nearly as a stoichiometric compound of composition near Me_{67}, as envisioned by Orville (1975), the isotherms at lower temperatures in Figure 9 would be straight lines parallel to the plagioclase axis and would cross the higher-temperature isotherms.

For these reasons the utility of the present work as a geothermometer is confined to higher Ca contents, probably only for plagioclase compositions greater than An_{70}. This is unfortunate, as scapolite-bearing granulites from the deepest portions of the crust, which may be present in many of the as yet little-studied nodule suites of explosive pipes, will have a sodic plagioclase because of the strong effect of high pressure in removing Ca from plagioclase into garnets and pyroxenes (Green, 1968). The use of hydrothermal high-pressure techniques as a possible means of obtaining equilibrium reversals in the lower-temperature regions has not yet been attempted, although ordinary experimental petrologic techniques may never succeed in reproducing the ordering state and equilibrium composition of relatively low-temperature scapolites and plagioclases close to the sodic

three-phase region. Thermochemical and theoretical treatments may eventually offer some hope for extension of the thermometer based on this mineral pair.

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